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**A Kinetic Model for Predicting
the Concentrations of Active
Halogens Species in Chlorinated
Saline Cooling Waters.**

A Final Report.

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Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A07; Microfiche A01

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Contract No. W-7405-eng-26

CHEMISTRY DIVISION

A KINETIC MODEL FOR PREDICTING THE CONCENTRATIONS OF ACTIVE HALOGENS
SPECIES IN CHLORINATED SALINE COOLING WATERS. A FINAL REPORT.*

W. R. Haag and M. H. Lietzke

* Research sponsored in part by the Division of Chemical Sciences, Office of Basic Energy Sciences, The U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

Date Published - August 1981

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ABSTRACT

A kinetic model has been developed for describing the speciation of chlorine-produced oxidants in seawater as a function of time. The model is applicable under a broad variety of conditions, including all pH ranges, salinities, temperatures, ammonia concentrations, organic amine concentrations, and chlorine doses likely to be encountered during power plant cooling water chlorination. However, the effects of sunlight are not considered. The model can also be applied to freshwater and recirculating water systems with cooling towers. The results of the model agree with expectation, however, complete verification is not feasible at the present because analytical methods for some of the predicted species are lacking.

INTRODUCTION

In a previous report¹ we described a kinetic model for predicting the concentrations of residual oxidants in chlorinated water discharged from power plants using freshwater for cooling. The model was verified² using chlorination data gathered at the Quad Cities Nuclear Plant located on the Mississippi River. We have now extended the model to be applicable to power plants located on estuaries or on the seacoast where saline water is used for cooling purposes. In addition, the previous model has been refined by the incorporation of halogen transfer reactions, breakpoint reactions, and the addition of alanine as a model organic amine (along with methylamine). The results presented here supersede

those given in an earlier version of the seawater model.³

The few models for following the time-course of chlorine disappearance in seawater which have heretofore been described in the literature⁴⁻⁷ are all empirical and therefore lack adaptibility to changing ammonia concentrations and chlorine demand conditions, and they cannot be expected to be valid outside the chlorine dose ranges and time periods studied. For example, Khalanski⁷ showed that the second-order decay model of Hostgaard-Jensen, et al.⁴ is not applicable at doses below 1.4 mg/l (as Cl_2) nor for contact times greater than ~ 100 minutes. Moreover, these models follow only total residual halogen disappearance and thus give little insight as to the chemical oxidant species in question. This model overcomes all these drawbacks by breaking down the overall chlorine decay process into simple chemical reactions.

Many of these reactions (such as methylchloramine formation) have well-defined kinetics with precisely-measured rate constants, whereas others either have not been studied kinetically or cannot as yet be broken down into simple processes, and therefore must be treated phenomenologically. The most important process of the latter type is the non-nitrogenous chlorine demand, which is a composite of many unknown reactions of various rates. Thus, a completely theoretical and predictive model is impossible at present, and, although the one given here is a reasonably good kinetic description of halamine chemistry, it makes no great strides towards a precise kinetic definition of non-amine seawater chlorine demand. Unfortunately, the overall precision

in predicting total residual halogen as a function of time is limited by the variability in non-amine seawater demand kinetics, which overshadows the relative refinement of the remainder of the model. Nevertheless, we feel that this work is of value because it (1) summarizes our present understanding of the chemistry of seawater chlorination; (2) points out areas which are in need of more research; (3) puts forth a model which is applicable under a broad variety of conditions; (4) presents a model which predicts the chemical oxidant species being discharged such that environmental impact assessment is more amenable; and (5) presents for the first time a kinetic model for the bromine-ammonia breakpoint system.

BACKGROUND

A. Chlorination Practices and Environmental Effects

Ninety percent of all U.S. electric power plants use chlorine for the prevention of slime formation in their cooling water systems.⁸ This is done because slime build-up blocks tube passages, accelerates corrosion, and reduces heat transfer efficiency. Typical chlorine doses are 0.5-10 mg/l for one-half to several hours per day. This amounts to an addition of about 30,000 tons of chlorine to our waterways annually for this purpose alone.⁹ The amount of water involved in such chlorination is also non-trivial. For example, the Quad Cities Nuclear Power Plant diverts nearly one-tenth the total flow of the Mississippi River through its cooling pipes,¹⁰ and the Calvert Cliffs Power Plant uses so much water that it has been called the fourth largest tributary to the Chesapeake Bay.¹¹ Therefore, any chemical

changes in the water brought about by chlorination will affect a large part of the local aquatic ecosystem. High chlorine doses have been the cause of numerous fish-kills, notably in the Saginaw Bay (1972)¹² and the James River estuary.¹³ These kills are generally attributed to direct toxicity of the hypohalites and/or halamines. Another effect is that many invertebrates and fishes tend to avoid even very low chlorine concentrations (0.005 mg/l ^{14,15}), preventing them from reaching breeding grounds. Further effects include direct toxicity and/or bioaccumulation of chlorination products such as haloforms and halo-organics, alteration of aquatic pheromones causing interference in chemical communications systems,¹⁶ loss of copper-chelating organics thus releasing cupric ions which can be harmful to phytoplankton,¹⁷ and direct, acute toxicity to microbiota, all of which may alter the local ecosystem.

It is therefore important to optimize chlorination practices such that maximal slimicidal effectiveness is achieved, while minimizing toxicity to higher aquatic organisms. Disinfection efficiencies vary greatly with each particular oxidant species,¹⁸ so it is important to be able to predict the species distribution and their persistence. For example, HOCl is about 80 times more effective than OCl^- ,¹⁸ presumably due to the greater permeability of the uncharged molecule through non-polar cell membranes. HOBr has a higher pK_a than HOCl (8.5 vs 7.5); therefore in the environmentally significant pH range 6-9, HOBr is mostly unionized giving better disinfection than HOCl , which is often greatly ionized. Monochloramine shows a much reduced

efficiency, whereas the bromamines are nearly as effective as HOBr and HOCl. Thus, bromine disinfection is desirable since it is little affected by pH or NH_3 concentration, and the bromine oxidants decompose faster resulting in lower overall toxicity to higher organisms. However, since chlorine rapidly oxidizes bromide to bromine, chlorination of saline waters containing bromide can achieve the same effect as using the more expensive bromine directly. This model will help predict to what extent chlorine oxidants are converted to bromine oxidants in saline waters. Unfortunately, the toxicities and slimicidal capacity of some of the compounds included in the model, particularly the bromochloramines and organic halamines, are largely unresearched. Nevertheless, one can see how modelling of chlorine-produced oxidant species might be useful in optimizing chlorination practices.

B. Summary of Seawater Chlorination Chemistry

The chemistry of saline water chlorination is summarized in Figure 1. First, molecular chlorine hydrolyzes rapidly and completely to form HOCl and HCl; this step was assumed to be instantaneous. Three items now compete for the HOCl produced: bromide, ammonia, and the non-amine "demand" which is a composite of inorganic and organic reducing agents and autodecomposition reactions (that is, everything else which is not clearly defined and consumes oxidants). Reaction with ammonia generates monochloramine and small amounts of dichloramine. Reaction with bromide produces HOBr, which in turn can react with any available amines to produce bromamines. The halamines are all unstable, eventually decomposing to form nitrogen gas or being reduced back to ammonia. However,

Figure 1. The chemistry of seawater chlorination. X represents Br or Cl.

their intermediate formation is an important consideration because their destruction is not immediate and they retain oxidizing properties which contribute to the toxic, total oxidant residual.

Inorganic bromamines are considered to exchange bromine rapidly and thereby co-exist in pH-dependent equilibrium distributions.^{18,19} On the other hand, chloramines exchange chlorine very slowly at pH 6-9, and thus one is for the most part concerned with the kinetic product,²⁰ namely monochloramine. Recent evidence has shown that both HOBr^{21,22} and the bromamines^{23,24} can brominate monochloramine to produce mixed-halamines, whose species-distribution kinetics remain largely uncharacterized.

The various halamines are subject to so-called "breakpoint" reactions, which are most rapid when the molar halogen to ammonia ratio is near 3/2, the stoichiometric ratio for the oxidation of ammonia to gaseous nitrogen. Simply stated, chlorine breakpoint may be envisioned as a reaction between monochloramine and dichloramine, while bromine breakpoint is primarily a reaction of dibromamine with tribromamine. All of these secondary oxidants are also subject to reduction by the demand, although the halamines do so somewhat slower than HOBr and HOCl.

The types of reactions for ammonia and its halogenated derivatives shown in Figure 1 also apply to organic amines, except for the breakpoint reactions. Organic halamines are generally more stable than inorganic ones, and their decomposition occurs by a variety of processes depending on the particular molecular structure. For example, β -alcoholamines fragment to give formaldehyde and ammonia,²⁵

N-chloroanilines rearrange to yield ring-chlorinated products,²⁶ N-haloamino acids decarboxylate to form aldehydes upon hydrolysis,²⁷⁻³¹ and N,N-dihaloamino acids decarboxylate and dehydrohalogenate to produce nitriles.²⁷⁻³⁰ Finally, one must also consider transfer reactions of positive halogen from inorganic halamines to organic amines yielding organohalamines. Such transfer is rather slow for chlorine³² but may be expected to be somewhat faster for bromine.

All the reactions in Figure 1 can occur simultaneously and the relative importance of each path depends on to what extent the characteristics of the water give it a competitive advantage. It is generally considered that monochloramine formation will dominate over HOBr formation in seawater containing 65 ppm Br^- when the ammonia concentration is above about 0.4 ppm. High ammonia concentrations can sometimes out-compete the demand,³³ giving a more persistent total residual in the form of monochloramine. Because ammonia concentrations in unpolluted seawater are generally very low and the bromide concentration is much greater than the chlorine dose, HOBr usually comprises most of the residual.

JUSTIFICATION FOR SPECIES MODELLED

Several workers have addressed the question of chlorine-produced oxidant speciation in saline waters.^{14,21-24,34-38} We feel that a major drawback to these studies has been the lack of acknowledgement of the possible presence of bromochloramines, whose existence has now been clearly established by Haag^{21,22} and independently by Trofe, et al.^{23,24} Sugam and Helz³⁶ have used a thermodynamic equilibrium

approach to show that bromine oxidants are ultimately favored over the analogous chlorine species, but their model did not include bromochloramines, presumably due to lack of data. Their method was admittedly invalid for practical predictions at normal contact times if any chloramines are formed, since their speciation reactions are kinetically limited. Johnson et al.³⁴ have used UV spectroscopy and an amperometric membrane electrode technique for speciation studies in which they concluded that NH_2Cl , HOBr , and the bromamines are the important products, their relative proportions depending on the conditions. Courtot and Peron³⁸ performed a similar study and came to the same basic conclusions. However, these results should not be taken as conclusive because both techniques employed were insensitive to the bromochloramines in the absence of standard spectra and proper calibration of the electrode for such compounds. Our model therefore includes the bromochloramines, despite the fact that they have never been directly observed in seawater chlorination studies, and it often predicts them to be major products.

A summary of all the compounds used in the model is given in Table I. Justifications for omitting similar known oxidants follow.

TABLE I
COMPOUNDS DESCRIBED KINETICALLY BY THE MODEL*

Non-oxidants	Hypohalous acids	Chloramines	Bromamines	Bromo-Chloramines
NH_3	HOCl	NH_2Cl	NH_2Br	NHBrCl
RNH_2^{**}	HOBr	NHCl_2	NHBr_2	NBr_2Cl
$\text{AlNH}_2^{\dagger}$		$\text{NCl}_3^{\ddagger}$	NBr_3	RNBrc1
Br^-		RNHCl	RNHBr	AlNBrCl
$\text{FASTCD}^{\#}$		AlNHCl	RNBrc2	
$\text{SLOWCD}^{\#\#}$			AlNHBr	
			AlNBr_2	

* The authors recognize that the amines and hypohalous acids are in equilibrium with their ionized forms which are by inference also being modelled. However, the halamines are very weak bases so their protonated forms do not contribute significantly to the total oxidant residual.

** RNH_2 = aliphatic amines modelled by CH_3NH_2 .

$\dagger$ AlNH_2 = free amino acids modelled by alanine.

$\#$ FASTCD = fast-acting, non-amine chlorine demand modelled as if it were a single compound.

$\#\#$ SLOWCD = slow-acting, non-amine chlorine demand modelled as if it were a single compound.

$\ddagger$ Freshwater system only.

A. Oxyhalogens

Non-nitrogenous oxidants ("free halogens") are limited to HOCl and HOBr. The reaction of HOCl with Br^- to form HOBr is obvious and well-documented.³³⁻⁴⁰ Bromide concentrations vary continuously from negligible in freshwater to ~65 mg/l in full strength seawater, the latter of which is greatly in excess of realistic chlorine doses. Sugam and Helz³⁶ have considered the possible formation of halogen complexes (e.g. BrCl , Br_3^- , BrCl_6^{-5} , etc.) in chlorinated seawater and concluded that no such species are thermodynamically stable above pH 6, despite the high concentration of Cl^- in seawater (0.54 M) favoring their formation.

Studies of the disproportionation of HOX to produce XO_3^- and X^- via the intermediate stage of HXO_2 (where $\text{X} = \text{Br}$ or Cl) allow us also to ignore these halites and halates, in the dark. (This model does not apply if sunlight is considered.)

The most rapid of such reactions is the catalytic oxidation of HOCl to ClO_3^- by hypobromous acid shown in the following cycle:⁴¹

Haag⁴² has shown these reactions, along with bromate formation, to be the major mode of chlorine disappearance in seawater at very

high doses (above 57.6 mg/l, the equivalent Br^- concentration). At more realistic doses, this set of reactions is potentially important only when amine concentrations are low, a free residual remains, the bromide ion concentration is such that roughly equal concentrations of HOBr and HOCl co-exist, and if the decay of oxidants is to be followed for more than a few hours.⁴² For a chlorine dose 1 ppm above the immediate demand, the Br^- concentration would need to be about 0.5 ppm, corresponding perhaps to the upper reaches of an estuary. We have disregarded this reaction sequence because of its overall relative slowness and because of the extremely narrow range of conditions to which it applies. Analogous reactions in the all-chlorine system (leading to chlorate) are four orders of magnitude slower ($k \approx 6.7 \times 10^{-6} \text{ M}^{-1} \text{ sec}^{-1}$)⁴¹ and have been ignored. The gradual formation of bromate would be expected ($k \approx 1.3 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$);⁴¹ however, Macalady et al.¹⁴ and Wong⁴³ have shown this not to occur in chlorinated seawater except under the influence of light. Furthermore, Helz et al.⁴⁴ concluded that bromate formation was not important in their study of chlorinated estuarine waters based on a lack of significant difference between nighttime and daytime chlorine decay studies. For these reasons halites and halates were not incorporated into the model.

A similar pair of reactions worth mentioning is the UV-light catalyzed auto-oxidation of hypohalites to O_2 and halide:

No account has been taken of the catalysis of this or any other reaction by light, chloride, bromide, or other seawater constituents

because the model is meant for processes occurring in the darkness of cooling pipes and because these effects have not been quantitated. In the case of hypochlorous acid in the absence of light, such auto-oxidation is exceedingly slow and for hypobromous acid it should be even slower. However, the trace metals present in seawater may well catalyze such a decomposition,⁴⁵ and so it has been incorporated as part of the seawater demand as will be discussed later.

B. Halamines

The relative importance of the remaining oxidants (the so-called combined halogens) depends on the distribution of amines in the water. Reports of ammonia concentrations in seawater^{6,7,46,47} range from < 0.001 ppm to 1.0 ppm. For unpolluted waters, these values are generally 0.05 mg/l or less.⁴⁷ This increases gradually as the salinity decreases such that freshwater concentrations are commonly in the range of 0.1 to 2 ppm, with typical wastewaters containing about 15 ppm.³²

The inclusion of organic nitrogen compounds is important because their halamines form faster than NH_2Cl by an order of magnitude or more, thus pulling active halogen away from the ammonia systems. Organic amines are generally found at somewhat higher concentrations than free ammonia and show less correlation with salinity. Analyses^{16,44,46,48} of several fresh-, estuarine-, and sea-waters give organic-N concentrations of < 0.05-2.7 mg/l as N, mostly in the range 0.2-0.45 mg/l, whereas typical values for wastewaters are 2-7 mg/l.^{16,32,49} However, much of this nitrogen is not reactive towards chlorine, at least not in such a way as to retain oxidizing power in the form of halamines. Peptide-bound, amino acid N, which is not attacked by chlorine²⁸ or bromine,²⁹

constitutes roughly 40-60% of the total dissolved organic N,⁵⁰ while reactive, free amino acids comprise only about 2-20%.^{48,51,52} The remaining 20-58% is made up of random amides, aliphatic amines, and heterocyclic N compounds (such as purines and pyrimidines). N-halo-amides form very poorly in water⁵³ and therefore can be ignored. Thus the important organic amines are free amino acids, which we have modeled collectively using alanine (AlNH_2), and the heterocyclic/aliphatic amines, for which methylamine (RNH_2) was taken as a model. Alanine was chosen because 1) it is one of the most abundant amino acids in both freshwater⁵¹ and seawater,⁵² 2) precise kinetic data are available on its formation and decomposition,³¹ 3) it is a convenient way to model the observations of Helz et al.⁴⁴ that considerable CO_2 and NH_3 are produced during the chlorination of estuarine waters (see Reactions 43 and 44 in appendix I), and 4) it is consistent with the observation of M. J. Tarao⁵⁴ that "...solutions of amino acids and peptones exhibit chlorine demand curves comparable with those characteristic of natural waters." Methylamine was chosen because it is the simplest organic amine, kinetic data on it are available, and it has halogenation rates similar to those of other organic amines.⁵³ A distinction between amino acids and aliphatic amines is necessary because their halamines have vastly different decomposition kinetics and products, as shown in Table II.

TABLE II
APPROXIMATE DECOMPOSITION HALF-LIVES OF ORGANIC HALAMINES
IN THE ABSENCE OF SUNLIGHT

HALAMINE	APPROXIMATE $t_{1/2}$, HOURS	PRODUCTS	REFERENCE
CH_3NHCl	450*	Unknown	22
CH_3NCl_2 , CH_3NBrCl , CH_3NBr_2	170	Unknown	22
N-Chloropiperidine	168	Unknown	55
N-Chloropyrrolidine	68	Unknown	56
Et_2NCl	58	Et_2NH and Et-N=CHCH_3	55
N-Bromopyrrolidine	33	Unknown	56
N,N-dichloropeptides	~ 24	Unknown	30
$\text{R-CH(CO}_2\text{H)NHCl}$	0.71	$\text{R-CHO} + \text{CO}_2 + \text{NH}_4\text{Cl}$	31
$\text{R-CH(CO}_2\text{H)NCl}_2$	$\lesssim 0.07$	$\text{R-C}\equiv\text{N} + \text{CO}_2 + \text{HCl}$	30

*The value for CH_3NHCl decomposition at pH 8.2 in the dark given in reference 22 is erroneously high.

Thus, aliphatic/heterocyclic amines tend to have a stabilizing effect on the total oxidant residual, whereas amino acids cause a destabilization.

In this model we have ignored the formation of NCl_3 and NBrCl_2 in saline waters. This is justified because NHCl_2 is needed as a precursor for both, but it is normally present in only small concentrations when bromide is present. This is true because reaction 19 normally outcompetes reaction 2:

Since both reactions share the same pH dependence, their relative rates will be independent of H^+ concentration but dependent on the molar ratio of Br^- to NH_2Cl . Assuming that 1 ppm of NH_2Cl had formed initially, reaction 19 will be at least ten times faster than reaction 2 even at a salinity of 0.5 ppt. Thus, any halamines formed in significant concentrations will contain at most one chlorine atom. The same arguments apply to organic chloramines, allowing us to neglect organic dichloramines, since their formation rates are similar to that of NHCl_2 .^{53,57} All this makes a good case for ignoring NHCl_2 itself; however, we have included it due to its importance as an intermediate in the chlorine breakpoint system. In the case of freshwater, the above competition does not exist and oligochlorination can occur. NBrCl_2 is omitted since no bromine-containing species can form in the absence of bromide, NCl_3 is included, and organic dichloramines are candidates for future inclusion.

SEAWATER CHLORINE DEMAND

A. Background

The basic premise of this model is that the total chlorine demand of seawater is the sum of demand due to nitrogenous compounds plus the demand due to everything else which reduces chlorine. For the purposes of this report we have used the term "chlorine demand" to mean ultimate, non-nitrogenous demand. In order to get an estimate of such chlorine demand we make use of total chlorine demand studies performed on seawaters that contain essentially no amines. The reports of several workers^{4-7,33,58,59} point out the need for more study in this area; however, the following generalizations can be made: 1) There is a true organic demand which can be saturated but is greatly variable. 2) Oxidant loss occurs in 3 phases: a rapid initial decay lasting $\lesssim$ 1-2 minutes, a slower decay lasting 1-2 hours, and finally a very slow but continuous loss, which is roughly linear with time and has no apparent limit. 3) In most cases the initial demand increases with increasing chlorine dose. This effect is likely part of the organic demand and becomes more noticeable at low doses and high temperatures. 4) Greater oxidant recoveries are obtained at pH 1.4 than at pH 4 using iodometric titrations when iodide is added before the acid. This difference is not due to bromate; it is probably an artifact in the method resulting from iodate formation or air oxidation of iodide, despite some rather unfounded claims⁶⁰ to the contrary.

The conclusions one would like to draw from these observations are that inorganic reducing agents react mostly in the rapid first phase, that the organic demand manifests itself in the first and second phases,

and that the long, slow, third phase is due to an auto-decomposition reaction of HOBr (perhaps catalyzed by some trace element⁴⁵ in the seawater). Wong⁴³ has shown that no bromate forms in the last phase even after 3.5 days, so we have modelled this loss by using the O₂-evolving decomposition (Equation 42 in Appendix I). The reasons for the increasing demand with increasing dose are complex, and not completely understood, and so this effect has been modelled empirically.

B. The Model

The computer program uses the following expression to calculate the chlorine demand as a function of chlorine dose at 20°C:

$$CD = 0.2648 + 0.2989CL - 0.02522CL^2 + 9.897 \times 10^{-4}CL^3 - 1.35 \times 10^{-5}CL^4,$$

where the demand (CD) and dose (CL) are in mg/l. This equation is an empirical fit of Wong and Davidson's⁵ data of "initial" demand in seawater versus dose and is valid only in the dose range 0-30 mg/l. Their "initial" demands correspond to phases 1 and 2 in this report and are obtained by extrapolating the linear portions (phase 3) of the chlorine demand vs time curves back to zero time. Thus, our "ultimate, non-nitrogenous demand" refers only to phases 1 and 2, with the linear 3rd phase being added for saline waters and not for freshwater, since no HOBr will be present in the latter. A plot of the above expression is given by curve A in Figure 2. It is assumed that this is a representative curve for most waters. However, adjustments are sometimes needed to model water with higher or lower demand. To do this, the model uses as input the demand value at a 2 mg/l dose at 20°C (termed the 2PPMD value). For the representative case, this corresponds to a demand of 0.77 mg/l, but for cleaner or more polluted waters it will be some lower or higher value. If we assume a dirty water

Figure 2. Ultimate, non-nitrogenous, chlorine demand as a function of dose and temperature. For A, C, and D 2PPMD = 0.77 mg/l; for B 2PPMD = 1.17 mg/l.

situation with a 2PPMD value of, say, 1.17 mg/l, this will have the effect of shifting the overall demand-dose curve up by 0.4 mg/l, as shown by curve B in Figure 2. Once the intercept of the curve is fixed using the 2PPMD value, suitable adjustments are made for temperature effects (curves D vs. A vs. C). These empirical corrections are based on Wong's data⁵⁸ and the mathematical expression for them are given at the top of page 3 in Appendix V. In Figure 2 the dashed line with a slope of unity indicates the maximum amount of chlorine which can be lost. Notice that at low doses the demand is often calculated to be greater than the dose, which means simply that not enough chlorine is being added to satisfy the potential demand. It should be stressed that regardless of the actual dose and temperature to be modelled, the 2PPMD value is used as input for the chlorine demand. The appropriate value for the given conditions is then calculated internally by the program. Although this method of estimating the demand is based on seawater data it is also applied at lower salinities, including freshwater, since the temperature and dose effects are similar.

With the demand thus determined, the program makes a distinction between phases 1 and 2 by arbitrarily assigning 70% of the demand to be "fast" and 30% to be "slow." The demand is thereby modelled as if it were two compounds with slow and fast second-order rate constants for reaction with the various oxidants (see Equations 49-61 in Appendix II). These rate constants are inputs to the program, making them adjustable parameters during data fitting. To complete the picture of total, non-nitrogenous demand, an empirical estimate of the zero-order rate constant, k_0 , for the very slow 3rd decay phase is made as a function of salinity, dose,

and temperature based on work by Wong^{5,58} (see Equation 42 in Appendix II for mathematical expressions).

Figures 3, 4, and 5 are a test of the above-described algorithm for predicting chlorine demand curves as a function of dose and temperature in seawater lacking amines. The inputted 2PPMD value was the representative 0.77 mg/l in all three cases, and the slow and fast demand rate constants were identical except at 1 mg/l dose, which required somewhat higher "slow" demand constants. However, the data in Figure 3 are difficult to interpret since the residuals were sometimes so low that artifacts may be involved. The good fits overall indicate that the model is reasonable, at least for this set of data, which is the only set of temperature-demand data available.

DISCUSSION OF MODEL REACTIONS AND THEIR KINETICS

Appendix I is a categorized list of the reactions used in this model. Appendix II gives details of the mathematical expressions for the rate constants and the differential rate laws for each reaction. In Appendix III, the differential rate expression for each reaction from Appendix II are combined to give the overall differential equations for each compound as they appear in the program. This section discusses the assumptions made in estimating rate constants and any other special considerations for the reactions in the model, in the order given in Appendix I. It is suggested that the reader keep Appendices I and II handy for continual reference.

One should keep in mind that, although the ionized forms of HOCl, HOBr, NH_3 , RNH_2 , and AlNH_2 do not react appreciably in any of the oxidant-interconversion reactions, the values used in the kinetic expressions are

Figure 3. Temperature-dependent, non-nitrogenous chlorine demand of sea-water at 1.0 mg/l dose. Experimental data of Wong:⁵⁸ □ 25 and 30°C, △ 40°C (averages of pH 1.4 and pH 4 titrations). Lines are the model predictions.

Figure 4. Temperature-dependent, non-nitrogenous chlorine demand of sea-water at 5.0 mg/l dose. Experimental data of Wong:⁵⁸ ○ 25°C, △ 40°C, ◇ 50°C (averages of pH 1.4 and pH 4 titrations). Lines are the model predictions.

Figure 5. Temperature-dependent, non-nitrogenous chlorine demand of sea-water at 10.0 mg/l dose. Experimental data of Wong:⁵⁸ ○ 25°C, △ 40°C, ◇ 50°C (averages of pH 1.4 and pH 4 titrations). Lines are the model predictions.

always total concentrations. That is, where we write $[\text{HOCl}]$ we actually mean $([\text{HOCl}] + [\text{OCl}^-])$; $[\text{NH}_3]$ means $([\text{NH}_3] + [\text{NH}_4^+])$, etc. Because of this convention, one must use observed rate constants, which account for such ionization, rather than theoretical ones. In Appendix II all rate constants apply to the 20-25°C range unless a temperature dependence is given.

