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BROMINE CHLORIDE— AN ALTERNATIVE TO CHLORINE FOR FOULING CONTROL IN CONDENSER COOLING SYSTEMS

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ABSTRACT

Bromine chloride was evaluated as a potential alternative to chlorine for fouling control in condenser cooling systems. Two properties of bromine chloride were examined: decay rate in estuarine cooling water and fouling control effectiveness.

The program was conducted at an 1100-MWe, fossil-fueled, two-unit generating facility using estuarine water for once-through condenser cooling. Chlorine and bromine chloride were applied continuously at levels of 0.5 ppm or less.

Fouling control effectiveness was determined by the extent of fouling control observed on glass panels exposed to treated and untreated cooling water, and on the basis of condenser performance data. Decay characteristics of bromine chloride were inferred from the analysis of cooling water by an amperometric back-titration method, which could evaluate residual oxidant concentrations of as little as 5 ppb.

The findings of the present study show that bromine chloride is an effective fouling control agent when applied on a continuous basis at a level of 0.5 ppm or less. Free hypobromous acid apparently was not present during cooling system transit. Fouling control resulted from the presence of bromamines.

The principal factor determining the amount of bromine chloride required to obtain adequate control was the temperature of intake cooling water. On the basis of decay characteristics of bromine chloride and the relationship between biocide concentration, temperature, and fouling, a control model was formulated which predicted the minimum amount of bromine chloride necessary to attain adequate fouling control.

Examination of the decay characteristics of bromine chloride and chlorine confirmed earlier reports that bromine chloride-induced oxidants dissipate faster from estuarine water than do chlorine-induced oxidants. The decay of both biocides showed a three-phase pattern. The initial phase was short, and the decay was rapid. First-order decay kinetics characterized the second phase, which persisted for about 10 min. In the third phase, oxidant decay was relatively slow.

Advantages and disadvantages of continuous and intermittent fouling control strategies are discussed on the basis of biological and environmental considerations.

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CHAPTER 1

RESULTS AND CONCLUSIONS

1. Bromine chloride, added in continuous low-level doses to the estuarine once-through cooling waters at one of the 575-MWe generating units at the Morgantown power plant, proved effective for controlling biofouling. Cooling water flows were 10 to 31 m^3/sec (370 to 1100 ft^3/sec); dose rates were 0.2 to 0.5 ppm BrCl; salinity was equal to or less than 7 parts per thousand (ppt); fouling coefficients were less than 0.06/day (see p. 27 of text).

2. On an equal weight basis, the continuous low-level application of bromine chloride and chlorine resulted in equally good control of biofouling in the condensers. On an equal molar basis, therefore, bromine chloride would be nearly twice as effective but would cost about 2½ times as much as chlorine at current market prices.

3. At ambient cooling water temperatures of 25° C and below, bromine chloride dose requirements for effective biofouling control were very temperature dependent, with no chemical addition necessary at temperatures below 14° C (57° C).

4. Because of the ambient levels of ammonia in the cooling waters, it was concluded that combined residuals, predominantly halamines, would be present after dosing with either chlorine or bromine chloride. Although it was not determined whether the chlorine addition resulted in the oxidation of bromide ion found in the estuarine water, it is a possibility that might explain the nearly equal effectiveness of the two halogens on an equal weight basis. In any case, free halogen residuals were assumed to be present in insufficient amounts for control of biofouling at this site.

5. At routinely used application levels, chlorine- or bromine chloride-induced oxidants dissipated in three decay phases. A very rapid oxidant loss was apparent in the first phase, which lasted less than 1 min. The order of the reaction was not determined. Quasi first-order decay kinetics characterized the second phase, which lasted about 10 min. In the third phase, oxidant decay was relatively slow; the order of the reaction could not be ascertained adequately.

6. In estuarine cooling water with ambient ammonia concentrations about equal to those of injected biocides and of 7 ppt salinity or less, bromine chloride-induced oxidants dissipated faster than chlorine-induced oxidants. The effluent of chlorobrominated cooling water contained only two-thirds to one-half the amount of oxidant present in chlorinated cooling water even though both fouling control agents were applied at equimolar concentrations.

7. The minimum amount of bromine chloride required to prevent the biofouling of the condenser cooling system could be predicted on the basis of water temperature, bromine chloride decay, and cooling water volume flow and transit time.

8. The concurrent fouling assay method used in the present investigation adequately reflected the extent of fouling control in the actual cooling system. Thus, this fouling assay method can be used to judge the effectiveness of a cooling water treatment strategy.

9. The precision and accuracy of the amperometric back titration method, as used in the present investigation for analyzing cooling water concentrations of chlorine- and bromine chloride-induced oxidants, appeared adequate for assessing the fouling control effectiveness of the two agents. The method did not provide information on the nature of the chemical species present during cooling water transit and their effects.

CHAPTER 2

RECOMMENDATIONS

1. In view of the fouling control efficacy of bromine chloride when applied continuously at relatively low concentrations (less than 1 ppm) and its relatively rapid dissipation compared to chlorine, its use as a fouling control agent for once-through cooling systems should be considered as an alternative to chlorine at estuarine sites where ambient levels of ammonia are relatively high (about one-half the applied bromine chloride dose) and salinities are less than 7 ppt.

2. In view of the satisfactory fouling control properties and dissipation characteristics of bromamines (this report) and the recent findings that slower decaying chloramines may cause acute toxicity to aquatic life (literature reports), it is evident that bromine chloride is a safer fouling control agent than chlorine.

3. Investigations should be initiated to explore the nature of the rapid, intermediate, and slow oxidant decay processes described in this report. Analytical techniques should be employed that characterize the chemical oxidant species. The relative importance of water quality parameters, such as pH, ammonia, salinity, and organic and inorganic constituents, to oxidant speciation should be established. Oxidant decay should be examined in terms of the type and concentration of oxidant-consuming constituents in natural waters. Insights into the aquatic chemistry of chlorine and bromine chloride could aid in refining the minimum biofouling control model developed in the present study and provide a basis for assessing the potential environmental hazards associated with the discharge of cooling water treated with chlorine or bromine chloride.

4. The common practice of chlorinating cooling water so that measurable quantities of hypochlorous acid are still present at the tailpipes of the condenser system should be re-examined in light of the present findings that halamines provide adequate fouling control for saline water (probably due to the oxidation of bromide ion to bromamines).

5. In light of the observed fouling control efficacy of continuous low-level chlorination and the striking concomitant reduction in the concentration of effluent oxidants, it is recommended that a similar fouling control strategy be explored for power plants using saline water and high-level intermittent chlorination. The efficacy of continuous low-level chlorobromination in fouling control should be explored at freshwater sites where the once-through cooling water is contaminated with ammonia.

CHAPTER 3

INTRODUCTION

The biofouling of condenser cooling systems causes frictional resistance to cooling water flow and loss of heat transfer efficiency. Thus, it presents a continuous maintenance problem for the power generating industry. Chlorine has been used effectively for many years to combat the growth of microbial slimes and such common biofoulers as molluscs, barnacles, bryozoa, hydroids, sponges, and tunicates on surfaces of bar-racks, screens, intake tunnels, water boxes, and condenser tube surfaces. However, recent investigations (e.g., Brungs, 1976; Eppley et al., 1976; Capuzzo et al., 1976; Bongers et al., 1975; Polgar et al., 1976; Stober and Hanson, 1974; and Roberts et al., 1975) showed that chlorine residuals in discharged cooling water from power plants can be toxic to aquatic life. Concerns about the biotoxicity of discharged chlorinated waste and cooling water have increased in response to recent findings that the reaction of chlorine with organic constituents of natural waters may form stable chloro-organics which could disrupt reproductive and other biological processes (Gehrs et al., 1974; Grothe and Eaton, 1975; Jolley et al., 1975; Patton et al., 1975; Eaton, 1973; Pitt et al., 1975). This potentially adverse impact on the inhabitants of receiving waters has motivated a search for alternative biocides for cooling water treatment.

Bromine chloride may be an attractive alternative to chlorine since bromamine, its most common derivative in ammonia-containing cooling water, is more reactive than the analogous chlorine compound, chloramine, and thus dissipates faster (Mills, 1973, 1975; Wackenhuth and Levine, 1974). Therefore, bromine chloride, if applied judiciously, may be less hazardous than chlorine.

The present project, designed to evaluate the effectiveness and environmental acceptability of bromine chloride as a potential alternative to chlorine for cooling water treatment, has three basic purposes:

- to determine the effectiveness of continuous low-level application of bromine chloride in maintaining cooling efficiency in once-through systems using low-salinity estuarine water for waste heat rejection

- to develop a procedure for estimating the minimum dosage of bromine chloride required for this purpose, taking into account temporal changes in water quality factors

- to assess the environmental acceptability of bromine chloride considering its dissipation characteristics relative to those of chlorine.

The program was conducted at the 1100-MWe, fossil-fueled, two-unit Morgantown, Maryland, generating facility operated by the Potomac Electric

Power Company on the Potomac River Estuary. For a description of site and plant design characteristics, see Bongers et al. (1975) and Appendix F.

Since biocide addition to the generating units could be controlled independently, the experimental design, formulated in consultation with the facility's operators, provided for concurrent testing of the two biocides. Although some limited mixing of the two cooling streams occurred before sampling could be completed -- somewhat complicating the interpretation of the findings --, concurrent use of both biocides eliminated the more severe problems of sequential dosing, i.e., contending with temporally varying environmental factors.

Two 15-day trials were made; continuous dose rates of 0.50 ppm BrCl and Cl_2 were used during trial I, August 1976, and dose rates of 0.15 and 0.35 ppm BrCl and Cl_2, respectively, were used during trial II, September 1976. Fouling control effectiveness was inferred from:

- observed biofouling rates on glass panels exposed to treated and untreated cooling water;
- monitoring data on residual concentrations of chlorine- and bromine chloride-induced oxidants in the cooling water;
- cooling system performance data.

Program findings, analysis, and interpretation are presented in the body of this report. The aqueous chemistry of chlorine and bromine chloride, raw data, and statistical treatments of biofouling data are included as Appendices A, B, and C. Economic, handling, and safety considerations of bromine chloride are addressed in Appendices D and E.

CHAPTER 4

ANALYTICAL PROCEDURES

Cl_2 AND BrCl MEASUREMENTS IN COOLING WATER

Reporting Procedure

Since we are concerned here with two halogens, chlorine (Cl_2) and bromine chloride (BrCl), concentrations will be reported as Total Oxidant [TOX], expressed as microequivalents per liter (μeq/ℓ) and ppm or ppb (parts per million or billion), in conformance with the standard procedure (APHA, 1975) for reporting Total Residual Chlorine concentrations. Thus, a concentration of 1 μeq of oxidant per liter corresponds to 35.5 ppb Cl_2 or 57.5 ppb BrCl. Oxidant levels were determined by the addition of iodide (I^-) at pH 4.

Titration Procedure

Three methods were tested for their ability to reliably measure low levels of total oxidant: potentiometric titration (Eppley et al., 1976); the NBS chlorine flux monitor (Marinenko et al., 1976); amperometric titration (APHA, 1975). The method selected for field use was a modified amperometric end-point detection procedure. Other techniques were rejected for several reasons. Although sufficiently precise and sensitive, the potentiometric method was not suitable for field use; near the titration end-point, time had to be allowed for the EMF to stabilize after each addition of titrant. This may not present a problem with automatic titrators working on the principle of the first or second derivative of EMF versus titrant volume, but, for manual titration, this proved very inconvenient.

The National Bureau of Standards (NBS) prototype chlorine flux monitor performed well when chlorine was introduced in a distilled water matrix. With natural water samples (i.e., those containing suspended material), it was difficult to maintain constant flow within the instrument, and changes in flow rate caused unacceptable calibration drift. There was a further problem with the response time of this instrument. About 2 minutes were required for the halogenated water to reach the electrode chamber, a delay which complicated the analysis of differences in decay properties of the two biocides. Because of these sampling difficulties, the prototype flux monitor was not used for field measurements.

The amperometric method chosen for field use is a particularly convenient technique because it relies only on detecting the appearance (back-titration) or disappearance (forward titration) of a current in excess of a residual current. Because it was essential to preserve the chemical conditions of samples collected in the field as of the moment of sampling, we developed a back-titration amperometric end-point detection method. Excess phenylarsine oxide (PAO) was added to the samples to fix all the available

oxidant and prevent it from decaying. (For example, a chlorinated cooling water sample containing 4.5 μeq/ℓ TOX, collected near the point of halogen injection, will lose TOX at the rate of about 0.6 μeq/ ℓ/min.) Excess PAO was then determined by back-titration with iodine solution of known concentration.

The principles of this method are described in Standard Methods (APHA, 1975), and it has been recommended as the only reliable standard method (Brungs, 1973). Because of the required detection limits, the following instrumentation set-up was employed.

A calomel reference electrode (Sargent-Welch #S-30490) and a platinum-hook indicating electrode (Sargent-Welch #S-30421) with a synchronous rotor (Sargent-Welch #S-76485) were used throughout this study. The indicating current was sensed by a picoammeter (Keithley, Model 616 Electrometer) with an output signal of 0 to 1 V. The output was fed to a strip chart recorder Philips #PM8110. When the strip chart was set to a 10-mV full scale sensitivity, small currents in excess of the background residual current, i.e., titration end points, became well-defined.

Titrant was added with a 2-ml capacity microburet (Gilmont #P-4200) with a delivery precision of ± 2 microliter. A 2-microliter addition of 0.00564N phenylarsine oxide (PAO) to a 500-ml solution (corresponding to 0.02 μeq/ℓ of TOX) yielded a 5% scale deflection on the strip chart, which far exceeded the less than 1% scale deflection of noise in the current trace. For back-titrations, where PAO was present in excess, the titrant was iodine solution. Since the iodine solution was about 1.3 times the normality of the PAO solution, the 2-microliter instrumental detection limit corresponded to about 0.03 μeq/ℓ of TOX.

The routine procedure used for TOX analysis in this study was as follows. Immediately prior to sample collection, 1 ml of KI solution (150 g/ℓ , fresh daily), one ml of pH 4 acetate buffer (APHA, 1975), and, with an Eppendorf micropipet, 500 or 1000 μl (depending on expected TOX concentration) of PAO solution (0.00564N, commercial) were put into a 500-ml sample bottle. A halogenated water sample was then collected in a 500-ml volumetric flask and poured into the bottle. Finally, the sample was titrated with an iodine solution (APHA, 1975), and TOX concentration at the time of collection was calculated from the formula:

$$[TOX] = \frac{5.63}{V_s}\left(V_{PAO} - V_{I_2}\,\frac{N(I_2)}{N(PAO)}\right)$$

where $[TOX]$ = total oxidant concentration (μeq/ℓ)

V_s = volume of sample (ml)

V_{PAO} = volume of PAO solution added (500 or 1000 μℓ)

V_{I_2} = volume of I_2 solution to end-point (μℓ)

$N(I_2)/N(PAO)$ = ratio of normalities of I_2 and PAO solution

It was necessary to complete a sample analysis within 40 minutes of the time KI and pH 4 buffer solutions were mixed to avoid oxidation of I^- to I_2. It was also necessary to redetermine the $N(I_2)/N(PAO)$ ratio at intervals of about 6 hours to compensate for slow and small changes in $N(I_2)$. Before use, all containers were soaked overnight in a concentrated Cl_2 solution and rinsed repeatedly with Cl_2-free deionized water.*

Precision and Detection Limit --

Table 4-1 contains the results of a comparison of [TOX] determinations in deionized and estuarine water. The estuarine water, with a salinity of 4.4 ppt, was collected at the Morgantown site. Chlorine from a $Ca(OCl)_2$ solution was added to 500-ml subsamples, which were already spiked with the required KI, buffer, and PAO reagents. On the basis of these data, we conservatively estimate the method's precision and detection limit for TOX in 500-ml samples to be 0.05 μeq/ℓ. This estimate was confirmed by an analysis of halogenated discharge cooling water at the Morgantown plant: for six determinations, the average and standard deviations were 2.09 and 0.05 μeq/ℓ, respectively.

Accuracy --

The accuracy of the technique has come into question because of recent observations by Carpenter and Macalady (1976). Using methods dependent on iodide oxidation, they found that [TOX] analyses were not quantitative for TOX in seawater. Therefore, we have examined the accuracy of the method by titrating saline solutions spiked with $Ca(OCl)_2$ and comparing results with those obtained by spiking deionized water.

Table 4-1 indicates no difference between the results of oxidant analyses of chlorinated deionized and estuarine water when KI, buffer, and PAO are present prior to chlorine addition. However, in field investigations, chlorine is present prior to reagent addition. For our accuracy tests, therefore, we added chlorine before the reagents. Since estuarine water contains components which consume oxidant, these tests were done with deionized water containing reagent grade salts. Solutions were mixtures of one or more of NaCl, KBr, and $NaHCO_3$, with Cl^-, Br^-, and HCO_3^- concentrations corresponding to seawater salinities from 5 to 35 ppt. The mixtures were designated as artificial seawater solutions (ASW).

The tests indicated that, for a range of TOX concentrations from 1 to 14 μeq/ℓ, the measured concentrations in solutions containing Cl^-, or Br^-, or both were always 5 to 15% lower than those in deionized water. There was no apparent correlation between the size of the TOX deficiency and Cl^- or Br^- concentration.

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* The source of deionized water at the Morgantown power plant was an on-site well. It was judged to be chlorine-free and iodine-demand free on the basis of forward and back-titrations, respectively. At our Baltimore laboratory, the water source is municipal, and distilled deionized water could only be made chlorine-free by boiling for 1 hour.

TABLE 4-1. RESULTS OF [TOX] ANALYSES BY BACK-TITRATIONS OF 500-ml SAMPLES OF ESTUARINE (EW) AND DEIONIZED (DW) WATER SPIKED WITH VARYING VOLUMES OF $Ca(OCl)_2$ SOLUTION

Volume of $Ca(OCl)_2$ solution (ml)	Water type	[TOX] (μeq/ℓ) Mean	S.D.*	No. of samples
0	DW	0.00	0.03	3
0	EW	0.00	0.02	2
1	EW	0.09	0.02	2
2	EW	0.19	0.04	2
5	EW	0.65	0.02	2
10	DW	1.11	0.02	5
10	EW	1.15	0.02	5
20	EW	2.35	0.05	2
40	DW	4.74	0.04	2
40	EW	4.77	0.03	2

* Standard Deviation

Figure 4-1 is a semi-logarithmic plot of TOX concentration versus time for four solutions. Each solution was divided into a series of 500-ml aliquots. The first aliquot in each series (time zero) was spiked with KI, buffer, and PAO prior to the addition of $Ca(OCl)_2$; the reagents were added to the other samples at the indicated times after $Ca(OCl)_2$ addition. The uppermost line indicates that, for deionized water or water containing only $NaHCO_3$, time has no effect on measured TOX levels. For the ASW solution ($NaCl + KBr + NaHCO_3$) and estuarine water, however, there are changes in [TOX] from its value at time zero. There was a 15% "loss" of TOX in the ASW System in 45 seconds, with no significant further changes with time. The change with time of [TOX] added to estuarine water was most dramatic: 50% of the [TOX] was lost in the first 45 seconds with first-order decay thereafter. This decay in estuarine water is discussed in Appendix A.

We have been able to characterize the loss of TOX in saline water as follows:

- the loss occurs in the presence of Cl^- or Br^-;
- the loss occurs immediately after chlorine addition and is insignificant thereafter;
- no loss occurs if I^- is present prior to chlorine addition (PAO and buffer need not be present);
- the loss cannot be attributed to oxidant demand since the addition of more $Ca(OCl)_2$ to the system after 10 minutes produces another 5 to 15% immediate loss of TOX.

We have not discovered the reason for the non-quantitative analysis of TOX in saline water. Since it occurs only in the presence of Cl^- or Br^- and in the absence of I^-, it is tempting to attribute it to a loss of Cl_2 or Br_2 gas via volatization at the point of halogen injection. The conversion of OCl^- to Cl_2 or Br_2 would be favored under these conditions but should not be significant at pH 7.5. Nevertheless, the loss occurs even when an alkaline chlorine solution is added to an alkaline saline solution. If bromate (BrO_3^-) or chlorate (ClO_3^-) were formed via the reactions:

$$3HClO = 2Cl^- + ClO_3^- + 3H^+$$

$$3HOBr = 2Br^- + BrO_3^- + 3H^+$$

they would not be detectable by the methods used for TOX, but still could account for the missing oxidant. Halate ion production is favored, but would be even more favored in the absence of Cl^- or Br^- where we have not observed a loss of TOX. Furthermore, Carpenter and Macalady (1976) could not detect (polarographically) BrO_3^- in chlorinated sea water.

There is indicated, however, the formation of some oxidant species -- one that forms in the absence of I^- and will not subsequently oxidize I^- to I_2. Although this portion of total oxidant is relatively small (5 to 15%), it should be noted that the term "TOX" in this report must be qualified to mean only that portion of the total oxidant which is measurable by the technique used.

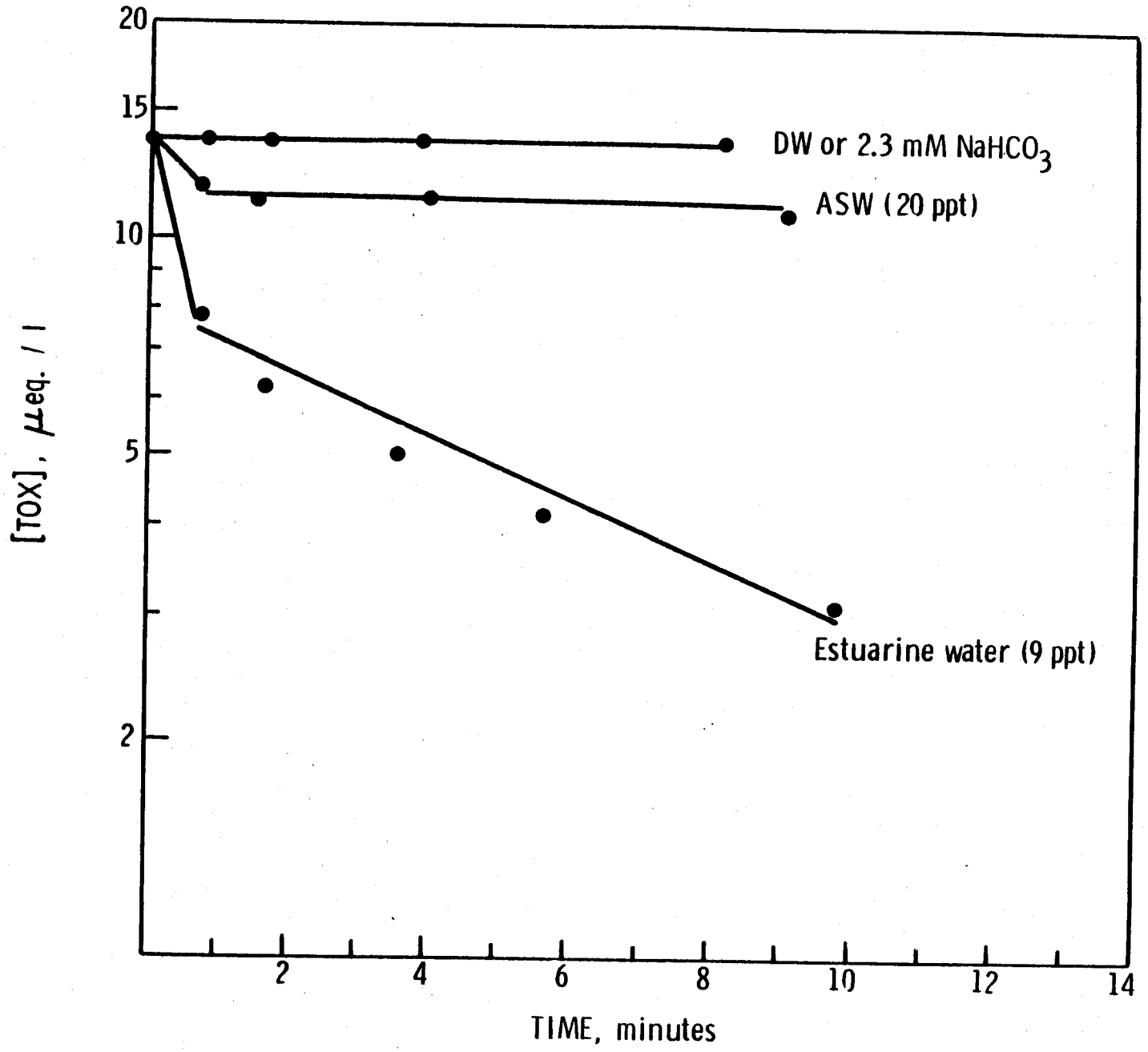

Figure 4-1. Time-dependent decay of TOX in solutions of $Ca(OCl)_2$ with deionized water (DW), $NaHCO_3$ solution, artificial sea water solution (ASW; 20 ppt salinity), and estuarine cooling water.

Interferences --

Three common constituents of estuarine water were tested for their ability to oxidize I^- and thus contribute anomalously to [TOX] measurements. The constituents were manganese dioxide, ferric oxide, and nitrite, which can yield I_2 via the reactions

$$MnO_2 + 4H^+ + 2I^- = I_2 + Mn^{2+} + 2H_2O$$

$$Fe(OH)_3 + 3H^+ + I^- = 1/2\ I_2 + Fe^{2+} + 3H_2O$$

$$NO_2^- + 2H^+ + I^- = 1/2\ I_2 + NO + H_2O \quad .$$

The two solid phase components are expected in estuarine water because of their ubiquitous presence in coatings on suspended material (Jenne, 1968). The nitrite ion can be expected to be present at a low micromolar level.

The reactions of ferric oxide and nitrite with I^- to form I_2 should not be thermodynamically significant at pH 4. It was observed that no I_2 was formed when systems containing 50 ppm Fe_2O_3 or 50 μM/ℓ NO_2^- were treated with KI, buffer, and PAO.

Of the three reactions, the one involving manganese dioxide is the most thermodynamically favored. During early experiments on the apparent loss of TOX in saline solutions, high concentrations of KI, up to 20 g/ℓ, were being used. These high levels of KI did not yield higher measured TOX concentrations, but, when 2 ppm MnO_2 was also present, detectable I_2 concentrations were obtained. However, at the KI concentration of 0.3 g/ℓ routinely used, no interference was observed with MnO_2 present at even 50 ppm.

Thus, the three possible interferents, when present at concentrations up to and exceeding those expected in estuarine cooling water, were not found to produce I_2 under normal analytical conditions. Conceivably, naturally occurring ferric and manganic solid phases could be more reactive than the commercial solids used here. The extent of natural interference was tested by comparing [TOX] analyses for control and actual samples. The results of such a test appear in Table 4-1 and show no evidence of I_2 formation from components other than the $Ca(OCl)_2$ added to estuarine water. Furthermore, numerous analyses of a single estuarine water sample showed good precision. This would not be the case if MnO_2 were reacting to produce I_2 since, as was seen when high KI concentrations were present, that reaction is not precisely reproducible. We are confident, therefore, that all TOX concentrations reported here represent only oxidant derived from the addition of Cl_2 or BrCl.

OTHER WATER QUALITY PARAMETERS

Ammonia

Ammonia concentrations were measured by the phenolhypochlorite method (Soloranzo, 1969). Water samples were collected in acid-washed polyethylene bottles and filtered through 0.45 μ Millipore filters within 20 minutes of collection. Fifty-ml samples of filtered water were spiked with 2 ml of

phenol solution, 2 ml of sodium nitroprusside solution, and 5 ml of alkaline-citrate-hypochlorite solution. All reagents were prepared as indicated by Soloranzo (1969), with hypochlorite solution made fresh daily and the others made fresh weekly.

Using a Beckman Model B spectrophotometer and 1-cm cuvettes, we measured absorbances at 640 nm 1 to 24 hours after reagent addition. No change in absorbance with time was observed as long as at least 1 hour was allowed for color development. Calibrations were made weekly using distilled water solutions of NH_4Cl. The factor relating concentration (in $\mu M/\ell$ NH_3-N) to absorbance was 60 ± 4 (standard deviation for nine data sets), which compares favorably with the factor of 6.5 reported by Soloranzo (using 10-cm cuvettes). One calibration, run by spiking estuarine water with NH_4Cl, yielded a concentration-to-absorbance factor of 58, thus indicating no need to correct absorbance for matrix effects. Beers law was obeyed to at least 22 $\mu M/\ell$. The reagent blank corresponded to a concentration of 1.2 $\mu M/\ell$; thus, the detection limit, defined as twice the concentration of the blank, was 2.4 $\mu M/\ell$. Among 38 duplicate determinations made during the experimental period, the average variation between duplicates was 7%.

Salinity, Temperature, pH, and Oxygen Concentration

These parameters were monitored instrumentally in intake cooling water. Probe readings of water conductivity (Riley and Skirrow, 1975) were corrected to their values at 25° C by the formula:

$$\Lambda_{25^\circ C} = \Lambda_T + (0.022)\ (T-25)$$

where T = temperature (°C)

Λ = conductivity (m Mhos/cm).

Conductivity was in turn related to salinity via the formula:

$$S(ppt) = \Lambda_{25}\ (0.578).$$

FOULING ASSAY PROCEDURE

To evaluate biofouling of treated and untreated cooling water, fouling chambers were deployed at four locations: the intake embayment (untreated cooling water), the circulators, the intake condenser water box, and the discharge canal (condenser effluent station). The design of the fouling chamber test system is illustrated in Figure 4-2.

Unfiltered estuarine water was delivered to each fouling chamber (FC in Figure 4-2) at the rate of 19 ± 1.2 ℓ/min (5.0 gal/min). The flow velocity in the chamber was approximately 30 cm/sec (1.0 ft/sec). The flow rate was controlled by means of an adjustable standpipe mounted in a 25-liter (6.6 gal) fiberglass volume control tank (VC in Figure 4-2), one tank for each set of two fouling chambers. Water passed by gravity from the volume control tank through a 7.6-cm (3.0-in) long PVC connector (3.8 cm, 1.5 in ID) to the fouling chambers. The water level in each fouling chamber could be controlled

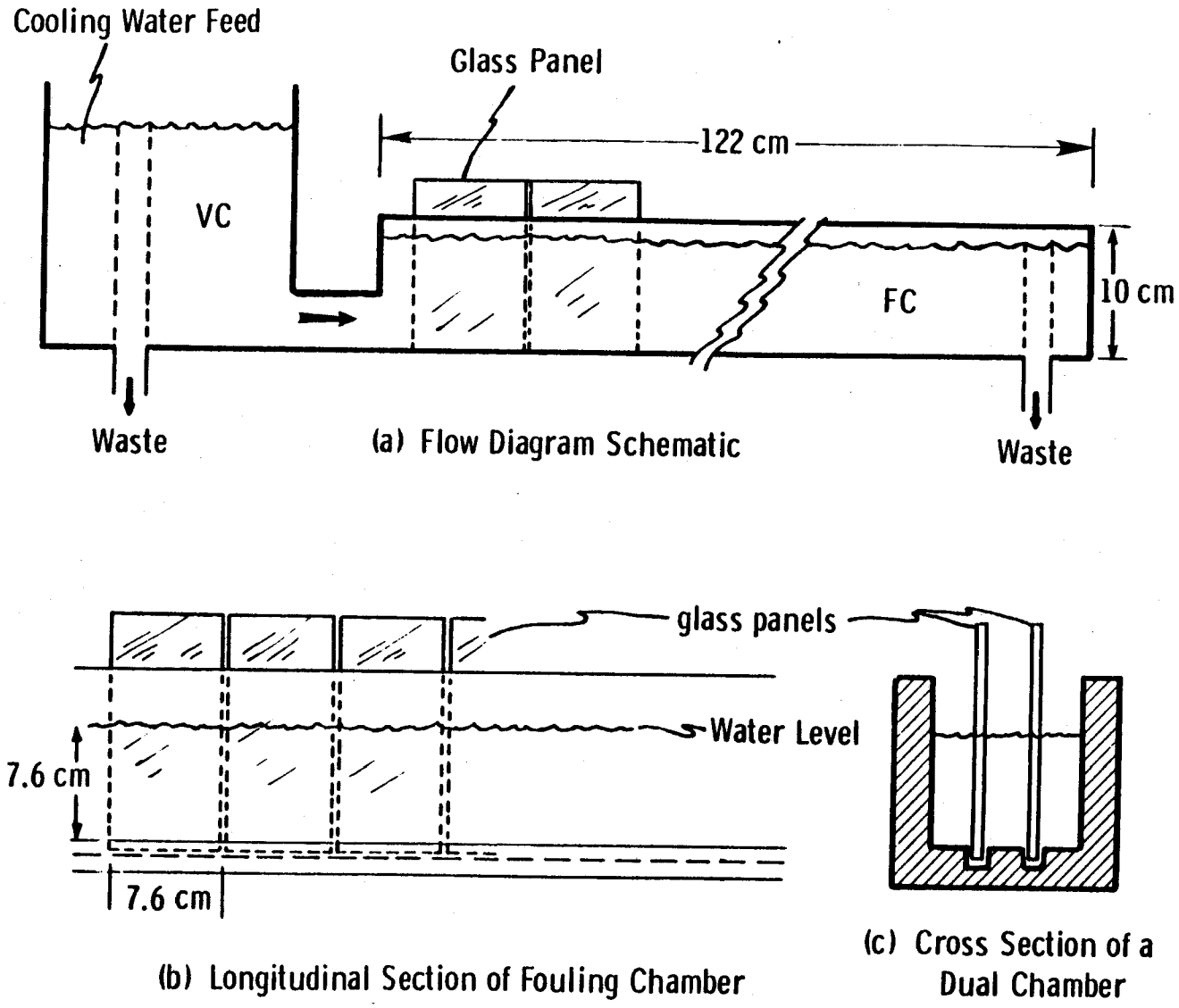

Figure 4-2. Diagram biofouling chamber.

independently by an adjustable standpipe at the discharge end. Duplicate fouling chambers were used at all stations with the exception of the condenser station, where a single fouling chamber was used; the volume flow of water at this location was insufficient to supply duplicate chambers.

