ATTACHMENT 2

THE RELATIVE TOXICITIES OF CONTINUOUS AND INTERMITTENT EXPOSURES OF CHLORINE AND BROMINE TO AQUATIC ORGANISMS

Prepared for

The Sodium Bromide/Bromine Chloride Industry Panel

Prepared by

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FOREWORD

The study was initiated at the request of The Sodium Bromide/Bromine Chloride Industry Task Force under contract to B & B Environmental Services, Inc. on October 10, 1990.

The test program was performed in accordance with the "Protocol for Testing of the Effects of Sodium Bromide on the Toxicity of Chlorine to Fresh and Saltwater Organisms," (Appendix B) and as amended by Protocol Amendment #1 (Appendix C). The Test Protocol and Amendment #1 were agreed upon by The Sodium Bromide/Bromine Chloride Industry Task Force, U.S. EPA, and B & B Environmental Services, Inc. The only deviation from the Test Protocol is the expression of oxidant as µeq/L rather than µg/L oxidant in the report. The rationale for expressing the oxidants as µeq/L rather than µg/L oxidant is given in the report.

In addition to the test program specified above, a program was developed by L. Bongers and W. Furth (included as Appendix A), designed to estimate the relative environmental impacts resulting from the application of chlorine and bromine for fouling control.

The undersigned certify that the test program was performed in accordance with the Test Protocol and Protocol Amendment #1.

Program Management:

Date:

Leonard H. Bongers, Ph.D. — 7-3-91

Dennis T. Burton, Ph.D. — 7-2-91

Daniel J. Fisher, Ph.D. — 7/2/91

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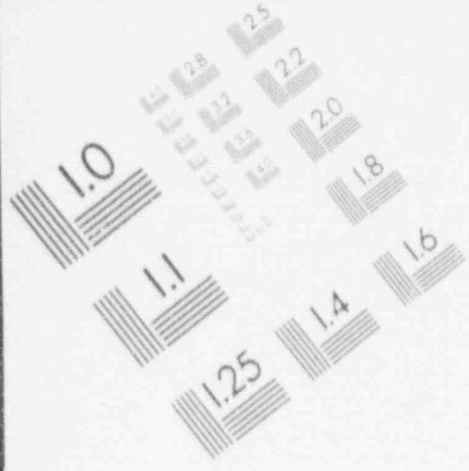
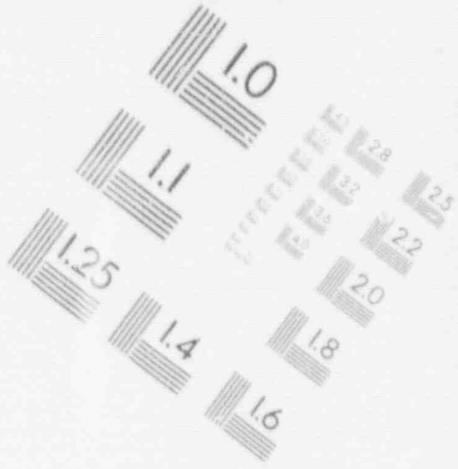
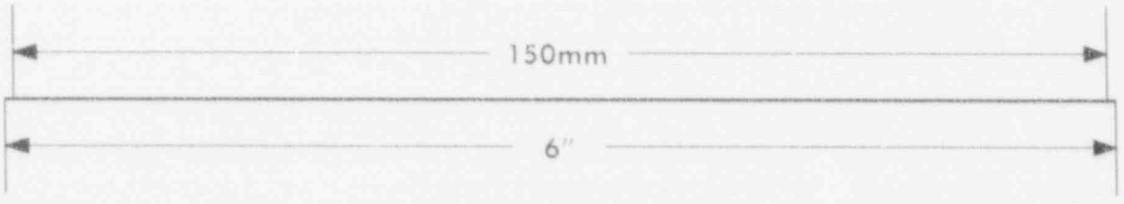
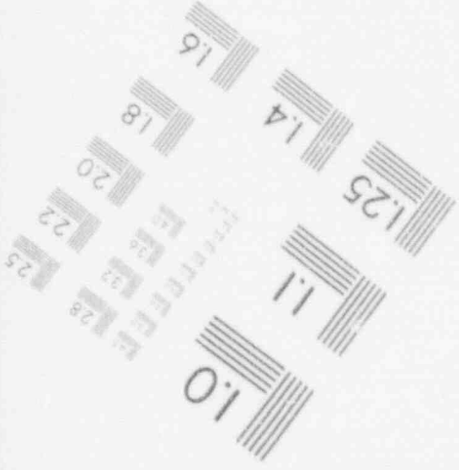
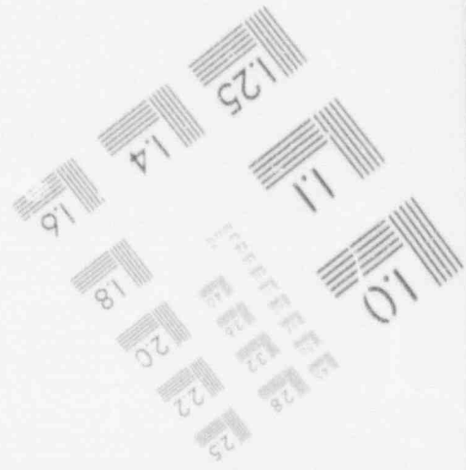
IMAGE EVALUATION TEST TARGET (MT-3)











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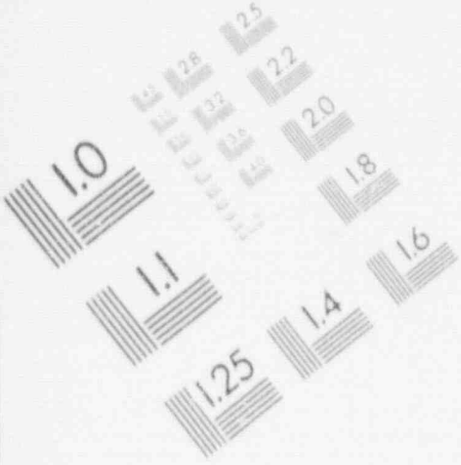

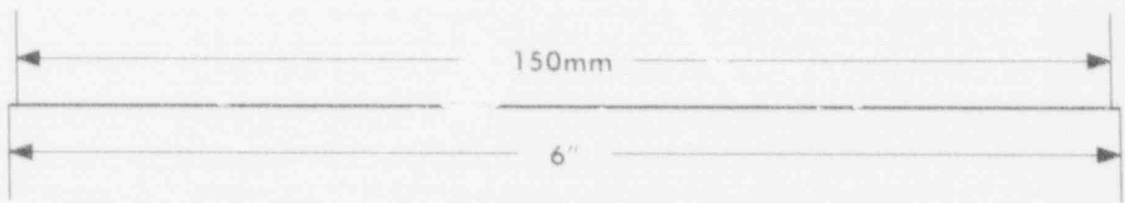

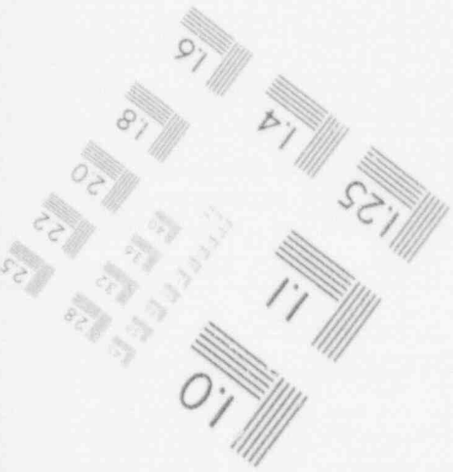

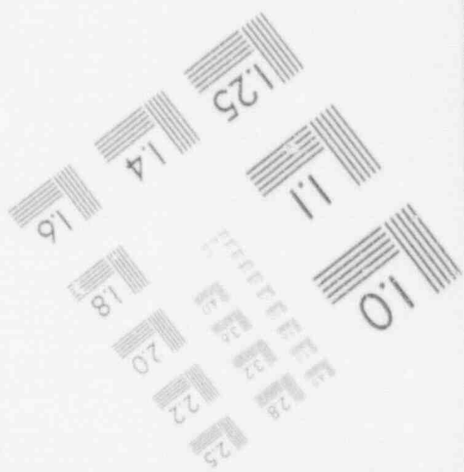

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ABSTRACT

Sodium bromide can be used to convert hypochlorous acid into hypobromous acid. Simultaneous addition of sodium bromide and chlorine to water used for powerplant condenser cooling could significantly reduce chlorine application rates because bromine oxidants are generated and considered more effective for controlling biofouling than chlorine oxidants.

Since such a change in biofouling control strategy could impact the environment, the biotoxicity characteristics of bromine oxidants were evaluated in terms of LC50 values. In order to ascertain potential effects of residual bromine oxidants on the environment, decay properties of bromine oxidants were compared to chlorine oxidants.

It was found that in four of six species tested, the bromine oxidants were about twice as toxic as the chlorine oxidants, while for two species the difference in toxicity was five fold. For continuous exposure to bromine oxidants, the 48-h LC50 for daphnids and the 96-h LC50 for amphipods could not be calculated because significant mortality occurred at the oxidant quantitation limit.

Oxidant decay properties were significantly different as well. Bromine oxidants decayed two to five times faster than chlorine oxidants.

Biotoxicity and chemical findings are in general agreement with data published previously.

Present data suggest that environmental benefits may result from the simultaneous application of sodium bromide with chlorine for biofouling control as compared to the application of chlorine without sodium bromide.

Preliminary computations based on present data indicate that these environmental benefits may be significant. The anticipated environmental benefits are attributable to the relatively rapid chemical decay of the bromine oxidants and also to the relatively lower amount of biocide needed for the same degree of biofouling control. Further details are given in Appendix A.

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I. INTRODUCTION

Chlorination by wastewater treatment plants and POTWs to eliminate the discharge of pathogenic organisms and the use of chlorine by electric utilities to inhibit biofouling are widespread practices. Laboratory research has shown, however, that chlorine-induced oxidants are toxic to both freshwater and saltwater aquatic organisms. Due to the relatively slow decay rate of these oxidants, they may be toxic to aquatic life when discharged into receiving waters.

The use of sodium bromide in conjunction with chlorine has been proposed as an alternative method to routine chlorination. When applied with chlorine, sodium bromide is oxidized by hypochlorous acid (HOCl) to hypobromous acid (HOBr) and sodium chloride. Due to the relatively low bond strengths, bromine residuals exhibit low stability and hence, should decay faster. In addition, they are more reactive than chlorine residuals, and should perform better as biocides. In cooling water containing ammonium salts, application of sodium bromide with chlorine should result in much lower levels of oxidant residuals because the slow-decaying chloramines would not be generated.

The objective of the present study was to provide a technical basis for assessing the potential environmental and operational benefits of using sodium bromide in conjunction with chlorine for the control of biofouling in power plant cooling systems.

Comparative data were obtained for both freshwater and saltwater organisms exposed to the two biofouling control options. The testing effort included:

- Measurements of acute toxicity effects on representative fresh- and saltwater organisms resulting from a continuous or intermittent exposure to chlorinated or brominated fresh- and saltwater.
- Evaluation of the effects of ammonia on the toxicity responses, and
- Measurements of decay rates in fresh- and in saltwater of chlorine- and bromine-induced oxidants.

Toxicity responses were expressed as 96-h LC50 values for all species tested with the exception of daphnids, for which 48-h LC50 values were estimated. Oxidant decays were computed as quasi-first order decay constants.

Findings presented in this report suggest that the relative potency of bromine-induced oxidants allows the amount of chlorine required for biofouling control to be reduced to about half the amount that is required in the absence of bromide.

The relatively rapid decay of bromine-induced oxidants is another promising feature resulting from the simultaneous addition of sodium bromide and chlorine. The combination of reduced biocide requirements for fouling control and the rapid decay of residual bromine oxidants may result in a significant decrease in environmental impact. Using toxicity data for golden shiner and rainbow trout, and oxidant decay values determined as part of the present study, sample calculations of the relative impacts of chlorine and bromine oxidants were performed. (For details see Appendix A.) These calculations indicate significant reduction in environmental impact, depending on biocide use for fouling control, and the relative amount of the riverflow and for condenser cooling.

II. MATERIALS AND METHODS

TEST MATERIALS

Test Species

Toxicity tests were performed on four freshwater and two saltwater species. The freshwater species included two invertebrates, the daphnid *Dapnia magna* and the amphipod *Hyalella azteca*, and two fish, the golden shiner *Notemigonus crysoleucas* and the rainbow trout *Oncorhynchus mykiss*. The two saltwater species were an invertebrate, the mysid *Mysidopsis bahia*, and a fish, the silverside *Menidia beryllina*. The life stage (length and weight, where appropriate) of each test species and the exposure conditions are given in Table 1. Daphnids and amphipods were obtained from in-house cultures; common shiners from Perry's Fish Farm in Petersburg, VA; and Rainbow trout from the U.S. Fish and Wildlife Service's Erwin National Fish Hatchery in Erwin, TN. Mysids were obtained from Chesapeake Cultures in Hayes, VA and silversides from Aquatic Indicators in St. Augustine, FL.

Test Compounds

Sodium hypochlorite (Lot #0276), was obtained from Lab Chem. Inc., Pittsburgh, Pennsylvania; sodium bromide (Lot #020290) from Ethyl Corp., Baton Rouge, Louisiana.