A. Halamine Formation and Hydrolysis

All of the halamine formation reactions, save trichloramine, are (or are assumed to be) very fast, being complete in less than a minute. Halamine formation rates increase with increasing basicity of the amine.⁵³ Thus, alkylamine and amino acid halamines form faster than the corresponding ammonia halamines. The hydrolysis of the N-Cl bond is very slow, whereas that of the N-Br bond is somewhat faster. Therefore we have assumed that the bromochloramines hydrolyze mostly to produce HOBr and a chloramine rather than HOCl and a bromamine (see for example Equations 9, 10, and 11). Some of the equations, particularly the alanine reactions, were added in the later part of the model development and their hydrolysis reactions were omitted for simplicity and because organohalamine formation equilibria are somewhat more favorable than their inorganic counterparts.

There is currently some controversy over the form for the kinetic rate law for monochloramine formation. Inman and Johnson^{35b} found that using a 0.8 power ammonia dependence (as is done in the model) gives better fits of the experimental data over a broader range of concentrations than does the original first order dependence found by Weil and Morris.⁶¹ Morris⁶² argues that the 0.8-power expression has no theoretical

justification and that one must therefore look for another explanation for the difference in the rate constant found by the two groups. Use of the 0.8 power dependence effects the relative rates of NH_2Cl versus HOBr formation. The calculated ammonia level for equal rates in seawater is 0.22 mg/l as N using the 0.8 power, but 0.61 mg/l if first order kinetics are assumed. For the present, either expression may be used, as long as the appropriate rate constants are employed.

Of the inorganic bromamines, only the rate of NH_2Br formation has been measured.⁶³ The intrinsic rates for NHBr_2 and NBr_3 were estimated to be about 200 and 5000 times slower, respectively, by comparison with NHCl_2 and NCl_3 formation, which are 1.8×10^4 and 2.5×10^6 times slower than NH_2Cl formation. The hydrolysis constants were calculated from the equilibrium constants estimated by Sugam.⁶⁴ This system will be discussed in greater detail along with the bromine breakpoint model.

The remaining unmeasured halogenation rates were estimated using the following assumptions as guidelines: 1) Bromamines form and hydrolyze faster than chloramines. 2) Organic amines and halamines halogenate faster than inorganic ones. 3) Chlorination of a bromamine is slower than bromination of a chloramine, which is in turn slower than bromination of a bromamine. Using the known rates of certain reactions as a starting point and then applying these rules leaves little freedom in choosing values for the unmeasured rate constants. Thus, it is highly unlikely that the estimated rates are off by more than 2-3 orders of magnitude. Before the measurements of Wajon,⁶³ we predicted the rate of monobromamine formation within a factor of 3 or 4 of the real value, using the above guidelines.

B. Bromide Oxidations

The rapid formation of HOBr requires no further discussion because it is well studied and its rate constant has been precisely measured.^{35a} The oxidation of Br^- by NH_2Cl is slow^{23,24} and relatively unimportant for the short contact times (≤ 1 hr.) normally modelled, but it does represent an important path for the conversion of chloramines into bromamines via bromochloramines. Equation 20 is actually a composite of a few steps:

but the protonation is a rapid equilibrium and the model assumes hydrolysis of BrCl to be instantaneous. Trofe et al.^{23,24} have shown that NHBrCl is a major product in this process. However, in a real situation one may assume that the HOBr generated can react not only with NH_2Cl to give a bromochloramine, but also with other amines, halamines, and the demand, to give other products as well. Therefore it is necessary to use Equation 20 to show the intermediate presence of HOBr rather than model the reaction as a direct conversion of NH_2Cl into NHBrCl .

C. Halogen Transfer

The N-Br bond is rather labile in aqueous media whereas the N-Cl bond is not.¹⁹ Therefore, inorganic bromamine disproportionations are expected to be very fast (as will be described later), while inorganic chloramine disproportionations may be ignored (above pH 6). Reaction 23 involves the transfer of a bromine atom from a bromamine to a chloramine. This is an

important link between the all-bromine and all-chlorine systems. This equation, along with Equation 9, accounts for NHBrCl formation subsequent to bromide oxidation by monochloramine (Equation 20). The rate constant for Reaction 23 is a crude estimate based on some information given by Trofe et al. in Reference 24.

Transfer of active chlorine from monochloramine to organic amines is in general thermodynamically favorable, but direct transfers (i.e. Equations 24 and 27) are slow.³² They outcompete the alternate mechanism (NH_2Cl hydrolysis followed by chlorination of the organic amine by the HOCl produced) only if NH_2Cl and the organic are both present at concentrations above about 10^{-5}M (0.14 mg/l as N)³², which is often the case, especially in wastewater discharges. Like NH_2Cl disproportionations, these transfers are acid catalyzed but roughly independent of pH in the range 6-9. Chlorine transfers from NHCl_2 are also to be expected; however, such reactions were omitted because NHCl_2 formation is generally very minor especially when organic amines are present. Direct bromine transfers from inorganic bromamines to organic amines (Equations 25, 26, 28 and 29) have not been studied but should be faster than the analogous chloramine reactions. We assumed that NHBr_2 , being less stable than NH_2Br , would react four times faster than NH_2Br , which reacts eight times faster than NH_2Cl , although these rates are rough estimates and could be much faster. Conservative guesses were made for fear of overestimating the importance of such reactions. Transfers from NBr_3 to organic amines were ignored on the basis that the unbrominated organic amine and NBr_3 are not likely to coexist for more than

a few seconds, since at the higher chlorine doses required for NBr_3 formation the organic amine should be rapidly brominated by HOBr .

D. Non-Breakpoint Decompositions

Equation 42 models the linear (zero order) 3rd decay phase in seawater found by Wong and Davidson⁵ for long contact times. This was discussed in the previous section on chlorine demand.

The decomposition of N-halamino acids to form aldehydes and nitriles in well-documented²⁷⁻³¹ (Reactions 43-46). The rates for monohalamino acids have been measured, whereas those for nitrile formation from dihalamino acids are based only on the statement by W. D. Stanbro³⁰ that "This reaction is more than an order of magnitude faster than N-chloro- α -amino acid decomposition." The formation of aldehydes and ammonia from monohalamino acids does not proceed directly as in Equations 43 and 44 but rather in two steps:

Here we make the reasonable assumption⁶⁵ that the intermediately-formed imine hydrolyzes instantaneously. This allows us to avoid modelling another nitrogen-containing species.

E. Halogen Demand

All of the residual oxidants have the potential for being reduced by the demand (Equations 49-61). As stated before, the demand was modelled as if it were two unique compounds reacting with each of the

oxidants with overall second-order kinetics. Because the demand is so complex, more detailed kinetic modelling was not warranted. Free hypohalites react much faster than halamines, and bromine oxidants react faster than their chlorine counterparts. No information was available on reaction rates of organic halamines or bromochloramines with the demand. Inorganic bromochloramines were included because of their similarity to bromamines, which are lost relatively rapidly to the demand. Aliphatic halamines were taken to react slowly due to their general stability, and halamino acid demand reactions were ignored since their autodecompositions are relatively fast and thereby more important. One important assumption we have made and which needs to be substantiated is that ammonia is regenerated when halamines are reduced by the demand. This effect, along with de-amination of N-halamino acids, can result in a build up of ammonia following its initial rapid decline upon chlorination.

BREAKPOINT REACTIONS

"Breakpoint" is the name given to reactions of halogens leading to the oxidation of ammonia to nitrogen, with concomitant reduction of positive halogen to halides. These reactions are most rapid when the molar ratio of halogen to ammonia is near 1.5 (the "breakpoint" in accord with the overall stoichiometry of the reaction systems:

where X represents bromine or chlorine. Such oxidations are slower at lower ratios because the oxidant becomes limiting and at higher ratios because the relatively more stable trihalamines form.

A. Chlorine Breakpoint

The chlorine breakpoint model consists of the following reactions:

These are the same reactions as are used in the model developed by Morris and Wei^{66,67} and later re-evaluated by Saunier and Selleck.⁶⁸

Saunier and Selleck found that the original model gave excellent results after revising some of the rate constants. Their results differed from those of Morris and Wei in that they found less NO_3^- and suggest that its formation is minimized by good initial mixing.

Oxidation of a small portion of the ammonia all the way to nitrate rather than just to nitrogen requires extra chlorine, thereby shifting the breakpoint up by a few tenths of a unit from 1.5. In the present model the revised rates were used, which should allow one to ignore HOCl loss by NO_3^- formation. However, it was opted to incorporate Reaction 33 in order to retain the capability of increasing the nitrate formation rate constant for poorly mixed systems, which are probably more representative of actual power plant chlorination conditions.

This model simplifies the Saunier and Selleck version by using the steady-state approximation for HNO. This was justified by earlier runs of the program which found HNO to be formed only in low concentration and remain nearly constant with time. Figure 6 is a comparison of the model results with some experimental data in a plug-flow reactor determined by Saunier and Selleck.⁶⁸ The model generates essentially the same curves as do Saunier and Selleck's calculations, which agree well with experiment. The main difference between the models in the prediction of somewhat less NCl_3 here, which results from the use of a smaller empirical trichloramine formation rate constant in this work. It is thus seen that use of the steady-state approximation does not cause a great loss of accuracy, whereas it considerably reduces the kinetic manipulation required.

Further simplification is achieved by using the same reaction rates below the breakpoint, even though the previous models were developed for above-breakpoint chlorination and it is known that NHCl_2 decomposes somewhat more slowly below Cl/N ratios of 1.5.⁶⁸ This simplification seemed justified since, in real situations, dichloramine seldom makes up a noticeable portion of the total oxidant residual, especially if any Br^- is present. Furthermore, in a complex mixture with other amines and varying demand it is often impossible to predict whether the dose is above or below the breakpoint.

Figure 7 is a typical chlorine breakpoint curve, as generated by the model, assuming zero chlorine demand and no nitrogenous compounds present other than NH_3 . Each point on the abscissa represents a separate experiment in which successively greater amounts of chlorine

Figure 6. Breakpoint chlorination kinetics. $T = 17.5^{\circ}\text{C}$, $\text{pH} = 7.2$, $[\text{NH}_3]_0 = 1.01 \text{ mg/l as N}$, initial molar Cl_2/NH_3 ratio = 2.63. Points - experimental data of Saunier and Selleck.⁶⁸ Lines - model predictions. $\bullet$ - Total oxidants, $\blacktriangle$ - HOCl , $\diamond$ - NH_2Cl , ∇ - NHCl_2 , $\square$ - NCl_3 .

Figure 7. Chlorine breakpoint model calculations. $T = 20^\circ\text{C}$, $\text{pH} = 7.0$, $[\text{NH}_3]_0 = 0.2 \text{ mg/l as N}$, ionic strength = 0.02, chlorine demand = $\text{AlNH}_2 = \text{RNH}_2$.

were added to 0.2 mg/l NH_3 . As more chlorine is added up to an initial chlorine to ammonia ratio of unity, more NH_2Cl is produced, but, for kinetic reasons, little or no NHCl_2 is formed. NH_2Cl in the presence of excess NH_3 is rather stable and therefore, after one hour the total residual chlorine (in the form of NH_2Cl) is still nearly equal to the initial chlorine added. Once there is a stoichiometric excess of chlorine over that needed to form NH_2Cl , considerable NHCl_2 is produced. Dichloramine decomposes and reacts indirectly with NH_2Cl (via Reactions 30 and 31) causing a reduction in total oxidants roughly proportional to the amount of NHCl_2 formed. At the breakpoint one has, in effect, a 50:50 initial mixture of NH_2Cl and NHCl_2 and the stoichiometry is ripe for total loss of chlorine by oxidation of NH_3 to N_2 . Beyond the breakpoint most of the NH_3 is readily oxidized within a few hours (except for some that formed NCl_3) and the excess chlorine remains as free hypochlorite. The chlorine residual now increases with the dose roughly as if no ammonia were present initially, except for a shift along the abscissa. Again, the good agreement of the computed curves with experiment⁶⁹ point to the validity of these chlorine breakpoint models.

B. Bromine Breakpoint

No models have previously been presented for the bromine breakpoint system. The suggested model appears to give good results; however, this conclusion should be taken as preliminary since it is based on comparison with only one set of experimental data.¹⁹

Johnson's studies of the bromamines^{19,70,71} indicate that bromine-ammonia breakpoint reactions involve di- and tribromamine, as opposed

to mono- and dichloramine in the all-chlorine system:

Cromer, Inman, and Johnson⁷⁰ suggest that reaction 35 is the preferred decomposition pathway because it has a rate constant roughly 1000 times larger than reaction 34. Experimental evidence⁷¹ indicates that reaction 36 should be kinetically unimportant above pH 6; however, it was found necessary to employ this reaction with a rate constant 35 times larger than the experimental value in order to successfully model NBr_3 decay at Br_2 to NH_3 ratios above the breakpoint at pH 7. (One might find some justification for doing this by considering the elevated rate a substitute for the known⁷¹ bromide catalysis for reaction 36 which the model otherwise ignores.) The breakpoint model is thus partly empirical.

It then becomes of critical importance to be able to predict which bromamine species will exist initially, since the breakpoint process will be fastest when di- and tribromamine are present in roughly equal concentrations. The bromamines are considered to exist in equilibrium distributions, as opposed to the chloramines, whose relative concentrations are determined by kinetics.²⁰ It will be shown here that the bromamine equilibria must be maintained by disproportionation reactions rather than by a series of formation-hydrolysis reactions, because the latter would reach equilibrium much more slowly than is observed by

experiment, i.e., several hours as opposed to several seconds. Table III gives thermodynamic data from which equilibrium constants may be calculated for the relevant processes. These equilibria are affected by the ionization of NH_3 and HOBr , giving the observed constants shown in Table IV. Note that $K_{6\text{obs.}}$ has the largest value, reflecting the dominance of NHBr_2 at bromine to ammonia ratios near unity and pH 7 to 8. The formation-hydrolysis reactions must be of minor importance in maintaining the bromamine equilibria because the hydrolysis rate constants would need to be much higher than predicted in order to maintain rapid equilibrium. Although the hydrolysis rate constants have not been measured, they are constrained to be less than about unity because it is unreasonable to allow k_6 or k_7 to be greater than k_{12} . (Each substituted bromine atom lowers the basicity of the amine making further halogenation slower.)

TABLE III

THERMODYNAMIC DATA ON THE BROMAMINES

<u>Compound</u>		<u>ΔG_f°, Kcal/mole</u>
$H_2O(l)$		-56.69
$NH_3(aq)$		- 6.35
$HOBr$		-19.7
NH_2Br		+18.4*
$NHBr_2$		+43.3*
NBr_3		+70.7*

<u>Formation-Hydrolysis</u>		<u>ΔG°, Kcal/mole</u>	<u>$K_{eq}(25^\circ C)$</u>
4)	$NH_3 + HOBr \rightleftharpoons NH_2Br + H_2O$	-12.24	$K_{12} = k_{12}/k_{-12} = 9.49 \times 10^8$
5)	$NH_2Br + HOBr \rightleftharpoons NHBr_2 + H_2O$	-12.09	$K_6 = k_6/k_{-6} = 7.37 \times 10^8$
6)	$NHBr_2 + HOBr \rightleftharpoons NBr_3 + H_2O$	- 9.59	$K_7 = k_7/k_{-7} = 1.08 \times 10^7$
<u>Disproportionation</u>			
21)	$2NH_2Br \rightleftharpoons NH_3 + NHBr_2$	+ 0.15	$K_D = k_D/k_{-D} = 0.78$
22)	$2NHBr_2 \rightleftharpoons NH_2Br + NBr_3$	+ 2.5	$K_{D1} = k_{D1}/k_{-D1} = 0.015$

* These estimates were graciously supplied by Dr. Richard Sugam and Dr. George Helz and are presented in Reference 64.

TABLE IV

OBSERVED EQUILIBRIUM CONSTANTS CORRECTED
FOR pH* AND IONIC STRENGTH†

<u>Keq(obs.)</u>	<u>pH 7</u>	<u>pH 8</u>
$K_{12}^{\text{obs.}}$	5.2×10^6	4.3×10^7
$K_6^{\text{obs.}}$	7.2×10^8	6.2×10^8
$K_7^{\text{obs.}}$	1.1×10^7	9.1×10^6
$K_D^{\text{obs.}}$	138	14.5
$K_{D1}^{\text{obs.}}$	0.015	0.015

* Operational definition of pH.

† Ionic strength = 0.10 (as used in Fig. 8)

Therefore, Equations 4-6 are kinetically limited, and in order to maintain equilibrium bromamine distributions during decomposition¹⁸ it is necessary to model equations 21 and 22 as true, rapid equilibria. It is important to note that Equations 21 and 22 are mathematically redundant, since they are simply linear combinations of Equations 4-6, but in order to be chemically correct both systems must be included because their kinetics are different. Disproportion rates of at least 10^4 l-mole⁻¹sec⁻¹ were found necessary to sustain equilibrium.

Figure 8 is a test of the bromine breakpoint model. LaPointe, Inman, and Johnson¹⁹ give an excellent discussion of this type of breakpoint curve. Briefly, the main differences between the all-bromine and

Figure 8. Bromine breakpoint curves. $T = 20^\circ\text{C}$, $\text{pH} = 7.0$, $[\text{NH}_3]_0 = 0.934$ mg/l as N, ionic strength = 0.10, Points - model predictions. Lines - experimental data of LaPointe et al.,¹⁹ $\circ$ - 5 minute residuals, Δ - 30 minute residuals.

all-chlorine systems are 1) a more rapid decomposition of bromine residuals; 2) the existence of considerable NHBr_2 and NBr_3 below breakpoint bromination levels, allowing decomposition to occur at lower doses and causing the flatter peak at halogen/N ratio 1.0 than in the all-chlorine system; 3) the formation and subsequent gradual decay of NBr_3 above the breakpoint, (that is, nearly all of the NH_3 can be converted into NBr_3 without converting any into N_2 , whereas N_2 evolution occurs extensively during NCl_3 production); and 4) nitrate formation appears to be negligible in the bromine system.

In Figure 8, the points are the values computed by the model and the dotted lines are the experimental curves of LaPointe et al.¹⁹ The computed curve represents the best fit obtained from trial-and-error estimation of the rate constants for Reactions 35 and 36. It is unfortunate that it was necessary to use empirically-derived rate constants for bromamine decompositions in light of the availability of experimental kinetic data determined by Johnson and coworkers.^{70,71} They developed the following expression,

$$-\frac{d[\text{NBr}_3]}{dt} = k_a [\text{NBr}_3] [\text{OH}^-] [\text{HOBr}]^{-1} + k_b [\text{NBr}_3]^2$$

to apply above the breakpoint where HOBr is in excess and tribromamine is the dominant bromamine, and

$$-\frac{d[\text{NHBr}_2]}{dt} = k_c [\text{NHBr}_2]^{2.5} [\text{NH}_3]^{-0.5} + k_d [\text{NHBr}_2]^2$$

below the breakpoint where ammonia is in excess and dibromamine predominates. It is interesting to note that, ignoring the k_b and k_d terms,

these equations reduce to

$$-\frac{d[\text{NBr}_3]}{dt} = k'_a[\text{NHBr}_2][\text{NBr}_3][\text{OH}^-]$$

and

$$-\frac{d[\text{NHBr}_2]}{dt} = k'_c[\text{NHBr}_2][\text{NBr}_3]$$

respectively. These equations can be combined to give

$$\frac{-d[\text{NHBr}_2]}{dt} = \frac{-d[\text{NBr}_3]}{dt} = (k'_c + k'_a[\text{OH}^-])[\text{NHBr}_2][\text{NBr}_3]$$

where $k'_c = 3.3(K_{12}\text{obs.}K_6\text{obs.})^{0.5}K_7\text{obs.}^{-1}$ and $k'_a = 1.18 \times 10^4 K_7\text{obs.}$ One has thus obtained rate equations which should apply both above and below the breakpoint, which was necessary, as in the chlorine system, because in real examples it is often impossible to predict on which side of the breakpoint a particular dose will fall. Using the observed equilibrium constant values given in Table IV, the NBr_3 decomposition equation becomes

$$-\frac{d[\text{NBr}_3]}{dt} = (18.7 + 1.3 \times 10^{11}[\text{OH}^-])[\text{NHBr}_2][\text{NBr}_3] + 0.34[\text{NBr}_3]^2$$

at pH 7. Use of this equation gave bromamine decomposition rates at least an order of magnitude too rapid, which resulted in poor fits of the experimental breakpoint curve (Figure 8). The empirically-fitted expression used in this model was:

$$-\frac{d[\text{NBr}_3]}{dt} = (894.6 + 1.18 \times 10^9[\text{OH}^-])[\text{NHBr}_2][\text{NBr}_3] + 12[\text{NBr}_3]^2$$

This equation gives considerably slower oxidant losses than the theoretical equation and has a somewhat smaller pH dependence. The need for an empirical rate law indicates that either (a) the estimated equilibrium constants are somewhat off, (b) the assumption of equilibrium for bromamine distributions is incorrect, (c) the measured rate constants are wrong, or (d) the kinetic rate laws have the wrong form. Since possibilities (c) and (d) are unlikely, one must conclude that either or both of choices (a) or (b) are correct. Changing the equilibrium constants would alter both the rate coefficients and the species distributions, both of which affect the overall rate. In particular, K_7 appears to be too high; lowering it would both bring the rate coefficients more in line with the empirical equation and alter the species distributions to give a more sharply defined breakpoint.

C. Mixed Halamine Breakpoint

No information was available in the literature to facilitate modeling of a breakpoint system in which both active chlorine and active bromine are present. For example, it is not known whether or not chloramines react with bromamines in breakpoint fashion. Nor is it known how or if the bromochloramines interact with themselves or the other halamines. Furthermore, there is little data available to help predict the bromochloramine species distribution as a function of pH, Br^- concentration and chlorine dose. The mixed halamine breakpoint model presented is therefore somewhat speculative.

The model consists of all the chlorine and bromine breakpoint reactions, the bromochloramine formation reactions (Equations 9, 10 and

23) and Equations 37-41 (see Appendix I). It was assumed that the bromochloramines do not interact with the chlorine breakpoint system but do so with the bromine system since chemically they resemble the bromamines more than the chloramines. No direct interaction between the bromine and chlorine systems was assumed. Furthermore, most of the bromochloramine reactions were assigned somewhat lower rate constants than those for the analogous all-bromine reactions. The influence of the mixed-halamine breakpoint system was thus limited because otherwise oxidant decomposition occurred too fast when compared with experimental seawater breakpoint curves. Note also that in Equations 37-41 the assumption was made that active chlorine is always reduced to chloride, whereas some of the combined bromine is released as free HOBr during breakpoint. This is a more likely pathway than assuming the release of free HOCl in light of the greater electronegativity of chlorine versus bromine. Needless to say, there is no direct experimental evidence to support or deny the occurrence of such reactions, but it was thought important to include them for the sake of completeness.

Figure 9 compares two experimental breakpoint curves with two hypothetical curves calculated by the model. Note that these are real examples which also contain non-nitrogenous demand, unlike Figures 7 and 8. In all cases the breakpoint lies above the theoretical 1.5 Cl/N molar input ratio. This is true not because of nitrate formation but (at least in part) because extra chlorine is required to satisfy the organic demand. It is interesting to note that as the chlorine dose is increased, the demand also rises, pushing the breakpoint to even higher ratios. The experiment of Courtot and Peron in Figure 9 (circles)

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Figure 9. Seawater breakpoint curves. $T \approx 20^\circ\text{C}$, $\text{pH} \approx 8.0$, ionic strength ≈ 0.72 , ○ - Brest, France (Courtot and Péron³⁸), $[\text{NH}_3]_0 = 0.108$ mg/l as N. □ - Dunkerque, France, 4/25/78 (Khalanski¹⁷), $[\text{NH}_3]_0 = 0.157$ mg/l as N. Solid line - model calculations, $[\text{NH}_3]_0 = 0.108$ mg/l as N, $\text{RNH}_2 = \text{AlNH}_2 = 0$, 2PPMD = 0.42 mg/l as Cl_2 . Dash-dotted line - model calculations, $[\text{NH}_3]_0 = 0.108$ mg/l as N, $\text{AlNH}_2 = 0.05$ mg/l as N, $\text{RNH}_2 = 0$, 2PPMD = 1.5 mg/l as Cl_2 .

appears to be a low-demand case. The corresponding model calculation (solid line) required the low 2PPMD value of 0.42 to bring the breakpoint down to a ratio of 2.0 from about 3.0 using the normal value of 0.77. However, organic demand effects are unlikely to be so large as to push the breakpoint up to a ratio of ~ 5.6 as observed by Khalanski.⁷ In fact, Khalanski found seawater breakpoints to occur mostly near ratios of 8-10 and sometimes as high as 17. A partial explanation for this may be the presence of organic amines, which were not measured by Khalanski. The dashed line in Figure 9 is a model calculation which assumed high demand (2PPMD = 1.5) and the presence of 0.05 mg/l alanine. It is seen that this had the dramatic effect of shifting the breakpoint from 2.0 to about 4.6. However, when Khalanski added stock ammonia solutions (which should contain negligible organic amines) to seawater, the shift in breakpoint was always greater than that predicted based on oxidation of NH_3 to N_2 . Thus, organic amine and demand effects are not the whole explanation.

Figure 10 shows the species distribution for a hypothetical seawater breakpoint curve. Again, the presence of demand shifts the breakpoint. As shown in the figure, the model predicts that NH_2Cl , NHBrCl , and NHBr_2 will be the dominant initial oxidants below the breakpoint, whereas HOBr , NBr_2Cl , and NBr_3 will predominate above the breakpoint. As in the all-bromine case, the decomposition is most rapid when roughly equal concentrations of dihalamines (NHBr_2 and NHBrCl) and trihalamines (NBr_3 and NBr_2Cl) are present. Likewise, short-time slopes for the total oxidant curve which are greater than unity above the breakpoint are to be expected due to the formation of trihalamines. At long times

Figure 10. Hypothetical seawater breakpoint model calculations. $T = 20^\circ\text{C}$, $\text{pH} = 8.0$, $[\text{NH}_3]_0 = 0.108 \text{ mg/l as N}$, ionic strength = 0.72, $\text{AlNH}_2 = \text{RNH}_2 = 0$, 2PPMD = 0.77 mg/l as Cl_2 .

these slopes should approach unity as the trihalamines decompose. The real situation appears to be somewhat different with slopes less than unity even at short contact times. Slopes less than unity can only be explained by a continuously increasing demand with increasing dose. This effect appears to be considerably greater for the French seawaters^{7,38} compared to the Massachusetts coastal waters used by Wong,⁵ to which the demand-dose curve was fitted for this model.