The fouling chambers were 122 cm (48 in) long by 5.1 cm (2.0 in) wide by 10.2 cm (4 in) high and constructed of 0.6-cm (0.25-in) PVC plate. Two rows of glass panels, 7.6 cm (3.0 in) by 12.7 cm (5.0 in) by 0.32 cm (0.125 in), were secured edge-to-edge in a vertical position in each fouling chamber (Figures 4-2a, b). Two grooves, 0.4 cm (0.16 in) deep by 0.35 cm (0.14 in) wide, were cut down the length of each fouling chamber to serve as alignment slots for equal exposure of both surfaces of the glass panels. The two rows of panels were positioned to provide 1.4 cm (0.56 in) clearance between each row and from the sides of the fouling chamber (Figures 4-2c).

The glass panels functioned as fouling substrates. At a water depth of 7.6 cm, the effective fouling area of each panel was approximately 116 cm^2 (7.6 cm x 7.6 cm x 2 sides). The leading and trailing edges of each panel were not available to fouling organisms because of the edge-to-edge configuration.

Ten clean panels were placed in each row of each fouling chamber at the beginning of each 15-day period. Because significant fouling occurred on exposed edges, it was necessary to add one non-experimental, or blank, panel at the first and last positions in each row. The 20 experimental panels (10 per row) were grouped into five serial, replicate partitions (IV in Table 4-2), each composed of four panels. This experimental configuration provided a balanced incomplete block design for proper statistical sampling. Four panels were removed from four different partitions every 3 days during the 15-day studies, as shown in the sampling schedule in Table 4-2. When an experimental panel was removed, it was replaced by a clean panel to eliminate free-edge exposure of the remaining panels.

All fouling chambers were kept in the dark throughout each study, except when panels were being removed or physical and chemical data were being collected. Flow rates were checked at least every 12 hours throughout all studies.

The material scraped from each panel was dried at 90° C for 24 hours and weighed to determine total dry weight. The material was then ashed for 2 hours at 500 to 550° C to burn off the organic portion of the fouling material. The inorganic residue weight was subtracted from the total dry weight to determine the amount of organic material originally present on the fouling substrate.

TABLE 4-2. SAMPLING DESIGN AND SCHEDULE

Fouling chamber		Sampling schedule		
Partition	Position	Day	Partition	Position
I	1 2 / 3 4	3	II	1
			III	1
II	1 2 / 3 4		IV	1
			V	1
III	1 2 / 3 4	6	I	2
			II	2
IV	1 2 / 3 4		III	2
			IV	2
V	1 2 / 3 4	9	I	3
			II	3
			III	3
			V	3
		12	I	4
			II	4
			IV	4
			V	4
		15	I	1
			III	4
			IV	3
			V	2

CHAPTER 5

FOULING CONTROL WITH BrCl AND Cl_2

One of the main concerns that led to the initiation of a study for evaluating BrCl as a potential alternative to chlorine was the observation that chlorine may react with ambient water constituents to produce long-lived residuals which are toxic to aquatic life. One of the purported desirable properties of BrCl is rapid dissipation of BrCl-induced oxidants and other reaction products after their passage through the condenser cooling system (Wackenhuth and Levine, 1974). As discussed in the previous sections and in Appendix A and as demonstrated elsewhere (Mills, 1975), BrCl-induced oxidants do indeed decay faster than Cl_2-induced oxidants, at least in low-salinity water.

BrCl should have a second important property if it is to be an acceptable alternative to chlorine: it should control biofouling as effectively as chlorine, either on a weight or a cost basis.

In this section, we present data on the decay kinetics of chlorine and bromine chloride in estuarine water and on the effectiveness of the two biocides. Effectiveness is measured in terms of fouling rates in the presence and absence of chlorine- and bromine chloride-induced oxidants. The effects of environmental parameters on the effectiveness of the biocide will be explored. (For discussion of concurrently assessed toxicity characteristics of the chlorobrominated effluent, see Bongers et al., 1977).

OXIDANT DECAY IN THE COOLING WATER

In order to facilitate a comprehensive analysis of the relationships between residual oxidant concentration and biofouling, we will first summarize our experimental findings and interpretations of oxidant decay in low-salinity estuarine water. A more extensive discussion of factors controlling the decay of Cl_2- and BrCl-induced oxidants is presented in Appendix A. The raw data on which this discussion is based are included in Appendix A as Table A-5.

The important parameters in oxidant characterization are the rate of decline of residual oxidant during cooling system transit and the free and combined halogen content of the oxidants. Examination of the time-dependent oxidant decay, illustrated for Cl_2 in Figure 5-1, reveals a three-phase decay pattern. At an applied dose of 0.5 ppm (14 μeq/ℓ), about half of the added oxidant was consumed within about half a minute (Phase 1, Figure 5-1); in the next phase (Phase 2, Figure 5-1), oxidant decay was distinctly slower, and the duration of this phase varied between 10 and 15 min. In the third

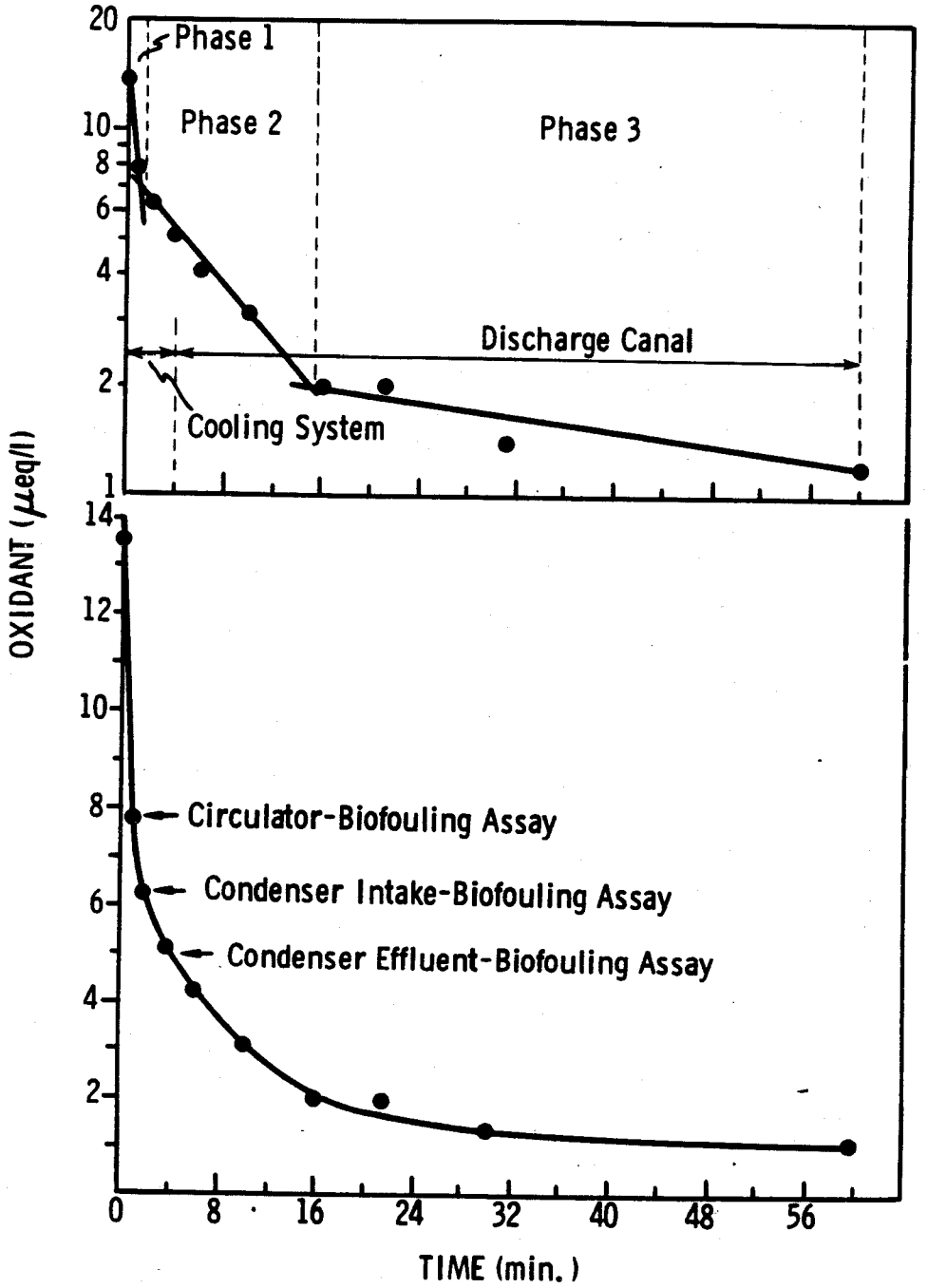

Figure 5-1. Typical time-dependent $Ca(OCl)_2$-induced oxidant decay in estuarine (<7 ppt salinity) cooling water. Bottom: arithmetic representation. Top: semilogarithmic transformation. For description of decay phases and biofouling assay procedures, see text.

phase, the rate of decline of titratable oxidant was much slower than that during the previous phases (often, further decline was not apparent after a contact time of about 30 min).

The decay pattern did not appear to be part of one single overall first-order process. Other models consistent with higher-order decay kinetics also indicated no single pattern.

Since 50% of the oxidant was lost in the very fast initial decay, and the third phase appeared to fit a first-order model with $b \approx -0.02\ min^{-1}$, the differences between the two biocides during the second phase were examined on the basis of a quasi first-order model. Table 5-1 summarizes the decay values measured for Cl_2 and BrCl between 13 July and 14 October 1976.

The overall average decay constants shown in the table for Cl_2 and BrCl were different at the 0.001 probability level, indicating that Br-Cl induced oxidants decayed faster than Cl_2-induced oxidants. While no strong correlation between k_1 values and measured water quality parameters was evident, there was a tendency for both Cl_2- and BrCl-induced oxidants to decay faster with increasing salinity. At salinities above 7 ppt, Cl_2-induced oxidants did not decay more slowly than the BrCl-induced oxidants. See Appendix A.

We want to emphasize that the pattern of oxidant decay described here applies strictly to low-salinity estuarine waters and applied biocide concentrations of 0.5 ppm (14 μeq/ℓ Cl_2, 8.7 μeq/ℓ BrCl) or less. Since prevailing salinities were below 7 ppt, and biocide doses were 0.5 ppm or less, the k_1 values reported in Table 5-1 were assumed to adequately describe oxidant decay during the field trials. These constants are, therefore, used in subsequent chapters for the formulation of a predictive, minimum biocide biofouling control model.

TABLE 5-1. COMPARISON OF AVERAGE QUASI FIRST-ORDER DECAY CONSTANTS (k_1)

Halogen	k_1 (ave)	k_1 (S.D.*)	Number of determinations
Cl_2	$-0.106\ min^{-1}$	0.048	20
BrCl	-0.127	0.032	17

* Standard Deviation

The analytical technique used to determine oxidant concentration of the cooling water did not permit analysis of free residual oxidant or the identification of the oxidant species. Back-titration at pH 7 generated very noisy, slowly drifting background currents, which made the instrument unsuitable for titrations at pH 4. However, we may assume that the concentration of free oxidant in the cooling water was negligible, at least during Phase 2 and Phase 3, for several reasons. First, we could infer that the 0.5 ppm application level was less than the chlorine demand (as defined by White, 1972, and APHA, 1975) of the cooling water since rechlorination of the same sample gave a three-phase decay pattern similar to that observed on the first application. The second reason for assuming "combined oxidants"

was that water quality measurements indicated that chloro- and bromo-derivatives could be formed. Thus, the ammonia content of the cooling water, and pH and temperature conditions favored conversion to halamine forms within seconds (for reaction kinetics, see Weil and Morris, 1949, and White, 1972).

Thus, we assumed that mainly combined residuals, and predominantly halamines, were present during cooling system transit.

EFFECTS OF BrCl- and Cl_2-INDUCED OXIDANTS ON FOULING RATES

Test Design

Biofouling was monitored at four stations. To determine biofouling potential of treated cooling water, glass panels mounted in fouling simulators were exposed to flowing cooling water at three power plant locations: (1) the circulators -- biocide contact time of the bypass stream was about 30 sec; (2) the intake condenser waterbox -- at this point, the biocide contact time was about 1 to 2 min; and (3) a discharge location -- at this station, the cooling water had an elevated temperature and a biocide contact time of about 5 min. (The biocide contact time at the condenser station varied from 0.7 to 2 min, and at the discharge station from 2 to 5 min, depending on the number of circulators in operation; see also Figure 5-1.) Intake cooling water collected at the trash racks in the intake embayment was used to determine the fouling potential of untreated cooling water. (For plant characteristics, see Appendix F.)

Biofouling control effectiveness of BrCl and Cl_2 was compared during two 15-day trials. During the first trial, the dose rates of BrCl and Cl_2 were 1360 kg (3000 lb)/day. For the volume of cooling water treated, the calculated dose levels were 510 ppb or, on a molar basis, 14.4 μeq/ℓ and 8.9 μeq/ℓ of chlorine and bromine chloride, respectively.

During the second test run, conducted in September 1976, biocide dose rates were considerably lower because of the lower ambient water temperatures prevailing during the month of September; i.e., since biofouling is strongly temperature-dependent, lower dose rates are needed at lower temperatures. Chlorine was injected at a level of 910 kg (2000 lb)/day (340 ppb; 9.6 μeq/ℓ), a dose rate commonly used during this part of the year. Bromine chloride was applied at the much lower level of about 360 kg (800 lb)/day (135 ppb; 2.4 μeq/ℓ) to allow comparison of the fouling control effectiveness of the two biocides on an equal cost basis, and to indicate the antifouling capability of presumed sub-optimal doses of bromine chloride.

Residual halogen levels were monitored for contact times of about 30 sec at the circulator stations, 1 to 2 min at the condenser intake waterbox (hereafter referred to as condenser station), and to 5 min at the discharge location. (The condenser discharge water was sampled at the inlet to a 40-ft long serpentine trough used for animal exposures and for evaluating biocide decay characteristics. For details, see Bongers et al., 1977.)

Fouling Control vs Biocide Concentration

The results of the two trials are recorded in Table 5-2 where the accretion of fouling material, in mg of accumulated dry weight over the specified time periods, is recorded by trial and test number, time, station location, and oxidant concentration for each biocide type. Accumulation of fouling material with time on glass panels is illustrated in Figures 5-2a, 5-3a, c, and 5-4a, c.

Dry weight values represent averages of eight replicate observations; oxidant concentrations are time-weighted average values based on the analysis of cooling water samples collected at the same locations where the fouling assays were conducted. The oxidant values thus represent the biocide concentrations experienced by the fouling communities accumulating at the respective locations. (Further details on dose rates are given in Appendix B. Analytical results and statistical treatment of biofouling assay data are presented in Appendix C.)

A review of all the data presented in Table 5-2 and Figures 5-2, 5-3, and 5-4 shows that fouling (of glass panels), in the absence of a biocide, proceeds quite rapidly at a temperature-dependent rate. This is evident when weight increases observed for tests 1 and 5 of trial I are compared with those for test 1 of trial II. During the September trial, when the ambient water temperatures were about 2° C below the August values, the accretion rate was much lower. Conceivably, this decrease in rate might be attributable to a decrease in abundance of fouling biota in the source water. (The importance of the ambient abundance of potential fouling biota on the rate of fouling is discussed in Chapter 6.) But, as indicated below and in Chapter 7, temperature variation appears to explain satisfactorily the differences between rates observed during the August and September trials.

The fouling rates observed in the cooling water at the circulator and condenser stations in the presence of BrCl were considered lower than those in the untreated water; the reduction was proportional to the oxidant concentration. For example, after 15 days exposure to an average of 3.1 and 1.8 μeq/ℓ of BrCl-induced oxidants, the amount of fouling material collected on the glass panels was only 5% and 16%, respectively, of that observed in the absence of biocide. (Compare tests 1, 2, and 3 of trial I in Table 5-2.) Similar trends are evident from comparisons of observations recorded for tests 5, 6, and 7 of trial I.

Dose-response interactions with chlorine as a biocide for cooling water treatment followed similar trends, as is apparent from the examination of tests 9, 10, and 11 of trial I, Table 5-2, and from Figures 5-2a, 5-3a, c, and 5-4a, c.

Although exhibiting the same general trends as observed during the first trial, dose-response interactions seen in the second trial did not allow further quantitative interpretations. Two factors may have accounted for this. First, the rate of fouling encountered during the September trial was much less than that observed during August. Consequently, the impact of sampling and analytical errors in September was more severe. More reliable data might have been acquired if the exposure period had been extended.

TABLE 5-2. ACCUMULATION OF FOULING MATERIAL ON GLASS PANELS FOR VARYING CONCENTRATIONS OF CONTINUOUSLY INJECTED BROMINE CHLORIDE AND CHLORINE

TEST DESCRIPTION				BIOCIDE			ACCRETION FOULING MATERIAL									
#	Date	Duration (Days)	Station location	Type	Concentration		DW_3*		DW_6		DW_9		DW_{12}		DW_{15}	
					(μeq/ℓ)	ppb	(mg)	(%)	(mg)	(%)	(mg)	(%)	(mg)	(%)	(mg)	(%)
I 1	11/8 - 26/8	15	Embayment				11	100	79	100	224	100	717	100	1318	100
2	11/8 - 26/8	15	Circulator	BrCl	3.1 ± 0.3	178	16	145	19	24	43	19	51	7	68	5
3	11/8 - 26/8	15	Condenser	BrCl	1.8 ± 0.2	103	22	200	49	62	95	42	152	21	215	17
4	11/8 - 26/8	15	Discharge	BrCl	1.4 ± 0.2	81	30	272	63	80	267	120	806	112	1589	121
5	17/8 - 26/8	9	Embayment				130	100	346	100	808	100				
6	17/8 - 26/8	9	Circulator	BrCl	2.9 ± 0.2	167	29	22	30	9	53	6				
7	17/8 - 26/8	9	Condenser	BrCl	2.0 ± 0.2	115	32	19	ND+	ND	118	15				
8	17/8 - 26/8	9	Discharge	BrCl	1.5 ± 0.2	86	25	96	536	154	1005	124				
9	17/8 - 26/8	9	Circulator	Cl_2	7.3 ± 0.5	259	24	18	64	18	91	11				
10	17/8 - 26/8	9	Condenser	Cl_2	4.9 ± 0.3	174	22	17	66	19	92	11				
11	17/8 - 26/8	9	Discharge	Cl_2	1.9 ± 0.2	67	59	45	254	73	571	71				
II 1	10/9 - 25/9	15	Embayment				13	100	42	100	77	100	170	100	297	100
2	10/9 - 19/9	9	Circulator	BrCl	1.1 ± 0.1	63	17	130	30	71	32	42				
3	10/9 - 19/9	9	Condenser	BrCl	0.9 ± 0.1	52	14	107	28	67	54	70				
4	10/9 - 25/9	15	Discharge	BrCl	1.0 ± 0.1	58	41	315	57	136	96	125	98	58	159	54
5	10/9 - 25/9	15	Circulator	Cl_2	5.3 ± 0.3	188	15	115	19	45	29	38	26	15	33	11
6	10/9 - 25/9	15	Condenser	Cl_2	3.3 ± 0.3	117	9	69	20	45	20	26	22	13	21	7
7	10/9 - 25/9	15	Discharge	Cl_2	1.6 ± 0.2	57	28	215	34	71	39	51	78	46	87	29

* DW_x is the total dry weight of fouling material accumulated in the specified period of time on 116-cm^2 (18-sq in) glass surface. The value is an average of replicates.

+ No Data

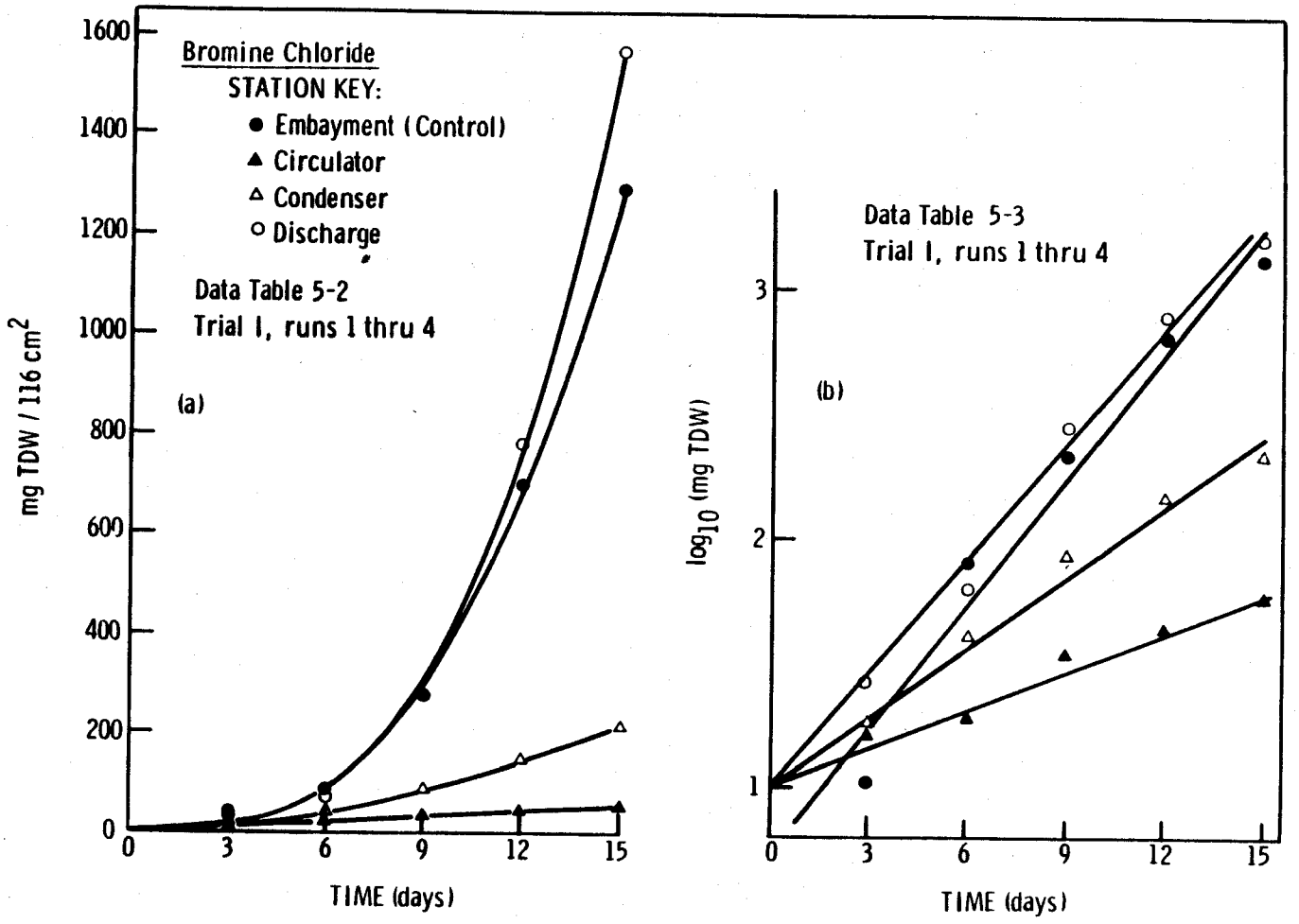

Figure 5-2. Accumulation with time of fouling material on glass panels exposed to BrCl-treated and untreated cooling water: (a) Ordinate expressed in total dry weight (TDW) per 116-cm^2 surface area; (b) Ordinate in base 10 logarithm of total dry weight. Average temperatures of the unheated and the heated cooling water were 24.9° C and 29.4° C, respectively.

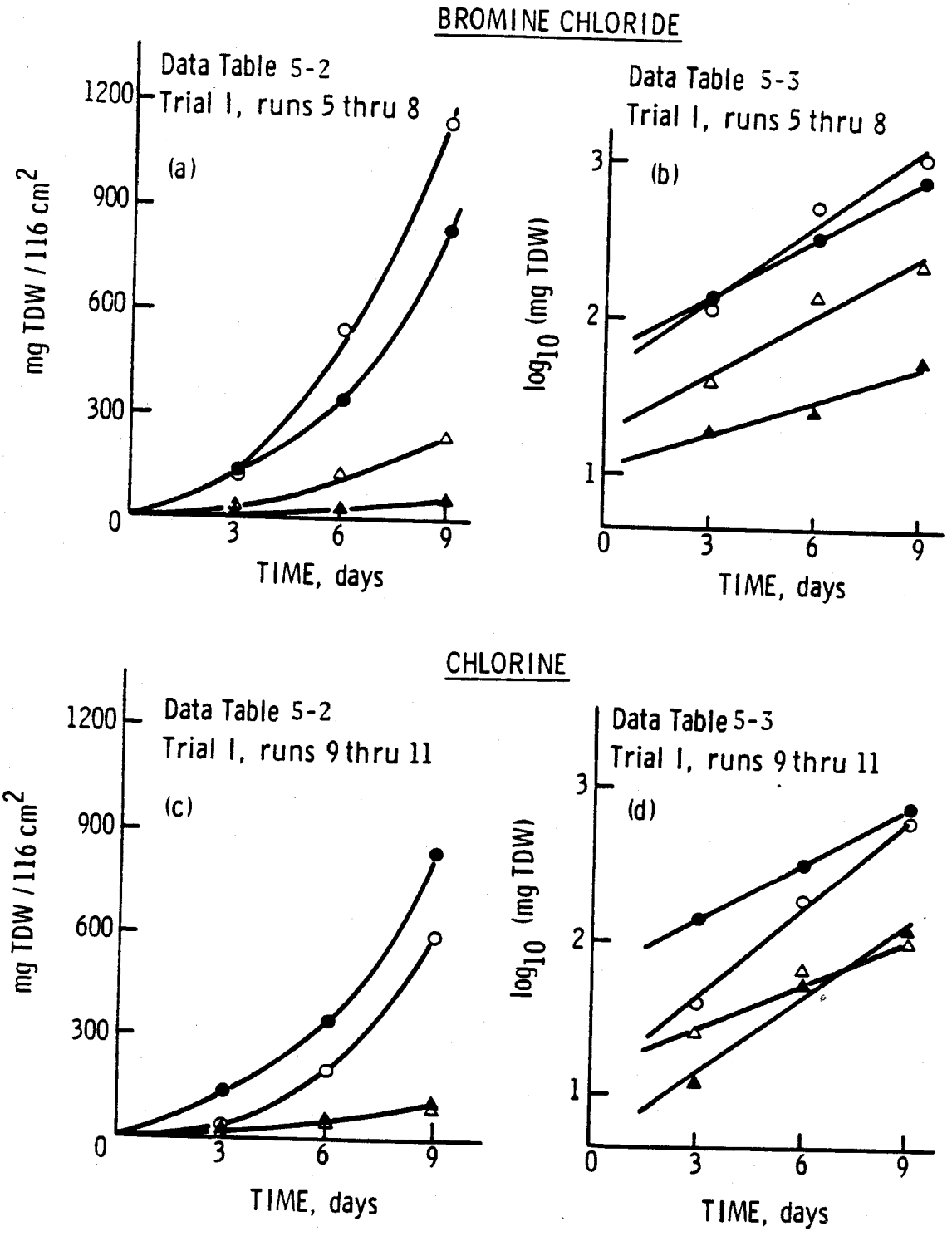

Figure 5-3. Accumulation with time of fouling material on glass panels exposed to BrCl-treated (a, b) and Cl_2-treated (c, d) cooling water. Average temperatures of the unheated and the heated cooling water were 24.9° and 29.4° C, respectively. Station key as in Figure 5-2.

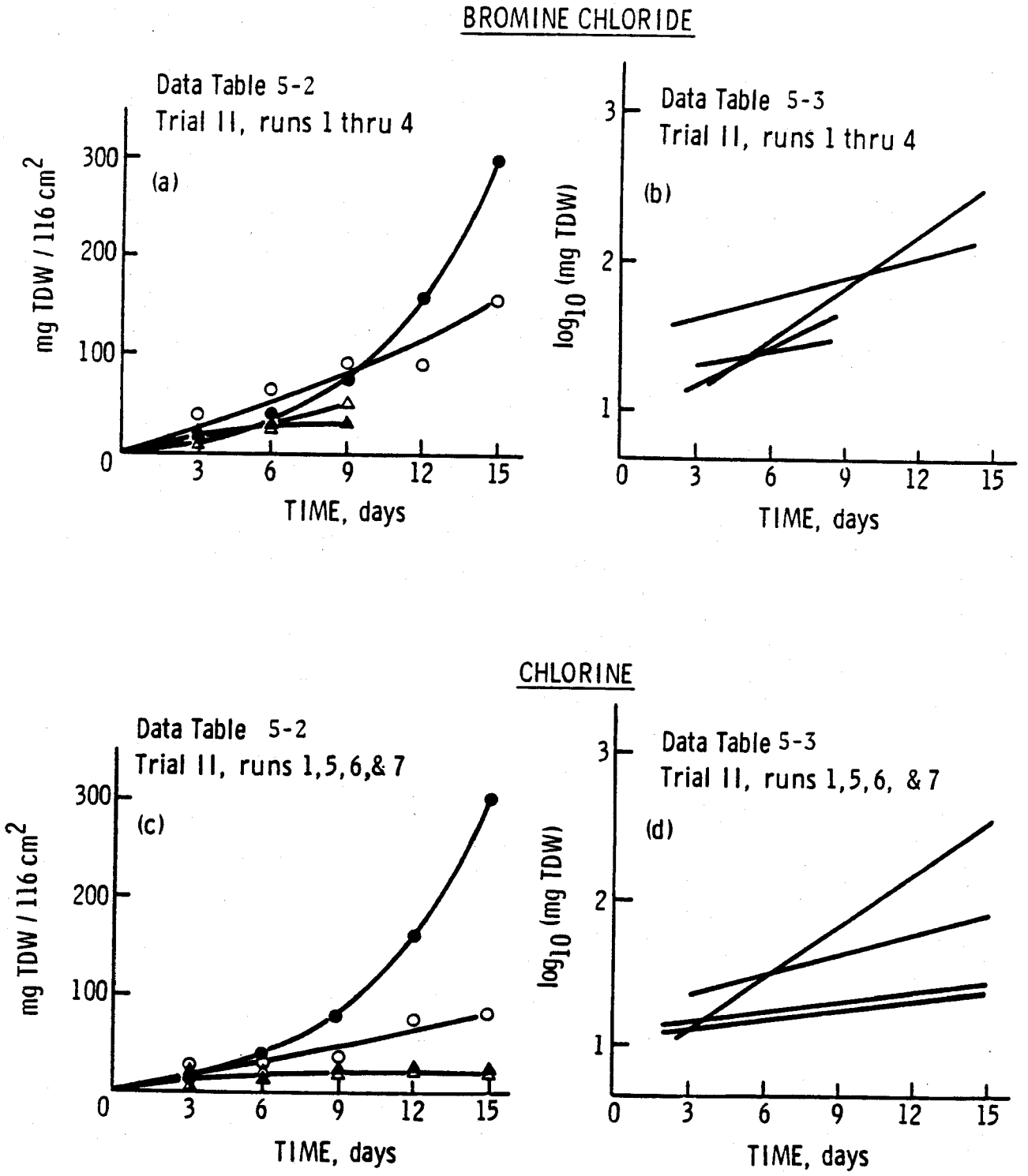

Figure 5-4. Accumulation with time of fouling material on glass panels exposed to BrCl-treated (a,b) and Cl_2-treated (c,d) cooling water. Average temperatures of the unheated and the heated cooling water were 22.9° C and 27.3° C, respectively.

Second, it appears that less biocide was necessary to inhibit biofouling during the September trial than anticipated. In particular, Cl_2 appears to have been added in excess (tests 5-7). Certain aspects of the September trial are important, however. The data (Table 5-2, tests 1 through 7, trial II, and Figures 5-4a and c) indicate that, even in the presence of an apparent oxidant excess, some buildup of fouling material will occur. Apparently, there is an immediate initial accumulation and attainment of some threshold value which remains reasonably constant with time, independent of biocide concentration. Whether the formation of this thin fouling layer can be prevented or in any way affects cooling system performance remains to be seen.

