TRIHALOMETHANE FORMATION POTENTIAL IN THE SACRAMENTO-SAN JOAQUIN DELTA MATHEMATICAL MODEL DEVELOPMENT

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The Resources Agency
Department of Water Resources
Division of Planning

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FOREWORD

The Sacramento–San Joaquin Delta is a source of drinking water for 20 million Californians. Formation of disinfection byproducts known as trihalomethanes, or THMs, is promoted by organic matter and bromide salts found in the Delta. Because these disinfection byproducts are a suspected threat to human health when present at sufficient levels, the Environmental Protection Agency has established a standard of 0.1 milligrams per liter for THMs in drinking water.

Two reports covering the Department of Water Resources' Delta THM precursor monitoring program have been previously published. The first is titled *The Delta as a Source of Drinking Water, Monitoring Results, 1983 to 1987*; the second is titled *Delta Island Drainage Investigation Report of the Interagency Health Aspects Monitoring Program, A Summary of Observations During Consecutive Dry Year Conditions, Water Years 1987 and 1988*. Both reports are available from the Department.

This report documents the Division of Planning's first attempt to mathematically describe THM precursors in the Sacramento–San Joaquin Delta. The model developed in this report, designed to simulate fate and movement of THM precursors and to simulate THM formation potential chemistry, will ultimately be used by the Division as a water quality planning tool. The present formulation has two important limitations. First, the model addresses Delta water quality and not tap water quality. This limitation exists because a relationship between THM formation potential and THMs at the consumer's tap has not been clearly defined for Delta water. Second, the model's ability to assess agricultural impacts on Delta water quality is limited by available drainage site data. No conclusion should be drawn from the model results presented in this report as the formulation is still preliminary.

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CHAPTER 1. SUMMARY

Background

A mathematical model is being developed by the Department of Water Resources (DWR) Division of Planning that will simulate the fate and movement of trihalomethane precursors within the Sacramento–San Joaquin Delta and predict trihalomethane formation potential speciation at existing and potential Delta export locations. Past research on trihalomethane formation potential in an estuarine environment is limited; therefore, creative formulations were required for the work reported here.

In 1979, the Environmental Protection Agency established a drinking water standard of 0.1 milligram 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 is that revised THM regulations may necessitate modifications in drinking water treatment processes, modifications in the operation of Delta export facilities, or a combination thereof. Additional studies have been undertaken and documented by DWR for the Interagency Delta Health Aspects Monitoring Program (IDHAMP), which is now under the Municipal Water Quality Investigations (MWQI) program.[1,2,3] These documents provide excellent background and detail on the items discussed in Chapters 2–4.

Purpose and Scope

The model is being developed with the intended purpose of assimilating existing hydrodynamic and water quality data into a tool that can be used in Delta planning studies. The model can be used to perform specific tasks such as:

- quantifying the relative contributions of THM precursors from freshwater inflows, agricultural discharges and tidal influences at existing and potential Delta export locations.
- evaluating incremental benefits of source water management alternatives to control THM precursor concentrations at export locations.
- providing guidance in setting data collection priorities and in determining spatial and temporal distribution of future data collection.

An overview of the model formulation is provided in Chapter 5.

Model Development

To model THM formation potential, it is critical to address both precursor effects and bromide effects. Precursor effects refer to the total amount of THMs that can potentially be produced on a molar basis. Precursor effects are influenced by the organic content of the source water. Precursor effects are also influenced by the established THM formation potential test conditions (e.g., chlorine dose, temperature, reaction time, and pH) and by inorganic sources of chlorine demand. In the model presented in this report, precursor effects are handled through the use of a simulation parameter called the total formation potential carbon (TFPC). Because DWR has established THM formation potential test conditions that are essentially "fixed," differences in TFPC are strongly influenced by differences in organic content between two waters.

Bromide effects, influential in the distribution of THM formation potential species, are handled through the use of a surrogate simulation parameter, chloride, and calculated parameters called the Bromine Incorporation Factor and Bromine Distribution Factors. Under constant test conditions, the Bromine Incorporation Factor is shown to be a nonlinear function of the ratio between chloride and TFPC molar concentrations. Bromine Distribution Factors, which estimate the molar distribution of the four THMFP species in a given water sample, are shown to be functions of the Bromine Incorporation Factor. These relationships were developed from a data base consisting of more than 2000 observations in the Delta between 1983 and 1990.

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An existing numerical hydrodynamics and water constituent transport model is used to mimic the fate and movement of precursor and bromide parameters from the upstream model boundaries to the downstream export locations. Used within the framework developed in this report, the transport model can be used to answer the following generalized question: Given certain precursor and bromide effects at the upstream model boundaries (e.g. Sacramento River at Greene's Landing, San Joaquin River at Vernalis, Bay–Delta interface at Benicia, agricultural drainage locations, and minor fresh water tributary inflows), what are the precursor concentrations, bromide concentrations and the resulting THM formation potential species distributions at Delta export stations? The numerical transport model and development of the overall THM formation potential model framework are discussed in Chapters 6 and 7.

Model Verification

The Bromine Incorporation Factor and Bromine Distribution Factor relationships were verified both internally and with an external data set of 1025 observations. The Bromine Incorporation Factor submodel was verified against a subset of the external data base (64 observations) that more or less represents DWR's THM formation potential test conditions. This data subset has constant reaction times of 168 hours and reaction temperature of 20°C. While the verification shows a good correlation between predicted and observed values, it also indicates that the submodel tends to overpredict at low values of the factor and to underpredict at high values of the factor. The difference in chlorine dose between the external data base and the dose utilized in DWR's test is a likely explanation for the model underprediction at high values of Bromine Incorporation Factor. Variability in other test conditions may also explain some of the deviation between model predictions and observed values.

The Bromine Distribution Factor relationships were verified against the entire external data set. The external data base follows the submodel relationships as well or better than the internal data base. This comparison shows that THM formation potential species distribute in a predictable fashion under varying test conditions. Model verification is presented in Chapter 7.

Model Application

Seven transport simulations were performed to illustrate potential model utility in meeting the following objectives: to quantify individual and cumulative impacts of THM precursor sources at Delta export locations and to simulate bromide effects at Delta export locations. Each simulation assumed historic hydrologic and water quality boundary conditions (July 1988) and each was performed in a steady state mode. Steady state mode was selected to simplify the analysis and was considered to be appropriate for illustrative purposes. Because of this and other simplifying assumptions associated with the simulations, **no conclusions should be drawn from the preliminary model results presented in this report.**

Conceptually, model utility in quantifying precursor impacts and bromide effects in the Delta was illustrated by the simulations. Model results were compared with historically observed values at seven locations in the Delta, including four export locations. Model results compared favorably with observed values at three of the four export stations (Clifton Court Forebay, Delta–Mendota Canal at Tracy Pumping Plant and Contra Costa Canal at Rock Slough). A less favorable model result at North Bay Aqueduct at Lindsey Slough was attributed to an inappropriate water quality boundary condition assignment for the Yolo Bypass. It was observed that agricultural drainage was influential at stations where model deviations were the greatest, thereby highlighting a need to more accurately describe agricultural drainage quality and quantity in the Delta. Model application is presented in Chapter 8.

Future Directions

Future directions in THM formation potential model development are discussed in Chapter 9. Areas identified for future enhancement include but are not limited to: developing an algorithm that describes THM precursor contributions from agricultural drainage; refining boundary conditions at Delta inflow locations; and defining relationships between THM formation potential, as measured in source waters, and THM concentrations in treated drinking water.

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CHAPTER 2. TRIHALOMETHANE FORMATION POTENTIAL

Chemistry of THM Formation

Public drinking water supplies are typically disinfected prior to distribution to consumers. Free chlorination is the predominant method of disinfection in water treatment practice. Although free chlorination provides a water safe from bacteriological contamination, it allows for the formation of several chemical by–products. Trihalomethanes (THMs) are one group of disinfection by–products formed when soluble organics are oxidized by free chlorine. THM compounds include: chloroform ($CHCl_3$), dichlorobromomethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), and bromoform ($CHBr_3$).

During disinfection, molecular chlorine reacts with water by the following reversible reactions:

$$Cl_2(aq) + H_2O \leftrightarrow HOCl + H^+ + Cl^- \quad (2\text{–}1)$$

$$HOCl \leftrightarrow H^+ + OCl^- \quad (2\text{–}2)$$

The relative amounts of hypochlorous acid (HOCl) and hypochlorite (OCl^-) produced in the above reactions are a function of pH. These chlorine species, known as free chlorine, are the disinfecting agents in the chlorination process. Free chlorine reacts with soluble organics to form THM compounds by the following reaction:

$$\text{Organics} + \text{Free Chlorine} \rightarrow \text{THMs} + \text{Other Disinfection By–Products} \quad (2\text{–}3)$$

If bromide is not present, chloroform is the only THM formed. If present, it competes with free chlorine to form brominated THM species, also known as bromomethanes. The chemical mechanism of THM formation in the presence of bromide is discussed in Chapter 4.

THM Regulations: Existing and Proposed

Currently, water utilities must reduce the total concentration of THMs to 0.10 mg/L to meet state and federal drinking water standards. This Maximum Contaminant Level (MCL) was not established strictly on the basis of health effects data but was set as a feasible level for compliance by water utilities. A lower MCL is being considered by the Environmental Protection Agency for human health protection.[1] The THM standard applies to drinking water in the distribution system, not at the source.

THM Formation Potential Test

In 1981 DWR developed a THM Formation Potential (THMFP) test to compare THM producing capacities of different Delta inflows and outflows. The THMFP test requires a high dose of chlorine to meet the chlorine demand of suspended and organic material in the samples and to maintain a chlorine residual during the holding period. While the test conditions do not reflect actual water treatment conditions, the IDHAMP Technical Advisory Group found the procedure acceptable for the purposes of comparing relative levels of THM precursors in Delta waters.[1]

In this procedure, THMFP samples are spiked with a dosage of 120 mg/L of chlorine, a concentration sufficiently high to meet the highest chlorine demand and maintain a residual after incubation at 25°C for seven days. Earlier DWR results showed this high chlorine dose was necessary for meeting the exceptionally high chlorine demand typically found in agricultural drain water samples. pH is not standardized in the test procedure. At the end of the incubation period, samples are dechlorinated and analyzed for THM compounds by the gas chromatograph purge and trap method.

A direct relationship between the THMFP test results and THM production under actual treatment conditions has not yet been developed. However, the amount of THMs formed during normal disinfection is influenced by the amount of precursor materials available. Therefore, a source water with high THMFP is generally indicative of a water that will contain high THM concentrations upon water treatment.

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CHAPTER 3. THM PRECURSORS: ORGANIC MATTER

Characteristics of Organic THM Precursors

As shown in Eq. 2–3, organics are the primary precursor in THM formation. Humic substances are generally considered to be the most important organic THM precursor in natural waters. Humic substances, which include humic and fulvic acids, are an extremely complex and diverse group of organic materials whose structure is not well defined. They are a mixture of poorly biodegradable decomposition products and by–products of natural organic matter produced by both plants and animals.[4] Because of the variability of humic substances, formation of THMs may vary with the different origins and properties of the humic substance.[1]

Channel and Drain Characteristics

Amy et al.[5] concluded that the organic THM precursors in Delta channel and agricultural drain water samples are significantly different in their character and propensity to form THMs. Organic matter in drain water was found to be more reactive and to have greater molecular size than organic matter in channel water in forming THMs. Because of these differences in reactivity and molecular size, concentrating effects of applied water has been discounted as the primary explanation for the high THMFP found in agricultural drains. Soil leaching is considered to be the dominant process that transports organic precursors into the drains.[1]

Delta Island Soil Characteristics

Delta islands are major storage pools of humic substances due to underlying organic soils. Delta soil types have been grouped into three broad classes: mineral, intermediate organic, and peaty organic.[6] All three soil types contain organic matter, with mineral soils the least amount (less than 10 percent) and peaty organic soils the most (50 to 80 percent). The composition and distribution of Delta soils is depicted in Fig. 1. Tests have shown composited Delta mineral and peat soil extracts to have THMFP values in the range of 27,000 μg/kg and 61,000 μg/kg, respectively.[7] This difference between soils indicates that THMFP is related to soil type and water saturation of the island soils.[1]

Conservative Characteristics

Dissolved organics have been observed to behave conservatively in waters with salinity less than 5000 mg/L,[8,9,10,11,12] the range generally found in the Delta. Humic substances, the most reactive organic fraction in forming THMs, are very resistant to natural biological degradation and tend to precipitate from solution only under extremely saline conditions.[13] Organic THM precursors can be treated as conservative constituents in Delta waters not only because of low salinities, but also because of short water residence times. With the exception of a few sloughs, Delta inflows are generally transported to export pumps or out into the bay in a few days or weeks.[1]

Sources of Organic THM Precursors

Delta waters receive organic materials from a variety of sources, including: agricultural drainage, surface runoff, wastewater treatment plant discharges, algal productivity, in–channel soils, levee materials, and riparian vegetation. Organic THM precursor contributions from agricultural drainage is currently under intense study. Results indicate that, in terms of concentration, agricultural drainage is a significant precursor source.[1] Preliminary studies by DWR have shown urban storm water runoff to have THMFP concentrations similar to those of agricultural drains,[2] whereas effluent from wastewater treatment plants does not appear to be a significant source of precursors in the Delta.[1] DWR has recommended that studies be undertaken to determine the impact of algal productivity on THMFP.[3]

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CHAPTER 4. THM PRECURSORS: BROMIDE

Chemistry of Bromomethane Formation

When water containing bromide ion is chlorinated, the bromide is oxidized to hypobromous acid according to the following reaction:

$$Br^- + HOCl \rightarrow HOBr + Cl^- \quad (4\text{-}1)$$

Hypobromous acid competes with free chlorine to produce THMs according to the general reaction:

$$\text{Organics} + HOCl + HOBr \rightarrow \text{THMs} + \text{Other Disinfection By-products} \quad (4\text{-}2)$$

If bromide is absent, chloroform ($CHCl_3$) is the only THM species produced in the above reaction. But if bromide is present during this reaction, the following bromomethanes are also produced: dichlorobromomethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$) and bromoform ($CHBr_3$).

Sources of Bromide

The major sources of bromide in the Delta are from sea water intrusion, agricultural drain discharges, and the San Joaquin River.[2] Connate waters are another source of bromide and may be significant in certain locations of the Delta.[1]

Significance of Bromide In THM Formation

Researchers have shown that molar yields of THMs increase with increasing bromide concentration.[16,17,18] Furthermore, THM speciation has been observed to shift toward the heavier bromomethanes as the concentration of bromide increases.[19] Because the atomic weight of bromine is heavier than that of chlorine (79.91 versus 35.45), the molecular weight of bromomethanes increase in proportion to the number of bromine atoms present: $CHCl_3$ [119.36], $CHCl_2Br$ [163.82], $CHClBr_2$ [208.28], and $CHBr_3$ [252.74]. Therefore, bromide not only increases the extent of THM formation on a molar basis, bromide also increases the extent of THM formation on a molecular weight basis. In addition to these problems, bromomethanes can complicate THM treatment processes and the health risks associated with bromomethanes may be greater than those of chloroform.

Summary of Previous MWQI Data Analyses

DWR has documented a number of observations related to Total Bromomethane Formation Potential (TBFP) based on THM data collected in the Delta.[1,2,3] TBFP was defined as the sum concentration of the three bromomethanes, i.e. $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$.

Electrical Conductivity and TBFP Correlation

Simple linear relationships were investigated between electrical conductivity (EC) and TBFP for channels and drains on a Delta-wide scale. These correlations were poorly defined, with coefficients of determination (r^2) of 0.66 and 0.54, respectively. Linear relationships were also investigated at individual monitoring stations. Correlations varied greatly by location; only three of twelve stations had r^2 values greater than 0.80. Based on these results, DWR concluded that inorganic constituents have a strong effect on TBFP at some stations; however, the use of EC, chloride, or TDS to predict TBFP on a Delta-wide scale is not appropriate because of poor correlation. It has been suggested that a multivariate analysis would reveal stronger relationships between EC and TBFP in the Delta.[20]

Bromide and Chloride Correlation

Because typical concentrations of bromide and chloride in open ocean water are about 65 mg/L and 19,000 mg/L, respectively,[4] the following relationship would be expected based solely on sea water intrusion:

THM	= THM concentration, μM
Br^-	= bromide concentration, mg/L
Cl_2	= chlorine dose, mg/L
T	= temperature, °C
TOC	= nonvolatile total organic carbon, mg/L
b_0,b_1,b_2,b_3,b_4,b_5	= model coefficients

Amy et al.[28] applied the Morrow and Minear model to additional data sets. Amy, Chadik, and Chowdhury[29] studied the effect of chlorination on nine natural waters located throughout the United States. From a set of 995 observations, the following multiple regression model was developed:

$$THM = b_o (UVA \times TOC)^{b_1} (Cl_2)^{b_2} (t)^{b_3} (T)^{b_4} (pH-2.6)^{b_5} (Br^- + 1)^{b_6} \quad (5\text{-}3)$$

Where:

THM	= THM concentration, μM
UVA	= absorbance of ultraviolet light at a wavelength of 254 nm, cm^{-1}
TOC	= total organic carbon, mg/L
Cl_2	= chlorine dose, mg/L
t	= reaction time, hrs
T	= temperature, °C
Br^-	= bromide concentration, mg/L
$b_0,b_1,b_2,b_3,b_4,b_5,b_6$	= model coefficients

The authors investigated a number of potential organic precursor parameters, including: TOC, UVA, relative fluorescence, and color. Statistically, the best overall organic precursor parameter for predicting THM was the multiple term (UVA x TOC). The chemical significance of this term is that TOC defines the precursor concentration while UVA defines the precursor reactivity in forming THMs.