HALOFORM PRODUCTION

Jolley^{16,72} has estimated that 0.5-3% of the chlorine added to freshwaters ends up in the form of chlorinated organics. Although much of this organic chlorine has formed by reaction with colloidal macromolecules,^{11,73} a significant portion is in the form of chromatographable, low-molecular-weight compounds.¹⁶ Chloroform is the most abundant of these low-molecular-weight chlorinated products.⁷⁴ As the salinity increases, more chlorine is converted into more-reactive bromine, resulting in both faster formation of bromo-organics and a greater percentage of brominated trihalomethanes (i.e. CHCl_2Br , CHClBr_2 , and CHBr_3).^{44,75,76} Chloroform and bromoform are known carcinogens in rodents⁷⁷ and therefore suspected carcinogens in man. Furthermore, in addition to the possibility of direct toxicity,^{78,79} their lipophilic character causes rapid bioaccumulation in fish and fish eggs^{78,79} (although depuration rates are also relatively fast). One would therefore like to predict haloform production since this will also affect the environmental impact of water chlorination.

The model gives an estimate of the total trihalomethane concentration (as measured by Direct Aqueous Injection Gas Chromatography) at

the end of the contact period based on an empirical relation found by Peters et al.⁸⁰ for reaction of chlorine with freshwater humic and fulvic acids:

$$\text{total haloforms (M)} = 0.01307 (\text{CDO})(1 + 14[\text{Br}^-]^{0.25})$$

where CDO is the molar Cl_2 concentration which has been lost by reaction with organic demand and $[\text{Br}^-]$ is the initial molar bromide concentration. The term $14[\text{Br}^-]^{0.25}$ was added to Peters et al.'s expression to account for more rapid haloform production when bromide is present. This term, based on Minear and Bird's work⁷⁶ results in a 3.4-fold increase in haloform yield at seawater salinities, with most of the effect being exerted at low bromide concentrations. Note that the above expression implies that about 13 mmol of chloroform are produced per mole chlorine consumed (in the freshwater case). Analysis of similar data found by Morris and Baum⁸¹ gave ratios in the range 11-122 mmol CHCl_3 /mole Cl_2 consumed. Morris and Baum used small model compounds which might be expected to give higher yields of haloforms than fulvic acids, which should have fewer active sites for haloform production per mole carbon. Thus, a ratio in the lower end of the range found by Morris and Baum appears appropriate for modelling natural waters. It should be pointed out that the relation given above is still a first approximation since the kinetics of haloform production often do not parallel chlorine consumption.⁸¹ Finally, no pH dependence was incorporated because total haloform production (free, dissolved haloforms + "residual" haloforms) is relatively insensitive to pH.⁸⁰ The effect of increasing pH is mostly to hydrolyze "residual" haloforms to free, dissolved haloforms.^{80,81}

No data to evaluate the validity of this portion of the model for natural waters could be found in the literature other than the report from which the empirical expression was obtained.

PRACTICAL EXAMPLES

A. Once-Through Cooling Systems

In the normal operating mode the computer program calculates the concentrations of residual oxidants as a function of time from the moment of chlorination. In the case of a once-through type cooling system, if the water velocity is constant in the cooling tubes, these values can easily be converted to concentrations as a function of distance from the point of chlorination. The concentration-distance profile calculated by the model will be maintained in the cooling system as long as chlorine is being added to the intake waters.

Figures 11-13 are concentration-time curves for chlorine-produced oxidant decay in samples representative of freshwater, estuarine water, and seawater. Some general trends in water quality on going from freshwater to seawater can be pointed out. First, the bromide concentration varies from near zero to ~ 65 mg/l resulting in a shift to the less-stable bromine oxidants. Second, the ammonia concentration decreases, causing a shift from combined oxidants to free oxidants (HOBr). Third, the organic carbon content decreases,⁸² at least for unpolluted samples, lowering the demand and allowing smaller chlorine doses. And finally, the pH increases from the 6.5-7.8 range to a nearly constant 8.1, thus affecting the many reaction rates which are pH-sensitive. Notably, the oxidation of bromide to bromine is slowed considerably in going from pH 7 to pH 8 while the formation rate of monochloramine is slightly

Figure 11. Oxidant decay for a representative freshwater case. $T = 25^\circ\text{C}$, $\text{pH} = 7.2$, ionic strength = 0, 2PPMD = 0.77 mg/l as Cl_2 .

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Figure 12. Oxidant decay for a representative estuary case. $T = 25^\circ\text{C}$, $\text{pH} = 7.65$, ionic strength = 0.43, salinity = 21.3 ppt, 2PPMD = 0.77 mg/l as Cl_2 .

Figure 13. Oxidant decay for a representative seawater case. $T = 25^\circ\text{C}$, $\text{pH} = 8.1$, ionic strength = 0.72, salinity = 35.5 ppt, 2PPMD = 0.77 mg/l as Cl_2 .

increased, helping the latter reaction compete with the former despite being at a disadvantage due to the high bromide concentrations. One may further generalize (as is shown by the chosen conditions in Figures 11-13) that, for unpolluted waters, chlorine doses in freshwater are typically below the breakpoint, in estuaries somewhere near the breakpoint, and in seawater above the breakpoint. (This will not be true for polluted waters wherein high NH_3 concentrations may preclude breakpoint chlorination even in seawater.) One thus has a noticeably more rapid loss of total oxidants in the case of an estuary than would be expected in freshwater or seawater. This behavior is verified, for example, in comparing chlorine consumption studies by Helz et al.⁴⁴ (estuary) and Eppley et al.³³ (seawater).

In this set of examples RNH_2 was omitted to make the diagrams simpler. In any case, the effect of aliphatic organic amines is simply to absorb active halogen in the production of alkyl halamines whose decomposition is negligible in a one-hour period (see Table II). A sample run which includes RNH_2 is given in Appendix VI. Here it is shown that for equal concentrations of NH_3 , RNH_2 , and AlNH_2 , most of the oxidant residual is tied up as organic halamines. The amino acid halamines decompose fairly rapidly, while the alkyl halamines are rather stable. In fact, the RNHBr concentration increases slightly due to release of HOBr in the bromine breakpoint process, which reacts with available RNH_2 , along with direct bromine transfer reactions.

Figure 11 shows the time-dependent species distributions when chlorine is added to freshwater containing ammonia and amino acids. Initially, NH_3 and AlNH_2 decrease rapidly by reaction with chlorine to

produce the corresponding monochloramines. Free chlorine is consumed rapidly and completely in these reactions and also in demand reactions. The bulk of the total residual consists of NH_2Cl , whose concentration declines gradually, partly by transfer of chlorine to AlNH_2 but mostly by reaction with the remaining demand. The latter reaction simultaneously causes an increase in NH_3 concentration. The deamination of AlNHCl further contributes to the increase in ammonia, this time at the expense of total organic amines. The slight loss of AlNH_2 is caused by chlorine transfer from NH_2Cl to produce AlNHCl . The overall situation is one in which the relatively high initial NH_3 concentration outcompetes the demand for reaction with added chlorine and prevents dichloramine formation, leaving a moderately stable residual in the form of NH_2Cl .

Figure 12 is the estuary case. As before, all the free chlorine is consumed in less than one minute. Bromide is converted into free bromine which is also used up immediately. Ammonia and AlNH_2 react rapidly to produce halamines, but this time bromamines and bromochloramines form in addition to monochloramine. Some breakpoint reactions are evident, resulting in a rapid loss of inorganic halamines. However, it is clear that one is still below the breakpoint because the initially-present ammonia is not converted completely into nitrogen and trihalamines. This is true despite the initial Cl_2/NH_3 ratio being greater than 1.5 because alanine and the demand absorb much of the free halogen, making the effective ratio less than 1.5. As in the freshwater case, ammonia builds up gradually due to reduction of NH_2Cl by the demand and deamination of AlNHCl and AlNHBr . AlNBrCl decomposes much more rapidly than

AINHCl or AINHBr but does not contribute to the increase in NH_3 . The overall situation here is one in which chloramines and bromamines are initially formed in roughly equal concentrations, but the chloramines are partially converted into less-stable bromochloramines both by direct transfer from dibromamine and by bromination with free HOBr released during rapid bromamine breakpoint reactions.

Figure 13 is the seawater case. Chlorine is quickly converted into bromine and both of these react with the demand. The demand outcompetes the small amounts of amines present resulting in a fast initial loss of total oxidants. The amines are all fully halogenated since there is an excess of added chlorine, resulting in increased stability for the inorganic halamine system but a decreased stability for the alanine halamines. The presence of considerable bromochloramines shows that monochloramine formation is still competitive with bromide oxidation even at such low ammonia concentrations. The overall situation is that free bromine makes up nearly all of the total residual because the amine concentrations are so low.

B. Freshwater Recirculating Systems with Cooling Towers

When the program is run for recirculating systems, it predicts average concentrations of oxidants in the cooling system rather than a concentration profile as a function of distance (i.e., time) in the cooling pipes. In this mode, extra terms of the form $+\text{RKINFL}[Y]_0$, $-\text{RKDSCH}[Y]$, and $-\text{RKEVAP}[Y]$ are added to the differential equations to account for the influx, discharge, and evaporation of compounds to and from the cooling system. Here $[Y]$ and $[Y]_0$ are the concentrations of the various species in the cooling system and intake water, respectively. RKINFL and RKDSCH

are the fractions of the total volume of water which are taken in and discharged per unit time. They are calculated by dividing the make-up rate and blow-down rate, respectively, by the total volume of the cooling system, assuming continuous blow-down. The inflow terms apply to all compounds in the make-up water, i.e., ammonia, organic amines, and demand, while the discharge terms apply to all species.

RKEVAP is an evaporation rate constant calculated by

$$\text{RKEVAP} = -(\text{QR}/\text{VCS})\ln(1-F),$$

where QR is the recirculating water flow rate (gallons/sec), VCS is the total volume of the cooling system, and F is an estimate of the fraction of oxidants lost by evaporation per pass through the cooling towers. Nelson⁸³ and Draley⁸⁴ have used F values in the range 0.3 - 0.6 in modeling recirculating systems. Somewhat lower estimates were used here because their F values incorporated other losses (i.e. breakpoint, oxidative deamination, and, in Draley's case, chlorine demand) which were considered separately in this model. The value of F reflects the volatility of the compound in question, and for amines this should increase upon chlorination since the ionization of chloramines is generally negligible. Thus, F was assumed to be significant for HOCl and chloramines, but was set to zero for amines and the demand. For purposes of this model, the inputted F values applies to HOCl, NCl₃, and RNHCl, while the values for NH₂Cl and AlNHCl were assumed to be three-tenths and one-tenth the inputted value, respectively. Evaporation of NHCl₂ was ignored since its concentration is normally minor. Although most of the chlorine in recirculating systems is generally considered to be lost to the organic demand,⁸⁵ some authors have suggested that evaporative losses can be significant.^{84,86}

For simplicity, it was assumed that the added chlorine is immediately dispersed throughout the cooling system. Furthermore, it was assumed that all the chlorine was added at once, even though chlorination normally occurs over a period of many minutes. However, this period is normally small compared to the chlorination cycle time, so instantaneous chlorination should be a reasonable model. The program can be easily altered to accept a chlorination feed time and feed rate if the need arises.

Table VIII in Appendix IV gives the input values for a sample run of the program in cooling tower mode. These are real chlorination conditions used at the Three Mile Island Nuclear Power Plant⁸⁵ before its infamous shut-down. The recommended operating procedure was to chlorinate at 6000 lbs/day for 40 minutes three times daily. This corresponds to a dose of 1.54 mg/l assuming instantaneous addition to the 13 million gallon cooling system. Figure 14 shows the model results for 15 chlorination cycles at a 1.54 mg/l dose. In the initial start up of the plant, the cooling system is filled with river water, whose characteristics are used as input to the program in this mode. Because the make-up flow is 11,500 gal/min and the blow-down rate is only 2,000 gal/min (i.e., 9,500 gal/min evaporate), the assumed-to-be non-volatile constituents of the river water - namely, demand and ammonium ion - have the potential for being concentrated by a factor equal to the make-up to blow-down ratio, which in this case is 5.63. The first 8 hours in Figure 14 show the kinetics of this concentration in the absence of added chlorine. One can see that compounds have been concentrated only by a factor of about 1.33, and thus 8 hours is not nearly enough time to reach the equilibrium levels in this example.

Figure 14. Freshwater chlorination cycles for a recirculating cooling tower system. Circles indicate the maximum monochloramine concentration at the beginning of the cycle.

In the first chlorination cycle, the following events occur. First, ammonia is rapidly consumed in forming NH_2Cl . Excess HOCl reacts more rapidly with the fast demand than with NH_2Cl . Thus, NHCl_2 formation is negligible and no breakpoint reactions can occur. Nevertheless, NH_2Cl is gradually destroyed by demand reactions, resulting in a regeneration of ammonia. Further input of ammonia from the make-up water causes its concentration to be greater at the end of the cycle than at the beginning. Likewise, fast demand increases from the inflow, but it never reaches the precycle level since, unlike ammonia, the demand already in the cooling system cannot be regenerated once it is consumed. Slow-acting demand is little affected due to outcompetition by NH_3 and fast demand, and so it increases as before chlorination.

The next few cycles see a repetition of this process. Fast demand is reduced overall, while slow demand and ammonia reach higher concentrations at the end of each cycle. In each case, the NH_2Cl formed equals the initial NH_3 concentration. Monochloramine persists longer the more the fast demand is reduced. However, the longer it persists, the more time it has to evaporate in the cooling towers. This causes a small reduction of end-of-cycle ammonia levels after cycle 4, since the NH_2Cl lost to evaporation does not regenerate NH_3 as does that lost to the demand.

Subsequent cycles (5-11) see an increased exertion of breakpoint reactions, which can now occur since the demand no longer prevents NHCl_2 formation. This explains both the decline in total ammonia and rise in fast-acting demand end-of-cycle levels. That is, NH_3 is converted to N_2 , and the demand effectively sees less total oxidants

because they are reduced to Cl^- in the same process. The breakpoint process is very rapid in this system, owing to the high temperature (43°C) and optimal pH (7.8), and it appears as a nearly instantaneous loss of initially-formed NH_2Cl in Figure 14 after cycle 8.

Finally, the system comes to equilibrium in the 12th cycle. Here, NH_3 and fast demand are consumed completely upon chlorination and a free residual persists for the first 40-50 minutes, causing the destruction of NH_2Cl . This continues until the breakpoint process is halted by the inflow of demand and NH_3 , which convert the HOCl into Cl^- and NH_2Cl , respectively. The latter effect causes the slight hump in the NH_2Cl curves in cycle 12 and thereafter. Subsequent NH_2Cl loss results mostly from reaction with fast demand and partly by discharge in the blow-down and evaporation. Slow demand is consumed slightly so long as HOCl remains, but its reaction with NH_2Cl is negligible at the equilibrium conditions in this example. Although dichloramine is an important intermediate during breakpoint, it is consumed so rapidly that its maximum concentration reaches only $0.13\mu\text{M}$ ($0.018\text{ mg/l as Cl}_2$) and so it is hardly measurable. Because of this, only unobservable traces of NCl_3 are formed, despite the presence of free HOCl .

The water conditions described by the model at equilibrium are in general agreement with those observed in the field.⁸⁵ Although it is not clear from the report⁸⁵ exactly when during the cycle the chemical analyses were made, the total NH_3 concentration ($\text{NH}_3 + \text{NH}_2\text{Cl}$) in the recirculating system was given as 0.05 mg/l , compared to the model prediction of $0.011 - 0.066\text{ mg/l}$. Likewise, the measured fast-acting demand was 0.64 mg/l , while the model values ranged from $0 - 0.72\text{ mg/l}$

during the cycle. Slow-acting demand varied from 2.1 - 2.3 mg/l for the model compared to a measured value of 3.7 mg/l. It is evident from Figure 14 that slow demand could be somewhat higher or lower without affecting the temporal patterns of the other species. Total chlorine residuals were found to decrease rapidly from 1.3 mg/l to about 0.3 - 0.4 mg/l in the first 10-20 minutes after chlorination was halted, followed by a much slower loss. Thus, the experiments indicate a moderately stable residual of 0.3 mg/l at 30 minutes following chlorination, while the model predicts a rather unstable 0.17 mg/l residual at 30 minutes. The increased stability observed in the field could easily be attributed to the formation of some aliphatic/heterocyclic chloramines, without greatly altering the remaining results. Organic amines were not measured in the experimental study.

The model estimates that, of the 1.54 mg/l chlorine dose, about 0.72 mg/l are consumed by the fast demand present initially, about 0.43 mg/l are used in breakpoint oxidation of ammonia, and about 0.18 mg/l react with the slow demand. The remaining 0.21 mg/l are lost to demand from the inflow, evaporation, and discharge. The good overall agreement with the chemical measurements suggests the validity of this chlorine mass balance. Furthermore, the ease of obtaining good fits with relatively small evaporation rate constants affirms the assertion that evaporative losses are minor,⁸⁵ contrary to the suggestions of Draley.⁸⁴

C. Laboratory Chlorination of Seawater Samples

The main goal of this work was to produce a model which could predict oxidant speciation and concentrations as a function of time.

Although a purely predictive capability was not tenable due to the variability of the demand, the model should be able to predict species distributions once the total oxidant decay curve has been fitted by adjusting the 2PPMD value and the halogen demand rate constants. The data of several workers^{5,7,33,58} were easily fitted in this manner, but these studies follow only total oxidant residuals and therefore a test of the oxidant speciation capability of the model was needed.

Figure 15 compares a seawater chlorination experiment performed by Inman and Johnson³⁴ with the corresponding model calculation. Very little data-fitting was performed, and the representative 2PPMD value of 0.77 mg/l was used. In Figure 15 the lines represent the model results and the points (with labels in parentheses) are the experimental data. The traces for total oxidants and NH_2Cl match reasonably well, but those for NHBr_2 do not. However, the calculated trace for NHBrCl agrees surprisingly well with the supposed experimental NHBr_2 points. This occurs in spite of the fact that the rate of formation of NHBrCl assumed by the model (Reaction 9) was an order of magnitude lower than that assumed for NHBr_2 (Reaction 5). Indeed, the amount of NHBrCl initially formed in the model calculations is near zero; rather, its formation is governed by bromine transfer from NHBr_2 to NH_2Cl as suggested by Trofe et al.²⁴ This type of transfer appears to preclude the coexistence of NHBr_2 and NH_2Cl in significant concentrations. These results point out the possibility that the oxidant measured by Inman

Figure 15. Experimental vs predicted oxidant speciation in chlorinated seawater. Points with parenthetical labels indicate data of Inman and Johnson.³⁴ Lines are the model calculations. $T = 23^{\circ}\text{C}$, $\text{pH} = 8.1$, $[\text{NH}_3]_0 = 2.0 \text{ mg/l as N}$, ionic strength = 0.67, salinity = 32.7 ppt, 2PPMD = 0.77 mg/l as Cl_2 , $\text{RNH}_2 = \text{AlNH}_2 = 0$, $[\text{Cl}_2]_0 = 5.0 \text{ mg/l as Cl}_2$.

and Johnson³⁴ using their membrane electrode was not NHBr_2 at all, but rather NHBrCl . Further support to this hypothesis is afforded by the evidence of Trofe et al.²⁴ that NHBr_2 and NHBrCl have similar electrochemical properties. It should be pointed out, however, that little confidence should be placed in the quantitation of the NHBrCl calculation. It is quite possible that NHBrCl decomposes more rapidly, or that the bromine transfer from NHBr_2 to NH_2Cl is an equilibrium process rather than unidirectional as was assumed by the model. In any case, it is quite likely that the measured electrode response was due, at least in part, to NHBrCl and not solely to NHBr_2 .

The unfortunate final conclusion of this comparison is that even the best oxidant speciation studies available to date are inadequate to fully test the model.

DISCUSSIONS AND RECOMMENDATIONS

Because so many reaction rates relative to seawater chlorination remain unmeasured, this model cannot be complete or final. We have instead attempted to summarize the present understanding of seawater chemistry relevant to cooling water chlorination practices, and present a framework of important reactions whose rates can later be added when data become available. It is our hope that future researchers will use Appendix II to choose reactions for kinetic studies.

It is difficult to assess the validity of our model because experimental verification is lacking. As might be expected, we found that total oxidant decay is strongly influenced by the presence of organic amines, which most seawater chlorination studies have failed to measure. Furthermore, simple analysis of total organic nitrogen is not enough,

since amino acids decompose so much more rapidly than aliphatic amines, and because peptide-bound nitrogen is not reactive toward halogens. Verification will require an extensive study which includes measurement of ammonia, total aliphatic/heterocyclic nitrogen, and free amino acid concentrations to be used as input to the program. Analysis of the reaction products will be difficult especially for the bromochloramines, since specific methods for their determination are lacking and because of the complex mixtures which are likely to form. Our overall conclusions as to the validity of the model are that it is in general agreement with experimental halamine species distributions, but that great variability in non-nitrogenous demand make predictions of total oxidant residuals somewhat tenuous.

The model calculations indicate that chlorination of ammonia will be important in seawater even at the lowest ammonia concentrations detectable by standard methods. Thus, it is predicted that NBr_2Cl should be an important fraction of the total combined residual in most chlorinated seawaters, the rest being made up by NBr_3 . Why has this compound never been detected? We suggest that it is either because NBr_2Cl and NBr_3 have nearly identical ultraviolet spectra, thus causing the misinterpretation that UV peaks near 258 nm are due only to NBr_3 , or that NBr_2Cl has such a low molar absorptivity that it is unobservable in the presence of NBr_3 , which has the highest known absorptivity of all the inorganic halamines. It is also possible, but unlikely, that NBr_2Cl decomposes so rapidly that it is undetectable after one minute. Such a possibility is greater for NHBrCl (which we predict should be important at lower Cl_2/NH_3 ratios) since dihalamines are generally less stable

than mono- or trihalamines. The formation of both mixed-halamines together is predicted to be greatest near the breakpoint, where their rapid decomposition could make observation difficult.

This raises another question, namely, what is the importance of mixed-halamine breakpoint reactions? Do the bromochloramines react with each other, with chloramines, or with bromamines to produce N_2 ? Do the chloramine and bromamine breakpoint systems interact? Can the bromochloramines be converted into bromamines in seawater before breakpoint reactions take their toll? Answers to such questions, along with the determination of analytic methods (UV spectra) for the bromochloramines, are of fundamental importance to the understanding of saline water chlorination chemistry and therefore warrant further research. Even the pure halogen breakpoint models are incomplete. The chlorine breakpoint models are valid only above the breakpoint. This may be a minor problem, but it would be of value to develop a model which is valid at all chlorine doses. The bromine-ammonia model was designed with this in mind; however, it lacks a thorough verification. Lastly, some explanation is needed for the unusually high breakpoint ratios ($Cl_2/NH_3 = 5-17$) observed by Khalanski⁷ in real seawater samples.

More research is needed to characterize the non-nitrogenous chlorine demand of seawater. While most workers agree that an organic demand exists, no quantitative studies have been performed. A study of the relation between seawater demand and total organic carbon would be valuable. Some other questions regarding the demand need answers: What are the compound(s) and/or catalyst(s) causing the decomposition of free bromine in the third slow phase? Is the increase in demand with

increasing dose real, or is it just a manifestation of higher reaction rates at higher doses? How fast do organic halamines react with the demand? In what fashion do halamines react with the demand? That is, can free ammonia and amines be released in such reactions or do amination reactions play a part (see Equations 51-56)? Can ammonia always outcompete the demand for reaction with chlorine as suggested by Eppley et al.³³ The data of Khalanski⁷ seem to contradict this. This is an indication that the organic constituents of seawater have oxidation rates varying as greatly as their concentrations.

Even the analytical methods for residual oxidant determinations in seawater need refinement. Unlike freshwater, the order of adding reagents appears to be of critical importance in any titrations employing iodide ion at low pH.⁸⁷ Is the difference in recoveries between pH 1.4 and pH 4 titrations real, or is it simply an artifact in the method caused by iodate formation or air oxidation of iodide? Moreover, the presence of iodate occurring naturally in seawater makes uncertain any measurements below 1.0 mg/l of Cl_2 ⁶⁰ if a low-pH titration is employed. Any studies measuring halogen residuals in seawater should carefully state the conditions of the analytical methods used.⁸⁸

Finally, it should be pointed out that this model was developed based on studies with chlorinated water samples in the laboratory. The inability of Helz et al.⁴⁴ to find good correlations between laboratory and field results casts doubt on the validity of extending the model results to actual field conditions. However, Carpenter et al.⁵⁶ found no significant differences between chlorine decomposition in "laboratory" samples and in the water as it passed through a power plant,

indicating that the effects observed by Helz et al.⁴⁴ were site-specific. Carpenter et al.⁵⁶ pointed out that studies at many coastal power plants will be required to establish the applicability of laboratory studies towards predicting actual discharge compositions.

CONCLUSIONS

1. A kinetic model has been developed for predicting the concentrations of various oxidants as a function of time in chlorinated seawater. The model was shown to be applicable under a broad variety of conditions, including all temperatures, chlorine doses, ammonia concentrations, organic amine concentrations, salinities (including freshwater), and pH levels likely to be encountered during power plant cooling water chlorination. The model applies to once-through, as well as recirculating systems. The effects of light are not included.
2. The ultimate goal of a purely predictive model is not feasible at present due to the great variability of the non-nitrogenous demand. However, oxidant speciation should be reasonably accurate once the total residual halogen decay curve has been fitted by adjusting the inputted demand value and/or demand rate constants.
3. Complete experimental verification of the model awaits the development of methods for analyzing complex mixtures of chloramines, bromamines, and bromochloramines.
4. Much research is needed to measure the many estimated rate constants used in the model and to identify the products of halamine reactions with the demand.

5. Analytical methods for determining chlorine-produced oxidants in seawater are uncertain at present and need refinement.
6. The concentration and form of organic amines should be measured in future seawater chlorination studies because they have a profound influence on the dynamics of halogen decay.
7. If the bromamines truly exist in equilibrium with each other, then these equilibria must be governed by direct disproportionation rather than by hydrolysis/formation reactions.
8. It can be stated with some confidence that the presently unobserved mixed halamine, NBr_2Cl , is being produced at power plants on the seacoast when NH_3 concentrations are relatively low, and is being discharged into oceans and estuaries with unknown environmental effects.

