Production of Halogenated Organics During Wastewater Disinfection

M. H. Roberts Jr.
Virginia Institute of Marine Science

Follow this and additional works at: https://scholarworks.wm.edu/reports

Part of the Marine Biology Commons

Recommended Citation

This Report is brought to you for free and open access by W&M ScholarWorks. It has been accepted for inclusion in Reports by an authorized administrator of W&M ScholarWorks. For more information, please contact scholarworks@wm.edu.
Production of Halogenated Organics During
Wastewater Disinfection

By

M. H. Roberts, Jr.
Virginia Institute of Marine Science
Gloucester Point, Virginia 23062

N. E. LeBlanc and D. R. Wheeler
Hampton Roads Sanitation District Commission
Virginia Beach, Virginia 23445

N. E. Lee, J. E. Thompson and R. L. Jolley
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

Special Report in Applied Marine Science and Ocean Engineering
No. 239

Virginia Institute of Marine Science
College of William and Mary
Gloucester Point, Virginia 23062
William J. Hargis, Jr., Director

December 1980
ACKNOWLEDGEMENTS

The Interagency Task Force on Chlorine received both technical and financial assistance from the Ethyl Corporation. Mr. John F. Balhoff of Ethyl Corp. designed the pilot plant system. Dr. J. Michael McEuen of Ethyl Corp. gave advice on experimental design, chemical analysis and other technical matters. In addition, Ethyl Corp. made available pilot plant equipment and bromine chloride for the study.

The authors wish to express their gratitude to Mr. Daniel Donnelly of the Annapolis Field Office of the U.S. Environmental Protection Agency who arranged for the trihalomethane analyses. The research for determination of nonvolatile halogenated organics was jointly sponsored by Hampton Roads Sanitation District (for the Va. Interagency Task Force on Chlorine) under DOE Agreement No. RTS 77-22 and the Division of Biomedical and Environmental Research, U.S. Dept. of Energy, under Contract W-7405-eng-26 with the Union Carbide Corporation.

Further acknowledgement is extended to Mr. George Kennedy of HRSD who operated the pilot plant, performed the sampling, and assisted in the preparation of this manuscript.

The authors wish further to acknowledge the support and advice of the various members of the Interagency Task Force on Chlorine, in particular Messrs. James Douglas, Norman Larsen, John R. Sutherland, and David Chance.

We also wish to express our thanks to Shirley Sterling and Tammy Miles who patiently typed the numerous revisions to this report. Final copy was prepared by the VIMS Report Center.
I. INTRODUCTION

Chlorine is the principle agent used in the disinfection of treated wastewater in Virginia as well as elsewhere in the United States. However, chlorine was implicated as the causative agent of a major fish kill in the James River during the spring of 1973 and again in 1974 (Bellanca and Bailey, 1977). This led to establishment of the Virginia Interagency Task Force on Chlorine. The Task Force was directed to investigate all aspects of chlorination of sewage wastes and to produce recommendations for action to avoid adverse impacts arising from the disinfection process.

Investigations included not only a review of relevant literature, but primary research as well. Initial research included studies of the effects of chlorine residues on estuarine species of phytoplankton (Roberts and Diaz, unpublished data; Roberts and Illowsky, unpublished data; Roberts, 1977; Bender et al., 1977), invertebrates and fishes (Roberts et al., 1975; Bender et al., 1977; Roberts and Gleeson, 1978; Roberts, 1978; Roberts et al., 1979; Roberts, 1980a, b; Laird and Roberts, 1980). Acute lethal doses (48 hr or 96 hr LC50's) ranged from 0.023 mg/l chlorine produced oxidants (CPO) for oysters to 0.84 mg/l for adult blue crabs. Natural phytoplankton communities exhibited a 50% reduction in primary productivity at applied chlorine doses of 0.29 to 1.91 mg Cl2/l (CPO could not be measured precisely in these static cultures, but some data suggests that after 60 minutes, CPO levels in the test cultures were one half or less of the applied dose).
The toxicity of two alternatives to chlorination were also studied: chlorination/dechlorination (Roberts, 1980c) and bromochlorination (Roberts and Gleeson, 1978). Dechlorination with sodium thiosulfate effectively eliminated toxicity of chlorination "residuals." However, application of dechlorination would mean additional costs for the disinfection process. Bromochlorination was observed to produce slightly less toxic "residuals" than chlorine. These residuals also decayed more rapidly than chlorine "residuals" (Roberts and Gleeson, 1978).

Bromochlorination as an alternative was sufficiently promising that a pilot-plant scale test was designed and conducted to compare directly the disinfection efficiency and toxicity of effluents from chlorination and bromochlorination. LeBlanc and McEuen (1978) and LeBlanc et al. (1978) described in detail the engineering of the pilot plant built at the James River Sewage Treatment Plant located in Newport News, Virginia. Briefly, a portion of the final treated waste effluent was diverted to the pilot plant prior to chlorination. A 100 gpm portion of the effluent was disinfected with chlorine gas via a standard vacuum injection system. A second 100 gpm portion of the effluent was disinfected with bromine chloride through a similar system modified to gasify the liquid BrCl prior to injection. Chlorination was controlled to maintain a specified 30 minute contact residual level while bromochlorination was controlled to maintain a specified 5 minute contact residual level. Experiments with this system showed that under optimized operating conditions either halogen
produced an effluent which meets the NPDES requirements for disinfection. Only 80-85% as much bromine chloride as chlorine was needed to achieve this result.

LeBlanc et al. (1978) and Roberts (1980a) described results of toxicity tests with each pilot plant effluent stream. In these tests, the 96 hr and 144 hr LC50's for spot, *Leiostomus xanthurus*, were virtually identical (0.25 mg/l for bromine chloride and 0.23 mg/l for chlorine). These concentrations could not be approached in the receiving water for the pilot plant system even with extreme deviations from the optimal mode of operation, deviations of a magnitude which would be unlikely to occur in a full-scale plant assuming reasonable plant management.

During the past several years there has developed a concern over the potential production of halogenated compounds in the disinfection process. Many of the halogenated compounds which could be generated may be carcinogenic, mutagenic or teratogenic. Rook (1974) and Rockwell and Larson (1978) reported the formation of haloforms (trihalomethanes) and chlorophenols by chlorination of natural waters. Production of these and other haloorganic compounds has been observed in drinking water (Bellar et al., 1974) and secondary treated effluents (Glaze and Henderson, 1975) after chlorination. Jolley (1973) observed a number of nonvolatile haloorganic compounds in treated sewage effluent following chlorination. Gaffney (1977) reported chlorobiphenyls and PCB's in chlorinated sewage wastes to which biphenyl had been added. Further, formation of halogenated
compounds has been a major issue at all three conferences on the environmental impact of chlorination (Jolley, 1976; Jolley et al., 1978; Jolley et al., 1980).

