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# **Methodology for Flow and Salinity Estimates in the Sacramento-San Joaquin Delta and Suisun Marsh**

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## **Chapter 9: Trihalomethane Formation Potential Modeling**

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# 9 Trihalomethane Formation Potential Modeling

*[Editor's Note: This is an electronic reprint of the original document. Electronic copies of the original figures were not available, thus the original figures are not included in this report.]*

The Sacramento-San Joaquin Delta is a source of drinking water for 20 million Californians. Because the Delta is part of a tidal estuary and its land use is predominantly agricultural, Delta waters tend to reflect high levels of bromides and organic material (Amy et al. 1990). Organics and bromides promote the formation of disinfection by-products (DBPs) in the presence of a strong oxidant. Trihalomethanes (THMs), one class of DBPs, are a suspected threat to human health when present in sufficient quantities in drinking water.

In 1979, the Environmental Protection Agency established a drinking water standard of 0.1 milligrams per liter for THMs. Anticipating revisions to the current standards and recognizing problems Delta water users may face in meeting more stringent requirements, DWR began a study of THM precursors in Delta waters. A conclusion drawn from that study was that revised THM regulations may necessitate modifications of drinking water treatment processes, modifications in the operation of Delta export facilities, or a combination thereof (DWR 1989). Besides THMs, the Environmental Protection Agency will be regulating a number of other DBPs. Those compounds most likely to be regulated include: trichloroacetic acid, dichloroacetic acid, total haloacetic acids, chloral hydrate, bromate, chlorate, and chlorite (Pontius 1991).

This chapter summarizes DWR's efforts to date in mathematically modeling THM formation potential (THMFP) in the Delta. The first section discusses current and upcoming publications related to this work. Future model enhancements, as identified in these publications, are briefly addressed. The second and third sections of this chapter present unpublished work that will be incorporated into the overall modeling framework.

## 9.1 Publications

The Division of Planning has recently published a report entitled Trihalomethane Formation Potential in the Sacramento-San Joaquin Delta: Mathematical Model Development (DWR 1991). The report documents DWR's initial efforts in modeling Delta THMFP. The contents of this report are summarized in two papers that will be published in the ASCE Journal of Water Resources Planning and Management (Hutton and Chung 1992a, 1992b).

Two potential areas for future model enhancement were identified in the above publications. The first enhancement outlined below is applicable to existing and potential Delta export stations while the second enhancement is applicable to model boundary stations:

1. Develop a correlation between THMFP values and expected tap water THM levels. The importance of such a correlation is that DWR's THMFP test assays the amount of precursor material in untreated source waters in the Delta, whereas drinking water

standards for THMs apply only to treated drinking water. A methodology to predict THM concentrations in a water distribution system from THMFP data is presented in the last section of this chapter.

2. Develop boundary conditions that relate DWR's precursor simulation parameter, TFPC (total THMFP as carbon), with a direct precursor measure. The importance of developing these boundary relationships is that TFPC is not well-suited for real time simulation, as a 7-day THMFP test must be performed to estimate its value at each boundary. A statistically-based precursor measure that has been proposed by Amy et al. (1987) is the product of total organic carbon (TOC) and ultraviolet absorbance at 254 nm (UVA), where TOC quantifies precursor concentration and UVA quantifies precursor reactivity in forming THMs. Work will commence on developing boundary relationships between TFPC and TOCxUVA as more data becomes available.

The following section summarizes a model enhancement that has been developed this past year and was completed subsequent to the publications discussed above.

## 9.2 Bromine Distribution Factors: Modified Formulation

Hutton and Chung (1992a,1992b) presented a mathematical model designed to analyze source water management alternatives in the Delta, with a specific focus on THMFP. Two empirical relationships were developed by the authors to describe impacts of bromide on the distribution of compounds measured by DWR's THMFP test. These relationships were based on 2000 samples of Delta channels and agricultural drains collected in the Delta between 1983 and 1990 under DWR's Municipal Water Quality Investigations (MWQI) program.

One empirical relationships, the Bromine Incorporation Factor, was originally defined by Gould et al. (1981) as the following dimensionless term:

$$\eta = \frac{\sum N[CHCl_{(3-N)}Br_N]}{\sum [CHCl_{(3-N)}Br_N]} \dots\dots\dots (1)$$

where:

$\eta$  = Bromine Incorporation Factor,  $0 \leq \eta \leq 3$   
 $N$  = number of bromide atoms in THM compound

The second empirical relationship developed by the authors was the Bromine Distribution Factors (**S**), a term defining a vector of THMFP species distribution functions:

$$\mathbf{S} = [s_0(\eta), s_1(\eta), s_2(\eta), s_3(\eta)] \dots\dots\dots (2a)$$

where:

$$s_0 = CHCl_3 \text{ Distribution Factor} = [CHCl_3] / [THMFP] \dots\dots\dots (2b)$$

$$s_1 = CHCl_2Br \text{ Distribution Factor} = [CHCl_2Br] / [THMFP] \dots\dots\dots (2c)$$

$$s_2 = \text{CHClBr}_2 \text{ Distribution Factor} = [\text{CHClBr}_2] / [\text{THMFP}] \dots\dots\dots(2d)$$

$$s_3 = \text{CHBr}_3 \text{ Distribution Factor} = [\text{CHBr}_3] / [\text{THMFP}] \dots\dots\dots(2e)$$

