TENNESSEE VALLEY AUTHORITY
KNOXVILLE, TENNESSEE 37902

MAR 30 1988

Mr. Ralph M. Sinclair
Manager, Permits Section
Tennessee Department of Health
and Environment
TERRA Building
150 Ninth Avenue, North
Nashville, Tennessee 37219-5404

Dear Mr. Sinclair:

SEQUOYAH NUCLEAR PLANT (SQN) - NPDES PERMIT NO. TN0026450 - NOTIFICATION OF USE OF CHLORINE/BROMINE TO CONTROL BIOFOULING

In accordance with Part III.D. of the NPDES permit, this is notification that TVA proposes to begin adding sodium bromide in addition to sodium hypochlorite to the essential raw cooling water (ERCW) system at SQN. In the past, sodium hypochlorite has been added to the ERCW system to control clams. TVA now believes it is necessary to treat the ERCW system to control biofouling and mitigate microbiologically induced corrosion (MIC). TVA proposes to use a chlorine-bromine mixture applied to the ERCW system continuously, year round. Industry experience has shown that a chlorine-bromine mixture is a more effective biocide than chlorine alone. Like chlorine, the bromine combines with organics to form bromamines, which are effective biocides and are less persistent than the chlorinated organics (chloramines) in the environment. The addition of bromine also reduces the amount of chlorine that is needed to provide the desired results. Therefore, the use of bromine reduces the total residual chlorine (TRC) and aids in compliance with the NPDES permit. In addition to the chlorine-bromine mixture, a biodispersant may also be added to increase penetration of the biofilm and thus make the biocide more effective.

TVA will likely contract with one of the following companies: NALCO, Betz Laboratories, or Calgon to supply the chlorine, bromine, and biodispersant chemicals; assist with the feeding of these chemicals into the ERCW system; and determine the effectiveness of the treatment program. The chlorine-bromine biodispersant can be applied in a premixed form or the chemicals can be added individually to obtain the desired mixture. The actual forms used will depend on which vendor is selected. The following products are being considered:

1. NALCO Company's Acti-brom 1338--Acti-brom 1338 is an aqueous solution containing sodium bromide and a biodispersant. Acti-brom 1338 would be injected simultaneously with sodium hypochlorite to obtain the desired bromine-chlorine mixture in the ERCW system.

2. Betz Laboratories' Slimicide C-78P--Slimicide C-78P is an organic granular material (bromochlorodimethyl hydantoin), that when dissolved in water releases both chlorine and bromine. No additional sodium hypochlorite is needed with this product.

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Betz Laboratories' Slimicide C-82--Slimicide C-82 is an aqueous solution of sodium bromide. It would be injected simultaneously with sodium hypochlorite to obtain the desired bromine-chlorine mixture in the ERCW system. This is an alternative to Betz Laboratories' Slimicide C-78P.

If this treatment is not fully effective, Betz Powerline 3690, a biodispersant, may also be used.

3. Calgon's H950--H950 is an aqueous solution of sodium bromide. H950 would be injected simultaneously with sodium hypochlorite to obtain the desired bromine-chlorine mixture in the ERCW system.

   If this treatment is not fully effective, Calgon's CL-361, a surfactant, or TRC 233, a biodispersant, may also be injected.

Product-specific information provided by the vendors are given in Enclosures 1 through 6. Included with this information is the name and general composition of each product, toxicity data, recommended dosages, users of the product, and EPA registration number, if applicable. Additional toxicity information compiled from the literature on chlorine-bromine mixtures is given in Enclosure 7.

TVA proposes to upgrade the present sodium hypochlorite feed system; the present system is unreliable and equipment problems have led to ineffective treatment. TVA also proposes to install a product-specific feed system for the bromide product ultimately selected. This will enable the feed rates for these chemicals to be closely controlled. Until permanent feed systems can be designed and installed, TVA plans to contract with one of the above-mentioned vendors for skid-mounted feed systems on a rental basis.

Actual dosage rates of sodium bromine and sodium hypochlorite are not known at this time. The specific dosages will vary depending upon the product selected, the number of ERCW pumps in operation, the water chemistry, and the severity of the biofouling. However, addition of the chlorine/bromine will be controlled such that the resulting TRC concentration in the diffuser discharge to the Tennessee River will not exceed 0.1 milligram per liter (mg/L). To help ensure that effective treatment is being provided and excess chemical is not added, the TRC level and microbiological activity will be monitored at various points within the ERCW system. The results of this monitoring program will be used to minimize chemical usage and serve as an operational control to avoid exceedances of the TRC effluent limitation established in the NPDES permit. If a biodispersant or surfactant is necessary for effective treatment, those additives would be fed at a rate of 3 to 10 mg/L depending on product selected and would pose no environmental threat due to low toxicity (as referenced in the enclosed literature).

Mr. Ralph M. Sinclair

The initial goal will be to provide enough chlorine/bromine to maintain a 0.5 to 0.7 mg/L total halogen residual at the ERCW heat exchangers. Once a vendor has been selected and a product-specific dosage rate determined, your office will be provided more specific data on the dosage rates. For example, Calgon estimates that the H-950 consumption would range from 32 to 190 pounds per day per ERCW pump in operation (ERCW pump rated at 9.85 MGD), depending on the feed ratio necessary to control the microbiological population, assuming an average chlorine demand of 0.4 mg/L, and maintaining a free residual of 0.5 to 0.7 mg/L total halogen. The estimated dosage rate for the Calgon product is considered representative of the dosage rate that would be required for any of the other products. Of course, variability in the dosage rate will occur depending on the concentration of bromine and chlorine in the specific product.

TVA requests that this information be made a part of the permit application for renewal of the SQN NPDES permit submitted October 1, 1987. TVA further requests that SQN be permitted to continuously inject chlorine, bromine, and biodispersant (from the list above) year round into the ERCW system for clam control and prevention/mitigation of microbiologically induced corrosion with the following effluent limitation and monitoring requirement: TRC of 0.1 mg/L at the diffuser discharge measured by multiple grab sample once per day. Multiple grab sample shall be defined as not less than four equally spaced grab samples during a one-hour period.

From discussions with your staff, we understand that when the permit is reissued, toxicity testing of the plant effluent will most likely be required on a seasonal basis. We propose to begin toxicity testing of the diffuser discharge shortly after the bromine/chlorine treatment begins. We will provide a copy of the toxicity testing procedures for your approval prior to initiating the tests.

The skid-mounted system for chlorine addition should be installed in time to began treatment for clam control later this spring. TVA would like to install the skid-mounted, bromine and biodispersant feed system so that treatment for MIC can begin as soon as possible. Therefore, we request that the permit be renewed or modified by July 1 to allow for the treatment of the ERCW system as described herein.

If your staff needs additional information or has any questions regarding this request, please have them call Madonna E. Martin at (615) 632-6695 in Knoxville.

Sincerely,

ORIGINAL SIGNED BY
RALPH H. BROOKS
Ralph H. Brooks, Director
Environmental Quality

Enclosures
cc: See page 4

MAR 3 0 1988

Mr. Ralph M. Sinclair

cc (Enclosures):

Mr. K. P. Barr, Acting Assistant Director
for Inspection Programs
TVA Projects Division
U.S. Nuclear Regulatory Commission
Region II
101 Marietta Street, NW., Suite 2900
Atlanta, Georgia 30323

Mr. Bruce R. Barrett, Director
Water Management Division
U.S. Environmental Protection
Agency, Region IV
345 Courtland Street, NE.
Atlanta, Georgia 30365

U.S. Nuclear Regulatory Commission
Attention: Document Control Desk
Washington, D.C. 20555

Mr. Philip L. Stewart, Manager
Chattanooga Field Office
Division of Water Pollution Control
2501 Milne Street
Chattanooga, Tennessee 37406-3399

Mr. G. G. Zech, Assistant Director
for Projects
TVA Projects Division
U.S. Nuclear Regulatory Commission
One White Flint, North
11555 Rockville Pike
Rockville, Maryland 20852

ENCLOSURE 1

Product Information for NALCO Company's

Acti-brom 1338

(This information was provided by NALCO for TVA's use in obtaining regulatory approval for the use of the specific product.)

EPA Registration Number: The EPA registration number for Acti-brom in recirculating systems is 1706-168. NALCO expects approval for the registration number for once-through systems any day.

NALCO

AQUATIC TOXICITY SUMMARY

ACTI-BROM 1338

The acute 96 hour static LC_{50} of Acti-Brom 1338 for the Rainbow Trout and Bluegill Sunfish was found to be greater than 1000 mg/L (ppm) for both species.

Corresponding 24 and 48 hour LC_{50}'s for Rainbow Trout were also greater than 1000 mg/L, respectively.

For Bluegill Sunfish the 24 and 48 hour LC_{50} values were also greater than 1000 mg/L.

The 96 hour observable no effect concentration noted for both Rainbow Trout and Bluegill Sunfish was 1000 mg/L.

Estimated Toxicity Rating = Essentially Non-Toxic

Respectfully submitted,

Claude H. Wolf
Corporate Toxicologist
March 1984
ABC/EH&S 279/F7903/84A209

Form 179

MATERIAL SAFETY DATA SHEET

NALCO

PRODUCT ACTI-BROM 1338 BIODISPERSANT

Emergency Telephone Number

Medical (312) 920-1510 (24 hours)

SECTION 1 PRODUCT IDENTIFICATION

TRADE NAME: ACTI-BROM 1338 BIODISPERSANT
DESCRIPTION: An aqueous solution of bromide salt and an oxyalkylate

NFPA 704M RATING 1 HEALTH 1 FLAMMABILITY 0 REACTIVITY 0 OTHER
0=Insignificant 1=Slight 2=Moderate 3=High 4=Extreme

SECTION 2 HAZARDOUS INGREDIENTS

Our hazard evaluation has identified the following chemical ingredient(s) as hazardous under OSHA's Hazard Communication Rule, 29 CFR 1910.1200. Consult Section 14 for the nature of the hazard(s).

INGREDIENT(S)	CAS #	APPROX.%
Sodium bromide	7647-15-6	40+

SECTION 3 PRECAUTIONARY LABEL INFORMATION

WARNING: Causes eye injury and skin irritation. Do not get in eyes. Avoid contact with skin and clothing. Wear goggles or face shield when handling. Avoid prolonged or repeated breathing of vapor. Use with adequate ventilation. Do not take internally.

Empty containers may contain residual product. Do not reuse container unless properly reconditioned.

SECTION 4 FIRST AID INFORMATION

EYES: Flush with water for 15 minutes. Call a physician.
SKIN: Wash thoroughly with soap and rinse with water. Call a physician.

NOTE TO PHYSICIAN: No specific antidote is known. Based on the individual reactions of the patient, the physician's judgment should be used to control symptoms and clinical condition.

CAUTION: If unconscious, having trouble breathing or in convulsions, do not induce vomiting or give water.

SECTION 5 HEALTH EFFECTS INFORMATION

PRIMARY ROUTE(S) OF EXPOSURE: Eye, Skin

EYE CONTACT: Can cause transient to moderate irritation.

NALCO CHEMICAL COMPANY ONE NALCO CENTER • NAPERVILLE, ILLINOIS 60566-1024
AREA 312-961-9500

SECTION 5 HEALTH EFFECTS INFORMATION (CONTINUED)

SKIN CONTACT: May cause irritation with prolonged contact.

SYMPTOMS OF EXPOSURE: A review of available data does not identify any symptoms from exposure.

AGGRAVATION OF EXISTING CONDITIONS: A review of available data does not identify any worsening of existing conditions.

SECTION 6 TOXICOLOGY INFORMATION

ACUTE TOXICITY STUDIES: Acute toxicity studies have been conducted on this product along with acute toxicity studies on the hazardous ingredient(s) in Section 2. The results are shown below.

PRIMARY EYE IRRITATION TEST (ALBINO RABBITS):
EYE IRRITATION INDEX DRAIZE RATING: 10.8/110.0 Minimally irritating

COMMENTS: No corneal opacity was noted. Iridial irritation which cleared three days after contact was noted. Slight to moderate conjunctivitis which cleared 7 days after contact was also noted. Results suggest transient irritation.

OTHER TOXICITY RESULTS:
Sodium bromide LD50 oral in rats is believed to be between 3,500 and 5,000 mg/kg.

SECTION 7 PHYSICAL AND CHEMICAL PROPERTIES

COLOR: Colorless	FORM: Liquid	ODOR: None
DENSITY:	12.2 lbs/gal.	
SOLUBILITY IN WATER:	Completely	
SPECIFIC GRAVITY:	1.46 @ 60 Degrees F	ASTM D-1298
pH (NEAT) =	7.1	ASTM E-70
VISCOSITY:	5 cps @ 72 Degrees F	ASTM D-2983
FREEZE POINT:	16 Degrees F	ASTM D-1177
FLASH POINT:	None (PMCC)	ASTM D-93

NOTE: These physical properties are typical values for this product.

SECTION 8 FIRE AND EXPLOSION INFORMATION

FLASH POINT: None (PMCC) ASTM D-93

EXTINGUISHING MEDIA: Not applicable

SECTION 9 REACTIVITY INFORMATION

INCOMPATIBILITY: Avoid contact with strong oxidizers (eg. chlorine, peroxides, chromates, nitric acid, perchlorates, concentrated oxygen, permanganates) which can generate heat, fires, explosions and the release of toxic fumes.

SECTION 10 PERSONAL PROTECTION EQUIPMENT

RESPIRATORY PROTECTION: Respiratory protection is not normally needed since the volatility and toxicity are low. If significant vapors, mists or aerosols are generated, wear a NIOSH approved or equivalent respirator, (ANSI Z 88.2, 1980 for requirements and selection).

For large spills, entry into large tanks, vessels or enclosed small spaces with inadequate ventilation, a pressure-demand, self-contained breathing apparatus is recommended.

VENTILATION: General ventilation is recommended.

PROTECTIVE EQUIPMENT: Use impermeable gloves and chemical splash goggles (ANSI Z 87.1 requirements and selection of gloves, goggles, shoes, etc.) when attaching feeding equipment or doing maintenance.

If clothing is contaminated, remove clothing and thoroughly wash the affected area. Launder contaminated clothing before reuse.

SECTION 11 SPILL AND DISPOSAL INFORMATION

IN CASE OF TRANSPORTATION ACCIDENTS, CALL THE FOLLOWING 24-HOUR TELEPHONE NUMBER (312-920-1510)

SPILL CONTROL AND RECOVERY:

Small liquid spills: Contain with absorbent material, such as saw dust, clay, soil or any commercially available absorbent. Shovel reclaimed liquid and absorbent into recovery or salvage drums for disposal. Refer to CERCLA in Section 14.

Large liquid spills: Dike to prevent further movement and reclaim into recovery or salvage drums or tank truck for disposal. Refer to CERCLA in Section 14.

DISPOSAL: If this product becomes a waste, it does not meet the criteria of a hazardous waste as defined under the Resource Conservation and Recovery Act (RCRA) 40 CFR 261, since it does not have

SECTION 11 SPILL AND DISPOSAL INFORMATION (CONTINUED)

the characteristics of Subpart C, (i.e. D001 through D017) nor is it listed under Subpart D.

As a non-hazardous liquid waste, it should be solidified before disposal to a sanitary landfill. Can be deep-well injected in accordance with local, state and federal regulations.

SECTION 12 ENVIRONMENTAL INFORMATION

AQUATIC DATA:

96 hour static acute LC50 to Bluegill Sunfish = Greater than 1,000 ppm

9- hour no observed effect concentration is 1,000 ppm based on no mortality or abnormal effects.

TOXICITY RATING: Essentially non-toxic

96 hour static acute LC50 to Rainbow Trout = Greater than 1,000 ppm

96 hour no observed effect concentration is 1,000 ppm based on no mortality or abnormal effects.

TOXICITY RATING: Essentially non-toxic

If released into the environment, see CERCLA in Section 14.

SECTION 13 TRANSPORTATION INFORMATION

DOT PROPER SHIPPING NAME/HAZARD CODE - PRODUCT IS NOT REGULATED DURING TRANSPORTATION

SECTION 14 REGULATORY INFORMATION

The following regulations apply to this product.

FEDERAL REGULATIONS:

OSHA'S HAZARD COMMUNICATION RULE, 29 CFR 1910.1200:
Based on our hazard evaluation, the following ingredient in this product is hazardous and the reason is shown below.

Sodium bromide - Eye irritant

NALCO

MATERIAL SAFETY DATA SHEET

PRODUCT ACTI-BROM 1338 BIODISPERSANT

Emergency Telephone Number
Medical (312) 920-1510 (24 hours)

SECTION 14 REGULATORY INFORMATION (CONTINUED)

CERCLA/SUPERFUND, 40 CFR 117, 302:
Notification of spills of this product is not required.

TOXIC SUBSTANCES CONTROL ACT (TSCA):
The chemical ingredients in this product are on the 8(b) Inventory List (40 CFR 710).

RESOURCE CONSERVATION AND RECOVERY ACT (RCRA), 40 CFR 261 SUBPART C & D:
If this product becomes a waste, it does not meet the criteria of a hazardous waste.

FEDERAL WATER POLLUTION CONTROL ACT, CLEAN WATER ACT, 40 CFR 401.15 (formerly Sec. 307), 40 CFR 116 (formerly Sec. 311):
None of the ingredients are specifically listed.

CLEAN AIR ACT, 40 CFR 60, SECTION 111, 40 CFR 61. SECTION 112:
This product does not contain ingredients covered by the Clean Air Act.

STATE REGULATIONS:

MICHIGAN CRITICAL MATERIALS:
This product does not contain ingredients listed on the Michigan Critical Materials Register.

STATE RIGHT TO KNOW LAWS:
This product does not contain ingredients listed by State Right To Know laws.

SECTION 15 ADDITIONAL INFORMATION

None

SECTION 16 USER'S RESPONSIBILITY

This product material safety data sheet provides health and safety information. The product is to be used in applications consistent with our product literature. Individuals handling this product should be informed of the recommended safety precautions and should have access to this information. For any other uses, exposures should be evaluated so that appropriate handling practices and training programs can be established to ensure safe workplace operations. Please consult your local sales representative for any further information.

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AREA 312-961-9500

MATERIAL SAFETY DATA SHEET

NALCO

PRODUCT ACTI-BROM 1338 BIODISPERSANT

Emergency Telephone Number
Medical (312) 920-1510 (24 hours)

SECTION 17 BIBLIOGRAPHY

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CASARETT AND DOULL'S TOXICOLOGY, THE BASIC SCIENCE OF POISONS, Doull, J., Klaassen, C. D., and Admur, M. O., eds., Macmillian Publishing Company, Inc., N. Y., 2nd edition, 1980.

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Title 29 Code of Federal Regulations Part 1910, Subpart Z, Toxic and Hazardous Substances, Occupational Safety and Health Administration (OSHA).

THRESHOLD LIMIT VALUES FOR CHEMICAL SUBSTANCES AND PHYSICAL AGENTS IN THE WORKROOM ENVIRONMENT WITH INTENDED CHANGES, American Conference of Governmental Industrial Hygienists, OH.

PREPARED BY: John J. Kasper, MSc., Manager Product Safety
DATE CHANGED: 03/27/86 DATE PRINTED: 09/23/87

NALCO CHEMICAL COMPANY
ONE NALCO CENTER • NAPERVILLE, ILLINOIS 60566-1024 • AREA 312-961-9500

January 14, 1988

Mr. W. A. Nestel
Tennessee Valley Authority
1N 54B Blue Ridge Place
1101 Market St.
Chattanooga, TN 37402-2801

Dear Mr. Nestel:

Thank you for inviting us to the TVA-Sequoyah Plant to discuss Acti-Brom. We enjoyed meeting with all of you.

Listed below are the answers to the questions which came up during our discussions.

7) **The use of bromine chemistry at Alcoa is still in the proposal stage-so there is no reference available. However, bromine chemistry is used at two (2) DuPont plants in the State of Tennessee. The contacts at these plants are:**
   - A) DuPont Chemical Co.- Old Hickory, TN
     Bob Berthold or Terry Barnes (Envir.)
     (615)847-6394
   - B) DuPont Chemical Co. - Memphis, TN
     Larry Hordon or Steve Hodorowsky (Envir.)
     (901)353-7100

If you need any further information, please contact me.

Sincerely,

Sandra M. Koeplin-Gall, Ph.D.
Utility Chemicals Group

SMKG/tlm
Enclosures

Reference List of Nuclear Plants

Using the Nalco Acti-Brom Program

Arizona Nuclear Power Project-Palo Verde Generating Station

Philadelphia Electric Company-Limerick Generating Station

Commonwealth Edison Company-Byron Generating Station

Commonwealth Edison Company-Dresden Generating Station

Houston Light and Power Compnay-South Texas Project

Northern States Power Company-Monticello Generating Station

Note: There are currently over 50 applications of Acti-Brom 1338 at both fossil and nuclear generating stations in the United States.

Utility Chemicals

Product Bulletin

U-1338

NALCO

ACTI-BROM™ 1338

CHLORINE ENHANCER BIODISPERSANT

Product Benefits

- Helps maximize turbine condenser efficiency
- Helps extend condenser tube life
- Can reduce maintenance costs
- Can reduce chlorine residual in the discharge
- Minimizes chlorine usage

Principal Uses

ACTI-BROM 1338 is used to enhance chlorine activity in utility cooling water systems. This product can be particularly useful in situations where biological control cannot be obtained within the legal chlorination time limits or where chlorine residuals are a problem.

General Description

ACTI-BROM 1338 is an aqueous solution containing a bromide salt and biodispersant designed to improve chlorine activity. Since ACTI-BROM 1338 is not a biocide, it is easy to handle and feed.

ACTI-BROM 1338 can be used with either gaseous chlorine or sodium hypochlorite.

Form	Colorless liquid
Density	12.2 lb/gal
ph (Neat)	8.0 (max)
Freeze Point	16°F
Viscosity (@ 72°F)	5 cp
Flash Point (PMCC)	None

Application

ACTI-BROM 1338 should be fed directly from the drum or bulk storage tank to a location in the chlorination system where it will be uniformly mixed and thoroughly distributed. The specific dosage of ACTI-BROM 1338 will vary depending upon the operating characteristics of your system, the water chemistry, and the severity of problems encountered. Your Nalco representative will recommend the optimum dosage necessary to ensure maximum program performance for your system.

ACTI-BROM 1338 is noncorrosive to materials normally used in feeding systems. For specific feeding and material compatibility instructions, consult your Nalco representative.

Handling and Storage

ACTI-BROM 1338 should be handled with caution. Do not get in eyes. Avoid contact with skin and clothing. In case of contact, immediately flush with large amounts of water for at least 15 minutes; for eyes, also get medical attention. Do not take internally. Keep out of reach of children.

Recommended in-plant storage limit is one year.

(Continued on Reverse Side)

NALCO CHEMICAL COMPANY
UTILITY CHEMICALS
ONE NALCO CENTER ◊ NAPERVILLE, ILLINOIS 60566-1024

Shipping

ACTI-BROM 1338 is available in bulk quantities; 55-gallon, non-returnable, lined steel drums weighing approximately 670 pounds net; or returnable stainless steel PORTA-FEED® units with a maximum capacity of 385 gallons.

The product is shipped from the nearest manufacturing or warehousing facility.

Chlorine Minimization with a Chlorine-Bromine-Biodispersant Mixture

NALCO

Reprint 369

Presented at the *American Power Conference*, 46th Annual Meeting,
April 23-25, 1984, Chicago, Illinois

CHLORINE MINIMIZATION WITH A CHLORINE-BROMINE-BIODISPERSANT MIXTURE

F. W. KRAEMER and A.F. GEPHART
Toledo Edison Company, Toledo, OH

S. KOEPLIN-GALL
Nalco Chemical Company

ABSTRACT

Biofouling is a problem in every utility. Toledo Edison-Bayshore Station has investigated several methods of biofouling control. The most effective method was an activated bromide chlorine mixture.

The activated bromide chlorine mixture demonstrates enhanced performance over chlorination alone. The activated bromide mixture is more effective at alkaline pH values than chlorine. It provides similar system performance at lower dosages and shorter treatment time periods than chlorine alone. Field studies have shown an 92% estimated yearly decrease in total oxidant utilizing an activated bromide mixture instead of chlorine alone. In addition, the activated bromide mixture never exceeded a concentration of 0.2 mg/l TRC; whereas, chlorine alone did. Corrosion rates for the activated bromide mixture were similar to chlorine alone, but overall corrosion should be less due to the shorter treatment time.

This paper will discuss the laboratory and field studies performed at Toledo Edison-Bayshore Station to determine the effectiveness of an activated bromide mixture. Studies involving biological control, total residual oxidant determinations and corrosion rates will be addressed.

INTRODUCTION

Fouling caused by microorganisms is a problem in electric utility systems. Extra fuel costs to the electric utility industry due to biofouling have been estimated at $400 million a year. With the costs of plant operation rising at a dramatic rate, any program that improves efficiency needs to be implemented.

The condenser is one largest single area that can affect plant efficiency. The temperatures inside a typical condenser provide an ideal environment for the growth of microorganisms. Even a few thousandths of an inch of slime deposit on a condenser tube — an almost invisible layer — has been shown to affect condenser efficiency, plant heat rate and maintenance costs. The slime layer forms a sticky surface which allows silt and other particles to adhere to the tube surface. In addition to heat transfer losses due to this insulating layer, corrosion and pitting can occur under these deposits, causing long term damage to the system.

Biofouling is generally controlled by chlorination with either gaseous chlorine or liquid sodium hypochlorite. Based upon Federal Power Commission data, about 65% of the 842 steam electric plants in their data base use chlorination for microbiological control. Chlorination practices have come under close scrutiny from the Environmental Protection Agencies due to the toxic by-products which are believed to form. Electric utilities specifically have been singled out for close regulation of their chlorine discharges. This has forced the electric utility industry to look at chlorine minimization and alternatives to chlorine to meet the strict discharge limits while maintaining adequate plant performance.