An important question, then, in the evaluation of bromochlorination as an alternative to chlorination is the potential for formation of various types of halogenated organics. A subproject of the pilot plant project was to analyze halogenated and unhalogenated wastes for halomethanes (volatile) and high molecular weight (nonvolatile) halogenated compounds. The results of these analyses form the subject for this report.
II. CONCLUSIONS

1. Unhalogenated effluent contained 3.8 µg/l chloroform, the origin of which is unknown.

2. Both chlorination and bromochlorination produced measurable amounts of trihalomethanes. Chloroform was the principal product of chlorination, bromoform the principal product of bromochlorination.

3. The chloroform observed following bromochlorination is that present in the unhalogenated waste and not produced by the bromochlorination.

4. Interhalogen trihalomethanes are not a significant fraction of the total trihalomethanes.

5. Initial dilution of effluents with receiving water markedly reduce the concentrations in the environment. For example, at the JRSTP, with a 20:1 dilution, the effluent concentrations convert to 0.4 µg/l chloroform and 0.6 µg/l bromoform.

6. Any nonvolatile halogenated by-products of disinfection in the pilot plant, if present, were at or below a concentration 1 µg/l, i.e. the detection limit of the analytical methods used.

7. No significant difference was found in the nonvolatile organic constituents detected in the undisinfected wastewater effluent sample and the samples of effluent disinfected with chlorine or bromine chloride.
III. RECOMMENDATIONS

1. The environmental impact of trihalomethanes should be evaluated by toxicity and bioaccumulation studies.
IV. MATERIALS AND METHODS

Pilot Plant

A pilot system was constructed at the James River Treatment Plant for a comparison of the effectiveness of bromine chloride and chlorine as disinfectants. This system was described in detail by LeBlanc et al. (1978) and will only be summarized in this report. Parallel chlorine and bromine chloride disinfection systems each received 0.14 MGD (100 gpm) of unhalogenated final clarifier effluent.

The chlorine disinfection pilot system was constructed to simulate full-scale plant operations. Gaseous chlorine, regulated by a chlorinator, was mixed via a vacuum injector with a recycle stream of chlorinated effluent to form a concentrated chlorine solution. This solution was contacted with secondary clarifier effluent. A portion of this flow was diverted to a 30 minute contact tank. Chlorine residual was measured after the 30 minute contact period.

Bromine chloride was injected into the secondary clarifier effluent in a manner similar to that for chlorine. Since bromine chloride was supplied as a liquid, it had to be vaporized with a heated water bath prior to injection into the recycle stream.

In addition to the 30 minute contact tanks, a small portion of the bromochlorinated final clarifier effluent was diverted to a 5 minute contact tank. The effluent residual after five minutes contact was used for bromine chloride dosage control since a previous
study (Ward et al., 1976) had shown that optimum control was achieved in this way.

**Analyses of Waste Characteristics**

General effluent physicochemical characteristics for final clarifier effluent were monitored daily throughout the study period. Hourly pH measurements were made using a Corning pH Meter Model 7. The daily pH was expressed as the 24-hr mean of these hourly measurements. Effluent flow rates were measured hourly and daily using Parshall flumes. A flow proportioned effluent sample of the final clarifier effluent was collected by the plant operators. This sample was refrigerated and shipped daily to the HRSD laboratory in Virginia Beach, Virginia. The chemical parameters monitored and analytical procedures used are summarized in Table 1.

**Sample Collection**

Samples of the final clarifier effluent from the James River Sewage Treatment Plant and the pilot plant were collected and shipped to the U.S. Environmental Protection Agency (USEPA), Annapolis Field Office and Oak Ridge National Laboratories (ORNL) for analysis of halogenated organic compounds. Three discrete effluent streams were sampled: final clarifier effluent prior to halogenation, chlorinated effluent and bromochlorinated effluent. Residuals were maintained in the halogenated systems at concentrations to be expected in normal operation. The halogen residuals were measured with a Fisher-Porter Amperometric Titrator.
Table 1. Analytical procedures used for physicochemical parameters in the Pilot Plant study.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>Analytical Instrument</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>In situ measurement</td>
<td>Field pH meter</td>
<td>APHA, 1976</td>
</tr>
<tr>
<td>Flow</td>
<td>In situ measurement</td>
<td>Plant flow meters</td>
<td>NA</td>
</tr>
<tr>
<td>BOD\textsubscript{5}</td>
<td>Membrane Electrode</td>
<td>YSI 57</td>
<td>APHA, 1976</td>
</tr>
<tr>
<td>TSS</td>
<td>Nonfiltrable residue</td>
<td></td>
<td>APHA, 1976</td>
</tr>
<tr>
<td>NO\textsubscript{2}, NO\textsubscript{3}-N</td>
<td>Automated Cadmium reduction</td>
<td>Technicon Auto Analyzer II</td>
<td>EPA, 1974</td>
</tr>
<tr>
<td>NH\textsubscript{3}-N</td>
<td>Automated colorimetric phenate</td>
<td>Technicon Auto Analyzer II</td>
<td>EPA, 1974</td>
</tr>
<tr>
<td>TKN</td>
<td>Automated phenate</td>
<td>Technicon Auto Analyzer II</td>
<td>EPA, 1974</td>
</tr>
<tr>
<td>Organic N</td>
<td>Calculation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NA - not applicable
A set of samples was taken from each effluent stream for volatile organic haloform analyses by the USEPA. Each set consisted of six 40 ml samples in glass vials which were filled over a 3-hr period, one vial every 30 minutes. Samples were drawn simultaneously from all three effluent streams. Care was taken to exclude air bubbles from these samples. The samples, eighteen in all, were immediately stored at 4°C until picked up at the plant by an EPA sampling team.

Concurrently with the collection of the EPA samples, composite samples from each of the effluent streams were collected for analyses of high molecular weight halogenated organics by ORNL. Seven liter polyethylene containers, previously rinsed with reagent grade acetone and air dried, were used for sample collection. Six containers per effluent stream were filled on six separate occasions with aliquots collected over a four hour period. After one 200 ml sample was removed for halogen residual analysis, the remainder of each 7 liter sample was frozen with dry ice. The total sample, consisting of six frozen containers per effluent stream, or approximately 40 liters per effluent, was immediately shipped by air express to the Oak Ridge National Laboratory. Each sample was assigned an alphanumeric identification number to insure data integrity.

**Trihalomethane Analysis**

James River Sewage Treatment Plant effluent samples collected for the EPA Annapolis Field Office were analyzed for the trihalomethanes, chloroform, dichlorobromomethane, dibromochloromethane and bromoform, using the EPA purge-and-trap procedure (Hall, 1979).
The purge-and-trap procedure is an extraction/concentration technique, which enhances the amount of trihalomethane injected into the gas chromatograph by a factor of 1000 over direct injection gas chromatography and by a factor of 200 over the interim liquid/liquid extraction method.