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APPENDIX I

REACTIONS MODELLED

Halamine Formation and Hydrolysis

Bromide Oxidation

Halogen Transfer

Breakpoint

Chlorine-Ammonia System

Bromine-Ammonia System

Mixed Halamine System

Other Decompositions

Halogen Demand

Equilibria

APPENDIX II

KINETIC DATA

$$(a) \quad +d[\text{NH}_2\text{Cl}]/dt = -d[\text{NH}_3]/dt = -d[\text{HOCl}]/dt = k_1[\text{NH}_3]^{0.8}[\text{HOCl}]$$

$$k_1 = 5.14 \times 10^8 \exp(-1550/T) \times (0.3017) \text{ l-mol}^{-1}\text{sec}^{-1}, T = ^\circ\text{K}$$

If the 0.8 power ammonia dependence is set equal to unity, then the factor 0.3017 should be omitted.

$$k_{1\text{obs}} = \frac{k_1}{K_a/[\text{H}^+] + 1 + K_a K_b/K_w + K_b[\text{H}^+]/K_w}$$

where K_a is the ionization constant of HOCl, K_b is the base dissociation constant of NH_3 , and K_w is the ionization constant of water. Note that equilibrium constants must be corrected for ionic strength in calculating observed rate constants. Ref: 35b, 61

$$k_{-1} = 8.7 \times 10^7 \exp(-8555.6/T) \text{ sec}^{-1}, T = ^\circ\text{K}. \quad \text{Ref: 89}$$

$$(a) \quad d[\text{NHCl}_2]/dt = -d[\text{NH}_2\text{Cl}]/dt = -d[\text{HOCl}]/dt = k_2[\text{NH}_2\text{Cl}][\text{HOCl}]$$

$$k_2 = 7.6 \times 10^7 \exp(-3673.9/T) \text{ l-mol}^{-1}\text{sec}^{-1}, T = ^\circ\text{K}$$

$$k_{2\text{obs}} = k_2/(K_a/[\text{H}^+] + 1).$$

Ref: 53

$$(b) \quad -d[\text{NHCl}_2]/dt = +d[\text{NH}_2\text{Cl}]/dt = +d[\text{HOCl}]/dt = k_{-2}[\text{NHCl}_2]$$

$$k_{-2} = 6.5 \times 10^{-7} \text{ sec}^{-1}.$$

Ref: 57b

$$(a) \quad +d[\text{NCl}_3]/dt = -d[\text{NHCl}_2]/dt = -d[\text{HOCl}]/dt = k_{48}[\text{NHCl}_2][\text{HOCl}]$$

$$k_{48\text{obs}} = 3.43 \times 10^5 \exp(-3522.9/T) \times$$

$$(1 + 10K_a/[\text{H}^+])/(1 + K_a/[\text{H}^+]) \text{ l-mol}^{-1}\text{sec}^{-1}, T = ^\circ\text{K}$$

This is a variation of an empirical fit of NCl_3 formation rates determined by Saunier and Selleck, who used the factor 25 in place of the factor 10 in the above expression.

Ref: 68

$$(b) \quad -d[\text{NCl}_3]/dt = +d[\text{NHCl}_2]/dt = +d[\text{HOCl}]/dt = K_{48}[\text{NCl}_3]$$

$$k_{-48} = 8.56 \times 10^8 \exp(-9058.9/T) \times$$

$$(1 + 5.88 \times 10^5 K_w/[\text{H}^+]) \text{ sec}^{-1}.$$

Ref: 68, 90

$$(a) \quad +d[\text{RNHCl}]/dt = -d[\text{RNH}_2]/dt = -d[\text{HOCl}]/dt = k_3[\text{RNH}_2][\text{HOCl}]$$

$$k_3 = 7.8 \times 10^9 \exp(-956.2/T) \text{ l-mol}^{-1}\text{sec}^{-1}, T = ^\circ\text{K}$$

$$k_{3\text{obs}} = \frac{k_3}{K_a/[\text{H}^+] + 1 + K_a K_{b3}/K_w + K_{b3}[\text{H}^+]/K_w}$$

where K_{b3} is the base dissociation constant of CH_3NH_2 and K_a and K_w are as defined above.

Ref: 53, 61

$$(b) \quad -d[\text{RNHCl}]/dt = +d[\text{RNH}_2]/dt = +d[\text{HOCl}]/dt = k_{-3}[\text{RNHCl}]$$

$$k_{-3} = 1.6 \times 10^{-6} \text{ sec}^{-1}.$$

Ref: 57b

$$(a) \quad +d[\text{NH}_2\text{Br}]/dt = -d[\text{NH}_3]/dt = -d[\text{HOBr}]/dt = k_{12}[\text{NH}_3][\text{HOBr}]$$

$$k_{12} = 7.5 \times 10^7 [2^{((T-20)/13.86)}] \text{ l-mol}^{-1}\text{sec}^{-1}, T = ^\circ\text{C}$$

$$k_{12}^{\text{obs}} = \frac{k_{12}}{K_{\text{HOBr}}/[\text{H}^+] + 1 + K_{\text{HOBr}}K_b/K_w + K_b[\text{H}^+]/K_w}$$

where K_{HOBr} is the ionization constant of HOBr, and K_b and K_w are as defined above. The temperature dependent expression is an empirical fit of the data in the reference and the kinetic expression applies only at $\text{pH} < 10$.

Ref: 68

$$(b) \quad -d[\text{NH}_2\text{Br}]/dt = +d[\text{NH}_3]/dt = +d[\text{HOBr}]/dt = k_{-12}[\text{NH}_2\text{Br}]$$

$$k_{-12} = k_{12}/9.493 \times 10^8 \text{ sec}^{-1}$$

This expression follows from an estimate of the free energy of formation of NH_2Br (see Tables III and IV, pages 38 and 39). Ref. 64

$$(a) \quad +d[\text{NHBr}_2]/dt = -d[\text{NH}_2\text{Br}]/dt = -d[\text{HOBr}]/dt = k_6[\text{NH}_2\text{Br}][\text{HOBr}]$$

$$k_6 = 3 \times 10^5 [2^{(T-25)/13.86}] \text{ l-mol}^{-1}\text{sec}^{-1}, T = ^\circ\text{C}$$

$$k_6^{\text{obs}} = k_6/(K_{\text{HOBr}}/[\text{H}^+] + 1)$$

This is an estimated value with an assumed temperature dependence similar to that of NH_2Br formation.

$$(b) \quad -d[\text{NHBr}_2]/dt = +d[\text{NH}_2\text{Br}]/dt = +d[\text{HOBr}]/dt = k_{-6}[\text{NHBr}_2]$$

$$k_{-6} = k_6/7.369 \times 10^8 \text{ sec}^{-1}$$

This expression follows from estimates of the free energies of formation of the bromamines (see Tables III and IV, pages 38 and 39).

Ref: 64

$$(a) \quad +d[\text{NBr}_3]/dt = -d[\text{NHBr}_2]/dt = -d[\text{HOBr}]/dt = k_7[\text{NHBr}_2][\text{HOBr}]$$

$$k_7 = 1.3 \times 10^4 [2((T-25)/13.86)] \text{ l-mol}^{-1}\text{sec}^{-1}, T = ^\circ\text{C}$$

$$k_{7\text{obs}} = k_7/(K_{\text{HOBr}}/[\text{H}^+] + 1)$$

This is an estimated value with an assumed temperature dependence similar to that of NH_2Br formation.

$$(b) \quad -d[\text{NBr}_3]/dt = +d[\text{NHBr}_2]/dt = +d[\text{HOBr}]/dt = k_{-7}[\text{NBr}_3]$$

$$k_{-7} = k_7/1.081 \times 10^7 \text{ sec}^{-1}$$

This expression follows from estimates of the free energies of formation of the bromamines (see Tables III and IV, pages 38 and 39).

Ref: 64

$$(a) \quad +d[\text{RNHBr}]/dt = -d[\text{RNH}_2]/dt = -d[\text{HOBr}]/dt = k_{13}[\text{RNH}_2][\text{HOBr}]$$

$$k_{13} = 9.0 \times 10^8 [2((T-20)/13.86)] \text{ l-mol}^{-1}\text{sec}^{-1}, T = ^\circ\text{C}$$

$$k_{13\text{obs}} = \frac{k_{13}}{K_{\text{HOBr}}/[\text{H}^+] + 1 + K_{\text{HOBr}}K_{b3}/K_w + K_{b3}[\text{H}^+]/K_w}$$

The value 9.0×10^8 was estimated based on data in the reference and assigned a temperature dependence the same as that of NH_2Br formation.

Ref: 63

$$(b) \quad -d[\text{RNHBr}]/dt = +d[\text{RNH}_2]/dt = +d[\text{HOBr}]/dt = k_{-13}[\text{RNHBr}]$$

$$k_{-13} = 1.6 \times 10^{-4} \text{ sec}^{-1}$$

Estimated value ($100 \times k_{-3}$).

$$(a) \quad +d[\text{RNBBr}_2]/dt = -d[\text{RNHBr}]/dt = -d[\text{HOBr}]/dt = k_9[\text{RNHBr}][\text{HOBr}]$$

$$k_9 = 1.4 \times 10^6 \text{ l-mol}^{-1}\text{sec}^{-1}, k_{9\text{obs}} = k_9/(\text{K}_{\text{HOBr}}/[\text{H}^+] + 1)$$

Estimated value ($\sim 5 \times k_6$, $\sim 10^{-3} \times k_{13}$).

$$(b) \quad -d[\text{RNBBr}_2]/dt = +d[\text{RNHBr}]/dt = +d[\text{HOBr}]/dt = k_{-9H}[\text{RNBBr}_2]$$

$$k_{-9H} = 0.5 k_9 \text{ sec}^{-1}$$

Estimated value (see Reaction 47).

$$(a) \quad +d[\text{NHBrCl}]/dt = -d[\text{NH}_2\text{Cl}]/dt = -d[\text{HOBr}]/dt = k_{10}[\text{NH}_2\text{Cl}][\text{HOBr}]$$

$$k_{10} = 3 \times 10^4 \text{ l-mol}^{-1}\text{sec}^{-1}, k_{10\text{obs}} = k_{10}/(\text{K}_{\text{HOBr}}/[\text{H}^+] + 1)$$

Estimated value ($\sim 100 \times k_2$, $\sim 0.1 \times k_6$).

$$(b) \quad -d[\text{NHBrCl}]/dt = +d[\text{NH}_2\text{Cl}]/dt = +d[\text{HOBr}]/dt = k_{-10}[\text{NHBrCl}]$$

$$k_{-10} = 2 \times 10^{-4} \text{ sec}^{-1}$$

Estimated value ($k_{-6} > k_{-10} > k_{-2}$).

$$(a) \quad +d[\text{NBr}_2\text{Cl}]/dt = -d[\text{NHBrCl}]/dt = -d[\text{HOBr}]/dt = k_{47}[\text{NHBrCl}][\text{HOBr}]$$

$$k_{47} = 3 \times 10^4 \text{ l-mol}^{-1}\text{sec}^{-1}, k_{47\text{obs}} = k_{47}/(K_{\text{HOBr}}/[\text{H}^+] + 1)$$

Estimated value.

$$(b) \quad -d[\text{NBr}_2\text{Cl}]/dt = +d[\text{NHBrCl}]/dt = +d[\text{HOBr}]/dt = k_{-47}[\text{NBr}_2\text{Cl}]$$

$$k_{-47} = 5 \times 10^{-4} \text{ sec}^{-1}$$

Estimated value ($2.5 \times k_{-10}$).

$$(a) \quad +d[\text{RNBrcCl}]/dt = -d[\text{RNHCl}]/dt = -d[\text{HOBr}]/dt = k_{11}[\text{RNHCl}][\text{HOBr}]$$

$$k_{11} = 5 \times 10^5 \text{ l-mol}^{-1}\text{sec}^{-1}, k_{11\text{obs}} = k_{11}/(K_{\text{HOBr}}/[\text{H}^+] + 1)$$

Estimated value ($\sim 20 \times k_{10}$, $\sim 0.3 \times k_9$).

$$(b) \quad -d[\text{RNBrcCl}]/dt = +d[\text{RNHCl}]/dt = +d[\text{HOBr}]/dt = k_{-11\text{H}}[\text{RNBrcCl}]$$

$$k_{-11\text{H}} = 0.3k_{11} \text{ sec}^{-1}.$$

Estimated value (see Reaction 48).

$$-d[\text{NHBrCl}]/dt = -d[\text{NH}_2\text{Br}]/dt = -d[\text{HOCl}]/dt = k_{\text{MXC}}[\text{NH}_2\text{Br}][\text{HOCl}]$$

$$k_{\text{MXC}} = 20 \text{ l-mol}^{-1}\text{sec}^{-1}, k_{\text{MXCobs}} = k_{\text{MXC}}/(K_a/[\text{H}^+] + 1)$$

Estimated value.

$$+d[\text{RNBrCl}]/dt = -d[\text{RNHBr}]/dt = -d[\text{HOCl}]/dt = k_{14}[\text{RNHBr}][\text{HOCl}]$$

$$k_{14} = 2 \times 10^4 \text{ l-mol}^{-1}\text{sec}^{-1}, \quad k_{14\text{obs}} = k_{14}/(K_a/[\text{H}^+] + 1)$$

Estimated value.

$$+d[\text{AlNHCl}]/dt = -d[\text{AlNH}_2]/dt = -d[\text{HOCl}]/dt = k_{33}[\text{AlNH}_2][\text{HOCl}]$$

$$k_{33} = 19 \, k_1/0.3017 \text{ l-mol}^{-1}\text{sec}^{-1}$$

$$k_{33\text{obs}} = \frac{k_{33}}{K_a/[\text{H}^+] + 1 + K_a K_{\text{bala}}/K_w + K_{\text{bala}}[\text{H}^+]/K_w}$$

where K_{bala} is the base dissociation constant for alanine. The value of k_{33} is 19 times the value k_1 would have assuming a first order ammonia dependence for monochloramine formation (see Reaction 1).

Ref: 53

$$+d[\text{AlNHBr}]/dt = -d[\text{AlNH}_2]/dt = -d[\text{HOBr}]/dt = k_{34}[\text{AlNH}_2][\text{HOBr}]$$

$$k_{34} = 3.8 \times 10^8 \text{ l-mol}^{-1}\text{sec}^{-1}$$

$$k_{34\text{obs}} = \frac{k_{34}}{K_{\text{HOBr}}/[\text{H}^+] + 1 + K_{\text{HOBr}} K_{\text{bala}}/K_w + K_{\text{bala}}[\text{H}^+]/K_w}$$

The value of k_{34} was taken equal to that for glycine bromination at 20°C. The kinetic expression applies only at $\text{pH} \lesssim 10$.

Ref: 63

$$+d[\text{AlNBrCl}]/dt = -d[\text{AlNHCl}]/dt = -d[\text{HOBr}]/dt \\ = k_{35}[\text{AlNHCl}][\text{HOBr}]$$

$$k_{35} = 1.75 \times 10^5 \text{ l-mol}^{-1}\text{sec}^{-1}, k_{35\text{obs}} = k_{35}/(K_{\text{HOBr}}/[\text{H}^+] + 1)$$

Estimated value ($\sim 0.33 \times k_{11}$, $0.5 \times k_{36}$).

$$+d[\text{AlNBr}_2]/dt = -d[\text{AlNHBr}]/dt = -d[\text{HOBr}]/dt = k_{36}[\text{AlNHBr}][\text{HOBr}]$$

$$k_{36} = 3.5 \times 10^5 \text{ l-mol}^{-1}\text{sec}^{-1}, k_{36\text{obs}} = k_{36}/(K_{\text{HOBr}}/[\text{H}^+] + 1)$$

Estimated value ($2 \times k_{35}$).

$$+d[\text{AlNBrCl}]/dt = -d[\text{AlNHBr}]/dt = -d[\text{HOCl}]/dt =$$

$$k_{37}[\text{AlNHBr}][\text{HOCl}]$$

$$k_{37} = 5 \times 10^4 \text{ l-mol}^{-1}\text{sec}^{-1}, k_{37\text{obs}} = k_{37}/(K_a/[\text{H}^+] + 1)$$

Estimated value ($\sim k_{14}$).

$$+d[\text{HOBr}]/dt = -d[\text{HOCl}]/dt = k_5[\text{HOCl}][\text{Br}^-]$$

$$k_5 = 4.7 \times 10^4 \exp(-754.9/T) \text{ l-mol}^{-1}\text{sec}^{-1}, T = ^\circ\text{K}$$

$$k_{5\text{obs}} = k_5/(K_a/[\text{H}^+] + 1).$$

Ref: 35a

$$+d[\text{HOBr}]/dt = +d[\text{NH}_3]/dt = -d[\text{NH}_2\text{Cl}]/dt = k_{\text{MXB}}[\text{H}^+][\text{Br}^-][\text{NH}_2\text{Cl}]$$

$$k_{\text{MXB}} = 1.417 \times 10^6 \text{ l}^2\text{-mol}^{-2}\text{sec}^{-1}.$$

Ref: 23, 24

$$(a) \quad +d[\text{NHBr}_2]/dt = +d[\text{NH}_3]/dt = -0.5d[\text{NH}_2\text{Br}]/dt = k_D[\text{NH}_2\text{Br}]^2$$

$$k_D = k_{-D}k_{6\text{obs}} k_{-12}/k_{-6}k_{12\text{obs}} \text{ l-mol}^{-1}\text{sec}^{-1} \text{ (See Reaction 22).}$$

$$(b) \quad +0.5d[\text{NH}_2\text{Br}]/dt = -d[\text{NHBr}_2]/dt = -d[\text{NH}_3]/dt = k_{-D}[\text{NHBr}_2][\text{NH}_3]$$

$$k_{-D} = 1 \times 10^4 \text{ l-mol}^{-1}\text{sec}^{-1} \text{ (see Reaction 22).}$$

$$(a) \quad +d[\text{NBr}_3]/dt = +d[\text{NH}_2\text{Br}]/dt = -0.5d[\text{NHBr}_2]/dt = k_{D1}[\text{NHBr}_2]^2$$

$$k_{D1} = 1 \times 10^4 \text{ l-mol}^{-1}\text{sec}^{-1}$$

$$(b) \quad +0.5d[\text{NHBr}_2]/dt = -d[\text{NH}_2\text{Br}]/dt = -d[\text{NBr}_3]/dt$$

$$= k_{-D1}[\text{NH}_2\text{Br}][\text{NBr}_3]$$

$$k_{-D1} = k_{D1}k_{6\text{obs}} k_{-7}/k_{-6}k_{7\text{obs}} = k_{D1}k_6k_{-7}/k_{-6}k_7 \text{ l-mol}^{-1}\text{sec}^{-1}$$

Reaction 21 is equal to (Reaction 5 - Reaction 4) and therefore the ratio k_D/k_{-D} is established once k_6 , k_{-6} , k_{12} , and k_{-12} are calculated. Likewise, Reaction 22 is equal to (Reaction 6 - Reaction 5) and the ratio k_{D1}/k_{-D1} is predetermined by k_6 , k_{-6} , k_7 , and k_{-7} . The values

for k_{-D} and k_{D1} are arbitrary, but $10^4 \text{ l-mol}^{-1}\text{sec}^{-1}$ was deemed to be the smallest number consistent with maintenance of an equilibrium distribution of bromamines under conditions likely to be encountered. Note that $k_{6\text{obs}}$ and $k_{12\text{obs}}$ must be used in Reaction 21 to account for ionization of NH_3 , but that these ionization effects cancel in calculating k_{-D1} .

Estimated from results presented in the reference.

Ref: 24

Average of alanine and glycine values in the reference. Ref: 32

Estimated value ($8 \times k_{41}$).

$$+d[\text{AlNHBr}]/dt = +d[\text{NH}_2\text{Br}]/dt = -d[\text{AlNH}_2]/dt = -d[\text{NHBr}_2]/dt$$

$$= k_{43}[\text{AlNH}_2][\text{NHBr}_2]$$

$$k_{43} = 40 \text{ l-mol}^{-1}\text{sec}^{-1}$$

Estimated value ($32 \times k_{41}$).

$$+d[\text{RNHCl}]/dt = +d[\text{NH}_3]/dt = -d[\text{RNH}_2]/dt = -d[\text{NH}_2\text{Cl}]/dt$$

$$= k_{44}[\text{RNH}_2][\text{NH}_2\text{Cl}]$$

$$k_{44} = 3.125 \text{ l-mol}^{-1}\text{sec}^{-1}$$

Estimated value (halfway between amino acid and morpholine averages in the reference).

Ref: 32

$$+d[\text{RNHBr}]/dt = +d[\text{NH}_3]/dt = -d[\text{RNH}_2]/dt = -d[\text{NH}_2\text{Br}]/dt$$

$$= k_{45}[\text{RNH}_2][\text{NH}_2\text{Br}]$$

$$k_{45} = 25 \text{ l-mol}^{-1}\text{sec}^{-1}$$

Estimated value ($8 \times k_{44}$).

$$+d[\text{RNHBr}]/dt = +d[\text{NH}_2\text{Br}]/dt = -d[\text{RNH}_2]/dt = -d[\text{NHBr}_2]/dt$$

$$= k_{46}[\text{RNH}_2][\text{NHBr}_2]$$

$$k_{46} = 100 \text{ l-mol}^{-1}\text{sec}^{-1}$$

Estimated value ($32 \times k_{44}$).

$$+d[\text{HNO}]/dt = -d[\text{NHCl}_2]/dt = k_{25}[\text{NHCl}_2]$$

$$k_{25} = 2.03 \times 10^{14} \exp(-3623.6/T) \times N_T K_w / [\text{H}^+] \text{ sec}^{-1}, T = ^\circ\text{K}$$

where N_T is the initial total ammonia concentration, in $\underline{\text{M}}$ (see Reaction 33). Ref: 68

$$-d[\text{NH}_2\text{Cl}]/dt = -d[\text{HNO}]/dt = k_{28}[\text{NH}_2\text{Cl}][\text{HNO}]$$

$$k_{28} = 1 \times 10^{-8} \exp(-3019.6/T) \text{ l-mol}^{-1}\text{sec}^{-1}, T = ^\circ\text{K}$$

(See Reaction 33).

Ref: 68

$$+d[\text{HOCl}]/dt = -d[\text{NHCl}_2]/dt = -d[\text{HNO}]/dt = k_{30}[\text{NHCl}_2][\text{HNO}]$$

$$k_{30} = 1.3 \times 10^9 \exp(-3019.6/T) \text{ l-mol}^{-1}\text{sec}^{-1}, T = ^\circ\text{K}$$

(See Reaction 33).

Ref: 68

$$-d[\text{HNO}]/dt = -0.5d[\text{HOCl}]/dt = k_{31}[\text{HNO}][\text{HOCl}]$$

$$k_{31} = 1 \times 10^7 \exp(-3019.6/T) \text{ l-mol}^{-1}\text{sec}^{-1}, T = ^\circ\text{K}$$

$$k_{31} \text{ obs} = k_{31} / (1 + K_a / [\text{H}^+]).$$

Ref: 68

Note: The steady state approximation was used in this model for HNO to eliminate a differential equation for it. The differential equations incorporating Reactions 30-33 then become:

$$\begin{aligned}
 -d[\text{NH}_2\text{Cl}]/dt &= \frac{k_{25}[\text{NH}_2\text{Cl}][\text{NHCl}_2]}{13[\text{NHCl}_2] + [\text{NH}_2\text{Cl}] + k_{\text{NO}_3}[\text{HOCl}]} \\
 -d[\text{NHCl}_2]/dt &= k_{25}[\text{NHCl}_2](1 + 13[\text{NHCl}_2]/(13[\text{NHCl}_2] + [\text{NH}_2\text{Cl}] + k_{\text{NO}_3}[\text{HOCl}])) \\
 +d[\text{HOCl}]/dt &= \frac{k_{25}[\text{NHCl}_2](13[\text{NHCl}_2] - 2k_{\text{NO}_3}[\text{HOCl}])}{13[\text{NHCl}_2] + [\text{NH}_2\text{Cl}] + k_{\text{NO}_3}[\text{HOCl}]}
 \end{aligned}$$

where $k_{\text{NO}_3} = k_{31\text{obs}}/k_{28}$ and the factor 13 arises from the ratio k_{30}/k_{28} .

$$+2d[\text{HOBr}]/dt = -d[\text{NHBr}_2]/dt = k_{27}[\text{NHBr}_2]^2$$

$$k_{27} = 13.3 \text{ l-mol}^{-1}\text{sec}^{-1}$$

Ref: 70, 92

Note errors on page 223 in ref. 70: the units on the rate constants should be $\text{M}^{-1}\text{hr}^{-1}$, not $\text{M}^{-1}\text{sec}^{-1}$.

$$+0.5d[\text{HOBr}]/dt = -d[\text{NHBr}_2]/dt = -d[\text{NBr}_3]/dt = k_{7p}[\text{NHBr}_2][\text{NBr}_3]$$

$$k_{7p} = 894.6 + 1.182 \times 10^9 K_w/[\text{H}^+] \text{ l-mol}^{-1}\text{sec}^{-1}$$

The pH independent term was empirically determined by fitting the pH 7.0 breakpoint curve given in reference 19. The pH dependence was estimated.

Ref: 19, 70, 71

$$k_{7D} = 12 \, \text{l-mol}^{-1}\text{sec}^{-1}$$

This value was used instead of the experimental value of 0.34 $\text{l-mol}^{-1}\text{sec}^{-1}$ in order to give the model a better overall fit in the high- Br_2/N -input region of the experimental bromine breakpoint curve in reference 19. Ref: 19, 71

$$k_{26} = 4.0 \, \text{l-mol}^{-1}\text{sec}^{-1}$$

Estimated value ($0.3 \times k_{27}$).

$$k_{7PX} = 0.15 \, k_{7P} \, \text{l-mol}^{-1}\text{sec}^{-1} \text{ (see Reaction 35).}$$

Estimated k_{7PX}/k_{7P} ratio.

(See Reaction 38).

$$+0.5d[\text{HOBr}]/dt = -d[\text{NHBrCl}]/dt = -d[\text{NBr}_2\text{Cl}]/dt$$

$$= k_{7\text{PX}2}[\text{NHBrCl}][\text{NBr}_2\text{Cl}]$$

$$k_{7\text{PX}2} = k_{7\text{P}} \text{ l-mol}^{-1}\text{sec}^{-1} \text{ (see Reaction 35).}$$

Estimated $k_{7\text{PX}2}/k_{7\text{P}}$ ratio.

$$+0.667d[\text{HOBr}]/dt = -d[\text{NBr}_2\text{Cl}]/dt = k_{7\text{D}}[\text{NBr}_2\text{Cl}]^2$$

(See Reaction 36).

$$-d[\text{HOBr}]/dt = k_8 \text{ mol-l}^{-1}\text{sec}^{-1}$$

$$k_8 = 1.567 \times 10^{-11} \text{ CL} \times \text{PS } \underline{\text{M}} \text{ sec}^{-1} \text{ for } \text{CL} < 7.5 \text{ and } T \leq 30^\circ\text{C}$$

$$k_8 = 1.175 \times 10^{-10} \text{ PS } \underline{\text{M}} \text{ sec}^{-1} \text{ for } \text{CL} \geq 7.5 \text{ and } T \leq 30^\circ\text{C}$$

$$k_8 = [1.567 \times 10^{-11} \text{ CL} + 9.40 \times 10^{-12} (T-30) \text{ PS } \underline{\text{M}}\text{-sec}^{-1} \text{ for } \\ \text{CL} < 7.5 \text{ and } T > 30^\circ\text{C}$$

$$k_8 = [1.175 \times 10^{-10} + 9.40 \times 10^{-12} (T-30) \text{ PS } \underline{\text{M}}\text{-sec}^{-1} \text{ for } \\ \text{CL} \geq 7.5 \text{ and } T > 30^\circ\text{C}$$

where CL is the chlorine dose in mg/l as Cl_2 and PS is the fraction percent salinity defined as $[\text{Br}^-]/65$ with $[\text{Br}^-]$ in mg/l. This zero-order decay is important only for long contact times (> 100 min) in chlorinated seawater with low ammonia and is a rough empirical fit of the data in the references.