The Toledo Edison-Bayshore Station began a chlorine minimization program in February of 1976. The Bayshore Station has 4 fossil fueled units. The intake bays are located directly across from the City of Toledo Sewage Treatment Plant. Each unit has a once through condenser which takes water from the Maumee River. Historically, slime and algae growth has been a problem in these condensers. Chlorine was necessary to control the microbiological growth. Analytical data gathered since 1980 have shown typical maximum TRC's of 1 to 3 mg/l.

A chlorine minimization study resulted in a 27% reduction in the pounds of chlorine used per year. However, this reduction did not reduce the Total Residual Chlorine (TRC) value to the 0.2 mg/l, which is specified in USEPA Guidelines. Dechlorination by either sodium sulfite or sulfur dioxide was considered. However, both methods were determined to be too expensive.

Alternatives to chlorination which could reduce the TRC value to 0.2 mg/l were investigated. Chlorine dioxide was tried during 1981. This program proved to be effective but only at a cost equal to four times the current chlorine costs. In addition, high capital expenditures would be needed for a permanent feed installation, and the safety of personnel and plant equipment would be jeopardized. Chlorine dioxide could probably meet

the TRC limits, but at an unjustifiably high cost. Consequently, other alternatives were sought.

A chlorine alternative, which used a chlorine, bromine and biodispersant mixture, was evaluated during 1982. This program is referred to as an activated bromide program since a bromide salt and biodispersant mixture are used in conjunction with chlorine to produce the oxidant species. The biodispersant assists in penetration of the biofilm.

This paper will discuss laboratory and field trial results obtained with the chlorine-bromine biodispersant or activated bromide mixture.

EXPERIMENTAL

Chlorine is used to activate the bromide and biodispersant mixture according to the following reaction:

$$HOCl + Br^- \rightarrow HOBr + Cl^-$$

The chlorine residual to bromide ratio can be varied to obtain a system which contains anywhere from a total bromine residual to a total chlorine residual. This is particularly important in systems with high ammonia levels since bromamines degrade more rapidly, and consequently, are not as persistent in the environment. This reduces the TRC and aids in compliance. Performance is also enhanced since bromamines are known to be more biologically active than chloramines.

Chlorine and bromine residuals can exist as either un-ionized or ionized species in water. The conversion from one species to another is pH dependent. This can be seen in Figure 1.

At pH 7.5, 50% of the available chlorine is HOCl and 50% is OCl^-. As the pH is increased, more ionized OCl^- is present relative to HOCl. OCl^- is known to be only 1/50 to 1/100 as effective a biocide as HOCl. It is important to use the most effective biocide possible, particularly in once-through systems where contact time is limited.

Figure 1 also shows the pH dependence of hypobromous acid. At pH 7.5, over 90% of the oxidant is present as HOBr. At pH 8.7, over 50% of the material is present as the un-ionized acid. There is also evidence that OBr^- is a more effective biocide than OCl^-, which further enhances the effective pH range of bromine residuals. These curves demonstrate that bromine residuals will provide better biocidal performance than chlorine in systems which operate at higher pH values.

Performance data generated in a laboratory compared the biocidal activity of chlorine alone and the activated bromide-chlorine mixture. These data are shown in Figures 2 and 3. At a typical contact time of 15 minutes, it takes 2.5 ppm of chlorine to achieve 0.001% survival. Under the same conditions, it takes only 1.25 ppm of the activated bromide-chlorine mixture.

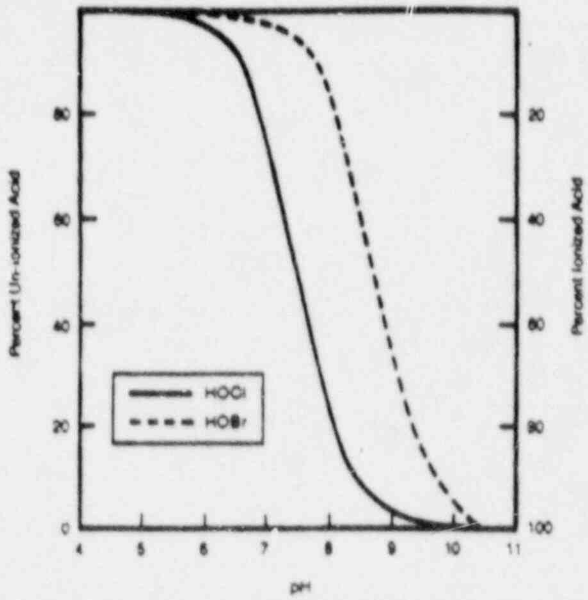


Figure 1 — *Distribution of aqueous chlorine and bromine solutions at various pH values*

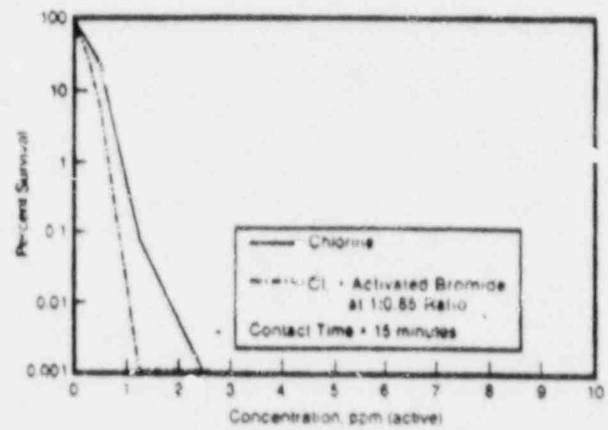


Figure 2 — *Percent survival vs dosage for chlorine and chlorine plus activated bromide after 15 minutes contact time.*

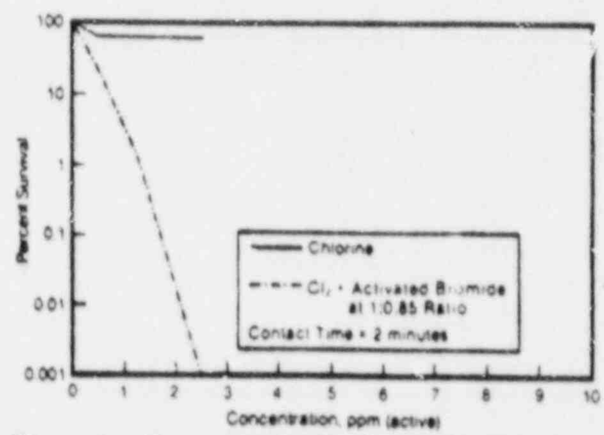


Figure 3 — *Percent survival vs dosage for chlorine and chlorine plus activated bromide after 2 minutes contact time.*

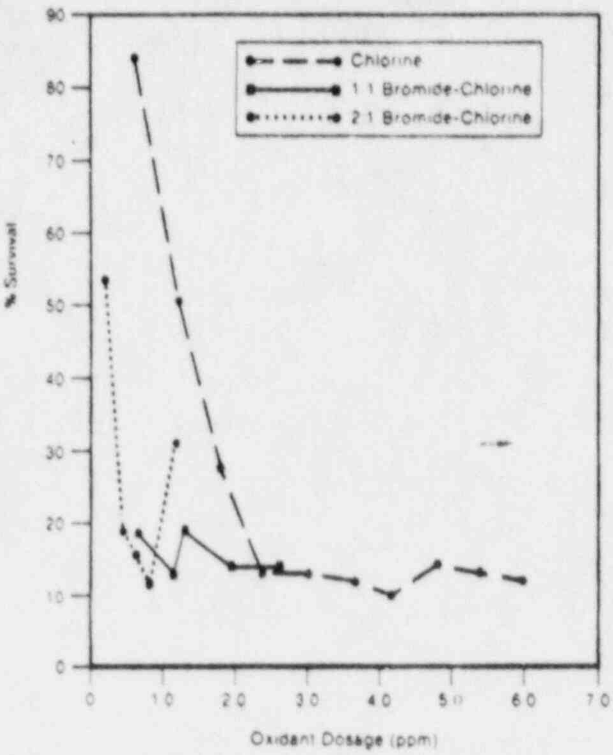


Figure 4 — *Laboratory data from May 10, 1983*

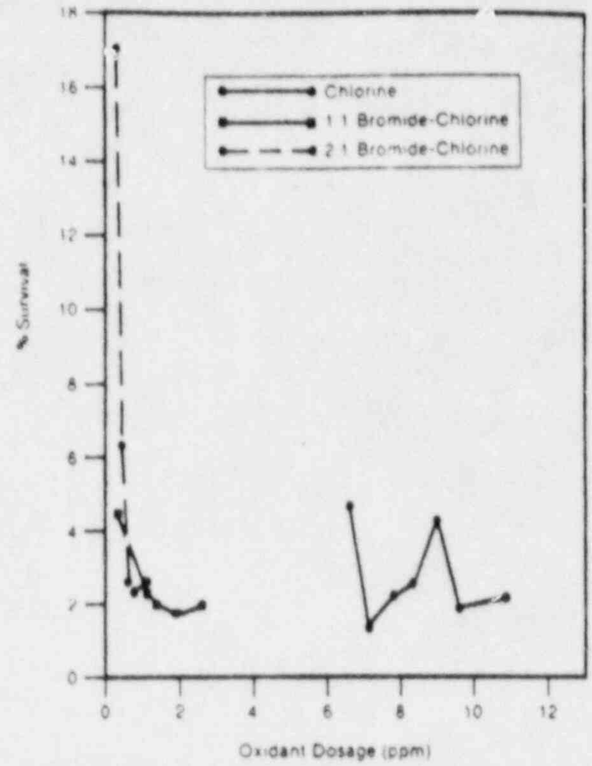


Figure 5 — *Laboratory data from June 7, 1983*

This effect is more pronounced when the contact time is reduced to only 2 minutes. In this situation, a chlorine dosage of 2.5 ppm allowed 75% survival. Under the same conditions, with 2.5 ppm of the activated bromide-chlorine mixture essentially sterile conditions were achieved in only 2 minutes.

As can be seen from these data, the activated bromide-chlorine mixture provides faster kills at lower dosages. For this reason, a field trial of this program at the Toledo Edison–Bayshore Station was undertaken.

PRELIMINARY FIELD TRIAL

The initial recommended treatment rate for this preliminary program was to reduce the current chlorination dosage in half and feed for only half the time. In addition, 0.85 pounds of the activated bromide mixture was to be added per pound of chlorine used. This resulted in an initial decrease in total oxidant of 46%.

The field trial at Toledo Edison, Bay Shore Unit No. 1 began in June, 1982, and was completed in July, 1982. Visual inspections verified that condenser cleanliness was maintained throughout the period. The total dosage concentration of the activated bromide-chlorine mixture over the entire period averaged 2.24 mg/l. During this same period, a sister unit, Bay Shore No. 2, was treated using chlorine alone at an average concentration of 9.11 mg/l. This represents a reduction of 75.4% in total oxidant usage based on concentration. In addition, it was necessary to chlorinate Bay Shore Unit No. 2 for a period of 60 minutes per day, or 3 times longer than Unit No. 1.

Based on these figures, a total of 584 lb of chlorine was used on Bay Shore Unit No. 2 while 23.9 lb of total oxidant was used on Bay Shore Unit No. 1. This represents a reduction of 95.9% in the pounds of oxidant used per day.

In addition to the cost savings realized by Toledo Edison, an estimated annual 409.5 ton reduction in total oxidant must also be considered as a benefit to the environment.

LABORATORY STUDIES

Laboratory studies during May and June of 1983, verified the effectiveness of the activated bromide-chlorine mixture with Maumee River water. These studies monitored total plate counts versus total oxidant dosage. The effect of two different chlorine-to-bromide ratios was also investigated. These data can be seen in Figures 4 & 5.

In May of 1983 (Figure 4), chlorine alone required 2.1 ppm to kill 80% of the bacteria present in the make-up water. Only 0.5 ppm of a mixture in a 2:1 ratio of bromide-to-chlorine was required for comparable kill. A mixture in a 1:1 bromide-to-chlorine ratio required 0.7

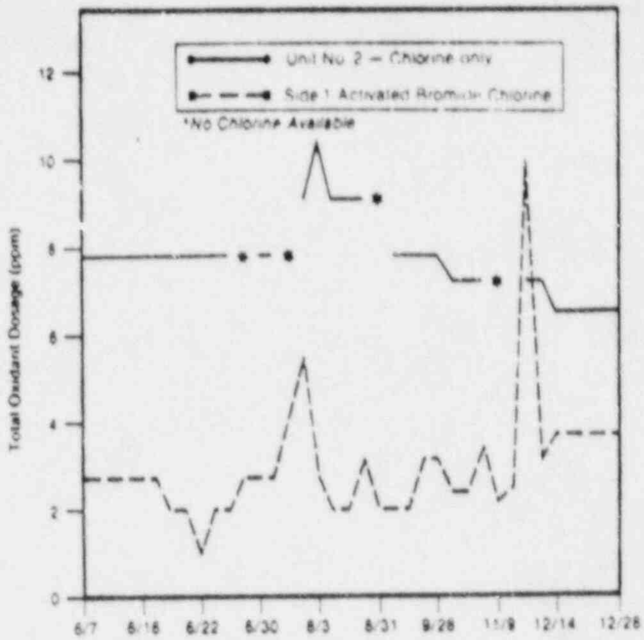


Figure 6 — *Total oxidant dosage for activated bromide chlorine vs chlorine*

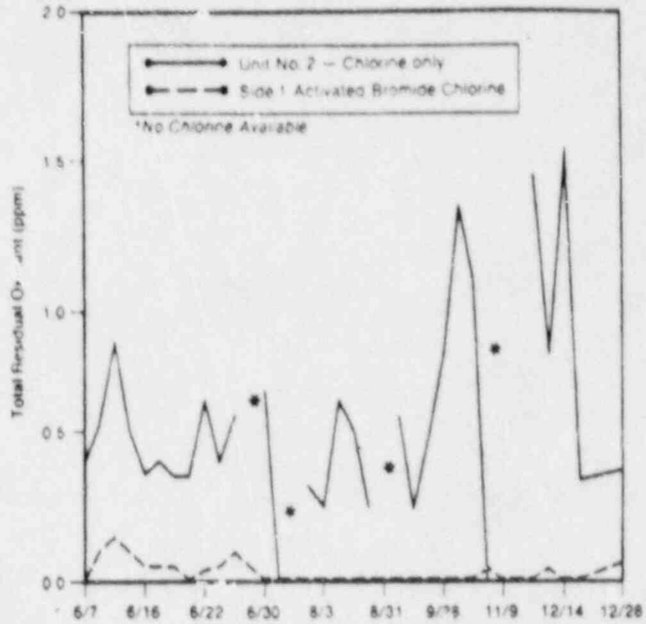


Figure 7 — *Total residual oxidant for activated bromide – chlorine vs chlorine*

ppm to accomplish the task. In this situation, 3-4 times more chlorine alone was required than either of the two activated bromide-chlorine mixtures.

This experiment was repeated again in June of 1983. These data can be seen in Figure 5. In this situation, chlorine alone required about 7 times the dosage that either of the chlorine-activated bromide mixtures did. These experiments clearly demonstrate the added efficacy which an activated bromide chlorine mixture provides.

CORROSION STUDY

Laboratory studies were also performed to determine the corrosiveness of the activated bromide-chlorine mixture versus chlorine alone. Mild steel, admiralty, and 304 stainless steel coupons were exposed to a chlorine and activated bromide-chlorine residual of 2 times and 1000 times the normal expected value. The results of these experiments are shown in Table I.

The data were taken for a 24 hour period. The corrosion rates are reported based on 24 hours of continuous treatment. These data were then recalculated to allow for a typical treatment time of only 1 hour per day. These data are listed under the expected corrosion rates.

If the treatment dosage remains below 2 times the normal value for only 1 hour per day, there should be no substantial corrosion of any of these metallurgies. However, 24 hour continuous treatment at 2 times the normal dosage will increase the corrosion to a marginally acceptable level.

If the dosage is increased to 1000 times the normal value, there will still be no substantial corrosion as long as the treatment time is one hour or less. 24 hour treatment at 1000 times the normal dosage will incur tremendous corrosion. These dosages would only be seen by the concentrated chlorine line. The system would normally dilute the chlorine well below this level.

FIELD TRIAL

The final test for the activated bromide chlorine mixture was a long term field trial on Unit No. 1 at the Toledo Edison Bayshore Station. During this trial, several parameters were monitored. The condenser was physically inspected whenever possible. Back pressure and total residual oxidant values were monitored. And finally, total plate counts were performed to determine the effect of the disinfectant on the microbiological population. Due to the risk of contamination on the No. 2 side of Unit No. 1 condenser during chlorination of Unit No. 2, only the No. 1 side of the No. 1 Unit condenser was used for this evaluation.

Bayshore Station No. 1 Condenser is dual-pass and has the capability of reversing flow. Side 1 was treated with the activated bromide-chlorine mixture for 10 minutes per day. Bayshore Station Unit No. 2, a sister unit, was treated with gaseous chlorine for a period of 60 minutes per day. This trial will continue through May 1984. The resulting data, through December 1983, can be seen in Table II and Figures 6 and 7. Figure 6 shows a comparison of the dosage of an activated bromide-chlorine mixture vs. chlorine alone. Figure 7 shows that the

Table I — *Corrosion results @ 70°F*

	ADM[1] (mpy)	MS[2] (mpy)	304 SS[3] (mpy)
Activated Bromide-Chlorine Mixture			
1000 times normal dosage (24 hours)	5.4	76.1	1.5
1000 times normal dosage (expected)	0.1	1.1	0.0
2 times normal dosage (24 hours)	0.2	4.7	0.1
2 times normal dosage (expected)	0.0	0.1	0.0
Chlorine Alone			
1000 times normal dosage (24 hours)	0.4	140.3	0.3
1000 times normal dosage (expected)	0.0	5.8	0.0
2 times normal dosage (24 hours)	0.2	5.1	0.0
2 times normal dosage (expected)	0.0	0.2	0.0

[1]*Admiralty*
[2]*Mild Steel*
[3]*Stainless Steel*

Table II — *Results of activated bromide-chlorine mixture vs chlorine alone*

	Unit 1 Side 1		Unit No. 2	
Date	Activated Bromide-Cl_2 Total Oxidant Dosage ppm	TRO[1]	Cl_2 Total Oxidant Dosage ppm	TRO[1]
6-7	2.7	0.00	7.8	0.40
6-13	2.7	0.10	7.8	0.52
6-14	2.7	0.15	7.8	0.80
6-15	2.7	0.10	7.8	0.50
6-16	2.7	0.05	7.8	0.36
6-17	2.7	0.05	7.8	0.40
6-20	2.0	0.05	7.8	0.35
6-21	2.0	0.00	7.8	0.35
6-22	1.0	0.04	7.8	0.60
6-23	2.0	0.05	7.8	0.40
6-27	2.0	0.10	7.8	0.55
6-28	2.7	0.05	—[2]	—[2]
6-30	2.7	0.00	7.8	0.63
7-5	2.7	0.00	7.8	0.00
7-11	3.8	0.00	—[2]	—[2]
7-20	5.5	0.00	9.1	0.32
8-3	2.7	0.00	10.4	0.25
8-10	2.0	0.00	9.1	0.60
8-17	2.0	0.00	9.1	0.50
8-23	3.1	0.00	9.1	0.25
8-31	2.0	0.00	—[2]	—[2]
9-7	2.0	0.00	7.8	0.55
9-14	2.0	0.00	7.8	0.25
9-21	3.2	0.00	7.8	0.48
9-28	3.2	0.00	7.8	0.75
10-19	2.4	0.00	7.2	1.35
10-26	2.4	0.00	7.2	1.10
11-1	3.4	0.04	7.2	0.00
11-9	2.2	0.00	—[2]	—[2]
11-16	2.5	0.00	—[2]	—[2]
11-23	9.9	0.00	7.2	1.45
11-30	3.1	0.04	7.2	0.76
12-14	3.7	0.00	6.5	1.52
12-21	3.7	0.01	6.5	0.33
12-28	3.7	0.07	6.5	0.37

[1] *Measured at the effluent stream outfall*
[2] *No chlorine available*

activated bromide-chlorine mixture never exceeded the USEPA Guidelines of 0.2 mg/l TRC. In fact, it seldom was above 0.1 ppm TRC; whereas, chlorine was frequently above this value.

From June through December, 1983, the No. 2 Unit had an average chlorine dosage of 7.85 mg/l, whereas the No. 1 Unit had an average dosage of 2.38 mg/l total oxidant (activated bromide-chlorine). The activated bromide-chlorine mixture was fed for 10 minutes per day. The chlorine alone was fed to No. 2 Unit for 60 minutes per day. This represents a yearly savings of 170,000 pounds of oxidant per unit. In addition to a significant savings of chemicals, it also allows the station to change from gaseous chlorine to activated bromide and chlorine solutions at a cost savings.

CONCLUSIONS

Chlorine minimization alone will not provide adequate biofouling control of the condensers at the Toledo Edison-Bayshore Station. Field and laboratory studies show that there would be frequent exceedances of the 0.2 mg/l TRC USEPA Guidelines. While a dechlorination system would prevent this, it would be expensive from both a chemical and equipment standpoint.

Chlorine dioxide can provide adequate microbiological control. However, this program would cost 4 times more than chlorine alone. In addition, personnel safety would be jeopardized.

An activated bromide-chlorine mixture was found to be an effective biofouling control agent. Laboratory studies demonstrate the effectiveness of this program at alkaline pH values. Laboratory and field studies show the effectiveness of this program at lower dosages than chlorine alone. In the eight-month field trial, a system treated with an activated bromide-biodispersant-chlorine mixture required 92% less oxidant than a similar system treated with chlorine alone. In addition, the unit treated with the activated bromide mixture never exceeded the 0.2 mg/l TRC USEPA Guideline.

This reduction in total oxidant represents a 27.6% cost savings over chlorine gas alone. It is also a significant environmental advantage since approximately 170,000 lb less oxidant per unit would be used by the Bayshore Station annually.

Corrosion rates for chlorine and activated bromide-chlorine mixtures are essentially the same. However, the activated bromide mixture will be operated for a much shorter time period. The overall corrosion should be less for this reason.

Overall, an activated bromide-chlorine mixture is the most cost effective method for the Toledo Edison-Bayshore Station to meet the USEPA Guidelines of 0.2 mg/l TRC and maintain a system free of microbiological growth.

NALCO CHEMICAL COMPANY
ONE NALCO CENTER • NAPERVILLE, ILLINOIS 60566-1024

Printed in U.S.A. 10-86

ENCLOSURE 2

Product Information for Betz Laboratories'

Slimicide C-78P

(This information was provided by Betz Laboratories for TVA's use in obtaining regulatory approval for the use of the specific product.)

EPA Registration Number: 5785-65-3876

Betz Industrial
The Water Management Division of Betz Laboratories, Inc.

product facts

BETZ® SLIMICIDE C-78P
MICROBIOCIDE

- Long-lasting protection–controlled biocide release
- Fast-dissolving granular form
- Generates effective concentrations rapidly
- Effective on bacterial, fungal, and algal fouling

DESCRIPTION AND USE

BETZ Slimicide C-78P is an effective, broad-spectrum microbiocide in a granular form. The product contains active bromine and chlorine in a stabilized form; they are released into the water in a controlled fashion as the granules dissolve.

Bromine and chlorine work together to provide effective control for a broad spectrum of slime-forming organisms. By controlling slime accumulations, Slimicide C-78P allows cooling towers and heat exchangers to operate at peak efficiency and reduces the tendency for underdeposit corrosion.

Slimicide C-78P is particularly well-suited for applications that require shock dosing. For example, the rapid dissolution rates typical of this product make possible effective biofouling control of utility surface condensers without exceeding total residual oxidant discharge limits.

BETZ Slimicide C-78P may be used alternately with other BETZ Slimicides to improve overall program effectiveness by reducing the development of microorganism strains that are resistant to a single biocidal agent.

Slimicide C-78P is registered with the Environmental Protection Agency for the control of bacterial, fungal, and algal slimes in industrial cooling towers, once-through cooling systems, brewery pasteurizers, air washers, influent water systems, such as flow-through filters and lagoons, and industrial water scrubbing systems.

TREATMENT AND FEEDING REQUIREMENTS

In small systems, BETZ Slimicide C-78P can be fed directly to the cooling water, pasteurizer, or air washer by means of a plastic or stainless steel feed device, such as a mesh bag or perforated container that provides gradual solution. For larger applications, a by-pass feeder is recommended to achieve consistent product residuals throughout the system. Betz offers a full range of feeder systems for applying Slimicide C-78P.

Proper treatment levels for BETZ Slimicide C-78P depend on many factors such as the nature and degree of severity of the microbial problem, system retention time, temperature, and other operating conditions. Typically, enough BETZ Slimicide C-78P is added to the system to maintain a 1-3 mg/L total halogen residual in the water for at least 4 hr daily. For best results, your Betz Industrial representative should determine the proper dosage for the specific system and the problem to be treated.

In all cases, the product must be applied in accordance with the use instructions on the BETZ Slimicide C-78P container label.

GENERAL PROPERTIES

Bromo-chloro hydantoin	93.5%
Inert ingredients	6.5%
Appearance	white granules
Bulk Density	64.5 lb/ft³ (1033 kg/m³)
EPA Reg. No.	5785-65-3876
pH (5% dispersion)	4.7
Solubility	1%

SAFETY PRECAUTIONS

A Material Safety Data Sheet containing detailed information relative to this product is available upon request.