Comparison of the fouling data for the discharge cooling water with those observed in the embayment water indicates that the rate of fouling is temperature-dependent. We observed (test 1 vs 4 and test 5 vs 8 of trial I and Figures 5-2a and 5-3a) that the accretion of fouling material in BrCl-treated cooling water, after a temperature rise of about 4.5° C, was higher in most instances than that of untreated cooling water at ambient temperature, even though significant quantities of oxidant were still present. (As will be shown subsequently, the differences became more pronounced after the temprature effects were corrected for the inhibitory effect of oxidant.) The fact that biofouling processes did recover so readily implied that the effects of BrCl treatment were transient in nature and, if biofouling community response is an indicator, probably caused little impact on the receiving water. Additionally, the fact that an increase in temperature can, at least in part, compensate for the inhibitory effects can provide insight into the nature of the inhibitor mechanism and, thus, a basis for formulating a more rational biocide dosing strategy.

The extent of biofouling recovery seen with BrCl during the August trial was not evident in any of the other trial I treatment conditions. This difference may have been the result of the relatively high initial dose rates used for chlorine (tests 9, 10, and 11 of trial I, and 5, 6, and 7 of trials I and II) and the low rate of fouling at the lower water temperatures. Clearly, our data are insufficient to determine whether the observed differences were due to the nature of the biocide.

To facilitate analysis of dose-response relationships, the logarithms of the accumulated fouling material weights were calculated (see Table 5-3). The log-transformed data were plotted against time on an arithmetic scale, as shown in Figures 5-2b, 5-3b, d, and 5-4b, d. Using the least squares method, we calculated coefficients a and b of the regression equation $y = a + bx$, where the regression coefficient b, the slope of the regression line, represented the growth constant of the fouling layer, defined here as the fouling coefficient (FC).

To characterize the effects of the BrCl-induced oxidants on FC, the data of tests 1 through 3 and 5 through 7 of the August trial were selected. Because of the strong temperature dependency of fouling processes, runs 4 and 8 (where the water temperature was higher due to condenser heating) of the August trial were not used for the analysis of the interaction between BrCl and FC.

TABLE 5-3. ACCUMULATION OF FOULING MATERIAL ON GLASS PANELS FOR VARIOUS OXIDANT CONCENTRATIONS AND WATER TEMPERATURES

Test # From Table 1		Temperature cooling water (° C)	Biocide			Accumulation of fouling material log 10 (mg DW) with time (days)*					a‡	b‡	r²●
			Type	Conc. (μeq/ℓ)	ppb	3	6	9	12	15			
I	1+	24.9		0	0	1.04	1.90	2.34	2.85	3.11	0.721	0.1697	0.96
	2+	24.9	BrCl	3.1	178	1.20	1.28	1.63	1.71	1.83	1.023	0.0563	0.94
	3+	24.9	BrCl	1.8	103	1.34	1.69	1.98	2.18	2.32	1.167	0.0817	0.97
	4+	29.4	BrCl	1.4	81	1.48	1.80	2.43	2.91	3.20	0.999	0.1517	0.98
	5+	24.9		0	0	2.11	2.54	2.92			{0.997** 1.767**	0.1283	1.00
	6+	24.9	BrCl	2.9	167	1.45	1.48	1.72			1.280	0.0450	0.83
	7+	24.9	BrCl	2.0	115	1.51	--	2.07			1.230	0.0933	--
	8+	29.4	BrCl	1.5	86	2.09	2.74	3.00			{0.706** 1.667	0.1600	0.96
	9	24.9	Cl_2	7.3	259	1.38	1.81	1.96			1.137	0.0967	0.93
	10	24.9	Cl_2	4.9	174	1.51	1.82	1.96			1.340	0.0683	0.92
	11	29.4		1.9	67	1.77	2.40	2.76			1.320	0.1650	0.98
II	1+	22.9	Cl_2	0	0	1.11	1.62	1.89	2.23	2.48	0.864	0.1117	0.98
	2	22.9	BrCl	1.1	63	1.23	1.48	1.51			1.127	0.0467	0.83
	3	22.9	BrCl	0.9	52	1.15	1.45	1.73			0.863	0.0967	1.00
	4	27.3	BrCl	1.0	58	1.61	1.76	1.98	1.99	2.20	1.413	0.0617	0.99
	5	22.9	Cl_2	5.3	188	1.18	1.28	1.46	1.42	1.52	1.113	0.0273	0.87
	6	22.9	Cl_2	3.3	117	0.95	1.30	1.30	1.34	1.32	1.008	0.0260	0.57
	7	27.3	Cl_2	1.6	57	1.45	1.53	1.59	1.88	1.94	1.279	0.0443	0.93

* Base 10 logarithms of weights reported in Table 5-2.

\+ Data used for model development.

‡ If we assume that accretion follows first-order kinetics within the specified 15-day time period, the coefficients a and b in equation $y = a + bx$ represent the y-intercept and the slope, respectively, of the time course.

** Represents the 6- to 15-day time span instead of the 0- to 9-day period.

● $r^2 = \frac{n\Sigma xy - \Sigma x \Sigma y}{n(n-1)s_x s_y}$

To evaluate the dependency of FC on oxidant concentrations, represented by [TOX] , the data observed at an average water temperature of 24.9° C were fitted to the equation y = a + bx. The following data were used

FC (day^{-1})	0.1697	0.1283	0.0563	0.0450	0.0817	0.0933
TOX (μeq/ℓ)	0	0	3.1	2.9	1.8	2.0

to obtain a regression coefficient b = -0.0323, a y intercept a = 0.1486, and a coefficient of determination r^2 = 0.89.

On the basis of these data, the relationship between the FC and [TOX] for an average cooling water temperature of 24.9° C can be described by the expression:

$$FC = 0.149 - 0.0323\,[TOX]\,, \qquad (5\text{-}1)$$

where FC = 0.149 represents the fouling coefficient in the absence of added oxidant. The observed data (open circles) and the calculated regression line are shown in Figure 5-5.

The FC-[TOX] interaction model, shown here, assumes a linear relationship over the full oxidant concentration range. This assumption may be invalid for relatively low and relatively high oxidant concentrations. For example, the model suggests that, at an average cooling water temperature of 24.9° C, fouling would be prevented at a [TOX] of 4.6 μeq/ℓ. At about half that value, we observed only a very small buildup, similar in magnitude to values observed at the lower cooling water temperatures in the presence of excess amounts of oxidant. Conceivably, this accumulation represented some minimal, unavoidable buildup. At any rate, further quantification of the dose-response interaction at the higher end of the oxidant concentration scale would require much longer exposure times than those used in our present investigations.

The linearity assumption may also be invalid at the lower end of the oxidant scale. Frequently, because biological processes are insensitive to or can compensate for the presence of relatively low concentrations of inhibitors, some threshold concentration of oxidant may be required before biological rate processes deviate from control values. In the present circumstances, the resolution of our test procedure will not extend to characterization of the FC-[TOX] dependency in this range, at least not under field conditions.

From an engineering point of view, dose-response interactions at the low and the high end of the oxidant scale are of limited practicality. While the effects of the very small bioaccumulation occurring at relatively high oxidant levels apparently do not perceptibly reduce condenser performance,

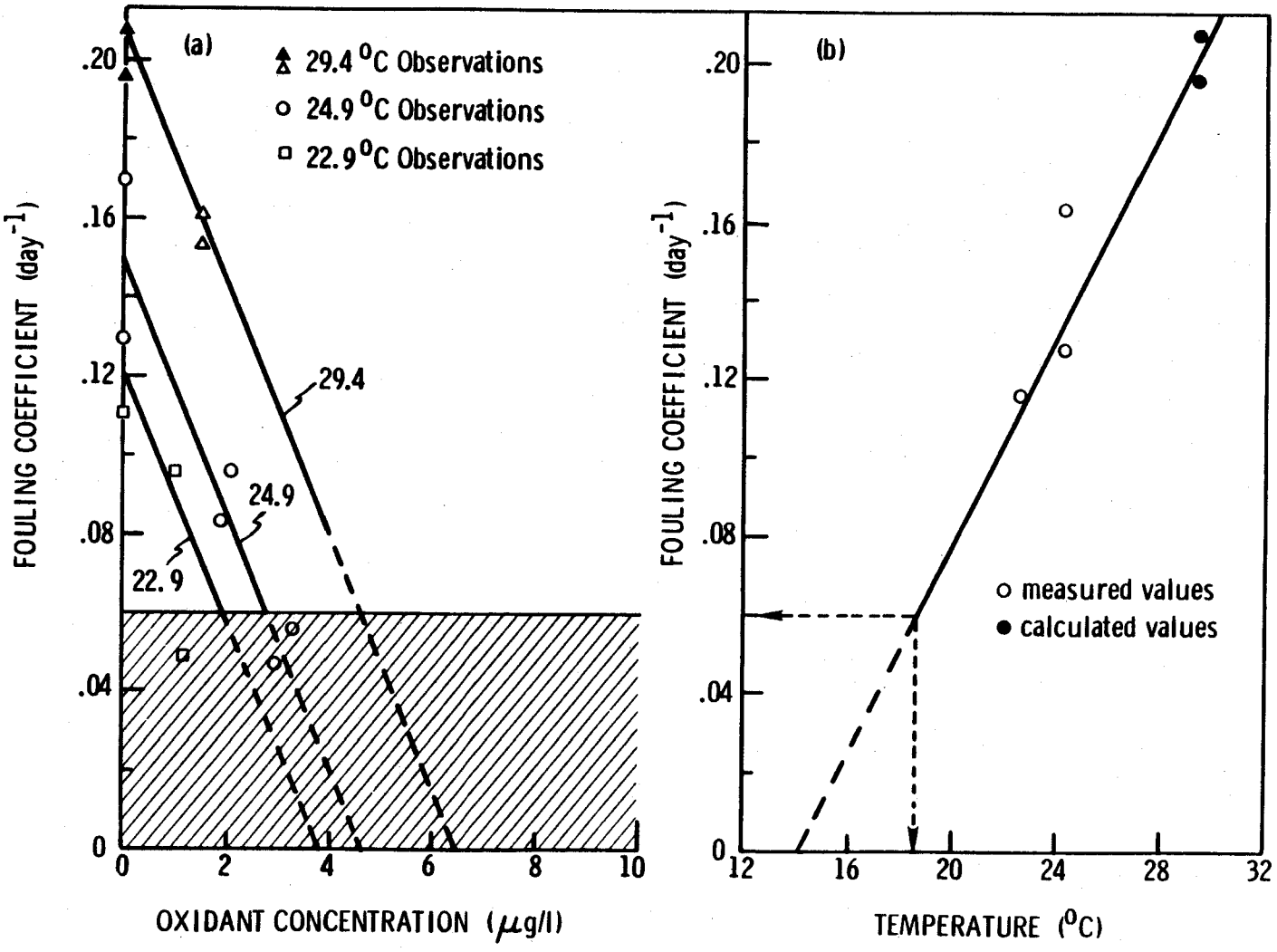

Figure 5-5. Relationship between fouling coefficient (day^{-1}) and

a. oxidant concentration (μeq/ℓ) for cooling water temperatures of 22.4°, 24.9°, and 29.4° C. In the shaded area, the rate of fouling is too low to evaluate with assay procedures used in the present study;

b. cooling water temperature (° C). Arrows indicate that the rate of fouling is too low, at a water temperature of about 18° C, to evaluate with present assay procedures.

the rapid accumulation which would occur at low oxidant levels would become immediately apparent by an unacceptable reduction in heat exchange efficiency in the condenser.

The FC- [TOX] dependence for chlorine-induced oxidants cannot be ascertained on the basis of available data. At 24.9° C, only two b values are available for chlorine (Table 5-3, tests 6 and 7, trial I), and, as stated earlier, the accumulation of fouling material in the presence of the relatively high chlorine concentrations (7.3 and 4.9 μeq/ℓ; 260 ppb and 174 ppb, respectively) was too small or the result of too little exposure time to allow accurate quantification. Therefore, further analyses of dose-response interactions will be restricted to BrCl data.

ENVIRONMENTAL FACTORS AFFECTING FOULING CONTROL

The influence of environmental factors on the effectiveness of chlorine and bromine chloride for fouling control has not been extensively studied. Not only is little known about the influence of water quality on the aqueous chemistry of these agents in marine environment, but the influence of environmental factors on the abundance of potential fouling biota has been explored even less.

We monitored four water quality parameters, salinity, dissolved oxygen, pH, and ammonia, plus water temperature in order to establish their importance on observed fouling rates. The findings are presented below.

Water Quality

From recent reports (Morris, 1975; Carpenter and Macalady, 1976) and discussions in previous sections and Appendix A, it is apparent that the salinity of the cooling water may profoundly affect the aqueous chemistry of chlorine in a marine environment. Salinity may also impact on biological processes. In an estuarine environment, the abundance and biotype of organisms capable of fouling condenser cooling systems may be governed by salinity and thus may vary within wide margins. Since dose-response relationships may be biotype dependent, salinity of the cooling water should be taken into consideration in determining required biocide dose rate.

During the August and September field investigations, the salinity of the cooling water remained relatively constant (5 ppt to 8 ppt, Table 5-4). For this reason, no attempts were made to relate this small variation in salinity to the extent of biofouling encountered during both tests.

Dissolved oxygen (DO) content of the cooling water is an important parameter to consider because of the suspected aerobic nature of the biological processes occurring in the fouling layer. The rates of nutrient utilization and bioaccretion may be controlled by oxygen depletion within the deeper fouling layers if the oxygen concentration in the external medium falls below certain levels. During our field trials, the DO content of the cooling

TABLE 5-4. SUMMARY OF WATER QUALITY CONDITIONS FOR EACH BIOCIDE DOSE RATE DURING THE TWO 15-DAY TEST RUNS

TEST CONDITIONS	TRIAL I		TRIAL II	
Biocide Dose Rates*	Cl_2	BrCl	Cl_2	BrCl
kg/day (continuous)	1360	1360	910	360
μeq/ℓ+	14.4	8.9	9.6	2.4
ppb	510	510	340	135
Water Quality Conditions	11 thru 26 Aug. 1976 Mean, ± S.D.‡	Range	10 thru 25 Sept. 1976 Mean, ± S.D.‡	Range
Ambient temp. (° C)	24.83 ± 1.4	26.5/22.0	22.94 ± 0.59	23.6/21.6
$[NH_3]$ (μmole/ℓ)	10.9 ± 3.6	16.3/ 5.1	3.9 ± 0.83	5.5/ 3.1
pH (range)		7.3 to 7.7		7.4 to 7.8
Salinity (ppt)		5 to 8		5 to 8
DO (ppm)	2.01 ± 0.56	3.3/1.1	4.04 ± 0.59	4.9/ 2.5

* Due to drift and dysfunctioning of the injection equipment, actual BrCl injection values varied, and daily adjustments were necessary.

\+ Microequivalents of bromine chloride- or chlorine-produced oxidants per liter.

‡ Mean ± 1 standard deviation.

water varied between 2 and 4 mg/ℓ. If oxygen contents in this range impose metabolic control, such factors should be taken into account in the interpretation of fouling rates observed in response to applied biocides.

There are no experimental data on the effects of DO on the rate of formation of a fouling layer on cooling system surfaces. However, the importance of DO may be evaluated on the basis of investigations dealing with biological rate processes in sewage sludge flocs and biofilms. Theoretical considerations and empirical investigations by Matson and Characklis (1976), LaMotta (1976), Hoehn and Ray (1973), and Mueller et al. (1968), who dealt with internal diffusion and substrate consumption in flocs and films, suggest that dissolved oxygen concentrations in the range reported here appear adequate to support unimpeded development of a fouling layer. This conclusion is based on the following considerations.

The highest dry weight accumulation of fouling material observed on a 116-cm^2 glass panel was 1,589 mg (Table 5-2). If a biological content of about 17% is assumed (Table 6-2), a biomass of 230 mg/100 cm^2 can be computed. To determine the apparent thickness of the biological layer, its density must be known. The density can be estimated on the basis of investigations carried out by Hoehn and Ray (1973) and Matson and Characklis (1976), who examined relationships between volumetric density and film thickness. Hoehn and Ray reported densities of 50 to 100 mg/cm^3 within a film thickness range of 50 to 100 microns. Assuming 100 mg/cm^3 as a representative density, we may compute a 230-micron layer thickness for the observed 230 mg of biological material/100 cm^2 area. From estimates by Matson and Characklis and Hoehn and Ray, we may further assume that the rate of metabolic processes in the exposed surface fouling layer will be limited by the availability of oxygen when the substrate total organic carbon content is 200 to 300 mg/ℓ. Since the total organic carbon of our source water is less than 10 mg/ℓ (USEPA, 1970), we may assume that oxygen contents of 2 to 4 mg/ℓ are not limiting fouling film development. This conclusion is supported by the observed growth response. Since first-order kinetics were obtained during the 15-day period, we may assume that oxygen limitation did not interfere with the development of the fouling film.

The pH value of the cooling water is an important parameter to consider in evaluating the effectiveness of chlorine and bromine chloride. The undissociated molecules (HOBr and HOCl) are the active species; the ionized species (OBr^- and OCl^-) are ineffective. Bromine chloride, therefore, has a significant advantage because dissociation of hypobromous acid occurs at a higher than ambient pH value. For example, at pH 8.0, 90% of an aqueous solution of BrCl would be present as the active species whereas, under similar conditions, only 19% of a chlorine solution would be active (Mills, 1975). With the prevailing pH values (7.3 to 7.8) and the noted differences between dissociation of Cl_2 and BrCl in this pH range, the need for examining pH effects on the effectiveness of the two biocides is evident.

However, for the present study, the pH of the cooling water is unimportant. Cooling water pH may be an important consideration when estimating chlorine dose rates for fouling prevention, especially when the presence of free chlorine is a deciding factor. But, because our cooling water contained a sufficient concentration of ammonia, and the chlorine and bromine chloride dose rates were relatively low, we may assume that halamine formation

(chloramines and bromamines) was essentially complete in all cases, and that no free chlorine or bromine was present in the cooling water.

This supposition was confirmed by water analysis data presented in Table 5-4 and by investigations by Morris (1975), Mills (1975), and Johnson and Sun (1975) on the aqueous reactions and toxicity of chlorine and bromine chloride in the presence of ammonia. During the first 15-day trial (Table 5-4), the average NH_3 concentration was 10.9 $\pm$ 3.6 μ mole/ℓ while the calculated chlorine and bromine chloride concentrations at the point of injection were 9.6 μeq/ℓ and 2.4 μeq/ℓ, respectively. Moreover, since HOBr and HOCl readily react with oxidizable cooling water constituents (e.g., Fe^{++}, Mn^{++}, NO_2^-, and organics), we may assume that ambient reactant levels during both test periods were more than sufficient to convert the injected biocides into the amine forms (2 μeq of chlorine or bromine chloride combine with 1 μ mole of NH_3).

Thus, for the present study, we may assume that combined residuals, primarily chloramines and bromamines, were the active species in fouling control.

Temperature Effects

The temperature of the cooling water may affect fouling control in two ways. First, the effectiveness of the biocide may increase with increasing temperature. A number of investigators, examining the effect of temperature on dose-response interactions, observed that sensitivity of biota to an inhibitor tended to increase with increasing temperatures, but the extent of the increase was frequently small and depended on biotype, physiological and developmental state, and the presence of extraneous substances and other milieu variables (Lamanna and Mallette, 1965; Capuzzo et al., 1976). For the present study, temperature effects on oxidant inhibition will be ignored.

Second, the temperature of the cooling water may stimulate fouling. Reports indicate that the temperature coefficient of biological processes can usually be presented by the traditional Arrhenius equation, at least within some narrow temperature range (e.g., Varma and Nepal, 1972; Rye and Matelis, 1968; Reynolds et al., 1975; Oppenheimer, 1970; and Kinne, 1970). For example, using a rotating disk unit, Davis and Pretorius (1975) examined temperature coefficients (Q_{10}) of biofouling and observed values of 1.38 between 10 and 30° C, -2.66 above 30° C, and 13.06 below 10° C. Q_{10} values of 2 were commonly observed. Fouling responses measured during the two field trials in the present study followed the traditional temperature response pattern.

The quantitative relationship between the observed accretion rates and temperature was established on the basis of the data recorded in Table 5-3. The following data sets were used to determine the dependency of FC (coefficient b in Table 5-3) on temperature:

FC (day^{-1})	0.1697	0.1283	0.1117	0.1969	0.2085
T (^oC)	24.9	24.9	22.9	29.4	29.4

The FC values used for the 29.4° C water temperature were calculated by correcting the observed values (Table 5-3, test runs 4 and 8 of trial I) for biocide effect. In making this correction, we assumed the potency of bromine chloride to be invariant with temperature within the specified range. Because the temperature span we are dealing with is relatively small (4.5° C), and the extent of biocide activity increase with temperature observed with some biological systems is relatively unpronounced (Capuzzo et al., 1976), we feel justified in making this simplifying assumption.

To make the correction for inhibitor effect on fouling, we used Eq. 5-1 to calculate a corrected value

$$FC_c = FC_m + 0.0323\ [TOX]$$

where FC_m is the measured value for T = 29.4°C in Table 5-3.

For runs 4 and 8, respectively, we obtain:

$$FC_c = 0.1517 + 0.0323 \cdot 1.4 = 0.1969$$

and

$$FC_c = 0.1600 + 0.0323 \cdot 1.6 = 0.2085 \quad .$$

These values are entered for T = 29.4°C in the table above.

Using the tabulated values, we then obtain:

$$FC = -0.1854 + 0.0132 \cdot T \quad . \qquad (5\text{-}2)$$

This expression, with a coefficient of determination $r^2 = 0.86$, suggests that FC increases by about a factor of 2.5 with an increase in ambient water temperature from 21° C to 31° C ($Q_{10} = 2.5$), and that FC approaches zero at an ambient water temperature of about 14° C. This latter value is substantially less than the 18° C commonly considered the water temperature at which fouling control is required. Practical applications of this temperature response will be discussed in Chapter 7.

CHAPTER 6

EFFECTS OF BROMINE CHLORIDE AND CHLORINE ON DEVELOPMENT OF BIOFOULING LAYERS

A truly effective fouling control strategy cannot be designed without a thorough understanding of the processes controlling the sequence of events which produce a buildup of fouling layers on cooling system surfaces. Understanding these processes can aid in the design of an optimal control technology in various ways. First, treatment of cooling water with BrCl or Cl_2 can be targeted at the more sensitive processes in the sequence of events. For example, injection cycling frequency in intermittent fouling control procedures could be synchronized with the occurrence of the event most vulnerable to biocide inhibition. Second, an appreciation of the relative importance of the environmental factors regulating the biological growth processes could aid in the formulation of a predictive, minimum dose, fouling control model.

The purpose of this section is to place fouling control of power plant cooling systems by BrCl in a broader biological perspective. Fouling processes occurring on panels exposed to the relatively static conditions in open marine environments will be compared to those observed in the dynamic environment of a power plant cooling system. Regulating processes, peculiar to the cooling system environment, will also be examined on the basis of information from recent bench-scale investigations on the formation of biological slimes under controlled environmental conditions. These studies have been particularly informative with respect to the mode of development of fouling communities.

EVENTS IN A STATIC AQUATIC ENVIRONMENT

Recent studies have addressed the broad theme of biofilm development on solid substrates in marine environments. The development is characterized by the occurrence of three distinct sequential phases.

The first phase involves the "conditioning" of the clean surface exposed to seawater; in the second phase, epiphytic microorganisms establish colonies on the conditioned surface; epifaunal communities are the subsequent colonizers, and their growth and reproduction are believed to contribute most of the biomass observed on solid substrates suspended in estuarine and marine environments.

During the primary event, glycoproteinaceous material and simple carbohydrates--common constituents of the relatively dilute nutrient environment--concentrate on the clean surface and "neutralize" specific surface textures (Sechler and Gunderson, 1972). Investigations by Neihof and Loeb (1972), Baier (1972), Marshall (1972), and Marshall et al. (1971) indicate that the formation of this film is a necessary precursor to the adhesion of bacterial colonies.

The organic and inorganic nutrients concentrated at the solid surface function as attractants to motile bacteria. Young and Mitchell (1972), exploring chemotactic responses of motile bacteria, observed that positive chemotactic compounds enhance the rate of attachment (the opposite response was elicited when toxic compounds were concentrated at the solid-liquid interface), and empirical evidence showed that accumulation and initial rate of growth of the attached periphytes are proportional to the organic carbon content of the medium.

The phase-2 primary periphytes, including Pseudomonas, Flavobacterium, and Achromobacter species as principal members, colonize the "primed" substrate within a matter of hours, and, according to Zobell (1943), Corpe (1972), and Marshall (1972), their populations increase, at least initially, at an exponential rate. A mechanistically important characteristic of the primary periphytes is their excretion of a polysaccharide slime, which is believed to be essential to their adherence to the solid surface. Phase-2 secondary periphytes, which, in turn, are succeeded by microalgae and protozoa, are Caulobacter, Hyphomicrobium, and Saprospira species (Corpe, 1972).

The observed ability of these gelatinous bacterial slimes to accumulate metals (U.S. Naval Institute, 1952) and aggregate particulate matter is of special interest in cooling system fouling since observations by Mangum and McIlhenny (1974) and McCoy (1974) indicate that cooling water chlorination results in the formation of iron and manganese precipitates.

The third phase in the accumulative process is the colonization of the fertile slime layer by early life stages of epifaunal communities. Although permanent bioadhesions to clean surfaces do occur, e.g., barnacle nauplii (Crisp, 1972), the slime layer apparently is a prerequisite for the attachment and adherence of many invertebrate fouling larvae (Knight-Jones and Crisp, 1953; Chet et al., 1975).

Since any organism which is capable of colonizing a surface is capable of becoming a fouling organism in estuarine environments, an extensive list of potential fouling organisms can be prepared. Table 6-1 presents a list of the common, potential foulers observed in the Potomac River estuary, their salinity preferences, and their reproductive and feeding modes.

The dominant organisms occurring on fouling panels are more limited in number. In the Patuxent River estuary, a tributary of the Chesapeake Bay in the same oligohaline regime as the Morgantown SES, the productive members of the fouling communities are the hydroids, tunicates, barnacles, tubeworms, bryozoa, and a tube-building amphipod (Cory, 1967).

The structure of the panel communities would be expected to reflect the reproductive cycles of the ambient communities. Investigations by Cory (1967) and Sutherland and Karlson (1972) indeed confirmed that the intensity of larval setting corresponds to their reproductive periods. In Chesapeake Bay, the primary reproductive period of the fouling animals mentioned above is summer. Some start in late spring and continue through early fall.

TABLE 6-1. ASSORTED LIST OF POTENTIAL FOULING ORGANISMS OBSERVED IN THE POTOMAC ESTUARY

Major group	Distributional range*			Reproduction season	Feeding type	Mode of reproduction
	Fresh-water	Estuarine	Marine			
PROTOZOA (single celled organisms)	VC	VC	VC	Reproduce throughout the year primarily in summer.	All feeding types occur in this group.	Sexual and asexual, primarily by cell division.
PORIFERA (sponges)	R	C	VC	Reproduce throughout the year primarily in summer.	Suspension feeders without nervous integration, weak ability to respond to external stimuli.	Asexual reproduction by budding or fragmentation and sexual reproduction with pelagic larval stages.
Microciona prolifera		x	x	Summer-Fall		
Haliclona permollis		x	x	Late Spring-Summer		
Cliona truitti		x		Summer		
CNIDARIA (hydrozoans)	VC	VC	VC	Reproduce primarily in warmer months, information not available on a species by species basis.	Suspension feeders, use tentacles to capture a wide range of food items.	Asexual reproduction by budding or fragmentation and sexual reproduction involving alteration of generations as well as pelagic larval stages.
Bimeria sp.		x				
Bouganvilla sp.		x	x			
Clytia longicyatha		x				
Cordylophora lacustris	x	x				
Membranipora tenuis		x				
Sertularid argentea			x			
Victorella pavida		x				
ENTOPROCTA (bryozoans)	R	C	VC	Reproduce primarily in warmer months.	Suspension feeders which use cilia to obtain a wide variety of particles from the surrounding waters.	Asexual reproduction by budding and sexual reproduction with pelagic larval stages.

(Continued)

TABLE 6-1. (Cont'd.) ASSORTED LIST OF POTENTIAL FOULING ORGANISMS OBSERVED IN THE POTOMAC ESTUARY

Major group	Distributional range*			Reproduction season	Feeding type	Mode of reproduction
	Fresh-water	Estuarine	Marine			
Urnatella gracilis	x	x		Information not available.		
Numerous species, not identified.		x	x	Information not available.		
POLYCHAETA (segmented worms)	A	VC	VC	Reproduce during all seasons, spring-fall spawners predominate.	Omnivores, feeding by filtering and ingesting sediments.	Sexual reproduction with pelagic larval stages. Eggs are often brooded.
Polydora lingi		x		Spring-early summer		
Polydora websteri		x		Information not available.		
MOLLUSCA (oysters and clams)	C	VC	VC	Reproduce during all seasons, spring-fall spawners predominate.	Suspension feeders with sensory perception of the water quality.	Sexual reproduction with pelagic larval stages.
Brachiodontes recurvus		x	x	Spring-Fall		
Congeria leucophyta		x		Spring-Fall		
Crassostrea virginica		x	x	Spring-Fall		
CIRRIPEDA (barnacles)	A	C	VC	Reproduce throughout the year, spring-fall spawners predominate.	Suspension feeders with sensory perception of the water quality.	Sexual reproduction with pelagic larval stages.
Balanus amphitrite		x	x	Spring-Fall		
Balanus improvisus		x	x	Spring-Fall		
AMPHIPODA	VC	VC	VC	Reproduce throughout the year, spring-fall spawners predominate.	Scavengers	Sexual reproduction with brooded young.
Corophium lacustre		x		Spring-Fall		

* A = Absent
R = Rare
C = Common
VC = Very Common
x = Dominant Species

In Chesapeake Bay, most of the productivity of panel communities occurs in July and August (Cory, 1967). Water temperature apparently is the dominant regulating factor in that it controls feeding and reproduction. When ambient water temperatures reach 20°C, accumulation due to production by epifaunal communities starts and usually continues until fall, when the water temperatures decrease to 20°C. This pattern is observed in Chesapeake Bay (Cory, 1967; Cory and Nauman, 1969) and other geographic locations (U. S. Naval Institute, 1952). As will be seen later, biocide use to prevent fouling of cooling systems usually starts when the ambient water temperature reaches 18°C to 20°C and is terminated in the fall when the ambient temperature declines to that value.

Another important factor having considerable bearing on the composition and development of the fouling community is the velocity of the water relative to the fouling surface. This, and other pertinent environmental factors are addressed in the next section.

COOLING SYSTEM FOULING PROCESSES AND THEIR CONTROL

A sequence of events similar to that involved in the biofouling of solid surfaces in marine and estuarine situations can be expected to occur under the more dynamic conditions prevailing in power plant cooling systems. An important difference lies in the flow regime. In a cooling system, flow velocities may vary from 15 to 30 cm/sec through the traveling screens up to 200 cm/sec through the condenser tubes. Since development and maintenance of the initial film and the subsequent attachment and feeding of epifaunal animals are affected (all of them differently) by the velocity of the cooling water, the nature of the fouling communities developing in a cooling system may vary spatially.

Another difference between the two environments is the magnitude of the initial rate processes. The objective of fouling control measures is to limit accumulation to a level which permits efficient operation; therefore, short-term phenomena in the initial events must be examined. To determine the importance of factors regulating processes resulting in the initial buildup, a relatively high sampling frequency is necessary. Therefore, the accumulation on the glass panels was assayed at 3-day intervals over a 15-day period, and the high replication of the sample scheme was designed to gain sufficient precision.

Fouling Layer Development

The kinetics of biomass accretion are evident from Figures 5-2b, 5-3b, and 5-4b. The weight contribution of the initial colonization is shown by the Y-axis intercept; the time-dependent buildup due to the growth of attached fauna (phase-3 activity) is illustrated by the series of curves reflecting the growth in the presence and absence of BrCl.

Inspection of the relation between weight increase (per 116 cm^2) and time (in days) indicates that biomass increases exponentially during the 15-day experimental period. Since the shape of these curves reflects the nature of biological processes, we can draw some inferences from them.

Apparently, for the given set of conditions, the observed rates of growth are the maximum attainable rates consistent with internal biological processes. The exponential increase in biomass continues until external factors impose limitations; biomass accretion then proceeds at a linear rather than exponential rate. This change in growth kinetics should be a consideration in defining the minimum biocide dose requirements. Furthermore, with the transition to linear growth, the nature of the metabolic processes of the deeper fouling layer may change, thus weakening the structural integrity of the whole layer. Large patches may then peel off the intake conduit and waterbox surfaces and block sections of the condenser system.

In view of the aerobic nature of the phase-3 activity, the transfer of biological reactants, such as organic carbon constituents and/or oxygen, from the external liquid and their penetration into the biomass may become limiting factors in its growth. The ability of a reactant to fully penetrate the attached biomass depends on biomass thickness, consumption rate of the reactant, and its bulk liquid concentration. The functional relationship between these variables may be estimated on the basis of bench-scale kinetic and mechanistic studies conducted by, e.g., Hoehn and Ray (1973), Matson and Characklis (1976), Characklis and Dydek (1976), Bintanja et al. (1976), La Motta (1976), Whalen et al. (1969), and Bungay and Harold (1971).