Ref: 5, 58

$$+d[\text{NH}_3]/dt = -d[\text{AlNHCl}]/dt = k_{38}[\text{AlNHCl}]$$

$$k_{38} = 8.731 \times 10^{15} \exp(-13,387/T) \text{ sec}^{-1}, T = ^\circ\text{K. Ref: 31}$$

$$+d[\text{NH}_3]/dt = -d[\text{AlNHBr}]/dt = k_{39}[\text{AlNHBr}]$$

$$k_{39} = 1 \times 10^{-4} \text{ sec}^{-1}$$

This is the N-bromoglycine value at pH 8.4 and 20°C given in reference 63 and is in accord with k_{38} at 20°C. Ref: 29, 30, 63

$$-d[\text{AlNBr}_2]/dt = k_{40}[\text{AlNBr}_2]$$

$$k_{40} = 30k_{38} \text{ sec}^{-1}$$

Estimated value. Justifications for the reaction products and rate are given in the references. Ref: 29, 30

$$-d[\text{AlNBrCl}]/dt = k_{40}[\text{AlNBrCl}]$$

(See Reaction 45.)

$$-d[\text{RNBr}_2]/dt = k_{-9}[\text{RNBr}_2]$$

$$k_{-9} = 7 \times 10^{-7} \text{ sec}^{-1}$$

Estimated based on results in this laboratory.

Ref: 21, 22

$$-d[\text{RNBrCl}]/dt = k_{-11}[\text{RNBrCl}]$$

$$k_{-11} = 7 \times 10^{-7} \text{ sec}^{-1}$$

Estimated based on results in this laboratory.

Ref: 21, 22

$$-d[\text{HOCl}]/dt = -d[\text{FASTCD}]/dt = k_{DI}[\text{HOCl}][\text{FASTCD}]$$

$$-d[\text{HOCl}]/dt = -d[\text{SLOWCD}]/dt = k_{DIS}[\text{HOCl}][\text{SLOWCD}]$$

$$K_{DJ} = 1 \times 10^4 \text{ l-mol}^{-1}\text{sec}^{-1}, k_{DIS} = 12.5 \text{ l-mol}^{-1}\text{sec}^{-1}$$

Values estimated based on the previous freshwater model. k_{DI} is fast, but slow enough to allow amine chlorination to outcompete demand reaction. Here, and in the remaining demand reactions (Reactions 50-61) the rate constants are suggested, average values and should be adjusted to give better fits of experimental data. Fast demand (FASTCD, phase 1) and slow demand (SLOWCD, phase 2) were arbitrarily assumed to be 70% and 30% of the initial total demand, respectively.

Ref: 1, 33

$$-d[\text{HOBr}]/dt = -d[\text{FASTCD}]/dt = k_{DJ}[\text{HOBr}][\text{FASTCD}]$$

$$-d[\text{HOBr}]/dt = -d[\text{SLOWCD}]/dt = k_{DJS}[\text{HOBr}][\text{SLOWCD}]$$

$$k_{DJ} = 3 \times 10^4 \text{ l-mol}^{-1}\text{sec}^{-1}, k_{DJS} = 37.5 \text{ l-mol}^{-1}\text{sec}^{-1}$$

Estimated values ($3 \times k_{DI}$, $3 \times k_{DIS}$). Bromine is more reactive than chlorine (see Reaction 49). Ref: 39

$$+d[\text{NH}_3]/dt = -d[\text{NH}_2\text{Cl}]/dt = -d[\text{FASTCD}]/dt = k_{DL}[\text{NH}_2\text{Cl}][\text{FASTCD}]$$

$$+d[\text{NH}_3]/dt = -d[\text{NH}_2\text{Cl}]/dt = -d[\text{SLOWCD}]/dt = k_{DLS}[\text{NH}_2\text{Cl}][\text{SLOWCD}]$$

$$k_{DL} = 10 \text{ l-mol}^{-1}\text{sec}^{-1}, k_{DLS} = 0.3 \text{ l-mol}^{-1}\text{sec}^{-1}$$

Estimated values ($k_{DI}/1000$, $k_{DIS}/50$).

$$+d[\text{NH}_3]/dt = -d[\text{NCl}_3]/dt = -d[\text{FASTCD}]/dt = k_{DL}[\text{NCl}_3][\text{FASTCD}]$$

$$+d[\text{NH}_3]/dt = -d[\text{NCl}_3]/dt = -d[\text{SLOWCD}]/dt = k_{DLS}[\text{NCl}_3][\text{SLOWCD}]$$

(See Reaction 51.)

$$+d[\text{NH}_3]/dt = -d[\text{NH}_2\text{Br}]/dt = -d[\text{FASTCD}]/dt$$

$$= 0.33k_{DK}[\text{NH}_2\text{Br}][\text{FASTCD}]$$

$$+d[\text{NH}_3]/dt = -d[\text{NH}_2\text{Br}]/dt = -d[\text{SLOWCD}]/dt$$

$$= 0.33k_{DKS}[\text{NH}_2\text{Br}][\text{SLOWCD}]$$

$$k_{DK} = 15 \text{ l-mole}^{-1}\text{sec}^{-1}, k_{DKS} = 0.5 \text{ l-mole}^{-1}\text{sec}^{-1}$$

Estimated values ($1.5 \times k_{DL}$, $1.5 \times k_{DLS}$).

$$+d[\text{NH}_3]/dt = -d[\text{NHBr}_2]/dt = -d[\text{FASTCD}]/dt = k_{\text{DK}}[\text{NHBr}_2][\text{FASTCD}]$$

$$+d[\text{NH}_3]/dt = -d[\text{NHBr}_2]/dt = -d[\text{SLOWCD}]/dt = k_{\text{DKS}}[\text{NHBr}_2][\text{SLOWCD}]$$

(See Reaction 53.)

$$+d[\text{NH}_3]/dt = -d[\text{NHBrCl}]/dt = -d[\text{FASTCD}]/dt$$

$$= k_{\text{DK}}[\text{NHBrCl}][\text{FASTCD}]$$

$$+d[\text{NH}_3]/dt = -d[\text{NHBrCl}]/dt = -d[\text{SLOWCD}]/dt = k_{\text{DKS}}[\text{NHBrCl}][\text{SLOWCD}]$$

(See Reaction 53.)

$$+d[\text{NH}_3]/dt = -d[\text{NBr}_3]/dt = -d[\text{FASTCD}]/dt = k_{\text{DK}}[\text{NBr}_3][\text{FASTCD}]$$

$$+d[\text{NH}_3]/dt = -d[\text{NBr}_3]/dt = -d[\text{SLOWCD}]/dt = k_{\text{DKS}}[\text{NBr}_3][\text{SLOWCD}]$$

(See Reaction 53.)

$$+d[\text{NH}_3]/dt = -d[\text{NBr}_2\text{Cl}]/dt = -d[\text{FASTCD}]/dt$$

$$= k_{\text{DK}}[\text{NBr}_2\text{Cl}][\text{FASTCD}]$$

$$+d[\text{NH}_3]/dt = -d[\text{NBr}_2\text{Cl}]/dt = -d[\text{SLOWCD}]/dt = k_{\text{DKS}}[\text{NBr}_2\text{Cl}][\text{SLOWCD}]$$

(See Reaction 53.)

$$+d[\text{RNH}_2]/dt = -d[\text{RNHCl}]/dt = -d[\text{FASTCD}]/dt = k_{\text{DM}}[\text{RNHCl}][\text{FASTCD}]$$

$$+d[\text{RNH}_2]/dt = -d[\text{RNHCl}]/dt = -d[\text{SLOWCD}]/dt$$

$$= k_{\text{DMS}}[\text{RNHCl}][\text{SLOWCD}]$$

$$k_{\text{DM}} = 0.2k_{\text{DL}} \text{ l-mol}^{-1}\text{sec}^{-1}, \quad k_{\text{DMS}} = 0.2k_{\text{DLS}} \text{ l-mol}^{-1}\text{sec}^{-1}$$

Estimated $k_{\text{DM}}/k_{\text{DL}}$ ratios.

$$+d[\text{RNH}_2]/dt = -d[\text{RNHBr}]/dt = -d[\text{FASTCD}]/dt = k_{\text{DM}}[\text{RNHBr}][\text{FASTCD}]$$

$$+d[\text{RNH}_2]/dt = -d[\text{RNHBr}]/dt = -d[\text{SLOWCD}]/dt = k_{\text{DMS}}[\text{RNHBr}][\text{SLOWCD}]$$

(See Reaction 58.)

$$+d[\text{RNH}_2]/dt = -d[\text{RNBrCl}]/dt = -d[\text{FASTCD}]/dt = k_{\text{DM}}[\text{RNBrCl}][\text{FASTCD}]$$

$$+d[\text{RNH}_2]/dt = -d[\text{RNBrCl}]/dt = -d[\text{SLOWCD}]/dt = k_{\text{DMS}}[\text{RNBrCl}][\text{SLOWCD}]$$

(See Reaction 58.)

$$+d[\text{RNH}_2]/dt = -d[\text{RNBr}_2]/dt = -d[\text{FASTCD}]/dt = k_{\text{DM}}[\text{RNBr}_2][\text{FASTCD}]$$

$$+d[\text{RNH}_2]/dt = -d[\text{RNBr}_2]/dt = -d[\text{SLOWCD}]/dt$$

$$= k_{\text{DMS}}[\text{RNBr}_2][\text{SLOWCD}]$$

(See Reaction 58.)

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$\begin{aligned} \log_{10} K_w = & -13.9965 + 7.608333 \times 10^{-2} \text{ CL} - 1.72836 \times 10^{-3} \text{ CL}^2 \\ & + 4.11271 \times 10^{-2} (T-25) \end{aligned}$$

where $T = ^\circ\text{C}$ and CL is the chlorinity in parts per thousand, which is related to the total salinity, S, by the equation $\text{CL} = 0.5511\text{S}$. The K_w equation is an empirical fit of experimental seawater $\text{p}K_w$ values given in the reference and is valid for $T = 0$ to 35°C and salinities of 0 to 44 ppt.

Ref: 92

$$K_{\text{ECL}} = [\text{HOCl}][\text{H}^+][\text{Cl}^-]/[\text{Cl}_2]$$

$$\begin{aligned} K_{\text{ECL}} = & 1.42691 \times 10^{-4} + 9.53502 \times 10^{-6} T + 1.91076 \times 10^{-8} T^2, \\ T = & ^\circ\text{C} \end{aligned}$$

This is an empirical fit of the data in the reference and is valid for $T = 0$ to 45°C .

Ref: 93

$$K_a = [\text{H}^+][\text{OCl}^-]/[\text{HOCl}]$$

$$\log_{10} K_a = -937.7/T + 0.149 \text{ CL}^{1/3} - 4.433, \quad T = ^\circ\text{K}$$

where CL is the chlorinity as defined above. This is an empirical fit determined by Sugam and Helz for $T = 10$ - 40°C and salinities of 0 to 34.7 ppt.

Ref: 94

$$K_{\text{HOBr}} = [\text{H}^+][\text{OBr}^-]/[\text{HOBr}]$$

$$\log_{10} K_{\text{HOBr}} = 2802.49 + 0.7335T - 80,670/T - 1115.1 \log_{10} T,$$

$$T = ^\circ\text{K}.$$

Ref: 95

$$K_{\text{NH}} = [\text{NH}_3][\text{H}^+]/[\text{NH}_4^+]$$

$$\begin{aligned} \ln K_{\text{NH}} = & \ln [8.44167 \times 10^{-11} + 6.22812 \times 10^{-12} T \\ & + 3.69317 \times 10^{-13} T^2 - 5.97755 \times 10^{-17} T^3 + 2.52447 \times 10^{-16} T^4] \\ & - 0.312494 \mu, \quad T = ^\circ\text{C} \end{aligned}$$

where μ is the ionic strength. This is an empirical fit of the estimated theoretical seawater values given by Whitfield (average of models 3 and 4) and the 25°C, experimental freshwater value given by Bates and Pinching. Valid near 25°C and for $\mu = 0$ to 0.8.

Ref: 96, 97

$$K_{\text{b3}} = [\text{CH}_3\text{NH}_3^+][\text{OH}^-]/[\text{CH}_3\text{NH}_2]$$

$$K_{\text{b3}} = 3.56464 \times 10^{-4} + 4.35750 \times 10^{-6} T - 6.58928 \times 10^{-8} T^2,$$

$$T = ^\circ\text{C}$$

This empirical fit of data in the reference is valid for $T = 0$ to 50°C.

Ref: 98

$$K_{\text{bala}} = [\text{AlNH}_3^+][\text{OH}^-]/[\text{AlNH}_2]$$

$$K_{\text{bala}} = 4.898 \times 10^{-5}.$$

Ref: 99

APPENDIX III

MODEL DIFFERENTIAL EQUATIONS

$$\begin{aligned}
d[\text{HOCl}]/dt = & -k_1[\text{NH}_3]^{0.8}[\text{HOCl}] + k_{-1}[\text{NH}_2\text{Cl}] - k_2[\text{NH}_2\text{Cl}][\text{HOCl}] \\
& + k_{-2}[\text{NHCl}_2] - k_{48}[\text{NHCl}_2][\text{HOCl}] + k_{-48}[\text{NCl}_3] - k_3[\text{RNH}_2][\text{HOCl}] \\
& + k_{-3}[\text{RNHCl}] - k_{\text{MXC}}[\text{NH}_2\text{Br}][\text{HOCl}] - k_{14}[\text{RNHBr}][\text{HOCl}] \\
& - k_{33}[\text{AlNH}_2][\text{HOCl}] - k_{37}[\text{AlNHBr}][\text{HOCl}] - k_5[\text{HOCl}][\text{Br}^-] \\
& + k_{25}[\text{NHCl}_2](13[\text{NHCl}_2] - 2k_{\text{NO}_3}[\text{HOCl}])/(13[\text{NHCl}_2] + [\text{NH}_2\text{Cl}] \\
& + k_{\text{NO}_3}[\text{HOCl}]) - k_{\text{DI}}[\text{HOCl}][\text{FASTCD}] - k_{\text{DIS}}[\text{HOCl}][\text{SLOWCD}]
\end{aligned}$$

$$\begin{aligned}
d[\text{HOBr}]/dt = & -k_{12}[\text{NH}_3][\text{HOBr}] + k_{-12}[\text{NH}_2\text{Br}] - k_6[\text{NH}_2\text{Br}][\text{HOBr}] \\
& + k_{-6}[\text{NHBr}_2] - k_7[\text{NHBr}_2][\text{HOBr}] + k_{-7}[\text{NBr}_3] - k_{13}[\text{RNH}_2][\text{HOBr}] \\
& + k_{-13}[\text{RNHBr}] - k_9[\text{RNHBr}][\text{HOBr}] + k_{-9\text{H}}[\text{RNBr}_2] - k_{10}[\text{NH}_2\text{Cl}][\text{HOBr}] \\
& + k_{-10}[\text{NHBrCl}] - k_{47}[\text{NHBrCl}][\text{HOBr}] + k_{-47}[\text{NBr}_2\text{Cl}] \\
& - k_{11}[\text{RNHCl}][\text{HOBr}] + k_{-11\text{H}}[\text{RNBrCl}] - k_{34}[\text{AlNH}_2][\text{HOBr}] \\
& - k_{35}[\text{AlNHCl}][\text{HOBr}] - k_{36}[\text{AlNHBr}][\text{HOBr}] + k_5[\text{HOCl}][\text{Br}^-] \\
& + k_{\text{MXB}}[\text{H}^+][\text{Br}^-][\text{NH}_2\text{Cl}] + 0.5k_{27}[\text{NHBr}_2]^2 + 2k_{7\text{P}}[\text{NHBr}_2][\text{NBr}_3] \\
& + 1.5k_{7\text{D}}[\text{NBr}_3]^2 + 0.5k_{26}[\text{NHBrCl}]^2 + 2k_{7\text{PX}}[\text{NHBrCl}][\text{NBr}_3] \\
& + 2k_{7\text{PX}}[\text{NHBr}_2][\text{NBr}_2\text{Cl}] + 2k_{7\text{PX}2}[\text{NHBrCl}][\text{NBr}_2\text{Cl}] \\
& + 1.5k_{7\text{D}}[\text{NBr}_2\text{Cl}]^2 - k_8 - k_{\text{DJ}}[\text{HOBr}][\text{FASTCD}] - k_{\text{DJS}}[\text{HOBr}][\text{SLOWCD}]
\end{aligned}$$

$$\begin{aligned}
d[\text{NH}_3]/dt = & -k_1[\text{NH}_3]^{0.8}[\text{HOCl}] + k_{-1}[\text{NH}_2\text{Cl}] - k_{12}[\text{NH}_3][\text{HOBr}] \\
& + k_{-12}[\text{NH}_2\text{Br}] + k_{\text{MXB}}[\text{H}^+][\text{Br}^-][\text{NH}_2\text{Cl}] + k_{\text{D}}[\text{NH}_2\text{Br}]^2 - k_{-\text{D}}[\text{NHBr}_2][\text{NH}_3] \\
& + k_{41}[\text{AlNH}_2][\text{NH}_2\text{Cl}] + k_{42}[\text{AlNH}_2][\text{NH}_2\text{Br}] + k_{44}[\text{RNH}_2][\text{NH}_2\text{Cl}] \\
& + k_{45}[\text{RNH}_2][\text{NH}_2\text{Br}] + k_{38}[\text{AlNHCl}] + k_{39}[\text{AlNHBr}] + k_{\text{DL}}([\text{NH}_2\text{Cl}] \\
& + [\text{NCl}_3])(\text{FASTCD}) + k_{\text{DLS}}([\text{NH}_2\text{Cl}] + [\text{NCl}_3])(\text{SLOWCD}) \\
& + 0.33k_{\text{DK}}[\text{NH}_2\text{Br}](\text{FASTCD}) + 0.33k_{\text{DKS}}[\text{NH}_2\text{Br}](\text{SLOWCD}) + (k_{\text{DK}}(\text{FASTCD}) \\
& + k_{\text{DKS}}(\text{SLOWCD}))([\text{NHBr}_2] + [\text{NHBrCl}] + [\text{NBr}_3] + [\text{NBr}_2\text{Cl}])
\end{aligned}$$

$$\begin{aligned}
d[\text{RNH}_2]/dt = & -k_3[\text{RNH}_2][\text{HOCl}] + k_{-3}[\text{RNHCl}] - k_{13}[\text{RNH}_2][\text{HOBr}] \\
& + k_{-13}[\text{RNHBr}] - k_{44}[\text{RNH}_2][\text{NH}_2\text{Cl}] - k_{45}[\text{RNH}_2][\text{NH}_2\text{Br}] \\
& - k_{46}[\text{RNH}_2][\text{NHBr}_2] + (k_{\text{DK}}(\text{FASTCD}) + k_{\text{DKS}}(\text{SLOWCD}))([\text{RNHBr}] \\
& + [\text{RNBrCl}] + [\text{RNBr}_2] + [\text{RNHCl}])
\end{aligned}$$

$$\begin{aligned}
d[\text{AlNH}_2]/dt = & -k_{33}[\text{AlNH}_2][\text{HOCl}] - k_{34}[\text{AlNH}_2][\text{HOBr}] - k_{41}[\text{AlNH}_2][\text{NH}_2\text{Cl}] \\
& - k_{42}[\text{AlNH}_2][\text{NH}_2\text{Br}] - k_{43}[\text{AlNH}_2][\text{NHBr}_2]
\end{aligned}$$

$$\begin{aligned}
d[\text{NH}_2\text{Cl}]/dt = & k_1[\text{NH}_3]^{0.8}[\text{HOCl}] - k_{-1}[\text{NH}_2\text{Cl}] - k_2[\text{NH}_2\text{Cl}][\text{HOCl}] \\
& + k_{-2}[\text{NHCl}_2] - k_{10}[\text{NH}_2\text{Cl}][\text{HOBr}] + k_{-10}[\text{NHBrCl}] \\
& - k_{\text{MXB}}[\text{H}^+][\text{Br}^-][\text{NH}_2\text{Cl}] - k_{32}[\text{NH}_2\text{Cl}][\text{NHBr}_2] - k_{41}[\text{AlNH}_2][\text{NH}_2\text{Cl}] \\
& - k_{44}[\text{RNH}_2][\text{NH}_2\text{Cl}] - k_{25}[\text{NH}_2\text{Cl}][\text{NHCl}_2]/(13[\text{NHCl}_2] + [\text{NH}_2\text{Cl}]) \\
& + k_{\text{NO}_3}[\text{HOCl}]) - k_{\text{DL}}[\text{NH}_2\text{Cl}](\text{FASTCD}) - k_{\text{DLS}}[\text{NH}_2\text{Cl}](\text{SLOWCD})
\end{aligned}$$

$$\begin{aligned}
d[\text{NHCl}_2]/dt = & k_2[\text{NH}_2\text{Cl}][\text{HOCl}] - k_{-2}[\text{NHCl}_2] - k_{48}[\text{NHCl}_2][\text{HOCl}] \\
& + k_{-48}[\text{NCl}_3] - k_{25}[\text{NHCl}_2](1 + 13[\text{NHCl}_2]/(13[\text{NHCl}_2] + [\text{NH}_2\text{Cl}]) \\
& + k_{\text{NO}_3}[\text{HOCl}]))
\end{aligned}$$

$$\begin{aligned} d[\text{NCl}_3]/dt = & + k_{48}[\text{NHCl}_2][\text{HOCl}] - k_{-48}[\text{NCl}_3] - k_{\text{DL}}[\text{NCl}_3][\text{FASTCD}] \\ & - k_{\text{DLS}}[\text{NCl}_3][\text{SLOWCD}] \end{aligned}$$

$$\begin{aligned} d[\text{NH}_2\text{Br}]/dt = & k_{12}[\text{NH}_3][\text{HOBr}] - k_{-12}[\text{NH}_2\text{Br}] - k_6[\text{NH}_2\text{Br}][\text{HOBr}] \\ & + k_{-6}[\text{NHBr}_2] - k_{\text{MXC}}[\text{NH}_2\text{Br}][\text{HOCl}] - 2k_{\text{D}}[\text{NH}_2\text{Br}]^2 \\ & + 2k_{-\text{D}}[\text{NHBr}_2][\text{NH}_3] + k_{\text{D1}}[\text{NHBr}_2]^2 - k_{-\text{D1}}[\text{NH}_2\text{Br}][\text{NBr}_3] \\ & + k_{32}[\text{NH}_2\text{Cl}][\text{NHBr}_2] - k_{42}[\text{AlNH}_2][\text{NH}_2\text{Br}] + k_{43}[\text{AlNH}_2][\text{NHBr}_2] \\ & - k_{45}[\text{RNH}_2][\text{NH}_2\text{Br}] + k_{46}[\text{RNH}_2][\text{NHBr}_2] - 0.33k_{\text{DK}}[\text{NH}_2\text{Br}][\text{FASTCD}] \\ & - 0.33k_{\text{DKS}}[\text{NH}_2\text{Br}][\text{SLOWCD}] \end{aligned}$$

$$\begin{aligned} d[\text{NHBr}_2]/dt = & k_6[\text{NH}_2\text{Br}][\text{HOBr}] - k_{-6}[\text{NHBr}_2] - k_7[\text{NHBr}_2][\text{HOBr}] + k_{-7}[\text{NBr}_3] \\ & + k_{\text{D}}[\text{NH}_2\text{Br}]^2 - k_{-\text{D}}[\text{NHBr}_2][\text{NH}_3] - 2k_{\text{D1}}[\text{NHBr}_2]^2 + 2k_{-\text{D1}}[\text{NH}_2\text{Br}][\text{NBr}_3] \\ & - k_{32}[\text{NH}_2\text{Cl}][\text{NHBr}_2] - k_{43}[\text{AlNH}_2][\text{NHBr}_2] - k_{46}[\text{RNH}_2][\text{NHBr}_2] \\ & - k_{27}[\text{NHBr}_2]^2 - k_{7\text{P}}[\text{NHBr}_2][\text{NBr}_3] - k_{7\text{PX}}[\text{NHBr}_2][\text{NBr}_2\text{Cl}] \\ & - k_{\text{DK}}[\text{NHBr}_2][\text{FASTCD}] - k_{\text{DKS}}[\text{NHBr}_2][\text{SLOWCD}] \end{aligned}$$

$$\begin{aligned} d[\text{NBr}_3]/dt = & k_7[\text{NHBr}_2][\text{HOBr}] - k_{-7}[\text{NBr}_3] + k_{\text{D1}}[\text{NHBr}_2]^2 \\ & - k_{-\text{D1}}[\text{NH}_2\text{Br}][\text{NBr}_3] - k_{7\text{P}}[\text{NHBr}_2][\text{NBr}_3] - k_{7\text{D}}[\text{NBr}_3]^2 \\ & - k_{7\text{PX}}[\text{NHBr}_2\text{Cl}][\text{NBr}_3] - k_{\text{DK}}[\text{NBr}_3][\text{FASTCD}] - k_{\text{DKS}}[\text{NBr}_3][\text{SLOWCD}] \end{aligned}$$

$$\begin{aligned} d[\text{RNHCl}]/dt = & k_3[\text{RNH}_2][\text{HOCl}] - k_{-3}[\text{RNHCl}] - k_{11}[\text{RNHCl}][\text{HOBr}] \\ & + k_{-11\text{H}}[\text{RNBrCl}] + k_{44}[\text{RNH}_2][\text{NH}_2\text{Cl}] - k_{\text{DM}}[\text{RNHCl}][\text{FASTCD}] \\ & - k_{\text{DMS}}[\text{RNHCl}][\text{SLOWCD}] \end{aligned}$$

$$\begin{aligned}
d[\text{RNHBr}]/dt &= k_{13}[\text{RNH}_2][\text{HOBr}] - k_{-13}[\text{RNHBr}] - k_9[\text{RNHBr}][\text{HOBr}] \\
&+ k_{-9\text{H}}[\text{RNBr}_2] - k_{14}[\text{RNHBr}][\text{HOCl}] + k_{45}[\text{RNH}_2][\text{NH}_2\text{Br}] \\
&+ k_{46}[\text{RNH}_2][\text{NHBr}_2] - k_{\text{DM}}[\text{RNHBr}][\text{FASTCD}] - k_{\text{DMS}}[\text{RNHBr}][\text{SLOWCD}]
\end{aligned}$$

$$\begin{aligned}
d[\text{RNBr}_2]/dt &= k_9[\text{RNHBr}][\text{HOBr}] - k_{-9\text{H}}[\text{RNHBr}_2] - k_{-9}[\text{RNBr}_2] \\
&- k_{\text{DM}}[\text{RNBr}_2][\text{FASTCD}] - k_{\text{DMS}}[\text{RNBr}_2][\text{SLOWCD}]
\end{aligned}$$