PACKAGING INFORMATION

BETZ Slimicide C-78P comes in granular form. It is supplied in 6.5-gal (25-L), polyethylene containers. Approximate net weight per container is 50 lb (23 kg).

BETZ LABORATORIES, INC.
4636 SOMERTON ROAD, TREVOSE, PA 19047

PRODUCT: SLIMICIDE C-78P

1/12/88 AQUATIC TOXICOLOGY

RAINBOW TROUT		
	96 HR. LC50	0.87 MG/L
DAPHNIA MAGNA		
	48 HR. LC50	0.47 MG/L
FATHEAD MINNOW		
	96 HR. LC50	0.25 MG/L

DEHALOGENATED SLIMICIDE C-78P

RAINBOW TROUT		
	96 HR. LC50	6100 MG/L
DAPHNIA MAGNA		
	48 HR. LC50	1300 MG/L
FATHEAD MINNOW		
	96 HR. LC50	8100 MG/L

BETZ LABORATORIES, INC.
4636 SOMERTON ROAD, TREVOSE, PA. 19047
BETZ MATERIAL SAFETY DATA SHEET
24 HOUR EMERGENCY TELEPHONE (HEALTH OR ACCIDENT) 215/355-3300

PRODUCT : SLIMICIDE C-78P

EFFECTIVE DATE 07-14-87
REV.: SEC.9

PRODUCT APPLICATION : SOLID MICROBIAL CONTROL AGENT.

-----SECTION 1-----------HAZARDOUS INGREDIENTS---------------

INFORMATION ON PHYSICAL HAZARDS, HEALTH HAZARDS, PEL'S AND TLV'S FOR SPECIFIC PRODUCT INGREDIENTS AS REQUIRED BY THE OSHA HAZARD COMMUNICATIONS STANDARD IS LISTED. REFER TO SECTION 4 (PAGE 2) FOR OUR ASSESSMENT OF THE POTENTIAL ACUTE AND CHRONIC HAZARDS OF THIS FORMULATION.

1-BROMO-3-CHLORO-5,5-DIMETHYLHYDANTOIN***CAS#16079-88-2;OXIDIZER;EYE AND SKIN IRRITANT;PEL:NONE;TLV:NONE.

-----SECTION 2-----------TYPICAL PHYSICAL DATA-----------------------

PH: 5% DISP. (APPROX.) 4.7
FL.PT.(DEG.F): >200 SETA(CC)
VAPOR PRESSURE(mmHG): NA
VISC cps70F: NA
EVAP.RATE: NA WATER=1
PHYSICAL STATE: GRANULES
ODOR: HALOGEN
SP.GR.(70F)OR DENSITY: 65 LBS.CU.FT.
VAPOR DENSITY(AIR=1): NA
%SOLUBILITY(WATER): 1
APPEARANCE: WHITE
FREEZE POINT(DEG.F): NA

-----SECTION 3-----------REACTIVITY DATA-----------------------------

OXIDIZING AGENT.DO NOT STORE OR MIX WITH REDUCING AGENTS

THERMAL DECOMPOSITION (DESTRUCTIVE FIRES) YIELDS ELEMENTAL OXIDES.

PRODUCT: SLIMICIDE C-78P

-----SECTION 4-----------HEALTH HAZARD EFFECTS-----------------------

ACUTE SKIN EFFECTS *** PRIMARY ROUTE OF EXPOSURE
MODERATELY IRRITATING TO THE SKIN.MAY BE CORROSIVE IN CONTACT WITH MOIST SKIN.

ACUTE EYE EFFECTS ***
SEVERE IRRITANT TO THE EYES

ACUTE RESPIRATORY EFFECTS ***
DUSTS CAUSE IRRITATION TO UPPER RESPIRATORY TRACT

CHRONIC EFFECTS OF OVEREXPOSURE***
NO EVIDENCE OF POTENTIAL CHRONIC EFFECTS.

MEDICAL CONDITIONS AGGRAVATED ***
NOT KNOWN

SYMPTOMS OF EXPOSURE ***
MAY CAUSE REDNESS OR ITCHING OF SKIN.

PRECAUTIONARY STATEMENT BASED ON TESTING RESULTS ***
MAY BE TOXIC IF ORALLY INGESTED.

-----SECTION 5------------FIRST AID INSTRUCTIONS---------------------

SKIN CONTACT***
REMOVE CLOTHING.WASH AREA WITH LARGE AMOUNTS OF SOAP SOLUTION OR WATER FOR 15 MIN.IMMEDIATELY CONTACT PHYSICIAN

EYE CONTACT***
IMMEDIATELY FLUSH EYES WITH WATER FOR 15 MINUTES.IMMEDIATELY CONTACT A PHYSICIAN FOR ADDITIONAL TREATMENT

INHALATION EXPOSURE***
REMOVE VICTIM FROM CONTAMINATED AREA.APPLY NECESSARY FIRST AID TREATMENT.IMMEDIATELY CONTACT A PHYSICIAN.

INGESTION***
DO NOT FEED ANYTHING BY MOUTH TO AN UNCONSCIOUS OR CONVULSIVE VICTIM DILUTE CONTENTS OF STOMACH.INDUCE VOMITING BY ONE OF THE STANDARD METHODS.IMMEDIATELY CONTACT A PHYSICIAN

-----SECTION 6-----------SPILL,DISPOSAL AND FIRE INSTRUCTIONS---------

SPILL INSTRUCTIONS***
VENTILATE AREA,USE SPECIFIED PROTECTIVE EQUIPMENT.SPILLED MATERIAL WHICH CAN NOT BE RECOVERED FOR RE-USE,SHOULD BE PLACED IN A WASTE DISPOSAL CONTAINER AND DISPOSED OF IN AN APPROVED PESTICIDE LANDFILL.SEE PRODUCT LABEL STORAGE AND DISPOSAL INSTRUCTIONS. PRODUCT RELEASES CHLORINE WHEN WET.SPILL RESIDUE MAY BE NEUTRALIZED WITH 3% HYDROGEN PEROXIDE SOLUTION.

DISPOSAL INSTRUCTIONS***
WATER CONTAMINATED WITH THIS PRODUCT MAY BE SENT TO A SANITARY SEWER TREATMENT FACILITY,IN ACCORDANCE WITH ANY LOCAL AGREEMENT,A PERMITTED WASTE TREATMENT FACILITY OR DISCHARGED UNDER A NPDES PERMIT
PRODUCT(AS IS)-
BURY IN AN APPROVED PESTICIDE FACILITY OR DISPOSE OF IN ACCORDANCE WITH LABEL INSTRUCTIONS

FIRE EXTINGUISHING INSTRUCTIONS***
FIREFIGHTERS SHOULD WEAR POSITIVE PRESSURE SELF-CONTAINED BREATHING APPARATUS(FULL FACE-PIECE TYPE).
DRY CHEMICAL,CARBON DIOXIDE,FOAM OR WATER

PRODUCT: SLIMICIDE C-78P

-----SECTION 7-----------SPECIAL PROTECTIVE EQUIPMENT----------------

VENTILATION PROTECTION***
ADEQUATE VENTILATION TO MAINTAIN DUST CONCENTRATIONS BELOW THE EXPOSURE LIMITS OF 10MG/M3(TLV) AND 15MG/M3(PEL) FOR NUISANCE OR INERT DUSTS
RECOMMENDED RESPIRATORY PROTECTION***
IF VENTILATION IS INADEQUATE OR SIGNIFICANT PRODUCT EXPOSURE IS LIKELY, USE RESPIRATOR WITH ORGANIC VAPOR,ACID GASSES AND DUST/MIST CARTRIDGES.
RECOMMENDED SKIN PROTECTION***
GAUNTLET-TYPE NEOPRENE GLOVES,CHEMICAL RESISTANT APRON
WASH OFF AFTER EACH USE.REPLACE AS NECESSARY
RECOMMENDED EYE PROTECTION***
AIRTIGHT CHEMICAL GOGGLES

-----SECTION 8-----------STORAGE AND HANDLING PRECAUTIONS-------------

STORAGE INSTRUCTIONS***
KEEP DRUMS & PAILS CLOSED WHEN NOT IN USE.
DO NOT EXPOSE TO MOISTURE
HANDLING INSTRUCTIONS***
GENERAL-IMMEDIATELY REMOVE CONTAMINATED CLOTHING,WASH BEFORE REUSE
SPECIFIC- OXIDIZER.EMITS TOXIC FUMES WHEN WET.

-----SECTION 9-----------FEDERAL REGULATIONS-------------------------

FIFRA(40CFR):EPA REG.NO. 5785-65-3876
OSHA(29CFR)-USE PROTECTIVE EQUIPMENT IN ACCORDANCE WITH 29CFR SECTIONS 1910.132-1910.134. USE RESPIRATORS WITHIN USE LIMITATIONS OR ELSE USE SUPPLIED AIR RESPIRATORS.
REPORTABLE QUANTITY: AS IS PRODUCT (HAZARDOUS SUBSTANCE)
NOT APPLICABLE
RCRA(40CFR): IF DISCARDED,THIS MATERIAL BEARS HWI# NOT APPLICABLE
DOT(49CFR)CLASSIFICATION: OXIDIZER
NFPA/HMIS : HEALTH - 3 ; FIRE - 1 ; REACTIVITY - 0 ; SPECIAL - OXY ; PE - C

****

HAROLD M. HERSH
ENVIRONMENTAL INFORMATION COORDINATOR

BETZ

slimicide C-78P

FOR CONTROL OF ALGAL, BACTERIAL AND FUNGAL SLIMES IN RECIRCULATING COOLING WATER SYSTEMS AND ONCE-THROUGH INDUSTRIAL COOLING WATER SYSTEMS.

PRECAUTIONARY STATEMENTS

HAZARDS TO HUMANS AND DOMESTIC ANIMALS

DANGER

CORROSIVE. Causes eye and skin damage. May be fatal if swallowed. Irritating to nose and throat. Avoid breathing dust. Do not get into eyes, on skin or on clothing. Wear goggles or face shield and rubber gloves when handling. Remove and wash contaminated clothing before reuse.

ENVIRONMENTAL HAZARDS

This pesticide is toxic to fish. Do not discharge into lakes, streams, ponds or public water unless in accordance with a NPDES permit. For guidance contact your Regional Office of the EPA.

PHYSICAL AND CHEMICAL HAZARDS

STRONG OXIDIZING AGENT. Mix only with water. Use clean, dry utensils and equipment. Do not add this product to any dispensing device containing remnants of any other product. Such use may cause a violent reaction leading to fire and explosion. Contamination with moisture, organic matter, or other chemicals may start chemical reaction with generation of heat, hazardous gases, and possible fire and explosion. In cases of contamination or decomposition, do not reseal container. If possible, isolate container in open air or well ventilated area. If necessary, flood with large volumes of water.

DIRECTIONS FOR USE

It is a violation of Federal law to use this product in a manner inconsistent with its labeling.

(Directions for Use continued on third panel)

BLOCH088-8511

Contents: GRANULES

ACTIVE INGREDIENT:	
1-Bromo-3-chloro-5,5-dimethylhydantoin	93.0%
INERT INGREDIENTS:	6.0%
Total	100.0%

AVAILABLE BROMINE: 62% AVAILABLE CHLORINE: 28%

EPA Reg. No. 5785-65-3878

EPA Est. No. 7011-MI-01

NET WEIGHT
AS MARKED ON CONTAINER

KEEP OUT OF REACH OF CHILDREN

DANGER

STATEMENT OF PRACTICAL TREATMENT

If swallowed, feed bread soaked in milk, followed by olive oil or cooking oil. Seek medical attention immediately.

In case of eye contact, flush eyes with cold water for at least 15 minutes. Seek medical attention promptly.

In case of skin contact, brush off excess chemical and flush skin with cold water for at least 15 minutes. If irritation develops seek medical attention.

A Material Safety Data Sheet containing more detailed information relative to this product is available upon request.

See left panel for additional Precautionary Statements.

RECIRCULATING COOLING WATER SYSTEMS

When used as directed, BETZ Slimicide C-78P effectively controls algal, bacterial and fungal slimes in commercial and industrial cooling towers, influent water systems such as flow through filters and lagoons, heat exchange water systems, industrial water scrubbing systems, brewery pasteurizers, and industrial air washing systems equipped with a mist eliminator. Add Slimicide C-78P using a bypass feeder or broadcast into an open area in the system such as a cooling tower basin or deck, where sufficient agitation is present to promote rapid mixing and dissolution.

DOSAGE RATES:
INITIAL DOSE: When the system is noticeably fouled, add Slimicide C-78P at the rate of 0.2 to 0.8 lb. per 1000 gallons of water contained in the system. Repeat initial dosage until at least one ppm bromine residual is established for at least 4 hours.

SUBSEQUENT DOSE: When microbial control is evident, add Slimicide C-78P at the rate of 0.1 to 0.3 lb. per 1000 gallons of water contained in the system. Repeat as needed to maintain at least one ppm bromine residual for at least 4 hours.

ONCE-THROUGH INDUSTRIAL COOLING WATER SYSTEMS

For the control of algal, bacterial and fungal slimes in once-through and closed-cycle fresh and sea water cooling systems, cooling ponds, canals and lagoons, add Slimicide C-78P to the system inlet water or before any other contaminated area in the system.

DOSAGE RATES:
INITIAL DOSE: When the system is noticeably fouled, add Slimicide C-78P at the rate of 0.2 to 0.8 lb. per 1000 gallons of water contained in the system. Repeat initial dosage until at least one ppm bromine residual is established for at least 4 hours.

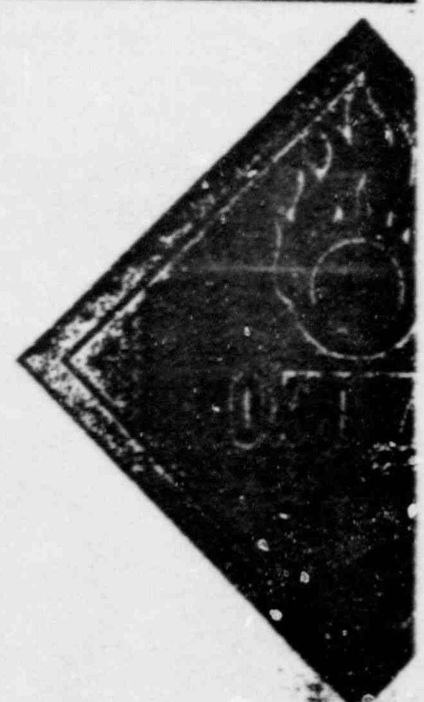
SUBSEQUENT DOSE: When microbial control is evident, add Slimicide C-78P at the rate of 0.1 to 0.3 lb. per 1000 gallons of water contained in the system. Repeat as needed to maintain at least one ppm bromine residual in the water for at least 4 hours.

STORAGE AND DISPOSAL

STORAGE: Keep product dry in tightly closed container when not in use. Store in a cool, dry, well ventilated area away from heat, open flames, organic chemicals and sunlight. Do not contaminate water, food or feed by storage or disposal. Open dumping is prohibited.

DISPOSAL: Wastes resulting from the use of this product may be disposed of on site or at an approved waste disposal facility. DO NOT REUSE EMPTY CONTAINER. Triple rinse the container (or equivalent). Then offer for recycling or reconditioning, or puncture and dispose of in a sanitary landfill, or incineration. Burn only if allowed by state and local authorities. If burned, stay out of smoke.

FOR INDUSTRIAL USE ONLY. Technical advice regarding specific site problems is available from BETZ.



Betz Industrial
The Water Management Division of Betz Laboratories, Inc.

Heartland District Office
208 Bob Wallace Avenue
Huntsville, AL 35801
205-536-1357

RECEIVED
CHEMISTRY BRANCH
JAN 20 '88

January 18, 1988

TVA
Lookout Place 5
South 61 E-C
1101 Market Street
Chattanooga, TN 37402-2801

Attention: Mr. William Nestel

Dear Mr. Nestel:

Enclosed is a package of information which addresses the questions you raised during our 1-14-88 meeting.

BIOCIDE REFERENCES

We offer two industrial plants as references within the state of Tennessee. I should note that both plants are using C-77P, rather than C-78P. Both products contain 93% 1-Bromo-3-Chloro-5, 5-dimethylhydantion. The C-77P product is compressed into tablet form for slow dissolving while the C-78P is granular and recently made available for a higher maximum dissolution rate (i.e. shock dosing).

E. I. DuPont de Nemours
Memphis, TN

Inland Container
New Johnsonville, TN

ENCLOSURE 3

Product Information for Betz Laboratories'

Slimicide C-82

(This information was provided by Betz Laboratories for TVA's use in obtaining regulatory approval for the use of the specific product.)

EPA Registration Number: 5785-66-3876

BETZ® LABORATORIES, INC.

Slimicide C-82

FOR USE AS A DISINFECTANT, [illegible] ALGICIDE AND [illegible]

[illegible] CONTINUED FROM PAGE ONE

ONCE-THROUGH COOLING WATER AND WASTEWATER TREATMENT SYSTEMS

When used as directed, Slimicide C-82 effectively controls algae, bacterial and fungal slimes in once-through fresh and sea water cooling systems and disinfects secondary and tertiary wastewater treatment systems.

[illegible] DOSE: Add Slimicide C-82 solution to the system at a 0.5 to 2.0 Slimicide C-82/oxidant [illegible] ratio. For example:

1) 2 to 8 pounds of chlorine gas (99.9%) per gallon of Slimicide C-82 solution;
2) 1.6 to 6.3 gallons sodium hypochlorite (12.5% available chlorine) per gallon of Slimicide C-82 solution.

INITIAL DOSE: When the system is noticeably fouled, add 0.008 to 0.06 gallons of Slimicide C-82 per 1000 gallons of water contained in the system, and oxidize with either gas chlorine (0.02 to 0.08 lbs gas chlorine per 1000 gallons contained volume), or sodium hypochlorite solution (0.02 to 0.07 gallons 12.5% sodium hypochlorite solution per 1000 gallons contained volume).

SUBSEQUENT DOSE: When microbial control is evident, add 0.004 to 0.05 gallons Slimicide C-82 solution per 1000 gallons of water contained in the system, and oxidize with either gas chlorine (0.008 to 0.08 lbs gas chlorine per 1000 gallons contained volume), or sodium hypochlorite solution (0.007 to 0.07 gallons 12.5% sodium hypochlorite solution per 1000 gallons contained volume).

Feed Slimicide C-82 either before or after the oxidant injection point into the water to be treated. To [illegible] rapid mixing of the treated water, Slimicide C-82 and oxidant is advised. Pump manufacturers can recommend the appropriate materials of construction and capacity for a pump to feed Slimicide C-82 or sodium hypochlorite solution. If used as the oxidant, chlorine gas must be handled and used only in accordance with practices recommended in the Chlorine Manual published by the Chlorine Institute, Inc., New York. Use chlorine gas only in well-ventilated areas.

Treatment levels of Slimicide C-82 and oxidant can best be measured [illegible] test kits for either bromine or chlorine. Tests should be made immediately after drawing water samples from the system. Use test kits according to directions.

1. When a bromine test kit is used, results can be read directly as ppm bromine.

2. When a chlorine test kit is used, results can be expressed in terms of bromine by multiplying chlorine values by the conversion factor 2.25.

[illegible] [illegible]

BETZ® LABORATORIES, INC.

Slimicide C-82

FOR USE AS A DISINFECTANT, [illegible] SLIMICIDE AND ALGICIDE

PRECAUTIONARY STATEMENTS
HAZARDS TO HUMANS AND DOMESTIC ANIMALS
WARNING

[illegible] MAY [illegible] EYE AND SKIN [illegible]. AVOID CONTACT WITH EYES. WEAR GLOVES AND SAFETY GOGGLES. WASH CONTAMINATED CLOTHING BEFORE REUSE.

ENVIRONMENTAL HAZARDS

DO NOT DISCHARGE INTO LAKES, STREAMS, PONDS OR PUBLIC WATERS UNLESS IN ACCORDANCE WITH AN NPDES PERMIT. FOR GUIDANCE, CONTACT YOUR REGIONAL OFFICE OF EPA.

PHYSICAL AND CHEMICAL HAZARDS

SLIMICIDE C-82 IS NOT FLAMMABLE. HOWEVER, IN FIRES [illegible] BY OTHER MATERIALS, [illegible] BROMIDE OR BROMINE MAY BE RELEASED. IN CASE OF FIRE, WEAR SELF-CONTAINED BREATHING APPARATUS.

Active Ingredient:

Sodium Bromide..........46%

Inert Ingredients..........54%

100%

CONTENTS: LIQUID
POUNDS PER GALLON: 12.6 (70F)
EPA REG. NO.: 5790-[illegible] EPA EST. NO.

WARNING KEEP OUT OF REACH OF CHILDREN
STATEMENT OF PRACTICAL TREATMENT

Eye Contact: Flush eyes with cold water for at least 15 minutes. If irritation persists, seek medical attention immediately.

Skin Contact: Prolonged contact can produce skin irritation. If skin contact occurs, wash with cold water for 15 minutes.

A Material Safety Data Sheet containing more detailed information relative to this product is available upon request.

DIRECTIONS FOR USE:

It is a violation of Federal law to use this product in a manner inconsistent with its labeling.

STORAGE AND DISPOSAL

STORAGE: Keep product in tightly closed original container when not in use. Store in a dry, well-ventilated area. Product should be stored at 30F or above.

DISPOSAL: Wastes resulting from the use of this product may be disposed of on site or at an approved waste disposal facility. Triple rinse the container (or equivalent). Then offer for recycling or reconditioning, or puncture and dispose of in a sanitary landfill, or incinerate. Burn only if allowed by state and local authorities. If burned, stay out of smoke.

RECIRCULATING COOLING WATER SYSTEMS

When used as directed, Slimicide C-82 effectively controls algae, bacterial and fungal slimes in commercial and industrial cooling towers, influent water systems such as flow through filters, heat exchange water systems and industrial water scrubbing systems.

DOSAGE RATES: Add Slimicide C-82 to the system at a 0.5 to 2.0 Slimicide C-82/ oxidant mole ratio. For example:

1) 2 to 6 pounds of chlorine gas (99.9%) per gallon of Slimicide C-82 solution,

2) 1.4 to 6.5 gallons sodium hypochlorite (12.5% available chlorine) solution per gallon of Slimicide C-82 solution.

INITIAL DOSE: When the system is noticeably fouled, add 0.001 to 0.020 gallons of Slimicide C-82 solution per 1000 gallons of water contained in the system and oxidize with either gas chlorine (0.008 to 0.092 lbs gas chlorine per 1000 gallons of contained water), or sodium hypochlorite solution (0.007 to 0.020 gallons of 12.5% sodium hypochlorite solution per 1000 gallons of contained water).

SUBSEQUENT DOSE: When microbial control is evident, add 0.0005 to 0.020 gallons of Slimicide C-82 solution per 1000 gallons of water contained in the system, and oxidize with either gas chlorine (0.004 to 0.092 lbs gas chlorine per 1000 gallons of contained water), or sodium hypochlorite solution (0.002 to 0.020 gallons of 12.5% sodium hypochlorite solution per 1000 gallons of contained water).

USE DIRECTIONS CONTINUED ON SECOND PANEL.

NET WT.: LBS.
LOT NO.

FOR INDUSTRIAL USE. Technical advice regarding specific site problems is available from BETZ.
[illegible] PANEL 1 OF 2

Manufactured For: BETZ Laboratories, Inc.

ATTACH PANEL TWO HERE

ATTACH PANEL TWO HERE

TREVOSE, PA 19047 BUSINESS PHONE: 215-355-3300 EMERGENCY(HEALTH OR ACCIDENT): 215-355-3300

Slimicide C-82
NET WT.:
LBS.
LOT NO.

Slimicide C-82
PROPER SHIPPING NAME:

DISCARD THIS TAB. THIS PRODUCT IS NOT REGULATED BY DOT.

CUSTOMER PART NO.

BETZ LABORATORIES, INC.
4636 SOMERTON ROAD, TREVOSE, PA.19047

PRODUCT: SLIMICIDE C-82

1/15/88

AQUATIC TOXICOLOGY

FATHEAD MINNOW	96 HR. LC50: 16,479 MG/L NaBr
DAPHNIA MAGNA	48 HR. LC50: 11,000 MG/L Br-
POECILIA RETICULATA	96 HR. LC50: 16,000 MG/L Br-
ORYZIAS LATIPES	96 HR. LC50: 24,000 MG/L Br-

Data supplied by manufacturer

ENCLOSURE 4

Product Information for Betz Laboratories'

Powerline 3690

(This information was provided by Betz Laboratories
for TVA's use in obtaining regulatory approval
for the use of the specific product.)

EPA Registration Number: Not Applicable

Betz Industrial

The Water Management Division of Betz Laboratories, Inc.

4636 Somerton Road
Trevose, PA 19047-6783
215-355-3300
Telex 173-148

January 21, 1988

Mr. William A. Nestel
Program Manager, Chemistry
TENNESSEE VALLEY AUTHORITY
Lookout Place 5
South 61 E-C
1101 Market Street
Chattanooga, TN 37402-2801

Dear Mr. Nestel:

Attached for your reference is a new Aquatic Toxicology data sheet for our biodispersant, Betz Powerline 3690. The data sheet has been revised to include the results of the aquatic toxicity evaluation on Daphnia magna conducted this week in order to provide TVA with a more complete environmental affairs package.

In our initial aquatic toxicity evaluation on rainbow trout conducted several years ago, Powerline 3690 exhibited such a low order of toxicity that no further studies were conducted on other aquatic organisms.

Betz Powerline 3690 was shown to produce 0% mortality on Daphnia magna at a dosage of 500 mg/L, the highest level tested. Normal application rates are on the order of 5 to 10 mg/L.

Thank you for the opportunity to be of service.