Trihalomethanes are extracted by an inert gas bubbled through the aqueous sample. The trihalomethanes, along with other organic constituents which exhibit low water solubility and a vapor pressure significantly greater than water, are efficiently removed from the aqueous phase. These compounds are swept from the purging device and trapped in a short column containing a suitable sorbent. After a predetermined period of time, the trapped components are desorbed by heating the column and backflushed onto the head of the gas chromatograph column for separation under programmed conditions. Measurement is accomplished with a halogen specific detector such as electrolytic conductivity or microcoulometric titration. Aqueous standards and unknowns are extracted and analyzed under identical conditions in order to compensate for extraction losses.

**Analysis of High Molecular Weight Compounds**

The basic analytical steps used to examine effluent samples for high molecular weight compounds were (1) concentration of samples, (2) separation of constituents, and (3) identification of constituents.

**Concentration**

The lower limit of detection for various compounds using high-pressure liquid chromatography (HPLC) is in the microgram range,
depending on the uv absorption of the individual compound. Since HPLC is limited to \( \leq 5 \text{ ml per sample} \) and the concentrations of specific contaminants in effluent samples may be \( \leq 10 \mu g/l \), it is necessary to concentrate wastewater effluents by factors up to 3000-fold prior to analysis. Lyophilization was chosen as the concentration method. Previous studies had shown this to be a convenient and suitable method that provided recovery of stable, nonvolatile organic compounds (Jolley et al., 1979).

Initially, the effluent was filtered through a Whatman No. 2 filter paper to remove suspended matter. The filtrate was transferred to a commercial-size lyophilizer for drying. After freeze-drying, the solids were acidified with acetic acid to destroy carbonate salts and centrifuged. The supernatant liquid was transferred to the freeze-dryer for a final reduction in volume. Water and acetate buffer were added to attain the desired liquid volume (\( \approx 50 \text{ ml} \)) and to adjust the pH to 4.5. Finally, the sample was well mixed, and the solids were separated by centrifugation. The supernatant liquid (effluent concentrate) was analyzed by liquid chromatography.

**Separation**

Liquid chromatography has proven useful for the separation and identification of numerous constituents in wastewater effluents. High-resolution anion exchange chromatographs have been demonstrated to possess sensitivity in the microgram range and are capable of detecting and quantifying many individual organic compounds in concentrates of complex aqueous effluent samples.
Both preparative-scale and analytical-scale chromatographs (Fig. 1) are used to separate and detect uv-absorbing compounds. The chromatograph consists primarily of a heated, high-pressure ion exchange column, a sample injection valve, a two-wavelength dual-beam uv photometer, a cerate oxidative monitor and a strip-chart recorder. The ion exchange column for each system is 50 cm in length and is constructed of type 316 seamless stainless steel tubing (0.45 to 1.0 cm ID), usually packed with strongly basic anion exchange resin. A 0.05 to 5.0 ml sample (the volume depends on the inside diameter of the ion exchange column and the nature of the sample) is applied to the column through a six-port injection valve mounted as near the top of the column as possible to minimize peak width.

The chromatograms are obtained by eluting the sample constituents from the resin column with an ammonium acetate-acetic acid buffer solution (pH 4.4). The acetate concentration of the buffer is gradually increased from 0.015 to 6.0 M. The uv absorbances of the column effluent are measured at 254 and 280 nm with a dual-beam flow-through photometer and are recorded on a strip chart.

**Identification of Constituents**

The preparation of samples for analysis, the separation of constituents, and the application of analytical methods to separated fractions involve an integrated and complex series of manipulations and investigative techniques. The preparative-scale liquid chromatograph system, which is coupled to a fraction collector, is capable of chromatographing a 5 ml sample with a resolution approaching that of the analytical column. The eluate fraction,
Fig. 1. Schematic of high-pressure liquid chromatography system.
containing an unknown constituent, is collected and processed through
the following analytical procedure so that the isolated constituents
can be identified and characterized.

Preparation of fractions for analyses. Eluted fractions
corresponding to individual chromatographic peaks from the anion
exchange separations are frozen at -60°C and lyophilized for removal
of the ammonium acetate-acetic acid buffer. The samples are then
dissolved in spectroscopic-grade methanol.

Ultraviolet spectrometry. For each of the collected fractions in
methanol solution, uv.spectra are obtained from 320 to 210 nm on a
Beckman DB-G recording spectrophotometer and compared with the uv
spectra of reference compounds obtained in the same manner.

Gas chromatography. Conversion of the nonvolatile constituents
to volatile compounds is necessary for analysis by gas chromatography.
The method of forming volatile derivatives of the nonvolatile
compounds was silylation with bis(tri-methyilsilyl)-trifluoroacetamide.
The samples are analyzed on a Tracor 222 gas chromatograph (Tracor,
Inc.) using flame ionization detection and dual packed columns
(0.25 in x 6 ft, 3% OV-1 on 100-120 mesh on Chromosorb Q, and 3% OV-17
on 100-120 mesh Gaschrom Q).

Mass spectrometry. Mass spectrometry was performed on aliquots
of the trimethylsilyl (TMS)-derivatized samples described above. The
TMS-derived samples were analyzed in a Finnigan Model 3000 high-
resolution quadrapole gas chromatograph-mass spectrometer (GC/MS)
scanning from 40 to 490 amu. The quadrapole GC/MS is interfaced to a
PDP 8/e (Digital Equipment Corp.) central processing unit (CPU) with a core memory of 12K. Acquisition of raw data is under computer control. An average of every three mass scans is plotted, and a continually developing reconstructed gas chromatogram (RGC) results. Peaks of interest were then compared by computer using the large Battelle library which holds 25,000 spectra (Anon., 1974, 1976). In addition, comparison of the fragmentation patterns with those of reference standards was routinely performed, and the methylene unit retention values resulting from gas chromatography were calculated and compared with those of standard reference compounds.
V. RESULTS

General Waste Characteristics

All samples for halogenated organic analyses were collected on 29 June 1978, approximately seven months after the disinfection efficiency and toxicity studies were completed (LeBlanc et al., 1978). The average effluent characteristics (flow rate, BOD₅, total suspended solids, pH, NO₂⁻-NO₃⁻-N, NH₃-N, TKN, organic N, chlorine application rate, chlorine residual₃₀) during the sampling period are shown in Table 2. For comparison, the monthly means for June 1978 and June 1977 are also presented.

During the sampling period, the plant effluent was more typical of a "good" secondary treatment plant effluent than indicated by monthly averages for June 1977 or 1978. During both months, nitrification occurred for extensive periods resulting in low NH₃-N/high NO₂⁻-NO₃⁻-N concentrations and high chlorine application rates to maintain the required 2 mg/l 30 minute chlorine residual.

The halogen application rates in the pilot plant during the sample collection period averaged 4.2 mg/l for chlorine and 4.3 mg/l for bromine chloride (Table 3). The average 30 minute chlorine residual was 2.07 mg/l, or virtually identical to the residual in the main plant (Table 2). The average 5 minute bromine chloride residual was 0.95 mg/l.
Table 2. Average daily unchlorinated final effluent physicochemical characteristics and chlorine usage from James River Treatment Plant.