$$\begin{aligned}
d[\text{NHBrCl}]/dt &= k_{10}[\text{NH}_2\text{Cl}][\text{HOBr}] - k_{-10}[\text{NHBrCl}] - k_{47}[\text{NHBrCl}][\text{HOBr}] \\
&+ k_{-47}[\text{NBr}_2\text{Cl}] + k_{\text{MXC}}[\text{NH}_2\text{Br}][\text{HOCl}] + k_{32}[\text{NH}_2\text{Cl}][\text{NHBr}_2] \\
&- k_{26}[\text{NHBrCl}]^2 - k_{7\text{PX}}[\text{NHBrCl}][\text{NBr}_3] - k_{7\text{PX}2}[\text{NHBrCl}][\text{NBr}_3] \\
&- k_{\text{DK}}[\text{NHBrCl}][\text{FASTCD}] - k_{\text{DKS}}[\text{NHBrCl}][\text{SLOWCD}]
\end{aligned}$$

$$\begin{aligned}
d[\text{NBr}_2\text{Cl}]/dt &= k_{47}[\text{NHBrCl}][\text{HOBr}] - k_{-47}[\text{NBr}_2\text{Cl}] - k_{7\text{PX}}[\text{NHBr}_2][\text{NBr}_2\text{Cl}] \\
&- k_{7\text{PX}2}[\text{NHBrCl}][\text{NBr}_2\text{Cl}] - k_{7\text{D}}[\text{NBr}_2\text{Cl}]^2 - k_{\text{DK}}[\text{NBr}_2\text{Cl}][\text{FASTCD}] \\
&- k_{\text{DKS}}[\text{NBr}_2\text{Cl}][\text{SLOWCD}]
\end{aligned}$$

$$\begin{aligned}
d[\text{RNBrCl}]/dt &= k_{11}[\text{RNHCl}][\text{HOBr}] - k_{-11\text{H}}[\text{RNBrCl}] + k_{14}[\text{RNHBr}][\text{HOCl}] \\
&- k_{-11}[\text{RNBrCl}] - k_{\text{DM}}[\text{RNBrCl}][\text{FASTCD}] - k_{\text{DMS}}[\text{RNBrCl}][\text{SLOWCD}]
\end{aligned}$$

$$\begin{aligned}
d[\text{AlNHCl}]/dt &= k_{33}[\text{AlNH}_2][\text{HOCl}] - k_{35}[\text{AlNHCl}][\text{HOBr}] \\
&+ k_{41}[\text{AlNH}_2][\text{NH}_2\text{Cl}] - k_{38}[\text{AlNHCl}]
\end{aligned}$$

$$\begin{aligned}
d[\text{AlNHBr}]/dt &= k_{34}[\text{AlNH}_2][\text{HOBr}] - k_{36}[\text{AlNHBr}][\text{HOBr}] - k_{37}[\text{AlNHBr}][\text{HOCl}] \\
&+ k_{42}[\text{AlNH}_2][\text{NH}_2\text{Br}] + k_{43}[\text{AlNH}_2][\text{NHBr}_2] - k_{39}[\text{AlNHBr}]
\end{aligned}$$

$$d[\text{AlNBrCl}]/dt = k_{35}[\text{AlNHCl}][\text{HOBr}] + k_{37}[\text{AlNHBr}][\text{HOCl}] - k_{40}[\text{AlNBrCl}]$$

$$d[\text{AlNBr}_2]/dt = k_{36}[\text{AlNHBr}][\text{HOBr}] - k_{40}[\text{AlNBr}_2]$$

$$\begin{aligned} d[\text{FASTCD}]/dt = & - [\text{FASTCD}] k_{\text{DI}}[\text{HOCl}] + k_{\text{DJ}}[\text{HOBr}] + k_{\text{DL}}[\text{NH}_2\text{Cl}] \\ & + k_{\text{DL}}[\text{NCl}_3] + 0.33k_{\text{DK}}[\text{NH}_2\text{Br}] + k_{\text{DK}}([\text{NHBr}_2] + [\text{NBr}_3] + [\text{NHBrCl}] \\ & + [\text{NBr}_2\text{Cl}]) + k_{\text{DM}}([\text{RNHCl}] + [\text{RNHBr}] + [\text{RNBrCl}] + [\text{RNBr}_2]) \end{aligned}$$

$$\begin{aligned} d[\text{SLOWCD}]/dt = & - [\text{SLOWCD}] k_{\text{DIS}}[\text{HOCl}] + k_{\text{DJS}}[\text{HOBr}] + k_{\text{DLS}}[\text{NH}_2\text{Cl}] \\ & + k_{\text{DLS}}[\text{NCl}_3] + 0.33k_{\text{DKS}}[\text{NH}_2\text{Br}] + k_{\text{DKS}}([\text{NHBr}_2] + [\text{NHBrCl}] \\ & + [\text{NBr}_3] + [\text{NBr}_2\text{Cl}]) + k_{\text{DMS}}([\text{RNHCl}] + [\text{RNHBr}] + [\text{RNBrCl}] \\ & + [\text{RNBr}_2]) \end{aligned}$$

APPENDIX IV

OPERATION OF THE FORTRAN PROGRAM

A listing of the computer program is given in Appendix V and a sample output is given in Appendix VI. The program can be operated in various modes depending on the conditions chosen:

TABLE V

OPERATION MODES OF THE FORTRAN PROGRAM			
<u>Mode</u>	<u>Conditions</u>	<u>Number of Species</u>	<u>Number of Differential Equations</u>
A	Saline waters with NH_3 , AlNH_2 and RNH_2	24	22
B	Saline waters with NH_3 and AlNH_2	19	17
C	Freshwaters with NH_3 , AlNH_2 and RNH_2	12	11
D	Bromine-ammonia breakpoint model	8	6
E	Saline waters with no amines	6	4

Although modes B - E are subsets of mode A (with the exception of NCl_3 inclusion in mode C only), the simplest mode should be chosen to minimize computer run time. All species are described kinetically using differential equations except two, bromide and total residual halogen, which are calculated by mass balance. Thus, as many as 22 differential equations are solved simultaneously.

The FORTRAN program has three major sections. The main program defines the initial conditions, converts all concentrations to molarity, and calculates observed rate constants from the theoretical ones based on the initial conditions. The first subroutine, KUTA, is called once for each chlorination cycle. It performs the integration of the needed simultaneous differential equations using a one-step Runge-Kutta-Merson technique. In this method, the step size of integration is varied such that the error in each integration (defined by the input term ACCURC) is held constant. The variable step-size capability increases efficiency since short intervals are taken only when needed, and larger intervals used when convergence is easier. Once the desired accuracy is obtained, the program moves to the next time step. The inputted values of ACCURC should thus be kept as large as possible, to minimize run time, but kept small enough to retain reasonable accuracy after allowing for decomposition of oxidants (roughly 3 - 6 orders of magnitude lower than the lowest molar concentration input term). KUTA also calculates the haloforms produced, corrects discharge concentrations for dilution if it applies, and performs bookkeeping of calculated concentrations to ensure proper output. The last subroutine, EQUA, is a list of the differential equations for each species as designated by the Y-array. Each term in the Y-array contains the concentration of a single specie at the current time interval. EQUA is called several times by KUTA for each time step during integration.

A definition list of input terms required by the program is given on the first and second pages of Appendix V. The data are supplied on four cards according to the format shown in Table VI.

TABLE VI

INPUT DATA FORMAT

Card No.	Field	Variable	Format
1	1-8	TMP	E8.0
	9-16	PH	E8.0
	17-24	BR	E8.0
	25-32	CL	E8.0
	33-40	CDO	E8.0
	41-48	NH3	E8.0
	49-56	RNH2	E8.0
	57-64	ALNH2	E8.0
	65-72	ACCURC	E8.0
	73-80	VCS	E8.0
2	1-10	RF	E10.0
	11-20	RF1	E10.0
	21-30	DLF	E10.0
	31-40	TO	E10.0
	41-49	T1	F9.0
	50	IT	A1
	51-59	TSTEP	E9.0
	60	ITS	A1
	61-65	IFLAG	I5
	66-70	NCLC	I5
	71-75	N	I5
	76-80	LSKIP	I5

TABLE VI (continued)

Card No.	Field	Variable	Format
3	1-8	KDI	E8.0
	9-16	KDJ	E8.0
	17-24	KDK	E8.0
	25-32	KDL	E8.0
	33-40	KDIS	E8.0
	41-48	KDJS	E8.0
	49-56	KDKS	E8.0
	57-64	KDLS	E8.0
	65-72	QR	E8.0
	73-80	F	E8.0
4	Every 3 spaces	J(I)	I3

The value of LSKIP needed increases with the complexity of the chemical system modelled and the accuracy desired, and decreases with increasing rates of oxidant loss. This is best determined by experience. Suggested values range from zero for fast-running freshwater cases up to 1000 or more for slow-running seawater cases with high amine concentrations. On the third card are entered the estimated rate constants for reaction of the various oxidants with the demand. These were left as adjustable parameters for facilitate data-fitting. Suggested values are given in the definitions list of input terms. The fourth card lists the subscripts corresponding to the compounds appropriate for the run, as designated in the definitions list of input terms. Table VII gives the subscripts for each mode, where the modes are defined in Table V. These subscripts can be listed in any order so long as 22 and 23 are at the end. Finally, Table VIII gives examples of input

TABLE VII

INPUT DATA FOR CARD 4

Mode	N	Ordered Subscripts
A	22	1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 24 22 23
B	17	1 2 4 5 6 7 8 9 12 14 16 17 18 19 20 21 24 22 23
C	11	1 2 3 4 5 8 14 15 16 17 18 22 23
D	6	4 6 7 8 12 14 22 23
E	4	4 5 6 17 22 23

data for a freshwater recirculating system and a seawater once-through system. These data correspond to the practical examples discussed in the previous sections.

TABLE VIII

EXAMPLES OF INPUT DATA

Variable	Freshwater Recirculating System	Seawater Once-through System
TMP	43.0 (deg C)	23.0 (deg C)
pH	7.8	8.1
BR	0	60.0 (mg/l)
CL	1.54 (mg/l)	5.0 (mg/l)
CDO	2.15 (mg/l)	0.77 (mg/l)
NH3	0.17 (mg/l)	2.0 (mg/l)
RNH2	0	0
ALNH2	0	0
ACCURC	1.0×10^{-11}	1.0×10^{-11}
VCS	1.3×10^7 (gal)	0
RF	187.5 (gal/sec)	1.0
RF1	33.33 (gal/sec)	1.0
DLF	1.0	1.0
TO	0	0
T1	480. (min)	40. (min)
IT	M	M
TSTEP	0.001 (min)	0.001 (min)
ITS	M	M
IFLAG	0	0
NCLC	15	1
N	11	17
LSKIP	170	800

J(I) (freshwater) 1 2 3 4 5 8 14 15 16 17 18 22 23

(seawater) 1 2 4 5 6 7 8 9 12 14 16 17 18 19 20 21 24 22 23

APPENDIX V

LISTING OF THE FORTRAN PROGRAM

THE PURPOSE OF THIS PROGRAM IS TO PREDICT THE CONCENTRATIONS
OF RESIDUAL OXIDANTS IN WATER DISCHARGED FROM POWER PLANT COOLING
SYSTEMS. THIS MODEL HANDLES ALL SALINITIES FROM FRESHWATER TO SEAWATER.

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DEFINITIONS OF INPUT TERMS

TMP AVERAGE TEMPERATURE OF WATER IN THE COOLING SYSTEM (DEG C)
PH PH OF THE WATER (OPERATIONAL DEFINITION OF PH)
BR BROMIDE ION CONCENTRATION IN MAKEUP WATER (PPM, AS BR). FOR PURPOSES
OF IONIC STRENGTH CORRECTIONS IT IS ASSUMED THAT THE BROMIDE
CONCENTRATION PARALLELS SALINITY.
CL AMOUNT OF CHLORINE ADDED (PPM, AS CL2)
CDO ULTIMATE, NON-NITROGENOUS CHLORINE DEMAND OF THE WATER (PPM, AS CL2)
AT A 2 PPM DOSE AND 20 DEG C.
NH3 TOTAL AMMONIA CONCENTRATION IN MAKEUP WATER (PPM, AS N)
RNH2 ORGANIC NITROGEN (CH3NH2) CONCENTRATION IN MAKEUP WATER (PPM, AS N)
ALNH2 FREE AMINO ACID (ALANINE) CONCENTRATION IN MAKEUP WATER (PPM, AS N)
ACCURC A NUMBER REFLECTING THE ACCURACY TO WHICH THE INTEGRATIONS ARE
TO BE PERFORMED. THIS SHOULD BE ABOUT 4-6 ORDERS OF MAGNITUDE LOWER
THAN THE SMALLEST MOLAR CONCENTRATION INPUT TERM.
VCS VOLUME OF THE COOLING SYSTEM (GALLONS). LEAVE BLANK IF UNKNOWN.
RF RATE OF MAKE-UP FLOW INTO COOLING SYSTEM (GALLONS PER SECOND)
RF1 RATE OF BLOWDOWN FROM COOLING SYSTEM (GALLONS PER SECOND)
QR RECIRCULATING WATER FLOW RATE (GALLONS PER SECOND)
RF, RF1, AND QR ARE NOT NEEDED FOR ONCE-THROUGH SYSTEMS. IF THEY ARE
UNKNOWN SET THEM EQUAL TO 1.0
F ESTIMATE OF THE FRACTION OF OXIDANTS LOST BY EVAPORATION PER PASS
THROUGH THE COOLING TOWER. SUGGESTED VALUES ARE 0-0.2. LEAVE BLANK
IF UNKNOWN.
DLF DILUTION FACTOR AFTER BLOWDOWN. THIS SHOULD BE A NUMBER GREATER THAN
OR EQUAL TO UNITY. OUTPUTTED DISCHARGE VALUES ARE CONCENTRATIONS
AFTER SIMPLE DILUTION WITH MAKE-UP WATER WITHOUT REACTION.
TO TIME AT START OF RUN. USUALLY TO = 0.
T1 DURATION OF RUN (EITHER IN MINUTES OR SECONDS)
IT IF IT=M OUTPUT WILL BE IN MINUTES. IF IT=S OUTPUT WILL BE IN SECONDS
TSTEP TIMESTEP TO BE TAKEN AT THE START OF THE INTEGRATION. THIS
MUST BE SHORT. SUGGESTED VALUE .001 MINUTES
ITS IF ITS=M TIMESTEP WILL BE IN MINUTES. IF ITS=S TIMESTEP WILL
BE IN SECONDS.
IFLAG INTEGER SPECIFYING WHETHER OUTPUT IS TO BE IN MOLARITY OR IN PPM. IF
IFLAG=0 OUTPUT IS IN MOLARITY. IF IFLAG=1 OUTPUT IS IN PPM. ALL
OXIDANTS ARE CALCULATED AS CL2, AMINES AS N, AND HALOFORMS AS CHCL3.
NCLC NUMBER OF CHLORINATION CYCLES. FOR ONCE-THROUGH SYSTEMS NCLC=1
N NUMBER OF DIFFERENTIAL EQUATIONS. FOR SALINE WATERS WITH RNH2 AND
ALNH2 N=22. FOR SALINE WATERS LACKING RNH2 N=17. FOR FRESHWATER N=11.
FOR THE BR BREAKPOINT MODEL N=6. FOR SEAWATER WITHOUT AMINES N=4.
LSKIP NUMBER OF LINES OF CALCULATED VALUES SKIPPED BETWEEN EACH PRINTED
LINE. THIS AVOIDS REAMS OF OUTPUT FOR SLOW-RUNNING CASES.

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C      KDI,KDJ,KDK,KDL  FAST DEMAND RATE CONSTANTS FOR HOCL, HOBR, BROMAMINES AND
C      BROMOCHLORAMINES, AND NH2CL, RESPECTIVELY. SUGGESTED VALUES ARE
C      10000, 30000, 15, AND 10, RESPECTIVELY. THESE MAY BE VARIED BY 1-2
C      ORDERS OF MAGNITUDE FOR FITTING EXPERIMENTAL DATA.
C      KDIS,KDJS,KDKS,KDLS  SLOW DEMAND RATE CONSTANTS FOR HOCL, HOBR, BROMAMINES
C      AND BROMOCHLORAMINES, AND NH2CL, RESPECTIVELY. SUGGESTED VALUES ARE
C      12.5, 37.5, 0.5, AND 0.3, RESPECTIVELY. THESE MAY BE VARIED BY 1-2
C      ORDERS OF MAGNITUDE FOR FITTING EXPERIMENTAL DATA.
C      J(I)  A LIST OF THE SUBSCRIPTS CORRESPONDING TO THE COMPOUNDS TO BE
C      MODELLED IN THIS RUN, AS CONTAINED IN THE Y-ARRAY:  Y1=NH2CL,
C      Y2=NHCL2, Y3=RNHCL, Y4=HOCL, Y5=FASTCD, Y6=HOBR, Y7=NHBR2, Y8=NX3,
C      Y9=NHBRCL, Y10=RNBR2, Y11=RNBRCL, Y12=NH2BR, Y13=RNHBR, Y14=NH3,
C      Y15=RNH2, Y16=ALNH2, Y17=SLOWCD, Y18=ALNHCL, Y19=ALNHBR, Y20=ALNBRCL,
C      Y21=ALNBR2, Y22=BROMIDE, Y23=TOTAL RESIDUAL HALOGEN, Y24=NBRL2CL
C
C      IMPLICIT REAL*8(A-H,O-Z)
C      REAL*8 MWCL/.70906D+02/,KBALA,NH3,KDL,KDN,KDIS,KDJS,KDKS,KDLS,KDHS
C      REAL*8 KA,KECL,KNH,KB3,KW,KHOB,KONA,KONAW,KH1,KH2,KH3,KDI,KDJ,KDK
C
C      COMMON /CONC/ CLHOL,BRHOL,BRHOLO,HCON,CDO,DLP,RK1OBS,RK2OBS,KW
C      1,RK3OBS,CHCL3,CHCL3P,NH3,RNH2,ALNH2,PS,RKINFL,RKDSCH,RKEVAP,DCO,
C      2DCOSLO,TDK,MUL,IPLAG,NN,NS,J,LSKIP
C      COMMON/MNH/KH1,KH2,KH3,RK6,RKH6,RK7,RKH7,RKXIB,RKXIC,RK5,RKXI,KDK,
C      1RKXIH,RK9,RKH9,RK11,RKH11,RK14,RK8,RK7PX,RK47,RKH47,RK7PX2,RKNO3,
C      3RK12,RKH12,RK13,RKH13,RK7P,RKD,RKMD,RKD1,RKMD1,RK7D,KDI,KDJ,RK48,
C      4KDL,KDN,KDIS,KDJS,KDKS,KDLS,KDHS,BK25,RK26,RK27,RK32,RK33,RKH48
C      5,RK34,BK35,RK36,RK37,RK38,RK39,RK40,RK41,RK42,RK43,RK44,RK45,RK46
C      DIMENSION Y(25),J(25)
C      DATA TEN,THOU/10.,1000./,MCR/'M'/
C
C      CDPCL(X)=0.264791+0.298892*X-0.0252245*X**2+9.8974D-4*X**3
C      1-1.35389D-5*X**4
C
C      READ INPUT.
C
C      3 READ(5,10,END=105) THP,PH,BR,CL,CDO,NH3,RNH2,ALNH2,ACCURC,VCS
C      READ(5,12) RP,RF1,DLP,T0,T1,IT,TSTEP,ITS,IPLAG,NCLC,N,LSKIP
C      READ(5,10) KDI,KDJ,KDK,KDL,KDIS,KDJS,KDKS,KDLS,QR,F
C      NS=N+2
C      READ(5,11) (J(I), I=1,NS)
C      10 FORMAT(10E8.0)
C      11 FORMAT(24I3)
C      12 FORMAT(4E10.0,P9.0,A1,E9.0,A1,4I5)
C      IF(THP.EQ.0) CALL EXIT
C
C      CALCULATE INFLOW (RKINFL), DISCHARGE (RKDSCH), AND EVAPORATION (RKEVAP)
C      RATE CONSTANTS FOR FRESHWATER COOLING TOWER SYSTEM MODELLING.
C
C      RKINFL=0.
C      RKDSCH=0.
C      RKEVAP=0.
C      IF(VCS.LT.0.01) GO TO 15

```



```

RKINFL=RF/VCS
RKDSCH=RF1/VCS
RKEVAP=-DLOG(1.-P)*QR/VCS
15 BDR=RF/RF1

```

```

C
C      CALCULATE THE CHLORINE DEMAND BASED ON CHLORINE DOSE AND TEMPERATURE.
C      SLOW DEMAND IS ASSUMED TO BE 30% OF THE TOTAL DEMAND.
C

```

```

CD=CDO
CDO=CDO+(CDFCL(CL)-CDFCL(2.))
CDO=CDO+(CDO-.25)/25.*(TMP-20.)
IF (TMP.GT.20.) CDO=CDO+0.073333*(TMP-20.)
IF (TMP.GT.20.0.AND.CL.LT.2.5) CDO=CDO+0.0293333*CL*(TMP-20.)
IF (CDO.LT.0.0.OR.CL.LE.0.) CDO=0.

```

```

C
C      PRINT THE INITIAL VALUES.
C

```

```

IF (N.EQ.6) WRITE(6,18)
18 FORMAT(1H1,T48,'BROMINE BREAKPOINT MODEL CALCULATIONS'////)
IF (N.EQ.11) WRITE(6,20)
20 FORMAT(1H1,T46,'FRESHWATER CHLORINATION MODEL CALCULATIONS'////)
IF (N.EQ.6.OR.N.EQ.11) GO TO 25
WRITE(6,22)
22 FORMAT(1H1,T47,'SEAWATER CHLORINATION MODEL CALCULATIONS'////)
25 WRITE(6,26)
26 FORMAT(T58,'INITIAL CONDITIONS'//2X,'PH      TEMP  CL ADDED (AS CL2)
1  CL DEMAND (AS CL2)  NH3 (AS N)  RNH2 (AS N)  ALNH2 (AS N)  DL
2F  HU/BD  VCS (G)  QR (G/SEC)  P')
WRITE(6,30) PH,TMP,CL,CDO,CD,NH3,RNH2,ALNH2,DLF,BDR,VCS,QR,P
30 FORMAT(2X,F4.2,F6.1,'C',F10.3,' PPM',F10.3,' PPM  I/O:',F5.3,F8.4,
1' PPM',F9.4,' PPM',
2F11.4,' PPM',F7.2,F6.2,1PE10.2,1PE11.2,0PF7.3/// T44,'CALCULATED I
3INITIAL CONCENTRATIONS (MOLES/LITER)'//T18,'H+',T31,'CL TOTAL',T44,
4'HOCL',T57,'OCL-',T70,'CL2',T83,'NH3',T96,'RNH2',T109,'ALNH2')

```

```

C
C      CALCULATE RATE AND EQUILIBRIUM CONSTANTS BASED ON TEMPERATURE
C

```

```

TDK=TMP+273.15
PS=BR/65.
SAL=PS*35.46
CHLRN=0.5511*SAL
SI=PS*0.72
GAMA=DEXP(-4.202D+6/(78.3*TDK)**1.5*DSQRT(SI)/(1.+1.5*DSQRT(SI)))
KW=TEN**(-13.9965+7.60833D-2*CHLRN-1.72836D-3*CHLRN**2
1+4.11271D-2*(TMP-25.))
KA=DEXP(-2.30259*(937.7/TDK-0.149*CHLRN** (1./3.)+4.433))
KHOB=2802.49+0.7335*TDK-80670/TDK-1115.1*DLOG(TDK)/2.3025
KECL=1.42691D-04+TMP*9.53502D-06+TMP*TMP*1.91076D-08
KNH=8.44167D-11+6.22812D-12*TMP+3.69317D-13*TMP**2-5.97755D-17*
1TMP**3+2.52447D-16*TMP**4
KB3= 3.56464D-04+TMP*4.35750D-06-TMP*TMP*6.58928D-08
KBALA=4.898D-5

```

C

```

RK1T=5.14D+8*DEXP(-1550.0/TDK)*0.302
KM1=DEXP(-13.036+TMP*.113091-TMP*TMP*3.27212D-04)
RK2T=1.17429D+02+TMP*3.57857D+00+TMP*TMP*2.12857D-01
KM2=6.5D-7
RK3T=2.33667D+08+TMP*3.26666D+06
KM3=1.6D-6
KDM=KDL*0.2
KDMS=KDLS*0.2
RK5=4.7D+4*DEXP(-754.9/TDK)
RK6=3.0D+5*2.**((TMP-25.)/13.86)
RKM6=RK6/7.369D+8
RK7=1.3D+4*2.**((TMP-25.)/13.86)
RKM7=RK7/1.081D+7
RKA8=1.1111111D-6*CL
IP(CL.GT.7.5) RKA8=8.3333333D-6
IP(TMP.GT.30.) RKA8=RKA8+6.66667D-7*(TMP-30.)
RKA8=RKA8*PS/70906.
RKM9=7.0D-7
RKM10=2.0D-4
RKM11=7.0D-7
RK12=7.5D7*(2.**((TMP-20.)/13.86))
RKM12=RK12/9.493D+8
RK13=9.0D+8*(2.**((TMP-20.)/13.86))
RKM13=1.6D-4
RK26=4.0
RK27=13.3
RK32=320.
RK38=8.731D+15*DEXP(-13387./TDK)
RK39=1.0D-4
RKA40=RKA38*30.
RKA41=1.25
RKA42=RKA41*8.
RKA43=RKA41*32.
RKA44=3.125
RKA45=RKA44*8.
RKA46=RKA44*32.
RKA47=5.0D-4
RKM48=1.417D+6

```

C

C

C

C

CALCULATE H+ CONC. AND CONVERT INITIAL PPM CONCENTRATIONS TO
MOLAL CONCENTRATIONS

```

HCON=TEN**(-PH)/GAMA
NH3=NH3/(THOU*14.007)
RNH2=RNH2/(THOU*14.007)
ALNH2=ALNH2/(THOU*14.007)
CLMOL=CL/(THOU*MWCL)
CDO=CDO/(THOU*MWCL)
BRMOL=BR/(THOU*79.916)

```

C

C
C

CORRECT RATE CONSTANTS FOR IONIC STRENGTH AND PH DEPENDENCE.

$DHC = 2.34404 * DSQRT(SI) / (1. + 1.5 * DSQRT(SI))$
 $KHOBR = DEXP(2.3026 * KHOBR - DHC)$
 $KNH = DEXP(DLOG(KNH) - 0.312494 * SI)$
 $KB3 = DEXP(DLOG(KB3) - DHC)$
 $KBALA = DEXP(DLOG(KBALA) - DHC)$
 $BRONA = KHOBR / HCON + 1.$
 $BRONAW = KHOBR / KW + HCON / KW$
 $KONA = KA / HCON + 1.$
 $KONAW = KA / KW + HCON / KW$
 $RK1OBS = RK1T / KONA / (1. + HCON / KNH)$
 $RK2OBS = RK2T / KONA$
 $RK3OBS = RK3T / (KONA + KONAW * KB3)$
 $RK5 = RK5 / KONA$
 $RK6 = RK6 / BRONA$
 $RK7 = RK7 / BRONA$
 $RK7D = 12.$
 $RK7P = 894.6 * (1. + 1.321D + 6 * KW / HCON)$
 $RK7PX = RK7P * 0.15$
 $RK7PX2 = RK7P$
 $RK9 = 1.4D + 6 / BRONA$
 $RKNX = 3.0D + 4 / BRONA$
 $RK11 = 5.D + 5 / BRONA$
 $RK12 = RK12 / BRONA / (1. + HCON / KNH)$
 $RK13 = RK13 / (BRONA + BRONAW * KB3)$
 $RK14 = 2.D + 4 / KONA$
 $RKNXC = 400. / KONA$
 $RK25 = 2.03D + 14 * DEXP(-3623.6 / TDK) * NH3 * KW / HCON$
 $RKNQ3 = 0.1 / KONA$
 $RK33 = (RK1T / 0.302 * 19.) / (KONA + KONAW * KBALA)$
 $RK34 = 3.8D + 8 / (BRONA + BRONAW * KBALA)$
 $RK35 = 1.75D + 5 / BRONA$
 $RK36 = 3.5D + 5 / BRONA$
 $RK37 = 5.D + 4 / KONA$
 $RK47 = 3.D + 4 / BRONA$
 $RK48 = 3.43D + 5 * DEXP(-3522.9 / TDK) * (1. + 10. * KA / HCON) / KONA$
 $RKN48 = 8.56D + 8 * DEXP(-9058.9 / TDK) * (1. + 5.88D + 5 * KW / HCON)$
 $RKMD = 1.D + 4$
 $RKD1 = RKMD$
 $RKD = RKMD * RK6 * RKN12 / RKN6 / RK12$
 $RKMD1 = RKD1 * RK6 * RKN7 / RKN6 / RK7$

C
C
C

CALCULATE INITIAL HOCL, OCL-, AND CL2 CONCENTRATIONS.

$HOCL = CLMOL / KONA$
 $OCL = CLMOL - HOCL$
 $CL2 = CLMOL * CLMOL * HCON / RECL$

C

PRINT INITIAL CONCENTRATIONS AND CORRECTED VALUES OF RATE
CONSTANTS.