All chlorine stock solutions were prepared from Lot #0276 containing 66 grams chlorine per liter. To prepare bromine stock solution, sodium bromide (NaBr) from Lot #020290, containing 527 grams NaBr per liter, was added to a solution of hypochlorous acid. In order to assure complete conversion of hypochlorous acid (HOCl) into hypobromous acid (HOBr), sodium bromide was added at 1.5 times the stoichiometric concentration of chlorine, in accordance with equation:

$$HOCl + 1.5\ NaBr \rightarrow HOBr + NaCl + 0.5\ NaBr$$

Thus, it is reasonable to assume that a stock solution containing chlorine and sodium bromide in the specified ratio will principally contain hypobromous acid, and no hypochlorous acid. (In the text these solution are referred to as chlorine/NaBr mixtures or as bromine solutions.)

Dilution Water

Unchlorinated groundwater from an on-site deep well was used for all tests using freshwater. For saltwater tests, estuarine water from the adjoining Parrish Creek was used. Both the freshwater and the saltwater were filtered to 1 µm and stored in 850 gallon holding tanks. The water in the holding tanks could be aerated and heated (titanium heaters) as necessary. For all organisms with the exception of rainbow trout the water temperature was maintained at 25°C; for rainbow trout the temperature was maintained at 15°C. For all saltwater tests the salinity of the estuarine water was increased to 20 ppt with Instant Ocean®. Water quality parameters are recorded in Tables 2 and 3. The groundwater was also tested for organic priority pollutants; none were detected above the level of detection.

TEST METHODS

Treatment Conditions

All tests with the exception of rainbow trout, were conducted at 25°C ± 2°C; tests with rainbow trout were conducted at 15° ± 1°C. Test temperatures were recorded continuously, and at no time did the temperature exceed the specified limits. Other conditions are as listed in Table 2 and Table 3.

The test organisms were exposed to either chlorine or bromine (i.e., chlorine/NaBr mixture) in a side-by-side flow-through exposure system. This allowed direct toxicity comparisons between both oxidants using the same dilution water. All organisms except the daphnids were exposed for 96 hours. The daphnids were exposed for 48 hours.

Two separate tests were conducted on each species. In one test, organisms were exposed continuously to a dilution series of oxidants. In the second test, organisms were exposed intermittently to a dilution series of oxidant for 40 minutes every 8 hours. The organisms were maintained in oxidant free conditions for the periods between exposures.

Initially, the method of Brooks et al. (1989) was used to maintain oxidant concentrations during the intermittent exposures. These investigators spiked the tanks with oxidant to obtain the desired exposure concentration. Then, a flow-through toxicant delivery system was turned on to maintain that concentration during the intermittent period. At the end of the period the toxicant delivery system was turned off, and the tanks were flushed with diluent water. This procedure was used for tests with the daphnids and the golden shiner. For the rest of the intermittent tests conducted in the present study, the toxicant delivery system was maintained under constant conditions, while the test chambers, containing the organisms, were transferred between halogenated test aquaria and non-halogenated flow-through holding tanks. Immediately following transfer of the organisms

to the holding tanks, the flow rate of diluent water into the tanks was increased to flush any total residual oxidants (TRO) that may have been transferred from the test aquaria.

The rainbow trout were held in 1 mm mesh nitex baskets with petri dish bottoms during the intermittent exposure periods. The petri dishes allowed for a small amount of liquid to cover the fish during transfers between treatment conditions.

The smaller organisms were tested in the continuous exposure chambers described below and transferred with a glass ladle between treatments. This allowed the organisms to remain immersed during the transfer. Although both intermittent procedures produced good "square-wave" intermittent exposure conditions, the latter transfer method appeared more convenient than the spiking procedure.

An additional continuous exposure study was conducted to compare the toxicity of chloramines and bromamines to daphnids and mysids. In these experiments, dilution water was dosed to 0.3 mg/L NH_4-N with ammonium chloride prior to delivery to the test system. This stoichiometric ratio of ammonia to oxidant, also used by Brooks et al, allows conversion of oxidants into amines. Bioassays conducted with these test solutions principally evaluate the biotoxicity of chloramines and bromamines.

Exposure System

A continuous flow delivery system similar to that used by Vanderhorst et al (1977) was used to create a stable oxidant exposure environment. Water from the diluent holding tanks was pumped to a 200 gallon constant head tank located above the exposure wet table. The smaller head tank was temperature controlled and aerated. The wet table holding the exposure aquaria was also temperature controlled. Diluent water was delivered by gravity through a 4 inch PVC delivery pipe suspended above the wet table. Overflow from the delivery pipe was diverted back into the large holding tanks. The flow rate through the delivery pipe was controlled by both a standpipe in the overhead tank and a PVC valve at the beginning of the delivery pipe. Excess water not used as dilution water was diverted from the overhead tank to the holding tanks through an overflow system. Diluent water was delivered from the delivery pipe to the test aquaria by adjustable glass siphons as shown in Vanderhorst et al (1977). Each siphon was inserted into a green nalgene stopper which was inserted into a hole drilled into the 4 inch delivery pipe. The flow rate from each siphon was adjusted to 190 mL/min for all halogenated treatments and 200 mL/min for the control.

Chlorine and bromine stock solutions were delivered at a rate of 10 mL/min to each treatment condition by Masterflex® pumps. Stocks of various TRO concentrations were made up using reverse osmosis water in 20 L glass carboys. NaBr was added to the NaOCl solution, stirred, and allowed to stand in the dark for 15 minutes prior to dosing of the stocks. The stocks were mixed thoroughly and allowed to stand for 1 to 2h prior to use. During the exposure periods, the 20 L carboys were covered with black plastic. New stock

solutions were made every 24 hours. Glass delivery tubes were inserted through silicone stoppers to the bottom of the stock bottles. Chlorine resistent Masterflex® tubing (C-FLEX®) was used to deliver the stock solutions through the pump heads to glass mixing funnels suspended below the diluent water siphons. After mixing, the halogen concentrations were delivered through tygon tubing to glass splitters which delivered equal volumes of treated or control water to two replicates per treatment.

The exposure aquaria (9.5 L) contained 7 L of solution. Flow into each aquaria was 100 mL/min. This allowed for a 90% molecular replacement time of approximately 2.5 hours. All tests were conducted in these aquaria using the same flow rate. In the continuous exposure tests, daphnids, amphipods, mysids, and silversides were suspended in glass chambers (5 cm diameter by 15 cm length) with nalgene screens on the bottoms. The test chambers were suspended in the test aquaria from a rocker-arm assembly which allowed the chambers to move vertically through the test aquaria. A complete vertical cycle was completed every 20 to 25 sec. This increased mixing of fresh toxicant into the chambers throughout the test. Control organisms were suspended in identical baskets. Rainbow trout and shiners were exposed in the aquaria without chambers. As discussed earlier, chambers and baskets (trout) were moved between exposure and holding tanks during the intermittent exposure tests.

Exposure Protocol

Each test (continuous or intermittent) consisted of five to six treatments per oxidant plus a control. In the chloramine/bromamine studies an additional ammonia control was added. Rainbow trout tests were conducted at a temperature of 15°C, while all other tests were conducted at 25°C. The light cycle for all the tests was 16 h light:8 h dark. Organisms were not fed during the tests except for the mysids which require live brine shrimp to survive 96 hours and amphipods which were fed micro-encapsulated artificial food. Prior to the start of each test the exposure system was operated until TRO concentrations in all test aquaria stabilized. The continuous flow tests were started by adding organisms to the stabilized test aquaria. To start the intermittent exposures for the amphipods, trout, mysids, and silversides, organisms were added to the exposure chambers in the holding tanks. After all of the chambers were loaded they were transferred to the test aquaria to start the exposure. After 40 min, the chambers were transferred to non-halogenated holding tanks. As discussed above, daphnids and shiners were kept in the test aquaria which were spiked and continuously dosed for 40 min, after which time chlorine was flushed from the system.

In the continuous exposure experiments, water samples were taken for TRO analysis at 1, 2, 4, 6, 8, 10, 12, 24, 36, 48, 60, 72, 84, and 96 h. TRO measurements for the intermittent exposures were taken at the beginning and end of each 40 min exposure period. Organism mortalities were recorded at 1, 2, 4, 8, 12, 24, 36, 48, 72, and 96 hours for the continuous exposures, and at 1, 2, 4, 8, 12, 16, 24, and every 8 hours thereafter until the conclusion of the test. Free available oxidant (FAO) was measured one time in each test

treatment during every test. Dissolved oxygen, conductivity or salinity, pH, alkalinity, and hardness were measured daily in each treatment. Temperature was recorded continuously in one control replicate in all tests.

During the chloramine/bromamine studies, total ammonia (NH_3-N) was measured in the diluent water holding tanks at the beginning and end of each tank refill. In addition, FAO, mono-, and di-halogenated amines were measured in each treatment tank once during each of these tests.

The bioassay test protocol was consistent with the test guidelines described in the Environmental Protection Agency's, "Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms" (USEPA 1985), with the exception of temperature. The test temperature for all species, except rainbow trout, was 25°C rather than 20°C. The rainbow trout test was conducted at 15°C rather than 12°C.

Measurements of Oxidant Concentration

The amperometric titration method, described in *Standard Methods*, (Method 4500-Cl D APHA et al. 1989), was used to determine total residual oxidants (TRO), and free available oxidant (FAO). Fischer Porter amperometric titrators (Model #17T2000) were used for all measurements. By using the high sensitivity mode, a forward titration, and a 200 mL sample, TRO quantitations limits were 15 µg/L TRO as chlorine and 34 µg/L TRO as bromine. With this sample size, 1 mL of PAO (0.00564N phenylarsene oxide) titrant equals 1 mg/L chlorine equivalents. Samples were analyzed immediately upon collection to avoid loss of oxidant due to holding. Total residual oxidant concentrations are presented as µg/L (ppb) TRO as chlorine or bromine. LC50 values are reported as ppb TRO as chlorine and as µeq TRO/L for the chlorine exposures and as ppb TRO as bromine and as µeq TRO/L for bromine exposures. The TRO as ppb bromine was calculated by multiplying the milliliters of titrant (PAO) used by 2.25 as described in the Fischer Porter titrator manual. LC50 values for the two treatments are compared on a µeq TRO/L basis. The concentration of TRO as ppb chlorine and bromine are converted to µeq TRO/L by dividing by 35.5 for chlorine and 79.9 for bromine.

Measurements of Oxidant Decay

These tests were conducted on the freshwater and saltwater used for the bioassay testing. The effects of sodium bromide on the decay of chlorine-induced oxidants were tested at 1.5 times the stoichiometric concentration of chlorine. The static decay tests were

made in 2 L Pyrex® beakers at 25°C in the dark. TRO measurements were made amperometrically by the same procedures described above for the bioassay tests.

Ammonia Measurements

Ammonia (NH_3-N) was measured using an ammonia-selective electrode and an Orion Model 901 Ion Analyzer. Method 4500-NH_3 described in *Standard Methods* (APHA et al. 1989) was used for the analysis.

III. RESULTS

CHLORINE AND BROMINE TOXICITIES

The toxicity data for continuous exposures are presented as LC50 and as ILC50 for intermittent exposures. These toxicity indicators are based on the average oxidant concentration per treatment. The LC50 represents the TRO concentration which is lethal to 50% of the test organisms exposed continuously over the test period. The ILC50 represents the TRO concentration which is lethal to 50% of the test organisms exposed intermittently for 40 minutes every 8 hours. The continuous exposure LC50 values are based on the average TRO concentrations over the entire length of the test period, while the ILC50 are based on the average TRO concentration for all of the 40-minute exposure periods during the test.

LC50 values are calculated from the mortality data in accordance with EPA Manual 600/4-85/013 (USEPA 1985). Where possible, the probit method was used. If the statistical criteria for a probit analysis were not met, an LC50 value was calculated by the moving average angle method. An EPA computer program was used for calculating all LC50 values (Stephan 1978).

The results of all toxicity tests are summarized in Table 4, while oxidant concentration for all treatment conditions are summarized in Tables 5 and 6.

From the examination of the results it appears that bromine-induced oxidants are more toxic than chlorine-induced oxidants when compared on a µeq TRO/L basis (see Table 4). On the other hand, when the comparisons are made on a weight basis (i.e., µg/L) chlorine-induced oxidants appear more toxic than bromine-induced oxidants in 12 of 14 cases tested. These apparent contradictions result from the difference in atomic weight of the two agents involved.

We prefer to express toxicity and chemical decay in terms of microequivalents per liter (µeq/L) for several reasons. One is that neither the speciation nor the relative contribution of individual oxidants to biotoxicity are known; another is that the TRO measurement method determines TRO concentrations in terms of iodine equivalents per unit volume. And, since there are differences between the toxicities of chlorine-induced and bromine-induced oxidants, and, their rates of decay, it would be misleading to convert TRO equivalents into either a weight-based chlorine value or a weight-based bromine value.

Also, to facilitate estimates of the relative environmental impacts of the two agents it is more convenient to perform calculations based on TRO values expressed in terms of chemical equivalents per unit volume.

Accordingly, in this report comparisons between the agents will be based on µeq chlorine TRO/L or µeq bromine TRO/L.

Results recorded in Table 4 indicate that for continuous exposures, bromine oxidants appear to be twice as toxic (1.93 ± 0.35) as chlorine oxidants in four of the six organisms; for the amphipods and silversides bromine oxidants are about five times as toxic (5.28 ± 0.53). A 48-h LC50 for daphnids and a 96-h LC50 for amphipods could not be calculated for continuous bromine exposure, because survival was less than 50% at the level of oxidant quantitation.

For intermittent exposures, bromine oxidants were, on the average, 1.7 times (1.67 ± 0.34) as toxic; but there was little difference among species.

In freshwater, daphnids and amphipods were most sensitive, both in continuous and intermittent exposures. In saltwater, the mysid was the most sensitive organism when exposed continuously to chlorine oxidants. The mysid and silverside were equally sensitive to continuous bromine exposure and also to both oxidants, when they were exposed intermittently.