Very truly yours,

BETZ INDUSTRIAL

Raymond M. Post

Raymond M. Post
Project Engineer

RMP/bw
Enc.

BETZ LABORATORIES, INC.
4636 SOMERTON ROAD, TREVOSE, PA. 19047

PRODUCT: POWERLINE 3690

1/21/88

AQUATIC TOXICOLOGY

DAPHNIA MAGNA

0% MORTALITY: 500 MG/L
48 HR. SCR.

RAINBOW TROUT

0% MORTALITY: 1000 MG/L
48 HR. SCR.

1/21/88

MAMMALIAN TOXICOLOGY

ORAL LD50 -NO DATA

DERMAL LD50 -NO DATA

SKIN IRRITATION SCORE-NO DATA

EYE IRRITATION SCORE-NO DATA

INHALATION-NO DATA

PRODUCT CONCENTRATION (ppm)	OXYGEN DEMAND (ppm) BOD	COD	TOC
1000	< 4	356	201

BETZ LABORATORIES, INC.
4636 SOMERTON ROAD, TREVOSE, PA. 19047
BETZ MATERIAL SAFETY DATA SHEET
24 HOUR EMERGENCY TELEPHONE (HEALTH OR ACCIDENT) 215/355-3300

PRODUCT : POWERLINE 3690 Bio Dispersant

EFFECTIVE DATE 11-11-87
SEC.8-MINOR CHANGE

PRODUCT APPLICATION : WATER-BASED DEPOSIT CONTROL AGENT.

-----SECTION 1-----------HAZARDOUS INGREDIENTS---------------

INFORMATION ON PHYSICAL HAZARDS, HEALTH HAZARDS, PEL'S AND TLV'S FOR SPECIFIC PRODUCT INGREDIENTS AS REQUIRED BY THE OSHA HAZARD COMMUNICATIONS STANDARD IS LISTED. REFER TO SECTION 4 (PAGE 2) FOR OUR ASSESSMENT OF THE POTENTIAL ACUTE AND CHRONIC HAZARDS OF THIS FORMULATION.

THIS PRODUCT CONTAINS NO HAZARDOUS INGREDIENTS BY OSHA REGULATIONS OR ANY STATE RIGHT-TO-KNOW REGULATIONS.

-----SECTION 2-----------TYPICAL PHYSICAL DATA-----------------------

PH: AS IS (APPROX.) 12.5	ODOR: NONE
FL.PT.(DEG.F): >200 SETA(CC)	SP.GR.(70F)OR DENSITY: 1.019
VAPOR PRESSURE(mmHG): ND	VAPOR DENSITY(AIR=1): ND
VISC cps70F: 11.7	%SOLUBILITY(WATER): 100
EVAP.RATE: ND WATER=1	APPEARANCE: COLORLESS
PHYSICAL STATE: LIQUID	FREEZE POINT(DEG.F): 31

-----SECTION 3-----------REACTIVITY DATA----------------------------

STABLE

THERMAL DECOMPOSITION (DESTRUCTIVE FIRES) YIELDS ELEMENTAL OXIDES.

PRODUCT: POWERLINE 3690

-----SECTION 4-----------HEALTH HAZARD EFFECTS-----------------------

ACUTE SKIN EFFECTS *** PRIMARY ROUTE OF EXPOSURE

SLIGHTLY IRRITATING TO THE SKIN

ACUTE EYE EFFECTS ***

MODERATELY IRRITATING TO THE EYES

ACUTE RESPIRATORY EFFECTS ***

MISTS/AEROSOLS MAY CAUSE IRRITATION TO UPPER RESPIRATORY TRACT

CHRONIC EFFECTS OF OVEREXPOSURE***

NO EVIDENCE OF POTENTIAL CHRONIC EFFECTS.

MEDICAL CONDITIONS AGGRAVATED ***

NOT KNOWN

SYMPTOMS OF EXPOSURE ***

MAY CAUSE REDNESS OR ITCHING OF SKIN.

-----SECTION 5------------FIRST AID INSTRUCTIONS--------------------

SKIN CONTACT***

REMOVE CONTAMINATED CLOTHING.WASH EXPOSED AREA WITH A LARGE QUANTITY OF SOAP SOLUTION OR WATER FOR 15 MINUTES

EYE CONTACT***

IMMEDIATELY FLUSH EYES WITH WATER FOR 15 MINUTES.IMMEDIATELY CONTACT A PHYSICIAN FOR ADDITIONAL TREATMENT

INHALATION EXPOSURE***

REMOVE VICTIM FROM CONTAMINATED AREA TO FRESH AIR.APPLY APPROPRIATE FIRST AID TREATMENT AS NECESSARY

INGESTION***

DO NOT FEED ANYTHING BY MOUTH TO AN UNCONSCIOUS OR CONVULSIVE VICTIM DILUTE CONTENTS OF STOMACH.INDUCE VOMITING BY ONE OF THE STANDARD METHODS.IMMEDIATELY CONTACT A PHYSICIAN

-----SECTION 6-----------SPILL,DISPOSAL AND FIRE INSTRUCTIONS---------

SPILL INSTRUCTIONS***

VENTILATE AREA,USE SPECIFIED PROTECTIVE EQUIPMENT.CONTAIN AND ABSORB ON ABSORBENT MATERIAL.PLACE IN WASTE DISPOSAL CONTAINER. THE WASTE CHARACTERISTICS OF THE ABSORBED MATERIAL,OR ANY CONTAMINATED SOIL, SHOULD BE DETERMINED IN ACCORDANCE WITH RCRA REGULATIONS. FLUSH AREA WITH WATER.WET AREA MAY BE SLIPPERY.IF SO,SPREAD SAND OR GRIT.

DISPOSAL INSTRUCTIONS***

WATER CONTAMINATED WITH THIS PRODUCT MAY BE SENT TO A SANITARY SEWER TREATMENT FACILITY,IN ACCORDANCE WITH ANY LOCAL AGREEMENT,A PERMITTED WASTE TREATMENT FACILITY OR DISCHARGED UNDER A NPDES PERMIT

PRODUCT(AS IS)-

INCINERATE OR BURY IN APPROVED LANDFILL

FIRE EXTINGUISHING INSTRUCTIONS***

FIREFIGHTERS SHOULD WEAR POSITIVE PRESSURE SELF-CONTAINED BREATHING APPARATUS(FULL FACE-PIECE TYPE).

DRY CHEMICAL,CARBON DIOXIDE,FOAM OR WATER

PRODUCT: POWERLINE 3690

-----SECTION 7-----------SPECIAL PROTECTIVE EQUIPMENT-----------------

VENTILATION PROTECTION***
ADEQUATE VENTILATION
RECOMMENDED RESPIRATORY PROTECTION***
IF VENTILATION IS INADEQUATE OR SIGNIFICANT PRODUCT EXPOSURE IS LIKELY, USE A RESPIRATOR WITH DUST/MIST FILTERS.
RECOMMENDED SKIN PROTECTION***
RUBBER GLOVES
WASH OFF AFTER EACH USE.REPLACE AS NECESSARY
RECOMMENDED EYE PROTECTION***
SPLASH PROOF CHEMICAL GOGGLES

-----SECTION 8-----------STORAGE AND HANDLING PRECAUTIONS------------

STORAGE INSTRUCTIONS***
KEEP DRUMS & PAILS CLOSED WHEN NOT IN USE.
REASONABLE AND SAFE CHEMICAL STORAGE
HANDLING INSTRUCTIONS***
GENERAL-IMMEDIATELY REMOVE CONTAMINATED CLOTHING,WASH BEFORE REUSE
SPECIFIC- ALKALINE.DO NOT MIX WITH ACIDIC MATERIAL.

-----SECTION 9-----------FEDERAL REGULATIONS-------------------------

OSHA(29CFR)-USE PROTECTIVE EQUIPMENT IN ACCORDANCE WITH 29CFR SECTIONS 1910.132-1910.134.
REPORTABLE QUANTITY: AS IS PRODUCT (HAZARDOUS SUBSTANCE)
NOT APPLICABLE
RCRA(40CFR): IF DISCARDED,THIS MATERIAL BEARS HWI# D002
DOT(49CFR)CLASSIFICATION: NOT APPLICABLE
NFPA/HMIS : HEALTH - 1 ; FIRE - 1 ; REACTIVITY - 0 ; SPECIAL - ALK ; PE - B

****

HAROLD M. HERSH
ENVIRONMENTAL INFORMATION COORDINATO

ENCLOSURE 5

Product Information for Calgon's

H950

(This information was provided by Calgon for TVA's use in obtaining regulatory approval for the use of the specific product.)

EPA Registration Number: 5785-66-10445

CALGON CORPORATION

SUBSIDIARY OF MERCK & CO., INC.

COOLING WATER TREATMENT

H-950

DESCRIPTION

H-950 Microbiocide is a bromine-donating compound in liquid form designed to supplement conventional chlorination for control of biofouling on heat exchange surfaces in once-through and recirculating cooling systems. When introduced into a chlorinated water stream, H-950 releases two powerful oxidizing hypohalous acids providing superior biocidal effectiveness at costs that approximate chlorination. H-950 also controls the growth of microorganisms in the bulk water and removes existing biofouling from system surfaces. Residual chlorine concentrations are greatly reduced so that discharge restrictions can be easily met.

ADVANTAGES

More Effective than Chlorine Alone

H-950 releases balanced amounts of hypobromous (HOBr) and hypochlorous (HOCl) acids. Lower total halogen is required to maintain microbiological control than when chlorine is used alone.

Hypobromous acid is a more effective biocide than hypochlorous acid, producing greater kills in a shorter period of time. The hypobromous acid formed is about four times more active than hypochlorous acid.

Effective Over a Wide pH Range

H-950 effectively controls microorganisms in cooling water systems over a pH range of 6.0-9.0. The hypobromite ion (OBr^-) is nearly as effective as undissociated hypobromous acid. The hypochlorite ion (OCl^-), which is the predominant form at pH >8.0, is significantly less effective than the hypochlorous acid. Therefore, at high pH, H-950 is more effective in maintaining microbiological control at lower treatment levels than chlorine fed alone.

Low Capital and Operating Costs

H-950 provides superior results at costs comparable to traditional chlorination. The injection of H-950 is simply integrated into the existing chlorine feed system. Your Calgon representative will recommend the proper size feed system to meet your specific needs.

Reduces Toxic By-Product Discharge

Chlorine reacts with naturally occurring organics in water to form toxic compounds such as trihalomethanes (THM's). By using H-950, chlorine feed is typically cut in half, significantly reducing THM formation and discharge.

Broad Spectrum Activity

H-950 provides broad spectrum control of slime-producing microorganisms such as bacteria, fungi, and algae in open recirculating cooling water systems.

Unaffected in the Presence of Ammonia

H-950 remains active in the presence of ammonia. When ammonia is present in cooling waters, both chlorine and bromine will react with it to form haloamines. The chloramines formed are less effective biocides. Bromamines have relatively the same biocidal effectiveness as hypobromous acid.

No Adverse Effect on System Wood or Metallurgy

H-950 releases balanced amounts of hypobromous and hypochlorous acids. Because lower total halogen is required for microbiological control, there is reduced potential for wood delignification or corrosion of system metallurgy.

EPA REGISTRATION

H-950 is registered by the United States Environmental Protection Agency (EPA Registration No. 5785-66-10445) as a biocide for use in recirculating and once-through cooling water systems.

DIRECTIONS FOR USE

Badly fouled systems MUST BE cleaned before treatment is begun.

Feed H-950 after the oxidant injection point into the water to be treated. Be sure rapid mixing of the treated water, H-950, and oxidant is achieved. Your Calgon representative will recommend appropriate feed equipment to assure complete mixing of the material.

Dosage Rates

Add H-950 to the system at 0.25 to 1.0 $NaBr/Cl_2$ mole ratio. For example:

1. 0.06-0.26 gallons H-950 per pound chlorine gas (99.9%).

2. 0.08-0.34 gallons H-950 per gallon sodium hypochlorite (12.5% available chlorine).

Initial Dose: When the system is noticeably fouled, add 0.001 to 0.020 gallons H-950 per 1000 gallons of water in the system and oxidize with either gaseous chlorine (.008 to .15 lbs. per 1000 gallons) or sodium hypochlorite solution (.006 to .12 gallons per 1000 gallons). Maintain a free halogen residual (0.1-0.3 ppm as Cl_2) for a minimum of one hour. Repeat as necessary until control is evident.

Subsequent Dose: When microbial control is evident, add 0.0005 to 0.020 gallons of H-950 per 1000 gallons of water in the system and oxidize with either gaseous chlorine (.004 to .15 lbs. per 1000 gallons) or sodium hypochlorite solution (.003 to .12 gallons per 1000 gallons).

Once-Through Cooling Water

Initial Dose: When the system is noticeably fouled, add 0.003 to 0.04 gallons of H-950 per 1000 gallons of water in the system and oxidize with either gaseous chlorine (0.02 to .30 lbs. per 1000 gallons) or sodium hypochlorite solution (.02 to .25 gallons per 1000 gallons). Maintain a free halogen residual (0.1-0.3 ppm Cl_2) for a minimum of one hour. Repeat as necessary until control is evident.

Subsequent Dose: When microbial control is evident, add 0.001 to 0.04 gallons H-950 per 1000 gallons of water in the system and oxidize with either gaseous chlorine (.008 to .30 lbs. per 1000 gallons) or sodium hypochlorite solution (.006 to 0.25 gallons per 1000 gallons).

CONTROL TESTING

The best indication of the successful application of H-950 is visual inspection of tower surfaces or monitoring changes in heat transfer on metal surfaces or process equipment. Usually, a free oxidant residual is required to achieve biological control. Use of on-site bacteria counts or microscopic examination provide relative indicators of system cleanliness and biological control. If bacteria counts are used,, note that counts may be high immediately after biocide addition. Counts will lower as control is achieved.

TYPICAL PROPERTIES

Active Ingredient	Sodium Bromide, 46%
Appearance	Clear Liquid
pH	7.3
Specific Gravity @ 77 F	1.42
Density, pounds per gallon	11.8
Odor	Odorless
Freeze Point, F	50

PACKAGING

H-950 is available in 55 gallon drums or delivered to on-site storage facilities via bulk or Calgon Bulk Liquid Service-Plus.SM

STORAGE AND HANDLING

The recommended minimum storage temperature is 50 F. H-950 should be stored in heat traced tanks or in an enclosed facility capable of maintaining 50 F.

PRECAUTIONS

Hazards to humans and domestic animals. Harmful if swallowed. Avoid breathing vapors. Irritation may develop from eye and skin exposure. Wear gloves and safety goggles. Avoid contact with skin and eyes. Wash contaminated clothing before reuse.

Environmental hazards. Do not discharge into lakes, streams, ponds, or public water unless in accordance with an NPDES permit. For guidance, contact your regional office of EPA.

Physical and chemical hazards. H-950 is not flammable. However, in fires fueled by other materials, hydrogen bromide or bromine may be released. Wear self-contaminated breathing apparatus.

Storage. Keep product in tightly closed original container when not in use. Store in a dry, well-ventilated area. Product should be stored at 50 F or above.

Disposal. Wastes resulting from the use of this product may be disposed of on site or at an approved waste disposal facility. Triple rinse the container (or equivalent). Then offer for recycling or reconditioning, or puncture and dispose of in a sanitary landfill, or incinerate. Burn only if allowed by state and local authorities. If burned, stay out of smoke.

Information concerning human and environmental exposure may be reviewed on the Material Safety Data Sheet and label for this product.

For additional information regarding incidents involving human and environmental exposure, call (412) 777-8000 and ask for the Health and Environmental Affairs Department.

For more information, contact your local Calgon Representative or write: Water Management Division, Calgon Corporation, P.O. Box 1346, Pittsburgh, PA 15230.

AQUATIC TOXICITY

HOCl[1]

Trout: LC_{50}, 96 Hr.	0.08-0.1 ppm
Minnows: LC_{50}, 96 Hr.	0.09 ppm
Bluegill: LC_{50}, 96 Hr.	0.18-0.33 ppm
Daphnia: LC_{50}, 48 Hr.	0.02-0.2 ppm

HOBr[2]

Trout: LC_{50}, 96 Hr.	0.23 ppm
Bluegill: LC_{50}, 96 Hr.	0.52 ppm
Daphnia: LC_{50}, 48 Hr.	0.71 ppm

[1] As Cl_2

[2] As Br_2

From Literature

1178-10/79 Experimental

MATERIAL SAFETY DATA SHEET

CALGON CORPORATION
SUBSIDIARY OF MERCK & CO., INC.

PRODUCT NAME H-850

SECTION I

MANUFACTURER'S NAME	Calgon Corporation	EMERGENCY TELEPHONE NO.	(412) 777-8000
ADDRESS	P.O. Box 1346, Pittsburgh, Pennsylvania 15230		
CHEMICAL NAME AND SYNONYMS	Sodium Bromide Solution	FORMULA	Multicomponent Liquid

SECTION II HAZARDOUS INGREDIENTS

PRINCIPAL HAZARDOUS COMPONENT (S)	%	ORAL LD_{50}	DERMAL LD_{50}	TLV (Units)
Sodium Bromide (CAS No. 7647-15-6)	35 - 45	> 5000 mg/kg	> 2000 mg/kg	None Established

SECTION III PHYSICAL DATA

BOILING POINT (°F)	> 212	SPECIFIC GRAVITY (H_2O=1)	1.34 - 1.5
VAPOR PRESSURE (mmHg.)	N/A	PERCENT VOLATILE BY VOLUME (%)	55
VAPOR DENSITY (AIR=1)	N/A	pH	N/A
SOLUBILITY IN WATER	Complete		
APPEARANCE AND ODOR	Colorless liquid, odorless		

SECTION IV FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (Method Used)	N/A	FLAMMABLE LIMITS N/A	Lel	Uel

EXTINGUISHING MEDIA: Water, CO_2, Foam, Dry Chemical

SPECIAL FIRE FIGHTING PROCEDURES: Exercise caution when fighting any chemical fire. A self-contained breathing apparatus and protective clothing are essential.

UNUSUAL FIRE AND EXPLOSION HAZARDS: None

N/A = Not applicable

Users of Calgon Chlorine/Bromine Chemistry in Tennessee

Aluminum Company of America

BASF Fibers

ENCLOSURE 6

Product Information for Calgon's

CL-361

(This information was provided by Calgon for TVA's use in obtaining regulatory approval for the use of the specific product.)

EPA Registration Number: Not Applicable

CL-361

Deposit Penetrant

DESCRIPTION

CL-361 is a unique liquid blend of deposit penetrants, surfactants, and polymeric dispersants formulated to enhance scale, deposit and corrosion control programs.

ADVANTAGES

- **Enhances Microbiological Treatment Results**
  CL-361 effectively penetrates slime deposits permitting the microbiocide to function cost effectively. The low foaming action which results from CL-361 feed facilitates slime penetration.
- **Deposit Control**
  CL-361 functions as a dispersant keeping inorganic and organic foulants fluidized to minimize deposition on equipment and on heat exchanger surfaces.
- **Improves Corrosion Control Programs**
  CL-361 promotes system cleanliness, resulting in increased heat transfer. Corrosion inhibitors function more effectively when metal surfaces are free of foulants. Improved system cleanliness also minimizes under deposit corrosion.

METHOD OF FEEDING

CL-361 should be fed at a point in the system where turbulent flow will assure good mixing. The product must be fed neat and must not be mixed with other water treatment chemicals prior to feeding. CL-361 may be fed continuously or intermittently depending on treatment objectives. Your Calgon representative will assist you in establishing a treatment program to fit your specific cost performance criteria.

CONTROL TESTING

Product performance is ultimately confirmed by periodic equipment inspections, as well as heat transfer and corrosion monitoring.

TYPICAL PROPERTIES

Appearance	clear, colorless liquid
pH	5.3
Specific Gravity @ 77° F	1.02
Density, pounds per gallon	8.5
Flash Point, ° F (TCC)	>200
Measured Freeze Point, ° F	30
Brookfield Viscosity @ 70° f, cps	15

PACKAGING

CL-361 is available in 5 gallon plastic pails (40 lbs. net, 43 lbs. gross), 55 gallon plastic drums (450 lbs. net, 474 lbs. gross), 275 gallon plastic disposable bins (2337 lbs. net, 2512 lbs. gross), or delivered to on-site storage facilities via bulk or Calgon Bulk Liquid Service-Plus℠.

SHIPPING

DOT Hazardous Class	Not Restricted
DOT Proper Shipping Name	Not Restricted
UN Number	Not Applicable

STORAGE AND HANDLING

The recommended minimum storage temperature for CL-361 is within the range of 30-35° F. Best if used within twelve (12) months from time of receipt. Preferably, product should not be allowed to freeze. If freezing occurs, product may separate. It may be possible to restore product integrity by slowly warming until product thaws and agitating.

COMPATIBILITY

Recommended materials for:

Bulk Storage Tanks - High density or cross-linked polyethylene, fiberglass with bisphenol, isophthalic, or vinyl ester liner resins, #304 or #316 stainless steel, epoxy phenolic, or vinyl ester lined steel.

Pump "Liquid Ends" and Piping - Polyethylene, polypropylene, PVC, 304SS, 316SS, Kynar, Hypalon, Viton or Teflon

Information concerning human and environmental exposure may be reviewed on the Material Safety Data Sheet for this product.

For additional information regarding incidents involving human and environmental exposure, call 412 777-8000 and ask for the Regulatory and Trade Affairs Department.

1179 10/79

MATERIAL SAFETY DATA SHEET

DATE September 17, 1987

0619-00-23-02-570

PRODUCT NAME CL-361

CALGON CORPORATION
SUBSIDIARY OF MERCK & CO., INC.

SECTION I

MANUFACTURER'S NAME	Calgon Corporation	EMERGENCY TELEPHONE NO.	(412) 777-8000
ADDRESS	P. O. Box 1346, Pittsburgh, Pennsylvania 15230		
CHEMICAL NAME AND SYNONYMS	Surfactant	FORMULA	Multicomponent Liquid

SECTION II HAZARDOUS INGREDIENTS

PRINCIPAL HAZARDOUS COMPONENT (S)	%	ORAL LD_{50}	DERMAL LD_{50}	TLV (Units)
This product would not be regarded to contain any hazardous				
ingredients according to OSHA Hazard Communication				
Standard (29 CFR 1910.1200).				

SECTION III PHYSICAL DATA

BOILING POINT (°F)	> 212	SPECIFIC GRAVITY (H_2O=1)	1.01 - 1.03
VAPOR PRESSURE (mmHg.)	Similar to Water	PERCENT VOLATILE BY VOLUME (%)	95
VAPOR DENSITY (AIR=1)	Similar to Water	pH	5.0 - 5.5
SOLUBILITY IN WATER	Complete		
APPEARANCE AND ODOR	Clear colorless liquid with mild organic odor		

SECTION IV FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (Method Used)	Not flammable	FLAMMABLE LIMITS Not Applicable	Lel	Uel
EXTINGUISHING MEDIA	Product is not flammable.			
SPECIAL FIRE FIGHTING PROCEDURES	None			
UNUSUAL FIRE AND EXPLOSION HAZARDS	None			

EFFECTS OF OVEREXPOSURE — The product is practically non-toxic through ingestion and dermal absorption. The acute oral LD_{50} (rats) is > 3.0 g/kg. The acute dermal LD_{50} (rabbits) is > 2 ml/kg. It is not a primary skin irritant. The Primary Irritation Index is 2.04/8 (rabbits). The product produced slight conjunctival irritation in rabbit eyes (Score after 24 hr - 2, Score after 48 hr - 0).

EMERGENCY AND FIRST AID PROCEDURES

Good First Aid should be followed in all cases of exposure.

In case of eye contact, flush with plenty of water for at least 15 minutes.
If irritation develops, call a physician.

SECTION - VI REACTIVITY DATA

STABILITY	STABLE	X	CONDITIONS TO AVOID	Unknown
	UNSTABLE			
INCOMPATABILITY (Materials to Avoid)	Strong bases			
HAZARDOUS DECOMPOSITION PRODUCTS	Unknown			
HAZARDOUS POLYMERIZATION	MAY OCCUR	NO X	CONDITIONS TO AVOID	Unknown

SECTION VII SPILL OR LEAK PROCEDURES

REPORTABLE QUANTITIES (RQ) IN LBS. OF EPA HAZARDOUS SUBSTANCES IN PRODUCT

1. N/A
2.
3.

NOTIFY EPA OF PRODUCT SPILLS EQUAL TO OR EXCEEDING N/A LBS.

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED — Dispose of in accordance with local, state and federal regulations. Dike area to contain as much spilled material as possible. Remove any remaining material by absorbing on vermiculite or other suitable absorbing material and place in a sealed metal container for disposal.

WASTE DISPOSAL METHOD

Flush with plenty of water and dispose of in accordance with local, state and federal regulations.

SECTION VIII SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (Specify Type)	Not Required			
VENTILATION	LOCAL EXHAUST	Not Required	SPECIAL	
Normal	MECHANICAL (General)	Not Required	OTHER	
PROTECTIVE GLOVES	Not Required		EYE PROTECTION	Not Required
OTHER PROTECTIVE EQUIPMENT	Not Required			

SECTION IX SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING

Wash thoroughly after handling. Keep container closed.
Exercise caution in the storage and handling of all chemical substances.

OTHER PRECAUTIONS

None

578 PREPARED BY Janet Mostowy

ENCLOSURE 7

Toxicity Data for Chlorine/Bromine
Mixtures

(This information was compiled from the literature.)