<table>
<thead>
<tr>
<th>Date</th>
<th>Flow (MGD)</th>
<th>BOD (mg/l)</th>
<th>TSS (mg/l)</th>
<th>pH</th>
<th>NO₃-NO₂-N (mg/l)</th>
<th>NH₃-N (mg/l)</th>
<th>TKN (mg/l)</th>
<th>Organic N (mg/l)</th>
<th>Applied (mg/l)</th>
<th>Residual (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/29/78</td>
<td>11.08</td>
<td>3</td>
<td>5</td>
<td>7.00</td>
<td>1.086</td>
<td>14.2</td>
<td>NS</td>
<td>NS</td>
<td>3.97</td>
<td>2.17</td>
</tr>
<tr>
<td>6/78¹</td>
<td>12.52</td>
<td>3</td>
<td>17</td>
<td>6.77</td>
<td>4.82</td>
<td>7.6</td>
<td>1.3</td>
<td>1.3</td>
<td>6.60</td>
<td>2.07</td>
</tr>
<tr>
<td>6/77¹,²</td>
<td>11.20</td>
<td>12</td>
<td>12</td>
<td>6.40</td>
<td>9.30</td>
<td>2.9</td>
<td>5.6</td>
<td>2.7</td>
<td>7.30</td>
<td>2.40</td>
</tr>
</tbody>
</table>

NS - no sample
¹ - daily means for the months specified
² - from LeBlanc et al., 1978
Table 3. Halogen application rates, halogen residuals and effluent flow rates during the sample collection period on 29 June 1978.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chlorine 30 min.</th>
<th>Bromine Chloride 5 min.</th>
<th>Flow Each System gpm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Applied mg/1</td>
<td>Residual mg/1</td>
<td>Applied mg/1</td>
</tr>
<tr>
<td>1</td>
<td>4.5</td>
<td>2.00</td>
<td>3.7</td>
</tr>
<tr>
<td>2</td>
<td>4.4</td>
<td>2.20</td>
<td>3.6</td>
</tr>
<tr>
<td>3</td>
<td>4.3</td>
<td>2.25</td>
<td>3.5</td>
</tr>
<tr>
<td>4</td>
<td>4.0</td>
<td>2.10</td>
<td>4.8</td>
</tr>
<tr>
<td>5</td>
<td>4.0</td>
<td>1.95</td>
<td>5.2</td>
</tr>
<tr>
<td>6</td>
<td>3.9</td>
<td>1.90</td>
<td>4.7</td>
</tr>
<tr>
<td>Average</td>
<td>4.2</td>
<td>2.07</td>
<td>4.3</td>
</tr>
</tbody>
</table>
Trihalomethanes

The influent to the pilot plant contained 3.8 µg/1 chloroform (Table 4). No other trihalomethane was observed in the influent. This background level of chloroform may have been present in drinking water of the service area, introduced by industrial operations, or it may have been formed during pretreatment chlorination performed at sewage pumping stations for odor control. We have no data to implicate any of these potential sources.

After chlorination in the pilot plant, the chloroform concentration was slightly more than doubled to 8.0 µg/1. Dichlorobromomethane and chlorodibromomethane were reported at concentrations equal to the detection limit. Thus the primary trihalomethane produced by chlorination was chloroform.

After bromochlorination, 3.1 µg/1 chloroform was found, only slightly less than the concentration in the influent. The primary trihalomethane produced during bromochlorination was bromoform (12.1 µg/1) with a trace of chlorodibromomethane but no detectable dichlorobromomethane.

High Molecular Weight Constituents

A large number of complex mass spectra was derived from each HPLC fraction of the three wastewater effluent samples examined. Preliminary examination and interpretation consisting of comparison with computer files (Anon., 1974, 1976) and several mass spectra compilations (Stanhagan et al., 1974; Markey et al., 1972; Markey et al., undated) have resulted in the identifications reported.
Table 4. Trihalomethane residuals observed in composited samples from pilot plant influent and effluents.

<table>
<thead>
<tr>
<th>Source</th>
<th>CHCl₃</th>
<th>CHCl₂Br</th>
<th>CHClBr₂</th>
<th>CHBr₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unhalogenated</td>
<td>3.8</td>
<td>ND*</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Chlorinated</td>
<td>8.0</td>
<td>0.3</td>
<td>0.3</td>
<td>ND</td>
</tr>
<tr>
<td>Bromochlorinated</td>
<td>3.1</td>
<td>ND</td>
<td>0.3</td>
<td>12.1</td>
</tr>
</tbody>
</table>

*ND - nondetectable; detection limit = 0.3
The total number of compounds identified by GC/MS analysis in the nondisinfected control sample was 19. An additional 54 compounds were tentatively identified by GC retention times. For the chlorinated sample, 25 compounds were identified by GC/MS, and 16 were tentatively identified by GC retention time. For the bromochlorinated sample, 42 compounds were identified by GC/MS, and 32 were tentatively identified by GC retention times.

**Liquid Chromatography**

A comparison of the apparent chemical effects on the uv-absorbing constituents due to disinfection by chlorination and bromochlorination is shown in a composite drawing (Fig. 2) of the three chromatograms obtained from analytical-scale liquid chromatography. The uv-absorbing constituents in the control sample, represented by the solid line, are offset below the chlorinated sample, represented by the dashed line, and the bromochlorinated sample, represented by the dash-dot line. Some destruction of uv-absorbing constituents in the control sample appears to have occurred by both disinfection processes. For example, the constituent peaks eluting at ~0.05, 3.5, 7.0 and 13.5 hr in the control sample are not present in either of the disinfected samples. The constituent peak eluting at ~1 hr is reduced by ~50% when disinfection was accomplished by chlorination and ~25% when bromochlorination was the disinfection technique. Similarly, differences occur in constituents eluting between 3 and 4.5 hrs. These differences, as well as others, can also be seen in the composite drawing of the three chromatograms obtained from the
Fig. 2. Composite analytical-scale chromatogram of control, chlorinated, and bromochlorinated secondary effluents.
preparative-scale liquid chromatograph (Fig. 3). The shift in peak position observed in the preparative-scale chromatogram is due to flow rate fluctuation and not the disinfection processes.

Gas Chromatography-Mass Spectrometry

Control sample. A preparative-scale chromatogram of the nondisinfected control sample showing the fractions used for mass spectral analysis is given in Figure 4. The numbers in parentheses represent the number of compounds tentatively identified by mass spectra in each fraction. A total of 15 combined fractions were chosen for derivatization by trimethylsilylation and analyzed in a Finnigan 3000 high-resolution quadrapole mass spectrometer scanning in the range of 40 to 490 amu. The nonvolatile compounds tentatively identified by mass spectra are listed in Table 5.