Conversion of chlorine oxidants into chloramimines, and bromine oxidants into bromamines appeared to increase toxicity, although this effect was less pronounced in case of the bromamines. This increase in toxicity is attributable to amines, and not to the formation of unionized ammonia. Under prevailing test conditions, the concentration of unionized ammonia was estimated at less than 15 and 17 pbb during the mysid and daphnid tests, respectively. These levels are well below reported toxicity values (USEPA 1985, 1989).

During each treatment condition, one sample also was analyzed for free available oxidant (FAO), as well as total residual oxidant (TRO). The results of these analyses are recorded in Table 7 (chlorine), Table 8 (bromine), and Table 9 (ammonia test).

FAO was observed more frequently at the high-concentration treatment conditions; with bromine as the treatment agent, FAO was also observed at low-concentration treatments. To what extent free available oxidant did contribute to the observed mortalities is unclear from the available data.

In the presence of 0.3 mg/L ammonia-nitrogen, FAO was not observed in chlorine treatments (Table 9). Addition of ammonia to bromine treatments did indicate the presence of relatively large concentrations of FAO. According to a personal communication with Dr. Franklin Handy of Great Lakes Chemical Corporation, West Lafayette, Indiana, the FAO observations in bromine treatments with ammonia are erroneous. Apparently, under such conditions, the amperometric titration method measures bromamines as FAO. Since ammonia was added in relative excess, we may assume complete conversion of bromine oxidants into bromamines. Thus, the observed toxicities reflect bromamine toxicities.

DECAY OF CHLORINE AND BROMINE INDUCED OXIDANTS

The effect of the addition of sodium bromide to a solution containing chlorine on oxidant decay is recorded in Table10, and illustrated in Fig. 1, where the natural logarithms of the total residual oxidant concentrations are plotted against time for solutions containing chlorine and chlorine/solutions to which sodium bromide is added. Figure 1 shows the decay in freshwater; in Fig. 2, similar data are shown for the decay in saltwater.

The test data reflect a two-phase, quasi first order oxidant decay, for both chlorine and bromine (i.e., chlorine/sodium bromide). In both cases, the initial relatively fast decay, defined as K1 (slope of ln [μeq TRO] vs time) was followed by a much slower decay, defined as K2.

In freshwater, (Table 11), sodium bromide increased the fast decay by a factor of about three (0.054 vs 0.016), while K2 was increased by a factor of 5 (0.005 vs 0.001).

In saltwater (Table 12) with sodium bromide, the fast decay (K1 = 0.084) was, on the average, about twice as fast as the fast decay observed in the presence of chlorine alone (K1 = 0.044). The slow decay (K2 = 0.009) was, on the average, about nine times the chlorine value (K2 = 0.001).

These data clearly indicate significant increases in the rates of the fast and slow oxidant decays when sodium bromide is applied simultaneously with chlorine.

As will be discussed in the next section and in Appendix A, the relatively rapid decay of bromine oxidants may significantly reduce the environmental impact resulting from biofouling control of powerplant cooling systems.

IV. DISCUSSION

LC50 values for chlorine TRO in the current study are consistent with toxicity values from the Environmental Protection Agency's water quality criteria for chlorine (USEPA 1984) when expressed as ppb chlorine TRO. The species mean acute values (SMAV) for *Daphnia magna* (27.7 ppb) and rainbow trout (62 ppb) reported in the water quality criteria are identical to values from the current study. The SMAV for amphipods of 267 ppb is similar to our value of 78 ppb considering the species *(Gammarus pseudolimnaeus)* and life stage differences. The somewhat lower SMAV of 127 ppb TRO for *Notemigonus crysoleucas* reported in the water quality criteria may be a factor of one low value (40 ppb) skewing the SMAV and the fact that sewage effluent was used as the dilution water in all the tests used to determine the SMAV.

There are no directly comparable values for *Mysidopsis bahia* or *Menidia beryllina* in the water quality criteria. The only mysid value reported was an LC50 of 162 ppb for *Neomysis sp.* determined at 15°C and a salinity of 28 ppt. The temperature difference between the two studies may explain the difference from our value of 62 ppb. There is one 96-h LC50 value of 54 ppb for *Menidia peninsulae* and a 96-h LC50 value of 37 ppb for *Menidia menidia* which form the basis for comparison with our present value of 143 ppb with *Menidi beryllina*. The value of 37 ppb was achieved using field collected adult silversides. The 96-h LC50 value of 54 ppb is an unpublished value cited in a paper by Goodman et al. (1983) for comparison with long term studies conducted with the same species. Compared to the no effects level of 40 ppb found by Goodman et al. for hatching success and survival, it seems likely that the 96-h LC50 of 54 ppb may be somewhat low.

Brooks et al. (1989) conducted an extensive study on continuous and intermittent toxicity of chloramines to a number of species. Results from his studies give comparable LC50 values to the current studies (48-h LC50 of 24 ppb TRO for *Daphnia magna* and a 96-h LC50 of 111 ppb for rainbow trout). These investigators also showed a 3- to 5-fold decrease in daphnid sensitivity during intermittent exposures (2 hours/day) and a 7-fold decrease in rainbow sensitivity, again very comparable to the present study. The common shiner *Notropis cornutus* was more sensitive to chloramines (96-h LC50 of 71 ppb) than the golden shiner was to chlorine in the present study. Species and exposure dissimilarities (ammonia vs no ammonia) could explain the differences in the LC50s.

Present tests indicate that continuous exposure to bromine oxidants appears to be about two times as toxic to four of the six species, compared to continuous exposure to chlorine oxidants. For the silversides and amphipods, the difference was five-fold. For continuous exposures to bromine oxidants the 48-h LC50 for daphnids and the 96-h LC50 for amphipods could not be calculated because their survival was less than 50% at the level of oxidant quantitation. With intermittent exposures, the difference in toxicity was on the average 1.7 times.

A similar difference in "potency" was also observed in a study by Bongers et al, 1977, and Liden et al, 1980, when the effectiveness of biofouling control by bromine chloride was compared to that of chlorine. These studies indicated that the more toxic bromine oxidants permitted the use of much lower amounts of biocide for fouling control. A 15-day trial, conducted on a powerplant cooling system using low-salinity estuarine water for heat rejection, indicated that, on an equimolar basis, bromine oxidants were two to three times more effective than chlorine oxidants.

In light of the observed fouling control efficacy of bromine oxidants, and their relatively rapid decay characteristics, the conversion of hypochlorous acid into hypobromous acid and bromine oxidants could significantly reduce the impact on the aquatic environment resulting from the control of biofouling of powerplant cooling systems. Beneficial effects from this conversion would be most pronounced at high ambient water temperatures and when a relatively large portion of the riverflow is used for condenser cooling.

Preliminary estimates of a reduction in environmental impacts is shown in Table 13, where the benefits of using sodium bromide in conjunction with chlorine are estimated for heat rejection into a freshwater stream. (Methodology, assumptions and calculation are given in Appendix A.)

This comparison which is based on rainbow trout and golden shiner data, indicates that significant reduction in environmental impact can be achieved, depending upon the amount of riverflow used for condenser cooling.

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Table 1. Information on organisms used in testing

Species	Test	Life Stage	Length mm(±SD)	Weight (mg ±SD)	
				Wet	Dry
Daphnid *(Daphnia magna)*	48-h Continuous	<24h	NA	NA	NA
	48-h Intermittent	<24h	NA	NA	NA
Golden shiner *(Notemigonus crysoleucas)*	96-h Continuous	Young	71.5(4.80)	3180(714)	890(225)
	96-h Intermittent	Young	74.9(6.09)	3300(701)	960(229)
Rainbow trout *(Oncorhynchus mykiss)*	96-h Continuous	15 day	24.0(1.23)	98.0(11.9)	17.2(2.01)
	96-h Intermittent	15 day	24.0(1.23)	98.0(11.9)	17.2(2.01)
Amphipod *(Hyalella azteca)*	96-h Continuous	juvenile	NA	NA	0.44(0.14)
	96-h Intermittent	juvenile	NA	NA	0.44(0.14)
Mysid *(Mysidopsis bahia)*	96-h Continuous	5 day	NA	NA	0.171(0.003)
	96-h Intermittent	5 day	NA	NA	0.169(0.003)
Silversides *(Menidia beryllina)*	96-h Continuous	8 day	10.6(0.93)	4.81(2.08)	0.96(0.42)
	96-h Intermittent	11 day	11.6(0.76)	8.24(1.57)	1.68(0.33)
Daphnid *(Daphnia magna)*	48-h Continous 300 µg/l Ammonia	<24h	NA	NA	NA
Mysid *(Mysidopsis bahia)*	96-h Continuous 300 µg/l Ammonia	5 day	NA	NA	0.168(0.005)

Table 2. Mean water quality (±SD) for the chlorine studies

Test	DO (mg/L)	pH	Cond/Salinity*	Alk. (as mg/L $CaCO_3$)	Hard. (as mg/L $CaCO_3$)
FRESHWATER					
Daphnid Continuous	8.5 (0.2)	7.31-7.71	333.3 (17.0)	152.5 (2.5)	144.5 (2.9)
Daphnid Intermit	8.4 (0.1)	8.21-8.34	366.7 (20.5)	108.3 (2.4)	161.0 (32.7)
Shiner Continuous	7.6 (0.2)	8.16-8.36	368.3 (25.3)	133.3 (16.5)	184.3 (20.0)
Shiner Intermit	6.8 (0.1)	7.41-7.68	350.0 (9.5)	100.0 (15.8)	145.5 (5.1)
Trout Continuous	7.7 (0.1)	7.20-7.64	334.0 (6.5)	132.0 (2.4)	160.0 (3.3)
Trout Intermit	7.7 (0.1)	7.20-7.64	334.0 (6.5)	132.0 (2.4)	160.0 (3.3)
Amphipod Continuous	8.0 (0.1)	7.84-8.00	363.0 (3.4)	165.0 (7.1)	138.0 (4.3)
Amphipod Intermit	8.0 (0.1)	7.84-8.00	363.0 (3.4)	165.0 (7.1)	138.0 (4.3)
Daphnid w/ Ammonia	8.6 (0.1)	7.35-7.90	341.2 (14.3)	159.0 (5.1)	142.0 (3.2)
SALTWATER					
Silversides Continuous	7.2 (0.2)	8.36-8.52	20.7 (0.45)		
Silversides Intermit	7.2 (0.2)	8.33-8.65	20.5 (0.44)		
Mysid Continuous	7.2 (0.2)	8.36-8.52	20.7 (0.45)		
Mysid Intermit	7.2 (0.2)	8.33-8.65	20.5 (0.44)		
Mysid w/ Ammonia	7.7 (0.1)	8.00-8.11	21.0 (0.82)		

* Conductivity expressed as µmhos/cm; salinity expressed as ppt

Table 3. Mean water quality (±SD) for the chlorine/NaBr study

Test	DO (mg/L)	pH	Cond/Salinity*	Alk. (as mg/L $CaCO_3$)	Hard. (as mg/L $CaCO_3$)
FRESHWATER					
Daphnid Continuous	8.7 (0.1)	7.28-7.77	331.2 (14.3)	160.0 (5.0)	145.0 (3.0)
Daphnid Intermit	8.4 (0.1)	8.21-8.34	366.7 (20.5)	110.0 (4.0)	178.7 (8.2)
Shiner Continuous	7.6 (0.2)	8.11-8.33	368.3 (25.3)	141.0 (15.9)	184.3 (20.0)
Shiner Intermit	6.8 (0.1)	7.41-7.68	350.0 (9.5)	100.0 (15.8)	145.5 (5.1)
Trout Continuous	7.5 (0.1)	7.24-7.41	334.0 (6.5)	132.0 (2.4)	160.0 (3.3)
Trout Intermit	7.5 (0.1)	7.24-7.41	334.0 (6.5)	132.0 (2.4)	160.0 (3.3)
Amphipod Continuous	8.0 (0.1)	7.81-8.01	363.0 (3.4)	165.0 (7.1)	138.0 (4.3)
Amphipod Intermit	8.0 (0.1)	7.81-8.01	363.0 (3.4)	165.0 (7.1)	138.0 (4.3)
Daphnid w/ Ammonia	8.6 (0.1)	7.33-7.89	341.2 (14.3)	159.0 (5.1)	142.0 (3.2)
SALTWATER					
Silversides Continuous	7.2 (0.2)	8.36-8.51	20.7 (0.45)		
Silversides Intermit	7.2 (0.2)	8.30-8.59	20.5 (0.44)		
Mysid Continuous	7.2 (0.2)	8.36-8.51	20.7 (0.45)		
Mysid Intermit	7.2 (0.2)	8.30-8.59	20.5 (0.45)		
Mysid w/ Ammonia	7.7 (0.1)	8.02-8.16	21.0 (0.82)		