Assuming functional forms dependent on  $\eta$ , Hutton and Chung (1992a) performed regression analyses on the MWQI data set to derive model coefficients that statistically describe the Bromine Distribution Factors. The resulting vector of distribution functions,  $\mathbf{S}_R$ , is given below in Eqs. 3a-3d:

$$s_0 = -.0285\eta^3 + .2613\eta^2 - .8703\eta + 1 \dots\dots\dots(3a)$$

$$s_1 = \frac{-.0446\eta^3 - .1888\eta^2 + .8659\eta}{\eta + 1} \dots\dots\dots(3b)$$

$$s_2 = -.0792\eta^3 + .1936\eta^2 + .1244\eta \dots\dots\dots(3c)$$

$$s_3 = .0250\eta^3 + .0351\eta^2 + .0017\eta \dots\dots\dots(3d)$$

$\mathbf{S}_R$  was verified against a THMFP data set developed under varying reaction conditions by Amy et al. (1987). An excellent correspondence was observed between  $\mathbf{S}_R$  and this data set, indicating that THMFP species distribute in a predictable fashion under varying test conditions (DWR 1991).

Some caution is necessary in the use of  $\mathbf{S}_R$ , however, as its predictions are not always constrained within the implied limits of distribution functions. For instance, Eqs. 3a and 3b give negative predictions at high values of  $\eta$ . But by definition, the functions should always be greater than or equal to zero. Also, as shown in Fig. 1, the sum of Eqs. 3a-3d is not equal to one for all values of  $\eta$ . But again by definition, the sum of the distribution functions should always equal one. The conditions cited above are not always satisfied because model coefficients were determined statistically, with the objective being to minimize sum-of-squares errors. Hutton and Chung (1992a) documented a simple approach to adjust the values predicted by  $\mathbf{S}_R$ .

A technique is presented in this section that solves analytically for Bromine Distribution Factor coefficients. A number of solution conditions are introduced to eliminate the need for a posteriori adjustments of model predictions. Solution results are evaluated by comparing predicted values with observed values from the MWQI data set and other THM data sets.

### 9.2.1 Theoretical Solution

A third order polynomial function dependent on  $\eta$  was assumed for each Bromine Distribution Factor such that:

$$s_i = a_i\eta^3 + b_i\eta^2 + c_i\eta + d_i \quad i = 0, 1, 2, 3 \dots\dots\dots(4)$$

Sixteen equations are required to arrive at a unique solution for the 16 unknown coefficients implied by Eq. 4. Ten conditions were identified to solve for the unknowns:

$$ds_0/d\eta = 0 \text{ at } \eta = 3 \dots\dots\dots(5a)$$

$$s_1 = 0 \text{ at } \eta = 0 \dots\dots\dots(5b)$$

$$s_1 = 0 \text{ at } \eta = 3 \dots\dots\dots(5c)$$

$$ds_1/d\eta = 0 \text{ at } \eta = 1 \dots\dots\dots(5d)$$

$$s_2 = 0 \text{ at } \eta = 0 \dots\dots\dots(5e)$$

$$s_2 = 0 \text{ at } \eta = 3 \dots\dots\dots(5f)$$

$$ds_2/d\eta = 0 \text{ at } \eta = 2 \dots\dots\dots(5g)$$

$$ds_3/d\eta = 0 \text{ at } \eta = 0 \dots\dots\dots(5h)$$

$$s_0 + s_1 + s_2 + s_3 = 1 \quad \forall \eta \dots\dots\dots(5i)$$

$$s_1 + 2s_2 + 3s_3 = \eta \quad \forall \eta \dots\dots\dots(5j)$$

Although only ten conditions are identified above, a unique solution can be found. Eqs. 5i and 5j are valid over the entire range of  $\eta$ , suggesting that these conditions can be employed to derive more than one equation. For example, Eqs. 5b and 5e are obvious restatements of Eq. 5j. Eq. 5j was derived by substituting Eqs. 2b-2e into Eq. 1.

The sixteen unknown coefficients were solved for in four steps: (i) First, Eqs. 5c and 5d were employed to solve for  $b_1$  and  $c_1$  in terms of  $a_1$ . Per Eq. 5b,  $d_1 = 0$ . (ii) Next, Eqs. 5f and 5g were employed to solve for  $b_2$  and  $c_2$  in terms of  $a_2$ . Per Eq. 5e,  $d_2 = 0$ . (iii) Substituting results from the previous steps into Eq. 5j,  $s_3$  coefficients were solved for in terms of  $a_1$  and  $a_2$ . A solution was found for  $a_1$  by employing Eq. 5h. (iv) Again, substituting results from the previous steps into Eq. 5i,  $s_0$  coefficients were solved for in terms of  $a_2$ . A solution was found for  $a_2$  by employing Eq. 5a.