Regression analysis indicted that THM formation theoretically commenced at pH 2.6 for the nine waters studied, therefore the parameter (pH -2.6) was utilized. Urano et al[26] found that chloroform formation commenced at pH 2.8. Natural bromide concentrations ranged from 0.010 - 0.245 mg/L; however, samples were spiked to increase the maximum value to 1.245 mg/L. The authors indicated that the bromide term can be deleted from the model with only a small loss of predictive accuracy. Other THM models have also been proposed.[30,31,32]

Past research on THM formation potential in estuarine or bromide-rich environments is limited. As a result, many of the previous modeling efforts do not consider bromide effects in THM formation and speciation. Also, as revealed in the literature, a typical objective of existing models is to evaluate finished water management alternatives through the description of THM reaction kinetics. Because this study is concerned with evaluating source water management alternatives in a bromide-rich environment, site-specific data and innovative formulations were essential in developing a model of the Sacramento-San Joaquin Delta to simulate raw water THM formation potential and speciation.

Conceptual Framework

The THMFP model is conceptually divided into two main components, 1) simulation of THM precursor transport and 2) simulation of THMFP species distribution. These components are addressed in detail in Chapters 6 and 7.

Fig. 2 illustrates the model flow logic and interaction between each model component. The purpose of the transport component is to determine THM precursor concentrations at existing and proposed export stations from known boundary conditions. Boundary conditions (transport model inputs) are denoted in the figure by a "B." Export water qualities (transport model outputs) are denoted in the figure by a "E." The objective of the THMFP distribution simulation component is to estimate concentrations of $CHCl_3$, $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$ that

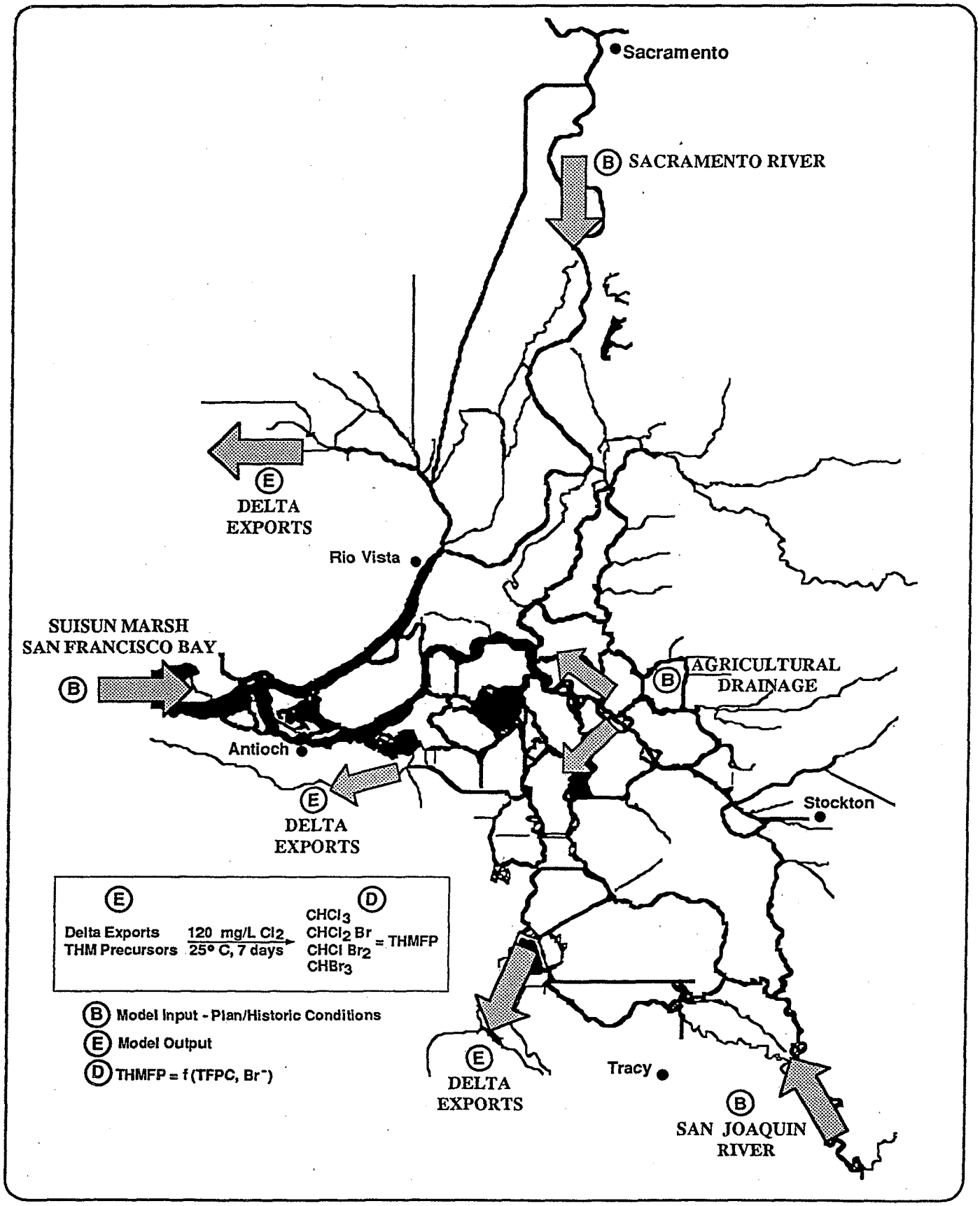

Figure 2. Model Boundary Conditions and Output

would be produced by a water sample under DWR's test conditions, assuming export water quality determined in the transport component. Simulation of THMFP species distribution is denoted by a "D" in Fig. 2. For example, given certain precursor concentrations at the model boundaries (e.g., Sacramento River at Greene's Landing, San Joaquin River at Vernalis, Bay–Delta interface at Benicia, agricultural drainage locations), what are the precursor concentrations and resulting THMFP species distributions at Delta export stations?

Parameter Selection

To model THMFP, it is critical to address both precursor effects and bromide effects. Precursor effects influence the total amount of THMs that are produced on a molar basis. Precursor effects are related to the organic content of the source water and are also related to the conditions established for the THMFP test. Bromide effects are influential in the distribution of species formed in the THMFP test. Bromide effects are related to ambient bromide concentration, organic content, and to established THMFP test conditions. Therefore, to model THMFP, parameters must be selected to represent organics, bromide, and THMFP test conditions.

Precursor Effects

Chlorine dose, reaction time, temperature and pH are identified in Eq. 5-3 as important parameters that describe precursor effects related to THMFP test conditions. Chlorine residual, another important parameter, was maintained relatively constant by Amy et al.[29] with a 3:1 chlorine to TOC ratio. Because chlorine dose, reaction time and temperature are "fixed" in DWR's THMFP test, it was not necessary to explicitly include these parameters in a description of precursor effects. Chlorine residual and pH, on the other hand, are allowed to vary in DWR's THMFP test. But as data is not generally available for these remaining test condition parameters (chlorine residual data has been collected in recent years), chlorine residual and pH were also excluded from a precursor effects description.

TOC is identified in Eq. 5-3 and generally throughout the literature as an important parameter that describes precursor effects related to organic matter. If all natural organic matter readily reacted with free chlorine to form THMs, then TOC or dissolved organic carbon (DOC) would be direct indicators of organic THM precursors. Not all organic compounds found in water are THM precursors, however. Good correlations have been obtained between TOC and DOC and THMFP for single water sources,[5,15,33,34] but when waters from different sources are included in a single comparison, the correlations are sometimes not as good.[35] This is because TOC and DOC tend to contain variable mixtures of organic matter that are active in forming THMs, the mixture being dependent on the source's particular watershed characteristics.

DWR has found very few clearly defined relationships between TOC or DOC and THMFP in Delta source waters. Figs. 3 and 4 illustrate the poor correlations in the Sacramento River at Greene's Landing and in the San Joaquin River at Vernalis. Elimination of a few outlying points does not improve the relationships significantly. Removing four outliers at Greene's Landing (Fig. 3) increases the r^2 value to 0.35. Removing one outlier at Vernalis (Fig. 4) increases the r^2 value to 0.17.

Specific formation potentials are nearly identical for the two Delta tributaries. The average specific THMFP at Greene's Landing is 133 μg/mg TOC; the average specific THMFP at Vernalis is 131 μg/mg TOC. Individual values at both locations are highly variable, however, with standard deviations of 57 μg/mg at Greene's Landing and 51 μg/mg at Vernalis. Reckhow and Singer[35] reported an average specific THMFP of 52 μg/mg TOC from seven different water sources. Differences in THMFP test conditions probably account for the discrepancy between the values reported by the researchers and DWR. The researchers utilized 20–60 mg/L chlorine doses and a three day reaction time, compared with a 120 mg/L chlorine dose and seven day reaction time utilized by DWR. Neither TOC nor DOC was selected as a surrogate measure of precursor effects in the Delta because of the poor correlations discussed above.

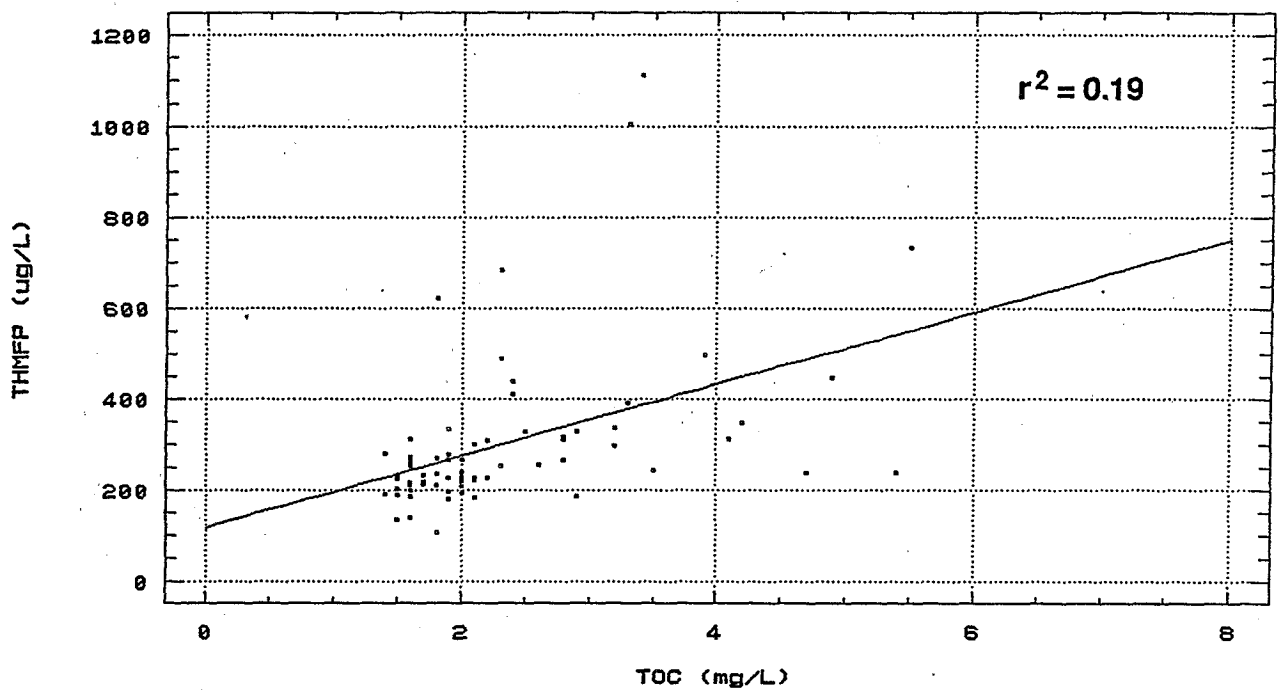

Figure 3. THMFP versus TOC at Greene's Landing

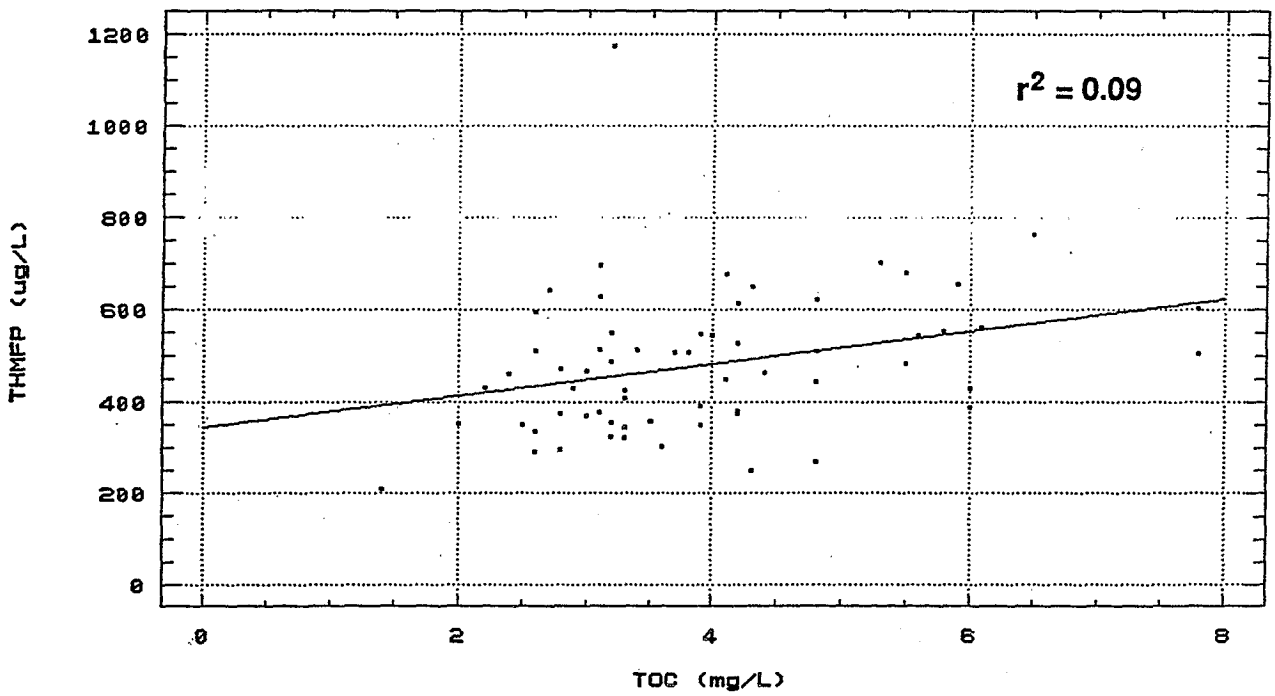

Figure 4. THMFP versus TOC at Vernalis

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UVA is also identified in Eq. 5-3 and elsewhere in the literature[15,33] as an indicator of organic THM precursors. UVA measurements permit the concentration of high molecular weight molecules (e.g. humic and fulvic acids) to be assessed in a semiquantitative fashion. In this way, UVA is more selective for THM precursors than is TOC or DOC.[36] UVA was not measured under the MWQI program until May 1990 and therefore was not selected as a surrogate measure of precursor effects in the Delta.

Research has shown that molar yields of THMs increase with increasing bromide concentration.[16,17,18] However, Amy et al. found molar THMFP to be relatively insensitive to bromide concentration.[29] Therefore, bromide was not selected as a parameter to describe precursor effects.