```

WRITE(6,40) HCON,CLHOL,HOCL,OCL,CL2,NH3,RNH2,ALNH2
WRITE(6,45) KW,KECL,KA,KHOB,KNH,KB3,KBALA,GANA,SI,SAL,RKINPL,
1RKDSCH,RKEVAP
WRITE(6,50) RK1OBS,KH1,RK2OBS,KH2,RK3OBS,KH3,RK5,RK6,RKH6,RK7,
1RKH7,RK7D,RK7P
WRITE(6,55) RK7PX,RK7PX2,RKD,RKMD,RKD1,RKMD1,RK8,RK9,RKH9,RKH,
1RKH,KNH,RK11,RKH11
WRITE(6,56) RK12,RKH12,RK13,RKH13,RK14,RKHXC,RKHXB,RK25,RK26,RK27,
1RK32,RK33,RK34
WRITE(6,57) RK35,RK36,RK37,RK38,RK39,RK40,RK41,RK42,RK43,RK44,
1RK45,RK46,RK47
WRITE(6,58) RKH47,RK48,RKH48,KDI,KDJ,KDK,KDL,KDH,KDIS,KDJS,KDKS,
1KDLS,KDMS
WRITE(6,60) T0,IT,T1,IT,TSTEP,ITS,ACCURC,LSKIP
IF(N.EQ.11) WRITE(6,99)
IF(N.NE.11) WRITE(6,100)
40 FORMAT(13X,1P8G13.3///T58,'OBSERVED CONSTANTS'//)
45 FORMAT(4X,'KW' KHYD(CL2) KA(HOCL) KA(HOBR) KA(NH4+) KB(MNH
12) KB(ALA) GANA MU SALINITY RKINPL RKDSCH RK
2EVAP'/1P13E10.2/)
50 FORMAT(4X,'K1' K-1 K2 K-2 K3 K-3
1 K5 K6 K-6 K7 K-7 K7D
2K7P'/1P13E10.2/)
55 FORMAT(4X,'K7PX' K7PX2 KD K-D KD1 K-D1
1 K8 K9 K-9 K10 K-10 K11
2K-11'/1P13E10.2/)
56 FORMAT(4X,'K12' K-12 K13 K-13 K14 KHX
1 KHXB K25 K26 K27 K32 K33
2K34'/1P13E10.2/)
57 FORMAT(4X,'K35' K36 K37 K38 K39 K40
1 K41 K42 K43 K44 K45 K46
2K47'/1P13E10.2/)
58 FORMAT(4X,'K-47' K48 K48 KDI KDI KDJ KDK
1 KDL KDM KDIS KDIS KDKS KDLS
2KDMS'/1P13E10.2/)
60 FORMAT(//T10,'T INITIAL =' ,P5.2,A1,5X,'T FINAL =' ,P7.2,A1,5X,
1'1ST TIME STEP =' ,P7.4,A1,5X,'ACCURC =' ,1PG9.2,5X,'LSKIP =' ,I5//)
99 FORMAT(2X,'TIME HOCL NH3 RNH2 ALNH2 NH2CL NHC
1L2 RNHCL ALNHCL NH2BR NHBR2 NCL3 SLOW CD PAST C
2D T.R.HAL.'/)
100 FORMAT(2X,'TIME HOCL NH3 RNH2 ALNH2 NH2CL NHC
1L2 RNHCL ALNHCL NH2BR NHBR2 NBR3 SLOW CD PAST C
2D T.R.HAL.'/)

```

C SET INITIAL NON-OXIDANT CONCENTRATIONS TO THEIR INPUT VALUES AND SET
C ALL OXIDANT AND HALOFORM CONCENTRATIONS TO ZERO.
C

DLF=1.000/DLF
DCOSLO=0.3*CD0
CD0=0.7*CD0
DC0=CD0
DO 101 I=1,24
101 Y(I)=0.
Y(5)=DC0
Y(14)=NH3
Y(15)=RNH2
Y(16)=ALNH2
Y(17)=DCOSLO
Y(22)=BRMOL
BRMOL=BRMOL
CHCL3 = 0.000
CHCL3P = 0.000

C MULTIPLY TIME UNITS BY 60 IF OUTPUT IS IN MINUTES INSTEAD OF SECONDS
C
C

MUL=1
IF(IT.NE.HCR) GO TO 62
TO=T0*60.
TI=T1*60.
62 IF(ITS.EQ.HCR) MUL=60
TSTEP=TSTEP*MUL

C SOLVE DIFFERENTIAL EQNS USING SUBROUTINES KUTA AND EQUA.
C KUTA IS CALLED ONCE FOR EACH CHLORINATION CYCLE.
C
C

NN=N
IMAX=700
DO 200 K=1,NCLC
T0=T0
T1=TI
CALL KUTA(T0,T1,Y,N,TSTEP,ACCURC,IMAX)
200 CONTINUE
GO TO 3
105 CONTINUE
STOP
END

C
C

SUBROUTINE KUTA (XN,XU,Y,N,H,ACCURC,IMAX)

IMPLICIT REAL*8 (A-H,O-Z)
 REAL*8 K1,K2,K3,K4,K5,KW,KM1,KM2,KM3,KDI,KDJ,KDK,NH3,MX,MX2
 1,KDL,KDM,KDIS,KDJS,KDKS,KDLS,KDMS
 LOGICAL QUIT

DIMENSION Y (25),YI (25),YN (25),K1 (25),K2 (25),K3 (25),K4 (25),K5 (25),
 1F (25),E (25),F1 (25),YH (25),HB (1500),HX (1500),BC (1500),TI (1500),
 2RB (1500),RB2 (1500),RBC (1500),AB (1500),AB2 (1500),ABC (1500),YA (25),
 3YB (25),J (25),MX2 (1500)

COMMON /CONC/ CLMOL,BRMOL,BRNOLO,HCON,CD0,DLP,RK1OBS,RK2OBS,KW
 1,RK3OBS,CHCL3,CHCL3P,NH3,RNH2,ALNH2,PS,RKINPL,RKDSCH,RKEVAP,DC0,
 2DCOSLO,TDK,MUL,IPLAG,NN,NS,J,LSKIP
 COMMON/NUM/KM1,KM2,KM3,RK6,RKM6,RK7,RKM7,RKMXB,RKNIC,RK5,RKNX,KDK,
 1RKNXH,RK9,RKM9,RK11,RKM11,RK14,RK8,RK7PX,RK47,RKM47,RK7PX2,RKM03,
 3RK12,RKM12,RK13,RKM13,RK7P,RKD,RKMD,RKD1,RKMD1,RK7D,KDI,KDJ,RK48,
 4KDL,KDM,KDIS,KDJS,KDKS,KDLS,KDMS,RK25,RK26,RK27,RK32,RK33,RKM48
 5,RK34,RK35,RK36,RK37,RK38,RK39,RK40,RK41,RK42,RK43,RK44,RK45,RK46

YA ARRAY CONTAINS CONVERSION FACTORS FROM MOLARITY TO PPM

DATA YA (1),YA (2),YA (3),YA (4),YA (5),YA (6),YA (7),YA (8),YA (9),YA (10),
 1YA (11),YA (12),YA (13),YA (14),YA (15),YA (16),YA (17),YA (18),YA (19),
 2YA (20),YA (21),YA (22),YA (23),YA (24)
 2 /70906., 141812., 70906., 70906., 70906.,
 370906., 141812., 212718., 141812., 141812., 141812., 70906., 70906.,
 414007., 14007., 14007., 70906., 70906., 70906., 141812., 141812., 79910.,
 570906., 212718./

INITIALIZE VARIABLES. ADD CHLORINE FOR THE NEXT CHLORINATION CYCLE.
 CALCULATE NEW CHLORINE-BREAKPOINT RATE CONSTANT FOR NEXT CYCLE.

Y (4)=Y (4)+CLMOL
 Y (23)=Y (23)+CLMOL
 RK25=2.03D+14*DEXP (-3623.6/TDK)*Y (14)*KW/HCON
 L=10000
 ITTER=0
 DO 5 I=1,24
 YN (I)=0.
 5 YB (I)=0.
 NC=1
 TI (1)=XN

FINAL VALUES FROM LAST CYCLE BECOME INITIAL VALUES FOR THIS CYCLE.

```

C      WRITE INITIAL CONCENTRATIONS IN MOLARITIES AND
C      STORE REMAINING VALUES OR...
C
      IF (IPLAG .EQ. 1) GO TO 600
      WRITE(6,71) XN,Y(4),Y(14),Y(15),Y(16),Y(1),Y(2),Y(3),Y(18),Y(12),
1Y(7),Y(8),Y(17),Y(5),Y(23)
71 FORMAT(F7.1,1P14E9.2)
      HB(1)=Y(6)
      MX(1)=Y(9)
      RB(1)=Y(13)
      RB2(1)=Y(10)
      RBC(1)=Y(11)
      AB(1)=Y(19)
      ABC(1)=Y(20)
      AB2(1)=Y(21)
      BC(1)=Y(22)
      MX2(1)=Y(24)
      GO TO 601

C      ...CONVERT TO PPM, WRITE INITIAL CONCENTRATIONS, AND
C      STORE REMAINING VALUES.
C
600 DO 621 I=1,NS
621   YB(J(I))=Y(J(I))*YA(J(I))
      WRITE(6,671) XN,YB(4),YB(14),YB(15),YB(16),YB(1),YB(2),YB(3),
1YB(18),YB(12),YB(7),YB(8),YB(17),YB(5),YB(23)
671 FORMAT(F7.1,14P9.5)
      HB(1)=YB(6)
      MX(1)=YB(9)
      RB(1)=YB(13)
      RB2(1)=YB(10)
      RBC(1)=YB(11)
      AB(1)=YB(19)
      ABC(1)=YB(20)
      AB2(1)=YB(21)
      BC(1)=YB(22)
      MX2(1)=YB(24)

C      PERFORM INTEGRATION USING SUBROUTINE EQUA. THE LOOP BETWEEN
C      LINES 40 AND 95 IS ITERATED FOR A GIVEN TIME STEP UNTIL THE
C      DESIRED ACCURACY IS OBTAINED.
C
601 QUIT=.FALSE.

```

```

DO 10 I=1,N
10  YN(J(I))=Y(J(I))
20  IF (H .GT. 6000.) H=6000.
    IF (XN+H.LT.XU) GO TO 30
    H=XU-XN
    QUIT=.TRUE.
30  CALL EQUA(YN,F1)
40  DO 50 I=1,N
    K1(J(I))=H*F1(J(I))/3.
50  YI(J(I))=YN(J(I))+K1(J(I))
    CALL EQUA(YI,F)
    DO 60 I=1,N
    K2(J(I))=H*F(J(I))/3.
60  YI(J(I))=YN(J(I))+K1(J(I))/2.+K2(J(I))/2.
    CALL EQUA(YI,F)
    DO 70 I=1,N
    K3(J(I))=H*F(J(I))/3.
70  YI(J(I))=YN(J(I))+3.*K1(J(I))/8.+9.*K3(J(I))/8.
    CALL EQUA(YI,F)
    DO 80 I=1,N
    K4(J(I))=H*F(J(I))/3.
80  YI(J(I))=YN(J(I))+3.*K1(J(I))/2.-9.*K3(J(I))/2.+6.*K4(J(I))
    CALL EQUA(YI,F)
    TEST=0.0
    DO 90 I=1,N
    K5(J(I))=H*F(J(I))/3.
    E(J(I))=(K1(J(I))-9.*K3(J(I))/2.+4.*K4(J(I))-K5(J(I))/2.)/5.
    TEST=DMAX1(TEST,DABS(E(J(I))))
90  CONTINUE
    IF (TEST.LT.ACCURC) GO TO 100
    ITTER=ITTER+1
    IF (ITTER.GE.INAX) GO TO 140
    H=H/2.
    QUIT=.FALSE.
95  GO TO 40

C
C      CALCULATE NEW CONCENTRATIONS AND TIME VALUE BY ADDING THE INCREMENTS
C      GENERATED ABOVE.
C
100 DO 110 I=1,N
    YH(J(I))=YN(J(I))
110  YN(J(I))=YN(J(I))+(K1(J(I))+4.*K4(J(I))+K5(J(I)))/2.
    XN=XN+H

C
C      THE INTEGRATION FOR THIS TIME STEP IS NOW COMPLETE.
C      SET CONCENTRATIONS TO ZERO IF THEY BECOME LESS THAN 10 TO THE -30
C      MOLAR AND UPDATE MASS BALANCE EQUATIONS.
C

```



```

DO 112 I=1,NS
112 IF(YN(J(I)).LT.1.D-30) YN(J(I))=0.
   YN(22)=BRHOL0-YN(6)-YN(7)*2.-YN(8)*3.-YN(9)-YN(10)*2.-YN(11)-YN(12)
   1)-YN(13)-YN(19)-YN(20)-YN(21)*2.-YN(24)*2.
   YN(23)=YN(1)+YN(2)*2.+YN(3)+YN(4)+YN(6)+YN(7)*2.+YN(8)*3.+YN(9)*2.
   1+YN(10)*2.+YN(11)*2.+YN(12)+YN(13)+YN(18)+YN(19)+YN(20)*2.
   2+YN(21)*2.+YN(24)*3.
   CD0=YN(5)
C
C       IF NO RESIDUAL HALOGEN REMAINS, STOP.
C
C       IF(YN(23).LE.0.) QUIT=.TRUE.
C
C       DO NOT PRINT CALCULATED VALUES UNTIL LSKIP IS REACHED.
C
114 IF(QUIT) GO TO 115
   L=L+1
   IF(L.LT.LSKIP) GO TO 118
   L=0
115 TY=XN/MUL
   NC=NC+1
   TI(NC)=TY
C
C       WRITE 1ST 14 NEWLY CALCULATED VALUES IN MOLARITIES AND STORE
C       REMAINING VALUES OR...
C
   IF (IFLAG.EQ.1) GO TO 700
   WRITE(6, 71) TY,YN(4),YN(14),YN(15),YN(16),YN(1),YN(2),YN(3),
1YN(18),YN(12),YN(7),YN(8),YN(17),YN(5),YN(23)
   IF(NW.EQ.11) GO TO 118
   HB(NC)=YN(6)
   MX(NC)=YN(9)
   RB(NC)=YN(13)
   RB2(NC)=YN(10)
   RBC(NC)=YN(11)
   AB(NC)=YN(19)
   ABC(NC)=YN(20)
   AB2(NC)=YN(21)
   BC(NC)=YN(22)
   MX2(NC)=YN(24)
   GO TO 118
C
C       ...WRITE 1ST 14 NEWLY CALCULATED VALUES IN PPM, IF SO DESIRED, AND
C       STORE REMAINING VALUES.
C
700 DO 721 I=1,NS
721   YB(J(I))=YN(J(I))*YA(J(I))

```

```

WRITE(6,671) TY,YB(4),YB(14),YB(15),YB(16),YB(1),YB(2),YB(3),
1YB(18),YB(12),YB(7),YB(8),YB(17),YB(5),YB(23)
IF(NN.EQ.11) GO TO 118
HB(NC)=YB(6)
MX(NC)=YB(9)
RB(NC)=YB(13)
RB2(NC)=YB(10)
RBC(NC)=YB(11)
AB(NC)=YB(19)
ABC(NC)=YB(20)
AB2(NC)=YB(21)
BC(NC)=YB(22)
MX2(NC)=YB(24)

C      INCREASE TIME STEP IF ACCURCY IS TOO GOOD AND PERFORM ANOTHER
C      INTEGRATION IF T FINAL HAS NOT BEEN REACHED.
C
118 IF (TEST.GE.ACCURC/32.) GO TO 120
H=H*DSQRT(2.D0)
ITTE=ITTE-1
120 IF (.NOT.QUIT) GO TO 20

C      T FINAL HAS BEEN REACHED. CALCULATE HALOFORM PRODUCED AND CORRECT
C      CONCENTRATIONS FOR DILUTION WITH MAKE-UP WATER.
C
CHCL3=CHCL3+0.01307*(DCO+DCOSLO-YN(5)-YN(17))*(1.+14.*BRMOLO**.25)
CHCL3P=CHCL3*1.1935D+5
125 DO 130 I=1,NS
130 Y(J(I))=YN(J(I))*DLP
Y(5)=Y(5)+(1.0-DLP)*DCO
Y(14)=Y(14)+(1.0-DLP)*NH3
Y(15)=Y(15)+(1.0-DLP)*RNH2
Y(16)=Y(16)+(1.0-DLP)*ALWH2
Y(17)=Y(17)+(1.0-DLP)*DCOSLO
Y(22)=Y(22)+(1.0-DLP)*BRMOLO

C      WRITE THE DISCHARGE VALUES AFTER DILUTION IF DLP IS NOT UNITY
C
IF (DLP.EQ.1.0) GO TO 540
WRITE (6,780)
780 FORMAT (/T50,'DISCHARGE VALUES'/)
IF (IFLAG.EQ.1) GO TO 785
WRITE(6,71) TY,Y(4),Y(14),Y(15),Y(16),Y(1),Y(2),Y(3),Y(18),Y(12),
1Y(7),Y(8),Y(17),Y(5),Y(23)
GO TO 540
785 DO 790 I=1,NS
790 YB(J(I))=Y(J(I))*YA(J(I))
WRITE(6,671) TY,YB(4),YB(14),YB(15),YB(16),YB(1),YB(2),YB(3),
1YB(18),YB(12),YB(7),YB(8),YB(17),YB(5),YB(23)
C

```

```

C      WRITE REMAINING VALUES IN MOLARITIES OR...
C
540 IF (NN.EQ.11.AND.IFLAG.EQ.1) GO TO 585
    IF (NN.EQ.11) GO TO 565
    WRITE(6,550)
550 FORMAT (//3X,'TIME      HOBR      NHBRCL      NBR2CL      RHHBR      R
1NBR2      RNBRCCL      ALHHBR      ALNBR2      ALNBRCL      BRONIDE'//)
    IF (IFLAG.EQ.1) GO TO 570
    DO 555 I=1,NC
555 WRITE(6,560) TI(I),HB(I),HX(I),HX2(I),RB(I),RB2(I),RBC(I),AB(I),
1AB2(I),ABC(I),BC(I)
560 FORMAT (F8.2,1P10E11.2)
    IF (DLP.EQ.1.0) GO TO 565
    WRITE(6,780)
    WRITE(6,560) TY,Y(6),Y(9),Y(24),Y(13),Y(10),Y(11),Y(19),Y(21),
1Y(20),Y(22)
565 WRITE(6,802) CHCL3
802 FORMAT (//10X,'HALOFORM CONC. =', 1PE9.2,' M'///)
    RETURN

C
C      ...WRITE REMAINING VALUES IN PPM.
C
570 DO 575 I=1,NC
575 WRITE(6,580) TI(I),HB(I),HX(I),HX2(I),RB(I),RB2(I),RBC(I),AB(I),
1AB2(I),ABC(I),RC(I)
580 FORMAT (F8.2,F10.5,9F11.5)
    IF (DLP.EQ.1.0) GO TO 585
    WRITE(6,780)
    WRITE(6,580) TY,YB(6),YB(9),YB(24),YB(13),YB(10),YB(11),YB(19),
1YB(21),YB(20),YB(22)
585 WRITE(6,803) CHCL3P
803 FORMAT (//10X,'HALOFORM CONC. ='0PF8.4,' PPM, AS CHCL3'///)
    GO TO 150
140 WRITE(6,10000)
10000 FORMAT(1X,'INAX EXCEEDED')
150 RETURN
    END

C
C

```

SUBROUTINE EQUA (Y,YP)

C
C

```

IMPLICIT REAL*8 (A-H,O-Z)
REAL*8 KH1,KH2,KH3,KDI,KDJ,KDK,NH3,KW
1,KDL,KDH,KDIS,KDJS,KDKS,KDLS,KDHS
COMMON /CONC/ CLMOL,BRMOL,BRMOL0,HCON,CD0,DLP,RK1OBS,RK2OBS,KW
1,RK3OBS,CHCL3,CHCL3P,NH3,RNH2,ALNH2,PS,RKINPL,RKDSCH,RKEVAP,DC0,
2DCOSLO,TDK,MUL,IPLAG,NN,NS,J,LSKIP
COMMON/NUM/KH1,KH2,KH3,RK6,RKH6,RK7,RKH7,RKHXB,RKHXC,RK5,RKH5,KDK,
1RKHXH,RK9,RKH9,RK11,RKH11,RK14,RK8,RK7PX,RK47,RKH47,RK7PX2,RKNO3,
3RK12,RKH12,RK13,RKH13,RK7P,RKD,RKHD,RKD1,RKH1,RK7D,KDI,KDJ,RK48,
4KDL,KDH,KDIS,KDJS,KDKS,KDLS,KDHS,RK25,RK26,RK27,RK32,RK33,RKH48
5,RK34,RK35,RK36,RK37,RK38,RK39,RK40,RK41,RK42,RK43,RK44,RK45,RK46
DIMENSION YP(25),Y(25),J(25)
IF(NN.EQ. 4) GO TO 300
DO 30 I=1,NN
30 IF(Y(J(I)).LE.0.) Y(J(I))=1.0D-35
IF(NN.EQ. 6) GO TO 200
IF(NN.EQ. 11) GO TO 80
IF(NN.EQ. 17) GO TO 100

```

C
C
C
C

DIFFERENTIAL EQUATIONS FOR SALINE WATERS WITH ALL AMINES

C

```

YP(1)=Y(4)*(RK1OBS*Y(14)**0.80-RK2OBS*Y(1))-KH1*Y(1)+KH2*Y(2)
1-RKH5*Y(6)*Y(1)-RKHXB*HCON*BRMOL*Y(1)-KDL*CD0*Y(1)
2-KDLS*Y(17)*Y(1)-RK41*Y(16)*Y(1)-RK44*Y(15)*Y(1)+RKHXH*Y(9)
3-RK32*Y(1)*Y(7)-RK25*Y(2)*Y(1)/(13.*Y(2)+Y(1)+RKNO3*Y(4))

```

C

```

YP(2)=RK2OBS*Y(1)*Y(4)-KH2*Y(2)-RK25*Y(2)*(1.+13.*Y(2)/
1(13.*Y(2)+Y(1)+RKNO3*Y(4)))

```

C

```

YP(3)=RK3OBS*Y(15)*Y(4)-KH3*Y(3)+RK44*Y(15)*Y(1)-KDH*CD0*Y(3)
1-RK11*Y(3)*Y(6)+0.3*RKH11*Y(11)-KDHS*Y(17)*Y(3)

```

C

```

50 YP(4)=KH1*Y(1)+KH2*Y(2)-RK2OBS*Y(4)*Y(1)-RK3OBS*Y(4)*Y(15)
1+KH3*Y(3)-KDI*CD0*Y(4)-RK5*Y(4)*BRMOL-RK37*Y(19)*Y(4)
2-RK1OBS*Y(14)**0.80*Y(4)-RKHXIC*Y(12)*Y(4)-RK14*Y(13)*Y(4)
3+RK25*Y(2)*(13.*Y(2)-2.*RKNO3*Y(4))/(13.*Y(2)+Y(1)+RKNO3*Y(4))
4-KDIS*Y(17)*Y(4)-RK33*Y(16)*Y(4)

```

C

```

52 YP(5)=-KDI*CD0*Y(4)-KDJ*CD0*Y(6)-KDK*CD0*(Y(7)+Y(8)+Y(9)+Y(24))
1-0.33*KDK*CD0*Y(12)-KDL*CD0*Y(1)-KDH*CD0*(Y(3)+Y(10)+Y(11)+Y(13))

```

C