"EFFICACY OF CHLORINE AND BROMINE MIXTURES AS BIOCIDES AND SUBSEQUENT ENVIRONMENTAL CONSEQUENCES--A REVIEW[1]"

Biocides are typically used in raw water systems of power plants to control biological fouling in various system components. Biofouling reduces system efficiency by creating more resistance to flow and by decreasing effectiveness of heat transfer. Essentially complete clogging can occur under extreme conditions. Biofouling can also result in corrosion in the system to the point that leaks develop.

As a result of these problems, power plants use toxic agents (biocides) to control these growths. However, biocides cannot distinguish target from non-target organisms. This creates environmental consequences once treated water is discharged to a receiving stream. The resulting dilemma is how to maintain plant efficiency and safety yet minimize environmental impacts from a control program.

The most commonly used biocide is chlorine because of its historical use, effectiveness, and low expense. It is usually injected as chlorine gas (CL_2) or as a hypochlorite such as sodium hypochlorite (NaOCl). Once injected into the system, there usually will be two forms of free chlorine--hypochlorous acid (HOCl) and the hypochlorite ion (OCl^-). In the presence of ammonia (NH_4) two forms

[1]This review was based on abstracts from various abstracting services.

of combined chlorine can exist--monochloramine (NH_2Cl) and dichloramine ($NHCl_2$). All of these are quite toxic to aquatic organisms (EPA, 1985). The relatively long life of the combined forms (approximately 20 hours) adds to the concern for environmental impact (Zeh, 1984). Toxicity of chlorine from power plant use has been thoroughly studied and will not be detailed here because of its extensive documentation (Heinle, 1976; Cherry et al., 1977; Morgan and Prince, 1978; Anderson et al., 1979; Fandrei and Collins, 1979; Seegret et al., 1979; Bean et al., 1980; Brooks et al., 1982; Howells, 1983; Brooks and Barton, 1984; Wang and Hanson, 1984; Hidaka and Tatsakawa, 1985; Moss et al., 1985).

Other implications from use of chlorine include formation of organochlorine compounds. Formation of these compounds is a concern because incorporation of chlorine into an organic molecule increases its lipophilic character and at the same time increases toxicity or bioaccumulation, or both (Kapperman et al., 1976). Another concern for formation of organochlorines is that they have been found to be carcinogenic and mutagenic and, if present in a drinking water supply, have potential to affect human health (Bean et al., 1983; Bull, 1984; Meier and Bull, 1984;).

Because of the problems associated with use of chlorine as a biocide, power plants, waste water treatment facilities, and drinking water supplies have investigated use of alternative biofouling/disinfection control techniques. One of the more promising alternatives is use of bromine in place of or in addition to chlorine.

Bromine is injected into the system as either bromine chloride (BrCl), a fuming red liquid potentially hazardous to the user (Nalco, 1982); sodium bromide (NaBr), a salt solution typically used in addition to chlorine; or 1-Bromo-3-chloro-5,5 dimethylhydantoin (BCDMH), a slow release biocide (Soracco et al., 1985).

Most available literature deals with efficacy and/or environmental impacts of using BrCl. Because the active bromine species should be the same regardless of the donor (Nalco, 1982), study results should be applicable to one another.

Although some studies have found that bromine is a better biocide than chlorine Mills, 1973a and 1973b), most have found a combination of bromine and chlorine to be more effective than using either alone (Nalco, 1982; Zeh, 1984). Toxicity of bromine has been found to be roughly equal to that of chlorine for copepods (Bradley, 1977) and benthic invertebrates (Venosa and Ward, 1978). Venosa and Ward also found chlorine to be more toxic to fathead minnows than bromine, yet bromine was more toxic to salmonid fishes than chlorine. Tests on chlorine residuals and bromine residuals have shown chlorine residuals reduce growth of fathead minnows at substantially lower levels than bromine residuals (0.033 compared to 0.34 mg/L, respectively; Ward and DeGraeve, 1978) and are more acutely toxic than bromine to juvenile ye not adult fathead minnows (Wilde et al., 1983). However, Wilde et al. also found that bluegill were more tolerant of chlorine than bromine residuals.

It appears bromine is an effective biocide and is more desirable environmentally because of its short life compared to

chlorine--approximately 10 minutes for bromine compared to 20 hours for similar chlorine compounds (Zeh, 1984). Bromine apparently offers another advantage when used in combination with chlorine in that it enhances the decomposition of the toxic chloramines by formation of NHBrCl (Trofe et al., 1980a and b). Most researchers concluded that the environmental consequences of bromine were less than chlorine (Mills, 1973a and 1973b; Wackenhuth and Levine, 1974; Groninger et al., 1978; Ward and DeGraeve, 1978; Zeh, 1984).

Although bioaccumulation of brominated compounds has been investigated much less extensively than chlorinated compounds, results of a study by Kuehl et al. (1978) suggest bioaccumulation of organobromine compounds in fish. A study by Hohlfield et al. (1983) also indicated potential for organobromine compounds to bioaccumulate, although they found levels less than 100 ppb in fish exposed to BrCl treated water; a level which they concluded posed no risk to human health.

FAEB 1012g

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ACUTE TOXICITY OF CHLOROBROMINATED AND CHLORINATED EFFLUENTS TO VARIOUS SPECIES[1]

	Chlorobrominated Effluent	Chlorinated Effluent
	96 Hour TL50 (mg/l)	96 Hour TL50 (mg/l)
Fathead Minnow *Pimephales promelas*	0.133-0.185	0.082-0.095
Northern Common Shiner *Notropis cornutus*	0.120-0.140	0.051
Pugnose Shiner *Notropis anogensus*	0.109-0.136	0.045
Western Golden Shiner *Notemigonus crysoleucas*	0.090	0.040
Lake Trout *Salvelinus namaycush*	0.102	0.060
Chinook Salmon *Oncorhynchus tschawytscha*	0.059	
Northern Yellow Bullhead *Ictalurus natalis*	0.177	
Northern black Bullhead *Ictalurus melas*	0.283	
Daphnia Magna	0.047-0.055	0.017

[1] Disenfection Efficiency and Residual Toxicity of Several Wastewater Disenfectants - Volume I, EPA-600/2-76-156, 10/76.

Bull. Environm. Contam. Toxicol. 27, 326-331 (1981)

Static Acute Toxicity of Sodium Bromide to Fathead Minnows*

H. C. Alexander,[1] J. A. Quick, Jr.,[2] and E. A. Bartlett[3]

[1]Research Associate, [2]Project Leader, and [3]Research Chemist, Environmental Sciences Research Laboratory, The Dow Chemical Co., Midland, MI 48640

This study was the first phase of a research program designed to examine the dynamics of sodium bromide uptake, biotransformation, and depuration in fish. This investigation was designed to determine the acute static toxicity of sodium bromide to the test species, *Pimephales promelas* Rafinesque. These data were used to select exposure levels for later long-term sodium bromide exposures.

MATERIALS

Test Material. The NaBr used was analyzed 99.9% pure from Lot 09049, Halogens Research, Michigan Division, The Dow Chemical Company, Midland, MI.

Dilution Water. Lake Huron water which had been passed through a carbon contactor and ultraviolet light sterilizer was used. Detailed analyses of this dilution water are given in Tables 1 and 2 (HUNEMORDER 1979).

Fish. Fathead minnows (original stock from U.S. EPA Laboratory, Duluth, MN) were hatched and reared in the Environmental Sciences Research (ESR) Laboratory. These animals were reared at 25 ± 2°C until about 60 days of age (subadults) and then slowly (≤1°C/day) acclimated to 12 ± 1°C. Typical holding and rearing conditions were 16 h light/day photoperiod at 215-2044 lux and a water flow rate >2 L/min. Fish were fed once or twice daily, *ad libitum*. The specially formulated diet mix is shown in Table 3 (MEHRLE 1976).

METHODS

A range-finding test was run in which two fish were placed in 1 L of each of seven widely varying concentrations of NaBr at 12 ± 1°C. This test indicated the LC50 was between 10,000-20,000 mg/L.

* Dow Chemical Company B-600-066-81

0007-4861/81/0027-0326 $01.20

TABLE 1. CARBON FILTERED RAW LAKE HURON WATER ANALYSES

Alkalinity

TABLE 1. CARBON FILTERED RAW LAKE HURON WATER ANALYSES

Date	pH	Conductivity µmhos/cm	Hardness mg/L as $CaCO_3$	Alkalinity mg/L as $CaCO_3$
4/5/79	7.7	158	110	79
5/29/79	7.7	200	134	85
7/2/79	7.7	190	110	87
7/18/79	7.6	200	95	77
9/10/79	7.9	188	103	86
10/12/79	8.0	198	102	78
11/20/79	8.1	185	105	80
1/7/80	7.8	155	97	80

TABLE 2. CARBON FILTERED RAW LAKE HURON WATER ANALYSES

Chemical Quality	mg/L
Alkylbenzene sulfonate	ND (0.1)
Arsenic	ND (0.001)
Barium	ND (1)
Cadmium	ND (0.01)
Calcium	26
Chloride	9.9
Chromium	ND (0.05)
Copper	ND (0.01)
Cyanide	ND (0.01)
Fluoride	0.09
Iron	0.01
Lead	ND (0.05)
Magnesium	7
Manganese	ND (0.05)
Mercury	ND (0.005)
Nitrate	0.20
Phenols	ND (0.001)
Polychlorinated Biphenyls	ND (0.010×10^{-3})
Selenium	ND (0.01)
Silver	ND (0.05)
Sulfate	19
Total Filterable Residue	146
Zinc	ND (0.5)

ND = Parameter was not detected followed by minimum detectable amount in parentheses.

SES

TABLE 3. FORMULATED SYNTHETIC DIET

Dry synthetic diet contains:

28% casein - 280 g per kg dry mix
15% gelatin - 150 g per kg mix
28% dextrin - 280 g per kg mix
4% mineral mix - 40 g per kg mix
9% vitamin mix - 90 g per kg mix
11% corn oil - 110 g per kg mix
5% salmon oil - 50 g per kg mix

Mix for 15 minutes and package.

Mix equal weights of dry mix and dechlorinated Lake Huron water and refrigerate.

This was followed by a definitive test (THE DOW CHEMICAL COMPANY 1978) in which the concentrations of NaBr were set close together using a 90% dilution factor, with concentrations ranging from 8,610-20,000 mg/L. For this test, ten fish were placed in 8 L of dilution water for 24 h with aeration. After 24 h, aeration was discontinued and toxicant added with 2 L of water to bring the total volume to 10 L in each vessel at the start of the test. Fish were exposed for 96 h at 12 ± 1 C with effects recorded and dead animals removed every 24 h. No food was provided during the test. The 16-h photoperiod was also used in the testing area at 915-1345 lux cool white fluorescent illumination. Death was confirmed by absence of opercular movement and lack of response to prodding. Measurement of surviving fish at test conclusion showed the average standard length and weight to be 26.8 mm and 0.285 g.

Statistical Calculations. The results from toxicity tests were used to calculate the LC50 value, i.e., the toxicant concentration which would kill 50% of the test organisms in a specified time period. This was done using a computer program of Finney's method of probit analysis (FINNEY 1952), Thompson's method of moving averages (THOMPSON 1947), and the binomial method (STEEL et al. 1960). The 95% confidence interval (a range within which there is 95% probability the real LC50 value lies) was also determined. Probit results are considered the most accurate (PARK 1979), and are reported when data fulfilled the probit program requirements. Otherwise, LC50's calculated by moving average are reported.

RESULTS AND DISCUSSION

The acute toxicity of sodium bromide to the fathead minnow is summarized below:

Exposure Period (Hours)	LC50 (mg/L)	Method of Calculation
24	18,441 (17,879-19,140)*	Moving Avg.
48	17,757 (16,929-18,668)	Probit
72	17,019 (16,084-18,137)	Probit
96	16,479 (15,614-17,428)	Probit

The moving average value for the 24-h LC50 is reported because the data did not fulfill the requirement for the probit analysis which requires at least two partial kills to achieve statistically valid results. There was a sufficient range of mortality during the remainder of the test to perform valid probit analyses.

Sodium bromide has a low toxicity to fathead minnows that is similar to that of sodium chloride. The 96-h LC50 for sodium chloride on fathead minnows has been reported by our laboratory as 10,610 (10,423-10,846) mg/L (BARTLETT 1978). This is 0.181 (0.178-0.185) moles per L or 0.362 (0.356-0.370) ionic equivalents per L. The 96-h LC50 value for sodium bromide of 16,479 (15,614-17,428) mg/L is 0.160 (0.152-0.169) moles per L or 0.320 (0.304-0.338) ionic equivalents per L. These toxicity values are close but still significantly different at P= 0.05 because of no overlap on the 95% confidence interval.

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*95% confidence intervals

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Accepted June 15, 1981

Ed Wilde (803)
450-2556

Bull. Environ. Contam. Toxicol. 31, 309-314 (1983)

Acute Toxicity of Chlorine and Bromine to Fathead Minnows and Bluegills

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The environmental acceptability of using chlorine as an antifouling [illegible] industrial cooling systems is a subject of increasing conc[illegible]. Several alternatives to chlorination have recently been prop[illegible] including the use of a bromine-based biocide, 1-bromo-3-ch[illegible],5-dimethylhydantoin (BCDMH). This compound has reportedly [illegible]performed chlorine in several cooling tower applications (MACCHIAROLO, et al. 1980; MATSON & CHARACKLIS 1982). However, information on the use of BCDMH in once-through cooling systems and the relative environmental acceptability of BCDMH in comparison to chlorine are lacking.

The objective of this study was to [illegible] the relative toxicity of chlorine and BCDMH to three types [illegible] fish in a freshwater system used for cooling a nuclear reactor.

METHODS AND MATERIALS

Flow-through 96-h toxicity tests were conducted in March 1982 using a mobile laboratory located adjacent to Par Pond, a reactor cooling reservoir at the Savannah River Plant (SRP) near Aiken, S. C. Two solenoid-activated proportional, flow-through dilutor systems as described by PELTIER (1978) were used for simultaneous testing of oxidant residual toxicity resulting from chlorine and BCDMH additions. Each system delivered approximately 100%, 75%, 60%, 35%, 20%, 2%, and 0% of stock solution of the appropriate biocide to duplicate test chambers using Par Pond water as diluent.

A Hydrolab 8000 system was used to make daily measurements of: dissolved oxygen, temperature, conductivity, and pH in the test chambers receiving 100%, 35%, 2%, and 0% biocide solutions. Alkalinity was measured by APHA standard methods (APHA 1980).

Juvenile (six-week-old) and yearling fathead minnows (*Pimephales promelas*) and young-of-the-year bluegills (*Lepomis macrochirus*) were used as test organisms. The fish were acclimated to Par Pond water for ten days prior to the tests. Juvenile minnows were fed daily during the acclimation and test periods. Ten of each of the three types of fish were placed in each of the duplicate chambers (a loading rate of <2.0 g fish/L of water). Each test chamber was 30.0 cm deep and had a capacity of 15 L. Juvenile fathead minnows

were placed in small glass holding chambers (8.2 cm x 20.0 cm x 15.5 cm) which were suspended in the test chambers. These holding chambers had a 3.0 cm x 8.2 cm Nitex screen (#0 mesh, 0.505 mm aperature) at each end to allow circulation through the chamber and prevent predation by the other test organisms.

Two 80 L stock solutions of each biocide were prepared daily. Chlorine stock solutions were prepared by adding reagent grade 5% sodium hypochlorite. BCDMH solutions were prepared by adding Bromicide® (Great Lakes Chemical Corp., Lafayette, Indiana). Stock biocide solutions were added to their respective dilutor systems for 1 h/day, 0, 24, 48, and 72 h after testing began.

Water samples (ca. 20 ml) were collected from each of the test chambers and tanks containing stock solutions at 10-minute intervals during the periods (ca. 2 h/day) that biocide residuals were measurable in the test chambers. Levels of total and free residual chlorine (TRC and FRC) were determined by the DPD spectrophotometric method (APHA 1980). Oxidant residuals resulting from BCDMH treatment were also routinely measured as chlorine by the DPD method; however, the DPD differentiation method (using glycine) was performed on a few representative samples to distinguish between bromine and chlorine residuals (WHITE 1978).

Median lethal concentrations (96-h LC_{50}'s) were determined by the probit, moving average, and binomial methods (STEPHAN, 1977). Log transformations of dose values were not used because a better goodness of fit was obtained in the majority of cases by using actual dose values. Biocide dosages were calculated as follows:

(1) 96-h peak = the single highest biocide residual detected during the four days of testing.

(2) 96-h mean maximum = the average maximum biocide residual detected during the four days of testing.

(3) 96-h intermittent exposure mean = the mean biocide residual level during the four ~2-h exposure periods.

(4) 96-h accumulative exposure = the total 96-h biocide exposure in mg/L residual x minutes of exposure (area under a time-concentration curve).

LC_{50}'s for TRC and TRB (total residual bromine measured as chlorine) exposure were statistically compared. Differences were considered significant if: greater LC_{50}/smaller LC_{50} > 1.96 $SE_{\underline{Diff}}$ (APHA, 1980).

RESULTS AND DISCUSSION

The DPD differentiation measurements showed that > 95% of the oxidant residual resulting from BCDMH treatment was bromine.

Therefore, residuals from this treatment were considered total and free residual bromine (TRB and FRB).

LC_{50} values computed by the three methods (probit, binomial and moving average) were similar. Values obtained by the moving average method are presented in Table 1. Juvenile fathead minnows were significantly more tolerant of TRB than TRC. TRC and TRB 96-h LC_{50} values for adult fathead minnows were not significantly different. Bluegills were significantly more tolerant of TRC than TRB.

Table 1. Comparative toxicity (LC_{50}'s and 95% confidence intervals) of intermittent (ca. 2 h/day) exposure to residual chlorine or bromine

Type of biocide dose computation and fish	Biocide	
	TRC	TRB
96-h peak (mg/L)		
Juv. fatheads	0.44(0.22-0.62)	1.21(0.96-1.42)*
Adult fatheads	1.56(1.34-1.79)	1.83(1.59-2.10)
Bluegills	2.48(2.20-2.64)	2.35(1.92-2.73)
96-h mean max. (mg/L)		
Juv. fatheads	0.39(0.21-0.53)	0.81(0.65-0.94)*
Adult fatheads	1.37(1.19-1.55)	1.17(1.03-1.31)
Bluegills	2.13(1.93-2.34)	1.43(1.28-1.62)*
96-h int. exp. mean (mg/L)		
Juv. fatheads	0.18(0.11-0.24)	0.35(0.28-0.41)*
Adult fatheads	0.58(0.51-0.65)	0.51(0.46-0.57)
Bluegills	0.88(0.81-0.98)	0.63(0.56-0.71)*
96-h accum. (mg/L x min)		
Juv. fatheads	85(48-113)	164(132-194)*
Adult fatheads	274(240-308)	248(221-276)
Bluegills	421(387-465)	301(271-338)*

* LC_{50}'s for TRC and TRB significantly different at 0.05 level.

Bluegills were significantly more tolerant of both biocides than were fathead minnows. Adult minnows were significantly more tolerant of both biocides than juvenile minnows.

Water quality data are summarized in Table 2. All values for parameters monitored during the tests were within acceptable testing limits (PELTIER, 1978), and variability over time or between test chambers was not substantial.

The percentage of total residual oxidant (TRO) consisting of free residual oxidant (FRO) was greatest at times of maximum exposure

Table 2. Summary of water quality measurements made in conjunction with the toxicity tests.

Parameter	Mean $\pm$ SE	Range
Temp (°C)	21.1 $\pm$ 0.1	19.9 - 22.9
pH	7.0 $\pm$ 0.1	6.7 - 7.1
DO (mg/L)	7.8 $\pm$ 0.1	6.5 - 9.1
Cond (umhos/cm)	66.6 $\pm$ 0.1	63 - 71
Alkalinity (mg/L)	15.3 $\pm$ 0.1	14 - 16

in tests with both biocides. The FRC and FRB contributions to TRC and TRB in test chambers receiving 100% stock biocide solutions averaged 83.2% and 62.2%, respectively during the 30 min periods of maximum exposure. FRC and FRB contributed 68.8% and 50.4%, respectively to TRC and TRB during all exposure periods in the test chambers receiving 100% biocide stock solution.

This was the second of two studies comparing effluent toxicity with chlorination and chlorination alternatives in an SRP reactor heat exchanger cooling system. The first study (WILDE et al. 1983) showed that oxidant residuals from chlorine dioxide were 2-4 times more toxic to three types of fish than those from chlorination. The present study showed that on the basis of 96-h LC_{50} values for halogen residuals, chlorine and BCDMH additions resulted in similar overall toxicity to fish. Compared to chlorine, BCDMH was more toxic to bluegills and less toxic to juvenile fathead minnows.

The LC_{50} values for TRC were substantially higher in this study than in the previous SRP study where nearly identical methods were used. However, the pattern of relative TRC toxicity with regard to fish type was the same; juvenile fathead minnows were least tolerant, and bluegills were most tolerant. Two factors which probably contributed to the greater tolerance to TRC in the present tests compared to previous tests were: 1) a longer acclimation period to the test water (10 days compared to 3 days), and 2) a lower average water temperature (21.1°C compared to 27.7°C). HEATH (1977) and BASS and HEATH (1977) concluded that water temperature did not significantly influence the 96-h LC_{50} values for bluegills intermittently exposed to chlorine. However, toxicity testing of several fish species by BROOKS and SEEGERT (1977) and SEEGERT and BROOKS (1978) clearly demonstrated the existence of a direct relationship between chlorine toxicity and temperature. DICKSON et al. (1977) also showed that chlorine was more toxic to goldfish at higher temperatures.

Although all fish toxicity studies are somewhat site and time specific, the intermittent biocide regime and relatively high percentage of FRO in the TRO make the present results more applicable to power plant cooling systems than to domestic wastewater treatment systems. BROOKS et al. (1982) have recently demonstrated significantly different toxicities among various forms of residual chlorine to three species of fish. MATTICE et al. (1981) determined that hypochlorous acid was about four times as toxic as hypochlorite ion to mosquitofish. Other workers (ZILLICH, 1972; BRUNGS, 1973; BASS & HEATH, 1977) previously concluded that free chlorine is more toxic to fish than combined chlorine.

There are no previous studies comparing BCDMH toxicity with chlorine toxicity. Bromine chloride has been shown to be similar or slightly less toxic than chlorine (BURTON & MARGREY, 1979; DEGRAEVE & WARD, 1977; LIDEN et al., 1980). These results along with those of the current study indicate that chlorine and bromine produce similar residual halogen toxicity to fish.

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STUDY ON THE TOXICITY OF SODIUM BROMIDE TO DIFFERENT FRESHWATER ORGANISMS

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Abstract—The toxicity of sodium bromide for freshwater organisms was tested using algae (*Scenedesmus pannonicus*), crustaceans (*Daphnia magna*) and fish (*Poecilia reticulata* and *Oryzias latipes*). Depending on the species tested, the acute toxicity varied from 44 to 5800 mg Br⁻/litre (LC_{50} values) and the No Observed Effect Concentrations (NOEC values) in the long-term tests varied from 7.8 to 250 mg Br⁻/litre. Bromide ion markedly impaired reproduction in both crustaceans and fish. Histologically no effects were observed in the long-term test with Oryzias, but in the reproduction test with Poe[illegible]yperplasia of the thyroid, atrophy and degeneration of the musculature and regressive change[illegible]e reproductive tract were observed. As a criterion of water quality, 1 mg Br⁻/litre has been proposed, on the basis of reproductive performance in the Poecilia test. The concentrations found in surface water frequently exceed this value and sometimes reach levels at which acute effects on water organisms can be expected.

Introduction

Chemical analyses have shown that bromide ion is present in Dutch surface waters in relatively high concentrations (Wegman, Hamaker & de Heer, 1983). However, as data on the toxicity of bromide to water organisms are lacking, it is impossible to evaluate these analytical data with respect to the effect on the aquatic ecosystem.

In this study, short-term and long-term toxicity tests were carried out with different species of freshwater organisms to get an impression about the possible environmental effects of bromide and to establish a water-quality criterion. Furthermore, attention was paid to possible histopathological effects in fish.

Experimental

Test material. The purity of the sample of sodium bromide used as the test compound in this study was 99.5%. It was obtained from J. T. Baker Chemicals (Deventer, The Netherlands).

Methods

Short-term toxicity tests were carried out with four different freshwater organisms (Table 1): the alga *Scenedesmus pannonicus*, a crustacean (*Daphnia magna*) and two fish (*Poecilia reticulata* and *Oryzias latipes*). Long-term tests were performed with Daphnia, Poecilia and Oryzias (Table 1). For a more detailed description of the test protocols and experimental conditions used with Scenedesmus, Daphnia and Poecilia, the rules of the Dutch Standardization Organization (1980; NEN 6501, 6502, 6504 & 6506) can be used as reference.

The long-term tests with Poecilia and Oryzias were also carried out according to those rules. At the end of the 4-week test with Poecilia and the 5-week test with Oryzias the remaining fish were killed with the anaesthetic MS_{222}® (Sandoz AG, Basel, Switzerland) and the length and weight of each fish was determined.

Normally a 3-week test with *Daphnia magna* and an egg-larval test with a fish, combined with a 4-day test with algae, may give a reasonable impression about the possible ecotoxicological effects of a compound (Adema, Canton, Slooff & Hanstveit, 1981). Because reproduction proved to be a very sensitive criterion in the test with Daphnia the effects on the F_0 and F_1 generations were also studied. To examine the reproduction of fish as well, an additional test was carried out with *Poecilia reticulata*.

All test organisms were obtained from standardized laboratory cultures. The compositions of the test media were as described previously (Canton & Slooff, 1982a), except for the medium used in the reproduction test with Poecilia. This test was performed some years ago when another standardized test medium was used for fish (for the composition, see Canton & van Esch, 1976).