Given the above limitations of surrogate measures and given the overall model objectives, the TFPC parameter was selected to simulate precursor effects in the Delta. Variation in TFPC is strongly indicative of differences in the organic content and organic reactivity of Delta waters, as DWR's THMFP test conditions are essentially "fixed." (Granted, differences in pH and chlorine residual may also contribute to varying TFPC values.) TFPC provides a single common basis for quantifying the precursor effects in various source waters. In contrast, utilizing TOC, UVA, or a product of the two parameters to represent organic precursors requires a more sophisticated model framework. Specifically, it would be necessary to model the fate and movement of additional water quality parameters that describe the chlorine demand and activity of each source water. And even if strong multivariate relationships were established, such a model would be much more complex to develop and calibrate. Furthermore, the data required to develop and calibrate such a model is not currently available in sufficient quantities on a Delta-wide basis.

The TFPC parameter is calculated directly from measured THMFP data as follows:

- Divide the mass concentration of each THMFP compound by its respective molecular weight and sum the four concentrations to yield a molar concentration of THMFP. Since the molar ratio of THMFP to TFPC is 1:1, this value is also the molar concentration of TFPC.
- To obtain a mass concentration of TFPC, multiply the molar concentration by 12, the atomic weight of carbon.

Bromide Effects

Bromide was not measured under the MWQI program until May 1990 and available data is limited. Therefore, a decision was made to utilize chloride as a surrogate measure of bromide in the Delta. By using chloride as a representative parameter of bromide effects, the model formulation implicitly assumes the ratio between these ions is consistent throughout the Delta. The ionic ratio has been observed to be most consistent in the western Delta and less consistent in agricultural drains and in the interior Delta where seawater intrusion is insignificant. Fortunately, these latter areas have not generally demonstrated significant bromide effects (because of low ionic concentrations and or high precursor concentrations), thereby minimizing any potential discrepancies. Modeling bromide effects is discussed at length in Chapter 7.

Assumptions

Several key assumptions were made in developing the THMFP model formulation. These assumptions are outlined below:

1. Precursor effects in the Delta can be simulated through the use of the TFPC parameter. Bromide effects can be simulated with a surrogate measure of bromide—chloride. The rationale for these assumptions is given in the above section, "Parameter Selection."

2. Precursor and bromide effects are known at the model boundaries, i.e. TFPC and chloride concentrations are specified as boundary conditions. Model boundaries include:

- Sacramento River at I Street Bridge. Water quality at this boundary is assumed to be identical with observed values at Greene's Landing.

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- San Joaquin River at Vernalis
- Cosumnes River
- Mokelumne River
- Yolo Bypass
- Other miscellaneous rivers and streams tributary to the Delta
- Bay–Delta interface at Benicia
- Agricultural drain sites

3. Fate and movement of TFPC and chloride within the Delta can be modeled with conservative constituent assumptions. The rationale for this assumption is discussed in Chapter 3.

4. Precursor effects are dependent only on the fate and movement of TFPC specified at model boundaries. Bromide effects are dependent on interactions between chloride (i.e. bromide) and TFPC at individual locations.

Limitations

Limitations of the THMFP model formulation are as follows:

1. A lack of flow and water quality data limits the ability of the model to assess TFPC contributions from agricultural drainage. DWR previously recommended an expansion of the MWQI monitoring program to include a larger number of Delta island drains.[1] Enhancing the boundary condition description at agricultural drains, as discussed in Chapter 9, will require additional data.

2. TFPC cannot be estimated a priori to predict THMFP; it must be calculated from historical THMFP measurements. Therefore, TFPC cannot be used as a parameter to model THMFP in a predictive or real–time operations mode. However, with adequate historical data at boundary conditions, TFPC can be used as a simulation parameter to model THMFP in a historical or planning mode. This limitation is not critical because the THMFP model was designed as a planning tool with which various planning alternatives can be evaluated in an incremental, or comparative manner. Establishing multivariate relationships between TFPC and directly measurable water quality parameters to describe freshwater and Bay–Delta boundary conditions would permit the model to be used in a predictive mode. This potential model enhancement is identified as an area of future research and is discussed further in Chapter 9.

3. Correlations have not been developed between DWR's THMFP data and THM formation in a water treatment system. The THMFP test conditions skew both the total and distribution of THMs formed relative to typical water treatment conditions, producing more total THMs but smaller fractions of bromomethanes. While this fact limits the model's applicability, the lack of an established correlation does not prohibit the model from being used for its intended purpose because a) source waters with high THMFPs tend to indicate waters that will produce high THMs during water treatment, and b) the model evaluates source water management alternatives, not treatment alternatives. Singer[37] offered the following limitations generally associated with THMFP tests:

> *The principal limitation in the use of the THMFP concept is that it is not intended to be used as a predictive device for determining the concentration of THMs reaching the consumers' tap. It is a measure of the precursor content of a given water....Nevertheless, it may be possible for a utility to develop its own predictive model provided a suitable data base can be established for the specific treatment and hydraulic conditions for that utility.*

Developing correlations between raw water THMFP and finished water THMs was previously identified as an area of future research[1,38] and is discussed further in Chapter 9.

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CHAPTER 6. MODELING FATE AND MOVEMENT OF THM PRECURSORS

DWR Delta Simulation Model

DWR has developed a numerical model to simulate hydrodynamics and water quality within the Sacramento–San Joaquin Delta. The model, called DWR Delta Simulation Model (DWRDSM), simulates flow, stage, velocity, and conservative water constituents at various locations in the Delta for a given hydrology and channel geometry. DWRDSM is an enhanced version of the Fisher Delta Model.[39,40] Solution schemes employed by the model are the Method of Characteristics and the Lagrangian Method for hydrodynamics and water quality, respectively. The model includes approximately 500 nodes, 600 channels and 13 open reservoirs or lakes. Fig. 5 shows a network representation of the Sacramento–San Joaquin Delta as used in DWRDSM. To simulate Delta hydrodynamics, flows are specified at the upstream boundaries and tidal stages are specified at the downstream boundary (Benicia). Export pumping demands and Delta consumptive use are also specified. To simulate water quality, concentrations are specified at all boundaries.

The transport model has been used by DWR to quantify the effects of levee breaks, changes in net flow, changes in agricultural discharges, waste discharge spreading, installation of salinity control structures, dredging and/or diking of levees, and changes in the size and location of forebays. The model has also been used to examine the effects of various operational schemes of the major water facilities in the Delta.

Flow and constituent transport in the Delta is a nonlinear function of a multitude of variables, including but not limited to: hydrology, channel geometry and roughness, tidal forcing, water project operations, agricultural water use, wind, barometric pressure, and density gradients. A number of simplifying assumptions are required to numerically describe the gross circulation and transport processes associated with this complex system within practical data and computational constraints.

DWRDSM Hydrodynamics

Delta hydrodynamics is described by governing equations for long wave, non–uniform unsteady flows in prismatic channels. Coupled with continuity equations, these governing equations are solved numerically for flow, stage and velocity at discrete locations. The fundamental assumptions made in deriving the governing equations are:

1. Flow is assumed to be one dimensional. Therefore, channel velocities are assumed to be uniform over each cross–section and the free surface is assumed to be horizontal across the section. This assumption implies that centrifugal effects due to channel curvature and Coriolis effects are negligible.

2. Pressure is assumed to be hydrostatic, i.e., vertical acceleration is neglected and fluid density is assumed to be homogeneous.

3. For each channel, turbulence and boundary friction are assumed to be approximated by an empirical friction factor, Manning's roughness coefficient. Manning's coefficients are utilized as calibration parameters in the numerical model.

DWRDSM Water Quality

The fate and movement of water quality constituents is assumed to be adequately explained by two distinct processes: advection and dispersion. Advection is largely dependent on flow velocities, which are determined by model hydrodynamics. Dispersion is modeled by assuming that the turbulent mass flux can be expressed as a weighted function of the horizontal concentration gradient in a channel. This weighting function is called the dispersion coefficient. Dispersion coefficients are utilized as calibration parameters in the numerical model.

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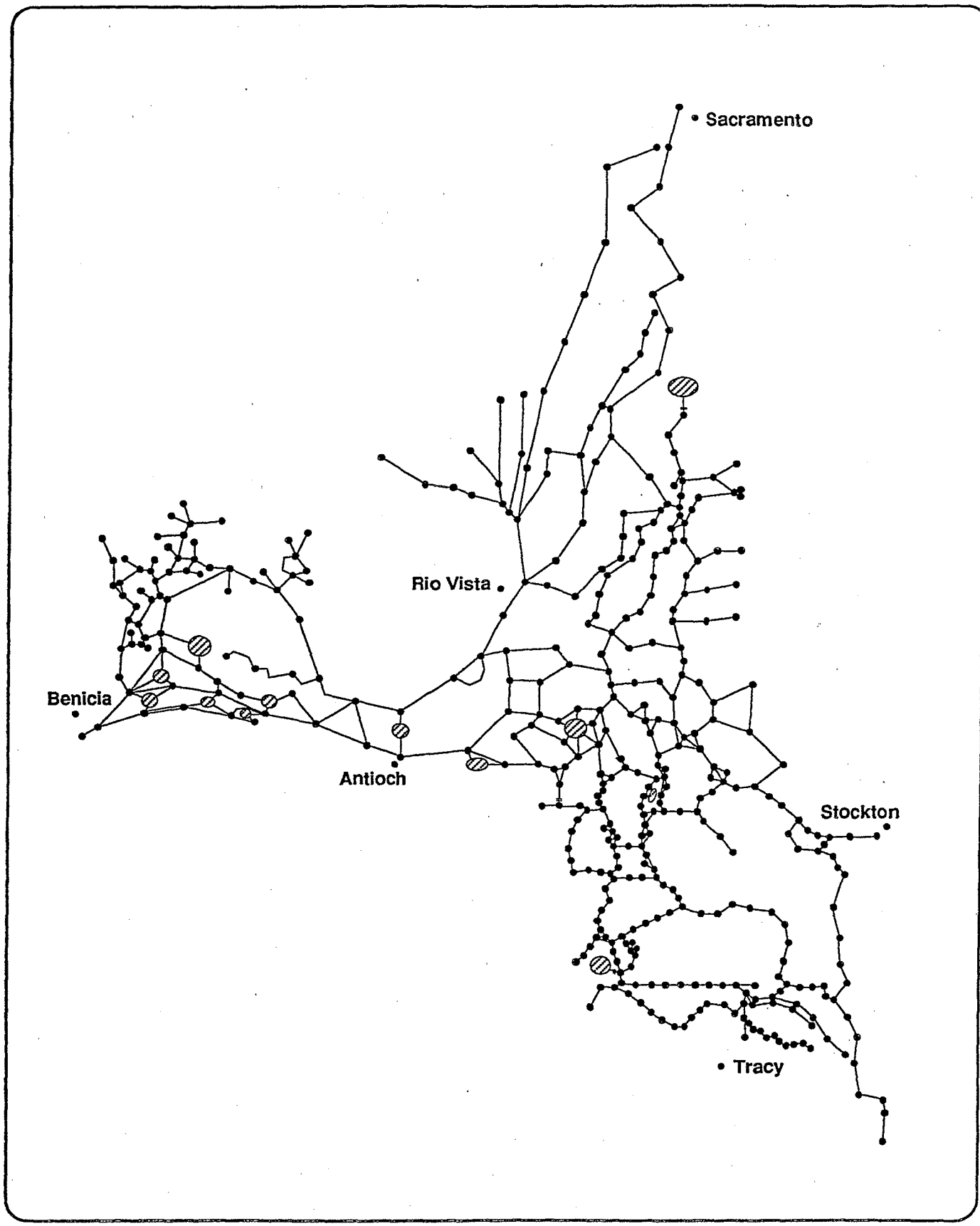

Figure 5. DWRDSM Delta Model Grid

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DWRDSM Calibration

The numerical model is calibrated with Delta 21field data to increase the accuracy of model output. DWRDSM hydrodynamics is calibrated by adjusting the values of Manning's roughness coefficient for each channel. DWRDSM water quality is calibrated by adjusting the values of the dispersion coefficient for each channel. The objective of the calibration is to reduce the differences between observed and calculated stage (for hydrodynamics) and between observed and calculated total dissolved solids concentration (for water quality). Two different methods are used to calibrate DWRDSM: a hand adjustment method and an automated method.[41] For the model runs described in Chapter 8, coefficients were calculated with the hand adjustment method using 1968 calendar year TDS data and May 1988 stage data.

Hand Adjustment Method

In the hand adjustment method, an initial model run is made with the calibration coefficients unadjusted, thereby establishing a base case. Runs are then made to adjust single channels or groups of channels. After each run, the difference between calculated and observed results are examined, either by means of plots or by mathematical measures of error such as root–mean–square (RMS). The coefficients are adjusted appropriately and another run is made. This procedure is repeated until a goodness–of–fit criterion is satisfied, a criterion ultimately determined by engineering judgement. The hand adjustment method has the advantage of utilizing knowledge of the system to efficiently select which channels to adjust and by how much. Examination of intermediate and final results with plots can lead to more insight than simply comparing a single, overall RMS value.

Automated Method

In the automated procedure, DWRDSM is automatically run by an algorithm called the Parameter Estimation Program (PEP).[42] After running the model, PEP examines the results, adjusts the calibration coefficients, and repeats the model run until a predetermined goodness–of–fit criterion is met. The advantages of the automated method are 1) once established, the calibration requires little manual intervention, 2) many small groups of channels can be calibrated as easily as a few large groups, resulting in a finer calibration, 3) calibrations can be easily revised, and 4) a consistent and objective calibration is achieved.

Different types of automated calibration methods are described below:

- **Normal & Amplitude Methods** — In the normal method, the RMS of the computed values minus the observed values is the objective function to be minimized. In the amplitude method, a sinusoidal curve(s) is fit to both the observed and calculated data. The difference between the sine curve amplitudes is then minimized. The amplitude method tends to remove datum errors and tends to avoid warping the calibration, a common result of trying to adjust for slight differences in phase between measured and computed data.
- **Unweighted & Weighted Methods** — In the unweighted method, measured and computed values (from either the normal or amplitude methods) are used without adjustment. In the weighted method, values are adjusted before the RMS error is computed, giving equal weight to monitoring station with low values as stations with large values. This weighting adjustment normalizes the values so that small values have the same influence in the calibration as large values.

Fate and Movement of THM Precursors with DWRDSM

The DWRDSM water quality component is calibrated to simulate the dispersion of total dissolved solids, a conservative constituent. Theoretically, the calibrated model should be able to simulate the transport of any conservative constituent. In accordance with theory, the model has been used successfully by DWR to study the fate and movement of chloride, another conservative constituent, with the same calibration coefficients. As discussed in Chapter 5, the THMFP model formulation requires DWRDSM to simulate the conservative transport of model parameters (TFPC and chloride) from boundary locations to Delta export locations.

Modes of DWRDSM Application

DWRDSM has generally been applied under one of three modes of operation: steady state incremental analysis, multi-year time series incremental analysis, and predictive or real time analysis.[41] A simple yet widely used application of planning models is the steady state incremental approach. Two steps characterize the steady state incremental approach as applied to DWRDSM:

1. DWRDSM is run for a well-understood "base condition" that incorporates existing Delta facilities and operations along with stream inflows representative of a year-type and season of interest. Assuming a tidal forcing function (typically a 19-year mean tide), the model is run until the hydrodynamics and water quality in the Delta do not change in a daily average sense. Steady state model output includes stage, velocity, flow and water quality.

2. The proposed structural or operational change is incorporated into the base condition model geometry, boundary conditions, or operations schedule. All other conditions are identical to the base condition. The results of this "plan condition" are compared with those of the base condition and the incremental differences are determined.

DWRDSM can also be operated in a time series incremental mode for multiple years. Similar to the steady state incremental mode, this application requires defined "base" and "plan" conditions. Outputs from DWR's statewide water operations model DWRSIM[43] can be used as input to the model when operated in time series incremental mode. DWRSIM output includes 57 years of monthly varying Delta export pumping, Sacramento River, San Joaquin River and miscellaneous stream inflows, and net Delta outflow to Suisun Bay. Time series output from base and plan conditions are compared to determine incremental differences.

Although DWRDSM is rigorously calibrated and verified against observed hydrodynamic and water quality data, use of absolute values from the model to predict impacts of structural or operational changes is not a prudent use of a planning model. Reliance on absolute values should be confined to simulating historic conditions and for model calibration and verification, given the uncertainties associated with prototype geometry, boundary conditions and mixing characteristics.