The resulting vector of theoretically-derived distribution functions,  $\mathbf{S}_T$ , is given below in Eqs. 6a-6d:

$$s_0 = -.0370\eta^3 + .3333\eta^2 - \eta + 1 \dots\dots\dots(6a)$$

$$s_1 = .1111\eta^3 - .6667\eta^2 + \eta \dots\dots\dots(6b)$$

$$s_2 = -.1111\eta^3 + .3333\eta^2 \dots\dots\dots(6c)$$

$$s_3 = .0370\eta^3 \dots\dots\dots(6d)$$

Although  $\mathbf{S}_T$  satisfies the conditions stipulated in Eqs. 5a-5j, it does not provide a good fit to observed data. Fig. 2 shows the theoretical solution superimposed on the MWQI data set. Figs. 3 and 4 show similar deviations between predicted and observed values, with Fig. 3 illustrating THMFP data developed by Amy et al. (1987) and Fig. 4 illustrating a simulated distribution system (SDS) THM data set developed by the Metropolitan Water District of Southern California (MWD). MWD's SDS THM test is described by Koch et al. (1991).

### 9.2.2 Modified Solution

As discussed above, the theoretical solution vector,  $\mathbf{S}_T$ , does not provide a good fit to the Bromine Distribution Factor data sets. Comparison of  $\mathbf{S}_R$  with  $\mathbf{S}_T$  gives some insight into shortcomings of the theoretical conditions. Alternate conditions were developed from this comparison to arrive at a modified solution vector,  $\mathbf{S}_M$ .

Not all of the theoretical conditions correspond with statistical characteristics of the MWQI data set. Regression analyses suggest that  $s_1$  and  $s_2$  reach maximum values at somewhat different values of  $\eta$  than specified in the theoretical conditions. Likewise, areas under the theoretical curves deviate from the areas under the regression curves. Integrating Eqs. 6a-6d reveals that the theoretical conditions produce four identical areas of 0.75. Areas under the regression curves, in contrast, are not equivalent. Integrating Eqs. 3a-3d results in the following areas: 0.86 for  $s_0$ , 0.59 for  $s_1$ , 0.70 for  $s_2$ , and 0.83 for  $s_3$ . This observation may suggest that a chemical preference exists for the formation of chloroform ( $\text{CHCl}_3$ ) and bromoform ( $\text{CHBr}_3$ ) over the other THM species, a consideration that was not modeled by the theoretical conditions.

One means of improving the data fit of the theoretical solutions is to assume a fourth order polynomial function for each Bromine Distribution Factor. Such an approach allows for the incorporation of additional conditions that describe data characteristics, e.g. maximum functional values or integrated functional values. Although valid, this approach was not employed because of its reliance on a more complex functional form. Instead, the third order functional form (Eq. 4) was maintained and the following 16 modified conditions were introduced with the purpose of improving fit to the MWQI data set:

$$s_0 = 1 \text{ at } \eta = 0 \dots\dots\dots(7a)$$

$$s_0 = 0 \text{ at } \eta = 3 \dots\dots\dots(7b)$$

$$ds_0/d\eta = 0 \text{ at } \eta = 3 \dots\dots\dots(7c)$$

$$\int s_0 d\eta = 0.85 \dots\dots\dots(7d)$$

$$s_1 = 0 \text{ at } \eta = 0 \dots\dots\dots(7e)$$

$$s_1 = 0 \text{ at } \eta = 3 \dots\dots\dots(7f)$$

$$ds_1/d\eta = 0 \text{ at } \eta = 1.05 \dots\dots\dots(7g)$$

$$\int s_1 d\eta = 0.60 \dots\dots\dots(7h)$$

$$s_2 = 0 \text{ at } \eta = 0 \dots\dots\dots(7i)$$

$$s_2 = 0 \text{ at } \eta = 3 \dots\dots\dots(7j)$$

$$ds_2/d\eta = 0 \text{ at } \eta = 1.90 \dots\dots\dots(7k)$$

$$\int s_2 d\eta = 0.75 \dots\dots\dots(7l)$$

$$s_3 = 0 \text{ at } \eta = 0 \dots\dots\dots(7m)$$

$$s_3 = 1 \text{ at } \eta = 3 \dots\dots\dots(7n)$$

$$ds_3/d\eta = 0 \text{ at } \eta = 0 \dots\dots\dots(7o)$$

$$\int s_3 d\eta = 0.80 \dots\dots\dots(7p)$$

Eqs. 7g and 7k are modified conditions that address deviations between the location of maximum values of  $s_1$  and  $s_2$ . Eqs. 7d, 7h, 7l and 7p are modified conditions that address deviations between areas under the functional curves. These latter conditions also satisfy the integrated forms of Eqs. 5i and 5j:

$$\sum \int s_i d\eta = \int d\eta = 3 \dots\dots\dots(8)$$

$$\int s_1 d\eta + 2 \int s_2 d\eta + 3 \int s_3 d\eta = \int \eta d\eta = 4.5 \dots\dots\dots(9)$$

The sixteen modified conditions (Eqs. 7a-7p) were employed to solve for 16 new coefficients. The resulting vector of modified distribution functions, **S<sub>M</sub>**, is given below in Eqs. 10a-10d:

$$s_0 = -.0222\eta^3 + .2444\eta^2 - .8667\eta + 1 \dots\dots\dots(10a)$$

$$s_1 = .0731\eta^3 - .4621\eta^2 + .7288\eta \dots\dots\dots(10b)$$

$$s_2 = -.0753\eta^3 + .1723\eta^2 + .1607\eta \dots\dots\dots(10c)$$

$$s_3 = .0296\eta^3 + .0222\eta^2 \dots\dots\dots(10d)$$

**S<sub>M</sub>** always gives predictions that lie within a meaningful distribution function range of zero to one. Furthermore, the distribution factor sum is always equal to one. Hence, predictions from **S<sub>M</sub>** do not require a posteriori corrections.