The possible factors affecting the transition to linear accretion were briefly scrutinized. Since biofilm activity is frequently reported in terms of the consumption of organic carbon per unit area and time, biomass accretion rates observed in the investigations were converted to organic carbon consumption rate based on the assumptions and computations given below.

The organic content of the biomass was determined for all treatment conditions. As shown in Table 6-2, the organic fraction averaged about 17% and the inert (ash) fraction about 83% of biomass. Since the ratio of organic to ash content appeared independent of treatment conditions, all biomass was considered to contain a biological fraction of 17%, which, for the present purpose, was assumed to consist of 50% carbon, i.e., 8.5% of the biomass was assumed to be organic C.

The consumption rate of organic C by the fouling layer was computed, assuming, arbitrarily, that 10% of the consumed organic C was assimilated and converted to biomass organic C. To compute organic C consumption as a function of temperature, Eq. 5-2 was solved for desired T values. Assuming a Y-intercept of 1.00, we obtained the following expressions for 20°, 25°, and 30° C, respectively:

$$C_{20} = 0.362 + 0.0786\ (t)$$

$$C_{25} = 0.362 + 0.1446\ (t)$$

$$C_{30} = 0.362 + 0.2106\ (t)$$

where t = time (days),

and,

C_x = base 10 logarithm of the mg organic C consumed/day/116-cm^2 surface area.

TABLE 6-2. ORGANIC FRACTION AS PERCENT OF TOTAL ACCUMULATED FOULING MATERIAL

For detailed data presentation, see Appendix C.
(Average % Organic Matter 17%)

Test # (see Table 5-2)	Station location	Biocide BrCl	Biocide Cl_2	Organic fraction %	Organic fraction Standard deviation	Organic fraction No. of samples
I, 1	Embayment	-	-	19.7	7.56	5
I, 5	Embayment	-	-	16.1	1.10	3
II, 1	Embayment	-	-	18.6	2.70	5
I, 2	Circulator	+	-	20.0	3.82	5
I, 6	Circulator	+	-	17.0	1.73	3
II, 2	Circulator	+	-	19.0	1.00	3
I, 9	Circulator	-	+	15.0	1.20	3
II, 5	Circulator	-	+	17.6	3.20	5
I, 3	Condenser	+	-	15.6	2.31	5
I, 7	Condenser	+	-	15.5	--	2
II, 3	Condenser	+	-	19.0	3.46	3
I, 10	Condenser	-	+	17.0	3.00	3
II, 6	Condenser	-	+	21.8	7.72	5
I, 4	Discharge	+	-	16.4	1.70	5
I, 8	Discharge	+	-	15.6	1.52	3
II, 4	Discharge	+	-	18.8	2.86	5
I, 11	Discharge	-	+	14.1	2.00	3
II, 7	Discharge	-	+	16.8	2.86	5

Table 6-3 shows the effects of three cooling water temperatures on the potential increase in organic C consumption with time. For a 25° C water temperature, in the presence of 3 μ eq/ℓ oxidant, the expression

$$C_{25}^{TOX} = 0.362 + 0.0534\ (t)$$

may be used.

The bulk organic C content of the cooling water was estimated on the basis of measurements of total organic carbon (TOC) in the Potomac River estuary (U.S.E.P.A., 1970), which showed an average value of about 6 mg/ℓ and a range between 11.6 and 0.63 mg/ℓ. Using high fluid velocities to minimize external diffusional resistance, LaMotta (1976) observed the rate of glucose utilization by the biofilm to be independent of bulk liquid concentration in the range between 16 and 2.3 mg glucose-C/ℓ, and exponential. The cooling water value of 6 mg/ℓ is within this range, and we also found exponential kinetics.

From LaMotta's data, a maximum rate of glucose-C consumption of 1856 mg/116 cm^2/day can be computed for a 320-micron film thickness. These values coincide with those projected using the expressions above relating organic C and temperature. At 20°, 25°, and 30° C, the "LaMotta maximum" would be reached at about the 37th day

$$(t_{20} = \frac{\log 1856 - 0.362}{0.0786}),$$

20th day

$$(t_{25} = \frac{\log 1856 - 0.362}{0.1446}),$$

and 14th day

$$(t_{30} = \frac{\log 1856 - 0.362}{0.2106}),$$

respectively. In the presence of 3μ eq/ℓ (172 ppb) BrCl, the maximum rate would be attained after 54 days.

The apparent fouling layer thickness, determined from available data at 24.9° C in the absence of BrCl, was 230 microns (Chapter 5). If film density remained unchanged, the 20-day projected film thickness would be 940 microns, which is about three times the value observed by LaMotta (1976).

Hoehn and Ray (1973), using their own observations and literature data, found that the transition from exponential to linear accretion occurred at a film thickness of about 200 microns. Maier's observations, quoted by Hoehn and Ray (1973), indicated that maximum glucose removal rates were about 10,000 mg glucose-C/day/116 cm^2, occurring at a film thickness of 1100 microns.

TABLE 6-3. ORGANIC C CONSUMPTION BY ACCUMULATED BIOMASS AS A FUNCTION OF TIME AND TEMPERATURE

(mg C/day/116 cm^2)

Time (Days)	Cooling water temperature			
	20° C No BrCl	25° C No BrCl	25° C 3μeq/ℓ(171ppb) BrCl	30° C No BrCl
5	6	12	4	26
10	14	64	8	294
15	35	340	15	3319
20	86	1795	27	3.7×10^4
25	212	9484	50	4.2×10^5

Values are calculated on the basis of the following expressions:

C_{20} = 0.362 + 0.0786 (t). No bromine chloride.

C_{25} = 0.362 + 0.1446 (t). No bromine chloride.

C_{30} = 0.362 + 0.2106 (t). No bromine chloride.

C_{25}^{TOX} = 0.362 + 0.0534 (t). 3μeq/ℓ bromine chloride.

t = time in days

These estimates of maximum film thickness and C consumption assume an adequate supply of oxygen for carbon metabolism. Observations by Hoehn and Ray (1973), Bungay et al. (1969), and Whalen et al. (1969) indicate that oxygen supply frequently becomes rate-limiting when bulk liquid nutrient concentrations are relatively high, and that biomass accretion is rarely limited by oxygen supply when bulk nutrient concentration is less than about 10 mg C/ℓ. In the present investigations, dissolved oxygen values were about 2 mg/ℓ; thus, we may assume that oxygen supply satisfied the demand. Conceivably, lower oxygen levels may well limit the attainable layer thickness to much lower values than those discussed above. Whether low bulk liquid concentrations control biomass accumulation sufficiently to obviate the need for cooling water treatment will largely depend on oxygen transfer characteristics at the liquid-fouling layer interface. Oxygen flux across the interface layer depends on its thickness, which is determined by the flow velocity at the surface.

Fouling Control Strategy

Fouling control procedures can now be considered in the context of the biological events addressed thus far. The control parameters to be considered are the minimum effective dose and the frequency and duration of each application. The control parameters will be explored for the three major biological events outlined above.

First, we may consider prevention of the development of the initial microbial layer, with the expectation that its prevention would inhibit the subsequent attachment of epifaunal organisms and might also reduce or prevent the accumulation of scale deposits.

Since the development of the microbial slime layer is initiated by the aggregation of microbes already present in the cooling water, the initial development most likely is extremely rapid. Whether attachment can be prevented is moot. Removal of the bacterial slime layer with BrCl or Cl_2 apparently is also very difficult. Required dose and contact time estimates may be based on empirical work by Characklis and Dydek (1976). Hypochlorite concentrations of 25 ppm were unable to inactivate an established slime biomass; additions of 250 ppm hypochlorite were required to completely remove the slime layer in 2 hours. The authors suggest that such high concentrations are required because chemical oxidation rather than bactericidal effect is needed for film detachment. Beauchamp (1969) reported that chlorine concentrations of 2 to 3 ppm, applied at 6-hour intervals for 15 min per cycle, prevented slime formation in a power plant cooling system. White (1972) notes that a dose as high as 4 ppm may be required for a few days to remove slime accumulations. In view of the relatively high chlorine levels necessary for removing an established slime layer, and existing environmental restrictions on such high levels, this method of controlling fouling does not look promising, at least for once-through cooling systems.

We may now consider the initial attachment of early life stages of epifaunal animals to the established microbial film and their subsequent exponential growth phase. The rationale for considering this approach is based on the common notion that early life stages are often more sensitive to control by Cl_2 or BrCl than their adult stages. Data in support thereof are provided by a number of investigators. For example, Beauchamp (1969) found that 0.5 ppm

chlorine, applied continuously, prevented fouling by mussels; 2 to 3 ppm applied for 15 min every 6 hours, did not control mussel fouling. Barnacle nauplii exposed for 5 min to 2.5 ppm total (applied) chlorine showed 80% mortality (McLean, 1973). Mangum and McIlhenny (1974) found that it takes several days and sometimes a full week for an adult barnacle to die in a 1 ppm chlorine environment. Straughan (1972) found that barnacle settlement could be controlled by intermittent application of 1 to 5 ppm chlorine once a week for 20 min.

White (1972) indicated that hard-shelled organisms could most effectively be controlled by continuous low-level chlorination that produced 0.25 to 0.5 ppm of free chlorine residuals at the condenser tailpipes. (This implies an applied dose of about 2 to 3 ppm for seawater.) Relini and Oliva (1972) reported that 0.3 ppm continuous chlorination prevented settlement of serpulids; for killing adults, a 1-hour exposure to 600 ppm of chlorine was required.

On the basis of a 2-year investigation, Lamb (1972) concluded that marine fouling can adequately be controlled by continuous application of less than 1 ppm chlorine, and that it was neither necessary to compensate for the chlorine demand of seawater nor to maintain a certain residual in the effluent in order to secure effective control. Investigating the relative merits of intermittent and continuous application, Mangum et al. (1972) showed that a high frequency of application and increased chlorination time per cycle were important factors for achieving effective control. White (1972) indicated that soft-bodied forms (e.g., bryozoa, sponges, tunicates) could be adequately controlled by intermittent chlorination yielding a 1-ppm concentration of free available chlorine at the end of a 1-hour contact time, with a repeat cycle of 8 hours.

From the data presented in previous chapters, it is evident that much lower concentrations than the ones shown above can achieve effective control in an estuarine environment. These results show that continuous low-level application of 0.5 ppm (applied dose) bromine chloride or chlorine can provide adequate protection during the summer, when ambient water temperatures are 25° C and the magnitude of fouling may be considered at its maximum. Lower dose rates were adequate with lower ambient water temperatures.

Our findings also indicate that it is not necessary to maintain a free available residual to achieve effective control. On the basis of White's (1972) definition of halogen demand, we may assume that the applied dose was less than the demand, and, on the basis of the ammonia content of the cooling water, it appears likely that the chemical species present during cooling system transit were chloramines and bromamines. These compounds apparently are effective fouling inhibitors.

Continuous application of bromine chloride or chlorine is considered a more effective control strategy than intermittent for the following reasons. During the exponential phase, biomass accretion is controlled by internal biological processes. Inhibition of those growth-regulating processes ought to be the most effective way of exerting control. The alternative to the control of the biological processes would be to meet the oxidant demand of the cooling water by chemically oxidizing nutrient constituents. This would limit growth by reducing the flow of energy and utilizable organic carbon from the bulk of the liquid to the biomass. Since energy and organic carbon are available in excess of need, oxidant addition would have to be adjusted to remove just that excess before an energy and carbon deficiency would be achieved.

Control of bioaccretion by continuous low-level application thus appears the most promising approach, unless destruction through chemical oxidation and subsequent removal of the biomass is the objective.

CHAPTER 7

DEVELOPMENT OF A BIOFOULING CONTROL MODEL AND ITS APPLICATION

Information on the effectiveness of bromine chloride in controlling glass panel fouling appears adequate to integrate the important effects of temperature and the responses of marine fouling organisms to bromine chloride into a single framework. However, to validate the model's application to the power plant cooling system, we must demonstrate that fouling control of the system is truly reflected by the glass panel fouling assays.

In the power industry, the effectiveness of cooling water treatment is routinely evaluated on the basis of condenser performance. Similar data were used here to relate glass panel fouling control to cooling system fouling control.

Condenser performance was inferred from the condenser "cleanliness factor," computed in accordance with the standard procedures used by steam plants in conducting condenser performance tests. Data on condenser performance, supplied by power plant personnel, are recorded in Table 7-1. The data, which were average values calculated on the basis of measurements taken once a day, showed little change over the 2-month period. On the basis of these data and opinions expressed by power plant personnel, we assumed that cooling system performance remained normal during the two periods when bromine chloride was used instead of chlorine, and, therefore, that glass panel fouling assays adequately reflected cooling system fouling control.

An additional assumption made was that chemical composition of the source water did not change drastically. Small variations in the so-called chlorine demand of the intake cooling water were ignored; to the extent that they occurred in the Potomac River estuary at the Morgantown site, it was assumed that they were not important in terms of fouling control when the cooling water was treated continuously.

MODEL DEVELOPMENT

A linear model structure was used to describe the relationship between biofouling, temperature, and concentration of bromine chloride residuals. The limited data output of the field trials did not permit consideration of interaction terms and more complex modeling procedures. As a first approximation, we postulate the following form:

TABLE 7-1. CONDENSER PERFORMANCE DURING AUGUST AND SEPTEMBER 1976 FOR CONDENSER HALF-SHELLS A AND B

Period	Biocide* (ppm)	Condenser Performance** A	Condenser Performance** B	Standard deviation A	Standard deviation B	Number of samples A	Number of samples B
8/1/76 to 8/10/76	Cl_2 0.35	75.07	80.96	3.07	6.66	7	7
8/11/76 to 8/28/76	BrCl 0.55	72.88	69.98	3.48	7.50	15	15
9/1/76 to 9/31/76	BrCl 0.15	73.91	68.51	7.52	7.22	20	20

*Applied feed rate. Application was continuous with the exception of short off-periods for maintenance. Data from Unit #1. Data supplied by Potomac Electric Power Company, Washington, D.C. 20006.

**Condenser performance is the actual heat transfer rate expressed as % of the expected heat transfer rate. For details see "Standards for Steam Surface Condensers"; Heat Exchange Institute; New York, N.Y. 10017, Sixth Ed, 1970.

$$FC = f\ (T,\ [TOX])$$

where FC = the coefficient of fouling (day^{-1})

T = the water temperature (^{o} C)

$[TOX]$ = the concentration of bromine chloride-induced oxidants, ($\mu eq/\ell$)

and assume that the function can be expressed as:

$$FC = A \cdot T + B \cdot [TOX] + C$$

where A, B, and C are constants (independent of T or [TOX]).

The ideal way of determining values for A, B, and C is by multiparameter regression. However, data at hand were insufficient for that purpose. Instead, we selected values for A and B from the expression for linear dependency of FC on T and FC on [TOX] , respectively, as shown in Chapter 5, Eqs. 5-1 and 5-2. Thus,

$$A = 0.0132 \text{ and } B = -0.0323\ .$$

The value of C (Eq. 7-1, above) can be determined by substituting FC = 0.149, A = 0.0132, and T = 24.9^{o} C in Eq. 7-1 for [TOX] = 0. Thus, C = -0.1797. The postulated conceptual model takes the following form:

$$FC = 0.0132 \cdot T - 0.0323\ [TOX] - 0.1797 \qquad (7\text{-}2)$$

From this expression, we calculated regression lines for relationships between fouling and oxidant levels for water temperatures of 29.4^{o} C, 24.9^{o} C, and 22.9^{o} C; plots of the observed dose-response interactions are shown in Figure 5-5.

With the exception of the observations made at 22.9^{o} C (Figure 5-5, squares), where data were limited, all values were used for model formulation. To test the validity of the model would require measurements of fouling material accretion over a range of environments and temperatures (at least 10° C) at biocide levels that inhibit the fouling from 20% to 70% of control values. Presently, such data are not at hand.

APPLICATION OF THE PROPOSED MODEL TO MORGANTOWN SES

The proposed computational methodology permits evaluation of bromine chloride dose requirements for fouling control at the Morgantown power plant, i.e., the minimum amount of continuously applied biocide required for maintaining cooling system performance. The factors to be considered are water temperature, "permissible" fouling coefficient, and the decay properties of the biocide in the cooling system.

The selection of a permissible fouling coefficient must be somewhat arbitrary because the relationship between cooling system performance and glass panel fouling (FC) has not been ascertained over a full season or over the normally occurring temperature range. One factor used in the selection of a permissible FC was the observation that FC values of 0.06 and 0.09 allowed efficient plant operation over a 15-day period during the summer of 1976. (The 0.06 and 0.09 values were observed at the circulator and condenser station, respectively; see Table 5-3.) Another factor considered was the common belief that cooling water treatment at the present site was not necessary until ambient water temperatures reached about 18°. The predicted FC value at 18° C is about 0.06 day^{-1} (see Figure 5-5b). On the basis of these two qualitative criteria, we assumed that the minimum bromine chloride dose needed to permit efficient plant operation was that where FC = 0.06.

When the 0.06 value is inserted in Eq. 7-2, the expression can be rearranged to give:

$$[TOX]_{condenser} = 0.41 \cdot T - 7.42 \qquad (7\text{-}3)$$

This expression can then be used to calculate minimum [TOX] values for cooling water temperatures in the range of 18° C to 30° C.

The two additional factors to be considered for determining the minimum biocide dose rate are the "immediate demand" of the incoming cooling water and the subsequent oxidant decay as a function of contact time. These factors depend on site-specific conditions and the configuration of the cooling system. For a given site, the immediate biocide demand of the cooling water may have short- and long-term components, depending on its content of oxidizable inorganic reductants (ferrous, manganous, nitrite, sulfide, and sulfite), organic compounds (phenols, aromatics, and amino acids), and ammonia, which may vary tidally, diurnally, and seasonally.

The immediate demand may also be a function of the amount of biocide initially added to the cooling water. As discussed earlier, the initial decay of added biocide was extremely rapid and could only be estimated from our field observations. Observations of residual oxidant levels at our first monitoring station after injection (circulator monitoring stations) indicated that about half of the injected oxidant concentration was consumed to satisfy the immediate demand before the cooling water reached the circulators. Subsequent decay of residual oxidant followed predictable first-order kinetics. Both the immediate demand and subsequent oxidant consumption were accounted for as described below.

Since condenser cleanliness is paramount to efficient performance of the cooling system, the oxidant level during condenser passage was considered critical to the overall performance of the system. To maintain the desired level of oxidant at this point in the system, the decay equation

$$\ln [TOX]_{circulator} = \ln [TOX]_{condenser} + 0.126 \cdot t \qquad (7\text{-}4)$$

was used to determine the decline in oxidant concentration as a function of contact time in the system between the circulators and the condensers. The quantity t depends on the number of functioning circulators. With one, two, or three circulators in operation, t equals 2, 1, or 0.67 min, respectively. Because of the three-phase decay characteristics discussed earlier, variation in t is restricted to values between 0.5 and 10 min.

To account for the immediate demand consumption, the [TOX] at the circulator was multiplied by a factor of two. Microequivalents oxidant were then multiplied by 57.5 to convert to micrograms of oxidant. The required minimum dose was calculated in terms of weight of bromine chloride per day, based on the volume flow of the cooling water and t as defined above.

By combining Eq. 7-3 and Eq. 7-4, we obtain:

$$\ln [TOX]_{circulator} = \ln (0.41\ T - 7.42) + 0.126 \cdot t\ .$$

We can calculate the injection concentration from the following expression:

$$\ln(C_i) = \ln (0.41\ T - 7.42) + 0.126 \cdot t - 2.16 \qquad (7\text{-}5)$$

where C_i is the concentration of biocide in ppm required at point of injection to keep FC at the condenser from exceeding 0.06 day^{-1}.

To calculate the minimum injection dose (D_i) in kg and lb of bromine chloride per day, expressions Eq. 7-6a and 7-6b, respectively, may be used:

$$\ln (D_i) = \ln (0.41\ T - 7.42) + \ln (V) + 0.126 \cdot t + 2.32 \qquad (7\text{-}6a)$$

$$\ln (D_i) = \ln (0.41\ T - 7.42) + \ln (V) + 0.126 \cdot t - 0.47 \qquad (7\text{-}6b)$$

where V is the cooling water volume flow in m^3/sec (7-6a) and cfs (7-6b). In Table 7-2, we record some typical dose rates and injection concentrations for BrCl, using cooling system design characteristics applicable to the Morgantown SES and an ambient temperature range appropriate for biocide addition.

TABLE 7-2. MODEL CALCULATIONS OF MINIMUM BROMINE CHLORIDE DOSE RATES (D_i) AND CONCENTRATION OF BROMINE CHLORIDE (C_i)* AT POINT OF INJECTION FOR A RANGE OF WATER TEMPERATURES AND COOLING WATER CONDENSER FLOW RATES

Ambient water temp. (°C)	$V = 10.36 m^3/sec$, $V = 370$ cfs, $t = 2$ min			$V = 20.44 m^3/sec$, $V = 730$ cfs, $t = 1$ min			$V = 30.80 m^3/sec$, $V = 1100$ cfs, $t = 0.67$ min		
	C_i (ppm)	D_i $\left(\frac{kg}{day}\right)$	D_i $\left(\frac{lb}{day}\right)$	C_i (ppm)	D_i $\left(\frac{kg}{day}\right)$	D_i $\left(\frac{lb}{day}\right)$	C_i (ppm)	D_i $\left(\frac{kg}{day}\right)$	D_i $\left(\frac{lb}{day}\right)$
20	0.116	106	234	0.102	184	406	0.098	266	586
21	0.177	161	355	0.156	281	619	0.149	406	895
22	0.237	217	478	0.204	377	831	0.201	546	1204
23	0.298	273	602	0.263	474	1045	0.252	685	1510
24	0.359	328	723	0.317	571	1259	0.304	825	1819
25	0.420	383	844	0.370	668	1473	0.355	965	2127
26	0.481	439	968	0.424	764	1684	0.406	1105	2436
27	0.542	495	1091	0.478	861	1893	0.458	1244	2743
28	0.602	551	1215	0.531	958	2112	0.509	1384	3051
29	0.663	606	1336	0.585	1055	2326	0.561	1524	3360
30	0.724	662	1459	0.638	1151	2538	0.612	1664	3668

*C_i is defined as the minimum bromine chloride requirement at point of injection to prevent the coefficient of fouling (FC) at the condenser from exceeding 0.06 day^{-1}.

MODEL VALIDATION

In its present form, the "minimum biocide model" provides a reasonable approximation of the minimum bromine chloride demand at the Morgantown site. The validity of the model for other environmental settings and other oxidant-producing biocides, such as chlorine, can be tested in two ways.

First, historical information on biocide use, collected under a variety of operating conditions and encompassing fresh and saline waters of known water quality, can be compared to model calculations. Such information, if it is based on comprehensive monitoring and includes some measure of residual fouling or condenser performance, ought to suffice for model calibration and verification.

The second, and most direct, method of calibrating the model and establishing its credibility is to collect dose-response data in representative environments over a range of ambient temperatures, providing a basis for comparisons between empirical observations and model calculations. Aquatic environments of special interest are the following:

- Freshwater environments with relatively high ammonia content. Data should be collected for both chlorine and bromine chloride as fouling control agents; bromine chloride, which forms reactive amines with ammonia, might be the more suitable biocide here, especially if chlorine forms less reactive, slower decaying chloramines. The difference in chemistry will affect the oxidant term B [TOX], Eq. 5-1, in the model; the difference in decay could affect the dose required (D_i in Eq. 7-6) to achieve adequate fouling control. Since the data collected would be peculiar to freshwater fouling species and freshwater communities and may affect both model terms, a freshwater model may be indicated.

- A low salinity (oligohaline or mesohaline) estuarine environment, as exists at the Morgantown site during the summer. In this region, where salinity varies from fresh water to about 10 ppt, the abundance and biotype of potential fouling biota are governed primarily by salinity and may oscillate within wide margins. Dose-response data collected at such a site would therefore cover a wide spectrum of estuarine species and could disclose species-specific differences in toxicity and temperature responses. In terms of model verification, data collected at a site such as Morgantown are essential for another reason. Morgantown is situated at the interface region where fresh and salt waters mix, and where freshwater run-off and estuarine dynamics may cause large shifts in salinity within short periods of time. Concurrent changes in the concentration of water constituents may affect the initial oxidant demand of the cooling water and alter decay properties of chlorine-induced oxidants. Both the biological factors outlined above and the chemical factors emphasized here could affect model parameters (A and B in Eq. 7-1) and indicate the need for an estuarine fouling control model.

- An intermediate salinity zone with salinity values varying between 10 and 20 ppt. A region could be selected which would be representative of both a marine and an estuarine environment in terms of biofouling potential. Dose-response data from such an environment would be most desirable for model calibration and verification since experience in Great Britain has shown that continuous low-level application of chlorine in such an environment provides an efficacious biofouling control methodology for once-through cooling systems.

- A marine environment with relatively high amounts of bromine (20 to 40 ppm). Both biological and non-biological factors of this environment could affect model parameters. The relative importance of species-specific effects could be examined by calibrating the basic model with dose-response data collected at a site where a broad spectrum of marine biota and communities is represented. The relatively high amounts of bromine present (in contrast to the two previous environments) could significantly modify chlorine-induced oxidant formation and decay, thus affecting the oxidant term of the model. Comparison of model calculations and empirical data could reveal the need for the formulation of a model sensitive to the specific characteristics of a marine environment.

Ultimately, the validity of the model will be determined by its utility in establishing a fouling control strategy which meets the specific demands of the electrical generating industry and limits environmental risks to an acceptable minimum.

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APPENDIX A

OXIDANT DECAY IN CHLORINATED AND CHLOROBROMINATED ESTUARINE COOLING WATER

Contents

Aqueous Chemistry of Cl_2 and BrCl in Low-Salinity Cooling Water

Test Procedures

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OXIDANT DECAY IN CHLORINATED AND CHLOROBROMINATED ESTUARINE COOLING WATER

AQUEOUS CHEMISTRY OF Cl_2 AND BrCl IN LOW-SALINITY COOLING WATER

Decay constants for Cl_2 and BrCl-induced oxidants have been calculated from observations and are reported in Table A-1. We have also attempted to correlate the formation and decay of halogen derivatives with ammonia and salinity concentrations in estuarine water. Please note that some of the conclusions reached are preliminary. Detailed test procedures and raw data on water quality and oxidant decay are given for further information.

The inorganic forms of dissolved Cl_2 and BrCl that may occur under the conditions prevailing during the field investigations can be shown schematically as follows:

- Chlorine

$$\left.\begin{array}{ll} Cl_2 + H_2O \rightarrow HCl + HOCl \text{ (hypochlorous acid)} \\ HOCl \rightarrow H^+ + OCl^- \text{ (hypochlorite ion)} \end{array}\right\} \text{"free chlorine"}$$

$$\left.\begin{array}{ll} HOCl + NH_3 \rightarrow H_2O + NH_2Cl \text{ (monochloramine)} \\ NH_2Cl + HOCl \rightarrow H_2O + NHCl_2 \text{ (dichloramine)} \\ NHCl_2 + HOCl \rightarrow H_2O + NCl_3 \text{ (trichloramine)} \end{array}\right\} \text{"combined chlorine"}$$

- Bromine Chloride

$$\left.\begin{array}{ll} BrCl + H_2O \rightarrow HCl + HOBr \text{ (hypobromous acid)} \\ HOBr \rightarrow H^+ + OBr^- \text{ (hypobromite ion)} \end{array}\right\} \text{"free bromine"}$$

$$\left.\begin{array}{ll} HOBr + NH_3 \rightarrow H_2O + NH_2Br \text{ (monobromamine)} \\ NH_2Br + HOBr \rightarrow H_2O + NHBr_2 \text{ (dibromamine)} \\ NHBr_2 + HOBr \rightarrow H_2O + NBr_3 \text{ (tribromamine)} \end{array}\right\} \text{"combined bromine"}$$

These reactions do not include organic derivatives and other forms of oxidized halogen such as halite, halate, or perhalate (XO_2^-, XO_3^-, XO_4^- where X represents Cl or Br). Moreover, near neutral pH, Cl_2 and BrCl do not exist in the unhydrolyzed form. Therefore, we will proceed under the simplifying assumption that the forms of halogen in our study were either "free" or "combined" as defined above. Furthermore, since the concentration of ammonia in the water exceeded that of oxidized halogen in most cases during this study, we will assume that the most prevalent forms of oxidized halogen were the mono- and dihalamines (see also White, 1972*).

Estuarine water of about 5 parts per thousand (ppt) salinity (a typical salinity at our experimental site) contains about 10 parts per million (ppm) bromide (Br^-) (Culkin, 1965). The following reaction for the oxidation of Br^- by HOCl has an equilibrium constant of 4×10^5 (Cotton and Wilkinson, 1962) and a second-order reaction rate constant of 1.8×10^5 liter/mole-minute (Farkas et al., 1949)

$$HOCl + Br^- = HOBr + Cl^- \qquad \text{(A-1)}$$

At this salinity, with the Br^- concentration much larger than that of HOCl (> 0.5 ppm) added during chlorination, it follows that there should be a 50% conversion of HOCl to HOBr about every 2 seconds near pH 7.5 (an average pH at the experimental site).

However, there are competing reactions which may prevent a quantitative conversion of oxidant from chlorine to bromine forms. Weil and Morris (1949) have described the kinetics of monochloramine formation:

$$HOCl + NH_3 = NH_2Cl + H_2O \quad . \qquad \text{(A-2)}$$

Their data indicate that, under conditions like those found in cooling water at the experimental site (pH 7 to 7.5; total ammonia and total oxidized halogen concentrations in the micromolar range; ammonia concentration greater than [TOX]), the half-life of free chlorine ($HOCl + OCl^-$) is less than 3 seconds. Since reactions (A-1) and (A-2) proceed with approximately equal rapidity, it is not possible to determine with any confidence which reaction will predominate.

Monochloramine could in turn be converted to monobromamine in estuarine water via the reaction:

$$NH_2Cl + Br^- = NH_2Br + Cl^- \quad . \qquad \text{(A-3)}$$

We do not know the kinetics of this reaction, but it is known that iodide (I^-) is not quantitatively oxidized by combined chlorine at pH values above 4.5 (APHA, 1975). Since iodide oxidation should proceed more easily than

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* For literature cited in this appendix, see List of References included in the main body of this report.

bromide oxidation, it may be that combined chlorine is stable in the presence of bromide in the pH range of natural waters.

Eppley et al. (1976), using a semiquantitative technique, showed that considerable amounts of bromine were formed upon chlorination of seawater. However, their conditions do not necessarily apply to Morgantown. For example, at Morgantown, the water is less saline (and therefore has less bromide) and contains more ammonia. Wackenhuth and Levine (1974) observed that adding BrCl to saline cooling water with high ammonia content resulted in lower oxidant levels in discharged water than did adding Cl_2.

The analytical method used in our study -- amperometric back-titration of solutions containing excess potassium iodide (KI) and phenylarsine oxide (PAO) at pH 4 -- detects total dissolved oxidant without discriminating between chlorine or bromine or among the various forms of each oxidized halogen. Therefore, we have reported our results in terms of microequivalents per liter (μeq/ℓ) of Total Oxidant (TOX)*. Our only chemical method of differentiating between Cl_2- and BrCl-treated solutions is to observe a difference in the decay characteristics between the induced oxidants. Although this is a rudimentary way of examining what are probably very complex chemical interactions, differences in decay characteristics do imply differences in the chemical speciation (all other decay-affecting parameters being equal), and the environmental benefits of BrCl versus Cl_2 can be inferred from such differences.

TEST PROCEDURES

Data for the characterization of TOX decay were obtained by one of the following test procedures.

1) Two gallons of halogenated water were collected in a bucket at a cooling water circulating pump. At predetermined intervals, 500-ml aliquots were transferred to bottles containing KI, PAO, and acetate buffer. This process essentially preserved the aliquot so that a later back-titration with I_2 yielded the TOX concentration at the time the aliquot was "pickled."

   This procedure was used to quantify TOX decay in 14 cases where BrCl was the added halogen and in 21 cases where Cl_2 was used. The same plastic bucket was used for all decay studies after being thoroughly cleaned and soaked overnight in a concentrated chlorine solution. The concentration of TOX was varied by changing the feed rate of halogen to cooling water.

2) A highly concentrated solution was obtained from the BrCl injection line, diluted with cooling water, and decay-monitored as in (1) above. Eight decay curves were obtained.

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* As a point of reference, it should be noted that 1 μeq/ℓ TOX is equivalent to 35.5 parts per billion (ppb) Cl_2 or 57.7 ppb BrCl.

3) Since plumbing problems precluded the collection of concentrated Cl_2 solutions from an injection line, commercial bleach was used as a Cl_2 source with a technique similar to (2) above to obtain six Cl_2 decay curves.