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CHAPTER 7. MODELING BROMINE INCORPORATION IN THM SPECIES

Purpose

Chapter 6 presents an existing numerical model, DWRDSM, as a tool to simulate the fate and movement of THM precursors in the Sacramento–San Joaquin Delta. The observations discussed in Chapter 4 make it clear that precursor transport alone does not completely describe the THM formation problem, but that aspects of THMFP chemistry must also be addressed, particularly the competition between HOCl and HOBr. Therefore, a complete model must also describe the interaction of organics and bromide in the presence of free chlorine to form chloroform and bromomethanes. Bromomethanes are significant relative to pure chloroform in that they exacerbate the problem of meeting THM standards, they are more complicated to control during water treatment, and they pose a potentially greater health risk. This chapter develops empirical relationships to characterize the distribution of THMFP species formed in the presence of free chlorine as a function of TFPC and chloride.

Bromine Incorporation Factor

Gould et al.[44] defined a term called the Bromine Incorporation Factor, η, to simplify management of THM data for a given water sample. The term consolidates all observed THM species into a single composite having the molecular formula $CHCl_{3-N}Br_N$, where N is the number of bromide atoms. Eq. 7–1 in Fig. 6 defines the term mathematically. Fig. 6 further illustrates the term with an example calculation using August 1988 data collected at Clifton Court Forebay.

The Bromine Incorporation Factor has a simple intuitive appeal. When η approaches zero, the molar distribution of THM species in a water sample is predominantly chloroform, the THM with zero bromide atoms. When η approaches three, the molar distribution of THM species in a water sample is predominantly bromoform, the THM with three bromide atoms. At intermediate values of η, a balanced molar distribution of THM species is indicated.

Further inspection of the mathematical definition reveals that the numerator is equivalent to the molar concentration of THMFP as bromide and the denominator is equivalent to the molar concentration of THMFP. But since the molar ratio of THMFP to TFPC is 1:1, the denominator is also equivalent to TFPC molar concentration. Therefore:

$$\eta = \frac{[THMFP - Br]}{[TFPC]} \qquad (7\text{–}2)$$

where:

η = Bromine Incorporation Factor

[THMFP–Br] = Bromine incorporated in THM species, μM

[TFPC] = Total Formation Potential Carbon, μM

Effects of Initial Conditions

Gould et al.[44] tested the effects of several water quality parameters on Bromine Incorporation Factor. The parameters tested were bromide concentration, pH, free chlorine (HOCl) dose, organic precursor concentration, and reaction time.

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$$\eta = \frac{\sum_{N=0}^{3} N \times [CHCl_{(3-N)}Br_N]}{\sum_{N=0}^{3} [CHCl_{(3-N)}Br_N]} \quad \text{..... (7-1)}$$

where:

η = Bromine Incorporation Factor, $0 \leq \eta \leq 3$

N = Number of Bromide atoms in THM species
(i.e. N = 0 for Chloroform; N = 3 for Bromoform)

EXAMPLE CALCULATION
August 1988 - Clifton Court Forebay

Given:

$[CHCl_3]$ = 230 µg/L = 1.93 µM
$[CHCl_2Br]$ = 120 µg/L = 0.73 µM
$[CHClBr_2]$ = 89 µg/L = 0.43 µM
$[CHBr_3]$ = 15 µg/L = 0.06 µM
THMFP = 230 + 120 + 89 + 15 = 454 µg/L

Calculation:

$$\eta = \frac{0(1.93)+1(0.73)+2(0.43)+3(0.06)}{1.93+0.73+0.43+0.06} = 0.56$$

Figure 6. Bromine Incorporation Factor: Mathematical Definition

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Bromine Incorporation Factor was observed to increase linearly with bromide at low concentrations of bromide. The relationship was observed to become asymptotic as η approached a maximum value at higher concentrations of bromide. Others[19,31,45] have also observed a shift toward more heavily brominated THM forms as the concentration of bromide increases. This relationship is believed to be due to the faster rate of bromine substitution reactions relative to chlorine substitution.[19]

At low bromide concentrations, a linear decrease in η was observed with increasing pH. At higher bromide concentrations, η increased moderately up to a pH of 8 and decreased moderately above pH 8. They concluded that bromine incorporation is more extensive at lower pH values and low bromide concentrations. They also concluded that the sensitivity of η to pH is modest at high bromide concentrations.

Bromine Incorporation Factor was observed to decrease with increased free chlorine dose at both low (0.4 mg/L) and high (4 mg/L) bromide concentrations. This relationship was also observed by the Metropolitan Water District of Southern California[46] at their Live Oak Reservoir, a storage facility receiving 100 percent SWP water. Bromine Incorporation Factor was also observed to decrease with increased organic precursor concentrations. This response was observed by others[19,31] and reflects a decrease in the bromide to precursor ratio. Finally, η was found to vary little with reaction time. Rebun et al.[45] also observed the same relationship.

Submodel Development

The strategy employed to model Bromine Incorporation Factor involved several sequential steps: 1) identifying important variables for which data was available, 2) analyzing data by regression analysis, and 3) selecting an appropriate submodel form. Both Delta channel and agricultural drainage data were utilized for submodel development.

Gould et al.[44] found bromide effects were influenced by ambient bromide concentration, organic content and certain established THM test conditions (i.e. chlorine dose and pH). Sensitivity of η to temperature and chlorine residual was not tested, and η was observed to be insensitive to reaction time.

Bromide was not measured under the MWQI program prior to May 1990; hence, a relationship between η and bromide could not be thoroughly investigated for Delta waters. As discussed in Chapter 5, a decision was made to utilize chloride as a surrogate measure of bromide in the Delta. Chloride was then identified as an important parameter in the Bromine Incorporation Factor submodel.

As discussed in Chapter 5, the TFPC parameter represents precursor effects associated with organic content and established THMFP test conditions. TFPC was also shown to be a component of the Bromine Incorporation Factor's mathematical definition in Eq. 7-2. Therefore, TFPC was also identified as an important parameter in the Bromine Incorporation Factor submodel.

Many of DWR's THMFP test conditions are "fixed," thereby reducing the number of parameters that contribute to variations in TFPC. Variable test conditions include pH and chlorine residual. Because these conditions are influential in bromine incorporation, some level of submodel error should be expected from the exclusion of these parameters (data is not generally available for these parameters, although chlorine residual data has been collected in recent years).

Fig. 7 shows the relationship between η and chloride as observed in over 2000 samples collected in the Delta between calendar years 1983 and 1990. All channel and agricultural drain samples collected for the MWQI program that included THMFP and chloride measurements and were not extreme outliers are shown. The relationship is identical to that reported by Gould et al.[44] for bromide. Because both chloride and TFPC were identified as potential variables in describing η, much of the data scatter in Fig. 7 is attributed to variation in TFPC.

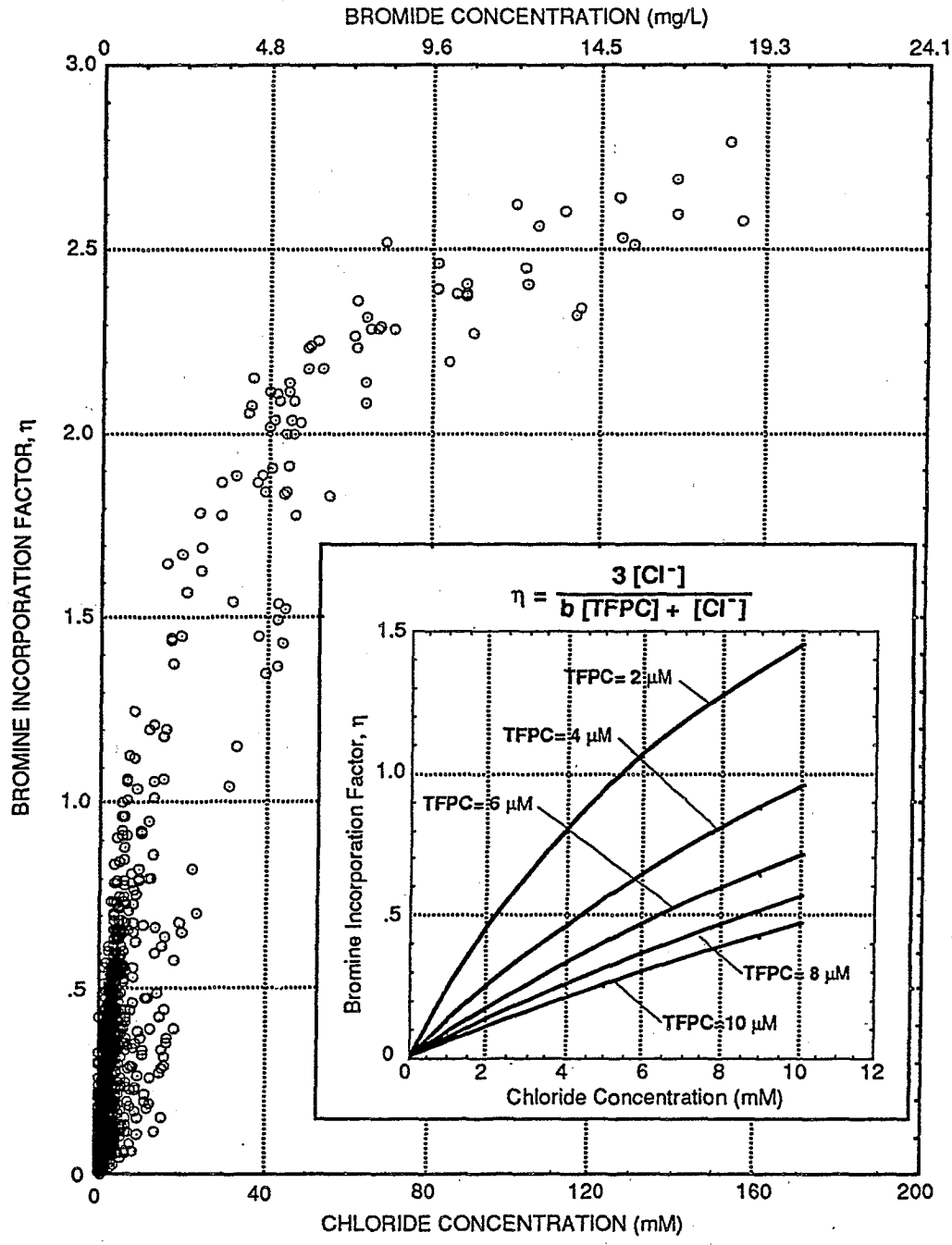

Figure 7. Bromine Incorporation Factor: MWQI Monitoring Data

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The 2000 samples were initially segregated into smaller data sets to screen Bromine Incorporation Factor submodel forms. Four data sets were defined by TFPC interval: 0–3 μM, 3–5 μM, 5–10 μM, and greater than 10 μM. Table 1 summarizes results of the regression analyses, including sample number (n), best-fit constants (a,b), coefficients of determination, (r^2), sum-of-squares error (SSE), and standard error of estimate (SEE). Many submodel forms were screened; four nonlinear forms are reported in Table 1. Submodel #1, a function of molar chloride concentration, is similar to the model proposed by Gould et al.[44] Molar chloride concentration is determined by dividing the mass concentration (e.g. mg/L) by its molecular weight of 35.45. Submodel #2 is a function of the same variable. Submodel #3, a function of both molar chloride and molar TFPC concentrations, mimics the mathematical definition of Bromine Incorporation Factor given in Eq. 7–1. Submodel #4 is also a function of chloride and TFPC. Fig. 8 shows best-fit curves for submodel 1–4 superimposed on the 3–5 μM TFPC data set.

Table 1. Initial Screening: Bromine Incorporation Factor Submodels

TFPC (μM)	n	Submodel Number	a	b	r^2	SSE	SEE
0–3	525	#1	.243	.552	.92	5.00	0.098
		#2	2.770	14.187	.96	2.68	0.071
		#3	.098	—	.58	25.49	0.220
		#4	.454	.168	.93	4.23	0.090
3–5	681	#1	.226	.528	.93	12.12	0.133
		#2	2.947	19.940	.97	4.82	0.084
		#3	.103	—	.56	78.44	0.339
		#4	.578	.196	.97	4.75	0.084
5–10	455	#1	.106	.738	.94	6.40	0.119
		#2	4.100	55.333	.95	5.52	0.110
		#3	.238	—	.82	17.51	0.196
		#4	.526	.144	.94	5.81	0.113
> 10	363	#1	.035	.919	.82	2.83	0.088
		#2	9.646	313.946	.83	2.67	0.086
		#3	.286	—	.73	4.32	0.109
		#4	.564	.134	.88	1.88	0.072

Submodel #1: $\eta = a[Cl^-]^b$

Submodel #2: $\eta = \dfrac{a[Cl^-]}{b + [Cl^-]}$

Submodel #3: $\eta = \dfrac{a[Cl^-]}{[TFPC]}$

Submodel #4: $\eta = \dfrac{a[Cl^-]}{[TFPC] + b[Cl^-]}$

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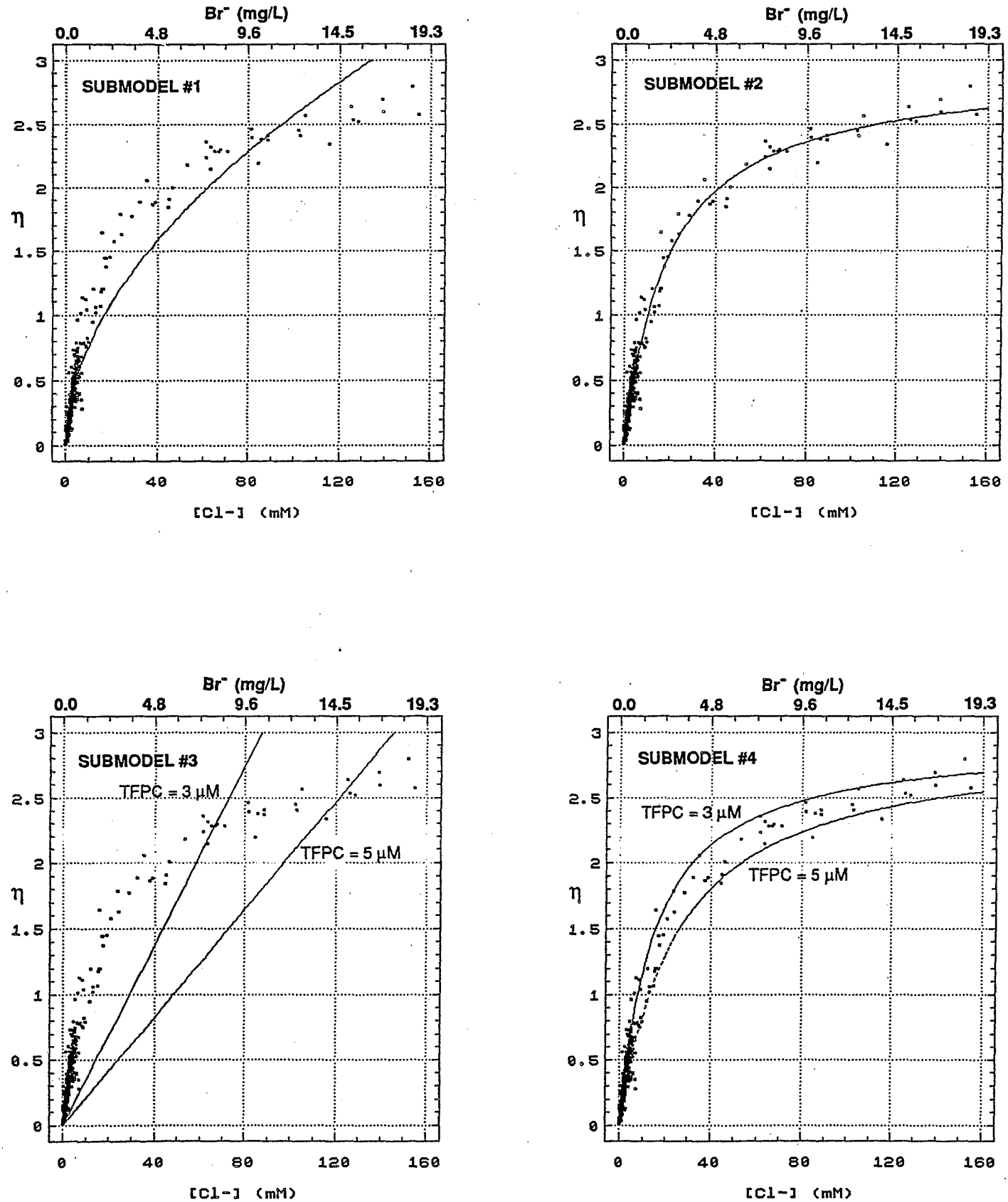

Figure 8. Bromine Incorporation Factor Submodels #1–#4: 3–5 µM TFPC Data Set

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Submodels #1 and #3 were discounted because of poor data fit. The former submodel gives poor predictions at high salinities, whereas the latter submodel gives poor predictions over the entire salinity range. Submodels #2 and #4 provided good fits over the entire data set, with r^2 between 0.83–0.97 for the former and 0.88–0.97 for the latter. Although submodel #2 was explicitly defined as a function of only one variable, its best-fit coefficients are strongly influenced by TFPC range. To illustrate the influence of TFPC range on submodel #2, data was regrouped into 14 data sets and regression analyses were performed to fit a modified form of the submodel. (Anticipating "b" to be proportional to TFPC, "a" was set equal to 3 in the modified submodel so that as "b" approaches zero, η approaches three, i.e. an infinitely large bromide to precursor ratio results in bromoform production only.) Results from these analyses are summarized in Table 2.