### 9.2.3 Verification of Modified Solution

The modified solution vector, **S<sub>M</sub>**, was verified against the original MWQI calibration data as well as the THMFP data set developed by Amy et al. (1987) and the SDS THM data set developed by MWD. **S<sub>M</sub>** is superimposed on these data sets in Figs. 2, 3 and 4. These figures show an excellent correspondence between the modified solutions and the data sets, indicating that **S<sub>M</sub>** is an appropriate model for the Bromine Distribution Factors under a variety of test conditions.

### 9.2.4 Conclusions

An analytical solution scheme was employed to solve directly for Bromine Distribution Factor model coefficients. The Bromine Distribution Factors have been shown elsewhere to be useful in characterizing the impact of bromide on the distribution of THMFP compounds (Hutton and Chung 1992a,1992b). The modified relationships are superior to those calibrated from regression analyses in that their predictions are always constrained within meaningful limits. These modified relationships were verified against three data sets that reflect a wide spectrum of water quality and reaction conditions.

Because the Bromine Distribution Factor functions have been shown to provide consistently good predictions over a wide range of water quality and reaction conditions, these relationships provide a potential link in developing correlations between data collected to measure precursor levels (i.e. high chlorine dose THMFP data) and data collected to estimate THM levels at the consumer's tap (i.e. SDS THM data). Employing the Bromine Distribution Factors and other relationships to correlate DWR's THMFP data with SDS THM data is discussed in the next section.

## 9.3 Correlating THMFP Data With SDS-THM Data

Measuring the tendency of water to form THMs or other DBPs is usually undertaken to accomplish one of two important objectives, either to estimate the total concentration of precursor material in a source water or to estimate the extent to which these precursors yield

THMs at the consumers' tap. The former objective, associated with evaluating precursor removal strategies and source water management alternatives, can be accomplished with a fixed high-chlorine dosage (high-dose) THMFP test. The latter objective, associated with evaluating DBPs likely to be formed under actual water treatment conditions, can be accomplished with a variable low-chlorine dosage (low-dose) THMFP test or a site-specific SDS test.

Design aspects of high-dose THMFP assays and SDS tests (or low-dose THMFP tests) reflect their differing objectives. To allow for unbiased comparisons of data between locations or periods of interest, standard conditions are of primary importance in high-dose assays. High chlorine doses minimize the differences in chlorine residual from one sample to another, and as observed by Reckhow and Edzwald (1991), assay values are independent of chlorine residual at high residual values. SDS tests, on the other hand, must be tailored to specific treatment systems and must reflect specific disinfection conditions (Reckhow and Edzwald 1991). At chlorine residuals typically employed during water treatment and distribution, THM formation is dependent on residual levels.

Given the differing objectives and design aspects of SDS tests and high-dose THMFP tests, it is not surprising that these tests provide information that is readily correlated only in a qualitative sense. Yet water supply decisions must ultimately consider how source water precursors translate into tap water quality for a given level of treatment. Recognizing the importance of understanding this relationship in the Delta, the California State Water Resources Control Board (1991) identified the need to develop a correlation between THMFP monitoring data and THM concentrations in treated drinking water. To provide such a link, this section presents a framework that correlates THM data collected under different reaction conditions. The framework is specifically employed to develop two models: one that predicts 24-hour SDS concentrations from 3-hr SDS measurements and one that predicts 24-hour SDS concentrations from high-dose THMFP measurements. The purpose of the former model is to provide a means of estimating distribution system THMs from treatment plant measurements. The purpose of the latter model is to provide a means of estimating distribution system THMs from source water precursor measurements. Correlation objectives are presented schematically in Fig. 5. Emphasis is placed on predicting THMs in a distribution system because this location is the best indicator of tap water quality. In addition to model development, model verification and applicability to source water management is also discussed.

### **9.3.1 Data Sets**

Three data sets are employed in this study. The first data set represents high-dose THMFP measurements. The latter data sets represent SDS measurements. Of these, one was developed to simulate chlorine contact time in a treatment plant (3-hour SDS data) and the other was developed to simulate chlorine contact time in a water distribution system (24-hour SDS data).

#### ***High-Dose THMFP Data***

DWR utilizes a high-dose THMFP test to assay precursor levels in Delta waters. Prior to the test, samples are filtered through a 0.45 millipore membrane filter. Filtration has only a minor impact in terms of precursor removal (DWR 1989). Samples are then subjected to a fixed free chlorine dose of 120 mg/L and incubated for a seven day period at 25°C. Finally, the samples

are dechlorinated using sodium thiosulfate and analyzed by the gas chromatograph purge and trap method. DWR found a high chlorine dose to be necessary in meeting demands exerted by agricultural drain samples, waters which tend to contain exceptionally high levels of organic precursors. High chlorine residuals are consistently produced by the THMFP test, suggesting that the precursor assay is independent of chlorine residual (Reckhow and Edzwald 1991). Samples are not buffered to a fixed pH value during the test.