Chlorinated sample. A preparative-scale chromatogram of the sample disinfected by chlorination showing the fractions subjected to GC/MS analysis is presented in Figure 5. A total of eleven fractions was prepared and analyzed by mass spectra, and the nonvolatile compounds tentatively identified are listed in Table 6.

Bromochlorinated sample. A preparative-scale chromatogram of the sample disinfected by bromochlorination showing the fractions subjected to GC/MS analysis is presented in Figure 6. Sixteen fractions from this sample were prepared and analyzed by mass spectra. The nonvolatile compounds tentatively identified are listed in Table 7.
Fig. 3. Composite preparative-scale chromatogram of control, chlorinated, and bromochlorinated secondary effluents.
Fig. 4. Chromatogram of uv-absorbing constituents in nondisinfected control secondary effluent.
Table 5. Identity of nonvolatile organic compounds found in fractions of unhalogenated sewage effluent.

| Fraction 7-10 | Lactic acid | Decamethyltetrasiloxane | Benzoic acid |
| Fraction 11-15 | Ethylene glycol ether | Benzoic acid | 2,2,4-Trimethyl-2,4,-disilapentane |
| Fraction 16-20 | Diglycolic acid | Benzoic acid | Stearic acid |
| Fraction 21-29 | Lactic acid | 3-Hydroxybutyric acid | Benzoic acid | Threonine | Arabino-1,5-lactone |
| Fraction 30-32 | Lactic acid | 3-Hydroxybutyric acid | Benzoic acid |
| Fraction 33-39 | Lactic acid | Benzoic acid | Palmitic acid |
| Fraction 40-44 | Benzoic acid |
| Fraction 45-47 | Myristic acid | Palmitic acid |
| Fraction 48-50 | Lactic acid | Benzoic acid | Palmitic acid |
| Fraction 51-61 | Phenol | Lactic acid | Benzoic acid | Palmitic acid | Terephthalic acid |
| Fraction 62-69 | Lactic acid | Urea | Benzoic acid | Phosphate | Palmitic acid | Stearic acid | Terephthalic acid |
| Fraction 76-86 | Lactic acid | Glycolic acid | Palmitic acid | Stearic acid | Decanoic acid |
| Fraction 99-110 | Lactic acid | 1,3-Propanediol | Benzoic acid | Phosphate | Palmitic acid | Stearic acid |
| Fraction 123-142 | Lactic acid | Benzoic acid |
| Fraction 158-175 | Benzoic acid |
Fig. 5. Chromatogram of uv-absorbing constituents in secondary effluent disinfected by chlorination.
<table>
<thead>
<tr>
<th>Fraction 10-16</th>
<th>Fraction 65-68</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic acid</td>
<td>Lactic acid</td>
</tr>
<tr>
<td></td>
<td>Urea</td>
</tr>
<tr>
<td></td>
<td>Benzoic acid</td>
</tr>
<tr>
<td></td>
<td>3,3-Dimethylhexane</td>
</tr>
<tr>
<td></td>
<td>Pentadecane</td>
</tr>
<tr>
<td></td>
<td>Tetradecane</td>
</tr>
<tr>
<td></td>
<td>Palmitic acid</td>
</tr>
<tr>
<td></td>
<td>2,5,10,14-Tetramethylpentadecane</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fraction 17-24</th>
<th>Fraction 81-100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic acid</td>
<td>Lactic acid</td>
</tr>
<tr>
<td>Serine</td>
<td>Urea</td>
</tr>
<tr>
<td></td>
<td>Pyruvic acid</td>
</tr>
<tr>
<td></td>
<td>Benzoic acid</td>
</tr>
<tr>
<td></td>
<td>Phosphate</td>
</tr>
<tr>
<td></td>
<td>Nor decane</td>
</tr>
<tr>
<td></td>
<td>2-Methyltetradecane</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fraction 25-35</th>
<th>Fraction 146-165</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic acid</td>
<td>Lactic acid</td>
</tr>
<tr>
<td>Erythritol</td>
<td>Urea</td>
</tr>
<tr>
<td></td>
<td>Pyruvic acid</td>
</tr>
<tr>
<td></td>
<td>Benzoic acid</td>
</tr>
<tr>
<td></td>
<td>Phosphate</td>
</tr>
<tr>
<td></td>
<td>Nor decane</td>
</tr>
<tr>
<td></td>
<td>2-Methyltetradecane</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fraction 36-43</th>
<th>Fraction 166-185</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lactic acid</td>
<td>Glycerol</td>
</tr>
<tr>
<td>1,3-Propanediol</td>
<td>Benzoic acid</td>
</tr>
<tr>
<td>3-Hydroxybutyric acid</td>
<td>Phosphate</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>Pentadecane</td>
</tr>
<tr>
<td>Hydroxymalonic acid</td>
<td>Stearic acid</td>
</tr>
<tr>
<td>Lauric acid</td>
<td>N-Tridecane</td>
</tr>
<tr>
<td>Xylose</td>
<td></td>
</tr>
<tr>
<td>Xylitol</td>
<td></td>
</tr>
<tr>
<td>Palmitic acid</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fraction 44-50</th>
<th>Fraction 166-185</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic acid</td>
<td>Glycerol</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>Benzoic acid</td>
</tr>
<tr>
<td></td>
<td>Phosphate</td>
</tr>
<tr>
<td></td>
<td>Pentadecane</td>
</tr>
<tr>
<td></td>
<td>Stearic acid</td>
</tr>
<tr>
<td></td>
<td>N-Tridecane</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fraction 52-59</th>
<th>Fraction 166-185</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyruvic acid</td>
<td>Glycerol</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>Benzoic acid</td>
</tr>
<tr>
<td></td>
<td>Phosphate</td>
</tr>
<tr>
<td></td>
<td>Pentadecane</td>
</tr>
<tr>
<td></td>
<td>Stearic acid</td>
</tr>
<tr>
<td></td>
<td>N-Tridecane</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fraction 60-64</th>
<th>Fraction 166-185</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic acid</td>
<td>Glycerol</td>
</tr>
<tr>
<td>Urea</td>
<td>Benzoic acid</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>Phosphate</td>
</tr>
<tr>
<td>4-Pyridoxic acid</td>
<td>Pentadecane</td>
</tr>
<tr>
<td></td>
<td>Stearic acid</td>
</tr>
<tr>
<td></td>
<td>N-Tridecane</td>
</tr>
</tbody>
</table>
Fig. 6. Chromatogram of uv-absorbing constituents in secondary effluent disinfected by bromine chloride.
Table 7. Identity of nonvolatile organic compounds found in fractions of bromochlorinated sewage effluent.