4) None of the above procedures yielded a value for a TOX concentration at time zero. Therefore, in three cases, identical volumes from a single cooling water source were spiked with identical aliquots of $Ca(OCl)_2$ solution. One of the water samples contained the pickling reagents prior to the $Ca(OCl)_2$ addition while the other samples were pickled at various times after that addition.

These procedures yielded the most useful decay data; the relationship between TOX concentration and time was well-defined, and solution conditions did not vary during a decay period. To obtain a relationship between TOX level and location, TOX decay was also observed by monitoring concentrations along the flow of halogenated cooling water as it moved through the intake conduits, the condenser, and down the discharge canal. However, this information was not as useful as "bucket data" in comparing halogens because (1) the relationship between time and location was not precise, and (2) in passing through the cooling system, TOX can be lost via the oxidation of fouling material on condenser surfaces.

Cl_2- AND BrCl-INDUCED OXIDANT DECAY PATTERNS

Figure A-1 shows the decay of TOX observed when $Ca(OCl)_2$ was added to estuarine cooling water; the fourth procedure above was used so that the TOX concentration at zero time was known. This figure illustrates the pattern which was routinely observed regardless of whether Cl_2 or BrCl was the added halogen. Initially, there was a very fast decay during which almost 50% of the TOX was lost during the first 30 seconds after halogen addition. Next, there was a fast decay which extended for 10 to 15 minutes; and finally, there was a period during which decay was so slow that often no difference could be seen between TOX levels at 30 and 60 minutes. In the few cases where TOX decay was followed beyond 60 minutes, the observed concentration change with time usually proved to be very small.

The second and third decay phases were always in evidence. The very fast initial decay was observed only when the fourth test procedure was used. However, comparisons of calculated TOX levels at the point of halogen injection with levels observed at the circulating pumps indicated that approximately 50% of both BrCl- and Cl_2-derived TOX was lost within about 30 seconds of halogen introduction to cooling water.

Figure A-2 is a transformation of Figure A-1 where the logarithm of TOX concentration is plotted against time. This plot would be a single straight line if decay were ideal first-order in accordance with the equation:

$$\frac{d\,[TOX]}{dt} = -k\,[TOX] \quad . \qquad \text{(A-4)}$$

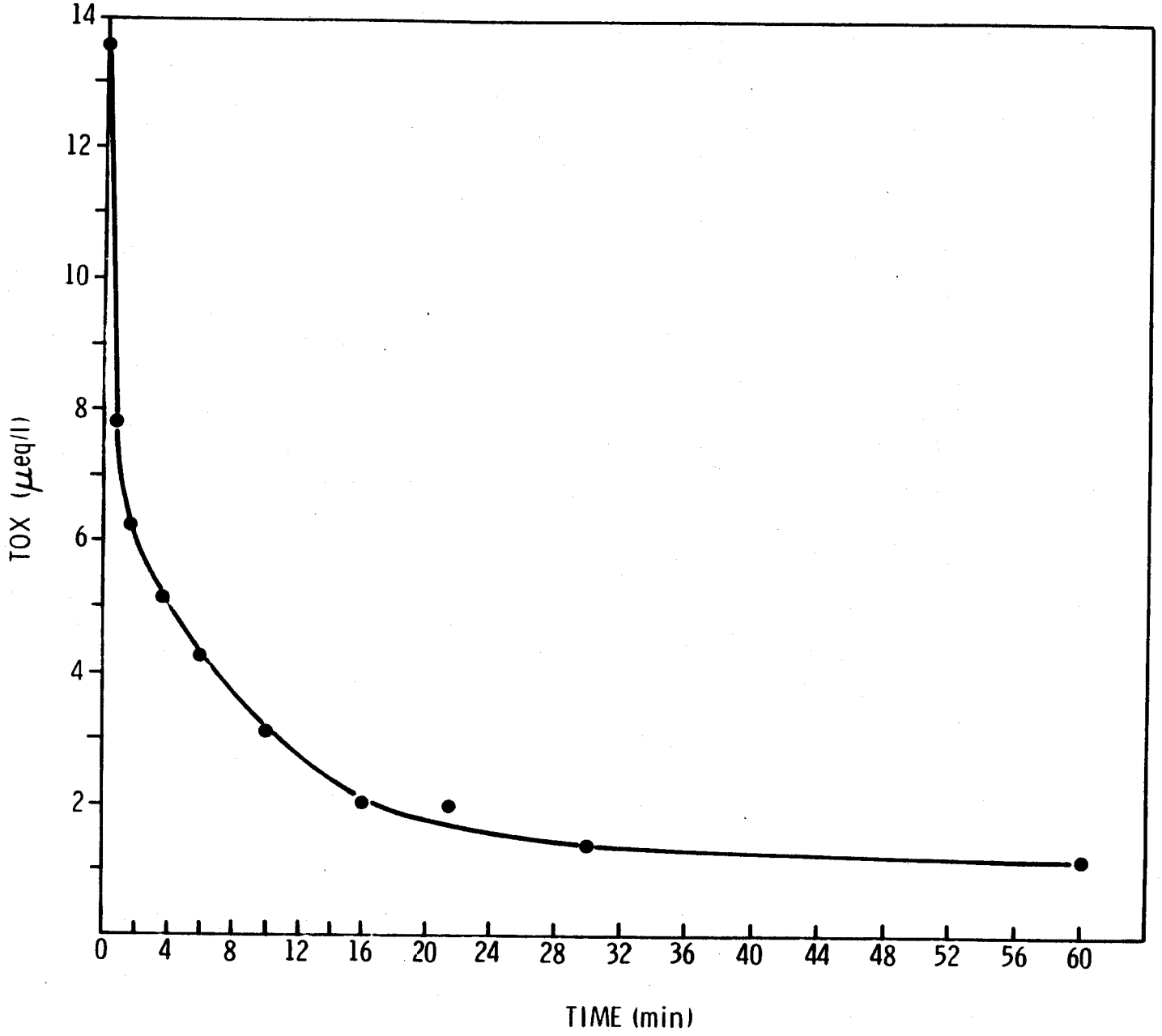

Figure A-1. Time-dependent decay of TOX for $Ca(OCl)_2$ added to estuarine water. This curve is representative of all TOX decay patterns observed during this study.

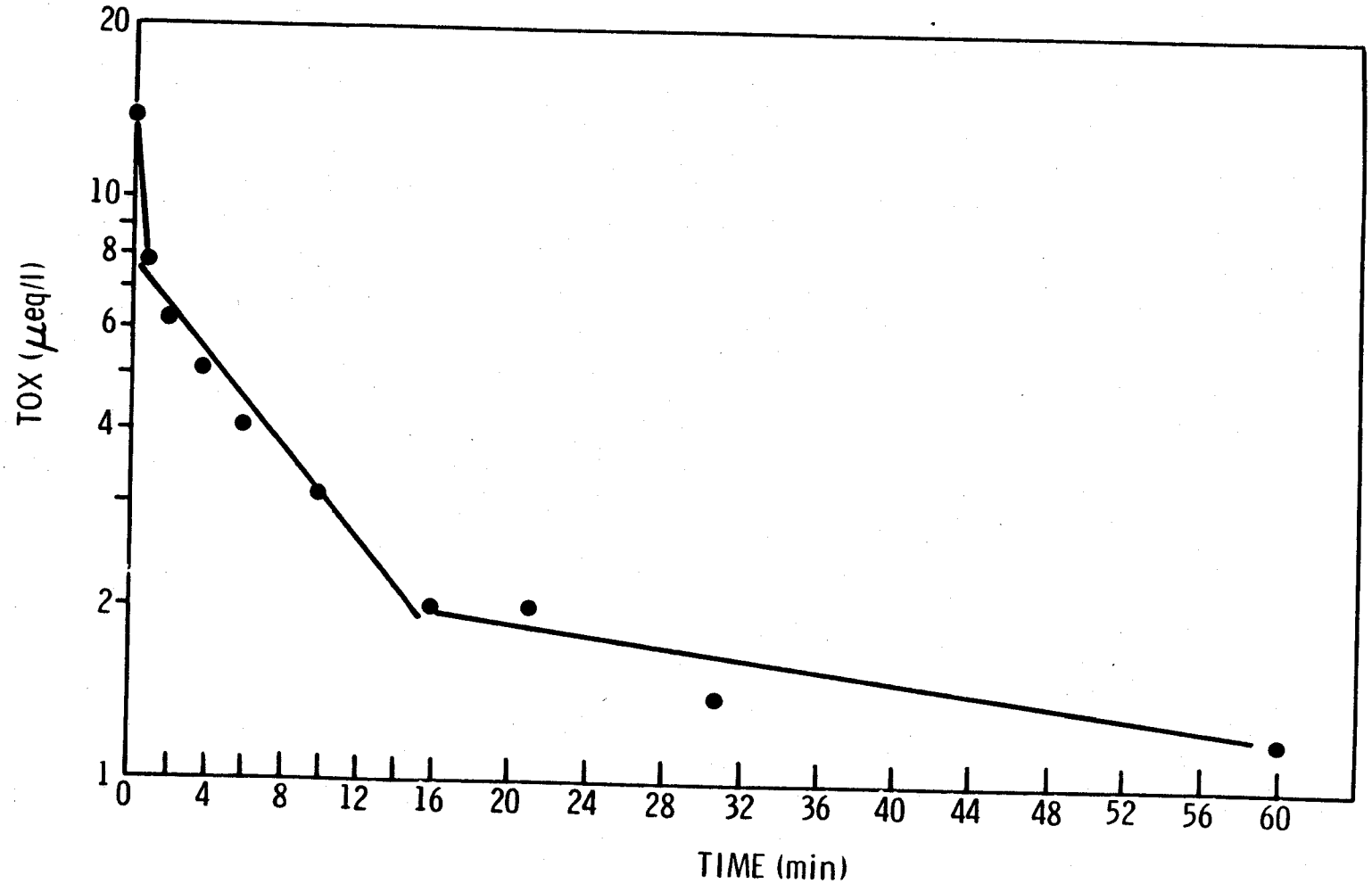

Figure A-2. Semi-logarithmic transformation of Figure A-1.

What is seen, though, are three separate lines corresponding to the three distinct decay periods indicated above. More complex transformations, consistent with higher order decay models of the form:

$$\frac{d\,[TOX]}{dt} = -k\,[TOX]^{a} \qquad \text{(A-5)}$$

where a > 1, do not yield curves with any less than three separate phases. On the other hand, simple zero-order decay cannot be used to describe the data since the rate of decay was observed to increase with increasing TOX concentration.

The very fast initial decay is not consistent with any model which describes the subsequent loss of TOX. As discussed in the section on Analytical Methods, this initial loss of TOX may be partly due to the inability of our analytical method to quantitatively measure all the TOX dissolved in saline solutions. However, a loss of 50% of TOX within 30 seconds of halogen addition to estuarine water is much larger than the 5 to 15% loss observed using saline solutions. Therefore, most of the initial decay of TOX is real and occurs via reactions which are much faster than those accounting for subsequent decay.

The decay after the initial 30 seconds is characteristic only of TOX in estuarine water and has been fitted to a two-phase quasi first-order model. From measurements taken from about 0.5 to 1 minute up to 10 to 15 minutes after halogen injection, we obtained five or six data points with a coefficient of determination (r^2) between ln [TOX] and time of > 0.96. The line defined by these points could not be extended indefinitely. The slow phase that followed also appeared to have first-order kinetics, with decay rates appearing to depend on TOX concentrations. However, this slow phase has not been very well quantified; it is described by only four (sometimes five) measurements over a 50-minute period, and r^2 between ln [TOX] and time is often low.

Table A-1 summarizes all decay data in terms of k_1 (decay constant for the 10- to 15-minute fast decay) and k_2 (decay constant for the slow decay). Coefficients of determination (r^2) are given for the k_2 values to indicate that these values are not always well defined. The raw data upon which these calculations are based are included as Table A-5.

FACTORS AFFECTING OXIDANT DECAY RATES

As can be seen from Figure A-3, where all derived k_1 constants are plotted against their dates of determination, there is a range of decay constants for both halogens. Therefore, before comparing decay constants between halogens, it is necessary to account for the variation in decay rate for a single halogen.

First, it should be noted that the fitting of the observations to a first-order decay model does not imply that decay rate is determined solely by TOX concentration. In general, there are two groups of cooling water

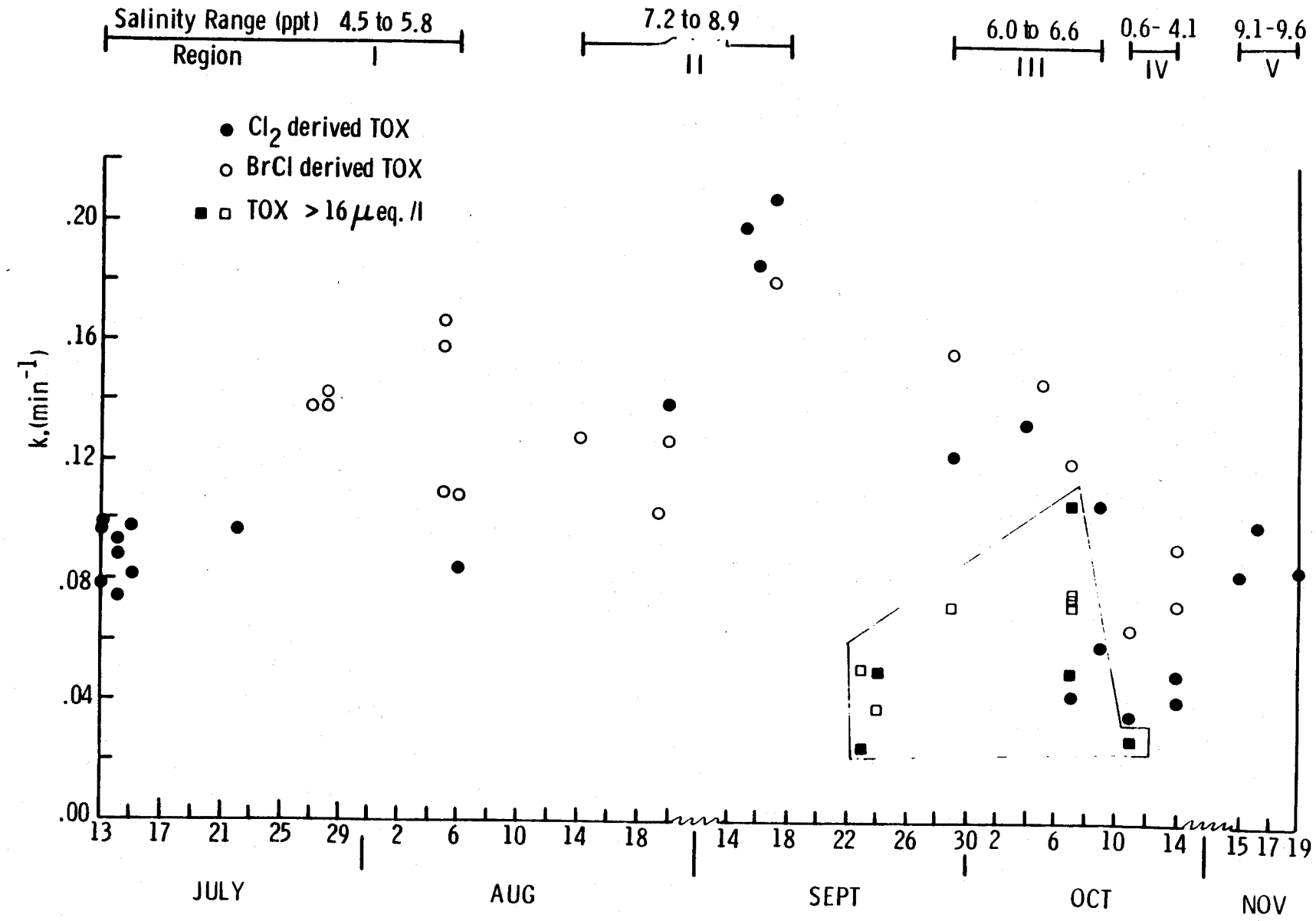

Figure A-3. First-order decay constants, k_1, plotted against their date of determination. Constants within box have been excluded from overall discussion of decay. See text for meaning of Regions I-V.

Table A-1. SUMMARY OF TOX DECAY DATA CALCULATED FOR A QUASI-FIRST ORDER MODEL

Explanation of Columns (left to right)

Run#	Position of a single decay determination within temporal sequence of all determinations. These numbers will aid in locating raw decay data in Table A-5.
Date/Time	Self-explanatory
$[TOX]_1$	The first concentration to fit the decay model. Except for runs 50, 51, and 52, it is the first measured concentration. The precision of TOX measurements is $\pm$ 0.5 μeq/ℓ (2 ppb Cl_2), except for some cases where the precision is $\pm$ 0.5 μeq/ℓ due to the lower volumes titrated.
k_1	Quasi-first order decay constant (slope of ln [TOX] vs time) for fast decay phase
T_F/[TOX]	Time and [TOX] for last point of fast decay and first point of slow decay period
$k_2(r^2)$	Decay constant for slow decay and r^2 for correlation of ln [TOX] with time. No constant was calculated if less than four data points were available.
$[TOX]_{60}$	The TOX concentration at 60 $\pm$ 10 minutes. (One hour after halogen addition, this 10-minute variation has no significant effect on TOX concentration.)
^oC, S (ppt) O_2, pH	Water quality parameters at time of cooling water collection (measured automatically)
$[NH_3]$	Ammonia concentration ($\pm$ 7%) measured within one hour of cooling water collection (Soloranzo, 1969)
Proc.	Procedure 1, 2, 3, or 4, as stated above under 2. TEST PROCEDURES

Table A-1 (continued). SUMMARY OF TOX DECAY DATA CALCULATED FOR A QUASI-FIRST ORDER MODEL

Run #	Date/Time	HALOGEN ADDED: Chlorine										
		$[TOX]_1$ (μ eq /ℓ)	k_1 (min^{-1})	$T_F/[TOX]$	k_2 (min^{-1}) (r^2)	$[TOX]_{60}$ (μ eq/ℓ)	Temp. (^oC)	Salinity (ppt)	O_2 (ppm)	pH	NH_3 (μ M / ℓ)	Proc.
	JULY											
1	13/0940	4.79	0.097	14/1.32	0.006 (0.99)	0.96	25.0	4.8	3.0	6.9	10.2	1
2	13/1150	5.97	0.078	6/3.97		1.04	25.0	4.5	3.6	7.0	7.6	1
3	13/1345	6.14	0.097	12/2.06	0.011 (0.86)	1.15	25.0	4.4	4.0	7.1	6.5	1
4	14/0950	10.37	0.074	17/3.01		1.32	24.5	5.1	3.3	7.0		1
5	14/1230	10.39	0.088	12/3.80	0.019 (0.94)	1.55	25.0	5.1	3.6	7.0	11.8	1
6	14/1405	9.72	0.093	12/3.38	0.014 (0.91)	1.55	25.5	4.9	3.7	7.0	9.2	1
7	15/0855	5.49	0.082	13/1.94	0.010 (1.00)	1.01	24.5	4.8	3.2	6.9	15.1	1
8	15/1115	6.87	0.098	11/2.42	0.018 (0.96)	0.90	24.0	4.5	4.7	6.7	9.3	1
9	22/0930	7.63	0.097	17/1.61	0.012 (0.76)	0.96	26.0	5.7	1.6	6.9		1
	AUGUST											
17	6/1150	4.48	0.085	18/0.99	0.010 (0.74)	0.65	26.0	4.5	1.4	7.0	9.0	1
20	20/1310	6.82	0.140	16/0.76	0.025 (0.98)	0.23	24.5	8.9	1.8	7.7	7.5	1
	SEPTEMBER											
22	15/1300	4.34	0.199	9/0.68	0.017 (0.89)	0.28	23.0	8.4	4.1	7.6	3.7	1
23	16/1350	4.82	0.186	9/0.79			23.0	7.8	4.0	7.7	4.5	1
25	17/1630	3.72	0.209	8/0.65	0.052 (0.99)	0.08	23.5	7.2	4.7	7.7	3.2	1
26	23/1230	67.2	0.025	12/50.3	0.008 (0.99)	35.1	22.0	8.1	3.1	7.7	3.4	3
29	24/1525	18.1	0.051	8/12.1	0.010 (0.86)	6.5	22.5	7.4	3.5	7.8	3.8	3
32	29/1635	6.85	0.123	9/2.20	0.026 (0.97)	0.62	21.0	6.0	4.0	7.7	6.6	1

Table A-1 (continued). SUMMARY OF TOX DECAY DATA
CALCULATED FOR A QUASI-FIRST ORDER MODEL

Run #	Date/Time	HALOGEN ADDED: Chlorine										
		$[TOX]_1$ (μeq /ℓ)	k_1 (min^{-1})	T_F/[TOX]	k_2 (r^2) (min^{-1})	$[TOX]_{60}$ (μeq/ℓ)	Temp. (^oC)	Salinity (ppt)	O_2 (ppm)	pH	NH_3 (μM / ℓ)	Proc.
	OCTOBER											
33	4/1025	5.32	0.134	14/0.99	0.015 (0.94)	0.48	20.0	6.4	4.2	7.5	12.8	1
36	7/1140	60.9	0.107	11/19.8	0.017 (0.95)	8.3	20.0	6.2	4.2	7.6	5.8	3
38	7/1555	26.0	0.050	9/17.5	0.009 (0.95)	10.1	20.0	6.3	4.0	7.6	6.7	3
40	7/1910	7.94	0.042	10/5.38	0.006 (0.95)	3.94	19.5	7.1	4.0	7.6		3
41	9/1045	5.27	0.105	16/1.13			19.5	6.5	3.9	7.4	4.2	1
42	9/1210	6.31	0.059	11/3.52	0.007 (0.97)		19.5	6.4	3.9	7.5	4.0	3
43	11/1115	16.59	0.028	16/10.73	0.011 (0.99)	6.68	19.0	0.9	5.0		11.8	1
44	11/1230	4.85	0.036	13/3.10	0.006 (0.93)	2.23	19.0	0.6	5.2		11.4	1
46	14/1005	6.73	0.050	15/3.30	0.008 (0.88)	2.20	18.0	4.1	3.2	7.4	> 100*	1
49	14/1435	7.01	0.041	14/4.17	0.006 (0.94)	3.07	18.0	3.8	3.9	7.6	13.6	1
	NOVEMBER											
50	15/1415	3.15	0.084	9/1.55								4
51	16/1200	7.97	0.101	12/2.23			18.0+	9.1		7.6		4
52	19/1230	7.77	0.085	16/2.00		1.21	17.5+	9.6		7.7		4

* Ammonia added
\+ Temp. higher than ambient since water taken from discharge canal

Table A-1 (continued). SUMMARY OF TOX DECAY DATA CALCULATED FOR A QUASI-FIRST ORDER MODEL

Run #	Date/Time	HALOGEN ADDED: Bromine Chloride										
		$[TOX]_1$ (μ eq /ℓ)	k_1 (min^{-1})	T_F/[TOX]	k_2 (min^{-1}) (r^2)	$[TOX]_{60}$ (μ eq/ ℓ)	Temp. (^oC)	Salinity (ppt)	O_2 (ppm)	pH	NH_3 ($\mu M/\ell$)	Proc.
	JULY											
10	27/1443	1.38	0.138	13/0.25	0.11 (0.42)	0.14	26.5	5.4	2.1	7.1		1
11	28/1030	2.17	0.138	11/0.51	0.017 (0.82)	0.28	25.5	5.5	1.6	7.0	10.5	1
12	28/1315	1.38	0.142	11/0.31	0.027 (0.97)	0.08	26.5	5.3	1.8	7.0	7.6	1
	AUGUST											
13	5/1040	1.58	0.158	11/0.28	0.039 (0.79)	0.06	26.0	5.4	2.0	6.9		1
14	5/1240	4.59	0.167	11/0.76	0.009 (0.55)	0.45	25.5	5.5	1.7	7.0		1
15	5/1420	4.85	0.110	15/0.90	0.013 (0.79)	0.51	25.5	5.6	1.8	7.0		1
16	6/1040	3.44	0.109	16/0.62	0.014 (0.93)	0.31	26.0	4.5	1.9	7.1	9.0	1
18	14/1100	3.58	0.128	16/0.48			25.0	7.6	1.6	7.4	10.9	1
19	19/1630	4.08	0.103	19/0.65		0.34					9.0	1
21	20/1445	4.17	0.126	16/0.65	0.006 (0.97)	0.42	24.0	8.7	1.8	7.7	6.5	1
	SEPTEMBER											
24	17/1520	5.63	0.190	11/0.93	0.018 (0.98)	0.37	23.5	7.2	4.7	7.7	3.4	2
27	23/1535	67.3	0.052	6/49.3	0.008 (0.88)	25.3	22.0	7.5	4.1	7.8	3.5	2
28	24/1310	49.7	0.038	13/31.4	0.010 (0.98)	19.0	22.5	7.4	3.5	7.8	3.8	2
30	29/1330	36.6	0.072	10/18.5	0.017 (0.87)		21.0	6.0	4.0	7.7	6.6	2
31	29/1430	6.85	0.143	9/1.80	0.012 (0.95)		21.0	6.0	4.0	7.7	6.6	2

Table A-1 (continued). SUMMARY OF TOX DECAY DATA CALCULATED FOR A QUASI-FIRST ORDER MODEL

Run #	Date/Time	HALOGEN ADDED: Bromine Chloride										
		$[TOX]_1$ (μ eq /ℓ)	k_1 (min^{-1})	$T_F/[TOX]$	k_2 (r^2) (min^{-1})	$[TOX]_{60}$ (μ eq/ℓ)	Temp. (^oC)	Salinity (ppt)	O_2 (ppm)	pH	NH_3 ($\mu M/\ell$)	Proc.
	OCTOBER											
34	5/1425	3.94	0.147	14/0.62		0.45	20.0	6.4	4.2	7.6	10.7	1
35	7/1015	58.2	0.073	13/23.7	0.020 (0.95)	9.7	19.5	7.1	4.1	7.6	6.0	2
37	7/1400	22.1	0.075	13/8.6	0.023 (0.97)	2.4	20.0	6.3	4.0	7.6	6.9	2
39	7/1725	9.15	0.121	9/3.35	0.026 (0.92)	0.76	19.5	7.1	4.0	7.6	6.7	2
45	11/1425	6.03	0.065	14/2.42	0.031 (0.98)	0.70	19.0	0.6	5.2			1
47	14/1150	8.28	0.073	16/2.85	0.030 (0.92)	0.68	17.5	3.4	3.5	7.6	> 100 *	1
48	14/1315	7.18	0.092	14/2.06	0.023 (0.92)	0.54	17.5	3.4	3.5	7.6	13.6	1

* Ammonia added.

characteristics which may affect the decay of TOX. The first group is represented by water quality parameters, such as pH, ammonia concentration* [NH_3], temperatures, and possibly salinity, that can affect the speciation of TOX. The second class consists of inorganic components that are oxidized by TOX, thereby resulting in TOX decay.

An example of the first type of effect would be a change in decay rate of Cl_2-induced oxidants due to the presence of NH_3 or a change in pH. These parameters will affect the partitioning of dissolved chlorine among the forms HOCl, OCl^-, NH_2Cl, and other chloramines. For a given oxidizable substrate, the rate of its oxidation (i.e., the rate of chlorine decay) may depend on the kinetics of its reaction with each particular form of oxidized chlorine. As indicated above, in saline waters there is the possibility that the number of oxidant species will be expanded due to the presence of Br^-. A second-order effect of salinity is the change in speciation among different forms of a single halogen due to the effect of ionic strength and complex formation on the thermodynamic activities of each individual species. This latter effect has recently been quantified by Sugam and Helz (1976) for the HOCl, OCl^- partitioning.

Regardless of the speciation of dissolved oxidant, no decay will occur unless something is oxidized. The most prevalent oxidizable substrate is water. Thermodynamically, the reactions of both dissolved Cl_2 and BrCl with H_2O to produce oxygen are favored. In practice, however, these reactions are extremely slow in the absence of ultraviolet (U.V.) irradiation. Using the fourth test procedure, we observed no decay of Cl_2 in distilled water. Since sunlight does not enter the cooling water system, halogenated water samples used for decay studies were normally not exposed to sunlight. When subsamples of estuarine water were divided so that half were exposed to sunlight (in a bucket) and half were not, there was no difference in TOX levels 1 hour after halogenation. This lack of a sunlight effect may be due to the natural turbidity of estuarine water.

While we have no measurements of oxidizable substances in cooling water, they must be present for TOX decay to occur. Eppley et al. (1976) observed that chlorine decay in natural seawater could be slowed by either the removal of particulate material or treatment of the water by U. V. irradiation prior to chlorination, i.e., removing or destroying oxidizable substrate. Consequently, it follows that TOX decay rate depends on both the quantity and quality of the oxidizable substrate.

A second avenue of TOX disappearance is via the formation of halogenated organic molecules. However, while this aspect of halogenation may be of prime importance in assessing environmental hazards of the process, it is negligible with regard to the loss of TOX. Jolley et al. (1975) observed that less than 3% of the Cl_2 added to two cooling water solutions became incorporated into stable chlorinated organics.

Given that TOX decay depends on both TOX speciation and quality and quantity of oxidizable substrate [S], the overall decay of TOX may be written as:

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* The term "ammonia" in this report is intended to include both forms of dissolved inorganic ammonia (NH_3 and NH_4^+).

$$\frac{d\ [TOX]}{dt} = -\sum k_{ij}\ [TOX]_i^{a_i}\ \ [S]_j^{b_j} \qquad \text{(A-6)}$$

where, for each combination of TOX species (i) and substrate (j), there is a kinetic expression of order ($a_i + b_j$) with a decay constant k_{ij}.

The speciation of dissolved halogen can, in theory, be calculated from thermodynamic data (properly corrected for effects of temperature and ionic strength) so that one can write:

$$[TOX]_i = g_i\ \ [TOX]\ . \qquad \text{(A-7)}$$

with $\Sigma g_i = 1$. The g_i values are functions of thermodynamic data and solution conditions. For a simple solution of Cl_2 in pure water at pH 7, for instance, $g_{HOCl} = 0.73$, and $g_{OCl^-} = 0.27$, as calculated from White (1972):

$$K = \frac{[OCl^-]\ \ [H^+]}{HOCl} = 10^{-7.43}\ .$$

The data obtained in this study are consistent with TOX decay being first order in [TOX]. Thus, if we use Eq. A-7 and set $a_i = 1$ for all i, Eq. A-6 becomes:

$$\frac{d\ \ [TOX]}{dt} = -[TOX] \sum k_{ij}\ g_i\ [S]_j^{b_j}\ . \qquad \text{(A-8)}$$

Comparing Eqs. A-8 and A-4 yields:

$$k = \sum k_{ij}\ g_i\ [S]_j^{b_j} \qquad \text{(A-9)}$$

where the left-hand member (k) is a quasi-first order constant derived from the observed decay data. It follows from Eq. A-9 that a series of decay determinations can yield the same empirical k value only if g_i and [S] remain constant, i.e., only if oxidant speciation and quantity and quality of oxidizable substrate remain constant. Furthermore, the observed decay will follow first-order kinetics only if [S] is large relative to [TOX] so that loss of [S] is insignificant.

The observed decays should be functions of oxidant speciation and [S]. However, two observations suggest that the relationship is not simple. First, a change from fast to slow decay within 10 to 15 minutes after halogenation was consistently observed; and secondly, when a water sample was re-halogenated about 1 hour following an initial halogenation, the decay curve obtained upon rehalogenation was identical in form to the one observed initially. Thus, the transition to the slow phase did not occur because all the available, easily oxidizable substrate was exhausted. Conceivably, after 10 to 15 minutes of contact, the supply of certain oxidant species was exhausted due to reaction with oxidizable substrate. Upon the readdition of a "fresh" supply of Cl_2 or BrCl,

the availability of such oxidant species could again permit rapid oxidation of substrate.

Implicit in this line of reasoning are two assumptions: first, with low-level chlorination or chlorobromination, only a small portion of the available oxidizable substrate is indeed oxidized; second, the Cl_2- and BrCl-induced oxidants are indeed reduced to Cl^- and Br^-. If, instead they were transformed to some oxidized form of halogen such as ClO_3^- or BrO_3^-, which cannot be determined by the analytical method, the observed decay would not be due to consumption of oxidant by oxidizable substances in cooling water. Since we have indications that some undetectable form of oxidant may be forming in saline solutions (Figure 4-1), we feel reasonably certain that decay in the estuarine system was due to an actual reduction (acceptance of electrons) of TOX.

EFFECTS OF AMMONIA AND SALINITY ON Cl_2- AND BrCl-INDUCED OXIDANT DECAY

We have investigated the differences between the decay of the Cl_2-induced and BrCl-induced oxidants in estuarine water. We have also attempted to determine the effects of water quality parameters on these decay rates.

Emphasis is on the relatively rapid decay, defined as k_1, occurring during the first 15 minutes of contact between the biocide and estuarine water. (The initial decay occurring during the first 30 seconds of contact is not considered in this discussion; since the first sample for oxidant analysis was usually collected about 30 seconds after mixing of the biocide and cooling water, often the very rapid initial decay phase was completed.) The relatively slow decays (k_2) occurring after the first 15 minutes are less important in continuous low-level chlorination or chlorobromination because the slow-phase oxidant loss is minimal with this mode of application. Thus, characterization of this phase is not crucial to determining either minimum dosage required for biofouling control or differences between the decay of Cl_2- and BrCl-derived oxidants.