```

70 YP(6)=RK5*Y(4)*BRMOL-KDJ*CD0*Y(6)-RK7*Y(6)*Y(7)-RKHX*Y(6)*Y(1)
1+RKHX6*Y(7)+0.5*RKH9*Y(10)-RK11*Y(3)*Y(6)+2.0*RK7P*Y(8)*Y(7)
2+RKHX7*Y(8)-RK8-RK35*Y(18)*Y(6)-RK36*Y(19)*Y(6)+1.5*RK7D*Y(24)**2
3-RK6*Y(12)*Y(6)-RK12*Y(14)*Y(6)+RKHX12*Y(12)-RK9*Y(13)*Y(6)
4+RKHX13*Y(13)-RK13*Y(15)*Y(6)+0.3*RKH11*Y(11)+0.5*RK27*Y(7)**2
5+RKHX47*Y(24)-KDJS*Y(17)*Y(6)-RK34*Y(16)*Y(6)+RKHXH*Y(9)
6+2.*RK7PX*(Y(7)*Y(24)+Y(8)*Y(9))-RK47*Y(9)*Y(6)+1.5*RK7D*Y(8)**2
7+2.*RK7PX2*Y(9)*Y(24)+RKHXB*HCON*BRMOL*Y(1)+0.5*RK26*Y(9)**2

```

C
 $YP(7) = RK6 * Y(12) * Y(6) - RKN6 * Y(7) - RK7 * Y(7) * Y(6) + RKN7 * Y(8)$
 $1 - KDK * Y(7) * CD0 - RK7P * Y(7) * Y(8) - RK27 * Y(7) ** 2 - RK7PX * Y(7) * Y(24)$
 $2 - RK43 * Y(16) * Y(7) - RK32 * Y(1) * Y(7) - RK46 * Y(15) * Y(7) - KDKS * Y(17) * Y(7)$
 $3 + RKD * Y(12) ** 2 - RKMD * Y(14) * Y(7) - 2.0 * RKD1 * Y(7) ** 2 + 2. * RKMD1 * Y(12) * Y(8)$

C
 $YP(8) = RK7 * Y(6) * Y(7) - RKN7 * Y(8) - KDK * Y(8) * CD0 - RK7PK * Y(8) * Y(9)$
 $1 + PKD1 * Y(7) ** 2 - RKMD1 * Y(12) * Y(8) - RK7P * Y(8) * Y(7) - RK7D * Y(8) ** 2$
 $2 - KDKS * Y(17) * Y(8)$

C
 $YP(9) = RKN1 * Y(6) * Y(1) - RKN1H * Y(9) + RK32 * Y(1) * Y(7)$
 $1 + RKN1C * Y(12) * Y(4) - RK26 * Y(9) ** 2 - KDKS * Y(17) * Y(9) - KDK * CD0 * Y(9)$
 $2 + RKN47 * Y(24) - RK47 * Y(9) * Y(6) - RK7PX * Y(8) * Y(9) - RK7PX2 * Y(9) * Y(24)$

C
 $YP(10) = RK9 * Y(13) * Y(6) - 1.5 * RKN9 * Y(10) - KDM * CD0 * Y(10)$
 $1 - KDHS * Y(17) * Y(10)$

C
 $YP(11) = RK11 * Y(3) * Y(6) - 1.3 * RKN11 * Y(11) + RK14 * Y(13) * Y(4)$
 $1 - KDM * CD0 * Y(11) - KDHS * Y(17) * Y(11)$

C
 $YP(12) = RK12 * Y(14) * Y(6) - RKN12 * Y(12) + RKN6 * Y(7) - 0.33 * KDKS * Y(17) * Y(12)$
 $1 - RK6 * Y(12) * Y(6) - RKN1C * Y(12) * Y(4) - 0.33 * KDK * CD0 * Y(12) + RK46 * Y(15) * Y(7)$
 $2 - 2.0 * RKD * Y(12) ** 2 + 2. * RKMD * Y(14) * Y(7) + RKD1 * Y(7) ** 2 - RKMD1 * Y(12) * Y(8)$
 $3 + RK32 * Y(1) * Y(7) - RK42 * Y(16) * Y(12) + RK43 * Y(16) * Y(7) - RK45 * Y(15) * Y(12)$

C
 $YP(13) = RK13 * Y(15) * Y(6) - RKN13 * Y(13) + 0.5 * RKN9 * Y(10) - RK9 * Y(13) * Y(6)$
 $1 - RK14 * Y(13) * Y(4) + RK45 * Y(15) * Y(12) + RK46 * Y(15) * Y(7)$
 $2 - KDM * CD0 * Y(13) - KDHS * Y(17) * Y(13)$

C
 $YP(14) = KNI * Y(1) + RKN12 * Y(12) - RK10BS * Y(14) ** 0.80 * Y(4) - RK12 * Y(14) * Y(6)$
 $1 + RKD * Y(12) ** 2 - RKMD * Y(14) * Y(7) + RK45 * Y(15) * Y(12)$
 $2 + RKNXB * HCON * BRHOL * Y(1) + RK38 * Y(18) + RK39 * Y(19) + RK41 * Y(16) * Y(1)$
 $3 + RK42 * Y(16) * Y(12) + RK44 * Y(15) * Y(1) + KDK * CD0 * Y(7) * Y(8) * Y(9) * Y(24)$
 $4 + KDL * CD0 * Y(1) + 0.33 * KDK * CD0 * Y(12) + 0.33 * KDKS * Y(17) * Y(12)$
 $5 + KDLS * Y(17) * Y(1) + KDKS * Y(17) * Y(7) * Y(8) * Y(9) * Y(24)$

C
 $YP(15) = KNI * Y(3) + RKN13 * Y(13) - RK30BS * Y(15) * Y(4) - RK13 * Y(15) * Y(6)$
 $1 - RK44 * Y(15) * Y(1) - RK45 * Y(15) * Y(12) - RK46 * Y(15) * Y(7)$
 $2 + (KDM * CD0 + KDHS * Y(17)) * (Y(3) + Y(10) + Y(11) + Y(13))$

C
 $YP(16) = -RK33 * Y(16) * Y(4) - RK34 * Y(16) * Y(6) - RK41 * Y(16) * Y(1)$
 $1 - RK42 * Y(16) * Y(12) - RK43 * Y(16) * Y(7)$

C
 $YP(17) = -KDLS * Y(17) * Y(1) - KDIS * Y(17) * Y(4) - KDJS * Y(17) * Y(6)$
 $1 - 0.33 * KDKS * Y(17) * Y(12) - KDKS * Y(17) * (Y(7) + Y(8) + Y(9) + Y(24))$
 $2 - KDHS * Y(17) * (Y(3) + Y(10) + Y(11) + Y(13))$

C
 $YP(18) = RK33 * Y(16) * Y(4) - RK35 * Y(18) * Y(6) + RK41 * Y(16) * Y(1) - RK38 * Y(18)$

C
 $YP(19) = RK34 * Y(16) * Y(6) - RK36 * Y(19) * Y(6) - RK39 * Y(19) + RK42 * Y(16) * Y(12)$
 $1 + RK43 * Y(16) * Y(7) - RK37 * Y(19) * Y(4)$

C

YP(20)=RK35*Y(18)*Y(6)+RK37*Y(19)*Y(4)-RK40*Y(20)

YP(21)=RK36*Y(19)*Y(6)-RK40*Y(21)

YP(24)=RK47*Y(9)*Y(6)-RKH47*Y(24)-RK7PX*Y(24)*Y(7)-KDK*CD0*Y(24)
1-RK7PX2*Y(9)*Y(24)-KDKS*Y(17)*Y(24)-RK7D*Y(24)**2
RETURN

DIFFERENTIAL EQUATIONS FOR FRESH WATERS WITH ALL AMINES

80 YP(1)=Y(4)*(RK1OBS*Y(14)**0.80-RK2OBS*Y(1))-KH1*Y(1)+KH2*Y(2)
1-KDL*CD0*Y(1)-KDLS*Y(17)*Y(1)-RK41*Y(16)*Y(1)-RK44*Y(15)*Y(1)
2-RK25*Y(2)*Y(1)/(13.*Y(2)+Y(1)+RKNO3*Y(4))
YP(2)=RK2OBS*Y(1)*Y(4)-KH2*Y(2)-RK25*Y(2)*(1.+13.*Y(2)/
1(13.*Y(2)+Y(1)+RKNO3*Y(4)))-RK48*Y(2)*Y(4)+RKH48*Y(8)
YP(3)=RK3OBS*Y(15)*Y(4)-KH3*Y(3)+RK44*Y(15)*Y(1)-KDH*CD0*Y(3)
1-KDMS*Y(17)*Y(3)
85 YP(4)=KH1*Y(1)+KH2*Y(2)-RK2OBS*Y(4)*Y(1)-RK3OBS*Y(4)*Y(15)+KH3
1*Y(3)-KDI*CD0*Y(4)-RK1OBS*Y(14)**0.80*Y(4)-KDIS*Y(17)*Y(4)
2+RK25*Y(2)*(13.*Y(2)-2.*RKNO3*Y(4))/(13.*Y(2)+Y(1)+RKNO3*Y(4))
3-RK33*Y(16)*Y(4)-RK48*Y(2)*Y(4)+RKH48*Y(8)
YP(5)=-KDI*CD0*Y(4)-KDL*CD0*(Y(1)+Y(8))-KDH*CD0*Y(3)
1-KDIS*Y(17)*Y(4)-KDMS*Y(17)*Y(3)
YP(8)=RK48*Y(2)*Y(4)-RKH48*Y(8)-KDL*CD0*Y(8)-KDLS*Y(17)*Y(8)
YP(14)=KH1*Y(1)-RK1OBS*Y(14)**0.80*Y(4)+KDLS*Y(17)*(Y(1)+Y(8))
1+KDL*CD0*(Y(1)+Y(8))+RK38*Y(18)+RK41*Y(16)*Y(1)+RK44*Y(15)*Y(1)
YP(15)=KH3*Y(3)-RK3OBS*Y(15)*Y(4)-RK44*Y(15)*Y(1)
1+KDH*CD0*Y(3)+KDMS*Y(17)*Y(3)
YP(16)=-RK33*Y(16)*Y(4)-RK41*Y(16)*Y(1)
YP(17)=-KDLS*Y(17)*(Y(1)+Y(8))-KDIS*Y(17)*Y(4)-KDMS*Y(17)*Y(3)
YP(18)=RK33*Y(16)*Y(4)+RK41*Y(16)*Y(1)-RK38*Y(18)
90 RETURN

DIFFERENTIAL EQUATIONS FOR SALINE WATERS WITHOUT RNH2

100 YP(1)=Y(4)*(RK1OBS*Y(14)**0.80-RK2OBS*Y(1))-KH1*Y(1)+KH2*Y(2)
1-RKHX*Y(6)*Y(1)-RKHXB*HCON*BRMOL*Y(1)-KDL*CD0*Y(1)
2-KDLS*Y(17)*Y(1)-RK41*Y(16)*Y(1)+RKHXH*Y(9)
3-RK32*Y(1)*Y(7)-RK25*Y(2)*Y(1)/(13.*Y(2)+Y(1)+RKNO3*Y(4))
YP(2)=RK2OBS*Y(1)*Y(4)-KH2*Y(2)-RK25*Y(2)*(1.+13.*Y(2)/
1(13.*Y(2)+Y(1)+RKNO3*Y(4)))
150 YP(4)=KH1*Y(1)+KH2*Y(2)-RK2OBS*Y(4)*Y(1)-KDI*CD0*Y(4)-RK5*Y(4)
1*BRMOL-RK1OBS*Y(14)**0.80*Y(4)-RKHX*Y(12)*Y(4)-KDIS*Y(17)*Y(4)
2+RK25*Y(2)*(13.*Y(2)-2.*RKNO3*Y(4))/(13.*Y(2)+Y(1)+RKNO3*Y(4))
3-RK33*Y(16)*Y(4)-RK37*Y(19)*Y(4)
152 YP(5)=-KDI*CD0*Y(4)-KDJ*CD0*Y(6)-KDK*CD0*(Y(7)+Y(8)+Y(9)+Y(24))
1-0.33*KDK*CD0*Y(12)-KDL*CD0*Y(1)

$YP(6) = RK5 * Y(4) * BRHOL - KDJ * CD0 * Y(6) - RK7 * Y(6) * Y(7) - RKHX * Y(6) * Y(1)$
 $+ RKH6 * Y(7) + 2.0 * RK7P * Y(8) * Y(7) + 2. * RK7PX * Y(9) * Y(8) + Y(7) * Y(24)$
 $1 - RK47 * Y(9) * Y(6) + RKH47 * Y(24) + 2. * RK7PX2 * Y(9) * Y(24) + 1.5 * RK7D * Y(8) ** 2$
 $2 + RKH7 * Y(8) - RKH - RK35 * Y(18) * Y(6) - RK36 * Y(19) * Y(6) + 0.5 * RK26 * Y(9) ** 2$
 $3 - RK6 * Y(12) * Y(6) - RK12 * Y(14) * Y(6) + RKH12 * Y(12) + RKHXH * Y(9)$
 $4 + .5 * RK27 * Y(7) ** 2 - KDJ * Y(17) * Y(6) - RK34 * Y(16) * Y(6) + 1.5 * RK7D * Y(24) ** 2$
 $5 + RKHXH * HCON * BRHOL * Y(1)$

C

$YP(7) = RK6 * Y(12) * Y(6) - RKH6 * Y(7) - RK7 * Y(7) * Y(6) + RKH7 * Y(8)$
 $1 - KDK * Y(7) * CD0 - RK7P * Y(7) * Y(8) - RK27 * Y(7) ** 2 - RK7PX * Y(7) * Y(24)$
 $2 - RK43 * Y(16) * Y(7) - RK32 * Y(1) * Y(7) - KDKS * Y(17) * Y(7)$
 $3 + RKD * Y(12) ** 2 - RKHD * Y(14) * Y(7) - 2.0 * RKD1 * Y(7) ** 2 + 2. * RKHD1 * Y(12) * Y(8)$

C

$YP(8) = RK7 * Y(6) * Y(7) - RKH7 * Y(8) - KDK * Y(8) * CD0 - RK7P * Y(8) * Y(7)$
 $1 - RK7PX * Y(8) * Y(9) + RKD1 * Y(7) ** 2 - RKHD1 * Y(12) * Y(8) - RK7D * Y(8) ** 2$
 $2 - KDKS * Y(17) * Y(8)$

C

$YP(9) = RKHX * Y(6) * Y(1) - RKHXH * Y(9) + RK32 * Y(1) * Y(7)$
 $1 + RKHX * Y(12) * Y(4) - RK26 * Y(9) ** 2 - KDKS * Y(17) * Y(9) - RK7PX * Y(9) * Y(8)$
 $2 + RKH47 * Y(24) - RK47 * Y(9) * Y(6) - KDK * CD0 * Y(9) - RK7PX2 * Y(9) * Y(24)$

C

$YP(12) = RK12 * Y(14) * Y(6) - RKH12 * Y(12) + RKH6 * Y(7) - 0.33 * KDKS * Y(17) * Y(12)$
 $1 - RK6 * Y(12) * Y(6) - RKHX * Y(12) * Y(4) - 0.33 * KDK * CD0 * Y(12)$
 $2 + RK32 * Y(1) * Y(7) - RK42 * Y(16) * Y(12) + RK43 * Y(16) * Y(7)$
 $3 - 2.0 * RKD * Y(12) ** 2 + 2. * RKHD * Y(14) * Y(7) + RKD1 * Y(7) ** 2 - RKHD1 * Y(12) * Y(8)$

C

$YP(14) = KH1 * Y(1) + RKH12 * Y(12) - RK10BS * Y(14) ** 0.80 * Y(4) - RK12 * Y(14) *$
 $1 * Y(6) + KDK * CD0 * Y(7) * Y(8) * Y(9) * Y(24) + RKHXH * HCON * BRHOL * Y(1)$
 $2 + RK38 * Y(18) + RK39 * Y(19) + RK41 * Y(16) * Y(1)$
 $3 + RK42 * Y(16) * Y(12) + RKD * Y(12) ** 2 - RKHD * Y(14) * Y(7)$
 $4 + KDL * CD0 * Y(1) + 0.33 * KDK * CD0 * Y(12) + 0.33 * KDKS * Y(17) * Y(12)$
 $5 + KDL * Y(17) * Y(1) + KDKS * Y(17) * Y(7) * Y(8) * Y(9) * Y(24)$

C

$YP(16) = -RK33 * Y(16) * Y(4) - RK34 * Y(16) * Y(6) - RK41 * Y(16) * Y(1)$
 $1 - RK42 * Y(16) * Y(12) - RK43 * Y(16) * Y(7)$

C

$YP(17) = -KDL * Y(17) * Y(1) - KDIS * Y(17) * Y(4) - KDJ * Y(17) * Y(6)$
 $1 - 0.33 * KDKS * Y(17) * Y(12) - KDKS * Y(17) * Y(7) * Y(8) * Y(9) * Y(24)$

C

$YP(18) = RK33 * Y(16) * Y(4) - RK35 * Y(18) * Y(6) + RK41 * Y(16) * Y(1) - RK38 * Y(18)$

C

$YP(19) = RK34 * Y(16) * Y(6) - RK36 * Y(19) * Y(6) - RK39 * Y(19) + RK42 * Y(16) * Y(12)$
 $1 + RK43 * Y(16) * Y(7) - RK37 * Y(19) * Y(4)$

C

$YP(20) = RK35 * Y(18) * Y(6) + RK37 * Y(19) * Y(4) - RK40 * Y(20)$

C

$YP(21) = RK36 * Y(19) * Y(6) - RK40 * Y(21)$

C

$YP(24) = RK47 * Y(9) * Y(6) - RKH47 * Y(24) - RK7PX * Y(24) * Y(7) - KDK * CD0 * Y(24)$
 $1 - RK7PX2 * Y(9) * Y(24) - KDKS * Y(17) * Y(24) - RK7D * Y(24) ** 2$
 RETURN

C

C

C DIFFERENTIAL EQUATIONS FOR THE BROMINE BREAKPOINT MODEL
C

```

200 YP(4)=-RK5*Y(4)*BRMOL
    YP(6)=RK5*Y(4)*BRMOL-RK7*Y(6)*Y(7)+RKN6*Y(7)+RKN7*Y(8)
    1-RK6*Y(12)*Y(6)-RK12*Y(14)*Y(6)+RKN12*Y(12)
    2+2.*RK7P*Y(7)*Y(8)+0.5*RK27*Y(7)**2
    3+1.5*RK7D*Y(8)**2
    YP(7)=RK6*Y(12)*Y(6)-RKN6*Y(7)-RK7*Y(7)*Y(6)+RKN7*Y(8)
    2-RK7P*Y(7)*Y(8)-RK27*Y(7)**2
    3+RKD*Y(12)**2-RKND*Y(14)*Y(7)-2.0*RKD1*Y(7)**2+2.*RKND1*Y(12)*Y(8)
    YP(8)=RK7*Y(6)*Y(7)-RKN7*Y(8)+RKD1*Y(7)**2-RKND1*Y(12)*Y(8)
    2-RK7P*Y(7)*Y(8)
    3-RK7D*Y(8)**2
    YP(12)=RK12*Y(14)*Y(6)-RKN12*Y(12)+RKN6*Y(7)-RK6*Y(12)*Y(6)
    1-2.0*RKD*Y(12)**2+2.*RKND*Y(14)*Y(7)+RKD1*Y(7)**2-RKND1*Y(12)*Y(8)
    YP(14)=RKN12*Y(12)-RK12*Y(14)*Y(6)+RKD*Y(12)**2-RKND*Y(14)*Y(7)
    RETURN

```

C
C
C
C

DIFFERENTIAL EQUATIONS FOR SEAWATER DEMAND WITHOUT AMINE SPECIES

```

300 YP(4)=-RK5*Y(4)*BRMOL-KDI*Y(4)*CDO-KDIS*Y(4)*Y(17)
    YP(5)=-KDI*Y(4)*CDO-KDJ*Y(6)*CDO
    YP(17)=-KDIS*Y(4)*Y(17)-KDJS*Y(6)*Y(17)
    YP(6)=RK5*Y(4)*BRMOL-KDJ*Y(6)*CDO-RK8-KDJS*Y(6)*Y(17)
    RETURN
END

```


SEAWATER CHLORINATION MODEL CALCULATIONS

INITIAL CONDITIONS

PH	TEMP	CL ADDED (AS CL2)	CL DEMAND (AS CL2)	NH3 (AS N)	RNH2 (AS N)	ALNH2 (AS N)	DLF	MU/BD	VCS (G)	OR (G/SEC)	F
8.10	20.0C	1.000 PPM	0.540 PPM	170.0.770	0.0500 PPM	0.0500 PPM	0.0500 PPM	5.00	1.00	0.0	0.0

CALCULATED INITIAL CONCENTRATIONS (MOLES/LITER)

CL	CL TOTAL	HOCL	OCL	CL2	NH3	RNH2	ALNH2
1.2470-08	1.4100-05	2.4670-06	1.1640-05	7.2740-15	3.5700-06	3.5700-06	3.5700-05

OBSERVED CONSTANTS

KW	KHYD(CL2)	KA(HOCL)	KA(HOBF)	KA(NH4+)	KB(MENH2)	KB(ALA)	GAMA	MU	SALINITY	RKINFL	PKDSCH	PKEVAP
4.210-14	3.410-04	5.880-08	6.290-10	3.170-10	1.740-04	2.040-05	6.370-01	7.200-01	3.550-01	0.0	0.0	0.0
K1	K-1	K2	K-2	K3	K-3	K5	K6	K-6	K7	K-7	K7D	K7P
3.400-03	1.840-05	4.790-01	6.500-07	9.970-05	1.600-06	6.260-02	2.220-05	3.170-04	9.640-03	9.370-04	1.200-01	4.890-03
K7PX	K7PX2	KD	K-D	KD1	K-01	K8	K9	K-9	K10	K-10	K11	K-11
7.330-02	4.890-03	3.130-05	1.000-04	1.000-04	6.820-05	1.570-11	1.330-06	7.000-07	2.860-04	2.300-04	4.750-05	7.000-07
K12	K-12	K13	K-13	K14	KHXC	KHXB	K25	K26	K27	K32	K33	K34
1.770-06	7.900-02	1.630-07	1.600-04	3.500-03	7.000-01	1.420-06	1.050-02	4.000-00	1.330-01	3.200-02	1.230-06	5.140-07
K35	K36	K37	K38	K39	K40	K41	K42	K43	K44	K45	K46	K47
1.670-05	3.330-05	8.750-03	1.280-04	1.000-04	3.850-03	1.250-00	1.000-01	4.000-01	3.130-00	2.500-01	1.030-02	2.860-04
K-47	K48	KH48	KD1	KD2	KDK	KDL	KDM	KDIS	KDJS	KDKS	KDLS	KDMS
5.000-04	1.750-01	9.710-05	1.000-04	3.000-04	1.000-01	1.200-01	2.400-00	1.250-01	3.750-01	5.000-01	5.000-01	1.000-01

T INITIAL = 0.0 M T FINAL = 60.00 M 1ST TIME STEP = 0.0010 M ACCURC = 1.000-10 LSKIP = 500

TIME	HOCL	NH3	RNH2	ALNH2	NH2CL	NHCL2	RNHCL	ALNHCL	NH2BR	NHBR2	NBR3	SLOW CD	FAST CD	T.R.HAL.
0.0	1.410-05	3.570-06	3.570-06	3.570-06	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.280-06	5.330-06	1.410-05
0.0	1.370-05	3.560-06	3.390-06	3.340-06	7.750-09	9.680-15	1.800-07	2.210-07	2.380-10	9.990-16	1.140-22	2.280-06	5.330-06	1.410-05
0.5	2.960-11	2.940-06	1.170-09	0.0	9.560-07	6.710-12	1.050-06	1.920-06	1.290-07	3.080-07	1.120-08	2.280-06	4.340-06	1.110-09
12.8	2.580-11	2.490-06	2.420-09	0.0	9.040-07	2.360-13	7.990-07	1.560-06	6.080-08	5.910-08	9.990-10	2.280-06	4.240-06	9.950-06
18.2	2.570-11	2.680-06	5.790-09	0.0	8.840-07	1.100-13	7.320-07	1.550-06	1.810-08	5.800-09	6.860-11	2.280-06	4.190-06	9.470-06
23.8	2.480-11	2.800-06	1.380-08	0.0	8.680-07	1.000-13	7.150-07	1.470-06	3.880-09	2.110-10	1.000-11	2.280-06	4.160-06	9.210-06
29.4	2.400-11	2.850-06	2.330-08	0.0	8.530-07	9.490-14	7.070-07	1.410-06	2.530-09	7.060-11	3.620-12	2.280-06	4.130-06	9.040-06
35.1	2.320-11	2.950-06	3.150-08	0.0	8.380-07	9.010-14	7.080-07	1.340-06	2.730-09	7.420-11	1.430-12	2.280-06	4.100-06	8.920-06
40.7	2.250-11	3.070-06	3.630-08	0.0	8.220-07	8.590-14	6.930-07	1.280-06	3.860-09	1.410-10	5.070-13	2.280-06	4.070-06	8.810-06
46.3	2.200-11	3.150-06	3.790-08	0.0	8.070-07	8.220-14	6.840-07	1.230-06	4.360-09	1.830-10	2.180-13	2.280-06	4.040-06	8.710-06
51.8	2.150-11	3.230-06	4.030-08	0.0	7.920-07	7.870-14	6.750-07	1.170-06	3.980-09	1.520-10	1.270-13	2.280-06	4.010-06	8.610-06
56.8	2.100-11	3.290-06	4.330-08	0.0	7.790-07	7.560-14	6.690-07	1.120-06	3.050-09	1.110-10	8.900-14	2.280-06	3.990-06	8.530-06
60.0	2.060-11	3.340-06	4.730-08	0.0	7.700-07	7.350-14	6.660-07	1.090-06	1.800-09	3.510-11	6.400-14	2.280-06	3.970-06	8.470-06

DISCHARGE VALUES

60.0 4.120-12 3.520-06 2.870-06 2.860-06 1.540-07 1.470-14 1.330-07 2.190-07 3.610-10 7.030-12 1.280-14 2.280-06 5.060-06 1.690-06

TIME	HOBR	NHBRCL	NBR2CL	RNHBR	RNBR2	RNBRCL	ALNHBR	ALNBR2	ALNBRCL	BROMIDE
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.130-04
0.00	1.750-08	5.720-15	2.550-21	2.130-09	5.300-14	2.250-12	6.640-09	4.140-14	1.990-12	8.130-04
6.51	2.200-09	1.320-07	2.580-05	2.460-02	3.530-07	2.140-06	2.410-07	9.450-08	3.290-07	8.090-04
12.85	9.250-10	1.490-07	3.300-09	2.140-08	3.680-07	2.380-06	1.910-07	4.080-08	1.550-07	8.090-04
18.22	2.610-10	1.430-07	2.770-09	2.900-06	3.720-07	2.430-06	1.750-07	1.720-08	6.880-08	8.100-04
23.76	7.580-11	1.330-07	1.960-05	2.770-08	3.720-07	2.440-06	1.670-07	5.920-09	2.420-08	8.100-04
29.41	3.500-11	1.230-07	1.380-09	3.000-08	3.710-07	2.440-06	1.600-07	2.040-09	8.490-09	8.100-04
35.06	0.0	1.130-07	9.800-10	3.350-08	3.700-07	2.430-06	1.540-07	9.340-10	3.970-09	8.100-04
40.71	0.0	1.050-07	7.240-10	3.990-08	3.700-07	2.430-06	1.480-07	7.290-10	3.150-09	8.100-04
46.26	0.0	9.690-08	5.630-10	4.880-08	3.700-07	2.430-06	1.430-07	7.640-10	3.300-09	8.100-04
51.89	4.940-11	8.370-08	4.460-10	5.560-06	3.700-07	2.420-06	1.370-07	7.030-09	3.020-09	8.100-04
56.77	4.250-11	8.380-08	3.680-10	6.200-08	3.700-07	2.420-06	1.320-07	6.150-10	2.630-09	8.100-04
60.00	2.400-11	8.010-08	3.190-10	6.460-08	3.700-07	2.420-06	1.290-07	4.750-10	2.030-09	8.100-04

DISCHARGE VALUES

60.00 4.810-12 1.800-08 6.390-11 1.290-08 7.390-08 4.840-07 2.590-08 9.490-11 4.050-10 8.130-04

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