* Conductivity expressed as µmhos/cm; salinity expressed as ppt

Table 4. Toxicity of Chlorine and Bromine on Freshwater and Saltwater animals

Common Name	Species Name	Toxicity Indicator	LC50 with Cl_2		LC50 with Cl_2 + NaBr	
			µeq TRO/L ± 95% C.I.	µg Chlorine/L ± 95% C.I.	µeq TRO/L ± 95% C.I.	µg Bromine/L ± 95% C.I.
FRESHWATER						
Daphnid	*Daphnia magna*	48-h Continuous	0.90 0.03 & 1.02	32 1 & 36	<0.42	<38[1]
Daphnid	*Daphnia magna*	48-h Intermittent	1.55 1.27 & 1.92	55 45 & 68	0.76 0.56 & 0.96	61 45 & 76
Golden Shiner	*Notemigonus crysoleucas*	96-h Continuous	8.57 7.19 & 10.09	304 253 & 358	3.61 2.96 & 4.43	288 236 & 353
Golden Shiner	*Notemigonus crysoleucas*	96-h Intermittent	16.13 14.24 & 18.44	572 505 & 654	9.90 8.80 & 11.31	790 702 & 903
Amphipod	*Hyalella azteca*	96-h Continuous	2.20 1.75 & 2.71	78 62 & 96	<0.39	<32[2]
Amphipod	*Hyalella azteca*	96-h Intermittent	8.49 7.1[illegible] & 10.21	301 252 & 362	4.17 3.41 & 5.10	333 272 & 407
Daphnid	*Daphnia magna*	48-h Continuous 300 µg/L Ammonia	<0.51	<18[3]	<0.39	<32[4]
Rainbow Trout	*Oncorhynchus mykiss*	96-h Continuous	1.66 1.41 & 2.00	59 50 & 71	0.85 0.68 & 1.02	68 54 & 81
Rainbow Trout	*Oncorhynchus mykiss*	96-h Intermittent	10.55 8.57 & 12.66	374 304 & 449	6.06 5.22 & 7.02	484 416 & 560

Table 4 (continued)

Common Name	Species Name	Toxicity Indicator	LC50 with Cl_2		LC50 with Cl_2 + NaBr	
			µeq TRO/L ± 95% C.I.	µg Chlorine/L ± 95% C.I.	µeq TRO/L ± 95% C.I.	µg Bromine/L ± 95% C.I.
SALTWATER						
Mysid	*Mysidopsis bahia*	96-h Continuous	1.75 1.47 & 2.09	62 52 & 74	1.16 0.93 & 1.41	92 74 & 113
Mysid	*Mysidopsis bahia*	96-h Intermi[illegible]	5.92 4.77 & 7.25	210 169 & 257	4.60 3.95 & 5.36	367 315 & 428
Silversides	*Menidia beryllina*	96-h Continuous	4.03 3.24 & 5.16	143 115 & 183	0.82 0.62 & 0.99	65 50 & 79
Silversides	*Menidia beryllina*	96-h Intermittent	5.44 4.20 & 6.79	193 149 & 241	4.31 3.67 & 5.13	344 293 & 410
Mysid	*Mysidopsis bahia*	96-h Continuous 300 µg/L Ammonia	<0.59	<21[5]	<0.62	<50[6]

1 Only 6 survivors at lowest concentration tested.
2 Only 1 survivor at lowest concentration tested.
3 No survivors at lowest treatment.
4 Only 8 survivors at lowest treatment.
5 Only 3 survivors at lowest treatment.
6 Only 2 survivors at lowest treatment.

NOTE: In all test solutions the concentration of total residual oxidants was measured as TRO equivalents, and expressed as micro equivalents per liter (µeq/L). The test results are expressed as micrograms/liter chlorine for all tests conducted with chlorine in the absence of added bromides. For tests conducted in the presence of bromides, toxicity is expressed as microgram/liter bromine. To convert bromine into "chlorine equivalents" divide the bromine concentration by 2.25. To convert chlorine into "bromine equivalents" multiply the chlorine concentration by 2.25.

Table 5. Chlorine TRO concentrations (in mg/L chlorine TRO) expressed as the mean (±SD) of all measurements made during the test period for each treatment

		TREATMENT CONDITIONS				
Test	Rep	1	2	3	4	5
		FRESHWATER				
Daphnid Continuous	A	24 ± 4.0	42 ± 5.0	76 ± 8.0	162 ± 8.0	306 ± 15.0
	B	24 ± 4.0	41 ± 6.0	73 ± 6.0	164 ± 12.0	314 ± 25.0
	C	24 ± 4.0	41 ± 5.0	74 ± 7.0	163 ± 10.0	310 ± 20.0
Daphnid Intermit	A	25 ± 4.8	40 ± 9.5	76 ± 7.9	153 ± 20.5	2 ± 28.3
	B	20 ± 7.5	45 ± 11.2	86 ± 14.4	159 ± 20.3	280 ± 14.1
	C	22 ± 6.9	43 ± 10.5	81 ± 12.5	156 ± 20.0	285 ± 19.1
Shiner Continuous	A	41 ± 5.0	72 ± 9.0	155 ± 10.0	312 ± 16.0	522 ± 13.0
	B	41 ± 6.0	73 ± 7.0	165 ± 14.0	308 ± 13.0	526 ± 19.0
	C	41 ± 6.0	73 ± 8.0	160 ± 13.0	310 ± 15.0	524 ± 16.0
Shiner Intermit	A	295 ± 33.0	418 ±39.0	670 ± 94.0	984 ± 125.0	1547 ± 40.0
	B	295 ± 30.0	411 ±45.0	677 ± 94.0	950 ± 88.0	1477 ± 6.0
	C	295 ± 31.0	416 ± 40.0	673 ± 93.0	967 ± 107.0	1512 ± 46.0
Amphipod Continuous	A	16 ± 4.4	35 ± 4.5	84 ± 6.9	159 ± 8.1	316 ± 20.7
	B	14 ± 4.4	36 ± 5.0	82 ± 8.6	157 ± 8.4	321 ± 14.3
	C	15 ± 4.5	35 ± 4.6	83 ± 7.7	158 ± 8.2	318 ± 18.3
Amphipod Intermit	A	36 ± 5.5	81 ± 7.7	153 ± 13.1	305 ± 29.5	631 ± 88.1
	B	35 ± 5.3	78 ± 11.2	153 ± 13.2	302 ± 27.4	626 ± 92.0
	C	35 ± 5.4	80 ± 8.8	153 ± 13.0	304 ± 27.8	629 ± 67.0
Daphnid Ammonia 0.3 mg/L	A	20 ± 3.0	35 ± 5.0	79 ± 9.0		
	B	16 ± 3.0	35 ± 6.0	69 ± 5.0		
	C	18 ± 4.0	35 ± 5.0	74 ± 9.0		

Table 5. Continued

Test	Rep	TREATMENT CONDITIONS 1	2	3	4	5
		SALTWATER				
Mysid Continuous	A	21 ± 6.0	38 ± 6.0	82 ± 10.0	156 ± 10.0	341 ± 54.0
	B	21 ± 2.0	39 ± 2.0	81 ± 12.0	159 ± 11.0	352 ± 54.0
	C	21 ± 4.0	38 ± 4.0	82 ± 11.0	157 ± 10.0	346 ± 53.0
Mysid Intermit	A	38 ± 6.7	72 ± 12.0	164 ± 21.2	348 ± 35.4	678 ± 37.4
	B	33 ± 4.4	68 ± 12.2	158 ± 22.7	331 ± 39.8	657 ± 43.8
	C	36 ± 5.6	70 ± 12.1	161 ± 22.0	339 ± 37.6	667 ± 41.5
Silversides Intermit	A	38 ± 6.7	72 ± 12.0	164 ± 21.2	370 ± 24.5	675 ± 34.2
	B	33 ± 4.4	68 ± 12.2	158 ± 22.7	350 ± 42.9	655 ± 49.3
	C	36 ± 5.6	70 ± 12.1	161 ± 22.0	360 ± 34.9	663 ± 43.0
Silversides Continuous	A	21 ± 6.0	38 ± 6.0	82 ± 10.0	148 ± 27.0	355 ± 43.0
	B	21 ± 2.0	39 ± 6.0	81 ± 12.0	151 ± 23.0	400 ± 14.1
	C	21 ± 4.0	38 ± 6.0	82 ± 11.0	150 ± 25.0	373 ± 40.0
Mysid Ammonia 0.3 mg/L	A	25 ± 4.8	40 ± 9.5	76 ± 7.9	153 ± 20.5	290 ± 28.3
	B	20 ± 7.5	45 ± 11.2	86 ± 14.4	159 ± 20.3	290 ± 14.1
	C	23 ± 6.9	43 ± 10.5	81 ± 12.5	156 ± 20.0	285 ± 19.1

Note: A&B: Values are average TRO concentrations for each treatment and replicant.
C: Values are the average TRO concentration for combined replicants of each treatment

Table 6. Bromine TRO concentrations (in mg/L bromine TRO) expressed in the mean (±SD) of all measurements made during the test period for each treatment

Test	Rep	TREATMENT CONDITIONS 1	2	3	4	5
		FRESHWATER				
Daphnid Continuous	A	34 ± 11.3	81 ± 15.8	140 ± 20.3	216 ± 24.8	387 ± 18.0
	B	43 ± 9.0	90 ± 20.3	155 ± 29.3	223 ± 31.5	365 ± 24.8
	C	38 ± 11.3	86 ± 18.0	146 ± 24.8	218 ± 29.3	376 ± 22.5
Daphnid Intermit	A	45 ± 12.6	90 ± 16.9	187 ± 29.3	351 ± 58.5	551 ± 47.7
	B	45 ± 0.0	88 ± 22.5	155 ± 22.5	342 ± 51.8	540 ± 63.7
	C	45 ± 8.8	88 ± 19.4	171 ± 30.4	347 ± 53.6	547 ± 46.4
Shiner Continuous	A	54 ± 11.3	90 ± 13.5	153 ± 20.3	333 ± 33.8	716 ± 31.5
	B	52 ± 11.3	83 ± 9.0	158 ± 18.0	349 ± 31.5	716 ± 40.5
	C	53 ± 11.3	88 ± 11.3	155 ± 20.3	342 ± 31.5	716 ± 33.8
Shiner Intermit	A	333 ± 74.3	486 ± 85.5	929 ± 110.3	1478 ± 155.3	2407 ± 423.0
	B	331 ± 76.5	493 ± 83.3	970 ± 123.8	1564 ± 182.3	2561 ± 373.5
	C	333 ± 74.3	491 ± 83.3	950 ± 119.3	1523 ± 171.0	2500 ± 378.0
Amphipod Continuous	A	36 ± 10.8	95 ± 20.3	182 ± 40.3	403 ± 38.7	776 ± 158.4
	B	29 ± 10.1	92 ± 22.1	182 ± 26.3	378 ± 44.1	776 ± 154.4
	C	32 ± 10.4	95 ± 20.9	182 ± 32.6	389 ± 42.3	776 ± 148.5
Amphipod Intermit	A	34 ± 11.3	92 ± 22.1	178 ± 33.1	380 ± 49.1	698 ± 142.0
	B	29 ± 9.0	88 ± 24.1	178 ± 27.6	365 ± 48.2	704 ± 149.2
	C	32 ± 10.1	90 ± 23.0	178 ± 30.6	374 ± 48.6	702 ± 143.1
Daphnid Ammonia 0.3 mg/L	A	34 ± 11.3	77 ± 15.8	149 ± 18.0		
	B	29 ± 11.3	65 ± 15.8	140 ± 20.3		
	C	32 ± 11.3	74 ± 15.8	144 ± 20.3		

Table 6. Continued

Test	Rep	TREATMENT CONDITIONS 1	2	3	4	5
Trout Continuous	A	32 ± 10.8	77 ± 13.7	142 ± 41.6	299 ± 65.0	623 ± 65.0
	B	27 ± 6.8	74 ± 15.3	140 ± 44.1	313 ± 75.4	608 ± 61.0
	C	29 ± 9.2	77 ± 14.4	142 ± 41.9	306 ± 67.7	614 ± 57.6
Trout Intermit	A	36 ± 10.4	81 ± 16.9	180 ± 37.4	392 ± 72.5	689 ± 55.6
	B	29 ± 8.1	77 ± 12.8	164 ± 41.0	412 ± 63.2	711 ± 63.2
	C	32 ± 9.9	79 ± 15.1	173 ± 39.4	401 ± 67.5	700 ± 59.6
SALTWATER						
Mysid Continuous	A	54 ± 9.0	97 ± 15.8	180 ± 36.0	443 ± 58.5	718 ± 130.5
	B	52 ± 11.3	101 ± 18.0	180 ± 40.5	407 ± 49.5	702 ± 101.3
	C	52 ± 11.3	99 ± 15.8	180 ± 38.3	425 ± 56.3	709 ± 112.5
Mysid Intermit	A	101 ± 15.1	225 ± 37.4	412 ± 58.1	745 ± 93.4	1436 ± 86.6
	B	81 ± 14.2	200 ± 35.8	374 ± 53.1	685 ± 88.4	1382 ± 115.7
	C	92 ± 17.1	213 ± 37.6	394 ± 57.6	716 ± 95.0	1409 ± 104.4
Silversides Continuous	A	54 ± 9.0	97 ± 15.8	180 ± 18.0	473 ± 22.5	781 ± 33.8
	B	52 ± 11.3	101 ± 18.0	178 ± 20.5	439 ± 49.5	781 ± 51.8
	C	52 ± 11.3	99 ± 15.0	178 ± 18.0	457 ± 38.3	781 ± 38.3
Silversides Intermit	A	101 ± 15.1	225 ± 37.4	412 ± 58.1	794 ± 74.7	1391 ± 50.0
	B	81 ± 14.2	200 ± 35.8	374 ± 53.1	698 ± 42.8	1260 ± 18.5
	C	92 ± 17.1	213 ± 37.6	394 ± 57.6	747 ± 64.4	1325 ± 77.4
Mysid Ammonia 0.3 mg/L	A	50 ± 5.9	90 ± 10.8	196 ± 22.7	356 ± 45.5	662 ± 103.7
	B	52 ± 8.3	88 ± 8.8	205 ± 13.1	362 ± 45.9	693 ± 148.5
	C	52 ± 7.0	90 ± 9.2	200 ± 18.7	358 ± 44.3	677 ± 124.2

Note: To convert bromine to chlorine equivalents, divide by 2.25.

A&B: Values are average TRO concentrations for each treatment and replicant.