The concentration ratios in the short-term and long-term tests were based on a ratio of $\sqrt[4]{10}$ (1.8) and $\sqrt{10}$ (3.2), respectively, except for the reproduction tests with Daphnia and Poecilia. The pH and oxygen content of the test solutions were checked immediately before the beginning of exposure and when fresh test solution was introduced or at the end of the test (in the case of a static test). Because of the high stability of sodium bromide in aqueous solutions and since no adsorption on glass occurs (J. H. Canton & R. C. C. Wegman, unpublished data), the actual concentrations were not measured during the test.

At the end of the reproduction test with Poecilia and the test with Oryzias all animals were immersed in Bouin fixative after being killed with MS_{222}. From the control group and the group exposed to 780 mg Br⁻/litre in the test with Oryzias, ten fish were embedded in one paraffin block and sectioned semiserially. In the test with Poecilia, all fish were em-

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Table 1. Test organisms, experimental conditions and toxicological criteria used in the short- and long-term toxicity tests

Test organism	Age	Exposure time (days)	Organisms (No./group)	Test vol./group (litres)	Temp.* (C)	Dosing	Renewal rate† (days)	Criteria
				Short-term tests				
Scenedesmus pannonicus	Logphase	4	10^6 cells/ml	0.15	23 ± 2	Static	—	Growth (biomass)
Daphnia magna	< 1 day	2	25	1	19 ± 1	Static	—	Mortality, abnormal behaviour
Poecilia reticulata	3–4 wk	4	10	1	23 ± 2	Pulsating	2	Mortality, abnormal behaviour
Oryzias latipes	4–5 wk	4	10	1	23 ± 2	Pulsating	2	Mortality, abnormal behaviour
				Long-term tests				
Daphnia magna	< 1 day	23	25	1	19 ± 1	Pulsating	2–3	Mortality, reproduction
Poecilia reticulata	3–4 wk	28	25	2	23 ± 2	Pulsating	2–3	Mortality, immobility, abnormal behaviour, growth
	8–9 months	124	10 M, 5F	30	23 ± 2	Pulsating	7	Mortality, immobility, abnormal behaviour, reproduction, histopathology
Oryzias latipes	> 6 hr (eggs)	34	30	1	23 ± 2	Pulsating	2–3	Mortality, immobility, abnormal behaviour, heart rate, hatching, growth, histopathology

*Lighting was on a light/dark cycle for all organisms except *S. pannonicus* (continuous, > 5000 lux); Daphnia 12 hr light, fish 14 hr light.

†Test solution was renewed once every 2, 2–3 or 7 days as indicated.

Table 2. Summary of the results of the short-term toxicity tests on sodium bromide

Test organism	Parameter	Results (g Br⁻/litre) at: 24 hr	48 hr	72 hr	96 hr
Scenedesmus pannonicus	EC_{50}*	5.8	7.8	8.5	10
	NOEC*	2.5	2.5	2.5	2.5
Daphnia magna	LC_{50}†	11	11		
	EC_{50}‡	5.8	5.8		
	NOLC†	7.8	7.8	-	
	NOEC‡	4.3	4.3	—	—
Poecilia reticulata	LC_{50}†	16	16	16	16
	EC_{50}‡	0.44	0.14	0.044	0.044
	NOLC†	7.8	7.8	7.8	7.8
	NOEC‡	0.25	0.078	0.025	0.025
Oryzias latipes	LC_{50}†	26	25	24	24
	EC_{50}‡	0.44	0.44	0.44	0.44
	NOLC†	7.8	7.8	7.8	7.8
	NOEC‡	0.25	0.25	0.25	0.25

NOE(L)C = No observed (specified) effect concentration

*E = growth.
†L = mortality.
‡E = mortality and abnormal behaviour.

bedded individually after being cut in sagittal or several transverse slices. Sections were stained with haematoxylin and eosin.

Results

The results of the short-term toxicity tests are summarized in Table 2. *Poecilia reticulata* was the most sensitive organism (EC_{50} = 44 mg Br⁻/litre), whereas the other test organisms proved to be far less susceptible (by a factor of 10 *c.* 100).

The results of the long-term toxicity tests are shown in Table 3. The lowest NOEC value (No Observed Effect Concentration) from these studies was 7.8 mg Br⁻/litre, which was derived from the reproductive performance of *Daphnia magna* and *Poecilia reticulata*. In the test with daphnids there was a concentration-related decrease in the total number of eggs produced per female per batch in the brood-chamber, as well as a concentration-related decrease in the viability of these eggs (Table 4). This phenomenon was also observed in the tests with the F_1 and F_2 generations.

At the three highest test concentrations (780, 3900 and 7800 mg Br⁻/litre) the fertility of Poecilia was not impaired during the first 5 weeks of exposure, but in a few cases prematures were born and the newborn fish were immobile or dead. After this period no

Table 3. Summary of the results of the long-term toxicity tests on sodium bromide

Test organism	Exposure time (days)	Criterion	$LC(EC)_{10}$ (g Br⁻/litre)	$LC(EC)_{50}$ (g Br⁻/litre)	NOEC (g Br⁻/litre)	$NOEC \times \frac{LC(EC)_{10}}{LC(EC)_{50}}$
Daphnia magna	23	Reproduction:				
		P generation	0.012	0.023	0.0078	0.0041
		F_1 generation	0.016	0.023	0.0078	0.0054
		F_2 generation	0.016	0.023	0.016	0.011
	19	Mortality	4.7	6.1	3.1	2.4
Poecilia reticulata	28	Mortality	7.8	12	2.5	1.6
		Mortality and behaviour	0.040	0.043	0.025	0.023
		Growth	—	—	0.25	—
	124	Mortality	—	>7.8	≥7.8	—
		Mortality and behaviour	0.15	0.17	0.078	0.069
		Reproduction	0.025	0.14	0.0078	0.001
Oryzias latipes	34	Mortality	0.62	1.5	0.78	0.32
		Mortality and behaviour	0.21	0.37	0.25	0.14
		Heart rate			< 7.8	
		Hatching			≥ 7.8	—
		Growth	—		0.78	—

NOEC = No observed effect concentration

Table 4. Results of the reproduction test with *Daphnia magna* (F_1 generation) exposed to sodium bromide

Br^- concn (mg/litre)	Cumulative no./female (% of control value) for: Eggs and newborns	Newborns
3.9	98	95
7.8	85	84
15.6	71	61
23.4	66	47
39.0	59	31
62.4	59	7

reproduction occurred at all and as the animals deteriorated all fish in these groups were killed after about 10 weeks of exposure and processed for histopathological examination. The animals in the other test groups (7.8 up to 390 mg Br^-/litre) were examined for a 124-day exposure period to determine the effects on reproduction. Up to 78 mg Br^-/litre, only the number of newborn fish was reduced; in the 390 mg Br^-/litre group there was also the birth of prematures in two cases.

The NOEC value for Oryzias was considerably higher, namely 250 mg Br^-/litre on the basis of mortality and abnormal behaviour. No effects were found at any of the tested concentrations (from 7.8 up to 7800 mg Br^-/litre) on the heart rate or the hatching of the embryos and neither were any deaths observed. After hatching, no effects were found up to 250 mg Br^-/litre. At higher concentrations fish showed abnormal behaviour and even (≥ 780 mg Br^-/litre) died.

During the toxicity tests no influence on pH or oxygen content of the test solutions could be observed.

Histology

Apart from background pathology (e.g. fatty infiltration of the liver, nephrosis, incidental hepatitis or granulomas), the Poecilia subjected to long-term exposure showed three major pathological lesions, namely thyroid hyperplasia, myopathy and regressive changes in the female reproductive tract (Table 5).

Thyroid hyperplasia (Fig. 1) was noted in the groups exposed to 78, 390, 780, 3900 and 7800 mg Br^-/litre. It was characterized by an increased quantity of follicles of varying size and shape, sometimes exhibiting folded or multilayered margins. In several animals, massive areas of thyroid epithelium were present, with few small colloidal spaces. The epithelium was generally cuboid to columnar, with nuclear enlargement, intracytoplasmic hyaline droplets and basophilic cytoplasm at its base. Colloid within the follicles was more granular than hyaline in appearance, or was even scarce or absent (Fig. 1). No alterations were observed in the pituitaries, but this organ was not invariably present in the sections from all the animals.

Myopathy (Figs 2 & 3) was observed in high incidence in the 3900- and 7800-mg Br^-/litre groups, whereas a minimal myopathy was present in a few cases in the control and 78-, 390- and 780-mg Br^-/litre groups and there was one marked case in the 7.8-mg Br^-/litre group. The lesion consisted of patchy or diffuse Zenkers degeneration of myofibrils, focal necrosis and invasion by macrophages. Usually isolated fibres or groups of fibres were affected in a more or less symmetrical pattern and the lesion could occur in any skeletal muscle, but was found most often in the tail muscles. Regeneration was poor or absent; degenerative changes were usually accompanied by atrophy of muscle fibres and fibrosis of the endomysium. The spinal cord, ganglia and nerve roots showed no relevant changes.

In Poecilia, the viviparous guppy, reproductive performance can be assessed from the histopathology of the female reproductive tract. Thus in the groups exposed to 390, 780, 3900 or 7800 mg Br^-/litre, a marked reduction in the number of foetuses was noted, along with regressive or degenerative changes of the reproductive tract, such as ovarian atrophy, cystic follicles and the occasional resorption of an advanced-stage foetus. No treatment-related changes were observed in the male reproductive organs.

In Oryzias, no treatment-related histopathological lesions were detected, not even in organ systems showing major lesions in Poecilia.

Table 5. Incidence of histopathological changes in *Poecilia reticulata* after long-term exposure to sodium bromide

Organ and finding		No. examined or affected after Br^- exposure (mg/litre) of: 0	7.8	78	390	780	3900	7800
Thyroid	No. examined ...	8	10	8	9	7	4	8
Hyperplasia		1	1	4	5	5	4	8
Musculature	No. examined ...	1	11	11	9	11	5	10
Atrophy slight		2		1	1	3	3	
marked			1				1	7
Degeneration slight		1	1	3	4	4	3	5
marked			1				1	4
Female reproductive tract	No. examined ...	7	9	7	9	7	3	6
Pregnancy		5	5	5	1	1 + 1*	1*	0
Regressive changes		0	0	0	2	4	3	6

*Resorption of advanced-stage foetus.

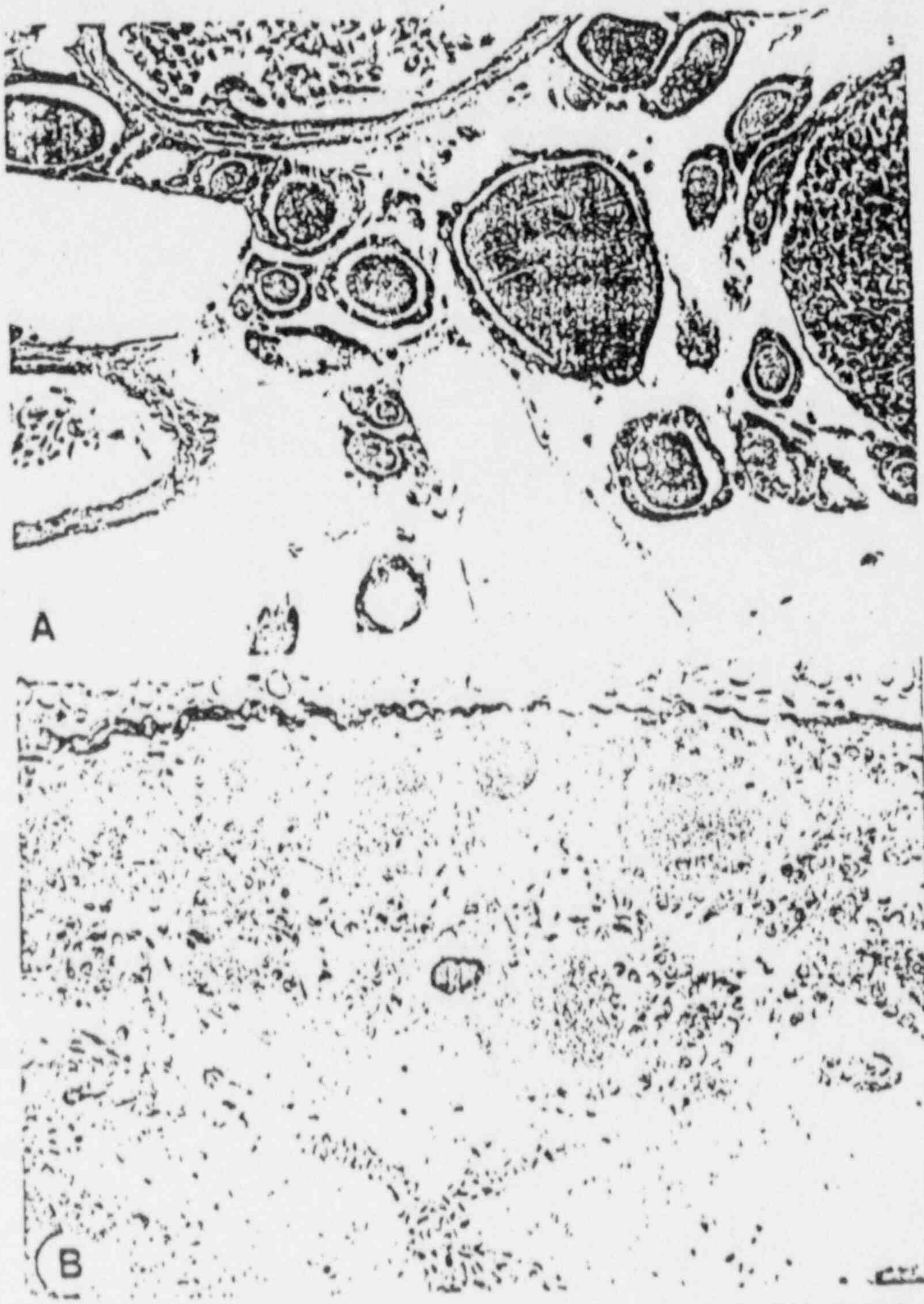

Fig. 1. Thyroid glands of *Poecilia reticulata*: (A) from control animal showing thyroid follicles dispersed in loose connective tissue around main blood vessels and hyaline colloid present within flat epithelium-lined follicles. (B) from an animal exposed to 7800 mg Br litre, showing hyperplasia of thyroid tissue with activated columnar cells forming irregular follicles containing granular colloid. Haematoxylin and eosin [illegible]

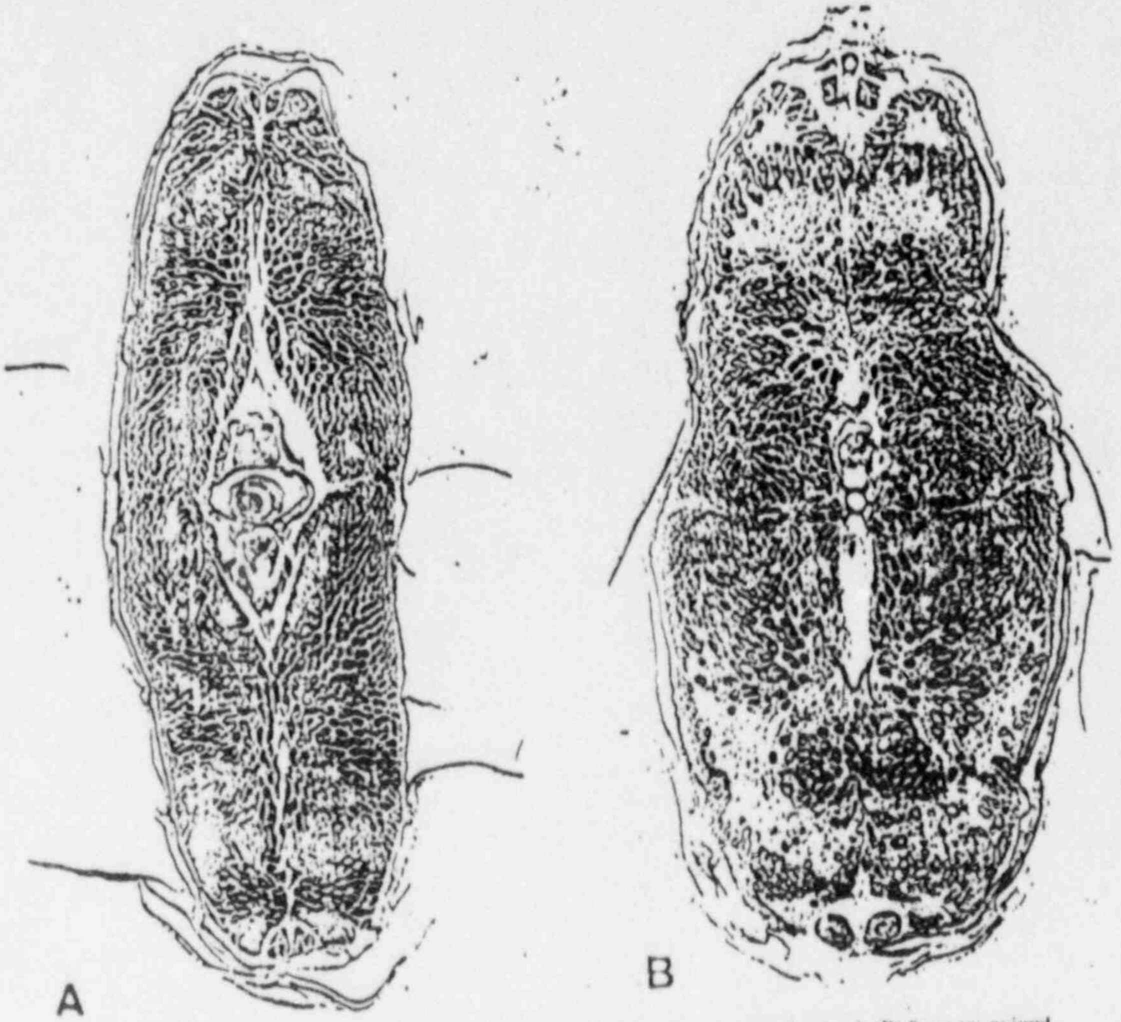

Fig. 2. Transverse section of the tail of *Poecilia reticulata*: (A) from control animal; (B) from an animal exposed to 7800 mg Br$^-$/litre, showing symmetrical muscular atrophy. H/E × 23.

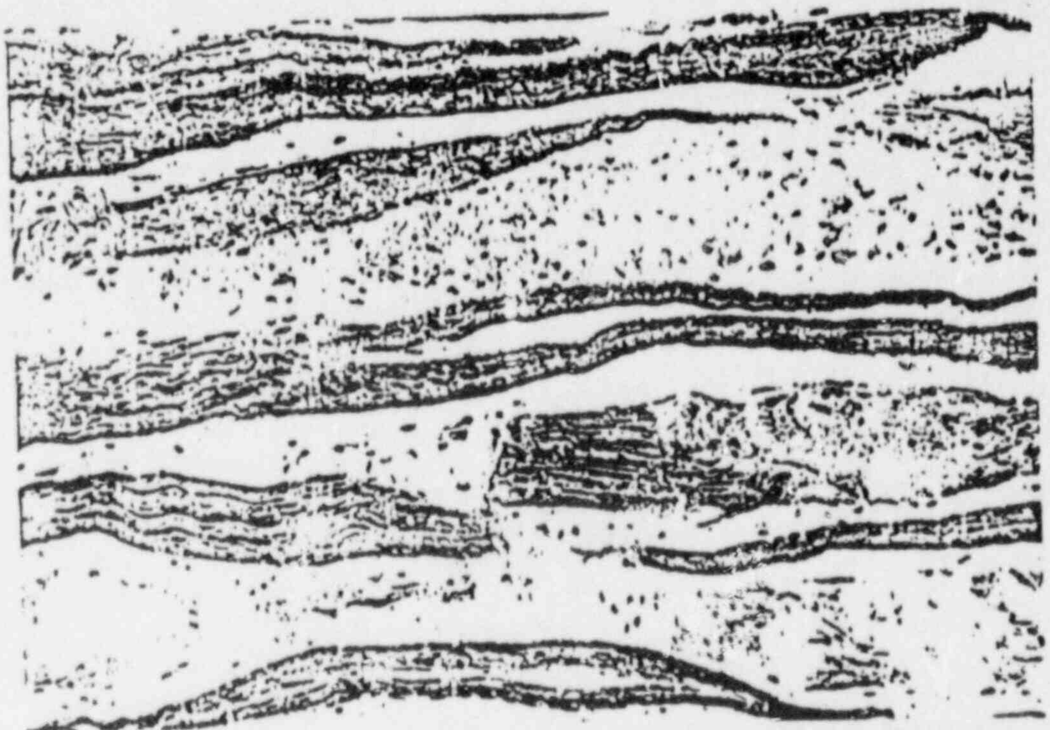

Fig. 3. Sagittal section of the tail muscles of *Poecilia reticulata* exposed to 7800 mg Br^-/litre, showing hyaline degeneration, necrosis and phagocytosis of individual muscle fibres. H/E × 230.

Discussion

Short-term toxicity studies

Depending on the freshwater organisms used, the results of the short-term toxicity tests (EC_{50} values) varied markedly, ranging from 44 to 5800 mg Br^-/litre (Table 2). In decreasing order of susceptibility the test organisms can be arranged as follows: (a) Poecilia, (b) Oryzias and (c) Daphnia together with Scenedesmus. Almost no decrease in $LC(EC)_{50}$ values could be observed during the tests, except for the EC_{50} values for Poecilia. With this fish a factor of 10 was found between the EC_{50} at 24 hour and at 96 hour. In the short-term tests with fish, abnormal behaviour proved to be a very sensitive criterion: the EC_{50} values (E = mortality and behaviour) were about 60-400 times lower than the LC_{50} values; in the test with daphnids this difference involved a factor of about 2.

Alexander, Quick & Bartlett (1981) established 16 g/litre as the 96-hour LC_{50} for *Pimephales promelas*, a value comparable to the LC_{50} values found in the present study.

Long-term toxicity studies

Daphnia. Sodium bromide proved to reduce strongly the reproduction capacity of *Daphnia magna*. Exposing the F_0 and also the F_1 generation, however, did not lead to lower NOEC values. Although the NOEC from the test with the F_1 generation was slightly higher (Table 3) this is not a realistic difference because the reproducibility of long-term tests with *Daphnia magna* is no better than a factor of 3.2 (Canton & Adema, 1978). The concentration-effect curves of the P, F_1 and F_2 generations were also approximately the same (see the EC_5, EC_{50} ratios in Table 3). Comparing the NOEC (E = reproduction) from the test with the P generation and the NOEC (E = mortality), a remarkable difference can be noted (about a factor of 400). Such a marked effect on reproduction has not been found in previous studies (Adema *et al.* 1981; Canton & Slooff, 1982a,b; Canton & Wegman, 1983). Comparing the NOEC and NOEC values from the long-term test with those from the short-term test it can be concluded that there is a marked difference between the NOEC values, but prolongation of the short-term test did not result in a lower NOEC value.

Poecilia. In the 4-week test with *Poecilia reticulata* a marked effect on the swimming behaviour of the fish was noted. This effect varied from reduced activity to immobility of the animals. An NOEC value of 25 mg Br^-/litre was found. A possible explanation for this phenomenon may be the myopathy observed microscopically. Since the effect on behaviour did not impair the growth of the animals in the 78- and 250-mg Br^-/litre groups (the NOEC for growth being about 10 times higher), the food intake was apparently not affected at these concentrations. The abnormal swimming behaviour was also noticed in the short-term test and the NOEC values (E = mortality and behaviour) in the short- and long-term tests were the same. Effects on behaviour were also observed in a 90-day toxicity study carried out in rats fed diets containing sodium bromide (van Logten, Wolthuis, Rauws *et al.* 1974). The animals on the highest bromide level did not groom themselves sufficiently and exhibited signs of motor incoordination of the hind limbs.

As in the experiments with Daphnia, impaired reproduction was noted in the experiment with adult Poecilia, a viviparous fish. In both organisms the same NOEC value (7.8 mg Br^-/litre) was found and bromide proved to have an embryotoxic effect. The NOEC value (E = mortality and behaviour) from this test is of the same order of magnitude as the NOEC value (E = reproduction) from the short-term test.

The reduction in offspring correlates with the regressive changes observed in the ovaries. As degenerative and atrophic changes were found, an effect of sodium bromide upon ovarian function is suggested and is consistent with ovarian changes found in the rat (van Logten *et al.* 1974). The results of the histopathological examination of Poecilia indicate furthermore a clear effect upon thyroid morphology and hence presumably upon its function. This morphological change corresponds with the thyroid hyperplasia observed in the rat (van Logten *et al.* 1974), a species in which in addition serum thyroxine was reduced along with a decrease in the amount of thyroxine in the thyroid follicles (as evidenced by an immunoperoxidase technique) whereas the serum thyrotropin level was elevated (Loeber, Franken & van Leeuwen, 1983). It is generally accepted that the fish thyroid is largely comparable to the mammalian gland. Several papers have been published on thyroid hyperplasia or even thyroid tumours induced in fish by iodine deficiency or antithyroid agents or of unknown aetiology (Harshbarger, 1979; Schlumberger, 1955; Woodhead & Ellet, 1967). A simple but satisfactory explanation for thyroid hyperplasia and hypothyroidism after sodium bromide exposure can be found in the competition between the two halogens, bromine and iodine, with respect to thyroxine synthesis.

The myopathy, characterized by myofibrillar degeneration, myophagia and atrophy, resembles the nutritional myopathy described by Cowey & Roberts (1978), Roberts (1978) and Helder (1979). In the present study, however, the myopathy was not associated with lipoid liver degeneration and steatitis. This suggests that vitamin E deficiency was not a major aetiological factor in this condition. Similar muscle lesions have been observed in the rat after oral administration of sodium iodide (Cantin, 1967). In rats given sodium bromide motor incoordination has been reported, but without histopathological lesions in the musculature (van Logten *et al.* 1974).