Samples have been collected monthly by DWR from 17 tributaries and channels in the Delta since 1983. Sample locations are shown in Fig. 6. Two of the 17 locations -- Sacramento River at Greene's Landing and Banks Pumping Plant -- are also employed by MWD as SDS sample locations. Therefore, parallel SDS and high-dose THMFP test values are available at these two locations. Parallel data collected between November 1990 and August 1991 are utilized in this study to correlate high-dose THMFP and SDS THM values.

### ***SDS Data***

To study chlorine disinfection by-products formation in their finished waters, MWD is collecting SDS data from the California State Water Project (SWP) and the Colorado River Aqueduct. In developing these data, samples are first jar treated to simulate treatment plant coagulation, flocculation, sedimentation and filtration. Samples are dosed with polymer and alum during jar treatment to minimize effluent turbidity; this chemical dosing also results in a reduction in precursor levels.

After jar treatment, samples are chlorinated and incubated for 3 and 24 hours to simulate contact time in a treatment plant and in a water distribution system, respectively. The 3-hour samples are dosed to maintain a free chlorine residual of approximately 1.0-1.5 mg/L and the 24-hour samples are dosed to maintain a residual of approximately 0.5-1.5 mg/L. Temperature is fixed at 25°C (summer conditions) and pH is buffered at 8.2 for both the 3-hour and 24-hour data sets. Details on MWD's SDS test are provided by Koch et al. (1991).

Forty-seven (47) 3-hour and 24-hour samples were collected between November 1990 and August 1991 at six sites within California. These sites are located in Fig. 7.

### **9.3.2 Correlation Framework**

Three statistical relationships are presented to correlate THM data collected under different reaction conditions. The first statistical relationship, total THM formation, addresses the impact of reaction conditions on precursor oxidation. The second and third statistical relationships, Bromine Incorporation Factor and Bromine Distribution Factors, address the impact of ambient water quality and reaction conditions on THM halogenation. When these relationships are employed within the framework discussed below and diagrammed in Fig. 8, individual THM species formation under one set of reaction conditions may be estimated from the THM formation measured under a different set of conditions.

### **Total THM Formation**

The first statistical relationship employed within the framework is between total THM formations measured under reaction conditions of interest. To develop such a relationship, parallel tests must be performed on the same water sample. Reckhow (1984) observed a proportional relationship between 3-day and 7-day high-dose THMFP concentrations. Reckhow and Edzwald (1991) observed the ratio of low-dose to high-dose THMFP concentrations to vary with precursor concentration. In this study, total molar THM formations were observed to relate proportionally, suggesting a model form:

$$[TTHM]_Y = b[TTHM]_X \dots\dots\dots(11)$$

where  $[TTHM]_Y$  is the total molar concentration under condition "Y" and  $[TTHM]_X$  is the total molar concentration under condition "X". An intercept is excluded from Eq. 11, as  $[TTHM]_Y$  should approach zero as  $[TTHM]_X$  approaches zero. If the objective is to develop a statistical relationship that estimates SDS values from measured THMFP values, the model constant in Eq. 11 would be derived by correlating SDS data (condition "Y") with THMFP data (condition "X"). The magnitude of the model constant is influenced by the relative difference in reaction conditions such as temperature, chlorine dose, pH and reaction time.

### **Bromine Incorporation Factor**

A second relationship, Bromine Incorporation Factor, must be established for the predicted reaction conditions, or condition "Y" following the above convention. Using the same example, if the objective is to develop a statistical relationship that estimates SDS values from measured THMFP values, the relationship must be developed from SDS data.

Gould et al. (1981) defined the Bromine Incorporation Factor,  $\eta$ , as a dimensionless term to describe the aggregate speciation of a given water sample. This term is defined as the molar THM concentration as bromide divided by the total molar THM concentration (see Eq. 1). When  $\eta$  approaches zero, the molar distribution of THM species is predominantly chloroform, the THM compound with zero bromide atoms. When  $\eta$  approaches three, the molar distribution of THM species is predominantly bromoform, the THM compound with three bromide atoms. At intermediate values of  $\eta$ , a balanced distribution of THM compounds is indicated.

Hutton and Chung (1992a) found the Bromine Incorporation Factor to be related to a surrogate bromide:precursor ratio in Sacramento-San Joaquin Delta waters under high-dose THMFP reaction conditions:

$$\eta = \frac{k\alpha}{\beta + \alpha} \dots\dots\dots(12)$$

where:

- k = bromine saturation level = 3
- $\alpha$  =  $[Cl^-]/[THMFP]$  (mM/ $\mu$ M)
- $\beta$  = regression constant = 5.48

This relationship was developed from 2000 high-dose THMFP measurements collected by DWR (1989,1990a,1990b) and verified with data collected under similar reaction conditions. Several empirical model forms were investigated by the authors.