C: Values are the average TRO concentration for combined replicants of each treatment

Table 7. Free available oxidant* and total residual oxidant (values in parenthesis) in chlorine test expressed as µg/L chlorine oxidants.

		TREATMENT CONDITIONS				
Test	Rep	1	2	3	4	5
FRESHWATER						
Daphnid Continuous	A	0 (10)	0 (30)	0 (80)	30 (140)	60 (330)
	B	0 (15)	0 (40)	0 (80)	20 (145)	80 (325)
Daphnid Intermit	A	0 (30)	0 (40)	0 (80)	20 (160)	160 (290)
	B	0 (20)	0 (50)	0 (80)	0 (160)	190 (250)
Shiner Continuous	A	0 (30)	0 (40)	0 (75)	0 (150)	0 (330)
	B	0 (20)	0 (45)	0 (70)	0 (145)	0 (320)
Shiner Intermit	A	0 (230)	40 (360)	440 (590)	900 (1010)	
	B	0 (260)	150 (340)	460 (600)	860 (950)	
Trout Continuous	A	0 (20)	0 (30)	0 (65)	0 (140)	0 (300)
	B	0 (10)	0 (40)	0 (60)	0 (140)	0 (300)
Trout Intermit	A	0 (20)	0 (30)	0 (65)	0 (140)	0 (300)
	B	0 (10)	0 (40)	0 (60)	0 (140)	0 (300)
Amphipod Continuous	A	0 (10)	0 (30)	0 (80)	30 (140)	60 (330)
	B	0 (15)	0 (40)	0 (80)	20 (145)	80 (325)
Amphipod Intermit	A	0 (10)	0 (30)	0 (80)	30 (140)	60 (330)
	B	0 (15)	0 (40)	0 (80)	20 (145)	80 (325)
SALTWATER						
Mysid Continuous	A	0 (25)	0 (40)	0 (90)	40 (160)	210 (315)
	B	0 (20)	0 (45)	0 (90)	30 (170)	220 (325)
Mysid Intermit	A	0 (30)	0 (60)	0 (160)	210 (390)	340 (670)
	B	0 (30)	0 (60)	0 (140)	230 (360)	380 (700)
Silversides Continuous	A	0 (25)	0 (40)	0 (90)	40 (160)	210 (315)
	B	0 (20)	0 (45)	0 (90)	30 (170)	220 (325)
Silversides Intermit	A	0 (30)	0 (60)	0 (160)	210 (390)	340 (670)
	B	0 (30)	0 (60)	0 (140)	230 (360)	380 (700)

* A value of 0 µg/L indicates FAO was not detected or quantifiable.

Table 8. Free available oxidant and total residual oxidant (values in parenthesis) in chlorine/NaBr test expressed as ug/L bromine oxidants*.

Test	Rep	TREATMENT CONDITIONS 1	2	3	4	5
FRESHWATER						
Daphnid Continuous	A	0 (23)	23 (113)	113 (203)	203 (450)	495 (698)
	B	0 (23)	23 (124)	113 (203)	225 (428)	450 (630)
Daphnid Intermit	A	0 (56)	0 (90)	0 (180)	68 (450)	473 (855)
	B	0 (45)	0 (113)	0 (158)	0 (473)	338 (788)
Shiner Continuous	A	0 (45)	0 (79)	45 (146)	113 (315)	495 (698)
	B	0 (56)	0 (90)	45 (180)	124 (338)	450 (630)
Shiner Intermit	A	135 (360)	135 (360)	495 (675)	630 (900)	1193 (1395)
	B	90 (360)	180 (405)	450 (585)	720 (968)	1418 (1710)
Trout Continuous	A	0 (23)	0 (68)	68 (180)	158 (270)	540 (698)
	B	0 (23)	0 (68)	68 (191)	180 (338)	585 (720)
Trout Intermit	A	0 (23)	0 (68)	68 (180)	158 (270)	540 (698)
	B	0 (23)	0 (68)	68 (191)	180 (338)	585 (720)
Amphipod Continuous	A	0 (23)	0 (113)	113 (203)	203 (450)	495 (698)
	B	0 (23)	0 (124)	113 (203)	225 (428)	450 (630)
Amphipod Intermit	A	0 (23)	23 (113)	113 (203)	203 (450)	495 (698)
	B	0 (23)	23 (124)	113 (203)	225 (428)	450 (630)
SALTWATER						
Mysid Continuous	A	23 (45)	45 (113)	158 (203)	338 (450)	653 (788)
	B	23 (45)	56 (101)	169 (180)	293 (383)	675 (731)
Mysid Intermit	A	0 (113)	0 (270)	135 (405)	630 (810)	1328 (1575)
	B	0 (68)	0 (203)	45 (383)	473 (743)	1418 (1530)
Silversides Continuous	A	23 (45)	45 (113)	158 (203)	338 (450)	653 (788)
	B	23 (45)	56 (101)	169 (180)	293 (383)	675 (731)
Silversides Intermit	A	0 (113)	0 (270)	135 (405)	630 (810)	1328 (1575)
	B	0 (68)	0 (203)	45 (383)	473 (743)	1418 (1530)

* To convert bromine to chlorine equivalents divide by 2.25.

Table 9. FAO, measured during the ammonia exposures as µg/L chlorine or bromine (µg/L Bromine/2.25 = µ/L chlorine equivalents)

Test	Replicants	FAO	TRO
Daphnid Chlorine	1(A)	0	20
	1(B)	0	10
	2(A)	0	35
	2(B)	0	30
	3(A)	0	70
	3(B)	0	65
Daphnid Chlorine/NaBr	1(A)	34	34
	1(B)	34	45
	2(A)	68	79
	2(B)	45	56
	3(A)	135	158
	3(B)	135	146
Mysid Chlorine	1(A)	0	20
	1(B)	0	20
	2(A)	0	40
	2(B)	0	40
	3(A)	0	85
	3(B)	0	80
	4(A)	0	160
	4(B)	10	165
	5(A)	0	270
	5(B)	0	280
Mysid Chlorine/NaBr	1(A)	45	45
	1(B)	56	56
	2(A)	68	68
	2(B)	79	79
	3(A)	158	181
	3(B)	135	151
	4(A)	315	360
	4(B)	293	349
	5(A)	585	675
	5(B)	630	810

Table 10. Oxidant decay,* measured as total residual oxidant equivalents (μeq, TRO) in fresh water and 20 ppt salt water upon the addition of chlorine, and chlorine plus 1.5 times the stoichiometric amount of NaBr.

Decay Time (min)	TRO (μeq/L)	TRO LN (μeq/L)		Decay Time (min)	TRO (μeq/L)	TRO LN (μeq/L)
Cl_2				Cl_2 + NaBr		
FRESH WATER						
0	25.35	3.233		0	25.35	3.233
5	21.27	3.057		5	15.41	2.735
15	19.01	2.945		10	14.65	2.684
30	18.31	2.907		30	13.10	2.573
90	15.21	2.722		85	11.27	2.421
170	13.38	2.594		160	10.48	2.349
270	13.18	2.579		260	8.39	2.189
360	12.68	2.540		350	7.61	2.029
SALT WATER						
0	28.17	3.338		0	28.17	3.338
5	20.85	3.037		4	14.93	2.703
10	19.15	2.952		10	12.96	2.562
20	17.32	2.852		18	11.83	2.471
50	15.77	2.758		30	9.72	2.274
110	13.52	2.604		90	6.48	1.869
170	12.82	2.551		150	5.07	1.623
260	10.85	2.384		240	3.38	1.218
380	9.01	2.198		360	2.25	0.811

* These observations are fitted to a two-phase first order model and plotted in Figure 1 (fresh water) and Figure 2 (salt water).

Table 11. Oxidant Decay,* Measured as Total Residual Oxidant (TRO) Equivalents in Freshwater

Test Time (min.)	TRO Range µgL Chlorine	K_1 (min^{-1})	r^2	K_1 (min^{-1})	r^2
		Chlorine			
240	900 - 495	0.015	0.848	0.001	0.988
360	900 - 450	0.010	0.775	0.001	0.806
1290	727 - 275	0.023	0.947	0.001	0.998
1345	840 - 250	0.017	0.812	0.001	0.983
	Avg ± SD	0.016 ± 0.005		0.001 ± 0.000	
	TRO Range µg/L Bromine	Chlorine Plus Bromide			
350	2025 - 608	0.055	0.818	0.002	0.986
380	1901 - 90	0.050	0.819	0.006	0.983
405	2036 - 338	0.061	0.829	0.003	0.983
525	1530 - <23	0.050	0.864	0.007	0.980
	Avg. ± SD	0.054 ± 0.005		0.005 ± 0.002	

* The test results are expressed as microgram/liter (µg/L) chlorine for all tests conducted with chlorine in the absence of added bromides. For tests with bromides added at 1.5 times the stoichiometric amount of chlorine, residual TRO concentrations are expressed as µg/L bromine. The observations were fitted to a two-phase first order model.

Table 12. Oxidant decay,* measured as Total Residual Oxidant (TRO) equivalents in 20 ppt saltwater

Test Time (min)	TRO Range µg/L Chlorine	K_1 (min^{-1})	r^2	K_2 (min^{-1})	r^2
		Chlorine			
380	1000 - 320	0.039	0.905	0.002	0.984
415	1000 - 350	0.055	0.889	0.001	0.887
705	1000 - 315	0.035	0.810	0.001	0.853
720	1000 - 310	0.048	0.926	0.001	0.936
	Avg ± SD	0.044 ± 0.009		0.001 ± 0.001	
	TRO Range µg/L Bromine	Chlorine Plus Bromide			
120	2205 - 360	0.085	0.873	0.008	0.998
240	2183 - 45	0.094	0.910	0.013	0.994
360	2250 - 180	0.073	0.798	0.005	0.972
395	2216 - 22	0.083	0.873	0.009	0.964
	Avg ± SD	0.084 ± 0.009		0.009 ± 0.003	

* The test results are expressed as microgram/liter (µg/L) chlorine for all tests conducted with chlorine in the absence of added bromides. For tests with bromides added at 1.5 times the stoichiometric amount of chlorine, residual TRO concentrations are expressed as µg/L bromine. The observations were fitted to a two-phase first order model.

Table 13. Estimates* of the relative environmental impact on a freshwater stream resulting from from the treatment of cooling water by chlorination in the presence and the absence of sodium bromide.

Effluent Flow as % of Riverflow	Rainbow Trout Impact Ratio Chlorine/Bromine	Golden Shiner Impact Ratio Chlorine/Bromine
0	1.19	2.21
10	1.45	3.37
25	2.38	5.15
50	6.71	22.9
100	9.41	97.1

Estimates for rainbow trout are based on the following inputs:

$$96\text{-}h\ LC50: \quad \frac{bromine}{chlorine} = \frac{0.85}{1.66}$$

$$96\text{-}h\ LC1: \quad \frac{bromine}{chlorine} = \frac{0.16}{0.48}$$

$$Oxidant\ decay: \quad \frac{K_1\ bromine}{K_1\ chlorine} = \frac{0.054}{0.016}$$

$$\frac{K_2\ bromine}{K_2\ chlorine} = \frac{0.005}{0.001}$$

Estimates for golden shiner are based on the following inputs:

$$96\text{-}h\ LC50: \quad \frac{bromine}{chlorine} = \frac{3.61}{8.57}$$

$$96\text{-}h\ LC1: \quad \frac{bromine}{chlorine} = \frac{1.11}{2.06}$$

$$Oxidant\ decay: \quad \frac{K_1\ bromine}{K_1\ chlorine} = \frac{0.054}{0.016}$$