The Fast-Decay Phase

For the present analysis, we have eliminated from consideration those k_1 values determined from runs where the first measured TOX concentration was greater than 16 μeq/ℓ (Runs 26-30, 35-38, 43; cf. Table A-1). Except for Run 43, the initial halogen concentration in all these cases exceeded the ammonia concentration. Therefore, instead of the amine species that are the major dissolved oxidants at lower halogen concentrations (White, 1972; Johnson and Overby, 1971), noncombined halogen species (hypohalite ion and hypohalous acid) were probably present. Since such differences in speciation may have resulted in anomalous decay constants, these runs were deleted from the data set. We also eliminated Runs 40 and 42 because alkaline commercial bleach was used as a chlorine source. As pointed out by Carpenter and Macalady (1976), chlorite ion may form during alkaline storage, and we do not know how chlorite reacts with the reagents used for oxidant analysis. Runs 46 and 47 were eliminated because ammonia was added in abnormally high concentrations, and Runs 4, 9, 13, 14, 15, 19, 40, 45, 50, 51, and 52 were not used because ammonia and/or salinity information was incomplete.

The runs included in the present analysis (10 BrCl and the 17 Cl_2) are recorded in Table A-2; representative runs are plotted in Figure A-4. From the relationship shown in Figure A-4 and a review of the k_1 values recorded in Table A-2, it is evident that the decay constants for both biocides vary over a relatively wide range. To determine to what extent measured water quality parameters could be responsible for the observed spread in decay constants, we tested the correlation of k_1 values with water temperature, dissolved oxygen, salinity, pH, and ammonia. We also tested the correlation of k_1 values with initial measured oxidant concentration since the existence of such a relationship would violate the assumption of first-order decay.

The coefficients of determination (r^2) for these correlations, recorded in Table A-3, show that the decay constant for Cl_2-induced oxidants is related to salinity and ammonia, but not to any of the other parameters. Since r^2 values for BrCl-induced oxidants are all less than 0.50, we can assume that the decay of bromine chloride in estuarine water is not significantly affected by any of the six parameters tested individually.

Because the Cl_2-decay constant showed NH_3 and salinity dependency, a prediction equation for chlorine decay was calculated by multiple linear regression, using the Table A-2 data sets. We obtained the relationship

$$k_1^{Cl_2} = -0.0508 + (0.004 \pm 0.002)\ [NH_3] - (0.018 \pm 0.004)\ [S] \qquad \text{(A-10)}$$

with a regression coefficient of 0.9051 and a standard error of estimate of $\pm$ 0.0230.

This relationship suggests that, at relatively low salinity values, the rate of oxidant decay will decrease with increasing ammonia concentrations. Conversely, at constant ammonia values, an increase in salinity will tend to speed up the rate of oxidant decay.

As pointed out earlier, these differences in decay may reflect differences in oxidant speciation occurring upon chlorine injection. At high ammonia concentrations, the reaction between HOCl and NH_3 (Eq. A-2) may predominate over the reaction between HOCl and Br^- (Eq. A-1). The formation of the relatively stable chloramines would then account for the rather slow decay observed under these conditions. At high salinity values, the Br^- would compete more effectively for the limited amount of HOCl than NH_3, thus allowing the formation of the more reactive hypobromous acid or bromamines.

Alternatively, one may postulate that the quality and quantity of oxidizable substrates in the cooling water change with salinity. At relatively high salinity values, therefore, the amounts of reduced organic and inorganic constituents, which react more rapidly with available oxidants, would be higher than in the fresher cooling water. Our data do not allow selection between the alternative hypotheses.

Obviously, the applicability of expression (A-10) for predicting chlorine-induced oxidant decay in estuarine water is limited to a certain range of salinity and ammonia values. The boundary conditions can be estimated on the basis of the decay characteristics observed with BrCl.

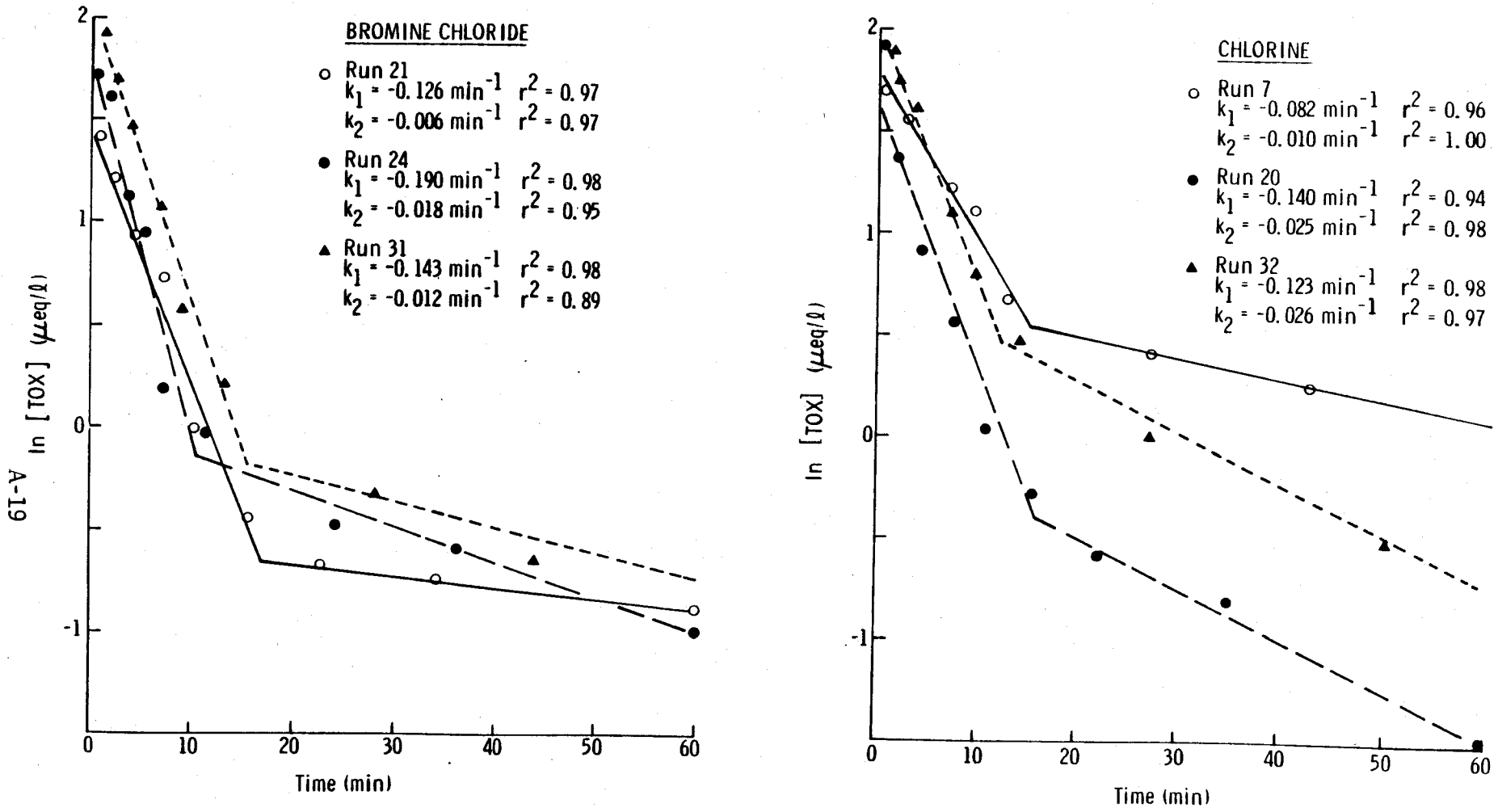

Figure A-4. Representative examples of the rapid (k_1) and slow (k_2) decay of Cl_2- and BrCl-induced oxidants in estuarine cooling water.

Table A-2. AMMONIA AND SALINITY EFFECTS ON THE DECAY OF BrCl- AND Cl_2-INDUCED OXIDANTS (Data from Table A-1)

Run Number	$[TOX]_1$ μeq/ℓ	$[TOX]_1$ ppb	Salinity ppt	NH_3 (μM/ℓ)	k_1 (min^{-1}) Obs.	k_1 (min^{-1}) Pred.	Pred/Obs.	k_2 (min^{-1}) Obs.
CHLORINE								
1	4.79	170	4.8	10.2	-0.097	-0.0924	0.95	-0.006
2	5.97	212	4.5	7.6	-0.078	-0.0980	1.26	----
3	6.14	218	4.4	6.5	-0.097	-0.1009	1.04	-0.011
5	10.39	369	5.1	11.8	-0.088	-0.0910	1.03	-0.019
6	9.72	345	4.9	9.2	-0.093	-0.0983	1.06	-0.014
7	5.49	195	4.8	15.1	-0.082	-0.0718	0.88	-0.010
8	6.87	244	4.5	9.3	-0.098	-0.0909	0.93	-0.018
17	4.48	159	4.5	9.0	-0.085	-0.0922	1.08	-0.010
20	6.82	242	8.9	7.5	-0.140	-0.1758	1.26	-0.025
22	4.34	154	8.4	3.7	-0.199	-0.1829	0.92	-0.017
23	4.82	171	7.8	4.5	-0.186	-0.1690	0.91	----
25	3.72	132	7.2	3.2	-0.209	-0.1639	0.78	-0.052
32	6.85	243	6.0	6.6	-0.123	-0.1286	1.05	-0.026
33	5.32	189	6.4	12.8	-0.134	-0.1096	0.82	-0.015
41	5.27	187	6.5	4.2	-0.105	-0.1474	1.40	----
44	4.85	172	0.9	11.8	-0.028	-0.1360	0.49	-0.006
49	7.01	249	3.8	13.6	-0.036	-0.0518	1.44	-0.006
Average					-0.1105	-0.1105	1.018	-0.016
Standard Deviation (±)					0.0507	0.0458	0.234	0.012
BROMINE CHLORIDE								
11	2.17	125	5.5	10.5	-0.139	-0.1180	0.85	-0.017
12	1.38	80	5.3	7.6	-0.072	-0.1184	1.64	-0.027
16	3.44	198	4.5	9.0	-0.109	-0.1087	1.00	-0.014
18	3.58	206	7.6	10.9	-0.163	-0.1400	0.86	----
21	4.17	240	8.7	6.5	-0.126	-0.1554	1.23	-0.006
24	5.63	308	7.2	3.4	-0.190	-0.1421	0.75	-0.018
31	6.85	394	6.0	6.6	-0.143	-0.1266	0.89	-0.012
34	3.94	227	6.4	10.7	-0.134	-0.1274	0.95	----
39	9.15	526	7.1	6.7	-0.100	-0.1384	1.38	-0.026
48	7.18	413	3.4	13.6	-0.092	-0.0931	1.01	-0.023
Average					-0.127	-0.1268	1.056	-0.0179
Standard Deviation (±)					0.035	0.0182	0.278	0.0072

Table A-3. COEFFICIENTS OF DETERMINATION (r^2)* BETWEEN k_1 AND VARIOUS WATER QUALITY PARAMETERS FOR BrCl- AND Cl_2-DERIVED OXIDANT

(Runs included in analysis are recorded in Table A-2)

Parameter	Chlorine		Bromine Chloride	
	r_2	No. Samples	r^2	No. Samples
S (ppt)	0.76	17	0.23	10
NH_3-N (μM/ ℓ)	0.50	17	0.20	10
pH	0.35	16	0.15	10
T (^oC)	0.03	17	0.01	10
O_2 (ppm)	0.00	17	0.13	10
$[TOX]_1$ (μeq/ ℓ)	0.43	17	0.00	10

*

$$r^2 = \frac{n \Sigma xy - \Sigma x \Sigma y}{n(n-1) S_x S_y}$$

If we assume that the postulated speciation hypothesis is correct, and that the ratio of the concentrations of Br^- and NH_3 determines the distribution of added oxidant between chloramine and bromamine constituents of the cooling water (reactions A-1 over A-2), the maximum rate of Cl_2-induced oxidant decay that can be attained would be equal to the rate of BrCl-induced oxidant decay. This latter rate can be estimated on the basis of the 10 data sets* recorded in Table A-2. The available data allow the calculation of the following relationship:

$$k_1^{BrCl} = -0.0686 + (0.001 \pm 0.005)\ [NH_3] - (0.009 \pm 0.011)\ [S] \qquad \text{(A-11)}$$

The multiple regression coefficient is 0.5188; the standard error of the estimate $\pm$ 0.0339. This expression indicates that the average decay rate is $-0.13\ min^{-1}$, and that the decay of bromine chloride-induced oxidant is relatively insensitive to variations in salinity and NH_3 concentrations.

Substitution of the average BrCl decay value in Eq. A-10 allows calculation of salinity and ammonia values at which Cl_2-induced and BrCl-induced oxidant decay rates are equal. Figure A-5 illustrates the results of these calculations. The relationship depicted indicates that, for a given ammonia concentration in the cooling water, the rate of oxidant decay, and therefore the advantage of BrCl over Cl_2 in limiting environmental impacts of biocide use, will depend on salinity.

The Slow-Decay Phase

As seen from Table A-4, no strong relationship exists between k_1 and k_2, nor does the exclusion of data (discussed above) from our analysis of k_1 constants greatly affect the average k_2 values. Most important, unlike k_1 values, there is no significant (at the 0.10 level) difference between slow decay constants for $BrCl^-$ and Cl_2-derived oxidant.

A crucial unanswered question is the reason for the change in decay rate observed 10 to 15 minutes after halogenation. We have already shown that the change cannot be due to a decrease in available oxidizable substrate: upon rehalogenation of a 1-hour old sample of halogenated estuarine water, the pattern of very fast initial decay followed by periods quantifiable by k_1 and k_2 constants is repeated. The change in decay rate must, therefore, be due to a change in the speciation of TOX, but we have no ready explanation for the observed behavior.

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* Ten data sets are insufficient for estimating three coefficients. Therefore, the derived relationship must be considered as tentative.

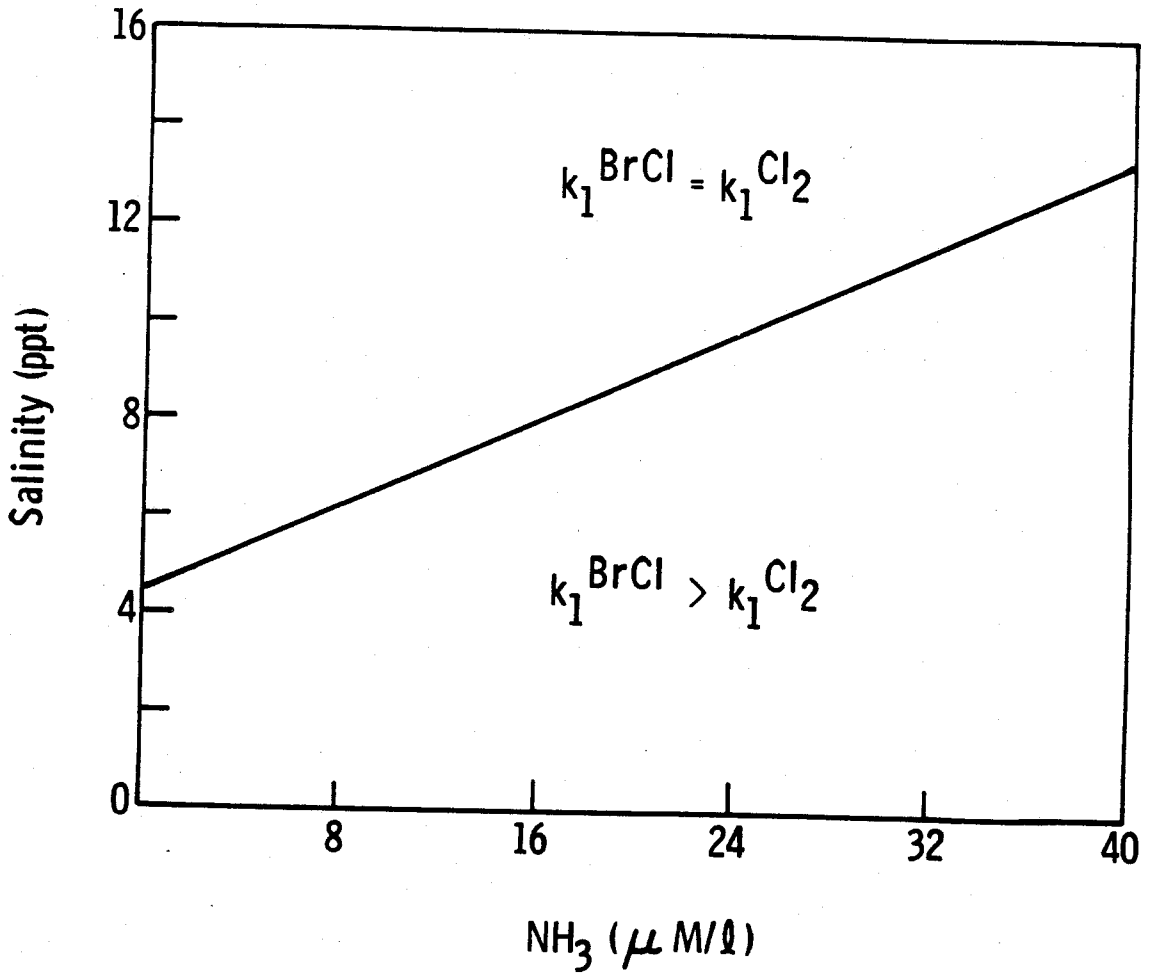

Figure A-5. Ammonia and salinity effects on decay constants of BrCl- and and Cl_2-induced oxidants.

TABLE A-4. SLOW DECAY CONSTANT, k_2, AND ITS RELATIONSHIP TO k_1
(Data from Table A-2)

	Cl_2	BrCl
Ave k_2 (min^{-1})	-0.016	-0.018
S.D. k_2	0.012	0.007
(k_1 x k_2) r^2	0.57	0.24
Number of samples	13	8

Potential Environmental Benefits of BrCl for Biofouling Control

While rigorous determination of factors affecting halogen decay remains to be done, the quasi-first order decay models discussed earlier can be used to estimate the relative advantage of replacing Cl_2 with BrCl in power plant applications. Consider a system where two streams from a single source of low salinity cooling water are halogenated with equimolar amounts of Cl_2 and BrCl. Within the initial 30 seconds, 50% of the TOX in both streams is lost, and, during the next 10 minutes, the Cl_2- and BrCl-derived TOX decays with first order constants of -0.11 min^{-1} and -0.13 min^{-1}, respectively (these constants are the overall averages from Table A-2). After 10 minutes, the ratio of TOX levels can be described by:

$$\frac{[TOX]_{BrCl}}{[TOX]_{Cl_2}} = e^{-0.20} = 0.82 \quad .$$

Thus, the TOX concentration of the BrCl-treated stream will be about 20% less than that of the Cl_2-treated stream. If the first-order decay were to last for 15 minutes instead of 10 minutes, the oxidant concentration of the chlorobrominated stream would be 30% less than that of the chlorinated stream.

If BrCl and Cl_2 were dosed on an equal weight, rather than equimolar, basis, the above ratios for $[TOX]_{BrCl}$ to $[TOX]_{Cl_2}$ would be 0.50 for a 10-minute decay and 0.45 for a 15-minute decay. Since equal weights of the two biocides are comparable in antifouling effectiveness (see Chapters 5 and 6), it is reasonable to expect a 50 to 60% decrease in effluent oxidant levels when Cl_2 is replaced with BrCl. Whether or not this decrease is significant in lowering any toxic effect of such treated effluents will depend on the absolute value of discharged TOX levels and the toxicity response of the biota of the receiving water.

Table A-5. SUMMARY OF RAW HALOGEN DECAY DATA

Key to Table Headings

1) Run number identified as #X. These numbers are the same as those used in Tables A-1 and A-2.

2) Type of halogen: Cl_2 and BrCl

3) The first number in parentheses (1 through 4) identifies test procedures as described in this Appendix under "Test Procedures."

4) The subsequent numbers in parentheses, separated by "/," are month and day, respectively.

Key to Columns

The first column is the biocide contact time in minutes; the second column is the oxidant concentration in μeq/ℓ observed at the specified time.

# 1 Cl_2, (1) (7/13)	
1.0	4.79
2.0	4.11
4.0	3.55
6.0	3.10
14.0	1.32
29.0	1.24
49.0	1.07
68.0	0.96

# 2 Cl_2, (1) (7/13)	
0.75	5.97
2.0	5.21
3.5	4.62
6.0	3.97
16.0	--
41.0	1.21
62.0	1.04

# 3 Cl_2, (1) (7/13)	
0.50	6.14
1.75	5.46
3.0	5.04
4.75	4.39
12.0	2.06
30.0	1.38
48.0	1.21
64.0	1.15

# 4 Cl_2, (1) (7/14)	
0.75	10.37
1.92	8.87
3.33	8.25
5.67	7.18
17.0	3.01
32.0	2.28
61.0	1.35

# 5 Cl_2, (1) (7/14)	
0.67	10.39
1.75	9.27
2.83	8.48
4.42	8.56
12.0	3.80
32.0	2.23
47.0	1.66
60.0	1.55

# 6 Cl_2, (1) (7/14)	
0.75	9.72
1.75	8.65
2.83	7.97
4.67	7.01
12.0	3.38
28.0	2.23
49.0	1.69
67.0	1.55

# 7 Cl_2, (1) (7/15)	
0.67	5.49
2.83	4.79
7.08	3.38
9.50	3.10
12.75	1.94
27.0	1.52
43.0	1.30
67.0	1.01

# 8 Cl_2, (1) (7/15)	
0.58	6.87
1.50	6.17
5.83	4.17
7.50	3.72
11.0	2.42
29.0	1.52
47.0	1.10
66.0	0.90

# 9 Cl_2, (1) (7/22)	
0.50	7.63
2.0	6.14
9.0	2.11
17.0	1.61
36.0	0.99
39.0	1.15
59.0	0.82
64.0	0.96

# 10 BrCl, (1) (7/27)	
0.67	1.38
1.50	1.21
2.67	1.10
4.50	0.99
13.0	0.25
39.0	0.31
54.0	0.20
59.0	0.14

# 11 BrCl, (1) (7/28)	
0.42	2.17
1.08	2.03
1.92	1.83
3.67	1.66
11.0	0.51
26.0	0.56
42.0	0.31
53.0	0.25
59.0	0.28

# 12 BrCl, (1) (7/28)	
0.42	1.38
1.25	1.30
2.42	1.13
4.58	1.07
11.0	0.31
24.0	0.25
35.0	0.20
62.0	0.08

# 13 BrCl, (1) (8/5)	
0.50	1.58
1.50	1.15
3.0	1.18
5.0	0.93
11.0	0.28
18.0	0.23
33.0	0.06
54.0	0.06

# 14 BrCl, (1) (8/5)	
0.58	4.59
1.75	3.77
3.58	2.99
6.50	2.17
11.0	0.76
20.0	0.54
35.0	0.39
49.0	0.45
60.0	0.45

# 15 BrCl, (1) (8/5)	
0.42	4.85
1.58	4.00
4.08	3.04
9.0	2.03
15.0	0.90
25.0	0.62
39.0	0.54
55.0	0.51

# 16 BrCl, (1) (8/6)	
0.42	3.44
1.50	2.90
4.17	2.08
8.42	1.41
15.75	0.62
26.50	0.45
48.0	0.34
63.0	0.31

# 17 Cl_2, (1) (8/6)	
0.50	4.48
1.50	3.86
4.08	2.87
9.17	2.00
18.0	0.99
27.0	0.79
42.0	0.62
59.0	0.65

# 18 BrCl, (1) (8/14)	
0.33	3.58
2.42	2.34
4.17	1.86
9.45	0.79
16.00	0.48
22.50	0.42

# 19 BrCl, (1) (8/19)	
0.50	4.08
1.50	3.35
3.50	2.68
7.50	1.97
12.45	0.85
19.00	0.65
26.25	0.37
51.0	0.34

# 20 Cl_2, (1) (8/20)	
0.42	6.82
2.00	3.92
4.25	2.48
7.58	1.77
10.67	1.04
15.50	0.76
22.33	0.56
35.17	0.45
59.0	0.23
68.0	0.25

# 21 BrCl, (1) (8/20)	
0.42	4.17
2.00	3.35
4.00	2.56
7.50	2.08
10.33	0.99
15.50	0.65
22.42	0.51
34.0	0.48
60.0	0.42

# 22 Cl_2, (1) (9/15)	
0.58	4.34
1.67	3.13
3.25	2.25
6.75	1.55
9.08	0.68
13.50	0.65
24.50	0.34
44.17	0.31
90.0	0.17

# 23 Cl_2, (1) (9/16)	
0.42	4.82
1.33	3.58
2.92	2.51
7.17	1.52
9.17	0.79
19.17	0.48
30.0	0.37

# 24 BrCl, (1) (9/17)	
0.50	5.63
1.42	4.54
3.33	3.24
4.92	2.62
7.17	1.21
11.0	0.93
23.75	0.62
36.33	0.56
60.0	0.37

# 25 Cl_2, (1) (9/17)	
0.42	3.72
1.33	2.68
3.50	1.55
6.25	1.13
8.25	0.65
14.75	0.39
26.0	0.25
47.0	0.08

# 26 Cl_2, (3) (9/23)	
0.33	67.2
1.25	63.8
2.42	62.1
5.37	57.7
7.70	55.0
11.62	50.3
24.33	46.1
38.33	41.0
55.50	35.1
114.50	29.0
263.33	19.0

# 27 BrCl, (2) (9/23)	
0.25	67.3
1.13	60.9
2.42	55.9
5.92	49.3
8.83	--
14.75	--
18.42	36.8
28.00	32.8
37.50	29.6
54.87	25.8
105.75	20.3

# 28 BrCl, (2) (9/24)	
0.33	49.7
1.25	46.8
2.75	43.2
5.67	39.8
8.30	34.2
12.50	31.4
20.22	28.4
30.72	24.6
47.77	21.0
63.17	19.0

# 29 Cl_2, (3) (9/24)	
0.33	18.1
1.33	17.4
2.92	15.2
6.17	13.4
8.30	12.1
14.50	10.3
26.33	8.1
43.33	6.9
66.75	6.5

# 30 BrCl, (2) (9/29)	
0.50	36.6
1.33	30.2
2.92	25.2
7.03	18.9
9.58	18.5
14.80	12.3
24.83	9.0
43.25	7.0
79.95	4.8

# 31 BrCl,(2) (9/29)	
0.92	6.85
2.08	5.52
3.50	4.34
6.75	2.99
8.83	1.80
13.08	1.24
27.92	0.73
44.17	0.54
73.67	0.42

# 32 Cl_2, (1) (9/29)	
0.67	6.85
1.58	5.83
3.50	4.59
7.42	3.10
9.42	2.20
13.83	1.63
26.83	0.99
49.92	0.62

# 33 Cl_2, (1) (10/4)	
0.42	5.32
1.25	4.79
3.25	3.89
6.83	2.70
9.00	1.41
13.58	0.99
22.25	0.85
33.50	0.62
61.25	0.48

# 34 BrCl, (1) (10/5)	
0.42	3.94
1.33	3.30
3.17	2.59
6.58	1.72
9.00	0.70
14.00	0.62
26.08	0.42
56.00	0.45

# 35 BrCl, (2) (10/7)	
0.33	58.2
1.17	52.1
2.83	44.9
5.58	35.9
7.67	30.2
12.67	23.7
25.25	--
32.83	14.0
45.25	10.8
59.33	9.7
267.0	5.0

# 36 Cl_2, (3) (10/7)	
0.50	60.9
1.09	54.1
2.25	49.4
3.75	--
4.92	32.7
10.92	19.8
18.92	15.5
35.42	10.8
46.67	9.5
61.17	8.3
183.0	4.5

# 37 BrCl, (2) (10/7)	
0.33	22.1
1.17	19.4
2.33	17.5
5.17	15.6
8.08	11.2
12.75	8.6
24.00	6.0
32.25	4.5
49.75	3.3
67.58	2.4
164.0	1.7

# 38 Cl_2, (3) (10/7)	
0.33	26.0
1.17	25.3
2.33	23.3
3.58	23.0
5.25	18.9
8.83	17.5
15.83	15.1
25.50	13.6
41.67	11.7
67.0	10.1
130.0	8.3

# 39 BrCl, (2) (10/7)	
0.50	9.15
1.67	7.52
3.17	6.28
6.17	4.65
8.50	3.35
14.50	2.25
24.75	1.46
36.00	1.13
51.08	0.85
62.83	0.76

# 40 Cl_2, (3) (10/7)	
0.58	7.94
1.42	7.55
2.67	7.15
4.58	6.73
6.25	5.80
10.25	5.38
20.75	4.73
30.00	4.56
41.67	4.34
60.75	3.94

# 41 Cl_2, (1) (10/9)	
0.42	5.27
1.58	4.68
3.50	3.86
6.42	3.01
8.67	1.89
12.67	1.38
15.83	1.13
26.00	0.82
40.25	0.76

# 42 Cl_2, (3) (10/9)	
0.58	6.31
1.50	5.94
2.67	5.61
4.50	5.30
5.50	4.51
10.58	3.52
20.67	3.18
29.83	3.01
44.83	2.79

# 43 Cl_2, (1) (10/11)	
0.42	16.59
1.42	15.94
4.00	14.68
8.00	13.32
11.00	11.69
16.42	10.73
25.58	9.41
34.50	8.56
44.50	7.72
60.00	6.68

# 44 Cl_2, (1) (10/11)	
0.42	4.85
1.58	4.56
3.67	4.25
7.16	3.86
9.75	3.27
13.33	3.10
22.50	2.73
32.25	2.56
64.00	2.23

# 45 BrCl, (1) (10/11)	
0.45	6.03
1.42	5.58
3.67	4.82
7.67	3.97
10.00	3.13
14.25	2.42
25.92	1.69
35.67	1.07
55.42	0.70

# 46 Cl_2, (1) (10/14)	
0.58	6.73
1.67	6.28
4.33	5.49
8.00	4.59
10.75	3.83
15.42	3.30
27.58	2.68
42.42	2.34
62.17	2.20

# 47 BrCl (1) (10/14)	
0.58	8.28
1.67	7.63
4.25	6.45
8.00	5.07
10.42	3.66
15.92	2.85
29.42	1.44
44.00	0.87
63.00	0.68

# 48 BrCl (1) (10/14)	
0.42	7.18
1.50	6.42
3.92	5.18
7.33	3.97
9.75	2.85
14.08	2.06
23.67	1.15
42.00	0.85
66.75	0.54

# 49 Cl_2, (1) (10/14)	
0.42	7.01
1.42	6.56
3.83	5.92
7.33	5.38
9.67	4.51
13.58	4.17
22.67	3.69
34.42	3.41
50.92	3.18
60.00	3.07

# 50 Cl_2, (4) (11/15)	
0.00	9.04
0.75	3.15
0.92	3.32
1.75	2.70
3.08	2.14
9.33	1.55

# 51 Cl_2, (4) (11/16)	
0.00	13.24
0.67	7.97
1.50	5.61
4.42	3.69
12.00	2.23

# 52 Cl_2, (4) (11/19)	
0.00	13.63
0.75	7.77
1.67	6.23
3.58	5.07
5.75	4.25
9.83	3.10
15.83	2.00
16.00	1.94
21.42	2.06
30.67	1.44
60.17	1.21

APPENDIX B

SUMMARY OF BrCl AND Cl_2 DOSE RATES (kg/day) AND TOX LEVELS (μeq/ℓ) AT THREE BIOFOULING SIMULATORS DURING TRIALS I AND II

Contents

Trial I (11 August - 26 August)

Trial II (10 September - 24 September)

SUMMARY OF BrCl AND Cl_2 DOSAGES (kg/day) AT THREE BIOFOULING SIMULATORS DURING TRIALS I AND II

TRIAL I (11 August - 26 August)

During this period, dose rates varied as follows:

Time Interval Date/Time	Date/Time	Applied Dosage (kg/day)
	Unit #1 (BrCl)	
11/0900	12/0050	1360
12/0050	12/0730	OFF
12/0730	16/1800	1360
16/1800	19/1630	OFF or between 725 and 1040
19/1630	24/0900	1360
24/0900	26/0900	725 to 1090
	Unit #2 (Cl_2)	
11/0900	12/0050	910
12/0050	12/0730	OFF
12/0730	14/1130	910
14/1130	15/2200	OFF
15/2200	16/0500	910
16/0500	26/0900*	910

*For this period, only two of three circulating pumps were in operation; thus, dose is equivalent to one of 1360 kg/day for a flow of three pumps. Each pump delivers $10.4 m^3$/sec.