To compensate for limited bromide data (bromide was not measured by DWR until May 1990), a decision was made to employ chloride as a surrogate measure of bromide in modeling the Bromine Incorporation Factor. By employing this surrogate measure, a consistent spatial distribution of chloride and bromide in the Delta is implicitly assumed. The ionic ratio has been observed to be most consistent in the western Delta where tidal influences are important and less consistent in agricultural drains and in the northern Delta where seawater influences are less significant. Agricultural drains and channels in the northern Delta have not generally demonstrated significant bromide effects in THM formation (i.e. low values of  $\alpha$ ), thereby minimizing any potential discrepancies (Hutton and Chung 1992a). Expressing the numerator and denominator of  $\alpha$  in molar units eliminates the bias of comparing THM compounds with different bromine fractions, thereby reflecting the relative amount of bromide and carbon precursor.

### ***Bromine Distribution Factors***

Eqs. 10a-10d were employed in this study to represent the Bromine Distribution Factors. Recalibration was not necessary, as these relationships have been shown to provide consistently good predictions over a wide range of water quality and reaction conditions (see Figs. 2-4).

### **9.3.3 Model Calibration #1: Correlating SDS Data Sets**

The correlation framework presented in Fig. 8 was first applied to develop a model that predicts 24-hour SDS concentrations from 3-hour SDS measurements. Relationships were calibrated for total molar THM formation and Bromine Incorporation Factor. As a preliminary analysis of the model, these relationships were employed in conjunction with Eqs. 10a-10d to predict 24-hour SDS concentrations from the 3-hour SDS calibration data. This analysis is considered to be preliminary because a true model verification should be accomplished with data other than those used for calibration.

### ***Total THM Formation***

Total molar THM formation correlation was excellent between the 3-hour samples and the 24-hour samples. The relationship, determined by linear regression and given in Eq. 13, has a  $r^2$  value of 0.98 (see Fig. 9).

$$[\text{TTHM}]_{24\text{-hr}} = 1.834 [\text{TTHM}]_{3\text{-hr}} \dots\dots\dots (13)$$

As expected, Eq. 13 reflects more oxidation of precursor material to THMs after 24 hours because of longer chlorine contact times. Eq. 13, which is based on 47 observations, suggests that total THM formation nearly doubles with the increased contact time.

## **Bromine Incorporation Factor**

To predict Bromine Incorporation Factor, 24-hour SDS data was fit by nonlinear regression to the model form given in Eq. 14, resulting in a r<sup>2</sup> value of 0.98 (see Fig. 10).

$$\eta = \frac{k}{1 + \beta^* \exp(-\gamma \ln \alpha^*)} \dots\dots\dots(14)$$

where:

$$\alpha^* = [\text{Br-}]/[\text{TTHM}]_{24\text{-hr}} (\mu\text{M}/\mu\text{M})$$

$$\beta^* = \text{regression constant} = 7.69$$

$$\gamma = \text{regression constant} = 1.38$$

In addition to providing a good match to the data, a rational basis exists for selecting this model form. Population growth tends to follow a pattern similar to Eq. 14. Analysis of such growth has revealed that the rate of growth is initially proportional to the size of the population. Later, however, some limiting factor (such as space or food) begins to decelerate growth until a saturation level is reached. Bromine incorporation into THM species can be thought to follow a pattern analogous to population growth, with bromine (HOBr) being analogous to the "population" and organic precursor (THM molecules) being analogous to the "space" or "food". Initially, for a fixed set of reaction conditions and a fixed concentration of precursor material, bromine incorporation is proportional to the natural logarithm of bromide concentration. But as bromination progresses, the number of available molecular reaction sites become limiting. Finally, a saturation level is approached as three bromine atoms are associated with each THM molecule (i.e.  $\eta=k=3$ ).

It is interesting to note that, when  $\gamma=1$ , the model form of Eq. 14 reduces to the model form presented in Eq. 12. Eq. 14 deviates from Eq. 12 in that a) bromide is used instead of a chloride surrogate in the molar ratio, and b) the molar ratio is dimensionless.

## **Preliminary Model Analysis**

Following the steps outlined in Fig. 8, the 3-hour SDS calibration data were employed to predict 24-hour SDS species concentrations. Total molar THM concentrations were transformed from 3-hour values to 24-hour values with Eq. 13. Transformed molar values were used in conjunction with observed molar bromide concentrations to predict  $\eta$  per Eq. 14. Bromine Distribution Factors were then estimated per Eqs. 10a-10d. Finally, individual species concentrations were calculated as the product of the total molar THM concentrations times the respective distribution factors times the respective molar weights.

Results from the preliminary model analysis are presented in Fig. 11 and show predicted versus observed 24-hour SDS species concentrations. The close comparisons between predicted and observed values indicate a good model calibration.

### 9.3.4 Model Calibration #2: Correlating SDS & THMFP Data Sets

Next, the correlation framework was applied to develop a model that predicts 24-hour SDS concentrations from high-dose precursor concentrations, i.e. 7-day THMFP samples. A relationship was calibrated for total molar THM formation but not for  $\eta$ . Eq. 14 serves as a useful relationship for Bromine Incorporation Factor as the objective is to predict 24-hour values. Similar to the previous calibration discussion, a preliminary model analysis is presented.