$$\frac{K_2\ bromine}{K_2\ chlorine} = \frac{0.005}{0.001}$$

Further details are given in Appendix A

Figure 1. Oxidant decay as µeq TRO in freshwater

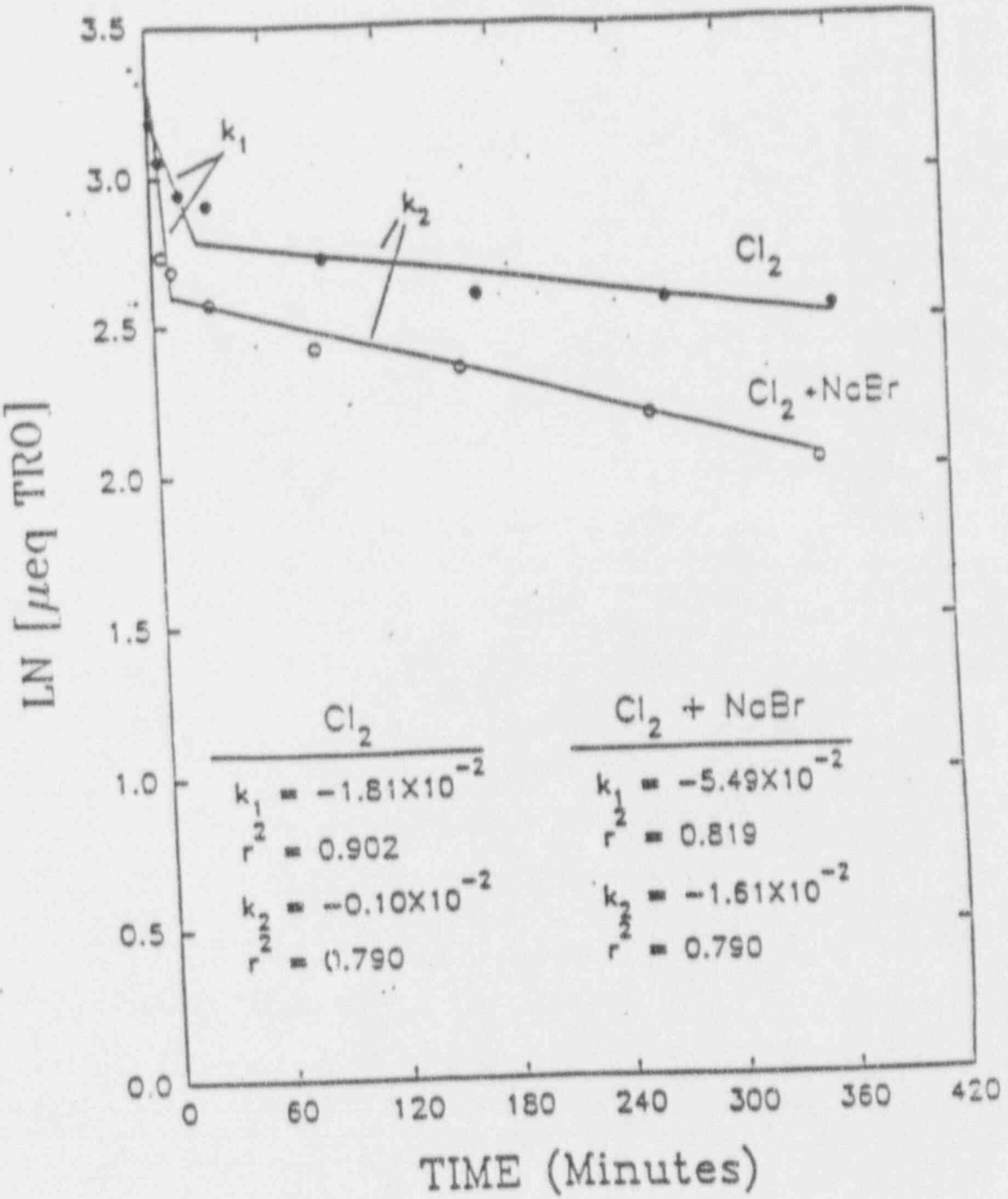
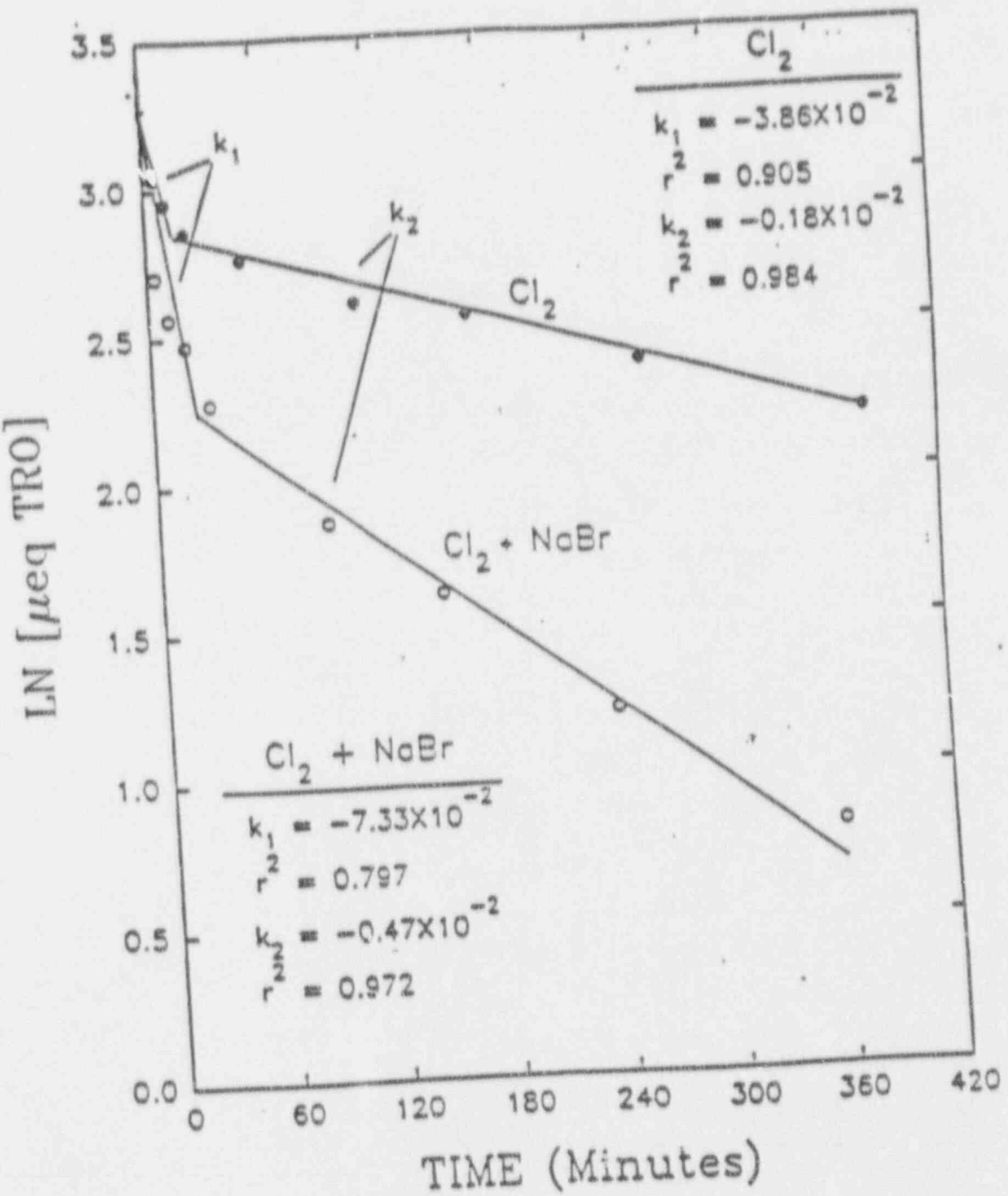


Figure 2. Oxidant decay as μeq TRO in saltwater



APPENDIX A

Relative Environmental Impact Estimates for Chlorine and Bromine Used for the Control of Biofouling Condenser Cooling Systems

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ABSTRACT

When used in combination with chlorine, sodium bromide can significantly reduce chlorine application requirements because the bromine oxidants generated under such conditions control biofouling more effectively. Also, since bromine oxidants dissipate two to five times faster than chlorine oxidants, the impact on the environment could be considerably less.

Therefore, although the LC_{50}'s for bromine oxidants are lower than the LC_{50}'s for chlorine oxidants, the effect of the more rapid decay combined with the lower demand could significantly reduce the environmental impact of biofouling control.

To evaluate the extent of the impact reduction and the factors affecting the reduction, the relative mortality risks were estimated for rainbow trout and golden shiner. In the calculations, the two test species (a freshwater and a saltwater species) were subjected to continuous biocide applications. It was further assumed that the electric facility used varying amounts of the flow of a freshwater stream for heat rejection.

Computations indicate that a significant reduction in impact can be expected when sodium bromide is used in conjunction with chlorine. The extent of the environmental benefits would increase when biocide application rates increase, as well as when a larger portion of the river flow is used by the electric facility for heat rejection.

These findings indicate that the anticipated reduction is principally attributable to the relatively rapid chemical decay of bromine oxidants and, to a lesser extent, also to the lower amount of bromine oxidants needed for the same degree of biofouling control.

A. PROBLEM STATEMENT

Since there is a viable alternative to chlorine for controlling biofouling of power plant cooling systems, the environmental consequences of changing from chlorine to the alternative must be ascertained. The alternative considered here is bromine, which is generated from chlorine when sodium bromide is simultaneously added to chlorine in the cooling water[1].

One way of evaluating the environmental impact of such a change is to estimate the relative mortality risks to which all the organisms are subjected when they are entrained in chlorinated or brominated water which flows through the cooling system. The impact estimate would also include the effects in the receiving waters which mix with the discharge.

The sample calculations, shown below, are based on mortality and chemical decay information collected as part of the present study[2]. The calculations provide a comparative impact estimate for rainbow trout and golden shiner.

The method is based upon a simple and understandable set of computations. Similar calculations can be made for other organisms for which the mortality and the no-effect threshold information is available.

B. ASSUMPTIONS

Throughout this appendix we shall use a Lagrangian approach: that is, we start with a parcel of water, and follow it through the plant and the transport and mixing in the river. The oxidant concentration in that parcel of water, as a function time, is the concentration defined in this manner. Further, the time integral of the concentration is also such a Lagrangian integral. Since this integral will be used to estimate the impact, we assume that the exposed organisms effectively follow the flow.

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[1]Please see text for added discussion.

[2]Please see text.

1. Physical Arrangement

The following sequence of events is assumed:

The biocide is introduced into the once-through cooling system.

It passes through the system, with no dilution, until it is returned to the river.

This river flows steadily away from the cooling water intake. In the river, the concentration of the biocide in the cooling water is diluted with the river water.

After a certain time, this dilution is effectively completed (i.e., the river is laterally well mixed); this mixed flow proceeds downstream with no additions or losses to the water.

2. Chemical Reactions

Based upon experimental data, it is assumed that the chemical (i.e. biocide) undergoes a two-phase quasi-first order decay process[3]. That is, if M(t) is the mass remaining at time t,

$$\frac{M(t)}{M(0)} = \begin{cases} \exp(-k_1 t) & 0 \le t \le t_1 \\ \exp(-k_1 t_1)\exp(-k_2[t-t_1]) & t_1 \le t < \infty \end{cases}$$

Let c(t) be the concentration[4], define

$$c_2 = c(0)\, e^{-k_1 t_1}$$

The concentration, including chemical decay and dilution, is

$$\frac{c(t)}{c(0)} = \frac{M(t)}{M(0)} \text{ divided by dilution factor}$$

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[3] Please see text.

[4] A notation table is provided at the end of this appendix

3. Mortality Relationships

One of the key assumptions is that the time integral of the concentration above a threshold concentration is a measure of the impact. The threshold concentration, of course, is the largest concentration which a specified organism can withstand for a long time period without suffering acute toxic effects. In absence of other information, a LC_1[3] value may be used in the computations.

For some organisms, the LC_{50} or LC_{100} concentrations, as a function of exposure time X, are reasonably accurately described by a hyperbola

$$Y = \frac{aX - b}{X - c} \quad (X > c)$$

where a, b, and c are constants[4]. In such a representation, the threshold is the concentration as X goes to infinity, that is, the constant a. This constant, even though it depends upon the organism and the biocide, should be reasonably independent of the mortality level. Also, the constant c, which has dimensions of time, is usually small compared to times of interest, such as 96 hours.

We can simplify this equation, as follows

$$Y\,T = constant$$

where

Y = *Concentration above threshold*

T = *Time beyond c*

and where the constant depends upon mortality level and, of course, the biocide and species considered. This equation is consistant with a dose-above-a-threshold evaluation approach.

4. Mixing

The hydrological mixing of the effluent with the receiving stream is complex and depends on site specific features. Even though this phenomena may be one of the few aspects of the over-all problem which is "solvable" from first or second principles we shall use only a very simple way of estimating the dilution. Presuming that the mixing process is not influenced by the choice of biocide, it

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[3] By $LC_{xx}(T)$ is meant the concentration which results in XX% mortality when exposed for T time. If T is not specified, assume it to be 96 hours.

[4] Please see Wang and Hanson, 1985, as referenced in the text.

is reasonable to assume that the comparative impact of two biocides is not significantly influenced by the exact nature of the mixing. Consequently, we shall assume that the amount of river water mixed with the effluent increases proportional with time, until all of the river flow is involved. It is further assumed that during this mixing the effluent is completely mixed lateral to it's flow (i.e., that it is independent of space, in the Lagrangian system), and that longitudinal mixing is negligible.

The dilution factor[7], with the above assumptions, is

$$MIN[\ \Psi,\ MAX[\ 1,\ 1+(\Psi-1)\frac{t-t_i}{t_e-t_i}\ ]\ ]$$

5. Measure of Impact

The time integral of the concentration over the threshold is

$$Z = \int_0^{\infty} \max[(c(t)-c_{TH}),0]\,dt$$

$$= \int_0^{t^*} [c(t)-c_{TH}]\,dt$$

where t^* is the time when $c(t) = c_{TH}$ and where c_{TH} is the threshold concentration.

To obtain the relative impact, we calculate

$$Z^* = \frac{Z}{c_{96}-c_{TH}}$$

where c_{96} is the concentration for LC_{50} at 96 hours. The quantity Z^* has the dimension of time. The relative impact between biocides 1 and 2 (namely, chlorine oxidants and bromine oxidants) will be the ratio of the above quantity calculated for each biocide, or

$$R_{1,2} = \frac{Z^1}{Z^2}\ \frac{c^2_{96}-c^2_{TH}}{c^1_{96}-c^1_{TH}}$$

where the superscripts refer to biocide 1 and 2. This ratio has no dimension. If it is larger than 1, biocide 1 has a larger impact than biocide 2. This ratio may reflect the comparative mortality.

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[7]please see notation section for definition of the symbols

C. SPECIAL CASES

Some special cases can be solved simply. For example, if we have no mixing with the river water, as would happen if all of the river water is used for cooling, we have

$$Z' + \frac{C_{TN} t'}{C_{96} - C_{TN}} = \begin{cases} \frac{1}{k_1} \frac{C(0) - C_{TN}}{C_{96} - C_{TN}} & \text{if } C_s \leq C_{TN} \\ \frac{(C(0) - C_s) k_2 + (C_s - C_{TN}) k_1}{k_1 k_2 (C_{96} - C_{TN})} & C_s > C_{TN} \end{cases}$$

In contrast, if the river flow is very large as compared to the effluent, and the concentration is immediately diluted to negligible levels as soon as the effluent reaches the river, then

$$Z' + \frac{t_r C_{TN}}{C_{96} - C_{TN}} = \frac{1}{k_1} \frac{C(0)}{C_{96} - C_{TN}} [1 - e^{-k_1 t_r}]$$

provided only that the concentration in the effluent just prior to entering the river is larger than either C_s or C_{TN}.