Table 2. Modified Submodel #2: Further Screening Analysis

$$\eta = \frac{3[Cl^-]}{b + [Cl^-]}$$

TFPC (μM)	Average TFPC (μM)	n	b	r^2	SSE	SEE
0.0– 2.0	1.62	169	18.923	.81	0.86	0.071
2.0– 2.5	2.26	157	15.818	.96	0.99	0.079
2.5– 3.0	2.75	199	15.783	.97	0.85	0.065
3.0– 3.5	3.26	240	18.735	.97	1.33	0.074
3.5– 4.0	3.74	194	20.111	.98	1.13	0.076
4.0– 4.5	4.24	131	20.077	.98	1.10	0.092
4.5– 5.0	4.73	116	23.708	.98	0.84	0.085
5.0– 6.0	5.46	161	28.901	.95	2.08	0.114
6.0– 7.0	6.47	93	32.616	.91	1.25	0.116
7.0– 8.0	7.44	92	35.467	.95	1.17	0.113
8.0–10.0	8.86	109	40.389	.92	1.45	0.115
10.0–15.0	12.08	137	55.038	.88	1.48	0.104
15.0–20.0	17.57	102	94.843	.72	0.33	0.057
> 20.0	26.27	124	119.623	.67	0.64	0.072

In Fig. 9, the regression coefficient "b" is shown to be a linear function of the average TFPC value. Prompted by this result, a final regression was performed on the entire 2000 point data set to fit the model form:

$$\eta = \frac{3[Cl^-]}{b[TFPC] + [Cl^-]} \qquad (7\text{–}3)$$

where:

$[Cl^-]$ = chloride, mM

[TFPC] = Total Formulation Potential Carbon, μM

b = regression coefficient = 5.482

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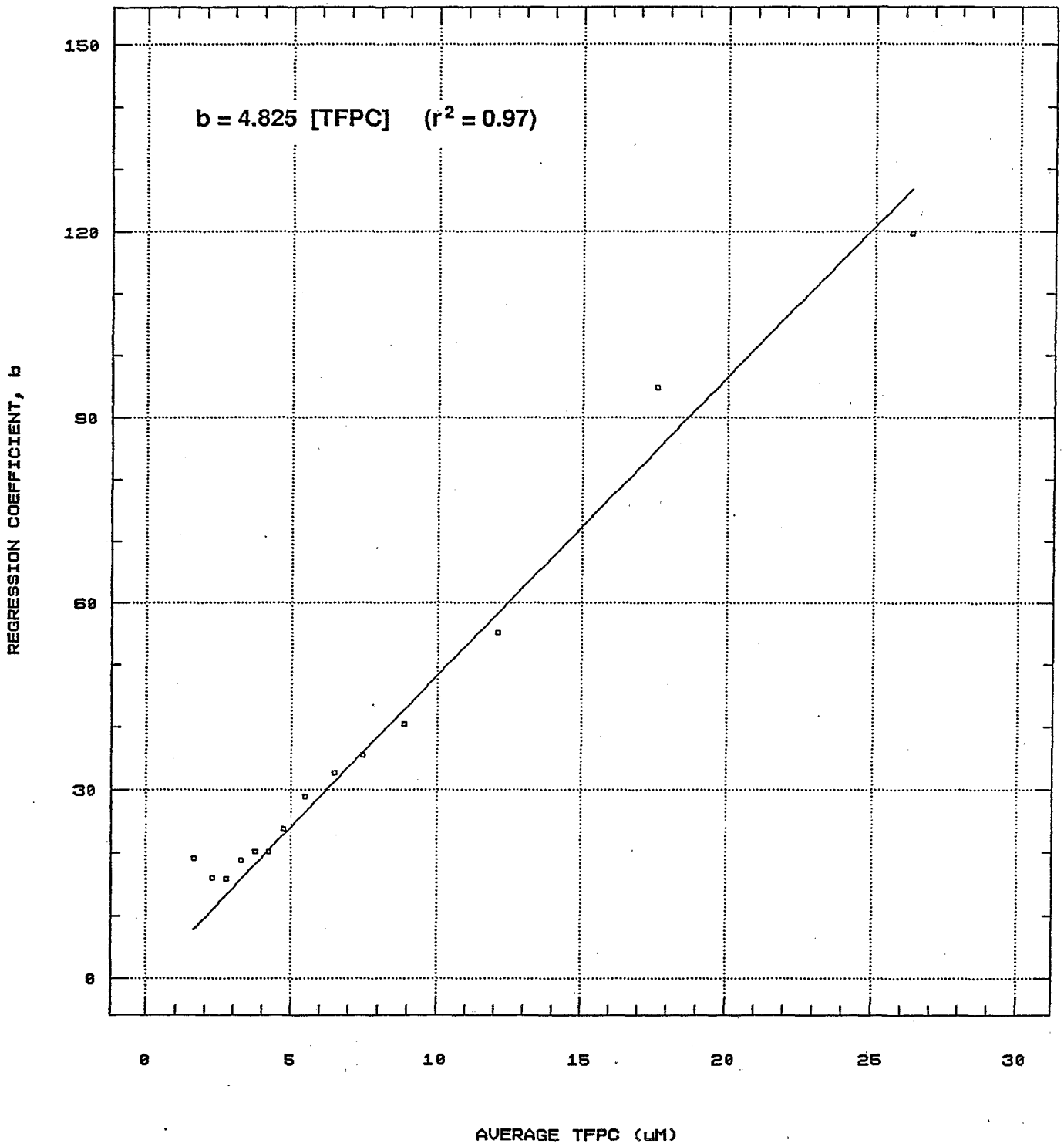

Figure 9. b as a Function of TFPC

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An r^2 value of 0.95, an SSE value of 19.86, and an SEE value of 0.099 were obtained for this relationship with the coefficient "b" equal to 5.482. This relationship, Submodel #5, was selected as the best submodel form to predict Bromine Incorporation Factor. Submodel #5 makes theoretical sense because it indicates the importance of the bromide to precursor ratio in influencing THMFP speciation. Eq. 7–3 can be rewritten in the form:

$$\eta = \frac{3[Cl^-]/[TFPC]}{b + [Cl^-]/[TFPC]} \quad \text{(7–4)}$$

to further highlight the importance of this ratio. Fig. 10 shows the data from Fig. 7 as a function of the molar chloride to TFPC ratio and superimposes the relationship given in Eq. 7–4. Fig. 11 compares observed and predicted values of η for submodel #5.

Spatial Variation

To analyze the spatial variation of η, measured values were plotted for eight stations in the Delta. The first four stations (see Fig. 12) represent export locations and include Banks Pumping Plant, Clifton Court Forebay, Delta–Mendota Canal, and Rock Slough. These stations are typically characterized by moderate concentrations of chloride and TFPC. The next four stations (see Fig. 13) represent boundary stations and include a composite of many agricultural drains, Greene's Landing, Mallard Island, and Vernalis. These stations represent diverse conditions and water qualities. Eq. 7–4 is superimposed on each data set in Figs. 12 and 13. Visually, model fit is good at all stations. The most scatter exists at high Cl:TFPC ratios for the composite agricultural drain data set.

Bromine Distribution Factors

The Bromine Incorporation Factor quantifies an average distribution of THM compounds in a water sample. To predict the concentrations of $CHCl_3$, $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$ that comprise this average value, a term called Bromine Distribution Factor is defined.

Bromine Distribution Factors, or s_N, define the proportion of TFPC that exists in each of the THMFP species for a given water sample. N denotes the number of bromide atoms in the THM species, a notation identical to that used by Gould et al.[44] in their definition of Bromine Incorporation Factor:

$$s_0 = CHCl_3 \text{ Distribution Factor} = \frac{[CHCl_3]}{[TFPC]} \quad \text{(7–5)}$$

$$s_1 = CHCl_2Br \text{ Distribution Factor} = \frac{[CHCl_2Br]}{[TFPC]} \quad \text{(7–6)}$$

$$s_2 = CHClBr_2 \text{ Distribution Factor} = \frac{[CHClBr_2]}{[TFPC]} \quad \text{(7–7)}$$

$$s_3 = CHBr_3 \text{ Distribution Factor} = \frac{[CHBr_3]}{[TFPC]} \quad \text{(7–8)}$$

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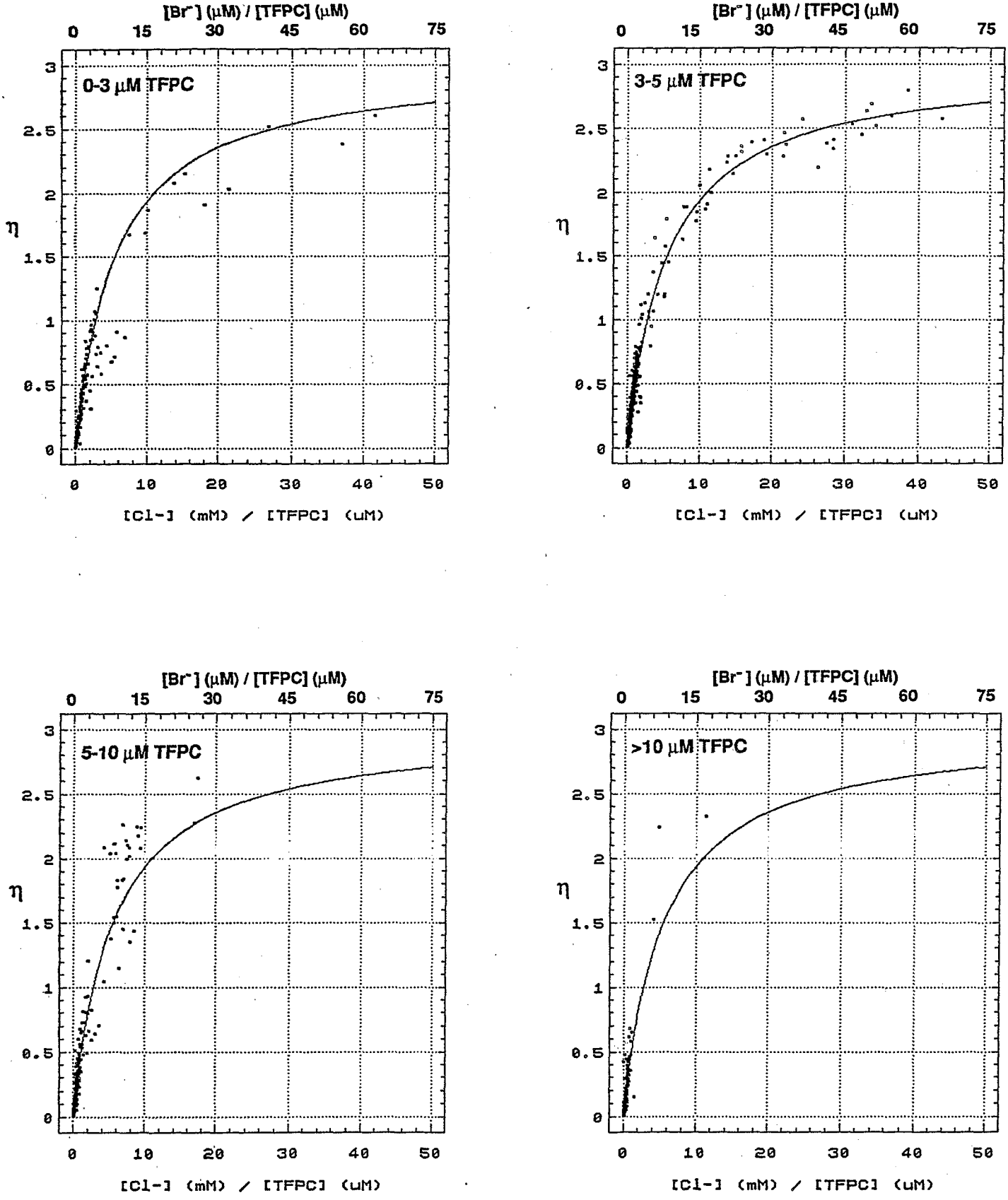

Figure 10. Bromine Incorporation Factor: Submodel #5

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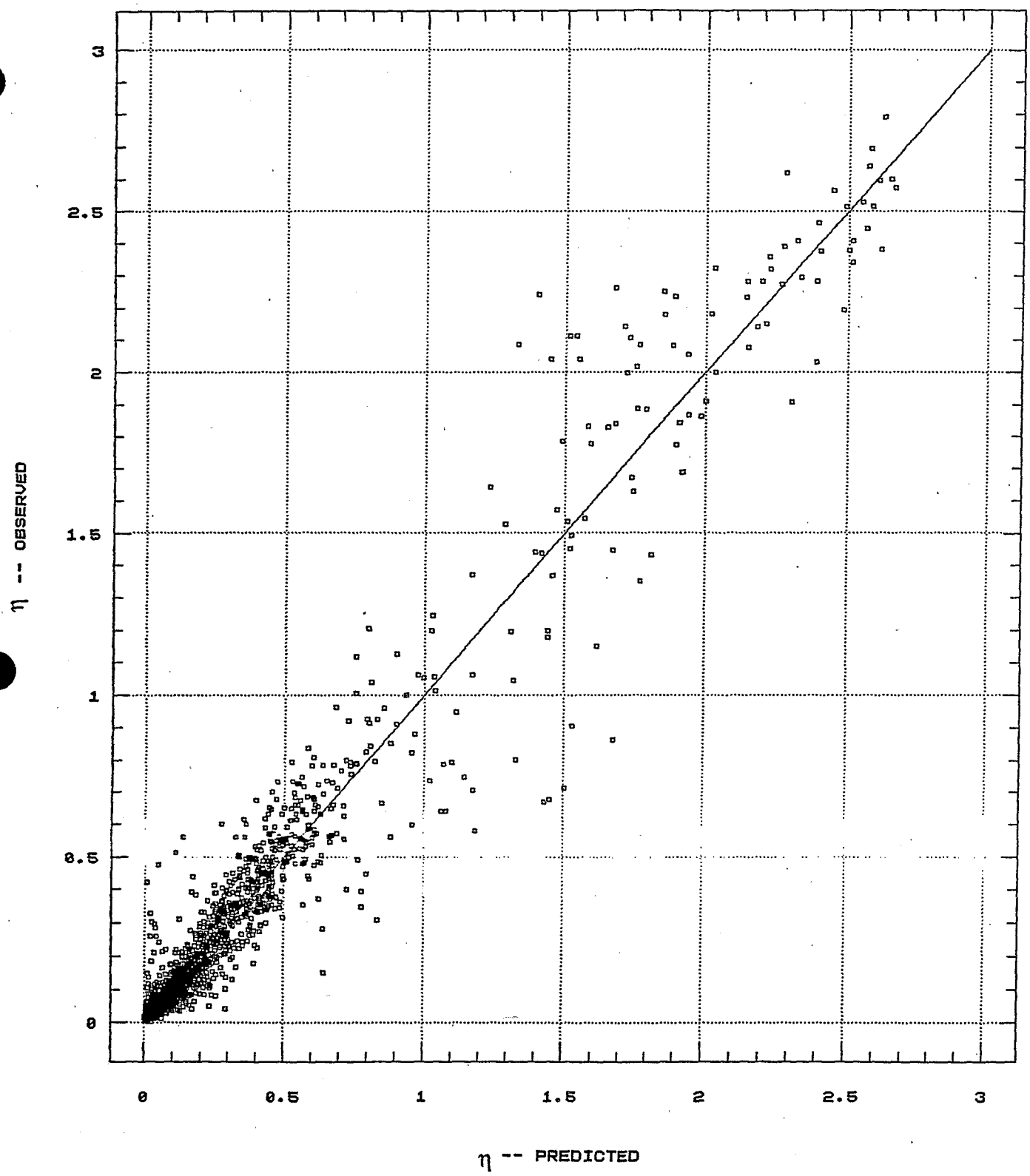