Total THM Formation. A poorly-defined linear relationship between 24-hr SDS formation and THMFP is given in Eq. 15 and shown in Fig. 12.

$$[\text{TTHM}]_{24\text{-hr}} = 0.197 [\text{THMFP}] \dots\dots\dots(15)$$

Eq. 15, which has a  $r^2$  value of 0.66 and is based on 18 observations, suggests that total molar THM formation under the high-dose THMFP conditions is nearly five times that of the formation under 24-hour SDS conditions. The observed increase is attributed to a longer reaction time and a higher chlorine dose.

Much of the data scatter shown in Fig. 12 is attributed to variation in precursor removal during SDS jar treatment. As suggested by Amy et al. (1987), precursor concentration in the SDS samples can be defined as the product of TOC and UVA, where TOC is related to precursor quantity and UVA is related to precursor reactivity. Fig. 13, which compares model fit to the level of SDS precursor removal, shows that Eq. 15 tends to (1) underpredict 24-hour formation at lower fractions of precursor removal and (2) overpredict 24-hour formation at higher fractions of precursor removal. To account for precursor removal variations in the SDS test, the dependent variable in Eq. 15 was modified such that:

$$[\text{THMFP}]^* = [\text{THMFP}] (1-R)^{-5.42} \dots\dots\dots(16)$$

where R is the precursor removal fraction resulting from SDS jar treatment. Based on observations that THM formation is related to precursor concentration as a power function (Amy et al. 1987), the exponent in Eq. 16 was determined by comparing  $[\text{THMFP}]$  values and raw water precursor values (TOCxUVA) on a log-log plot.  $[\text{THMFP}]^*$  represents the expected high-dose THMFP of a water subjected to precursor removal by jar treatment.

Another linear regression was performed, resulting in the following relationship:

$$[\text{TTHM}]_{24\text{-hr}} = 0.341 [\text{THMFP}]^* \dots\dots\dots(17)$$

Eq. 17, shown in Fig. 14, provides a much better fit to the data and has an  $r^2$  value of 0.89. Eq. 17 suggests that, for the same amount of precursor material, total THM formation increases by a factor of three with increased reaction time and chlorine dose.

Another potential source of data scatter, in addition to precursor removal variation, is pH variation associated with DWR's unbuffered THMFP test. Unfortunately, the impact of pH variation cannot be evaluated at this time as it is not being measured by DWR. Chlorine residual

is another varying factor in DWR's THMFP test. However, observations by Reckhow and Edzwald (1991) suggest that at high chlorine residuals (such as those produced by DWR's test), assay results are independent of chlorine residual. Because Eq. 17 is based on limited sampling, correlation "strength" or "weakness" is not conclusive at this time.

**Preliminary Model Analysis.** Again following the steps outlined in Fig. 8, the THMFP calibration data were employed to predict 24-hour SDS species concentrations. Total molar THM concentrations were transformed from THMFP values to 24-hour values with Eq. 17. Transformed molar values were used in conjunction with observed molar bromide concentrations to predict  $\eta$  per Eq. 14. Bromine Distribution Factors were then estimated per Eqs. 10a-10d. Finally, individual species concentrations were calculated as the product of the total molar THM concentrations times the respective distribution factors times the respective molar weights.

Results from the preliminary model analysis are presented in Fig. 15 and show predicted versus observed 24-hour SDS species concentrations. Again, close comparisons between predicted and observed values indicate a good preliminary model calibration.

### **9.3.5 Model Verification**

Limited data does not permit a thorough model verification at this time. However, three parallel observations provide a hint of the model's effectiveness in predicting 24-hour SDS concentrations from high-dose THMFP measurements. Data on SDS precursor removal is not available for these parallel observations; hence, Eq. 15 is used instead of Eq. 17 to predict total THM formation. Comparisons of model predictions and observed values, which look quite promising, are summarized in Table 1 and are discussed below.

#### ***July 1989 Observations***

In their verification of SDS results with observed distribution system concentrations, Koch et. al. (1991) reported 14-hour and 24-hour SDS values produced by raw influent water to MWD's Jensen Filtration Plant during July 1989. While all four THM species concentrations are reported for the 14-hour sample (see column 4 of Table 1), only a total THM concentration of 145  $\mu\text{g/L}$  is reported for the 24-hour sample. During both observations, influent to the plant was 100 percent SWP water. Banks Pumping Plant supplies the SWP; hence, assuming additional precursor sources to the SWP are negligible, THMFP measurements at Banks represent the precursor load at Jensen. To account for an approximately one year travel and retention time between Banks and Jensen, 12-month average THMFP and bromide values (see column 2) were calculated from observed data to predict SDS concentrations. Predicted 24-hour SDS values, given in column 3 of Table 1, compare favorably with the observed 14-hour values in column 4. The total THM value of 143  $\mu\text{g/L}$  is nearly identical to the reported 24-hour value of 145  $\mu\text{g/L}$ .

#### ***August 1990 Observations***

Parallel THMFP and 20-hour SDS measurements were taken from samples collected at Banks Pumping Plant and Greene's Landing on August 6, 1990. Predicted 24-hour SDS values at Banks, given in column 6, compare reasonably well with observed 20-hour SDS values (see column 7) except for a substantial overprediction of bromoform. Predicted 24-hour SDS values

at Greene's, given in column 9, compare closely with observed 20-hour SDS values (see column 10) except for a substantial overprediction of chloroform. SDS precursor removal may be influential in the differences between predicted and observed values. For example, if precursor removal for the Greene's Landing SDS sample was 77% ( $R = 0.77$ ), the correlation framework would predict SDS values nearly identical to those reported.