D. CALCULATED CASES

1. Impact of Decay Times

Several computations were made for the chlorine oxidants (biocide 1) and bromine oxidants (biocide 2), with the emphasis on determining the impact of their different chemical decay times. The ratio of the total river flow to the effluent flow was used as a parameter.

The physical parameters are shown in Table 1, and the chemical and biological parameters are shown in Table 2a. The organism for which impact is calculated is the Rainbow Trout. In order to evaluate the impact of the chemical decay times, the initial concentration in the cooling water is twice the LC_{50} concentration for both biocides.

The impacts, t' and the impact ratio were calculated for the various amounts of effluent flow, as compared to the river flow, with these parameters. The results are shown in Table 3a. In that table, both t' and Z' have the dimensions of minutes.

From these computations it is evident that bromine ha less of an adverse impact than chlorine. For example, if the cooling system borrows 25% of the river flow, the impact of bromine is only about 40% of the impact of chlorine. Additional computation were made

which showed that the benefits of bromine over chlorine increases as both initial concentrations are increased. With hindsight, this is what one would expect.

Not surprisingly, the larger the fraction of the river that is used for cooling, the larger the relative benefits of bromine. The "reason" for the advantage, in all cases, is the more rapid chemical decay of bromine as compared to chlorine.

2. Combined Impact

The computations discussed above dealt principally with the difference in the decay times. Additional computations, to include the impact of different initial concentrations relative to the LC_{50} levels, have to be made.

Sample computations were made for the Golden Shiner. For this organism the chlorine and the bromine LC_{50} concentration are shown in Table 2b. The no-effect threshold levels, as well as the initial selected concentrations are also shown in that table. It should be noted that the ratio of the initial concentration to the LC_{50} values are different for the two biocides. These initial concentrations were selected on the basis of a methodology developed by Bongers et al 1977 and Liden et al 1980. The stated biocide concentrations would control biofouling to operationally acceptable levels at an ambient temperature of 25°C. The results of the sample calculations are shown in Table 3b.

E. CONCLUSIONS

These sample computations indicate that a significant reduction in the environmental impact may result from using bromine instead of chlorine for biofouling control. This anticipated reduction is attributable to the relatively rapid chemical decay of the bromine oxidants, and also to the relatively lower amount of bromine needed for the same degree of biofouling control.

For the chemical and toxicity data used, the "benefits" of bromine (i.e., reduced mortality) would have a tendency to increase as biocide demand increases and/or the cooling water flow increases relative to the river flow.

With hindsight, this is what one would expect. Thus qualitative common sense is matched by the computational method, which has the added advantage of being both unemotional and quantitative.

Critical issues not addressed are:

The effects of changes in oxidant decay which may result from changes in water quality;

LC_{50} values significantly different from those used in these sample computations;

"Stationary" organisms, such as benthics which reside in the mixing zone, and organisms which enter the cooling water after it is discharged; and

Intermittent biocide applications instead of the continuous application as used in the present computations.

Table 1 Physical Inputs

t_a	60 minutes
t_r	5 minutes
Effluent Flow/ River Flow	0, 10%, 25%, 50%, and 100%

Table 2a Chemical and Biological Input

Rainbow Trout

	Chlorine	*Bromine*	
$c(0)$	3.32	1.70	$\mu eq/l$
c_{96}	1.66	0.85	$\mu eq/l$
$\frac{c(0)}{c_{96}}$	2	2	-
c_{TR}	0.48	0.16	$\mu eq/l$
k_1	0.016	0.054	min^{-1}
k_2	0.001	0.005	min^{-1}
t_1	15	15	min

Table 2b Chemical and Biological Input

Golden Shiners

	Chlorine	*Bromine*	
$c(0)$	9.44	2.66	$\mu eq/l$
c_{96}	8.57	3.61	$\mu eq/l$
$\frac{c(0)}{c_{96}}$	1.10	.737	-
c_{TR}	2.06	1.11	$\mu eq/l$
k_1	0.016	0.054	min^{-1}
k_2	0.001	0.005	min^{-1}
t_1	15	15	min

Table 3a Results of Computations

Rainbow Trout

Ψ^{-1}	*Chlorine*		*Bromine*		$R_{1,2}$
	Z'	t'	Z'	t'	
0	11.4	5	9.61	5	1.19
0.10	24.0	32	16.6	26	1.45
0.25	61.0	323	25.6	57	2.38
0.50	336	1010	50.1	188	6.71
1.00	1148	1709	122.	326	9.41

Table 3b Results of Computations

Golden Shiners

Ψ^{-1}	*Chlorine*		*Bromine*		$R_{1,2}$
	Z'	t'	Z'	t'	
0	5.39	5	2.44	5.	2.21
0.10	9.95	21	2.96	8.5	3.37
0.25	17.6	50	3.41	11	5.15
0.50	88.3	604	3.85	14	22.9
1.00	433.	1297	4.46	28	97.1

Notation

Symbol	Definition	Dimension	
a, b, c	Constants	various	
$c(t)$	Concentration	$\mu eq/l$	*
c_{96}	LC_{50} concentration, 96 hrs	$\mu eq/l$	*
c_s	$c(0)\, e^{-k_1 t_1}$	$\mu eq/l$	
c_{TN}	Threshold concentration	$\mu eq/l$	*
$k_{1,2}$	Exponents in chemical decay	min^{-1}	
$M(t)$	Mass measure	-	
Ψ^{-1}	Ratio of effluent flow to total river flow	-	
$R_{1,2}$	Ratio of Z^* for biocide 1 to Z^* for biocide 2	-	
t	Time, time=0 is at introduction of biocide	min	
t_1	Break time, chemical equation	min	
t_2	Time when mixing complete	min	
t_3	Time when effluent reaches river	min	
t^*	Time when $c(t) = c_{TN}$	min	
T	$X - c$	time	
X	Exposure time in [illegible]tion	hrs	
Y	Concentration, specified mortality	mg/l	
Y	$Y - c_{TN}$	conc.	
Z	Defined in text	time conc.	*
Z^*	Defined in text	time	

* Note:
Superscripts refer to biocides

APPENDIX B

Relative Environmental Impact Estimates for Chlorine and Bromine
Used for the Control of Biofouling Condenser Cooling Systems

PROTOCOL FOR THE TESTING OF THE EFFECTS OF SODIUM BROMIDE ON THE TOXICITY OF CHLORINE TO FRESH AND SALTWATER ORGANISMS

Prepared for

The Sodium Bromide/Bromine Chloride
Task Force

Prepared by

Leonard H. Bongers, Ph.D.
Dennis T. Burton, Ph.D.

August 1990

FOREWORD

This protocol was prepared at the request of the Sodium Bromide/Bromine Chloride Task Force by Leonard H. Bongers, Ph.D., B&B Environmental Services, Inc. and Dennis T. Burton, Ph.D., Johns Hopkins University's Applied Physics Laboratory, Environmental Sciences Group. The test protocol is designed in accordance with suggestions submitted by EPA (Mr. Charles Kaplan's memo of March 16, 1990) to the Task Force.

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INTRODUCTION

Chlorination of wastewater by POTWs to eliminate the discharge of pathogenic organisms and the use of chlorine by electric utilities to inhibit biofouling are a widespread practice. Research has shown, however, that chlorine-induced oxidants, since they decay relatively slowly, may be toxic to aquatic life when discharged into receiving waters.

The use of sodium bromide in conjunction with chlorine may solve this problem. When applied with chlorine, sodium bromide is oxidized by hypochlorous acid (HOCl) to hypobromous acid (HOBr) and sodium chloride. Due to the relatively low bond strengths, bromine residuals exhibit low stability. They are more reactive than chlorine residuals and, thus, should perform better.

In cooling water containing ammonium salts, application of sodium bromide with chlorine should result in much lower levels of oxidant residuals because the slow-decaying chloramines would not be generated.

The protocol outlined here is designed to evaluate the decay of oxidants generated by chlorine in fresh and salt water in the presence and in the absence of sodium bromide and to determine the effect of sodium bromide on the biotoxicity.

PROGRAM OBJECTIVE

The objective of the proposed test program is to compare residual biotoxicities to representative fresh water and salt water organisms exposed to water chlorinated in the presence of sodium bromide with similar water chlorinated in the absence of added sodium bromide.

TECHNICAL APPROACH AND METHODS

Oxidant Analysis

The chlorination of fresh and salt water may result in the formation of a large number of reaction products having varying kinetic constants and oxidizing capacity. The amperometric titration method, described in Standard Methods, 408C (APHA 1985), will be selected to determine total residual oxidants (TRO). Since it is essential to preserve the chemical conditions as of the moment of sampling, a back-titration amperometric end-point detection method will be selected. Fixation of oxidants at the time of sampling may be necessary because free oxidant, and especially bromine oxidants, decay relatively rapidly. Otherwise, the measurements could result in a substantial over-estimate of toxicity.

To implement the method, excess phenylarsine oxide (PAO) will be added to the samples to fix available oxidant. Unreacted PAO will be determined by back titration with iodine solution of known concentration using an amperometric titrator for endpoint detection.

Potentiometric methods also will be evaluated to determine whether direct-mode measurements provide sufficient sensitivity, accuracy and precision. If performance satisfies program objectives, the technique will be employed for routine TRO monitoring.

We anticipate the amperometric back titration method to be able to routinely detect TRO levels of 0.01 mg/L and quantify levels of 0.02 mg/L of chlorine equivalents.

Exposure Procedure

In view of the anticipated rapid oxidant decay, special provisions were necessary to create a reasonably stable environment for animal exposure. The design selected, illustrated in Fig. 1, will, at constant biocide feed rate, obtain steady-state oxidant decay along the length of the channel. Withdrawal of test fluid at a given location along the decay channel will yield fluid of constant total residual oxidant level.

Diluent water (fresh or salt water) (A; Fig. 1) and stock halogen solution (chlorine or chlorine plus sodium bromide) (B; Fig. 1) will be continually mixed in a mixing chamber (C; Fig. 1). The halogen stock solutions, the concentrations of which will be determined during the initial phases of the study, will be held in glass containers wrapped in black plastic to exclude all light. Water leaving the mixing chamber will flow through the PVC decay module of 10' sections (D; Fig. 1) to allow for decay of the oxidants. Halogenated water will be delivered from the decay module to replicate test aquaria (F; Fig. 1) at points which provide a geometric series of five test concentrations. We will attempt to include one concentration in the geometric series that kills 84 to 100% of the test organisms and one concentration that kills between 0 to 16% of the test organisms. Observations will be made at a minimum of 1, 2, 4, 8, 12, 24, 36, 48, 72 and 96 hours. Observations of abnormal behavior, immobility, loss of equilibrium, etc. will be recorded.

The test aquaria will be sized so that loading of the fish will not exceed 0.5 g/L. Loading will be less for the invertebrates. All test aquaria will be held in a constant temperature water bath (E; Fig. 1). All materials for both the chlorine and chlorine/sodium bromide test systems will be PVC, silicon, or glass. Dissolved oxygen and temperature will be measured in all test chambers in replicate A during the period T0 to T24 and T48 to T72 hours of the study; replicate B during the period T24 to T48 and T72 to T96. Conductivity or salinity and pH will be measured by standard procedures at the beginning and end of each test and every 24 hours in all controls, and the high, medium, and low halogen concentrations. Total Residual Oxidants (TRO) concentrations are to be measured, as a minimum, at 1, 2, 4, 6, 8, 10, 12, 24, 36, 48, 60, 72, 84, and 96 hours. TRO is to be measured in each test chamber for all replicates.

Test procedures and statistical analyses will be performed in accordance with EPA/600/4-85/013 with the following exceptions: 1) all test temperatures will be 25 ± 2°C except for rainbow trout which will be run at 15 ± 1°C, and 2) reference toxicant information will be supplied for daphnids and mysids only.