Figure 11. Bromine Incorporation Factor: Observed versus Predicted Values

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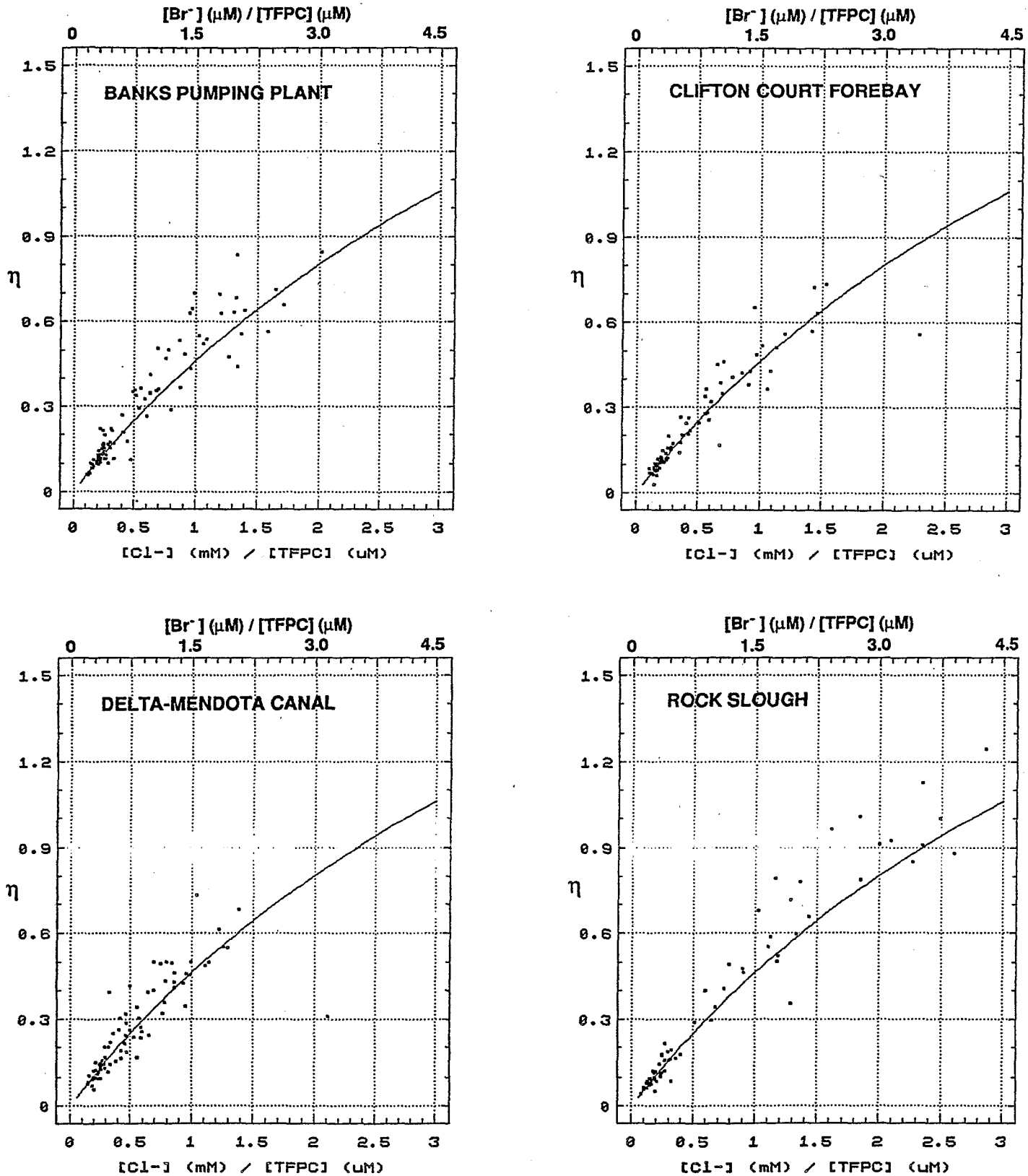

Figure 12. Bromine Incorporation Factor at Export Stations

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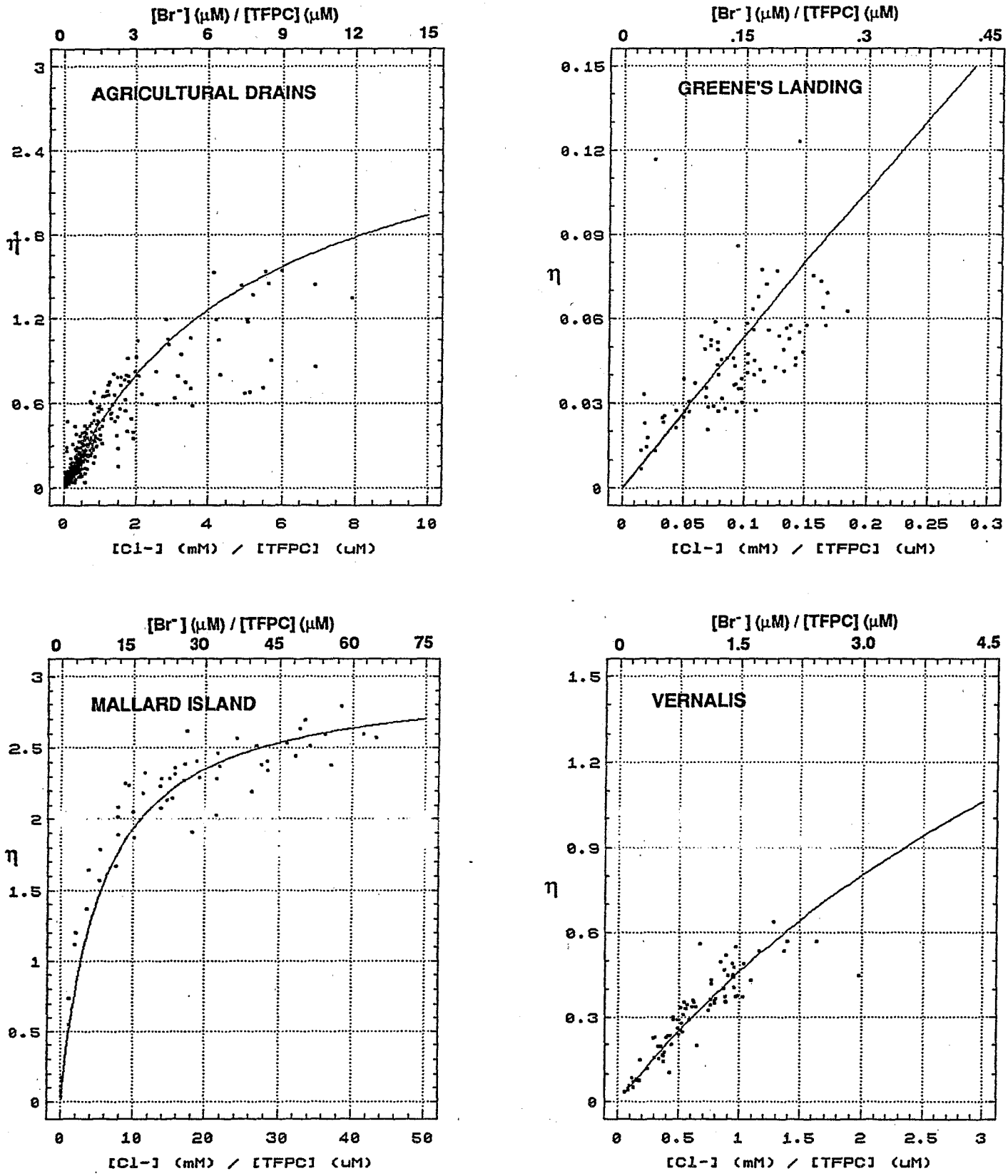

Figure 13. Bromine Incorporation Factor at Boundary Stations

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Based on the above definitions, the theoretical sum of Bromine Distribution Factors is one. Because η describes the distribution of THM species, η was suspected to be the key variable in predicting s_N. Regression analyses were performed on the entire 2000 sample data set to fit observed data to the following polynomial submodel forms:

$$s_0 = -.0285\eta^3 + .2613\eta^2 - .8703\eta + 1 \qquad r^2 = 1.00;\ SSE = 0.28;\ SEE = 0.012 \quad (7\text{–}9)$$

$$s_1 = \frac{-.0446\eta^3 - .1888\eta^2 + .8659\eta}{\eta + 1} \qquad r^2 = .95;\ SSE = 0.70;\ SEE = 0.019 \quad (7\text{–}10)$$

$$s_2 = -.0792\eta^3 + .1936\eta^2 + .1244\eta \qquad r^2 = .96;\ SSE = 0.57;\ SEE = 0.017 \quad (7\text{–}11)$$

$$s_3 = .0250\eta^3 + .0351\eta^2 + .0017\eta \qquad r^2 = .99;\ SSE = 0.18;\ SEE = 0.009 \quad (7\text{–}12)$$

Correlations are very high, with r^2 values ranging from 0.95 to 1.00. Hence, the assumption that η is the key variable in predicting s_N appears to be justified.

Fig. 14 plots s_N as a function of observed values of η for all four THMFP species. Regression curves are superimposed on each plot. The plots illustrate relationships that can be intuitively explained by the definition of η. For example, as η approaches zero, the $CHCl_3$ Distribution Factor (s_0) approaches one and the remaining distribution factors approach zero, i.e., the predominant THM compound is chloroform. As η approaches three, the $CHBr_3$ Distribution Factor (s_3) approaches one and the remaining distribution factors approach zero, i.e. the predominant THM compound is bromoform. At intermediate values of η, no THM compound is dominant.

Model Verification

Mathematical models are typically verified with data other than the original data base used for calibration. In this section, the model is verified with an external THMFP data base. Model predictions are also compared with the original MWQI data base as an internal measure of model error.

Internal Verification

Regression analyses presented thus far quantify the ability of submodels to 1) estimate η from observed values of chloride and TFPC and 2) estimate s_N from observed values of η. To quantify error associated with the sequential use of the Bromine Incorporation Factor and Bromine Distribution Factor submodels, Fig. 15 compares observed values of s_N (from observed values of η) against with predicted values of s_N (from predicted values of η). Differences between observed and predicted values were compared with two approaches.

The first approach used to internally verify the model was to calculate the standard error of estimate (SEE) for each THMFP species. SEE values are included on each graph in Fig. 15. Assuming normal distributions, about 67 percent of the observed values of s_N fall within one SEE of the model predictions and about 95 percent of the observed values fall within two SEEs of the model predictions.

The second approach used to internally verify the model was to conduct regression analyses of predicted values of s_N against observed values of s_N. With this approach, a perfect model would yield a regression equation with an intercept of zero, a slope of 1.00 and a r^2 value of 1.00. Results for each THMFP species are as follows:

$$s_0,\ \text{predicted} = 0.027 + 0.972\, s_0,\ \text{observed} \qquad r^2 = 0.94 \quad (7\text{–}13)$$

$$s_1,\ \text{predicted} = 0.006 + 0.926\, s_1,\ \text{observed} \qquad r^2 = 0.84 \quad (7\text{–}14)$$

$$s_2,\ \text{predicted} = 0.006 + 0.915\, s_2,\ \text{observed} \qquad r^2 = 0.88 \quad (7\text{–}15)$$

$$s_3,\ \text{predicted} = 0.001 + 0.910\, s_3,\ \text{observed} \qquad r^2 = 0.92 \quad (7\text{–}16)$$

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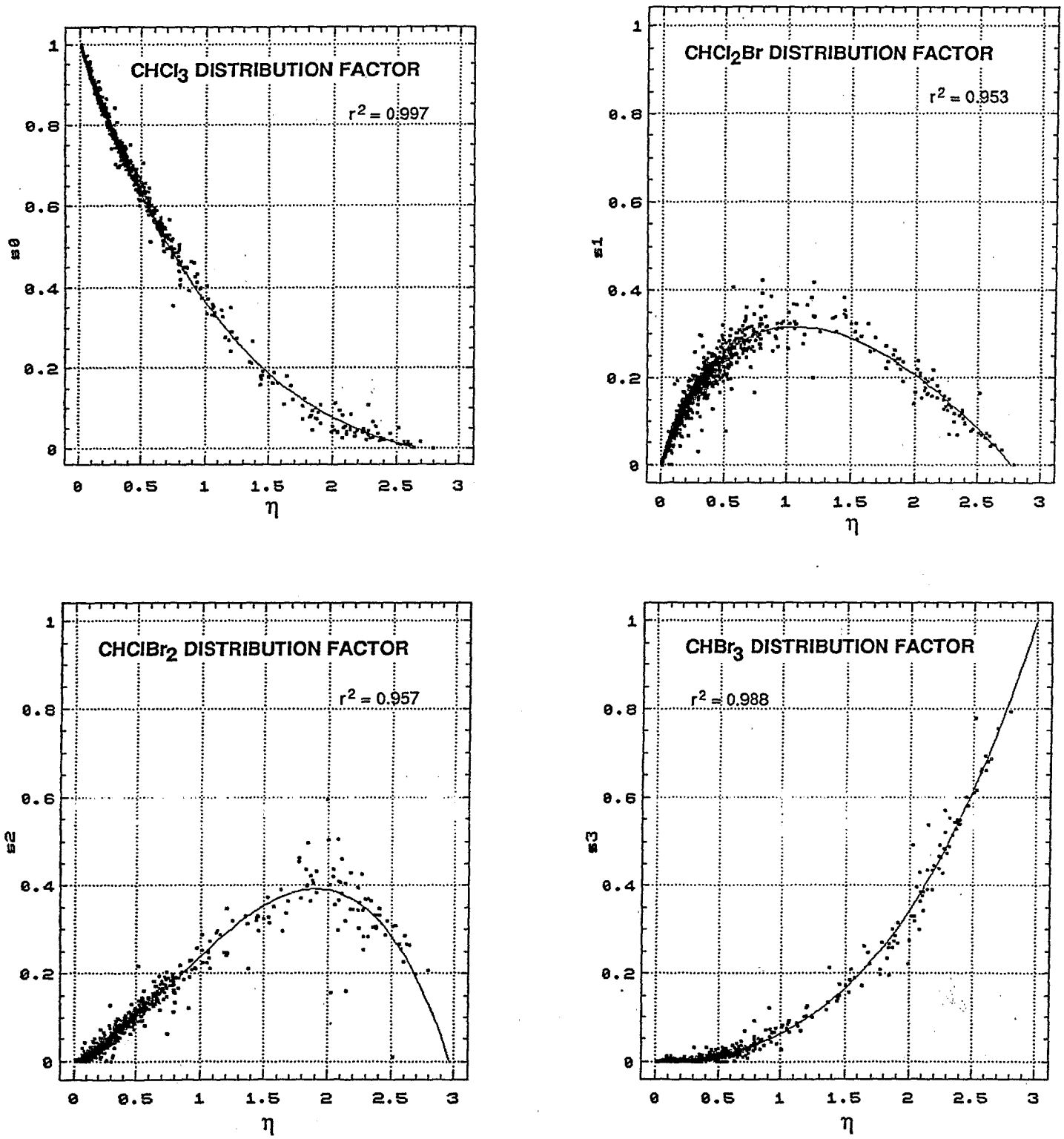

Figure 14. Bromine Distribution Factors

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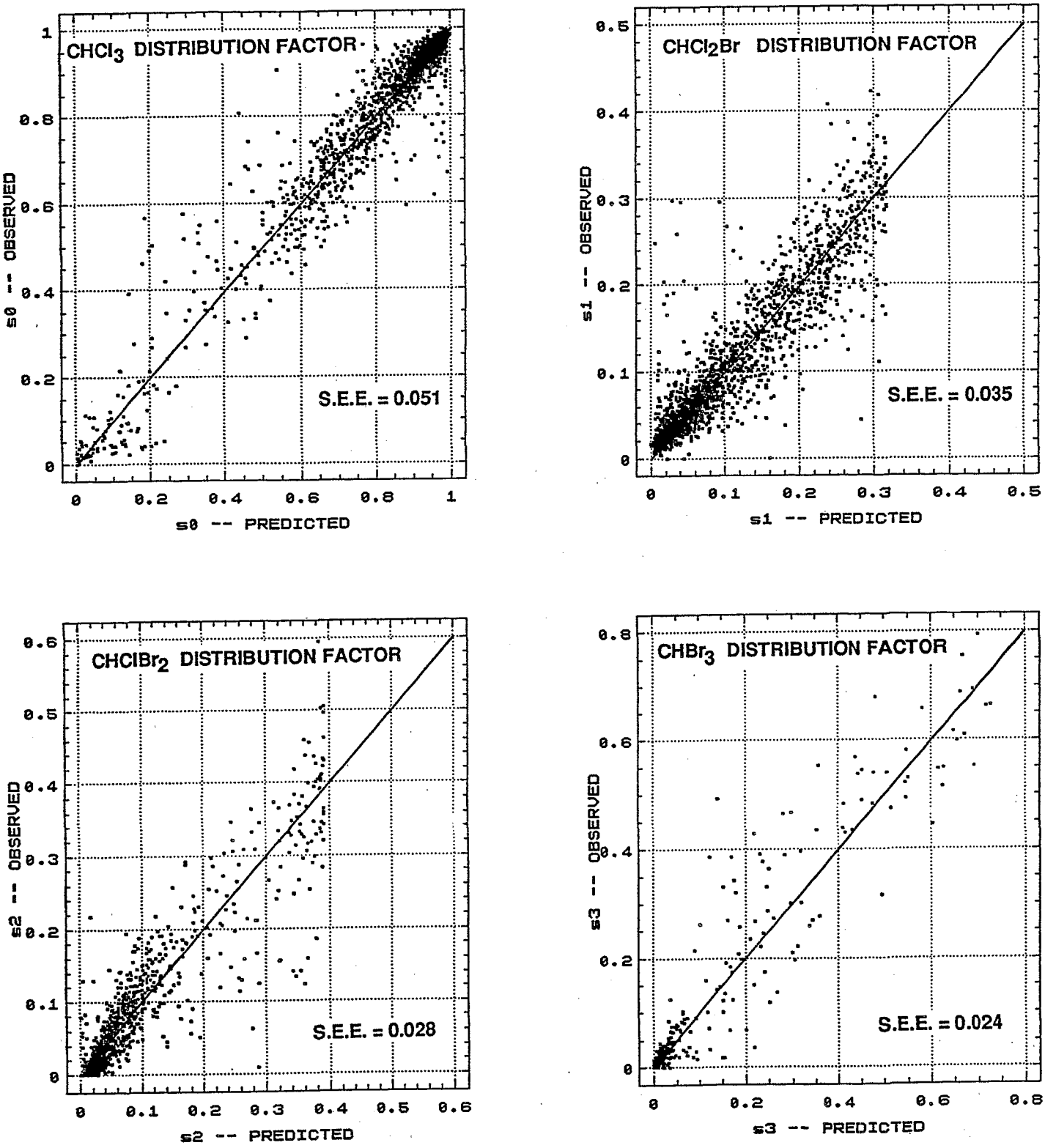

Figure 15. Bromine Distribution Factors: Observed versus Predicted Values

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Intercepts, slopes and correlations indicate that the model generally provides good predictions; the best preditions being for s_0.