Within discreet regions of the total test period, the August TOX levels are summarized as follows:

Time interval		Circulating pumps				Water box				Discharge			
Date/Time	Date/Time	Mean (μ eq/ℓ)	S.D.	min/max	(n)*	Mean (μ eq/ℓ)	S.D	min/max	(n)*	Mean (μ eq/ℓ)	S.D.	min/max	(n)*
										Unit #1 (BrCl)			
11/0900	12/0050	3.9 (224)**	0.4	3.4/4.5	(4)	2.6 (150)	0.4	2.3/3.2	(4)	1.8 (104)	0.4	1.5/2.3	(4)
12/0050	12/0730	BrCl + Cl_2 OFF											
12/0730	14/1130									1.5 (186)	0.2	1.1/1.6	(11)
14/1130	15/2300	3.4 (196)	0.2	3.0/3.6	(17)	2.2 (127)	0.2	1.7/2.6	(17)	0.9 (52)	0.2	0.7/1.1	(3)
15/2300	16/1800									1.4 (81)	0.2	1.2/1.6	(4)
16/1800	19/1630	BrCl OFF or fluctuating								1.1 (63)	0.1	1.1/1.2	(4)
19/1630	24/0900	4.0 (230)	0.3	3.6/4.4	(5)	2.6 (150)	0.2	2.4/2.8	(5)	1.7 (98)	0.1	1.6/1.8	(4)
24/0900	26/0900	1.9 (109)	0.3	1.7/2.4	(5)	1.3 (75)	0.1	1.1/1.4	(5)	1.5 (86)	0.2	1.4/1.7	(5)
										Unit #2 (Cl_2)			
11/0900	12/0050	5.4 (192)	0.2	5.3/5.7	(4)	4.2 (149)	0.3	3.9/4.6	(4)	2.5 (89)	0.3	2.2/2.9	(4)
12/0050	12/0730	BrCl + Cl_2 OFF											
12/0730	14/1130	5.1 (181)	0.4	4.2/5.8	(12)	3.9 (138)	0.3	3.6/4.4	(11)	2.1 (75)	0.1	1.9/2.3	(11)
14/1130	15/2200	Cl_2 OFF											
15/2200	16/0500	4.9 (174)	--	--	(1)	3.8 (135)	0.2	3.9/3.6	(2)	1.7 (60)	--	--	(1)
16/0500	26/0900+	7.3 (259)	0.5	6.7/7.9	(10)	4.9 (174)	0.3	4.5/5.2	(8)	1.9 (167)	0.2	1.4/2.1	(17)

*(n) = No. of samples

+During this period, only two of three circulating pumps were in operation.

**Values in parentheses are biocide concentrations in ppb.

TRIAL II (10 September - 24 September)

During this period, dose rates for each halogen remained constant at 910 kg/day for Cl_2 and 360 kg/day for BrCl with all three pumps in each unit operating. The TOX levels (in μeq/ℓ) at the three biofouling simulators on each unit are summarized as follows:

	Unit 1 (BrCl)			Unit 2 (Cl_2)		
	Mean	S.D.	No. of Samples	Mean	S.D.	No. of Samples
Circulator	1.1 (63)*	0.1	14	5.0 (178)*	0.3	18
Water box	0.9 (52)	0.1	14	3.3 (117)	0.3	17
Discharge	1.0 (58)	0.1	15	1.6 (59)	0.2	17

*Values in parentheses are biocide concentrations in ppb.

APPENDIX C

FOULING ASSAY INFORMATION

Contents

Organic and Inorganic Dry Weight Content of Fouling Material Accumulated on Glass Panels

Statistical Evaluation of Biofouling in Presence and Absence of Biocides

FOULING ASSAY INFORMATION

ORGANIC AND INORGANIC DRY WEIGHT CONTENT OF FOULING MATERIAL ACCUMULATED ON GLASS PANELS

The organic and inorganic dry weight contents of fouling material accumulating with time of exposure on 116-m^2 glass panels are presented. The data are recorded in Tables C-1, C-2, C-3, and are given by time (day) of sampling, biocide type, and station location.

Table C-1. MEAN TOTAL DRY WEIGHT, ORGANIC WEIGHT, AND INORGANIC WEIGHT AT DAYS 3, 6, 9, 12, AND 15 FOR THE 15-DAY TESTS CONDUCTED DURING THE FIRST STUDY 11 AUGUST 1976 TO 26 AUGUST 1976 (Weight Values Represent 116-cm^2 Glass Panel Area)

Test Conditions				Days of Fouling Exposure					
	Biocide			Day 3 (14 August 1976)					
Station Location	Type	Mean Conc.[a] (μeq/l)	(ppb)	Total Weight(mg)	n[c]	Organic Weight(mg)	n	Inorganic Weight(mg)	n
Embayment		0.0	0	11.39(±3.589)[b]	8	3.79(±1.158)	8	7.60(±3.439)	8
Circulator	Cl_2					no data			
Condenser	Cl_2					no data			
Discharge	Cl_2					no data			
Circulator	BrCl	3.1	178.25	16.13(±4.851)	8	3.79(±0.682)	8	12.34(±4.275)	8
Condenser	BrCl	1.8	103.50	22.36(±10.099)	4	4.39(±0.978)	4	17.97(±9.175)	4
Discharge	BrCl	1.4	80.50	29.82(±8.409)	7	5.11(±2.038)	7	24.71(±6.457)	7

[a] Mean concentration for trial period

[b] ± 1 S.D.

[c] Number of samples

Table C-1 (continued)

Test Conditions				Days of Fouling Exposure					
	Biocide			Day 6 (17 August 1976)					
Station Location	Type	Mean Conc. (μeq/l)	(ppb)[a]	Total Weight(mg)	n	Organic Weight(mg)	n	Inorganic Weight(mg)	n
Embayment		0.0	0	78.96(±10.471)	8	14.03(±1.855)	8	64.93(±10.242)	8
Circulator	Cl_2					no data			
Condenser	Cl_2					no data			
Discharge	Cl_2					no data			
Circulator	BrCl	3.1	178.25	19.47(±5.490)	8	4.57(±1.033)	8	14.90(±4.545)	8
Condenser	BrCl	1.8	103.50	49.29(±25.593)	4	7.48(±2.836)	4	41.81(±22.793)	4
Discharge	BrCl	1.4	80.50	63.34(±28.273)	8	11.58(±3.660)	8	51.76(±24.759)	8

[a]Mean concentration for 15 days

Table C-1 (continued)

Test Conditions				Days of Fouling Exposure					
				Day 9 (20 August 1976)					
Station Location	Type	Mean Conc.[a] (μeq/l)	(ppb)	Total Weight(mg)	n	Organic Weight(mg)	n	Inorganic Weight(mg)	n
Embayment		0.0	0	224.98(±26.599)	8	36.75(±4.025)	8	188.23(±22.704)	8
Circulator	Cl_2					no data			
Condenser	Cl_2					no data			
Discharge	Cl_2					no data			
Circulator	BrCl	3.1	178.25	42.95(±10.120)	8	7.12(±1.312)	8	35.83(±9.395)	8
Condenser	BrCl	1.8	103.50	95.28(±17.319)	4	13.70(±1.338)	4	81.58(±17.379)	4
Discharge	BrCl	1.4	80.50	267.12(±53.039)	8	39.66(±6.196)	8	227.46(±47.019)	8

[a] Mean concentration for 15 days

Table C-1 (continued)

Test Conditions				Days of Fouling Exposure					
	Biocide			Day 12 (23 August 1976)					
Station Location	Type	Mean Conc.[a] (μeq/l)	(ppb)	Total Weight(mg)	n	Organic Weight(mg)	n	Inorganic Weight(mg)	n
Embayment		0.0	0	716.75(±166.149)	8	112.43(±29.517)	8	604.32(±136.831)	8
Circulator	Cl_2					no data			
Condenser	Cl_2					no data			
Discharge	Cl_2					no data			
Circulator	BrCl	3.1	178.25	51.44(±11.381)	8	40.57(±8.230)	8	10.87(±4.877)	8
Condenser	BrCl	1.8	103.50	151.58(±45.578)	4	22.38(±8.357)	4	129.20(±37.920)	4
Discharge	BrCl	1.4	80.50	806.85(±187.589)	8	141.57(±31.645)	8	665.28(±156.938)	8

[a]Mean concentration for 15 days

Table C-1 (continued)

Test Conditions				Days of Fouling Exposure					
	Biocide			Day 15 (26 August 1976)					
Station Location	Type	Mean Conc. (μeq/l)	(ppb)[a]	Weight(mg)	n	Weight(mg)	n	Weight(mg)	n
Embayment		0.0	0	1318.26(±223.394)	8	206.14(±33.300)	8	1112.12(±191.107)	8
Circulator	Cl_2					no data			
Condenser	Cl_2					no data			
Discharge	Cl_2					no data			
Circulator	BrCl	3.1	178.25	67.63(±22.255)	8	10.42(±2.772)	8	57.21(±19.573)	8
Condenser	BrCl	1.8	103.50	215.35(±60.085)	4	29.62(±6.123)	4	185.73(±53.980)	4
Discharge	BrCl	1.4	80.50	1588.50(±640.376)	8	230.53(±82.062)	8	1357.97(±560.704)	8

[a]Mean concentration for 15 days.

Table C-2. MEAN TOTAL DRY WEIGHT, ORGANIC WEIGHT AND INORGANIC WEIGHT AT DAYS 3, 6, AND 9 FOR THE 9-DAY TESTS CONDUCTED DURING THE FIRST STUDY 17 AUGUST 1976 TO 26 AUGUST 1976 (Weight Values Represent 116-cm^2 Glass Panel Area)

Test Conditions				Days of Fouling Exposure					
	Biocide			Day 3 (20 August 1976)					
Station Location	Type	Mean Conc.[a] (μeq/l)	(ppb)	Total Weight(mg)	n[c]	Organic Weight(mg)	n	Inorganic Weight(mg)	n
Embayment		0.0	0	130.39(±22.158)[b]	5	20.11(±3.057)	5	110.28(±19.370)	5
Circulator	Cl_2	7.3	259.15	24.12(±10.189)	10	3.93(±1.367)	10	20.19(±8.995)	10
Condenser	Cl_2	4.9	173.95	21.83(±3.663)	5	4.37(±0.972)	5	17.46(±4.025)	5
Discharge	Cl_2	1.9	67.45	58.73(±11.610)	10	8.40(±1.543)	10	50.33(±10.204)	10
Circulator	BrCl	2.9	166.75	29.47(±6.076)	5	4.58(±1.629)	5	24.89(±5.284)	5
Condenser	BrCl	2.0	115.00	31.74(±5.023)	4	5.45(±0.879)	4	26.29(±4.339)	4
Discharge	BrCl	1.5	86.25	125.25(±26.495)	5	20.52(±4.412)	5	104.73(±22.233)	5

[a] Mean concentration for trial period

[b] ± 1 S.D.

[c] Number of samples

Table C-2 (continued)

Test Conditions				Days of Fouling Exposure					
	Biocides			Day 6 (23 August 1976)					
Station Location	Type	Mean Conc.[a] (μeq/l)	(ppb)	Total Weight(mg)	n	Organic Weight(mg)	n	Inorganic Weight(mg)	n
Embayment		0.0	0	346.40(±38.536)	5	58.98(±6.912)	5	287.42(±33.088)	5
Circulator	Cl_2	7.3	259.15	63.96(±24.781)	10	9.73(±3.493)	10	54.23(±21.513)	10
Condenser	Cl_2	4.9	173.95	65.86(±24.105)	5	11.08(±5.295)	5	54.78(±18.988)	5
Discharge	Cl_2	1.9	67.45	254.64(±95.945)	10	40.55(±22.581)	10	214.09(±75.608)	10
Circulator	BrCl	2.9	166.75	29.71(±5.781)	5	5.68(±1.447)	5	24.03(±4.383)	5
Condenser	BrCl	2.0	115.00			no data			
Discharge	BrCl	1.5	86.25	536.09(±88.358)	5	91.37(±11.816)	5	444.72(±76.589)	5

[a]Mean concentration for 9 days.

Table C-2 (continued)

Test Conditions				Days of Fouling Exposure					
				Day 9 (26 August 1976)					
Station Location	Type	Mean Conc.[a] (μeq/l)	(ppb)	Total Weight(mg)	n	Organic Weight(mg)	n	Inorganic Weight(mg)	n
Embayment		0.0	0	808.46(±247.854)	5	125.56(±40.980)	5	682.90(±206.996)	5
Circulator	Cl_2	7.3	259.15	91.00(±35.355)	10	12.30(±4.780)	10	78.70(±30.834)	10
Condenser	Cl_2	4.9	173.95	91.71(±20.542)	5	12.81(±2.807)	5	78.90(±17.943)	5
Discharge	Cl_2	1.9	67.45	571.10(±177.274)	10	70.52(±18.838)	10	500.58(±159.334)	10
Circulator	BrCl	2.9	166.75	52.77(±7.533)	5	8.59(±0.833)	5	44.18(±6.823)	5
Condenser	BrCl	2.0	115.00	118.39(±74.920)	4	16.28(±10.847)	4	102.11(±64.255)	4
Discharge	BrCl	1.5	86.25	1005.49(±278.485)	5	142.93(±33.641)	5	862.56(±244.866)	5

[a]Mean concentration for 9 days.

Table C-3. MEAN TOTAL DRY WEIGHT, ORGANIC WEIGHT AND INORGANIC WEIGHT AT DAYS 3, 6, AND 9 FOR THE 9-DAY TESTS AND DAYS 3, 6, 9, 12, AND 15 FOR THE 15-DAY TESTS CONDUCTED DURING THE SECOND STUDY 10 SEPTEMBER 1976 TO 25 SEPTEMBER 1976 (Weight Values Represent 116-cm^2 Glass Panel Area)

Test Conditions				Days of Fouling Exposure					
	Biocides			Day 3 (13 September 1976)					
Station Location	Type	Mean Conc.[a] (μeq/l)	(ppb)	Total Weight(mg)	n[c]	Organic Weight(mg)	n	Inorganic Weight(mg)	n
Embayment		0.0	0	13.33(±3.160)[b]	8	3.14(±0.785)	8	10.19(±2.609)	8
Circulator	Cl_2	5.3	188.15	15.05(±1.175)	8	3.03(±0.468)	8	12.02(±1.309)	8
Condenser	Cl_2	3.3	117.15	8.88(±1.165)	4	2.31(±0.292)	4	6.57(±1.291)	4
Discharge	Cl_2	1.6	56.80	28.25(±10.144)	8	5.35(±2.447)	8	22.90(±7.869)	8
Circulator	BrCl	1.1	63.25	16.80(±5.151)	8	3.44(±0.880)	8	13.36(±4.376)	8
Condenser	BrCl	0.9	51.75	13.62(±3.263)	4	3.10(±1.463)	4	10.52(±2.165)	4
Discharge	BrCl	1.0	57.50	41.32(±18.098)	8	6.00(±1.032)	8	35.32(±17.880)	8

[a] Mean concentration for trial periods

[b] ± 1 S.D.

[c] Number of samples

Table C-3 (continued)

Test Conditions				Days of Fouling Exposure					
	Biocides			Day 6 (16 September 1976)					
Station Location	Type	Mean Conc.[a] (μeq/l)	(ppb)	Total Weight(mg)	n	Organic Weight(mg)	n	Inorganic Weight(mg)	n
Embayment		0.0	0	42.33(±10.006)	8	7.60(±1.051)	8	34.73(±9.195)	8
Circulator	Cl_2	5.3	188.15	18.64(±4.763)	8	3.57(±0.999)	8	15.07(±3.951)	8
Condenser	Cl_2	3.3	117.15	20.35(±2.605)	4	4.29(±1.081)	4	16.06(±1.535)	4
Discharge	Cl_2	1.6	56.80	33.65(±8.303)	8	5.81(±1.356)	8	27.84(±7.129)	8
Circulator	BrCl	1.1	63.25	29.78(±7.375)	8	5.58(±1.317)	8	24.20(±6.123)	8
Condenser	BrCl	0.9	51.75	28.32(±13.204)	4	4.75(±1.939)	4	23.57(±11.274)	4
Discharge	BrCl	1.0	57.50	56.70(±16.035)	8	10.64(±3.282)	8	46.06(±12.879)	8

[a]Mean concentration for 15 days.

Table C-3 (continued)

Test Conditions				Days of Fouling Exposure					
	Biocides			Day 9 (19 September 1976)					
Station Location	Type	Mean Conc.[a] (μeq/l)	(ppb)	Total Weight(mg)	n	Organic Weight(mg)	n	Inorganic Weight(mg)	n
Embayment		0.0	0	76.77(±18.652)	8	14.27(±2.945)	8	62.50(±15.782)	8
Circulator	Cl_2	5.3	188.15	28.56(±14.143)	8	4.97(±1.531)	8	23.59(±12.787)	8
Condenser	Cl_2	3.3	117.15	20.39(±14.603)	4	5.84(±4.798)	4	14.55(±10.744)	4
Discharge	Cl_2	1.6	56.80	38.50(±6.972)	8	7.24(±1.313)	8	31.26(±5.714)	8
Circulator	BrCl	1.1	63.25	31.85(±7.425)	8	6.13(±1.287)	8	25.72(±6.218)	8
Condenser	BrCl	0.9	51.75	53.77(±6.580)	4	9.22(±3.757)	4	44.55(±5.515)	4
Discharge	BrCl	1.0	57.50	95.68(±26.254)	8	21.74(±11.669)	8	73.94(±28.075)	8

[a]Mean concentration for 15 days.

Table C-3 (continued)

Test Conditions				Days of Fouling Exposure					
	Biocides			Day 12 (22 September 1976)					
Station Location	Type	Mean Conc.[a] (μeq/l)	(ppb)	Total Weight(mg)	n	Organic Weight(mg)	n	Inorganic Weight(mg)	n
Embayment		0.0	0	169.75(±50.225)	8	28.09(±6.347)	8	141.66(±44.048)	8
Circulator	Cl_2	5.3	188.15	25.50(±12.347)	8	3.08(±1.497)	8	22.42(±10.983)	8
Condenser	Cl_2	3.3	117.15	22.39(±8.904)	4	2.04(±1.349)	4	20.35(±8.765)	4
Discharge	Cl_2	1.6	56.80	77.99(±16.504)	8	9.55(±2.933)	8	68.44(±13.770)	8
Circulator	BrCl					no data			
Condenser	BrCl					no data			
Discharge	BrCl	1.0	57.50	97.78(±25.091)	8	17.59(±3.852)	8	80.19(±21.554)	8

[a]Mean concentration for 15 days.

Table C-3 (continued)

Test Conditions				Days of Fouling Exposure					
	Biocides			Day 15 (25 September 1976)					
Station Location	Type	Mean Conc.[a] (μeq/l)	(ppb)	Total Weight(mg)	n	Organic Weight(mg)	n	Inorganic Weight(mg)	n
Embayment		0.0	0	297.95(±47.455)	8	50.03(±62.02)	8	247.92(±41.966)	8
Circulator	Cl_2	5.3	188.15	33.22(±22.549)	8	6.31(±2.242)	8	26.91(±20.520)	8
Condenser	Cl_2	3.3	117.15	21.07(±5.891)	4	5.02(±1.741)	4	16.05(±4.445)	4
Discharge	Cl_2	1.6	56.80	86.52(±20.003)	8	15.09(±2.685)	8	71.43(±17.380)	8
Circulator	BrCl					no data			
Condenser	BrCl					no data			
Discharge	BrCl	1.0	57.50	159.37(±26.977)	8	29.98(±3.686)	8	129.39(±23.509)	8

[a]Mean concentration for 15 days.

STATISTICAL EVALUATION OF BIOFOULING IN PRESENCE AND ABSENCE OF BIOCIDES

All studies (both the 15-day and 9-day tests in the first and second study periods) were analyzed statistically as a four factor partial hierarchal analysis of variance (ANOVA). Before the ANOVA statistics were performed, all data were checked to determine if the assumption of homogeneity of variance held. It was found that, in all cases for all three variables (total dry weight, organic weight, and inorganic weight), the largest variance in each case was several fold greater than the smallest one; therefore, several transformations (e.g., log transformation, square root transformation, etc.) were used to homogenize the variance. The log transformation was found to be the most appropriate; therefore, all data were log-transformed before the ANOVA was performed.

The four factors used in the ANOVA for each of the three study variables were: (1) station (see Table C-4 for station codes), (2) day, (3) fouling chambers nested within station, and (4) replicate fouling substrates nested within fouling chambers. There were seven levels in the station factor: three BrCl stations, three Cl_2 stations, and one reference station. The day factor consisted of five levels in the 15-day tests (days 3, 6, 9, 12, and 15) and three levels in the 9-day tests (days 3, 6, and 9). Duplicate fouling chambers were nested within all stations during the 15-day trials and the 9-day trial of the second study, with the exception of the BrCl and Cl_2 condenser stations where only one fouling chamber was used because of the flow conditions. Because of the initiation sequence of the 9-day trial during the first study period, fouling chambers could only be run in duplicate at the Cl_2 circulator station and the Cl_2 discharge station. The replicates nested within fouling chambers consisted of four levels (five levels in the case of some 9-day tests in the first study period); four (or five in the 9-day test) fouling substrates were located in specified positions within partitions in the fouling chamber (see Chapter 4: "Analytical Procedures," Table 4-2: Sampling Design and Schedule).

Initial four factor ANOVA on log-transformed total, organic, and inorganic weights for all 15- and 9-day tests showed that no significant difference ($P>0.01$) existed between duplicate fouling chambers nested within stations. No significant differences ($P>0.01$) were found among replicate fouling substrates nested within each fouling chamber. That is, no significant difference occurred among replicate fouling substrates down the length of the fouling chambers. Significant ($P<0.01$) station, day, and station-by-day interactions were found in all studies for all three variables. The station and day factors were subsequently treated as a two factor ANOVA. The method of fitting constants as described by Bancroft (1968) for use with ANOVA with unbalanced designs was used in the two factor ANOVA.

Several tests were used to elucidate the station-by-day interactions. An ANOVA for station effect at each of the levels of the day factor was performed. If a significant effect was found, Tukey's multiple range test (Winer, 1971) was used to determine where significant differences occurred among the stations (including the reference station) at each day for each variable. After the station effects were determined, an ANOVA for day effect at each level of the station factor was performed. If a significant effect was found between stations, Tukey's test (Winer, 1971) was used to detect significant differences among pairwise comparisons among the days.

Significant differences were found for station effects at each level of the day factor in all studies. The specific differences by day among the BrCl, Cl_2, and reference stations for all three variables are summarized in Tables C-5 to C-7. Table C-5 is a summary of Tukey's test (Winer, 1971) of the among mean station comparisons of all BrCl stations at days 3, 6, 9, 12, and 15 for the 15-day trial conducted between 11 August 1976 and 26 August 1976. A summary of the among mean station comparisons of all BrCl and Cl_2 stations for the 9-day trials conducted from 17 August 1976 to 26 August 1976, is presented in Table C-6. Table C-7 is a summary of the 9-day and 15-day trials conducted during September 1976.

Significant differences were also found for day effects at each level of the station factor in all studies. The specific differences by station among the days for all three variables are summarized in Tables C-8 to C-10. Table C-8 is a summary of Tukey's test (Winer, 1971) of the among mean day comparisons of each station for the 15-day trial conducted during the first study (11 August 1976 and 26 August 1976). A summary of the among mean day comparisons of each station for the 9-day trials conducted between 17 August 1976 and 26 August 1976 is presented in Table C-9. Table C-10 is a summary of the 9-day and 15-day trials conducted during September 1976.

Literature Cited

Bancroft, T.A. Topics in Intermediate Statistical Research. Iowa State Univ. Press, Ames. 129 p. 1968

Winer, B.J. Statistical Principles in Experimental Design. McGraw Hill, New York. 387 p. 1971

Table C-4. STATION IDENTIFICATION CODES FOR TABLES

Station	Station Identification Code
Embayment (reference)	Emb-R
Unit I circulator-BrCl	Cir-B
Unit I condenser-BrCl	Con-B
Unit I discharge-BrCl	Dis-B
Unit II circulator-Cl_2	Cir-C
Unit II condenser-Cl_2	Con-C
Unit II discharge-Cl_2	Dis-C

Table C-5. SUMMARY OF THE STATISTICAL ANALYSES OF THE AMONG MEAN STATION COMPARISONS OF ALL BROMINE CHLORIDE STATIONS AT DAYS 3, 6, 9, 12, AND 15 FOR THE 15-DAY TEST CONDUCTED DURING THE FIRST STUDY 11 AUGUST 1976 TO 26 AUGUST 1976[a,b]

Day 3 Total Weight

Station	Emb-R	Cir-B	Con-B	Dis-B
Emb-R	--	NS	*	*
Cir-B		--	NS	*
Con-B			--	NS
Dis-B				--

Day 3 Organic Weight

Station	Emb-R	Cir-B	Con-B	Dis-B
Emb-R	--	NS	NS	NS
Cir-B		--	NS	NS
Con-B			--	NS
Dis-B				--

Day 3 Inorganic Weight

Station	Emb-R	Cir-B	Con-B	Dis-B
Emb-R	--	NS	*	*
Cir-B		--	NS	*
Con-B			--	NS
Dis-B				--

[a]Concentrations with an * were significantly different at $P<0.01$; concentrations with NS were not significantly different at $P>0.01$.

[b]See Table C-4 for station identification codes.

Table C-5 (continued)

Day 6 Total Weight

Station	Cir-B	Con-B	Dis-B	Emb-R
Cir-B	--	*	*	*
Con-B		--	NS	*
Dis-B			--	NS
Emb-R				--

Day 6 Organic Weight

Station	Cir-B	Con-B	Dis-B	Emb-R
Cir-B	--	NS	*	*
Con-B		--	NS	*
Dis-B			--	NS
Emb-R				--

Day 6 Inorganic Weight

Station	Cir-B	Con-B	Dis-B	Emb-R
Cir-B	--	*	*	*
Con-B		--	NS	*
Dis-B			--	NS
Emb-R				--

Table C-5 (continued)

Day 9 Total Weight

Station	Cir-B	Con-B	Dis-B	Emb-R
Cir-B	--	*	*	*
Con-B		--	*	*
Dis-B			--	NS
Emb-R				--

Day 9 Organic Weight

Station	Cir-B	Con-B	Dis-B	Emb-R
Cir-B	--	*	*	*
Con-B		--	*	*
Dis-B			--	NS
Emb-R				--

Day 9 Inorganic Weight

Station	Cir-B	Con-B	Emb-R	Dis-B
Cir-B	--	*	*	*
Con-B		--	*	*
Emb-R			--	NS
Dis-B				--

Table C-5 (continued)

Day 12 Total Weight

Station	Cir-B	Con-B	Emb-R	Dis-B
Cir-B	--	*	*	*
Con-B		--	*	*
Emb-R			--	NS
Dis-B				--

Day 12 Organic Weight

Station	Cir-B	Con-B	Emb-R	Dis-B
Cir-B	--	*	*	*
Con-B		--	*	*
Emb-R			--	NS
Dis-B				--

Day 12 Inorganic Weight

Station	Cir-B	Con-B	Emb-R	Dis-B
Cir-B	--	*	*	*
Con-B		--	*	*
Emb-R			--	NS
Dis-B				--

Table C-5 (continued)

Day 15 Total Weight

Station	Cir-B	Con-B	Emb-R	Dis-B
Cir-B	--	*	*	*
Con-B		--	*	*
Emb-R			--	NS
Dis-B				--

Day 15 Organic Weight

Station	Cir-B	Con-B	Emb-R	Dis-B
Cir-B	--	*	*	*
Con-B		--	*	*
Emb-R			--	NS
Dis-B				--

Day 15 Inorganic Weight

Station	Cir-B	Con-B	Emb-R	Dis-B
Cir-B	--	*	*	*
Con-B		--	*	*
Emb-R			--	NS
Dis-B				--

Table C-6. SUMMARY OF THE STATISTICAL ANALYSES OF THE AMONG MEAN STATION COMPARISONS OF ALL BROMINE CHLORIDE AND CHLORINE STATIONS AT DAYS 3, 6, AND 9 FOR THE 9-DAY TEST CONDUCTED DURING THE FIRST STUDY 17 AUGUST 1976 TO 26 AUGUST 1976[a,b]

Day 3 Total Weight

Station	Con-C	Cir-C	Cir-B	Con-B	Dis-C	Dis-B	Emb-R
Con-C	--	NS	NS	NS	*	*	*
Cir-B		--	NS	NS	*	*	*
Cir-C			--	NS	*	*	*
Con-B				--	NS	*	*
Dis-C					--	*	*
Dis-B						--	NS
Emb-R							--

Day 3 Organic Weight

Station	Con-C	Cir-C	Cir-B	Con-B	Dis-C	Emb-R	Dis-B
Cir-C	--	NS	NS	NS	*	*	*
Con-C		--	NS	NS	NS	*	*
Cir-B			--	NS	NS	*	*
Con-B				--	NS	*	*
Dis-C					--	*	*
Emb-R						--	NS
Dis-B							--

[a]Concentrations with an * were significantly different at P<0.01; concentrations with NS were not significantly different at P>0.01.

[b]See Table C-4 for station identification codes.

Table C-6 (continued)

Day 3 Inorganic Weight

Station	Con-C	Cir-C	Cir-B	Con-B	Dis-C	Dis-B	Emb-R
Con-C	--	NS	NS	NS	*	*	*
Cir-C		--	NS	NS	*	*	*
Cir-B			--	NS	*	*	*
Con-B				--	*	*	*
Dis-C					--	*	*
Dis-B						--	NS
Emb-R							--

Day 6 Total Weight

Station	Cir-B	Cir-C	Con-C	Dis-C	Emb-R	Dis-B
Cir-B	--	*	*	*	*	*
Cir-C		--	NS	*	*	*
Con-C			--	*	*	*
Dis-C				--	NS	*
Emb-R					--	NS
Dis-B						--

Table C-6 (continued)

Day 6 Organic Weight

Station	Cir-B	Cir-C	Con-C	Dis-C	Emb-R	Dis-B
Cir-B	--	NS	NS	*	*	*
Cir-C		--	NS	*	*	*
Con-C			--	*	*	*
Dis-C				--	NS	*
Emb-R					--	NS
Dis-B						--

Day 6 Inorganic Weight

Station	Cir-B	Cir-C	Con-C	Dis-C	Emb-R	Dis-B
Cir-B	--	*	*	*	*	*
Cir-C		--	NS	*	*	*
Con-C			--	*	*	*
Dis-C				--	NS	*
Emb-R					--	NS
Dis-B						--

Table C-6 (continued)

Day 9 Total Weight

Station	Cir-B	Con-C	Cir=C	Con-B	Dis-C	Emb-R	Dis-B
Cir-B	--	NS	NS	*	*	*	*
Con-C		--	NS	NS	*	*	*
Cir-C			--	NS	*	*	*
Con-B				--	*	*	*
Dis-C					--	NS	NS
Emb-R						--	NS
Dis-B							--

Day 9 Organic Weight

Station	Cir-B	Cir-C	Con-C	Con-B	Dis-C	Emb-R	Dis-B
Cir-B	--	NS	NS	NS	*	*	*
Cir-C		--	NS	NS	*	*	*
Con-C			--	NS	*	*	*
Con-B				--	*	*	*
Dis-C					--	NS	*
Emb-R						--	NS
Dis-B							--

Table C-6 (continued)

Day 9 Inorganic Weight

Station	Cir-B	Con-C	Cir-C	Con-B	Dis-C	Emb-R	Dis-B
Cir-B	--	NS	NS	*	*	*	*
Con-C		--	NS	NS	*	*	*
Cir-C			--	NS	*	*	*
Con-B				--	*	*	*
Dis-C					--	NS	NS
Emb-R						--	NS
Dis-B							--

Table C-7. SUMMARY OF THE STATISTICAL ANALYSES OF THE AMONG MEAN STATION COMPARISONS OF ALL BROMINE CHLORIDE AND CHLORINE STATIONS AT DAYS 3, 6, AND 9 FOR THE 9-DAY TEST AND DAYS 3, 6, 9, 12, AND 15 FOR THE 15-DAY TEST CONDUCTED DURING THE SECOND STUDY 10 SEPTEMBER 1976 TO 25 SEPTEMBER 1976[a,b]

Day 3 Total Weight

Station	Con-C	Emb-R	Con-B	Cir-C	Cir-B	Dis-C	Dis-B
Con-C	--	NS	NS	NS	NS	*	*
Emb-R		--	NS	NS	NS	*	*
Con-B			--	NS	NS	*	*
Cir-C				--	NS	NS	*
Cir-B					--	NS	*
Dis-C						--	NS
Dis-B							--

Day 3 Organic Weight

Station	Con-C	Con-B	Cir-C	Emb-R	Cir-B	Dis-C	Dis-B
Con-C	--	NS	NS	NS	NS	NS	*
Con-B		--	NS	NS	NS	NS	NS
Cir-C			--	NS	NS	NS	NS
Emb-R				--	NS	NS	NS
Cir-B					--	NS	NS
Dis-C						--	NS
Dis-B							--

[a]Concentrations with an * were significantly different at $P<0.01$; concentrations with NS were not significantly different at $P>0.01$.

[b]See Table C-4 for station identification codes.