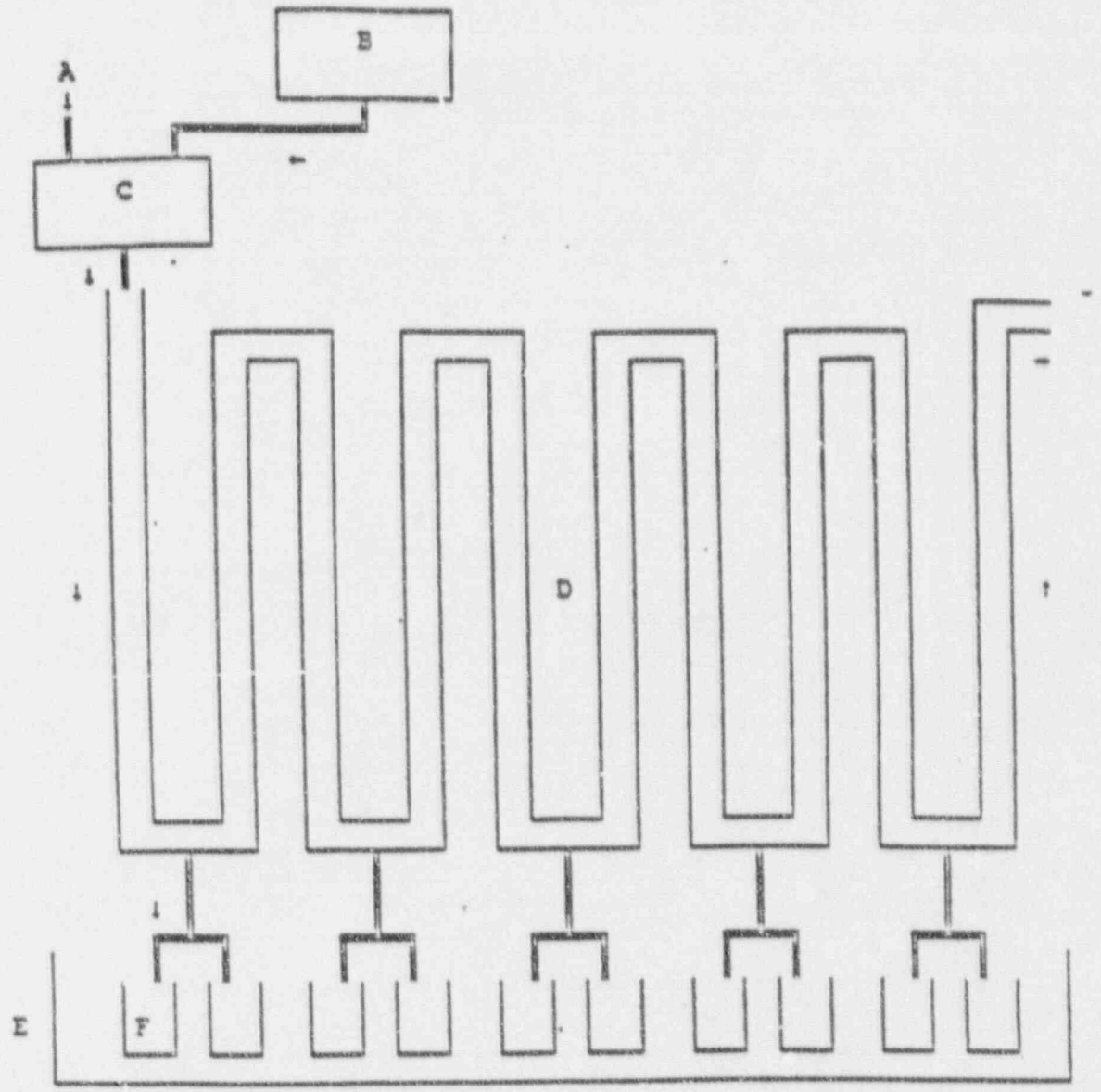

Figure 1. Schematic of oxidant decay channel used for side by side comparison of test solutions containing chlorine in one channel while the parallel channel (not shown) contains a mixture of chlorine and sodium bromide. The decay modules will be constructed from PVC schedule 40 pipe with inside diameter of 2, 3, or 4 inches.

A = Diluent Water
B = Halogen Tank
C = Mixing Chamber
D = Module
E = Water Bath
F = Test Aquaria

Test Organisms and Exposure Conditions

Flow-through tests will be performed on early life stages of the following organisms:

Fresh water organisms:

Species	Age or Size
Rainbow trout (Oncorhynchus mykiss)	15-30 days old ± 48 h
Common shiner (Notropis sp.)	1 to 2 inches
Amphipod (Gammarus sp. or Hyallella sp.)	Juvenile
Waterflea (Daphnia magna)	< 24 hr old

Salt water organisms:

Atlantic silverside (Menidia menidia)*	7-11 days old ± 24 h
Mysid shrimp (Mysidopsis bahia).	1-5 days old ± 24 h

Biotoxicities will be expressed as:

Rainbow trout	96-h LC50
Common shiner	96-h LC50
Amphipod	96-h LC50
Waterflea	48-h LC50**
Atlantic silverside	96-h LC50
Mysid shrimp	96-h LC50.

The waterflea and mysid shrimp will be obtained from the Johns Hopkins University/Applied Physics Laboratory (JHU/APL) Culture Facility located at Shady Side, Maryland, where the studies will be conducted. Rainbow trout, common shiner, amphipod, and Atlantic silverside will be obtained from various suppliers. Each species will be exposed to chlorinated water and chlorinated/brominated water in separate systems run side by side.

All species will be tested by definitive continuous flow acute toxicity test procedures described above. Briefly, five test concentrations plus control with two replicates of 10 organisms minimum per replicate will be used. All exposures will be 96 hours with the exception of the water flea which will be 48 hours. The acclimation and test temperature for all of the test animals, with the exception of rainbow trout, will be 25 (±2)°C. Rainbow trout will be acclimated and tested at 15 ± 1°C. Non-chlorinated deep well water, which has an average alkalinity of ≈156 mg/L as $CaCO_3$, hardness of ≈190 mg/L as $CaCO_3$, and pH of ≈7.8, will be used

* In the event that the Atlantic silverside minnows are not available commercially, the inland silverside minnow (Menidia beryllina) may be substituted.

** An attempt will be made to provide a 96-h LC50.

for the freshwater organisms. Filtered Chesapeake Bay water 8-12 ppt augmented with sea salts to a salinity of ≈ 20 ppt will be used for the salt water organisms. Dissolved oxygen concentrations will be maintained at a minimum of 4.0 mg/L at 25°C and 6.0 mg/L at 15°C. The photo period will be held at 16 hours light, 8 hours dark for all studies.

Treatment Conditions

For each organism tested, each set of paired treatment conditions 1.A and 1.B; 2.A and 2.B; 3.A and 3.B shall be conducted simultaneously.

Using test organisms and exposure procedure identified above, the following treatment conditions will be tested:

Treatment Condition 1.A: Continuous application of Cl_2 and Cl_2/NaBr; rainbow trout, common shiner, amphipod, waterflea; groundwater.

Two test runs will be made with the listed fresh water organisms. Groundwater will be used in this test series. For each test run, a constant rate of chlorine without sodium bromide will be fed to one decay channel whereas sodium bromide will be added to the second channel at 1.5 times the stoichiometric concentration of chlorine. The animals will be exposed to biocide concentrations from approximately 1 mg/L TRO to the residual level remaining after a decay time of approximately 90 minutes. Ninetysix-h LC50s will be determined for all animals with the possible exception of the waterflea.

Treatment Condition 1.B: Continuous application of Cl_2 and Cl_2/NaBr; Atlantic silverside and mysid shrimp; 20 ppt salt water

Two test runs will be made with the marine organisms listed earlier. Estuarine water (20 ppt salinity) will be used for this test series. Biocide applications will be as in Treatment Condition 1.A. Ninetysix-h LC50s will be determined.

Treatment Condition 2.A: Intermittent application of Cl_2 and Cl_2/NaBr; common shiner and water flea; groundwater.

To evaluate the effect of intermittent biocide application, elevated levels of biocide will be applied for 40 minutes at 8-h intervals. Chlorine will be injected in both channels, whereas one channel will receive, in addition, NaBr at 1.5 times the stoichiometric concentration of chlorine. Intermittent LC50s will be calculated.

Treatment Condition 2.B: Intermittent application of Cl_2 and Cl_2/NaBr; Atlantic silverside and mysid shrimp; 20 ppt salt water.

The test run will be as described under Treatment Condition 2.A, except that salt water will be used.

Treatment Condition 3.A: Ammonia; Cl_2; waterflea; groundwater.

To evaluate the effect of chloramines on biotoxicity, waterfleas will be exposed to groundwater chlorinated in the presence of ammonia. The test channels described earlier will be used for this test series as well. A forty-eight-h LC50 will be calculated. In addition to TRO, FAO shall be determined on a 12-h interval in the stock solution and the highest exposure concentration tested.

Treatment Condition 3.B: Ammonia; Cl_2/NaBr; mysid; 20 ppt salt water.

To evaluate the effects of bromamines on biotoxicity, the test procedure described under 3.A will be repeated using chlorine in combination with sodium bromide. This will include the determination of FAO as in 3.A.

Additional Tests

Die-away Tests

These tests will be designed to measure oxidant decay with time in the dark. TRO measurements will be started at approximately 0.3 mg/L and measurements shall be continued until a concentration of approximately 0.02 mg/L or less is obtained. A sufficient number of measurements shall be obtained to allow a reasonable plot of the data. A total of four tests will be performed as follows:

Freshwater with chlorine $\pm$ sodium bromide

Salt water with chlorine $\pm$ sodium bromide.

At predetermined intervals, a 200-ml aliquot will be taken, fixed with FAO, and analyzed for residual oxidant.

Free Available Oxidant Measurements

Using Standard Methods 408C (1985), FAO will be determined in addition to TRO, once during a test run when sodium bromide is added to the groundwater, and once during a test run when sodium bromide is absent.

Table 1. Summary Test Results

Treatment Condition Chambers	Test Fluid*	Conc	Controls	Number of Species	Runs	Exposure
1A Cl2 vs Cl2/NaBr	GW 2	5	1	4	2	88
1B Cl2 vs Cl2/NaBr	SW 2	5	1	2	2	44
2A Cl2 vs Cl2/NaBr	GW 2	5	1	2	2	44
2B Cl2 vs Cl2/NaBr	SW 2	5	1	2	2	44
3A Cl2 vs Cl2+NH4	GW 2	5	1	1	2	22
3b Cl2/NaBr vs Cl2/NaBr+NH4	GW 2	5	1	1	2	22

* GW: groundwater
SW: salt water

Quality Assurance and Quality Control

The Toxicity Testing Group of JHU/APL has a quality assurance/quality control program for all phases of its toxicity projects. The objective of the program is to assure that: 1) all results are representative and valid; 2) provisions are made to identify and correct any deficiencies in testing procedures or reports; 3) results of all studies provide a satisfactory basis for comparison with other studies; and 4) confidence in the results of the Toxicity Testing Group services is sufficient to assure their reliability to the sponsor, regulatory agencies and the public. For further details see the JHU/APL manual entitled "Standard Operating Procedures for Acute Effluent Toxicity Tests with Freshwater and Salt Water Organisms." July 1987. This SOP manual is submitted to provide quality assurance and quality control information for this study. However, this manual, dated July 1987, is incomplete insofar as it does not reflect all conditions planned for this study. To the extent that any condition in the SOP is inconsistent with the condition stated in the protocol, the condition in the protocol shall govern.

REPORTING PROCEDURES

Total Residual Oxidant Reporting

All oxidant measurements will be reported in mg/L. When bromide (Br^-) is added to chlorinated water, the oxidizing capacity of the solution will be expressed as mg/L oxidant, or as chlorine equivalents. No attempt or speculation will be made on what chemical species constitute the oxidants.

LC50 Reporting

The definitive acute toxicity data will be analyzed statistically in accordance with EPA document 600/4-85/013.

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THE TESTING OF THE EFFECTS OF SODIUM BROMIDE ON THE TOXICITY OF CHLORINE TO FRESH AND SALTWATER ORGANISMS

Test Schedule

1. Design, Installation, & Testing Of Set-up		
1.1 * Order and receive control equipment;	completion	10/15/90
1.2 * Design and assembly of modules;	completion	10/15/90
1.3 * Installation of control equipment;	completion	10/31/90
1.4 * Pre-op test runs;	completion	11/15/90
1.5 * Program checkout,including analytical		11/15/90
2. Biotoxicity Test Runs		
2.1 * Treatment condition 1A and/or 1B; 3 species		11/16 to 12/31
2.2 * Treatment condition 1A and/or 1B; 3 species		1/1 to 1/31
2.3 * Treatment condition 2A and 2B		2/1 to 3/8
2.4 * Treatment condition 3A and 3B		3/11 to 3/31
3. Die-away Test		12/1/90 to 1/3
4. Final Draft Report		5/1/91

APPENDIX C

Protocol Amendment #1

December 3, 1990

PROTOCOL AMENDMENT # 1

The following three revision to the protocol entitled "Protocol for the Testing of the Effects of Sodium Bromide on the Toxici.y of Chlorine to Fresh and Saltwater Organisms" were discussed and approved by USEPA representatives.

1. Test Species
   The protocol specified the common shiner as one of the test animals for treatment conditions 1A and 2A. Because of availability problems, the golden shiner will be used in stead of the common shiner for treatment conditions 1A and 2A.

2. Size of the Shiner
   The protocol specified the size of the shiner as 1 to 2 inches. Since test animals of that size were not available from commercial dealers, a larger size will be tested. Thus, for treatment conditions 1A and 2A, golden shiners in the size range of 2.5 to 3.5 inches will be used.

3. Oxidant Delivery System
   Because of the size of the golden shiner, the oxidant delivery system described and illustrated in figure 1 of the protocol. cannot be employed. Instead, a continuous-flow oxidant delivery system will be used, which is similar to the system described by J.R. Vanderhorst et al. in Bull. Environ. Contam. Toxicol. 17: 577-584; 1977. This system consists of individual stock solutions for each halogen concentration. Each stock solution is metered via a Masterflex pump to a mixing chamber and mixed with deluent water. The halogenated feed from each mixing chamber will then be split to each treatment rep..cate. The aquaria, housing the test animals, will be submerged in a constant temperature bath. There will be no changes to the analytical procedures specified in the protocol. All analyses will be performed as described in the protocol.

Program management:

D.T. Burton

Dennis T. Burton, Ph.D.

L.H. Bongers

Leonard H. Bongers, Ph.D.

Program Sponsor:

L.L. Wen

Louise L. Wen, Ph.D.
Chairperson, NaBr/BrCl Panel

ETHYL CORPORATION
Health and Environment Department

Toxicology and
Regulatory Affairs

Ethyl Tower
451 Florida Street
Baton Rouge, LA 70801

December 7, 1990

Dr. Leonard H. Bongers
B&B Environmental Services, Inc.
431 Drury Lane
Baltimore, MD 21229

Dear Leonard:

Enclosed is a signed protocol amendment for the NaBr test. Please include it as an addendum in the final study report.

Looking forward to see you next week.

Sincerely,

Louise L. Wen, Ph.D.
Chairperson
NaBr/Br Industry Panel

LLW:ab
080LLW90
Enclosure

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