### 9.3.6 Application to Source Water Management

Hutton and Chung (1992b) reported the use of mathematical modeling techniques to simulate the fate and movement of THM precursors in the Sacramento-San Joaquin Delta. The authors presented model simulation results in terms of THMFP. While THMFP gives much insight into precursor levels in source waters, it gives only limited insight into typical finished drinking water quality. The framework presented in this paper is well-suited for estimating drinking water THM concentrations from such THMFP model results. Utility of the correlation framework in evaluating source water management alternatives is illustrated with a hypothetical problem defined as follows:

*Due to concerns with THMs in treated water from the Sacramento-San Joaquin Delta, operating strategies are modified and facilities are strategically constructed so that salinity intrusion into the Delta from San Francisco Bay is greatly reduced. The resulting water quality impact is as follows: Br- is reduced from 0.51 mg/L (150 mg/L Cl-) to 0.17 mg/L (50 mg/L Cl-). Precursor loads are not impacted by modified operations and facilities. What incremental improvement in water quality, in terms of THMs, is expected at export locations?*

This hypothetical problem is evaluated at three precursor levels (as measured by high-dose THMFP) for the defined "base" and "plan" conditions. In the first set of calculations, individual THM species are expressed as high-dose THMFP concentrations. In the second set of calculations, the correlation framework is invoked to express individual THM species as SDS 24-hour concentrations.

Fig. 16 summarizes THMFP values calculated for 3 precursor levels under base and plan conditions. The plan condition results in a reduction of total THMFP mass concentration by approximately 10 percent. While chloroform increased by 30 to 60 percent, all bromomethane species decreased dramatically:  $\text{CHCl}_2\text{Br}$  was reduced by 50 to 60 percent,  $\text{CHClBr}_2$  was reduced by 70 percent, and  $\text{CHBr}_3$  was reduced by 90 percent.

Fig. 17 summarizes 24-hour SDS values calculated for the same precursor levels and under the same base and plan conditions. A SDS precursor removal of 60% ( $R = 0.60$ ) is assumed. The plan condition results in a reduction of total THMFP mass concentration by approximately 20 percent. Chloroform increased dramatically by approximately 400 to 900 percent and  $\text{CHCl}_2\text{Br}$  increased by 40 to 200 percent.  $\text{CHClBr}_2$  increased by 10 percent at precursor level "I" and was reduced by 30 to 50 percent at the other precursor levels.  $\text{CHBr}_3$  was reduced by 80 to 90 percent.

This hypothetical problem shows that, even when used within a context of incremental analyses, the statistical relationships are very sensitive to the type of data selected -- SDS or high-dose

THMFP. Fig. 18 compares the incremental variation in results from Figs. 16 and 17, focusing on precursor level "II". While both analyses predict chloroform concentrations to increase under plan conditions, the latter predicts a significantly larger change on a percentage basis. A striking difference also exists between the  $\text{CHCl}_2\text{Br}$  estimates, with THMFP values showing an incremental decrease and SDS values showing an incremental increase. And while both analyses predict  $\text{CHClBr}_2$  and  $\text{CHBr}_3$  concentrations to decrease under plan conditions, the incremental decreases vary. Therefore, to estimate incremental responses in drinking water quality to changes in source water quality even in a qualitative sense, high-dose THMFP data should be transformed into equivalent SDS values.

### **9.3.7 Conclusions**

A mathematical framework that correlates THM data collected under different reaction conditions was presented. The framework was specifically employed to develop two models: one that predicts 24-hour SDS concentrations from 3-hr SDS measurements and one that predicts 24-hour SDS concentrations from high dose THMFP measurements. The purpose of the former model is to provide a means of estimating distribution system THMs from treatment plant measurements. The purpose of the latter model is to provide a means of estimating distribution system THMs from source water precursor measurements. This latter model is particularly important to DWR, as an extensive amount of high-dose THMFP data has been collected in the Sacramento-San Joaquin Delta since 1983. Emphasis is placed on predicting THMs in a distribution system because this location is the best indicator of tap water quality.

Model calibrations and verifications, although generally quite good, are considered to be preliminary because of limited SDS data available for this study. The models will be recalibrated and verified as more data becomes available. The most significant aspect of the calibration exercise is that it shows THM data collected under different reaction conditions can be related mathematically. The preliminary calibration also reveals a need to account for jar treatment precursor removal when comparing SDS measurements with THMFP measurements.

The correlation framework is also shown to be an important link in using high-dose THMFP data to evaluate source water management alternatives. A hypothetical problem illustrates that incremental analysis of alternatives is extremely sensitive to the type of values employed, SDS or THMFP. This finding is particularly important to DWR in its evaluation of management alternatives in the Sacramento-San Joaquin Delta.

## **9.4 Overall Model Framework**

Figure 19 schematically presents the current overall framework in modeling THMFP of Delta waters and in estimating corresponding drinking water THM concentrations. This framework employs the DWR Delta Simulation Model (DWRDSM) to simulate fate and movement of bromide and THM precursors in conjunction with the modified empirical relationships and correlations discussed in this chapter.

## 9.5 References

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