External Verification

Model verification was also conducted with an external data base. The external data base was developed by Amy et al.[29] The data set received from the authors included 1,025 samples with chlorine residuals greater than zero. The data set reported in the literature included 995 samples. This slightly larger data set was utilized to verify the Bromine Incorporation Factor and Bromine Distribution Factor submodels.

To verify the Bromine Incorporation Factor submodel, the external data base was segregated to isolate data points that more closely reflect DWR's THMFP test conditions. A total of 64 data points were selected so that reaction time was equal to seven days and reaction temperature was equal to 20°C. While other parameters such as pH, bromide and TOC are within the ranges observed in the Delta, the range of chlorine dose (1.5–69 mg/L) utilized in the external data base is much lower than DWR's test dose of 120 mg/L. Fig. 16 plots the 64 data points along with the curve given in Eq. 7–4 as a function of the molar ratio of bromide to TFPC. The chloride to TFPC ratio in Eq. 7–4 was multiplied by 1.5 to "convert" it to an equivalent bromide to TFPC molar ratio, assuming an open ocean water correlation between bromide and chloride (see Eq. 4–4). Fig. 16 shows a good visual comparison between the external data base and the Bromine Incorporation Factor submodel given in Eq. 7–4. A SEE value of 0.132 compares favorably with the SEE value of 0.099 computed for the MWQI data calibration of Eq. 7–4. A regression analysis of predicted values against observed values was conducted. Again, a perfect model would yield a regression equation with an intercept of zero, a slope of 1.00 and a r^2 value of 1.00. The analysis resulted in an intercept of 0.079, a slope of 0.865, and a r^2 value of 0.92. Although the correlation is pretty good, the intercept and slope indicates that the model tends to overpredict at low values of η and underpredict at high values of η. The difference in chlorine dose between the external data base and the MWQI data base is a likely explanation for the model underprediction at high values of n. Variability in temperature (T=25°C under DWR test conditions) and variability in pH may also explain some of the deviation between model predictions and observed values.

To verify the Bromine Distribution Factor submodels, the entire data base was utilized to compare predicted and observed values. Fig. 17 plots the 1025 data points along with the curves given in Eqs. 7–9 through 7–12 as functions of observed Bromine Incorporation Factor. The external data base visually follows the submodel relationships as well or better than the MWQI data base (compare with Fig. 14). Similarities between SEE values for the external data base (see Fig. 17) and for the MWQI data base (see Eqs. 7–9 through 7–12) confirm this visual observation. Regression analyses of predicted values against observed values were conducted, resulting in the following:

$$s_0, \text{predicted} = -0.012 + 1.024\, s_0, \text{observed} \qquad r^2 = 1.00 \qquad (7\text{–}17)$$

$$s_1, \text{predicted} = -0.004 + 0.958\, s_1, \text{observed} \qquad r^2 = 0.96 \qquad (7\text{–}18)$$

$$s_2, \text{predicted} = -0.008 + 0.964\, s_2, \text{observed} \qquad r^2 = 0.99 \qquad (7\text{–}19)$$

$$s_3, \text{predicted} = 0.002 + 0.930\, s_3, \text{observed} \qquad r^2 = 0.99 \qquad (7\text{–}20)$$

Intercepts, slopes and correlations indicate that the model provides excellent predictions of Bromine Distribution Factors. This comparison shows that THMFP species form in a predictable fashion under varying test conditions. Because Eqs. 7–17 through 7–20 were developed with observed (and not predicted) values of η, the intercepts, slopes and correlations from these equations should not be directly compared with those given in Eqs. 7–13 through 7–16.

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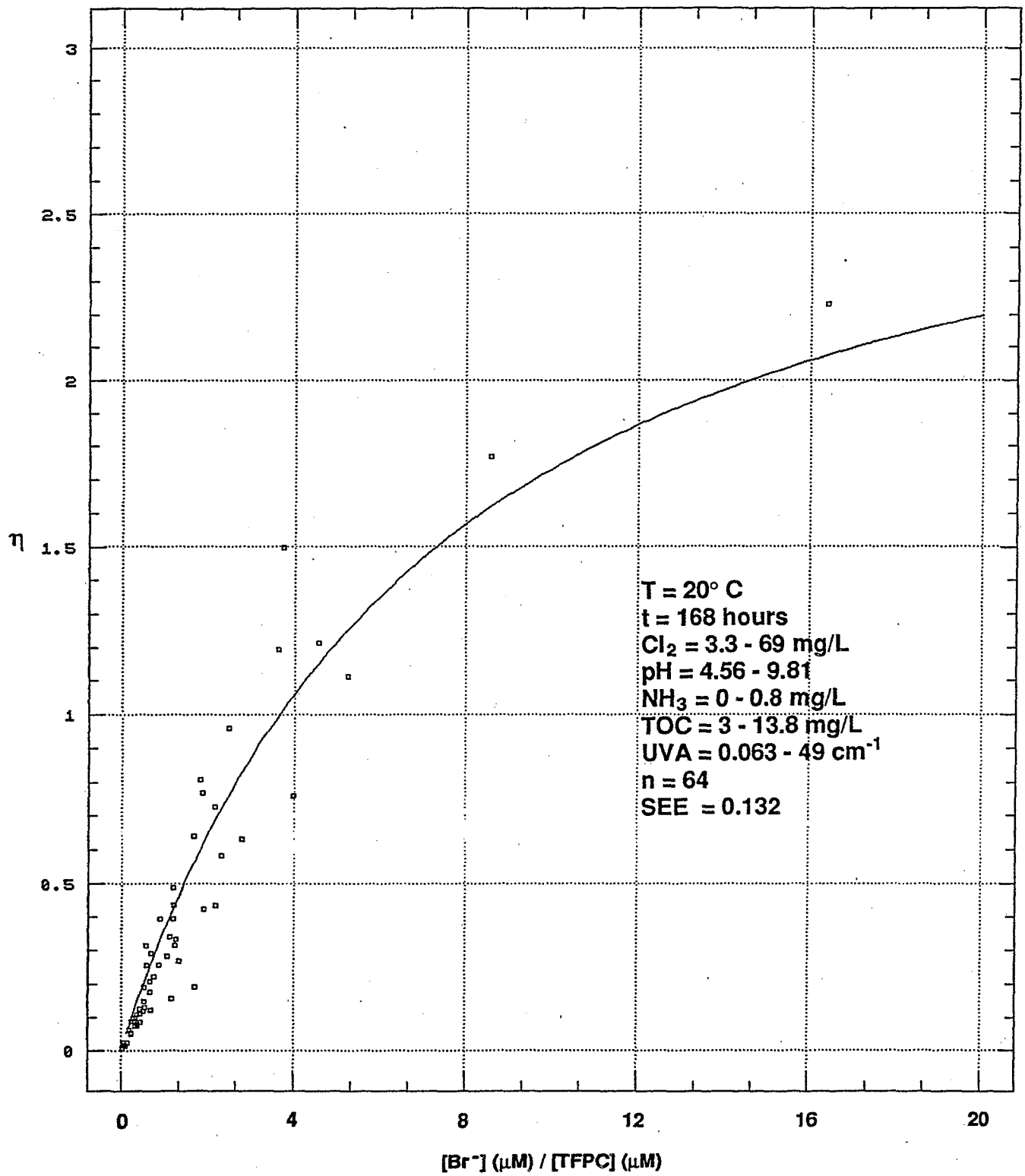

Figure 16. Bromine Incorporation Factor Verification

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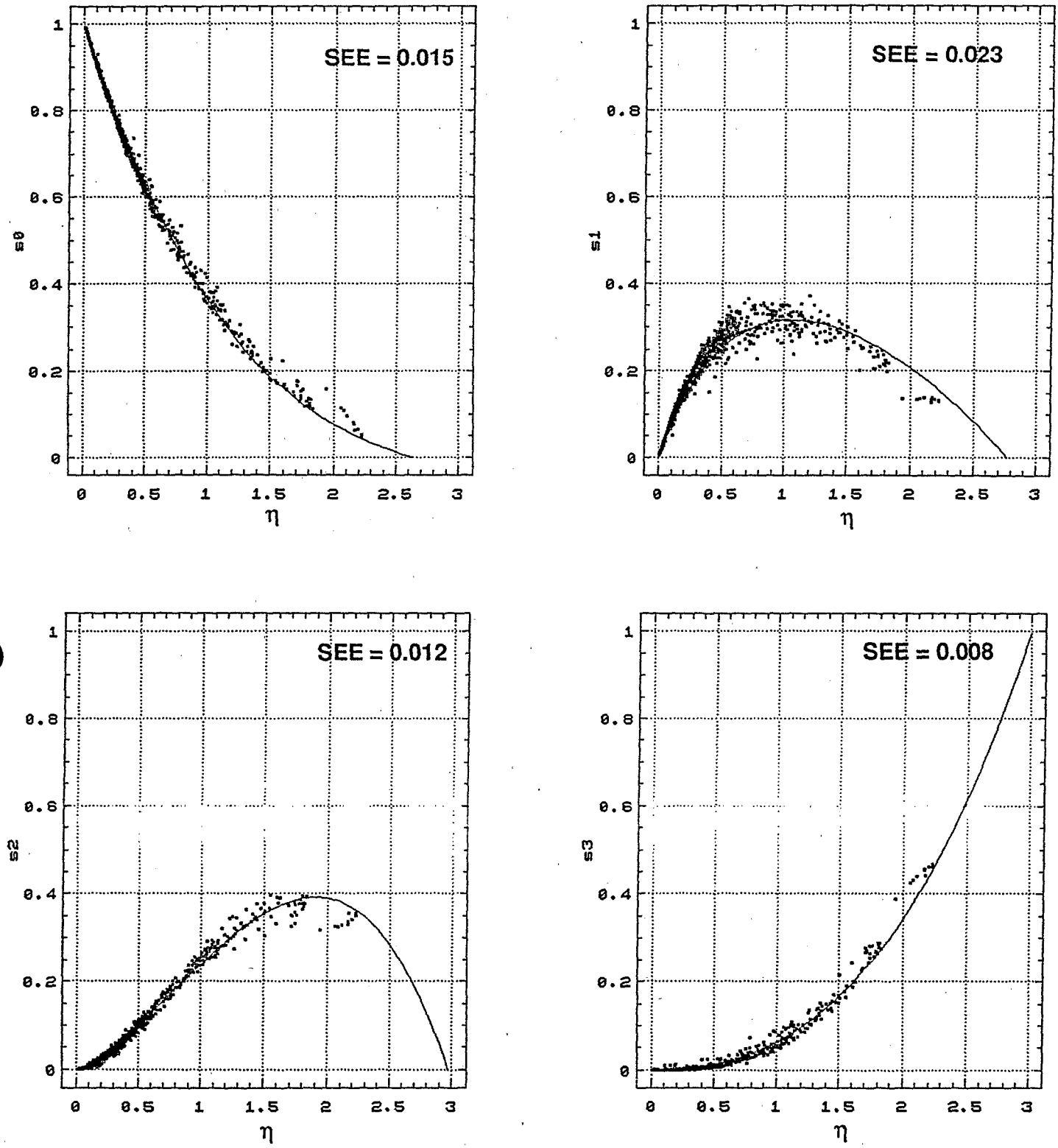

Figure 17. Bromine Distribution Factors Verification

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Example Problem

To partially illustrate the model framework established in this report, an example problem is presented in Fig. 18 and is discussed further below. The problem specifically shows how the precursor simulation model (DWRDSM) and the THMFP empirical relationships (Bromine Incorporation Factor and Bromine Distribution Factors) fit within the overall model framework. DWRDSM was run in a steady state mode to simulate transport of TFPC and total dissolved solids (TDS) in the Delta during the month of July 1988 (see Chapter 8). Historic water quality observations were input as boundary conditions. Simulation model results at Clifton Court Forebay were utilized as input to the following steps:

1. Simulation model results are converted to units consistent with Eq. 7–3. If TDS or EC is used to simulate salinity transport (as was the case in the example), an appropriate conversion must be made to determine chloride concentration.

2. After water quality parameters are converted to appropriate concentration units, the Bromine Incorporation Factor is determined from Eq. 7–3 with $b = 5.482$.

3. Bromine Distribution Factors are calculated as a function of the Bromine Incorporation Factor determined in Step 2. If a calculation results in a negative number, that distribution factor is assumed to be zero. An s_0 value of 0.46 means that 46 percent of the TFPC is in the form of $CHCl_3$. An s_1 value of 0.31 means 31 percent of the TFPC is in the form of $CHCl_2Br$. After all four distribution factors are calculated, the values are summed. Theoretically, the sum should equal one. If the sum does not equal one as in the example, a correction is made in Step 5.

4. THMFP molar concentrations are calculated as the product of Bromine Distribution Factors and TFPC.

5. THMFP mass concentrations are calculated as the product of molar concentration and molecular weight. Because the distribution factor sum is not equal to one in the example, the mass concentrations is divided by the Bromine Distribution Factor sum.

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PROBLEM STATEMENT: A transport model simulation of THM precursors in the Delta during July 1988 was conducted (details are provided in Chapter 8). Results indicated the following precursor concentrations at Clifton Court Forebay gates:

TFPC = 30 µg/L
TDS = 473 mg/L

Estimate THMFP species and total THMFP mass concentrations at Clifton Court Forebay.