Oryzias. In the long-term test, *Oryzias latipes* proved to be about 10-30 times less sensitive than Poecilia with respect to the NOEC values (Table 3). The same difference was also found in the short-term tests. The NOEC value (250 mg Br^-/litre) is identical to that from the short-term toxicity test, as was observed in the test with Poecilia.

The failure of Oryzias to develop pathological lesions at 780 mg Br^-/litre may be attributed to the shorter exposure-time and the lower test concentrations when compared with the reproduction test in Poecilia.

Proposal for a water-quality criterion

The NOEC-values from this study (short- and long-term tests) can be compared with those established for other freshwater organisms such as bacteria (*Pseudomonas fluorescens*), cyanobacteria (*Microcystis aeruginosa*), plants (*Lemna minor*), insects (*Culex pipiens*), hydrozoans (*Hydra oligactis*), molluscs (*Lymnaea stagnalis*) and amphibians (*Xenopus laevis*) (W. Slooff & J. H. Canton, unpublished data). In decreasing order of toxicity (on the basis of NOEC values), the organisms can be arranged as follows: Pseudomonas, Microcystis, Scenedesmus, Lemna (NOEC: 2500 mg/litre), Hydra (780 mg/litre), Oryzias (250 mg/litre), Culex (78 mg/litre), Xenopus (25 mg/litre) and Daphnia, Poecilia and Lymnaea (7.8 mg/litre). In the Lymnaea test, reproduction was again the most sensitive criterion. Thus it appears that bromide has a marked effect on the reproduction of water organisms. Reproduction has proved to be a sensitive criterion also in the rat (van Leeuwen, den Tonkelaar & van Logten, 1983).

From the experiments with various freshwater organisms it is concluded that Daphnia and Poecilia appear to be highly sensitive to bromide, the NOEC being 7.8 mg Br^-/litre. In a previous study (Canton & Slooff, 1979), the lowest NOL(E)C × LC(EC)$_{50}$/LC(EC)$_{50}$ value was proposed as a criterion for water quality. For bromide this value is 1 mg Br^-/litre on the basis of the effects observed on reproduction in Poecilia (Table 3).

The highest concentrations of bromide in surface water determined by Wegman *et al.* (1983) in the "Poelpolder" had a median value of about 10 mg Br^-/litre and a maximum of about 40 mg Br^-/litre. The high values were found during the main fumigation season. Thus, it can be expected that the use of methyl bromide as a soil fumigant in glasshouses might have an adverse effect on the aquatic environment. The concentrations of bromide in surface water are sometimes so high that even acute effects can be expected.

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Acclimation of fathead minnows and lake trout to residual chlorine and bromine chloride

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Chlorine has been used for many years as a wastewater disinfectant, and the toxicity of chlorinated wastewater is well documented.[1,2] Recently bromine chloride has been considered as a possible alternate method of disinfecting wastewater,[3-5] but knowledge of the toxicity of chlorobrominated effluent to aquatic life was limited to static, acute toxicity tests with fathead minnows in chlorobrominated effluent.[6] More recent research by the authors, which was conducted using a flow-through system, showed that although chlorobrominated effluent was toxic to some types of aquatic life, it was considerably less toxic than chlorinated effluent.[7]

While conducting acute and life cycle toxicity studies, it was noticed that if total residual chlorine (TRC) or total residual bromine chloride (TRBC) levels were relatively low initially and then gradually increased, fish seemed to be able to tolerate higher residual levels than they would have been able to tolerate without previous exposure. In other words, they seemed to be able to acclimate to the TRC or TRBC in the effluent. Past research has indicated that fish are able to acclimate to changes in water temperature[8,9] and dissolved oxygen (DO) concentrations,[10] although extremes of either parameter can be lethal. Because no data were available concerning the ability of fish to acclimate to TRC or TRBC in effluent, several experiments were conducted to test this possibility. The objectives were: 1. to determine if fathead minnows and lake trout previously exposed to sublethal levels of TRC and TRBC in effluent were able to acclimate and survive in effluent having levels of TRC or TRBC above their respective 96-hour TL_{50} values; 2. to determine the maximum level of TRC in effluent that fathead minnows can tolerate for 7 days after previous exposure to sublethal TRC levels; and 3. to determine relationships between acclimation time, concentrations of TRC during acclimation, and degree of acclimation achieved by fathead minnows.

Since these tests were conducted as a supplement to higher priority research, the authors were not able to explore this phenomenon as completely as would have been desirable. However, it seemed that the previously unreported nature of this data made any information that could be obtained worthwhile.

METHODS AND MATERIALS

These studies were conducted at the Grandville, Mich., Wastewater Treatment Plant as part of a larger project concerning effluent disinfection and residual toxicity.[7] The Grandville Wastewater Plant is an activated sludge plant which receives wastewater primarily from domestic sources and usually produces a high quality effluent. During the period of these studies, the treatment plant's effluent was chlorinated with a manual feed system adjusted with the aid of a continuously operating residual chlorine monitor. Five and seven-tenths liters per minute (1.5 gpm) of chlorinated final effluent, which normally had 1.0 to 1.5 ± 0.5 mg/l TRC, was pumped from the chlorine contact chamber to the bioassay laboratory after approximately 35 minutes of contact time. One hundred and thirty-two liters per minute (36 gpm) of nondisinfected effluent was pumped from the plant's final settling tanks to the effluent treatment building where 2.5 mg/l of bromine chloride was applied. After a 30-minute contact time, 5.7 l/min (1.5 gpm) was pumped to the bioassay laboratory for toxicity testing.

The dilution water for the bioassay laboratory was aerated well water passed through an iron removal filter. This water was of sufficient quality to enable fathead minnows and *Daphnia magna* to grow and reproduce satisfactorily. The chlorinated effluent and well water were heated to 23°C for tests with fathead minnows.

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The chlorobrominated effluent was chilled to approximately the temperature of unheated well water (14° ± 1°C) for tests with lake trout. Proportional diluters[11] with some refinements were used to deliver duplicate streams of 100 percent effluent and well water and 6 intermediate effluent concentrations of 60, 36, 21.6, 13.0, 7.8, and 4.7 percent to randomly selected test chambers. Only PVC pipe, silicone cement, stainless steel, neoprene rubber, and glass materials were used in the construction of the diluters. The test chambers were 600 × 290 × 300 mm (28.4 l) glass aquaria which received one volume every 2.6 hours, or 9.2 tank volumes per 24-hour period. Although DO measurements were not made in the tanks used in these tests, daily DO measurements in equivalent concentrations of the life cycle study tanks indicated that sufficient oxygen supplies were always available to test animals.

Significant differences between previously exposed and previously unexposed (control) groups were determined using the two sample *t*-test.[13] A linear regression analysis was used to test the relationship between survival times of acclimated and nonacclimated fish.[13]

Levels of TRC and TRBC were measured in the test chambers with a polarograph using the amperometric titration method.[12]

The first study consisted of 4 duplicate tests using 10 fathead minnows each. These tests were conducted over a 7-week period. Each test group was randomly exposed to one of a series of sublethal chlorinated effluent concentrations (4.7 to 13 percent) for 1 week, then transferred to a slightly higher concentration for the next week. This procedure was continued until each group of fish was finally subjected to chlorine concentrations which were higher than the 96-hour TL_{50} values for fathead minnows (0.082 and 0.095 mg/l) which were calculated from flow-through bioassay test results.[7] At that time, a control group of unexposed fish was isolated in the same test tank and the mortality of both groups was monitored. If the previously exposed group survived for 1 week, it was transferred to the next higher concentration. The mean (all means are arithmetic means) TRC exposure level and survival time for each week was calculated for each sample group.

A second group of four acclimation tests was conducted using lake trout in chlorobrominated effluent. In the first three tests, 18 fish were exposed to sublethal (0.011 to 0.068 mg/l) concentrations of chlorobrominated effluent for **4 to 9 days, and then placed in effluent having TRBC levels well above their 96-hr TL_{50} values.** The fourth group (control) had no exposure to residual bromine chloride before being placed in effluent containing lethal concentrations of TRBC. The mean TRBC exposure level and the mean survival time was calculated for each test group.

A third group of tests was conducted to determine the time required for fathead minnows to acclimate to chlorinated effluent, and to determine what levels of TRC were most conducive to acclimation. (See Table III to facilitate a better understanding of this portion of the study.) Two groups of 10 fathead minnows were acclimated for 1 and 2 hours to 0.070 mg/l TRC in effluent, and then placed in effluent having mean TRC levels of 0.302 to 0.349 mg/l. A third (control) group of 10 unacclimated fathead minnows were concurrently placed in effluent having mean TRC levels of 0.332 mg/l. In addition, fathead minnows were acclimated for 3 to 8 hours at 1-hour intervals in chlorinated effluent having TRC levels of 0.036 to 0.049 mg/l, which was near half of the calculated 96-hour TL_{50} value for that species, and 0.074 to 0.093 mg/l, which was near the previously determined 96-hour TL_{50} values (0.082 and 0.095 mg/l).[7] After each group of 10 fish was exposed for the specified length of time, it was placed in a concentration of chlorinated effluent having TRC levels well above their 96-hour TL_{50}. Concurrently, 10 previously unexposed (control) juvenile fathead minnows were placed in duplicate test chambers having similarly high TRC levels. The mortality and TRC levels were monitored in each tank until all of the previously exposed and control fish were dead. The mean TRC level and mean survival time was calculated for each test and control group.

Our previous studies[7] showed that the effluent containing both TRC and TRBC was not inherently acutely toxic to either fathead minnows or lake trout. Therefore, there were no fish exposed to similar nondisinfected effluent concentrations to serve as a control.

RESULTS

Fathead minnows previously exposed to sublethal TRC levels tolerated higher TRC levels than our observed 96-hr TL_{50} values (0.082 to 0.095 mg/l) for at least 7 days (Table I). Fathead minnows survived with no mortality for 1 week at TRC levels of 0.113, 0.116, 0.110, 0.134, and 0.138 mg/l, all of which were higher than our previously determined TL_{50}

relatively high TRBC concentration (1.066 mg/l). Of the 18 fish, 22 percent were still alive after 5 hours. Although the time to total mortality was not known, the 4 fish remaining alive after 5 hours of exposure were stressed and probably died within the next hour. Assuming that the remaining fish died after 6 hours of exposure, the mean survival time of this group was 3.7 hours. By comparison, 18 previously unexposed (control) lake trout that were placed in effluent having considerably lower TRBC levels (0.647 mg/l) had a mean survival time of 2.1 hours (Table II). Our 96-hour TL_{50} value determined in earlier flow-through tests with lake trout in chlorobrominated effluent was 0.102 mg/l) The second test subjected lake trout to mean TRBC levels of 0.029 mg/l for 9 days before they were introduced into a tank having 0.664 mg/l TRBC. The mean survival time of this test group was 10.8 hours. Test three subjects were exposed to 0.011 mg/l TRBC for 9 days and then placed in effluent containing 0.641 mg/l TRBC. Their mean survival time was 7.2 hours. These data suggest that Test 2 fish were able to tolerate similar residual levels for a longer period of time because of prior exposure to a slightly higher TRBC concentration (0.029 mg/l) than Group 3 (0.011 mg/l). Groups 2 and 3 survived significantly ($p = 0.05$) longer than their controls in similar TRBC concentrations.

Table III presents survival comparisons between 14 groups of 10 fathead minnows, each acclimated to chlorinated effluent for 1 to 8 hours, and their respective control groups which lacked previous exposure to chlorinated effluent. Those fish previously exposed to mean TRC levels of 0.070 mg/l for 1 and 2 hours showed little difference in mean survival time when compared with controls exposed to a similar test concentration. Of the 12 remaining groups of test fish, 6 were previously exposed to mean TRC levels having a range of 0.036 to 0.049 mg/l for 3 to 8 hours, while the remaining 6 groups of test fish were previously exposed to higher TRC levels of 0.074 to 0.095 mg/l for 3 to 8 hours. In every instance, the fish that had previous exposure to residual chlorine survived longer (mean survival time of 4 hours) than did control fish (mean survival time of 4 hours).

Those fish previously exposed to the 6 lowest TRC levels (0.036 to 0.049 mg/l) for 3 to 8 hours were able to survive in high TRC levels longer (mean survival time of 6.3 hours) than fish that had previous exposure to mean TRC levels of 0.074 to 0.095 mg/l (mean survival time of 5.6 hours). Also, those fish acclimated to TRC concentrations of 0.036 to 0.049 mg/l showed a greater difference in mean survival time when compared to control fish than did the fish acclimated to mean TRC levels of 0.074 to 0.095 mg/l. With the exception of the test group previously exposed to 0.070 mg/l for 1 and 2 hours, and those previously exposed to 0.042 mg/l TRC for 3 hours, all other test groups survived significantly longer than did control fish ($p = 0.05$).

In addition, a linear regression analysis performed between length of acclimation and length of survival when exposed to high TRC levels indicated that there was a statistically significant (0.001 level of significance) linear relationship between those two variables. The

TABLE II. Survival of lake trout in chlorobrominated effluent.*

Test Number 1	
$\bar{x}$ TRBC concentration to which fish were previously exposed	0.068 mg/l
Length of previous exposure	4 days
$\bar{x}$ TRBC concentration in which fish were tested	1.066 mg/l
$\bar{x}$ survival time at test residual	3.7 hours†,‡
Test Number 2	
$\bar{x}$ TRBC concentration to which fish were previously exposed	0.029 mg/l
Length of previous exposure	9 days
$\bar{x}$ TRBC concentration in which fish were tested	0.664 mg/l
$\bar{x}$ survival time at test residual	10.8 hours‡
Test Number 3	
$\bar{x}$ TRBC concentration to which fish were previously exposed	0.011 mg/l
Length of previous exposure	9 days
$\bar{x}$ TRBC concentration in which fish were tested	0.641 mg/l
$\bar{x}$ survival time at test residual	7.2 hours‡
Control	
$\bar{x}$ TRBC concentration to which fish were previously exposed	0.000 mg/l
Length of previous exposure	0 days
$\bar{x}$ TRBC concentration in which fish were tested	0.647 mg/l
$\bar{x}$ survival time at test residual	2.1 hours

* Eighteen lake trout were used in each test ($\bar{x}$ total length 39 mm, $\bar{x}$ weight 0.7 g).

† Calculation based upon all fish having died by 6 hours of exposure. After 5 hours of exposure 4 of the 18 fish were still alive, although they were severely stressed and probably died soon thereafter.

‡ Survival time significantly longer than control fish ($p = 0.05$).

TABLE I. Survival of fathead minnows* with and without previous exposure to chlorinated wastewater.

Duplicate Test Number		Week of Test 1	2	3	4	5	6	7
1	Mg/l TRC	0.056	0.063	0.113	0.504			
	% Effluent Concentration	13	21.6	36	60			
	$\bar{x}$ Survival Time†	NM§	NM	NM	17.5‖			
	$\bar{x}$ Survival Time‡			14	1.1			
	Mg/l TRC	0.052	0.064	0.116	0.512			
	% Effluent Concentration	13	21.6	36	60			
	$\bar{x}$ Survival Time†	NM	NM	NM	19.5‖			
	$\bar{x}$ Survival Time‡	—		56.5	1.4			
2	Mg/l TRC	0.021	0.036	0.064	0.233			
	% Effluent Concentration	7.8	13	21.6	36			
	$\bar{x}$ Survival Time†	NM	NM	NM	39.7#			
	$\bar{x}$ Survival Time‡							
	Mg/l TRC	0.018	0.047	0.069	0.215			
	% Effluent Concentration	7.8	13	21.6	36			
	$\bar{x}$ Survival Time†	NM	NM	NM	37.6#			
	$\bar{x}$ Survival Time‡							
3	Mg/l TRC	0.007	0.016	0.033	0.100	0.306		
	% Effluent Concentration	4.7	7.8	13	21.6	36		
	$\bar{x}$ Survival Time†	NM	NM	NM	NM	62.6‖		
	$\bar{x}$ Survival Time‡					3.6		
	Mg/l TRC	0.007	0.029	0.043	0.113	0.318		
	% Effluent Concentration	4.7	7.8	31	21.6	36		
	$\bar{x}$ Survival Time†	NM	NM	NM	NM	26.8‖		
	$\bar{x}$ Survival Time‡					2.6		
4	Mg/l TRC		0.008	0.021	0.042	0.134	0.241	
	% Effluent Concentration		4.7	7.8	13	21.6	36	
	$\bar{x}$ Survival Time†		NM	NM	NM	NM	77.3‖	
	$\bar{x}$ Survival Time‡						2.1	
	Mg/l TRC		0.012	0.022	0.070	0.138	0.224	0.359
	% Effluent Concentration		4.7	7.8	13	21.6	36	60
	$\bar{x}$ Survival Time†		NM	NM	NM	NM	20% Mortality	25.6§
	$\bar{x}$ Survival Time‡						3	1.3

* $\bar{x}$ total length 33.4 mm, $\bar{x}$ weight 0.74 g.
† Mean survival time (hours) of 5 previously exposed fish.
‡ Mean survival time (hours) of 5 previously unexposed fish.
§ No mortality during that week.
‖ Survival time significantly longer than previously unexposed fish at the 0.05 level of significance.
\# No control fish exposed. (Previously conducted acute toxicity tests indicated that fathead minnows had a mean survival time of 9.5 hours when exposed to similar (0.198 mg/l) concentrations of TRC in effluent.)

values for that species. Also, at higher residual levels (0.215 to 0.512 mg/l), previously exposed fathead minnows survived for 10 to 37 times longer (17.5 to 77.3 hours) than did their respective unexposed control groups (1.1 to 3.6 hours).

There also appears to be a trend for fathead minnows to show increased tolerance for high TRC concentrations as length of exposure to sublethal TRC levels increases. For example, in Test 2 (Table I), fathead minnows survived for 39.7 and 37.6 hours when subjected to 0.223 and 0.215 mg/l TRC after 3 weeks of exposure to sublethal TRC levels. However, in Tests 3 and 7, fathead minnows survived for 62.6 and 77.3 hours when exposed to 0.306 and 0.241 mg/l TRC following 4 weeks of exposure to sublethal TRC levels. Test number 4 shows a similar trend.

Lake trout which were exposed to sublethal levels of TRBC showed a similar ability to acclimate to lethal levels (Table II). The first test group was exposed to mean TRBC levels of 0.068 mg/l for 4 days prior to exposure to a

than previously unexposed fish. A similar phenomenon has been observed in a life cycle toxicity test with fathead minnows in chlorinated effluent. While 96-h TL_{50} values for fathead minnows are 0.082 and 0.095 mg/l TRC, 100 percent of the test fish survived for 106 days at mean TRC concentrations of 0.129 mg/l. One explanation for this long survival in relatively high TRC concentrations is that the test animals acclimated to residual chlorine during the early days of the life cycle test when measured TRC values were low.[7]

In addition, experience has indicated that tolerance to TRBC concentrations above the TL_{50} level decreases after several days of exposure to halogen-free water. For example, in life cycle toxicity tests with fathead minnows in chlorobrominated effluent, a decreased tolerance to TRBC was observed following a 3.5-day period when, because of mechanical failure, the test animals were not exposed to residual bromine chloride.[7]

While halogen acclimation was observed in just two species, other fishes probably also possess this capability, which might have survival value in natural conditions. For instance, in situations where low levels of residual chlorine are continuously added to a stream, such as below the discharge of a chlorinated effluent, resident populations might develop an increased tolerance for residual chlorine. This increased tolerance might enable the animals to survive in, or escape unusually high chlorine residuals such as might occur when the treatment plant discharges effluent with high TRC concentrations or during periods of low stream flow. An example of high TRC levels in a receiving stream was reported by Jackson[14] who found TRC levels ranging as high as 1.40 mg/l in receiving water below the Howell (Mich.) Wastewater Treatment Plant. It is possible, however, that fish residing in water having TRC levels below their TL_{50} value might suffer some adverse sublethal effects, such as reduced ability to avoid predators or reduced reproductive capacities.

Hart[15] discusses the fact that surprisingly few fish kills have been observed where the chlorinated effluents of wastewater treatment plants are discharged into natural waters. He suggests that one possible reason for the lack of reported fish kills is that fish are capable of detecting and avoiding potentially lethal concentrations of toxic materials. Sprague and Drury[16] and Summerfelt and Lewis[17] also discussed avoidance reactions of fishes to certain chemicals. The halogen acclimation that has been observed might facilitate avoidance actions by lengthening the time interval available for fishes exposed to high halogen concentrations to find a more hospitable environment, and might also be an explanation for the lack of observed fish kills when TRC concentrations are unusually high.

Studies to determine the lethality of chlorinated effluents generally use test animals which have never been exposed to, and thus have no increased tolerance for, residual chlorine. If halogen acclimation does occur in fish populations living in environments where they are regularly exposed to low residual chlorine concentrations, then it is possible that the chlorine tolerance limits determined in many studies do not apply to those regularly exposed resident fish, but rather to fish which may be transient and have not had recent halogen exposure.

CONCLUSIONS

This study leads to conclusions regarding the acclimation of juvenile fathead minnows and lake trout to TRC and TRBC in secondary effluent.

1. Fathead minnows and lake trout with previous exposure (longer than 2 hours) to chlorinated or chlorobrominated effluent respectively were capable of tolerating high levels of TRC or TRBC for longer periods of time than fish that were not previously exposed to either halogen.

2. For fathead minnows there was a linear relationship between duration of previous exposure and tolerance to residual halogen levels in excess of 96-hour TL_{50} values.

3. The acclimation of fathead minnows to TRC was most apparent after 4 or more hours of exposure to low TRC concentrations.

4. Even after long-term exposure to sublethal levels of TRC in effluent, fathead minnows were not able to survive high TRC concentrations.

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Effects of chlorobrominated and chlorinated cooling waters on estuarine organisms

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The environmental acceptability of chlorine as a universal disinfection agent for both industrial and municipal water and wastewater treatment processes recently has become the topic of considerable discussion. The widespread use of chlorine for the treatment of large volumes of cooling waters in thermoelectric power plants has become a primary cause of concern.[1] The chronic and acute effects of chlorine and its reaction by-products on aquatic organisms have been reviewed extensively by Tsai,[2,3] Brungs,[4,5] and Becker and Thatcher.[6] Investigations by Jolley[7] and Glaze and Henderson[8] have further identified many chlorinated organic and inorganic compounds from chlorine-treated municipal and industrial wastewaters that are potentially carcinogenic to man. Thus, several alternatives to chlorine have been suggested by the U.S. Environmental Protection Agency (EPA)[9] for wastewater treatment. The U.S. Nuclear Regulatory Commission[10] and Burton and Liden[11] have summarized the chlorine alternatives for biofouling control in power-plant condenser cooling systems.

Some proposed chlorine alternatives include bromine chloride, ozone, chlorine dioxide, hydrogen peroxide, ultraviolet radiation, and numerous other coatings and physical or chemical treatment.[11] Of these, bromine chloride (BrCl) has emerged as a prime candidate as a substitute biocide. Bromine chloride has been shown to be an effective disinfectant of wastewater.[12] In addition, Wackenhuth and Levin,[13] Bongers *et al.*,[14,15] and Burton and Margrey[16] have demonstrated bromine chloride's effectiveness as a biofouling control agent in thermoelectric power plant cooling systems using estuarine waters. Relatively little information is available, however, concerning the toxicity of bromine chloride and its chemoreaction by-products to estuarine floral and faunal species. A preliminary report of $BrCl$-Cl_2 toxicity to fish[17] and the results of a detailed comparative $BrCl$-Cl_2 biotoxicity study[18] comprise the only such work published concerning estuarine species.

Continuous-flow bioassays were conducted during August 1976 to compare the effects of chlorobrominated and chlorinated condenser cooling effluents on several selected estuarine food-chain organisms. Two fish species, Atlantic menhaden (*Brevoortia tyrannus*) and spot (*Leiostomus xanthurus*), two bivalve species, American oyster (*Crassostrea virginica*) and brackish water clam (*Rangia cuneata*), and the copepod *Acartia tonsa* were chosen because of their importance either to commercial or recreational fishing or as food-chain items in eastern U.S. estuarine regions. Naturally occurring phytoplankton communities were used for comparative productivity and respiration studies.

These studies were conducted at Potomac Electric Power Company's Morgantown Steam Electric Station, an 1100 MW, twin-unit, fossil-fueled power plant, located on the Potomac River, Charles County, Md. Comparison of the residual biotoxicities, as well as biofouling control efficacies[14] of the halogenated effluents, was accomplished by chlorobrominating the cooling water of one unit and chlorinating the cooling water of the second unit. The two biocides were applied continuously at 0.5 mg/l or less to the respective condenser cooling structures during the field trials.

METHODS AND MATERIALS

Bioassay apparatus. Chlorobrominated and chlorinated condenser discharge waters were pumped continuously to large, 0.75-m-high × 1.22-m-wide × 2.44-m-long troughs constructed of 1.9-cm-thick marine plywood covered with polyester-resin-impregnated fiberglass. The troughs were partitioned with four 0.64-cm-thick methyl methacrylate polymer dividers, which were spaced equidistantly across the troughs. Each was secured to opposite ends of the trough to form a 12-m-long serpentine channel. Cooling water inflow rates were maintained at 0.38 l/s, resulting in hydraulic residence periods of approximately 60 minutes in all troughs, simulating cooling water retention times observed in the plant's discharge canal. A third trough, supplied with dechlorinated (sodium thiosulfate) cooling water, served as a reference exposure trough. In all studies, test organisms were retained in the troughs at positions where the cooling waters had "aged" approximately 5, 30, and 60 minutes after halogenation.