Table C-7 (continued)

Day 3 Inorganic Weight

Station	Con-C	Emb-R	Con-B	Cir-C	Cir-B	Dis-C	Dis-B
Con-C	--	NS	NS	NS	NS	*	*
Emb-R		--	NS	NS	NS	*	*
Con-B			--	NS	NS	*	*
Cir-C				--	NS	NS	*
Cir-B					--	NS	*
Dis-C						--	NS
Dis-B							--

Day 6 Total Weight

Station	Cir-C	Con-C	Con-B	Cir-B	Dis-C	Emb-R	Dis-B
Cir-C	--	NS	NS	NS	NS	*	*
Con-C		--	NS	NS	NS	*	*
Con-B			--	NS	NS	NS	*
Cir-B				--	NS	NS	NS
Dis-C					--	NS	NS
Emb-R						--	NS
Dis-B							--

Table C-7 (continued)

Day 6 Organic Weight

Station	Cir-C	Con-C	Con-B	Cir-B	Dis-C	Emb-R	Dis-B
Cir-C	--	NS	NS	NS	NS	NS	*
Con-C		--	NS	NS	NS	NS	*
Con-B			--	NS	NS	NS	*
Cir-B				--	NS	NS	NS
Dis-C					--	NS	NS
Emb-R						--	NS
Dis-B							--

Day 6 Inorganic Weight

Station	Cir-C	Con-C	Con-B	Cir-B	Dis-C	Emb-R	Dis-B
Cir-C	--	NS	NS	NS	NS	*	*
Con-C		--	NS	NS	NS	*	*
Con-B			--	NS	NS	NS	NS
Cir-B				--	NS	NS	NS
Dis-C					--	NS	NS
Emb-R						--	NS
Dis-B							--

Table C-7 (continued)

Day 9 Total Weight

Station	Con-C	Cir-C	Cir-B	Dis-C	Con-B	Emb-R	Dis-B
Con-C	--	NS	NS	*	*	*	*
Cir-C		--	NS	NS	*	*	*
Cir-B			--	NS	NS	*	*
Dis-C				--	NS	NS	*
Con-B					--	NS	NS
Emb-R						--	NS
Dis-B							--

Day 9 Organic Weight

Station	Cir-C	Con-C	Cir-B	Dis-C	Con-B	Emb-R	Dis-B
Cir-C	--	NS	NS	NS	NS	*	*
Con-C		--	NS	NS	NS	*	*
Cir-B			--	NS	NS	*	*
Dis-C				--	NS	NS	*
Con-B					--	NS	*
Emb-R						--	NS
Dis-B							--

Table C-7 (continued)

Day 9 Inorganic Weight

Station	Cir-C	Con-C	Cir-B	Dis-C	Con-B	Emb-R	Dis-B
Cir-C	--	NS	NS	*	*	*	*
Con-C		--	NS	NS	NS	*	*
Cir-B			--	NS	NS	*	*
Dis-C				--	NS	NS	NS
Con-B					--	NS	NS
Emb-R						--	NS
Dis-B							--

Day 12 Total Weight

Station	Con-C	Cir-C	Dis-C	Dis-B	Emb-R
Con-C	--	NS	*	*	*
Cir-C		--	*	*	*
Dis-C			--	NS	*
Dis-B				--	*
Emb-R					--

Table C-7 (continued)

Day 12 Organic Weight

Station	Con-C	Cir-C	Dis-C	Dis-B	Emb-R
Con-C	--	*	*	*	*
Cir-C		--	*	*	*
Dis-C			--	NS	*
Dis-B				--	NS
Emb-R					--

Day 12 Inorganic Weight

Station	Con-C	Cir-C	Dis-C	Dis-B	Emb-R
Con-C	--	NS	*	*	*
Cir-C		--	*	*	*
Dis-C			--	NS	*
Dis-B				--	NS
Emb-R					--

Day 15 Total Weight

Station	Con-C	Cir-C	Dis-C	Dis-B	Emb-R
Con-C	--	NS	*	*	*
Cir-C		--	*	*	*
Dis-C			--	*	*
Dis-B				--	*
Emb-R					--

Table C-7 (continued)

Day 15 Organic Weight

Station	Con-C	Cir-C	Dis-C	Dis-B	Emb-R
Con-C	--	NS	*	*	*
Cir-C		--	*	*	*
Dis-C			--	*	*
Dis-B				--	NS
Emb-R					--

Day 15 Inorganic Weight

Station	Con-C	Cir-C	Dis-C	Dis-B	Emb-R
Con-C	--	NS	*	*	*
Cir-C		--	*	*	*
Dis-C			--	*	*
Dis-B				--	*
Emb-R					--

Table C-8. SUMMARY OF THE STATISTICAL ANALYSES OF THE AMONG MEAN DAY COMPARISONS OF EACH STATION FOR THE 15-DAY TESTS CONDUCTED DURING THE FIRST STUDY 11 AUGUST 1976 TO 26 AUGUST 1976[a]

Embayment (Reference) - Total Weight

Day	3	6	9	12	15
3	--	*	*	*	*
6		--	*	*	*
9			--	*	*
12				--	*
15					--

Embayment (Reference) - Organic Weight

Day	3	6	9	12	15
3	--	*	*	*	*
6		--	*	*	*
9			--	*	*
12				--	*
15					--

Embayment (Reference) - Inorganic Weight

Day	3	6	9	12	15
3	--	*	*	*	*
6		--	*	*	*
9			--	*	*
12				--	*
15					--

[a]Days with an * were significantly different at P<0.01; days with NS were not significantly different at P>0.01.

Table C-8 (continued)

Unit I Circulator (BrCl) - Total Weight

Day	3	6	9	12	15
3	--	NS	*	*	*
6		--	*	*	*
9			--	NS	NS
12				--	NS
15					--

Unit I Circulator (BrCl) - Organic Weight

Day	3	6	9	12	15
3	--	NS	*	*	*
6		--	*	*	*
9			--	NS	NS
12				--	NS
15					--

Unit I Circulator (BrCl) - Inorganic Weight

Day	3	6	9	12	15
3	--	NS	*	*	*
6		--	*	*	*
9			--	NS	NS
12				--	NS
15					--

Table C-8 (continued)

Unit I Condenser (BrCl) - Total Weight

Day	3	6	9	12	15
3	--	*	*	*	*
6		--	*	*	*
9			--	NS	*
12				--	NS
15					--

Unit I Condenser (BrCl) - Organic Weight

Day	3	6	9	12	15
3	--	NS	*	*	*
6		--	*	*	*
9			--	NS	*
12				--	NS
15					--

Unit I Condenser (BrCl) - Inorganic Weight

Day	3	6	9	12	15
3	--	*	*	*	*
6		--	*	*	*
9			--	NS	NS
12				--	NS
15					--

Table C-8 (continued)

Unit I Discharge (BrCl) - Total Weight					
Day	3	6	9	12	15
3	--	*	*	*	*
6		--	*	*	*
9			--	*	*
12				--	*
15					--

Unit I Discharge (BrCl) - Organic Weight					
Day	3	6	9	12	15
3	--	NS	*	*	*
6		--	*	*	*
9			--	NS	*
12				--	NS
15					--

Unit I Discharge (BrCl) - Inorganic Weight					
Day	3	6	9	12	15
3	--	*	*	*	*
6		--	*	*	*
9			--	*	*
12				--	*
15					--

Table C-9. SUMMARY OF THE STATISTICAL ANALYSES OF THE AMONG MEAN DAY COMPARISONS OF EACH STATION FOR 9-DAY TESTS CONDUCTED DURING THE FIRST STUDY 17 AUGUST 1976 TO 26 AUGUST 1976[a]

	Embayment (Reference) - Total Weight		
Day	3	6	9
3	--	*	*
6		--	*
9			--
	Embayment (Reference) - Organic Weight		
Day	3	6	9
3	--	*	*
6		--	*
9			--
	Embayment (Reference) - Inorganic Weight		
Day	3	6	9
3	--	*	*
6		--	*
9			--
	Unit I Circulator (BrCl) - Total Weight		
Day	3	6	9
3	--	NS	*
6		--	*
9			--

[a]Days with an * were significantly different at P <0.01; days with NS were not significantly different at P>0.01.

Table C-9 (continued)

Unit I Circulator (BrCl) - Organic Weight			
Day	3	6	9
3	--	NS	*
6		--	NS
9			--

Unit I Circulator (BrCl) - Inorganic Weight			
Day	3	6	9
3	--	NS	*
6		--	*
9			--

Unit I Condenser (BrCl) - Total Weight		
Day	3	9
3	--	*
9		--

Unit I Condenser (BrCl) - Organic Weight		
Day	3	9
3	--	*
9		--

Unit I Condenser (BrCl) - Inorganic Weight		
Day	3	9
3	--	*
9		--

Table C-9 (continued)

Unit I Discharge (BrCl) - Total Weight			
Day	3	6	9
3	--	*	*
6		--	*
9			--

Unit I Discharge (BrCl) - Organic Weight			
Day	3	6	0
3	--	*	*
6		--	NS
9			--

Unit I Discharge (BrCl) - Inorganic Weight			
Day	3	6	9
3	--	*	*
6		--	*
9			--

Unit II Circulator (Cl_2) - Total Weight			
Day	3	6	9
3	--	*	*
6		--	NS
9			--

Table C-9 (continued)

Unit II Circulator (Cl_2) - Organic Weight			
Day	3	6	9
3	--	*	*
6		--	NS
9			--

Unit II Circulator (Cl_2) - Inorganic Weight			
Day	3	6	9
3	--	*	*
6		--	NS
9			--

Unit II Condenser (Cl_2) - Total Weight			
Day	3	6	9
3	--	*	*
6		--	NS
9			--

Unit II Condenser (Cl_2) - Organic Weight			
Day	3	6	9
3	--	*	*
6		--	NS
9			--

Table C-9 (continued)

Unit II Condenser (Cl_2) - Inorganic Weight			
Day	3	6	9
3	--	*	*
6		--	NS
9			--

Unit II Discharge (Cl_2) - Total Weight			
Day	3	6	9
3	--	*	*
6		--	*
9			--

Unit II Discharge (Cl_2) - Organic Weight			
Day	3	6	9
3	--	*	*
6		--	*
9			--

Unit II Discharge (Cl_2) - Inorganic Weight			
Day	3	6	9
3	--	*	*
6		--	*
9			--

Table C-10. SUMMARY OF THE STATISTICAL ANALYSES OF THE AMONG MEAN DAY COMPARISONS OF EACH STATION FOR THE 9-DAY AND 15-DAY TESTS CONDUCTED DURING THE SECOND STUDY 10 SEPTEMBER 1976 TO 25 SEPTEMBER 1976[a]

Embayment (Reference) - Total Weight					
Day	3	6	9	12	15
3	--	*	*	*	*
6		--	*	*	*
9			--	*	*
12				--	*
15					--

Embayment (Reference) - Organic Weight					
Day	3	6	9	12	15
3	--	*	*	*	*
6		--	*	*	*
9			--	*	*
12				--	*
15					--

Embayment (Reference) - Inorganic Weight					
Day	3	6	9	12	15
3	--	*	*	*	*
6		--	*	*	*
9			--	*	*
12				--	*
15					--

[a] Days with an * were significantly different at P<0.01; days with NS were not significantly different at P>0.01.

Table C-10 (continued)

Unit I Circulator (BrCl) - Total Weight			
Day	3	6	9
3	--	*	*
6		--	NS
9			--

Unit I Circulator (BrCl) - Organic Weight			
Day	3	6	9
3	--	NS	*
6		--	NS
9			--

Unit I Circulator (BrCl) - Inorganic Weight			
Day	3	6	9
3	--	*	*
6		--	NS
9			--

Unit I Condenser (BrCl) - Total Weight			
Day	3	6	9
3	--	*	*
6		--	*
9			--

Table C-10 (continued)

Unit I Condenser (BrCl) - Organic Weight

Day	3	6	9
3	--	NS	*
6		--	NS
9			--

Unit I Condenser (BrCl) - Inorganic Weight

Day	3	6	9
3	--	*	*
6		--	*
9			--

Unit I Discharge (BrCl) - Total Weight

Day	3	6	9	12	15
3	--	NS	*	*	*
6		--	*	*	*
9			--	NS	*
12				--	*
15					--

Table C-10 (continued)

Unit I Discharge (BrCl) - Organic Weight

Day	3	6	9	12	15
3	--	NS	*	*	*
6		--	NS	*	*
9			--	NS	*
12				--	NS
15					--

Unit I Discharge (BrCl) - Inorganic Weight

Day	3	6	12	9	15
3	--	NS	*	*	*
6		--	NS	*	*
12			--	NS	*
9				--	NS
15					--

Unit II Circulator (Cl_2) - Total Weight

Day	3	6	12	9	15
3	--	NS	NS	*	*
6		--	NS	NS	*
12			--	NS	NS
9				--	NS
15					--

Table C-10 (continued)

Unit II Circulator (Cl_2) - Organic Weight

Day	3	6	12	9	15
3	--	NS	NS	NS	*
6		--	NS	NS	*
12			--	NS	NS
9				--	NS
15					--

Unit II Circulator (Cl_2) -Inorganic Weight

Day	3	6	12	9	15
3	--	NS	NS	NS	*
6		--	NS	NS	*
12			--	NS	NS
9				--	NS
15					--

Unit II Condensor (Cl_2) - Total Weight

Day	3	9	6	15	12
3	--	*	*	*	*
9		--	NS	NS	NS
6			--	NS	NS
15				--	NS
12					--

Table C-10 (continued)

	Unit II Discharge (Cl_2) - Organic Weight				
Day	3	6	9	12	15
3	--	NS	NS	*	*
6		--	NS	NS	*
9			--	NS	*
12				--	NS
15					--

	Unit II Discharge (Cl_2) - Inorganic Weight				
Day	3	6	9	12	15
3	--	NS	NS	*	*
6		--	NS	*	*
9			--	*	*
12				--	NS
15					--

APPENDIX D

ECONOMIC AND AVAILABILITY CONSIDERATIONS OF BROMINE CHLORIDE

ECONOMIC AND AVAILABILITY CONSIDERATIONS OF BROMINE CHLORIDE

Cost comparisons of cooling water treatment with Cl_2 vs BrCl are given below. These estimates are based on biocide cost information supplied by Dow Chemical (personal communication, Dr. Jack Mills) and Ethyl Corporation (personal communication, Dr. A. H. Filbey). Biocide costs were based on a price of $0.22 per kg for chlorine and $0.55 per kg for BrCl (costs of transportation and injection were assumed to be the same for both biocides). In comparing the two biocides, it was assumed that effective treatment resulted from a continuous chlorine or bromine chloride input of 0.5 ppm. For a dosage of 1350 kg/day of each biocide (the amount required to maintain a concentration of 0.5 ppm in the cooling stream) and a condenser flow of 31 m^3/sec, continuous injection of chlorine and bromine chloride would cost $300/day and $750/day, respectively. In other words, chlorobromination of cooling water may be 2½ times the cost of chlorination.

The price for bromine chloride, presently $0.55 per kg, would probably decline if mass production were initiated. Future pricing of this product may follow cost trends of similar developmental products as they achieve adult status. Although the price of bromine chloride is relatively insensitive to fluctuations in the cost of energy*, future increases in the cost of power may change this situation.

Bromine chloride is made by mixing stoichiometric quantities of bromine and chlorine (Mills, 1975). The present U. S. bromine chloride production capacity is estimated at 45 million kg per year. The capacity could probably be increased several fold within months, based on an estimate of the capacity expandable within a year and/or adjustments in bromine end-use.

In 1975, the total bromine production capacity in the United States was over 225 million kg, divided among the five bromine producers: Dow, Ethyl Corporation, Great Lakes, Michigan Chemical, and Arkansas Chemical. Ethyl Corporation, Great Lakes, and Dow control about 85% of the U. S. bromine production capacity. With the 1976 increase in production, the total U. S. capacity is estimated at about 250 million kg per year. If this production were totally dedicated to bromine chloride, it would yield 360 million kg of bromine chloride.

The capacity for base bromine production could be easily and substantially increased by drilling additional brine wells and expanding surface facilities. Well capacity presently increases by 10% per year. The present known underground bromine brine reserves in Arkansas and Michigan will afford at least a 100-year bromine supply at present consumption levels.

* The energy cost of BrCl and Cl_2 production is approximately 1 to 2 kwh per pound; that of O_3 is 10 to 12 kwh per pound.

Additionally, there are large seawater reserves. Much of the present bromine production is committed to various end-uses, including brominated organic and inorganic products. About 50-55% of the bromine produced is used to manufacture ethylene dibromide, a lead scavenger for gasoline. This market is declining at about 10% per year because of the use of unleaded gasoline in automobiles. Additional quantities of bromine thus will be available in the future.

The present domestic consumption of chlorine for condenser cooling water treatment is estimated at 27 million kg per year. This is about 0.5% of the domestic annual chlorine production (Chemical Marketing Reporter, 1973). If all power plants switched to BrCl, 27 million kg per year would be required for cooling water treatment.* The production of this amount of BrCl would require 18 million kg of bromine, which is about 7% of the present domestic production.

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* Assuming that BrCl effectiveness, as determined in the present study, applies nationally.

REFERENCES

Chemical Marketing Reporter. 1973. Schnell Publishing Company, Inc. New York, New York. May 1973.

APPENDIX E

THE SHIPPING, STORAGE, AND FEEDING OF BROMINE CHLORIDE

Contents

Shipping Bromine Chloride

Unloading and Storage

Bromine Chloride Feeding

Materials of Construction

Handling Precautions

THE SHIPPING, STORAGE, AND FEEDING OF BROMINE CHLORIDE

(Prepared by Dr. Jack Mills, Dow Chemical, Midland, Mich.)

Bromine chloride shipping, storage, and feeding closely parallel chlorine technology, with some important differences. For details concerning the shipping and handling of bromine chloride; the reader is referred to "Bromine Chloride Handbook," Form No. 101-15-72, supplied by the Dow Chemical USA, Inorganic Chemicals Department, Midland, Michigan 48640, and "Bromine Chloride for Treating Cooling Water and Wastewater," supplied by Ethyl Corporation, 1600 W. Eight Mile Rd., Ferndale, Michigan 48220. In addition to summarizing the chemical and physical properties of bromine chloride, these references describe unloading procedures, materials of construction, corrosivity, analysis, environmental properties, and safe handling practices.

SHIPPING BROMINE CHLORIDE

Bromine chloride is classified by the Department of Transportation (DOT) as a corrosive liquid. It is available from Dow in tank cars, and in cylinders and 3000-pound containers for development use. At the present time, Special Permit DOT-E 6602 authorizes shipment of bromine chloride and bromine chloride mixtures in steel tank trucks and tank cars similar to those used for chlorine:

- DOT Specification MC-331 tank motor vehicles having cargo tanks of 225 psig service pressure and minimum wall thickness of 0.625 inch.

- DOT Specification 105A500W tank cars or 106A500X tanks.

The DOT permit restricts the loading limit of tank cars to 110,000 pounds, and their outage must be not less than 2%. Smaller cylinders, such as 150 pounds or less, do not require a DOT Special Permit but fall under the DOT regulations covering corrosive liquids found in paragraphs 173-244 and 173-245 of the Code of Federal Regulations on Transportation.

At the present time, bromine chloride shipments and use are regulated under the Environmental Protection Agency Experimental Use Permit No. 464-EUP-47, issued July 9, 1976, under the provisions of the Federal Insecticide, Fungicide, and Rodenticide Act.

UNLOADING AND STORAGE

Chlorine unloading facilities, including unloading lines made of steel, can be used for bromine chloride. However, for longer service, it is recommended that Kynar-lined steel pipe or its equivalent be used to transfer liquid bromine chloride.

Bromine chloride should always be removed from a cylinder or tank car as a liquid because the dissociation above the liquid produces a chlorine-rich vapor. Therefore, cylinders loaded with BrCl contain dip tubes for easy removal of the liquid under its own pressure. When liquid is withdrawn by the prescribed method, its composition will remain substantially constant throughout the removal process. On unloading bromine chloride from 3000-pound cylinders or tank cars, special care must be taken to use the proper (liquid) angle valve.

In some locations subject to low winter temperatures, the vapor pressure in a tank car or cylinder may not be sufficient for unloading. The car or cylinder may then be unloaded by padding - i.e., by the addition of completely dry, oil-free, compressed air or nitrogen, similar to the procedure for chlorine padding. However, because of its lower vapor pressure (30 psig) and higher density (2.34 g/cc), BrCl may require padding more frequently than chlorine normally does.

Tank cars loaded with bromine chloride are equipped with ball check valves. If the valve is opened too rapidly, the ball check valve will close, and BrCl will not flow. The liquid angle valve should never be used to regulate the flow rate of BrCl. This valve must be kept completely open to allow the excess flow valve to close if the unloading line is broken.

The same instructions for storage of chlorine also apply to bromine chloride storage. The corrosivity of BrCl to steel is sufficiently low (0.93 mils/yr) to allow storage in steel-constructed cylinders and tank cars for extended periods of time. However, it is recommended that BrCl not be stored for more than 5 years in cylinders.

BROMINE CHLORIDE FEEDING

Bromine chloride can be utilized either in liquid or gaseous form. Generally, it is withdrawn from containers as a liquid, piped to an evaporator, changed to a gas, and fed through process equipment to the application point. Capital Controls Company, Colmar, Pennsylvania, has developed a bromine chloride vapor feed system which is a modification of their vacuum operated gas chlorinator.

In contrast to chlorine feed systems, which require an evaporator only at high feed rates, BrCl vapor feed systems always include an evaporator. The evaporator may consist of a chamber immersed in a controlled, heated water bath, which increases the temperature of the BrCl liquid, causing it to boil. Bromine chloride liquid enters the chamber and maintains the required liquid level and

pressure necessary to meet the vaporization rate for the gas demand. The gas released passes through the chamber and is super-heated as it leaves en route to a vacuum regulator. The vacuum regulator, connected to a remote flow meter, reduces the pressure to a negative (vacuum) pressure. The metered gas is directed to the ejector which creates the vacuum and mixes the gas with a water system. The BrCl solution is piped from the ejector to the point of application or diffuser. If the vacuum is lost, the vacuum regulator will shut off, stopping BrCl flow.

The BrCl feed system should be located in a room that is heated to 60° F minimum and contains provisions for exhausting gas, should a leak develop. Gas lines should not be routed through cool areas as this may cause BrCl reliquefaction in the process piping. If the application point is remote from the equipment area, piping the BrCl solution to the required area is recommended. Before start-up, the BrCl feed system should be tested for leaks, using the prescribed method suggested by the equipment manufacturer.

The estimated cost of the BrCl feed system is comparable to that of a similar-sized chlorine system which includes the cost of a chlorine evaporator; there will be additional cost depending on the choice of materials of construction. The cost of the 4000 pound per day development system for feeding bromine chloride at the Morgantown station was approximately $9500. Capital Controls Company should be consulted for additional information concerning future pricing of various size feeder systems for bromine chloride.

MATERIALS OF CONSTRUCTION

Piping should be of schedule 80 seamless black iron or carbon steel. Cast iron piping, fittings or equipment should never be used for BrCl service since the possibility of failure is greater with such materials, and the consequences of failure are likely to be serious. When bending of carbon steel piping is necessary, it is best bent hot and stress relieved to prevent it from becoming hard and brittle and to reduce the likelihood of failure in service.

Pipeline joints should preferably be flanged or welded. If threaded joints are necessary, extreme care must be taken to obtain clean, sharp pipe threads to ensure pressure-tight joints. Following the pipe-thread cutting operation, the pipe should be reamed and wiped with a solvent-soaked rag to remove cuttings and cutting oil. Solvents such as trichloroethylene or perchloroethylene are suitable for this purpose. Alcohols or hydrocarbons should never be used. A small amount of a linseed oil and white lead paste is recommended as a pipe dope.

Piping should be well supported, protected against extremes in temperature, and adequately sloped to allow drainage. Long liquid BrCl lines are not recommended, but, if used, they should be provided with shut-off valves at each end. A properly designed expansion chamber, with a volume equivalent to 20% of the volume of the pipe section, should be installed between the shut-off valves at the highest point. Its purpose is to absorb increases in the volume of BrCl caused by increases in temperature, and thus prevent hydrostatic rupture of a full line. The Dow Chemical Company may be consulted on installation.

Acceptable fittings include schedule 80 forged-steel welding tees and ells, cast steel 300-pound flanged ells and tees with ASA-faced and-drilled small tongue-and-groove facings, and forged-steel, 2,000-pound screw-end elbows and tees.

Asbestos, impregnated with Teflon polytetrafluoroethylene, and graphite-lubricated asbestos are common packing materials.

Gaskets should be of 3% antimony lead or of bonded asbestos fiber as per Military Specification MIL-A-17472 (Navy) or equivalent. For pipe smaller than 2 inches, 1/16-inch thick gaskets should be used; for pipe 2 inches or larger, gaskets should be 1/8 inch thick. Rubber gaskets are attacked by liquid BrCl and should never be employed.

Pressure gauges should be designed for BrCl service and be either the diaphragm-protected type or the forged-steel, welded bourdon tube type. Suitable diaphragms may be of Monel, silver, or tantalum. A pressure range of not less than 0-250 psig is desirable. Gauge glasses are a potential source of danger and are not recommended on BrCl equipment.

Special care should be taken in avoiding plastic materials which may be attacked by liquid BrCl or its concentrated vapors. Polyvinyl chloride and ABS plastic, which are common to chlorine feeding systems, should be avoided. Plastic pipes made of PVC can be used to carry a water stream containing bromine chloride from the point of injection. Kynar, Teflon, Viton, and other equivalent highly resistant plastics are recommended as replacements for rubber, PVC, or ABS plastics.

HANDLING PRECAUTIONS

Bromine chloride is a heavy, highly corrosive, fuming liquid with a sharp, harsh, penetrating odor. Chemically, it is a very active oxidizing agent, both as a liquid and a vapor. Liquid BrCl rapidly attacks the skin and other tissues, producing irritation and burns which heal very slowly; even comparatively low concentrations of vapor are highly irritating and painful to the respiratory tract.

The warning properties of BrCl are such that a person will avoid gross overexposure if he is capable of getting to fresh air. However, repeated day-long exposures to low levels may be injurious.

For emergencies, the preferred protection consists of self-contained breathing apparatus; a rubber, neoprene, or suitable plastic slicker suit; neoprene rubber gloves; rubber boots or high rubber shoes; and chemical worker's goggles. Full-face plastic shields with forehead protection should be worn in addition to chemical worker's goggles when complete face protection is desirable.

In case of gross vapor contact, immediately remove the victim to fresh air, keep him warm and quiet, and call a physician immediately. If the person shows signs of lung irritation, coughing, or respiratory embarrassment, 100% oxygen should be administered by properly trained personnel.

In case of contact with liquid bromine chloride, the affected area should be flooded immediately with copious quantities of water from a safety shower or other source of flowing water, and medical help summoned. All contaminated clothing, including shoes, should be removed as quickly as possible while the victim is under the shower. Washing should be continued for at least 15 minutes and, if medical help has not arrived by then, continued for another 15-minute period. Contaminated clothing should be washed before reuse.

If eye contact is made, the affected eye should be immediately irrigated with copious quantities of running water. Eye fountains are preferable for irrigation, but, if one is not available, a bubbler drinking fountain or a hose with a liberal, gentle flow may be utilized. The eyelids should be held apart during irrigation to ensure contact of water with all accessible tissues of the eyes and the lids. Eyes should be washed continuously for at least 15 minutes and medical attention obtained immediately.

In the event that a BrCl leak is detected, it should be immediately located and stopped. Even small leaks can create a safety hazard and cause serious corrosion to equipment in the area. Ammonia should be used to detect leaks.

The following decontaminants should be kept immediately at hand where BrCl is handled (water-safety showers and eye-wash fountains should be provided for washing contaminated skin and eyes, as well as a hose for rinsing away neutralized spillage):

- Anhydrous Ammonia - Cylinders of anhydrous ammonia should be available for decontamination of atmosphere containing BrCl fumes.
- Lime Slurry or Dry Soda Ash - A slurry of hydrated lime or dry soda ash may be applied to liquid BrCl spills to neutralize them.
- Potassium Carbonate or Sodium Carbonate Solution - These solutions are prepared by dissolving five pounds of the carbonate in 10 quarts of water. They are best for neutralizing halogen spills because their heats of solution and reaction are lower than those of lime.

APPENDIX F

SITE AND PLANT CHARACTERISTICS OF THE MORGANTOWN STEAM ELECTRIC STATION

Contents

Location and River Characteristics Near the Site

Cooling Water Flow

SITE AND PLANT CHARACTERISTICS OF THE MORGANTOWN STEAM ELECTRIC STATION

LOCATION AND RIVER CHARACTERISTICS NEAR THE SITE

PEPCO's Morgantown Steam Electric Station (SES) is located on the Potomac River estuary in Charles County, Md. The site is approximately equidistant from Washington, D. C., and near the confluence of the river with Chesapeake Bay. At this point (near the Rt. 301 bridge), the river is estuarine, with a mean cross-sectional area of 19.1×10^3 m^2 (205×10^3 ft^2). Average water depth is about 7 m (23 ft).

The flow regime is typical of a partially mixed estuary subject to moderately strong tidal currents. Distinct non-tidal flows are developed, directed downstream in the surface layers, and upstream at depth. The difference in volume transports between the two layers is the accumulated freshwater input from upstream of the site. Freshwater flow past the plant ranges typically between 140 to 1400 m^3/sec (5000 to 50000 cfs). The more apparent, oscillating tidal flows transport between 10 and 20 times the freshwater volume transport on the average (root mean square). Mean peak tidal velocities are approximately 0.5 m/sec (1.4 fps).

COOLING WATER FLOW

A once-through cooling system is employed at the plant to reject the waste heat of the twin 570-MWe generating units. Separate condenser systems cool each unit. The condenser discharge from both condensers enters a long discharge canal,which returns the thermally elevated cooling water to the river through a momentum jet located 0.5 km (0.3 mi) upstream of the intake.

Cooling water is drawn from the river through a deep-water intake structure. Lower layer withdrawal is accomplished by a combination of a curtain wall reaching 10 m (33 ft) below the mean low water level and an intake channel dredged to 15.2 m (50 ft), extending from the river channel to the curtain wall. The intake channel is 520 m (1700 ft) long and 106 m (350 ft) wide.

Since temperature and salinity vary continuously through the annual cycle, the vertical density structure of the river water determines the degree of selectivity in deep-water withdrawal. As long as salinity differences of at least 0.1 ppt exist vertically, the curtain wall is effective in drawing water from layers 10 m (33 ft) below the surface. This situation prevails during most of the year. Because there are longitudinal temperature and salinity gradients in the river that vary tidally, the depth of flow separation near the curtain wall may also change with a tidal period.

The cooling water, drawn in underneath the curtain wall at average velocities of 0.09 to 0.15 m/sec (0.3 to 0.5 fps), is mixed rapidly in an intake embayment (25000 m^3) before entering the intake ports located behind the bar racks and traveling screens. The pumphouse, which is the site of chlorine injection into the cooling stream, is also located behind the bar racks and vertical traveling screens. There are two sets of three pumps, one set per generating unit. The maximum condenser flow per generating unit is 31 m^3/sec; the cooling water transit time (intake to outfall) is 65 min.

At full plant load, the heat absorbed by the cooling water amounts to 1.6×10^{11} BTU per day. During passage through the condenser system, an abrupt rise in water temperature, about 6 to 7° C, occurs. Temperature decay through the discharge canal is slow, amounting to less than 10% of the rise across the condensers. The phytoplankton, zooplankton, fish eggs and larvae, and other small organisms present in the cooling water will experience a thermal dose of about 400 C degree-min for a 65-min transit time and an average temperature rise of 6°C.

In addition to thermal stresses, biota entrained in the cooling water may be affected by mechanical stresses caused by abrasion, velocity shear, and rapid pressure changes, estimated at 1.3 atmospheres. Although the effects of mechanical stresses have not been quantitatively determined, they should be considered in evaluating biocide and thermal stresses.

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16. ABSTRACT The report gives results of a comparison of bromine chloride and chlorine for fouling control in condenser cooling systems, by evaluating their decay rate in estuarine cooling water and their fouling control effectiveness. The program was conducted at an 1100-MWe, fossil-fueled, two-unit generating facility using estuarine water for once-through cooling. The halogens were applied continuously at doses of 0.5 ppm or less. Fouling control was evaluated by observing the accumulation of fouling on glass panels exposed to treated and untreated cooling water, and on condenser performance data. Decay characteristics of the halogens were evaluated by measuring residual oxidant concentrations using an amperometric back-titration method sensitive to 5 ppb. Fouling control resulted from the presence of bromamines expected from the rapid reaction of free hypobromous acid with the ambient levels of ammonia present. Dosing requirements depended primarily on cooling water temperature. Using BrCl decay and fouling response to treatment data, a control model was formulated which predicted minimum BrCl dose necessary to attain adequate fouling control. BrCl was found to be effective when dosed continuously at 0.5 ppm and less. Oxidant residuals resulting from BrCl treatment were found to dissipate more rapidly in the estuarine water than did the chlorine-induced oxidants.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Cooling Systems	Stationary Sources	13A
Condensers (Liquefiers)	Bromine Chloride	07A
Fouling Prevention		13H
Bromine Halides		07B

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