<table>
<thead>
<tr>
<th>Fraction 7-9</th>
<th>Fraction 66-72</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl-a.-mercaptoacetate</td>
<td>Urea</td>
</tr>
<tr>
<td>Glycerol</td>
<td>Phosphate</td>
</tr>
<tr>
<td>Fraction 10-12</td>
<td>Fraction 73-80</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>Lactic acid</td>
</tr>
<tr>
<td></td>
<td>Benzoic acid</td>
</tr>
<tr>
<td></td>
<td>Phosphate</td>
</tr>
<tr>
<td></td>
<td>Nordodecane</td>
</tr>
<tr>
<td></td>
<td>Nonadecane</td>
</tr>
<tr>
<td></td>
<td>Nitrophenyl butyrate</td>
</tr>
<tr>
<td></td>
<td>Diethyl-o-phthalate</td>
</tr>
<tr>
<td>Fraction 13-16</td>
<td>Fraction 142-160</td>
</tr>
<tr>
<td>o-Hydroxybutyric acid</td>
<td>o-Decylhydroxylamine</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>2-Propyl-1-heptanol</td>
</tr>
<tr>
<td>Inositol</td>
<td>2,6-Ditertbutyl-4-methylphenol</td>
</tr>
<tr>
<td></td>
<td>Nordodecane</td>
</tr>
<tr>
<td></td>
<td>2,2,3,3-Tetramethylhexane</td>
</tr>
<tr>
<td></td>
<td>Diethyl phthalate</td>
</tr>
<tr>
<td></td>
<td>Di-n-butyl-3-methylglutarate</td>
</tr>
<tr>
<td></td>
<td>Thymol</td>
</tr>
<tr>
<td>Fraction 17-19</td>
<td>Fraction 184-197</td>
</tr>
<tr>
<td>o-Hydroxybutyric acid</td>
<td>Benzoic acid</td>
</tr>
<tr>
<td>Glycerol</td>
<td>2-Propyl-1-heptanol</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>o-Decylhydroxylamine</td>
</tr>
<tr>
<td>Threitol</td>
<td>Dodecane</td>
</tr>
<tr>
<td>Glucitol</td>
<td>2,6-Ditertbutyl-4-methylphenol</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>Nordodecane</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>Diethyl phthalate</td>
</tr>
<tr>
<td></td>
<td>Di-n-butyl-3-methylglutarate</td>
</tr>
<tr>
<td></td>
<td>Perillen</td>
</tr>
<tr>
<td>Fraction 20-22</td>
<td>Fraction 225-240</td>
</tr>
<tr>
<td>o-Hydroxybutyric acid</td>
<td>3-Methyl-1,2-cyclopentanediol</td>
</tr>
<tr>
<td>Glycerol</td>
<td>2-Propyl-1-heptanol</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>4,8-Dimethylundecane</td>
</tr>
<tr>
<td>2-Hydroxyisobutyric acid</td>
<td>Diethyl phthalate</td>
</tr>
<tr>
<td>Xylose</td>
<td>Nordodecane</td>
</tr>
<tr>
<td>Lauric acid</td>
<td>Di-n-butyl-3-methylglutarate</td>
</tr>
<tr>
<td>Myristic acid</td>
<td>Nordodecane</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>Diethyl phthalate</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>Di-n-butyl-3-methylglutarate</td>
</tr>
<tr>
<td></td>
<td>Perillen</td>
</tr>
<tr>
<td>Fraction 25-26</td>
<td>Fraction 241-260</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>Benzoic acid</td>
</tr>
<tr>
<td>Glycerol</td>
<td>3,5,5-Trimethylhexanol</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>Nordonane</td>
</tr>
<tr>
<td>2-Hydroxyisobutyric acid</td>
<td>2-6-Ditertbutyl-4-methylphenol</td>
</tr>
<tr>
<td>2-Hydroxyisobutyric acid</td>
<td>Diethyl phthalate</td>
</tr>
<tr>
<td>Xylose</td>
<td>Diisobutyl adipate</td>
</tr>
<tr>
<td>Lauric acid</td>
<td>Pentyhexadecane</td>
</tr>
<tr>
<td>Myristic acid</td>
<td>Butyl carbobutoxymethyl phthalate</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td></td>
</tr>
<tr>
<td>Stearic acid</td>
<td></td>
</tr>
<tr>
<td>Fraction 27-31</td>
<td></td>
</tr>
<tr>
<td>Glycerol</td>
<td></td>
</tr>
<tr>
<td>Phosphate</td>
<td></td>
</tr>
<tr>
<td>Malic acid</td>
<td></td>
</tr>
<tr>
<td>Glucitol</td>
<td></td>
</tr>
<tr>
<td>Palmitic acid</td>
<td></td>
</tr>
<tr>
<td>Stearic acid</td>
<td></td>
</tr>
<tr>
<td>Fraction 44-48</td>
<td></td>
</tr>
<tr>
<td>Lactic acid</td>
<td></td>
</tr>
<tr>
<td>1,3-Propanediol</td>
<td></td>
</tr>
<tr>
<td>Phosphate</td>
<td></td>
</tr>
<tr>
<td>Oxalic acid</td>
<td></td>
</tr>
<tr>
<td>Palmitic acid</td>
<td></td>
</tr>
<tr>
<td>Fraction 52-57</td>
<td></td>
</tr>
<tr>
<td>Benzoic acid</td>
<td></td>
</tr>
<tr>
<td>2-6-Ditertbutyl-4-methylphenol</td>
<td>Diethyl phthalate</td>
</tr>
<tr>
<td>Diethyl phthalate</td>
<td></td>
</tr>
<tr>
<td>Diisobutyl adipate</td>
<td></td>
</tr>
<tr>
<td>Pentyhexadecane</td>
<td></td>
</tr>
<tr>
<td>Butyl carbobutoxymethyl phthalate</td>
<td></td>
</tr>
</tbody>
</table>
Gas chromatography. In addition to the GC/MS analysis, each fraction was analyzed by gas chromatography. Several compounds were tentatively identified by comparison of retention times with reference standards (Table 8). These are considered tentative identifications because in most cases mass spectral confirmation was not obtained. A typical gas chromatogram resulting from the analysis of a single HPLC fraction after derivatization is shown in Figure 7.
Table 8. Constituents in nondisinfected (control), chlorinated and bromochlorinated wastewater effluents. Tentative identifications based on HPLC (anion exchange) elution position and gas chromatographic (OV-1 and OV-17 packed columns) retention position.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>HPLC fractions in control effluent</th>
<th>HPLC fractions in chlorinated effluent</th>
<th>HPLC fractions in bromochlorinated effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Hydroxyphenylacetic acid</td>
<td>7-10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>7-10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-Methoxyphenylacetic acid</td>
<td>7-10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Methylhistidine</td>
<td>7-10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Methoxyphenyl-propionic acid</td>
<td>7-10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arabitol</td>
<td>7-10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Urea</td>
<td>7-10, 11-15</td>
<td>10-12</td>
<td></td>
</tr>
<tr>
<td>Melatonin</td>
<td>7-10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Methylhistamine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fucose</td>
<td>16-20</td>
<td>17-24</td>
<td>10-12, 25-26</td>
</tr>
<tr>
<td>Leucine</td>
<td>11-15</td>
<td>11-15</td>
<td>13-16</td>
</tr>
<tr>
<td>5,6-Dihydroxyuracil</td>
<td>11-15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Thiouracil</td>
<td>11-15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glucuronic acid</td>
<td>11-15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,5-Dihydroxybenzaldehyde</td>