Fish. Juvenile Atlantic menhaden (*Brevoortia tyrannus*) and spot (*Leiostomus xanthurus*) were seined from the Potomac River near the Morgantown plant. The fish were acclimated for 30 days in separate 1 000-l tanks that were supplied continuously with dechlorinated (sodium thiosulfate) discharge water at flow rates of approximately 0.19 l/s. Basic water quality of the acclimation water, monitored daily, was as follows (mean ± standard deviation): temperature = 30.9 (± 1.31) °C; pH = 7.0 (± 0.62); dissolved oxygen (DO) = 3.8 (± 1.23) mg/l; ammonia – N = 0.3 (± 0.28) mg/l; and salinity = 2.1 (± 0.71) ‰. Maintenance diets of trout chow for menhaden and fresh, finely chopped menhaden for the spot were apportioned to the fish on a twice-daily schedule, during both acclimation and test periods.

Fish were transferred to submerged nylon cages (0.18 m × 0.33 m × 0.71 m) located in the troughs at positions of 5, 30, and 60 minutes of halogen decay, as described above. Approximately 30 menhaden and 20 spot were distributed randomly to segregated, paired cages. Observations of fish mortality were made at hours 1, 2, 4, 16, and 24 during the first 24 hours, and twice daily thereafter during the 19-day (menhaden) and 20-day (spot) exposure periods. Total length and wet-weight data of dead menhaden and spot were recorded at each inspection. Mean (± standard deviation) total lengths and wet weights were 76.8 (± 8.89) mm and 5.9 (± 2.90) g for all menhaden, and 75.0 (± 8.03) mm and 6.8 (± 2.31) g for all spot.

Bivalves. Juvenile specimens, with shell lengths ≤ 7.5 cm, of American oyster (*Crassostrea virginica*) and brackish water clam (*Rangia cuneata*) were obtained from the mesohaline (5 to 18 ‰ salinity) region of the Potomac River. The shellfish were acclimated for at least 2 weeks before experimentation, in 200-l tanks receiving dechlorinated condenser cooling effluents. Basic water quality of acclimation water was identical to that used for fish acclimation.

Groups of 20 oysters and 25 clams were retained in vertically suspended, nylon-mesh "socks" located at the 5-, 30-, and 60-minute positions in the exposure troughs. Before immersion, to quantitate new shell deposition, the outer shell margin of all oysters was filed smooth; a 3-mm notch was filed in the shell margin of each clam. Test animals were inspected for mortalities three times each week during the 15-day exposure. New shell deposition was measured after the end of the experiment.

Copepods. *Acartia tonsa* from a laboratory-maintained culture were utilized to determine the effects of bromine chloride and chlorine on survival at both condenser effluent (31°C) and ambient (22°C) temperatures. The copepods were acclimatized to the test temperatures for 2 days before use, in screened containers located in the reference troughs. Test organisms were contained in 500-ml bioassay chambers, which were screened at both inflow and outflow ports to prevent escape of *A. tonsa* and introduction of undesirable organisms. Halogenated water was siphoned continuously from the troughs' three positions to the respective copepod chambers. Total survival of *A. tonsa* was determined after 24-hour exposure periods.

Phytoplankton. Entrained phytoplankton communities were used to evaluate the toxic effects of bromine chloride and chlorine on energy-fixing and respiratory processes of primary producers. Cooling water samples were obtained at various times during the day from the Plant intake embayment (reference) and from the discharge ends of the biotoxicity troughs. Portions of these samples were used to determine oxygen evolution and oxygen consumption (respiration) rate according to the phytoplankton metabolic rate measurement techniques given in "Standard Methods."[18] Dissolved oxygen determinations

TABLE 1. Total residual oxidant concentrations of chlorobrominated, chlorinated, and dechlorinated condenser cooling waters during fish and bivalve testing periods.

Treatment*	Halogen Concentrations (mg/l): Mean (± Standard Deviation)	Range
B5	0.081 (±0.0123)	<0.002–0.103
B30	0.045 (±0.0077)	<0.002–0.073
B60	0.020 (±0.0124)	<0.002–0.068
C5	0.062 (±0.0051)	<0.002–0.089
C30	0.032 (±0.0063)	<0.002–0.0[illegible]
C60	0.014 (±0.0039)	<0.002–0.0[illegible]2
R5	<0.002	—
R30	<0.002	—
R60	<0.002	—

* B = BrCl, C = Cl_2, R = Reference, dechlorinated; 5, 30, and 60 following letters denote approximate halogen decay times (minutes).

[illegible] made by the titration procedures described by Carpenter.[20] Chlorophyll *a* and carbon-fixation (^{14}C) determinations were conducted with the methods of Strickland and Parsons.[21] All water samples used for photosynthesis, respiration, chlorophyll *a*, and carbon assimilation studies were incubated for 4 hours before analysis in a shallow tub receiving a continuous supply of ambient Potomac River water. Phytoplanktonic oxygen evolution and respiration values were expressed as milligrams O_2 per milligram Chl *a* per hour and carbon-fixation values as milligrams ^{14}C per milligram Chl *a* per hour.

Water quality. Analysis of the chlorobrominated, chlorinated, and reference (dechlorinated) condenser effluents for basic water quality parameters indicated small but consistent differences between treatments during all phases of this study. The mean temperature (31.2° ± 1.23°C) of the chlorinated and reference stations, receiving Unit II condenser discharges, was consistently higher (0.7°C) than the mean temperature of the chlorobrominated station at Unit I (30.5° ± 1.51°C). No significant differences were found among other mean basic water quality parameters, between all stations; the parameters were as follows (mean ± standard deviation): pH = 7.1 (± 0.49); DO = 4.1 (± 0.1) mg/l; ammonia − N = 0.2 (± 0.38) mg/l; and salinity = 2.0 (± 0.63) ‰. Basic water quality analyses were conducted using procedures detailed in "Standard Methods"[19] and by Soloranzo (ammonia − N).[22] Total residual oxidant concentrations shown in Table I were measured twice daily and varied during these studies because of plant equipment malfunctions. Two temporary plant shutdowns for equipment repair occurred, during which periods the oxidant levels of < 0.002 mg/l were recorded. However, the downtime interruptions totaled less than 8 hours. Halogen determinations were conducted using a modified amperometric technique detailed in Bongers *et al.*[14]

RESULTS AND DISCUSSION

Fish. Juvenile *B. tyrannus* and *L. xanthurus* were both tolerant of the test conditions. Survival of menhaden and spot exposed for 19 and 20 days, respectively, to chlorobrominated and chlorinated condenser effluents exceeded 70% in all groups (Table II). Statistical analyses of the menhaden data using both ANOVA and Student's *t* tests[23] indicated that there were no differences ($P > 0.05$) in survival between bromine chloride, chlorine, and reference treatments (survival data from concentrations of each halogen were pooled for analysis because of small sample sizes). No differences were found in survival of chlorobrominated spot compared to either chlorinated or reference groups. Survival of chlorine-treated spot was significantly ($P < 0.05$) less than that of the reference fish. It is interesting to note, however, that a linear relationship between halogen concentration and spot survival was evident, that is, decreased residual oxidant levels accompanied by decreased survival, and that no such relationship was found for the menhaden data.

Few studies have been conducted comparing the toxicities of bromine chloride and chlorine to estuarine organisms. The 48- and 96-hour BrCl median lethal concentration (LC50) values reported by Roberts and Gleeson[15] for menhaden (0.22 mg/l) and spot (0.22 and 0.21 mg/l) were much higher than the total residual oxidant levels used in this study (Table II), where relatively minor mortality was observed. Roberts and Gleeson[15] found that bromine chloride was considerably less toxic to menhaden than chlorine, based on 96-hour Cl_2 LC50 values reported by the Virginia State Water Control Board,[24] although the Water Control Board LC50 values were suspected to be underestimated. Gullans *et al.*[25] reported that a total residual chlorine concentration (0.12 mg/l), which was double the

TABLE II. Mean survival of selected estuarine species exposed to chlorobrominated, chlorinated, and dechlorinated (reference) condenser cooling effluents.[a]

	Mean Survival at Given Mean Halogen Concentrations in mg/l (%)								
	BrCl			Cl_2			Reference[b]		
Species	0.081	0.045	0.020	0.062	0.032	0.014	R5	R30	R60
Teleost[c]									
Brevoortia tyrannus	86.7	100.0	96.8	96.5	100.0	96.7	100.0	100.0	93.1
Leiostomus xanthurus	80.9	75.0	73.1	78.3	76.0	73.9	82.3	--	87.0
Bivalve[d]									
Crassostrea virginica	100.0	90.0	100.0	100.0	92.0	100.0	—	100.0	—
Rangia cuneata	100.0	90.0	95.0	100.0	80.0	100.0	—	100.0	—

[a] Mean water temperatures 30°-31°C.
[b] R5, R30, R60 refer to positions in bioassay troughs corresponding to cooling water "ages" of 5, 30, and 60 minutes. Residual oxidant levels at all reference stations were <0.002 mg/l during studies.
[c] 19- and 20-day exposures for *B. tyrannus* and *L. xanthurus*, respectively.
[d] 15-day exposures.

maximum Cl_2 residual oxidant level used in this study (0.062 mg/l, Table II), caused 50% mortality among menhaden after 96 hours at 23°C.

Studies conducted by Middaugh *et al.*[26] showed that 50% mortality of juvenile spot had occurred after 8-day exposures to 0.06 mg/l total residual chlorine at 15°C. No deaths were observed among fish subjected to either 0.04 or 0.02 mg/l total residual chlorine at 10° or 15°C test temperatures.[26] In the present study, juvenile *L. xanthurus* were affected at all Cl_2-total residual oxidant concentrations (Table II), resulting in significantly lower mean survival of chlorine-treated fish compared with reference. However, the analyses indicated that neither halogen treatment was more deleterious than the other to the survival of either menhaden or spot.

Bivalves. Survival of juvenile oysters and clams was unaffected after 15-day exposures to the chlorobrominated or chlorinated condenser effluents (Table II). All mortalities recorded for *C. virginica* and *R. cuneata* were attributed to apparent suffocation of individuals that had escaped from the retaining "socks" and had fallen into the anaerobic layer present in the trough bottoms.

Restricted shell deposition, indicative of sublethal stress, was evident among juvenile oysters exposed to the halogenated effluents (Table III). An analysis of variance of the data using the *F*-test[22] indicated that while significantly more ($P < 0.05$) shell was generated among reference oysters compared to either halogenated group, no difference was found between BrCl and Cl_2 treatments. There was a positive relationship between shell deposition and total residual oxidant concentration for both chlorobrominated and chlorinated oysters. A significant difference ($P < 0.05$) within halogen treatments was found only between oysters exposed to 0.062 and 0.014 mg/l Cl_2-total residual oxidant. No significant difference in deposition among BrCl concentrations was found. Growth of *Rangia*, however, was apparently undeterred by either chlorobrominated or chlorinated effluents (Table III), as all test animals surviving had completely refilled the 3-mm notch that had been filed in the shell perimeter.

While BrCl- or Cl_2- residual oxidants do not appear to be acutely lethal to *C. virginica* or *R. cuneata* at residual oxidant concentrations < 0.1 mg/l, the results show an evident sublethal effect. Several other authors have documented oyster shell growth suppression by bromine chloride and chlorine in instances of sublethal exposures. Roberts and Gleeson[15] reported effective concentrations (EC50's) of 0.10 and 0.16 mg/l BrCl and 0.023 mg/l Cl_2, which inhibited juvenile *C. virginica* shell growth after 96 hours. Shell deposition also was controlled among oysters exposed up to 120 hours to 0.01 mg/l chlorine-produced oxidants.[27] Long-term 11-week exposure of mussels (probably *Mytilus*) to 0.2 mg/l Cl_2 resulted in 96% survival accompanied by < 10% increases in mean shell lengths.[28]

The restricted shell deposition observed among oysters in this study probably can be attributed to a combination of "avoidance" of the chlorobrominated and chlorinated effluents by shell closure and possible impairment

TABLE III. Mean shell deposition by juvenile American oysters and brackish water clams exposed to chlorobrominated and chlorinated condenser effluents.[a]

Mean Halogen Concentration (mg/l)	Mean Shell Deposition (mm ± standard error)	
	C. virginica	*R. cuneata*[b]
BrCl		
0.081	2.6 ± 0.13	≥3.0
0.045	2.7 ± 0.13	≥3.0
0.020	2.8 ± 0.17	≥3.0
Cl_2		
0.062	2.3 ± 0.15	≥3.0
0.032	2.7 ± 0.21	≥3.0
0.014	3.0 ± 0.21	≥3.0
Reference		
R30[c]	3.5 ± 0.17	≥3.0

[a] Test duration of 15 days.
[b] All clams refilled notches in shells.
[c] R30 refers to position in bioassay trough corresponding to where cooling waters were 30 minutes old. Reference total residual oxidant levels were <0.002 mg/l for the duration of the study.

of physiological and metabolic processes within the oysters. Chlorine shell-closure responses of oysters[?] or disruption of other normal feeding patterns, as shown with *Balanus*,[20] may restrict the total intake of food materials over time, thus resulting in lower fitness of the test organisms indicated by net decreases in oyster condition and gonadal indices.[?] Changes in physiological processes similar to those reported to occur in fish[22,23] as well as changes in metabolic pathways of oysters [illegible] caused by halogen exposures and resulting in [illegible] animal fitness also may have contributed to the lack of growth of oysters in this study.

Copepods. The effects of short-term 24-hour exposure to BrCl- and Cl_2-treated cooling waters on the survival of *Acartia tonsa* are summarized in Table IV. *Acartia* subjected to chlorobrominated waters at 31° and 22°C had higher mean total survival than either chlorinated (31°C) or reference (31° and 22°C) groups. However, no statistically significant ($P > 0.05$) differences were found between treatments using the Student's *t*-test for two means.[22] No significant differences in survival were found among either BrCl or reference *A. tonsa* tested at 31° and 22°C, although higher mean survival was observed among both groups at 22°C (see Table IV). Unexpectedly, a direct relationship was found between BrCl dosage and survival, that is, with lower BrCl-total residual oxidant concentrations, lower survival occurred. Conversely, an expected indirect relationship between Cl_2 or reference concentrations and survival, with higher survival corresponding to lower oxidant levels, was observed. These analyses do not offer an explanation for these anomalous results.

Chlorobrominated solutions also were found to be less toxic than chlorinated waters to *Acartia* by Roberts and Gleeson.[18] The 48-hour LC50 BrCl values reported by Roberts and Gleeson[18] were 0.12 and 0.11 mg/l at 20° and 25°C, respectively. Concurrent tests using chlorine yielded LC50 values of 0.067 and 0.029 mg/l, indicating that the 0.05 mg/l 48-hour LC50 Cl_2 value previously reported by Roberts *et al.*[25] was apparently an overestimation.[18] Similar tests using freshwater *Daphnia magna* indicated that chlorobrominated wastewater effluents were less toxic to the copepods than chlorinated effluents after 48-hour exposures.[17] Total residual bromine chloride concentrations of 0.037 and 0.055 mg/l and a total residual chlorine concentration of 0.017 mg/l caused 50% mortalities among *Daphnia*

TABLE IV. Mean survival of *A. tonsa* exposed to chlorobrominated and chlorinated condenser cooling waters.[a]

Halogen	Residual Concentration (mg/l)	Mean Survival at Given Test Temperature (%)	
		31°C	22°C
BrCl	0.096		90.1
	0.087	83.3	
	0.061	—	81.2
	0.052	83.3	—
	0.049	—	83.3
	0.047	75.0	
Cl_2	0.088	64.6	—
	0.029	62.7	
	0.016	83.4	
Reference[b]	R5	60.0	78.1
	R30	76.2	84.2
	R60	81.0	91.3

[a] 24-hour exposure periods. Tests conducted using condenser effluents (31°C) and pre-condenser cooling waters (22°C).
[b] R5, R30, and R60 refer to positions in bioassay trough corresponding to cooling water "ages" of 5, 30, and 60 minutes. Residual oxidant levels at all reference stations were <0.002 mg/l during studies.

during those 48-hour tests.[37] The results of the present study indicate that the residual toxicity of chlorobrominated waters is less than that of chlorinated waters, although at a statistically insignificant level.

Zooplankton mortalities resulting from power plant entrainment have been attributed to mechanical, thermal, and biocide stresses as well as combinations of the three. Work by Carpenter *et al.*[38] indicated that copepod mortalities were caused by hydraulic and mechanical stresses occurring during through-plant entrainment, but the relationships of excess temperature and chlorine to copepod mortality could not be discerned from their experimental design.

Several authors have shown, however, that zooplankton (copepods) are tolerant of relatively large changes in temperature and that pumping stress also may contribute little to mortality. Davies and Jensen[39] found that copepod mortality, comparing intake and discharge canal samples, was unaffected by ambient temperatures at Lake Norman and Indian River power plants, but that at the James River plant motility of copepods decreased with increased temperature. Similarly, *A. tonsa* had less than 30% total mortality when exposed to an 11°C thermal increase.[40] Results of on-site studies by Heinle[41] demonstrated that copepod mortalities from circulator pump stress was insignificant. Shear stress, acceleration, and abrasional forces in many plant configurations may be the major nonbiocidal or nonpumping contributors to zooplankton mortality during cooling system entrainment.[42]

Chlorination has been identified by several authors[39, 41, 43] as the major agent causing extensive zooplankton mortalities in power plants. Onsite studies by Davies and Jensen[39] showed that chlorination of condenser cooling waters resulted in significant copepod mortalities at total residual chlorine concentrations ≤ 1.0 mg/l. Heinle[41] observed similar decreases in copepod survival during chlorination cycles at Maryland power plants (unknown total residual chlorine concentration). Analysis of the results from the present study did not indicate any significant halogen-survival effects at representative discharge total residual oxidant levels < 0.1 mg/l. However, higher zooplankton mortality rates would have been expected with cooling water from within the cooling system closer to the point of biocide introduction (circulator pumps in this study), where total residual oxidant concentrations more closely approximated the 0.5-mg/l applied rate. Studies by McLean[40] and Gentile *et al.*[43] have shown that *A. tonsa* subjected to 2.5 mg/l total residual chlorine had 50% and < 10% total survival, respectively, after 5-minute exposures. Gentile *et al.*[43] also found that groups of *A. tonsa* had 50% survival after a 2-hour exposure to 1.0 mg/l total residual chlorine. The effects of initially applied total residual oxidant concentrations between 0.5 and 1.5 to 2.0 mg/l may not contribute directly to the immediate death of entrained zooplankton, but may increase the possibility of mechanically caused mortality occurring after the initial biocide shock, depending on time of exposure and temperature. Residual biocide concentrations < 0.1 mg/l total residual oxidant discharged into the receiving stream would probably have minimal effect on natural zooplankton populations.

Phytoplankton. Severe depression of photosynthetic processes and significantly increased respiration rates of entrained phytoplankton communities occurred during both chlorobromination and chlorination of condenser cooling waters (Table V). Reductions in primary producers' oxygen evolution ranged between 77 and 388% below that of unentrained reference samples. Similarly, carbon-fixation rates (^{14}C assimilation) were limited to 39 to 60% of untreated sample values (Table V) by both halogen treatments. Entrainment also resulted in increased phytoplankton respiration rates ranging between 56 and 1 276% greater than those recorded for reference samples. Analysis of the data[33] (ANOVA) did not indicate any significant differences ($P. > 0.05$) in photosynthetic or respiratory process changes between chlorobrominated treatments. No differences in rate changes were found either among BrCl-total residual oxidant concentrations (0.086 and 0.035 to 0.086 mg/l) or among Cl_2-total residual oxidant concentrations (0.067 and 0.067 to 0.121 mg/l). Photosynthesis and respiration rates at different sample times during each day (see Table V) were equally affected by all biocide treatments and levels.

Chlorination of condenser cooling waters has been demonstrated to contribute in varying degrees to the suppression of primary productivity of entrained phytoplankton. Some controversy exists concerning the combined effects of biocides (chlorine or bromine chloride) and thermal increase. Several studies[44-47] clearly demonstrated depression of productivity during periods of chlorination, as

TABLE V. Effects of bromine chloride and chlorine treatments on photosynthetic and respiratory processes of entrained phytoplankton.[a]

Oxidant	Date and dosage (mg/l)	Time	O_2 Evolution in Light (mg/mg Chl a·h)[b]		O_2 Consumption in Dark (mg/mg Chl a·b)		C Fixation in Light (mg ^{14}C/mg Chl a·h)	
			Reference	Experimental	Reference	Experimental	Reference	Experimental
BrCl	8/25; 0.086	0800	17.5	−9.5[b]	5.2	27.3	0.23	0.09
		1030	26.3	−12.8	2.9	26.4	0.28	0.13
		1230	22.0	−33.6	24.2	76.9	—	—
	8/30; 0.035-0.058	0800	36.2	−59.7	10.5	77.0	0.41	0.12
		0930	43.0	−8.7	3.4	46.8	0.31	0.11
		1030	25.7	−31.2	17.1	31.2	0.42	0.12
		1130	9.6	−27.6	32.2	50.2	0.41	0.13
Cl_2	8/25; 0.067	0800	37.3	−50.9	4.7	55.8	0.32	0.11
		1030	24.4	−12.7	5.3	35.8	0.10	0.06
		1230	32.0	−37.1	27.4	52.7	—	—
	8/30; 0.067-0.121	0800	39.9	9.1	9.5	22.7	0.30	0.14
		0930	21.2	−21.9	5.8	21.9	0.32	0.13
		1030	28.0	−53.8	16.3	70.3	0.38	0.12
		1130	47.1	−73.0	36.2	109.5	0.49	0.18

[a] Results indicate combined effects of biocide treatment and plant ΔT (31° to 35°C). Reference values are from ambient temperatures (24° to 28°C) and no biocide.
[b] Negative values indicate decreases in O_2 evolution.

was also observed in this study. Total inhibition of phytoplankton activity resulting from chlorination of cooling waters also has been reported.[45, 48, 49] However, thermal increases from low ambient temperatures (< 20°C) have resulted in either no effect[45, 50] or increased primary production.[48] Thermal stress from base temperatures > 20°C also has been demonstrated to have no effect[50] or to have depressed primary productivity.[46, 48] The sampling scheme used in this study did not allow for differentiation between BrCl and Cl_2 stresses and ΔT (7°C). However, based on the results of similar studies[45, 47] it appears that the observed changes in phytoplankton activities in this study were primarily caused by the initial exposure to the applied 0.5 mg/l BrCl- or Cl_2-total residual oxidant.

CONCLUSIONS

The toxic effects of chlorobrominated and chlorinated power plant cooling waters on estuarine organisms appear to be similar with respect to the lethal and sublethal response indicators used in this study. Similar total survival of menhaden and spot, as well as oysters and *Rangia* exposed to BrCl- and Cl_2-treated effluent indicates that the toxicities of the residual oxidants were similar for both halogens. Lack of dissimilarities in oyster and clam shell deposition between chlorobrominated and chlorinated effluents is further indication of equivalence of the two halogens' residual toxicities. Shell growth inhibition of bivalves living in areas affected by the plant's discharge would undoubtedly occur during periods of biocide utilization for biofouling control, usually from late spring to mid-fall. However, while growth might in fact be limited by biocides during this period, normal growth probably would resume after cessation of biocide use. Fish encountering bromochlorinated or chlorinated condenser cooling effluents in the discharge area of receiving streams probably would be unaffected by the low-level halogen residuals and would be likely to avoid unsatisfactory conditions, if possible.

The results of this study demonstrated that bromine chloride appears to be less toxic to zooplankton than equivalent levels of chlorine, although the difference was statistically insignificant. The data from our study probably are more indicative of survival of copepods and other similar zooplankton exposed to bromine chloride or chlorine residuals in the mixing areas of the plant's discharge, where residual oxidant levels would be < 0.1 mg/l. Mortality rates of zooplankters encountering initial biocide (BrCl or Cl_2) concentrations

> 0.5 mg/l during primary phases of through-plant entrainment probably would be higher than those rates observed in this study. Subsequent mechanical and physical stresses also could be expected to increase death and injury to entrained organisms.

Biocide effects on entrained phytoplankton activity appear to be identical regardless of halogen treatment. Although the data from this study did not delineate the separate roles of biocidal, mechanical, and physical stresses to phytoplanktonic processes, it is apparent from these data and the literature that initially applied minimum concentrations of BrCl or Cl_2, which effectively control biofouling in estuarine cooling systems, would contribute substantially to the inhibition of photosynthetic processes of entrained phytoplankton communities. Increased respiration rates observed in this study may have been caused by oxidative bacterial activity, stimulated by the sudden availability of organic material, presumably from dead phytoplankton.

The effects on phytoplankton of residual oxidant discharges into receiving streams, although not investigated as part of this study, appear to be confined to an area within several kilometers of the discharge point.[45] Outside of this area, Fox and Moyer[46] reported complete recovery of photosynthetic processes to pre-entrainment levels. Indications of the possibility of these recovery processes are evident in the carbon-fixation data presented in this study, where only partial inhibition of ^{14}C-assimilation by BrCl and Cl_2 after 4 hours incubation suggests that total destruction of the phytoplankton community did not occur.

The evidence presented in this study and by other investigators suggests that the effects on aquatic organisms of chlorobrominated power plant cooling waters are similar and in some cases not as severe as the effects of equivalent chlorinated waters. Bromine chloride's more rapid decay rate may make it a more desirable antifouling alternative to chlorine. However, it is important that more comparative tests be conducted to define any differences in toxicities of bromine chloride or chlorine residual oxidants. These tests would be necessary before chlorobromination can be conside[red] as an environmentally acceptable alternative to chlorine for disinfec[ti]on and biofouling control.

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