<td>11-15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Asparagine</td>
<td>11-15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Methylglucoside</td>
<td>11-15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3-Dimethylxanthine</td>
<td>11-15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonate</td>
<td>11-15</td>
<td></td>
<td>13-16</td>
</tr>
<tr>
<td>Fructose</td>
<td>11-15</td>
<td></td>
<td>13-16</td>
</tr>
<tr>
<td>Quinoline-5-aldehyde</td>
<td>11-15</td>
<td></td>
<td>13-16</td>
</tr>
<tr>
<td>Alanine</td>
<td>16-20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>l-Aminobutyric acid</td>
<td>16-20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Homoveratic acid</td>
<td>16-20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-Methyl adenine</td>
<td>16-20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glutamine</td>
<td>16-20</td>
<td>17-24, 36-43</td>
<td>36-43</td>
</tr>
<tr>
<td>Sorbose</td>
<td>16-20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Constituent</td>
<td>HPLC fractions in control effluent&lt;sup&gt;1&lt;/sup&gt;</td>
<td>HPLC fractions in chlorinated effluent&lt;sup&gt;2&lt;/sup&gt;</td>
<td>HPLC fractions in bromochlorinated effluent&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>-----------------------------------------</td>
<td>-----------------------------------------------</td>
<td>-------------------------------------------------</td>
<td>----------------------------------------------------------</td>
</tr>
<tr>
<td>Lysine</td>
<td>16-20</td>
<td>17-24, 25-35</td>
<td>20-22</td>
</tr>
<tr>
<td>Cystine</td>
<td>16-20</td>
<td></td>
<td>25-26</td>
</tr>
<tr>
<td>Asparagine</td>
<td>16-20</td>
<td></td>
<td>81-100</td>
</tr>
<tr>
<td>Proline</td>
<td></td>
<td></td>
<td>27-31</td>
</tr>
<tr>
<td>3-Methoxy-4-hydroxyphenyl-ethylamine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzoic acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-Pyridoxic acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sucrose</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tartaric acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aconitic acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tyramine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-Hydroxytryptophol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Histidine</td>
<td>21-29</td>
<td>25-35</td>
<td>27-31</td>
</tr>
<tr>
<td>Glutamic acid</td>
<td>21-29</td>
<td>25-35</td>
<td>27-31</td>
</tr>
<tr>
<td>Mannitol</td>
<td>21-29</td>
<td>25-35</td>
<td>27-31</td>
</tr>
<tr>
<td>1-Methylxanthine</td>
<td>21-29</td>
<td>25-35</td>
<td>27-31</td>
</tr>
<tr>
<td>N-Acetylmannosamine</td>
<td>21-29</td>
<td>25-35</td>
<td>27-31</td>
</tr>
<tr>
<td>Pyruvic acid</td>
<td></td>
<td></td>
<td>27-31</td>
</tr>
<tr>
<td>2-Mercaptopropionic acid</td>
<td></td>
<td></td>
<td>27-31</td>
</tr>
<tr>
<td>5-Methylcytosine</td>
<td></td>
<td></td>
<td>27-31</td>
</tr>
<tr>
<td>Ribose</td>
<td></td>
<td></td>
<td>27-31</td>
</tr>
<tr>
<td>Quinaldic acid</td>
<td></td>
<td></td>
<td>27-31</td>
</tr>
<tr>
<td>Cysteic acid</td>
<td></td>
<td></td>
<td>27-31</td>
</tr>
<tr>
<td>Cytidine</td>
<td></td>
<td></td>
<td>27-31</td>
</tr>
<tr>
<td>2-Hydroxypurine</td>
<td></td>
<td></td>
<td>27-31</td>
</tr>
<tr>
<td>3,4-Dideoxypentonic acid</td>
<td></td>
<td></td>
<td>27-31</td>
</tr>
<tr>
<td>2-Hydroxycinnamic acid</td>
<td></td>
<td></td>
<td>27-31</td>
</tr>
<tr>
<td>2-Hydroxycinnamic acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Constituent</td>
<td>HPLC fractions in control effluent</td>
<td>HPLC fractions in chlorinated effluent</td>
<td>HPLC fractions in bromochlorinated effluent</td>
</tr>
<tr>
<td>--------------------------------------------</td>
<td>-----------------------------------</td>
<td>--------------------------------------</td>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>N-Methyl-4-aminobenzoic acid</td>
<td>33-39</td>
<td>44-50</td>
<td></td>
</tr>
<tr>
<td>Glycolic acid</td>
<td>40-44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-Methyl-2-aminobenzoic acid</td>
<td>45-47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-Hydroxyuridine</td>
<td>45-47</td>
<td></td>
<td>36-43, 44-50</td>
</tr>
<tr>
<td>Phenylacetamide</td>
<td></td>
<td>36-43</td>
<td></td>
</tr>
<tr>
<td>Glucopyranolactone</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Methyluracil</td>
<td></td>
<td>36-43</td>
<td></td>
</tr>
<tr>
<td>4-Acetylbenzoic acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ketoglutaric acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Picolinic acid</td>
<td>44-50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mandelic acid</td>
<td>44-50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Hydroxybenzaldehyde</td>
<td>44-50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8-Hydroxyquinoline</td>
<td></td>
<td></td>
<td>44-48</td>
</tr>
<tr>
<td>2,5-Dihydroxybenzaldehyde</td>
<td></td>
<td></td>
<td>44-48</td>
</tr>
<tr>
<td>Hydantoin-5-acetic acid</td>
<td></td>
<td></td>
<td>44-48</td>
</tr>
<tr>
<td>Isoleucine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-Methoxycinnamic acid</td>
<td>48-50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Methylxanthine</td>
<td>48-50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Methylxanthine</td>
<td>48-50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Malonic acid</td>
<td>51-61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Methylaminobenzyl alcohol</td>
<td>51-61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7-Methylguanine</td>
<td>51-61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7-Methyluric acid</td>
<td>51-61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glyoxylic acid</td>
<td></td>
<td></td>
<td>60-64</td>
</tr>
<tr>
<td>Inosine</td>
<td>62-69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stearic acid</td>
<td>78-36, 99-100</td>
<td>78-36, 99-110</td>
<td>65-68, 81-100</td>
</tr>
<tr>
<td>Adipic acid</td>
<td>76-86</td>
<td></td>
<td>166-185</td>
</tr>
<tr>
<td>Adenosine</td>
<td>76-86</td>
<td></td>
<td>81-100</td>
</tr>
</tbody>
</table>
Table 8 (concluded)

<table>
<thead>
<tr>
<th>Constituent</th>
<th>HPLC fractions in control effluent&lt;sup&gt;1&lt;/sup&gt;</th>
<th>HPLC fractions in chlorinated effluent&lt;sup&gt;2&lt;/sup&gt;</th>
<th>HPLC fractions in bromochlorinated effluent&lt;sup&gt;3&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Aminobenzoic acid</td>
<td>99-110</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Methoxyphenylpropionic acid</td>
<td>99-110</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Caffeine</td>
<td>99-110</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>123-142</td>
<td>81-100</td>
<td>142-160</td>
</tr>
<tr>
<td>1-Methylindole</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td></td>
<td>146-165</td>
<td></td>
</tr>
<tr>
<td>Phosphate</td>
<td></td>
<td>146-175,166-185</td>
<td></td>
</tr>
<tr>
<td>Indole propionic acid</td>
<td></td>
<td>166-185</td>
<td></td>
</tr>
<tr>
<td>2-Acetoxybenzoic acid</td>
<td></td>
<td></td>
<td>241-260</td>
</tr>
</tbody>
</table>

1 Fractions are indicated on Fig. 3.

2 Fractions are indicated on Fig. 4.

3 Fractions are indicated on Fig. 5.
Fig. 7. Typical gas chromatogram from single derivatized high-pressure liquid chromatography fraction.
VI. DISCUSSION

The amounts of trihalomethane produced in the halogenation process were extremely small. In the chlorination process, only 0.09% (by weight) of the chlorine applied is accounted for as chloroform in the effluent. The yield of bromoform after bromochlorination is four times greater or 0.37% of the bromine chloride applied.

Upon chlorination of the sewage effluent, the principal chlorine constituents expected are hypochlorous acid, hypochlorite ion, and monochloramine (White, 1972). Under the operating conditions at the time of sampling, the first two forms would be expected to react almost instantaneously to produce monochloramine although the residual analyses were not performed to discriminate between "free" and "combined" residuals. Monochloramine is not usually considered a strong oxidizing agent. Thus only in the immediate vicinity of the injector would sufficient reactive chlorine be available to produce chloroform.

After bromochlorination, the principal residuals expected are hypobromous acid, hypobromite ion, and dibromamine (Mills, 1975). All of these compounds are strong oxidizing agents and presumably capable of reacting with organic compounds to produce bromoform. Presumably this greater reactivity of the principal bromine residuals accounts for the increased yield of trihalomethane after bromochlorination.

At the James River Sewage Treatment Plant, the initial dilution rate for the effluent entering the river is 20:1 which would result in
estuarine concentrations of 0.4 µg/l chloroform or 0.6 µg/l bromoform. Bieri et al. (1980) have reported that trihalomethane concentrations in the James River are generally less than 0.1 µg/l. However, chloroform concentrations at a station adjacent to the JRSTP outfall sometimes reach 0.6 µg/l. No bromoform was observed at this station. However, in this study Bieri et al. (1980) did observe similar levels of bromoform in the vicinity of electricity generating plants including the VEPCO plant at Yorktown, Virginia (0.6 µg/l) and the PEPCO plant at Morgantown, Maryland (7.2 µg/l maximum). Production of bromoform in these cases presumably results from initial rapid reaction of chlorine with the bromide in saline waters followed by reaction of the bromine produced with dissolved organic compounds. While bromoform was not expected or observed near the outfall of any sewage treatment plant following chlorination, it would be expected at sewage treatment plants following bromochlorination.

The toxicity of trihalomethanes to marine organisms is apparently unknown and only a small amount of data exists for freshwater species. Birge et al. (1979) reported a LC50 for hatching of rainbow trout eggs exposed to chloroform (flow-through system) of 2.03 mg/l (soft water) and 1.24 mg/l (hard water). Larvae were unaffected when exposed for an additional 96 hrs. Recently LeBlanc (1980) reported 24 hr and 48 hr LC50's for the water flea *Daphnia magna* exposed to chloroform and bromoform (static system). The values for *Daphnia magna* were an order of magnitude or more, higher than those for trout eggs. The 24 hr and 48 hr LC50 for *D. magna* exposed to chloroform were both 29 mg/l, those to bromoform were 56 and 46 mg/l, respectively.
Trabalka and Burch (1978) reported a 96 hr LC50 for *Daphnia pulex* exposed to bromoform of 44 mg/l. The difference in toxicity between trout and *Daphnia* may be largely due to the difference in test methods since both compounds are highly volatile. The difference may also reflect the use of measured chloroform concentration (Birge *et al.*, 1979) versus nominal concentration (LeBlanc, 1980; Trabalka and Burch, 1978).

If one assumes that marine species have sensitivity to chloroform and bromoform similar to that of freshwater species, one would expect an LC50 between 1 and 100 mg/l. These concentrations are 10,000 to 1,000,000 times higher than the concentrations expected in receiving waters immediately adjacent to the JRSTP outfall.

No halogenated high molecular weight compounds were detected in any samples. This was either because such halogenated compounds were not present in large enough concentrations to be detected by the mass spectrometer or they were sufficiently nonvolatile even after derivatization that they were not detected by the mass spectrometer.

The reason for the almost ubiquitous presence of benzoic acid in the eluate fractions from the high molecular weight constituent analyses is not known at this time. This phenomenon may result from the degradation of a larger molecular complex during derivatization with the silylating reagent. Thus, many of the uv-absorbing constituents separated by HPLC may actually represent larger molecular complexes containing simpler moieties such as benzoic acid, stearic acid, palmitic acid, etc. This phenomenon has been observed before in
the analysis of natural and highly polluted waters. The phenomenon is not believed to be attributable to microbial action on the constituents because each eluate fraction is frozen, processed, lyophilized while in the frozen state, and stored when dry at -20°C or as a methanol solution at 0°C. Under these conditions, microbial action on the chromatographic constituents is not anticipated.
LITERATURE CITED


Roberts, M. H., Jr. 1978. Effects of chlorinated sea water on
and D. H. Hamilton, Jr. (eds.), Water Chlorination:
Science Publ. Inc., Ann Arbor, MI.

xanthurus*) exposed to bromochlorinated and chlorinated sewage in

Roberts, M. H., Jr. 1980b. A flow-through toxicity testing system
for molluscan larvae as applied to halogen toxicity in estuarine
Testing Materials, Philadelphia, PA.

Roberts, M. H., Jr. 1980c. Detoxification of chlorinated sewage
effluent by dechlorination in estuarine water. Estuaries
3:184-191.

Roberts, M. H., Jr., R. J. Diaz, M. E. Bender and R. J. Huggett.
1975. Acute toxicity of chlorine to selected estuarine species.

Roberts, M. H., Jr. and R. A. Gleeson. 1978. Acute toxicity of
bromochlorinated seawater to selected estuarine species with a
comparison to chlorinated seawater toxicity. Mar. Environ. Res.
1:19-30.