STEP 1: Calculate TFPC and Chloride Molar Concentrations

$$[TFPC] = \frac{30\ \mu g/L}{12\ \mu g/\mu mole\ C} = 2.50\ \mu M$$

per salinity relationship [47]:

$$Cl^- = -47.95 + 0.4751 \times TDS = 177\ mg/L$$

$$[Cl^-] = \frac{177\ mg/L}{35.45\ mg/mmole} = 4.99\ mM$$

STEP 2: Calculate Bromine Incorporation Factor (η)

$$\eta = \frac{3\,[Cl^-]}{5.482 \times [TFPC] + [Cl^-]}$$

$$\eta = \frac{(3)(4.99)}{(5.482)(2.50) + 4.99}$$

$$\eta = 0.80$$

STEP 3: Calculate Bromine Distribution Factors (s_N)

$$S_0 = -.0285\eta^3 + .2613\eta^2 - .8703\eta + 1$$

$$S_0 = -.0285\,(.80)^3 + .2613\,(.80)^2 - .8703\,(.80) + 1$$

$$S_0 = 0.46$$

$$S_1 = (-.0446\eta^3 - .1888\eta^2 + .8659\eta) / (\eta + 1)$$

$$S_1 = (-.0446\,(.80)^3 - .1888\,(.80)^2 + .8659\,(.80)) / (.80 + 1)$$

$$S_1 = 0.31$$

$$S_2 = -.0792\eta^3 + .1936\eta^2 + .1244\eta$$

$$S_2 = -.0792\,(.80)^3 + .1936\,(.80)^2 + .1244\,(.80)$$

$$S_2 = 0.18$$

$$S_3 = .0250\eta^3 + .0351\eta^2 + .0017\eta$$

$$S_3 = .0250\,(.80)^3 + .0351\,(.80)^2 + .0017\,(.80)$$

$$S_3 = 0.04$$

$$\Sigma s_N = 0.46 + 0.31 + 0.18 + 0.04 = 0.99$$

STEP 4: Calculate Preliminary THMFP Molar Concentrations

$$[CHCl_3] = S_0 \times [TFPC] = 0.46 \times 2.50\ \mu M = 1.15\ \mu M$$

$$[CHCl_2Br] = S_1 \times [TFPC] = 0.31 \times 2.50\ \mu M = 0.775\ \mu M$$

$$[CHClBr_2] = S_2 \times [TFPC] = 0.18 \times 2.50\ \mu M = 0.45\ \mu M$$

$$[CHBr_3] = S_3 \times [TFPC] = 0.04 \times 2.50\ \mu M = 0.10\ \mu M$$

STEP 5: Calculate Revised THMFP Mass Concentrations

Adjust preliminary values such that $\Sigma s_N = 1.00$

$$CHCl_3 = \frac{1.15\ \mu M}{0.99} \times 119.36\ \mu g/\mu mole = 139\ \mu g/L$$

$$CHCl_2Br = \frac{0.775\ \mu M}{0.99} \times 163.82\ \mu g/\mu mole = 128\ \mu g/L$$

$$CHClBr_2 = \frac{0.45\ \mu M}{0.99} \times 208.28\ \mu g/\mu mole = 95\ \mu g/L$$

$$CHBr_3 = \frac{0.10\ \mu M}{0.99} \times 252.74\ \mu g/\mu mole = 26\ \mu g/L$$

Total THMFP = 139 + 128 + 95 + 26 = 388 µg/L

Figure 18. THMFP Model Methodology: Example Problem

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CHAPTER 8. APPLICATION OF THE THMFP MODEL

Modeling Objectives

Several DWRDSM simulations were made to illustrate two specific applications of the Sacramento–San Joaquin THMFP model. The first application was to quantify individual and cumulative impacts of fresh water inflows, tidal influences, and agricultural drainage on TFPC concentrations at Delta export locations. To quantify individual source water impacts, TFPC transport simulations were run for each major source. The second model application was to evaluate the ability of the Bromine Incorporation Factor and Bromine Distribution Factor submodels developed in Chapter 7 to simulate bromide effects in the Delta. Bromide effects are dependent on predicted values of TFPC and chloride at specific locations. To evaluate the second application, a salinity transport simulation was also performed and resulting THMFP estimates were compared with historic data.

DWRDSM was operated in a steady state mode to illustrate its application within the overall THMFP model framework. To arrive at steady state conditions from a set of historically observed boundary conditions, the model was allowed to iterate until predicted values did not change in a daily average sense. Although DWRDSM is not typically operated in a steady state mode to simulate historic conditions, this mode was selected to simplify the analysis. Steady state analysis was considered to be more appropriate than time series analysis because the present formulation does not attempt to describe transient processes involved in THM precursor movement to and from Delta islands. Finally, steady state analysis was considered to be appropriate since the overall objective is to illustrate rather than to reach quantitative conclusions. As stated in the introduction, **no conclusions should be drawn from the preliminary model results presented in this report.**

Modeling Scenarios

Seven model simulations, as described below, were performed to meet the stated modeling objectives. Each scenario assumes TFPC boundary conditions as measured under the MWQI program during July 1988. Water year 1988 was selected because average monthly values were already compiled by DWR to study the effect of agricultural drainage on export water quality.[1] July was specifically selected because it represents a peak drainage period due to increased irrigation in the Delta.

- Scenario 1 — Impact of Sacramento River (TFPC = 21 μg/L) as the sole source of organic THM precursors in the Delta.
- Scenario 2 — Impact of San Joaquin River (TFPC = 54 μg/L) as the sole source of organic THM precursors in the Delta.
- Scenario 3 — Impact of the Bay-Delta interface at Benicia (TFPC = 78 μg/L) as the sole source of organic THM precursors in the Delta. Because THMFP data is not available at Benicia, the boundary condition was determined by trial and error to approximate an average historical value at Mallard Island, the MWQI monitoring station closest to Benicia.
- Scenario 4 — Impact of peat island agricultural drainage (TFPC = 199 μg/L) as the sole source of organic THM precursors in the Delta. Fig. 1 shows the areal extent of peaty organic soils in the Delta. Peat island return flows of 296 cfs and their distribution among 29 DWRDSM nodes was based on DWR's July 1979 Delta consumptive use estimates (see Table 3).

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Table 3. Peat Island Discharge Distribution, Scenario 4		
Node #	**Island Name(s)**	**Drainage (cfs)**
32	McDonald	1.31
35	Mandeville, Medford	11.52
38	Webb	4.59
39	Venice	7.43
42	Bradford, Webb	17.75
44	Jersey	5.74
86	Palm	3.14
93	Bacon, Holland	15.11
98	Holland	3.34
100	Bacon	11.95
121	Lower Jones	20.26
130	Mandeville	17.10
135	Mildred	4.49
138	Quimby	22.72
140	McDonald	1.07
143	Lower Jones	8.21
195	Woodward	4.09
216	Holland	1.58
224	Webb	4.59
226	Bethel	1.51
243	King, Rindge	22.13
245	Empire	13.38
247	King	2.84
250	Terminus	15.09
251	Bouldin, Venice	13.51
266	Brack, Staten	20.11
268	Terminus	15.09
269	Staten	25.91
Total Peat Island Discharge		296.00

- Scenario 5 — Impact of mineral/intermediate organic island agricultural drainage (TFPC = 84 μg/L) as the sole source of organic THM precursors in the Delta. Fig. 1 shows the areal extent of mineral/intermediate organic soils in the Delta. Mineral island return flows of 1311 cfs and their distribution among 157 DWRDSM nodes was based on DWR's July 1979 Delta consumptive use estimates (see Table 4).

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Table 4. Mineral Island Discharge Distribution, Scenario 5		
Node #	**Island Name(s)**	**Drainage (cfs)**
1	River Junction, Kasson	46.05
3	McMullin Ranch, Kasson	12.20
23	Lower Roberts, Elmwood	11.11
40	Lower Andrus	20.20
42	Twitchell	17.75
45	Sherman	19.03
60	El Pescadero, Pico, and Naglee	13.47
63	El Pescadero	25.91
66	El Pescadero	11.62
67	Fabian	11.25
70	Fabian	12.25
80	Victoria	13.01
111	Union East, Drexler	10.04
113	Union West, Drexler, Honker Lake	15.36
138	Rough and Ready, Middle Roberts	22.72
148	Lower Roberts	17.37
150	Pico and Naglee	36.10
162	Mossdale 2, Paradise Junction	11.20
163	Mossdale 2, Paradise Junction	11.06
198	Undesignated Area	10.54
200	Undesignated Area	10.54
223	Undesignated Area	34.95
241	Shima, Smith Ranch	13.07
242	Bishop, Atlas	13.95
246	Shin Kee	14.54
253	Pierson, Stone Lake, Ehrhardt Club	68.69
257	New Hope	26.02
262	New Hope	14.69
298	Merritt, Lisbon	41.26
306	Grand	22.91
314	Netherlands	26.93
316	Prospect, Hastings, Egbert, Liberty	34.44
319	Yolano	14.66
320	Hastings, Yolano, Peter Pocket	25.92
321	Hastings	11.42
335	Freeport Area	54.57

Table 4. Mineral Island Discharge Distribution, Scenario 5 (continued)		
Node #	Island Name(s)	Drainage (cfs)
336	Clarksburg Area	11.15
337	Hood Area	14.49
350	Brannon, Ryer, Ida	29.62
——	Drainage from 118 nodes, each less than 10 cfs	479.00
Total Mineral/Intermediate Organic Island Discharge		1,311.00

- Scenario 6 — Cumulative impact of all TFPC sources modeled in Scenarios 1–5 and a number of smaller freshwater inflows. Because THMFP data for the Mokelumne and Cosumnes Rivers were not available for the 1988 water year, July 1984 data were used.[1] Miscellaneous eastside streams were assumed to have TFPC values equal to the Mokelumne River; Yolo Bypass was assumed to have TFPC values equal to the Sacramento River. This last assumption may be questionable, as Yolo Bypass acts as a drainage channel in the summer, picking up surface runoff from agricultural fields. However, no data is available to evaluate this assumption.
- Scenario 7 — Cumulative impact of all salinity sources into the Delta. TDS was measured at boundary locations during July 1988.[48] TDS and other boundary conditions are summarized in Table 5.

Table 5. July 1988 Boundary Conditions Using DWRDSM			
Inflows	**Q (cfs)**	**TDS (mg/L)**	**TFPC (μg/L)**
Sacramento River	14,642	94	21
San Joaquin River	1,357	510	54
Cosumnes River	5	94	25
Mokelumne River	19	94	36
Yolo Bypass	43	94	21
Misc. Streams	173	94	36
Bay at Benicia	(1)	18,300	78
Peaty island return flows	(2)	(2)	199
Mineral island return flows	(2)	(2)	84
Outflows	**Q (cfs)**	**TDS (mg/L)**	**TFPC (μg/L)**
SWP pumping	3,241	–	–
CVP pumping	4,479	–	–
Contra Costa Canal	247	–	–
North Bay Aqueduct	121	–	–
Net channel depletions	4,450	–	–
Net Delta outflow	3,701	–	–
(1) 19-year mean tide assumed (2) varies by island			

Modeling Assumptions

In addition to assuming steady state conditions and the water quality boundary conditions noted in Table 5, a number of additional assumptions were required to simulate the modeling scenarios.

- July 1988 hydrology was assumed to follow historic inflow, outflow and pumping values compiled in DWR's DAYFLOW data base.[49] Net flow directions, which represent average tidal conditions during July 1988, are depicted in Fig. 19.
- The difference between agricultural channel diversions and returns was assumed to emulate the consumptive use pattern of July 1979, a similar hydrologic period.
- A 19-year mean tidal cycle was assumed as the tidal forcing function in the Delta.
- Salinity from agricultural drainage was assumed to emulate the pattern observed in the Delta during 1954 and 1955.[6]
- TFPC was assumed to act as a conservative constituent in the Delta and to represent precursor effects. Both of these assumptions are discussed at length in Chapters 3 and 5.
- TDS was assumed to act as a conservative constituent in the Delta and represent bromide in the Delta. Salts are generally considered to act conservatively in natural waters. Correlations between TDS and chloride have been well established in the Delta.[47] And for water exported from the Delta through the SWP, the ionic ratio between chloride and bromide appears to be similar to that of open ocean water.[21,22]

Results

Results from the seven model scenarios are summarized herein. To emphasize the individual impact on export water quality from each precursor source, TFPC at Clifton Court Forebay inlet gates is reported for each scenario.

Scenario 1

Fig. 20 shows the influence of the Sacramento River on TFPC transport is substantial throughout most of the Delta. Since most Delta inflow comes from the Sacramento River, this result is not too surprising. Scenario 1 estimates the Sacramento River contributes 19 μg/L TFPC at Clifton Court Forebay under steady state conditions. DWRDSM reached steady state in approximately 70 days of simulation.

Scenario 2

Fig. 21 shows the influence of the San Joaquin River on TFPC transport is limited to the southern part of the Delta. This result can be explained by the net flow directions shown in Fig. 19. The model run predicts that San Joaquin River water flows entirely toward the Central Valley Project (CVP) Delta-Mendota Canal intake. An identical flow pattern was observed in the field[1] by tracing selenium under similar low flow conditions. Scenario 2 indicates that the San Joaquin River does not contribute TFPC at Clifton Court Forebay under steady state low flow conditions. DWRDSM reached steady state in approximately 12 days of simulation.

Scenario 3

Fig. 22 shows the influence of the Bay-Delta interface on TFPC transport is limited to the western Delta. A boundary condition at Benicia was not available from existing TFPC data to directly perform this model run. Therefore, a trial and error method was employed to determine an appropriate value.

Through trial and error, it was determined that a TFPC boundary condition of 78 μg/L at Benicia produced results comparable with observed values at Mallard Island. Mallard Island, for which a 52 μg/L TFPC concentration was measured, is the Delta monitoring location most representative of Suisun Marsh and San Francisco Bay influences.

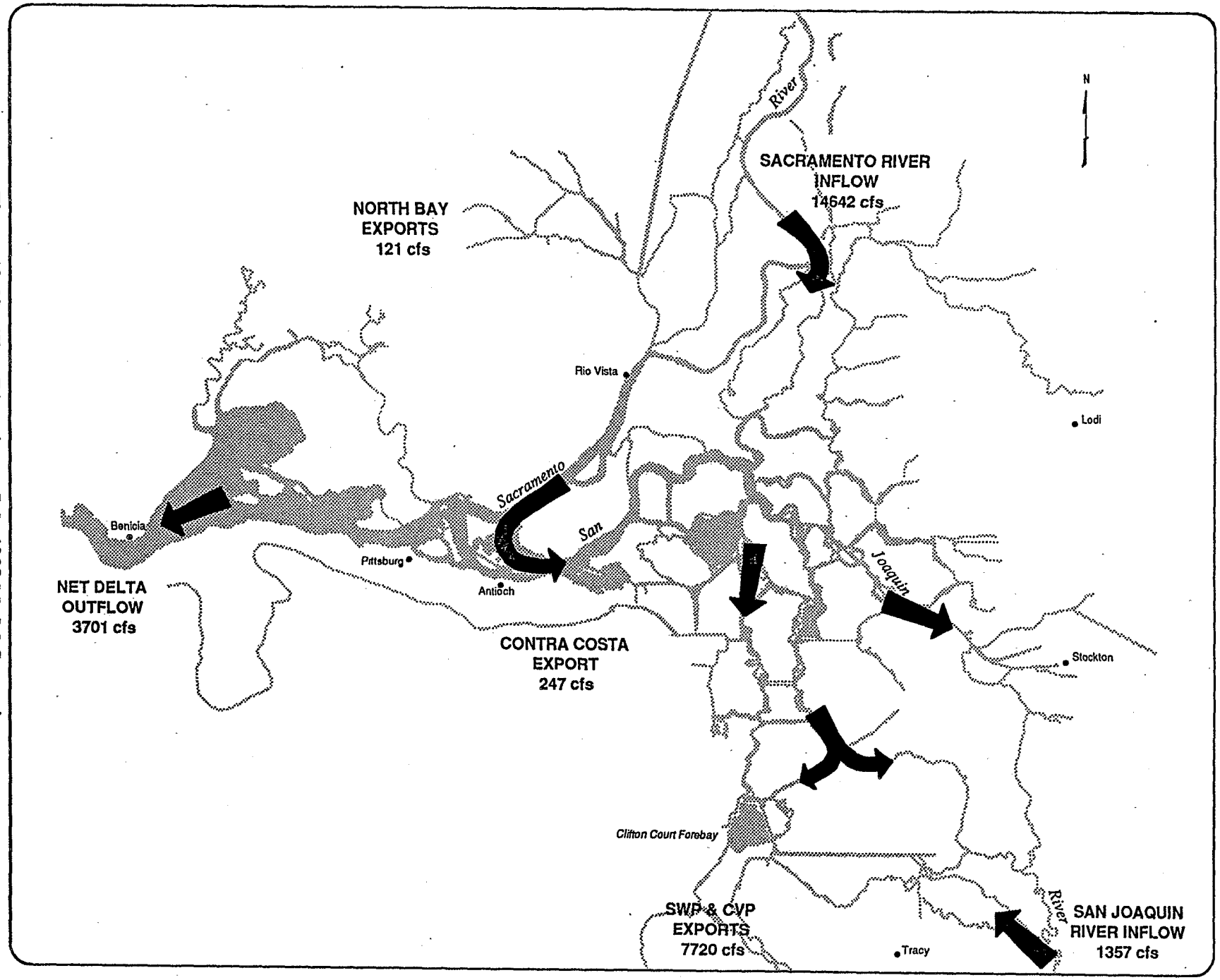

Figure 19. Net Flow Directions: July 1988 Model Scenarios

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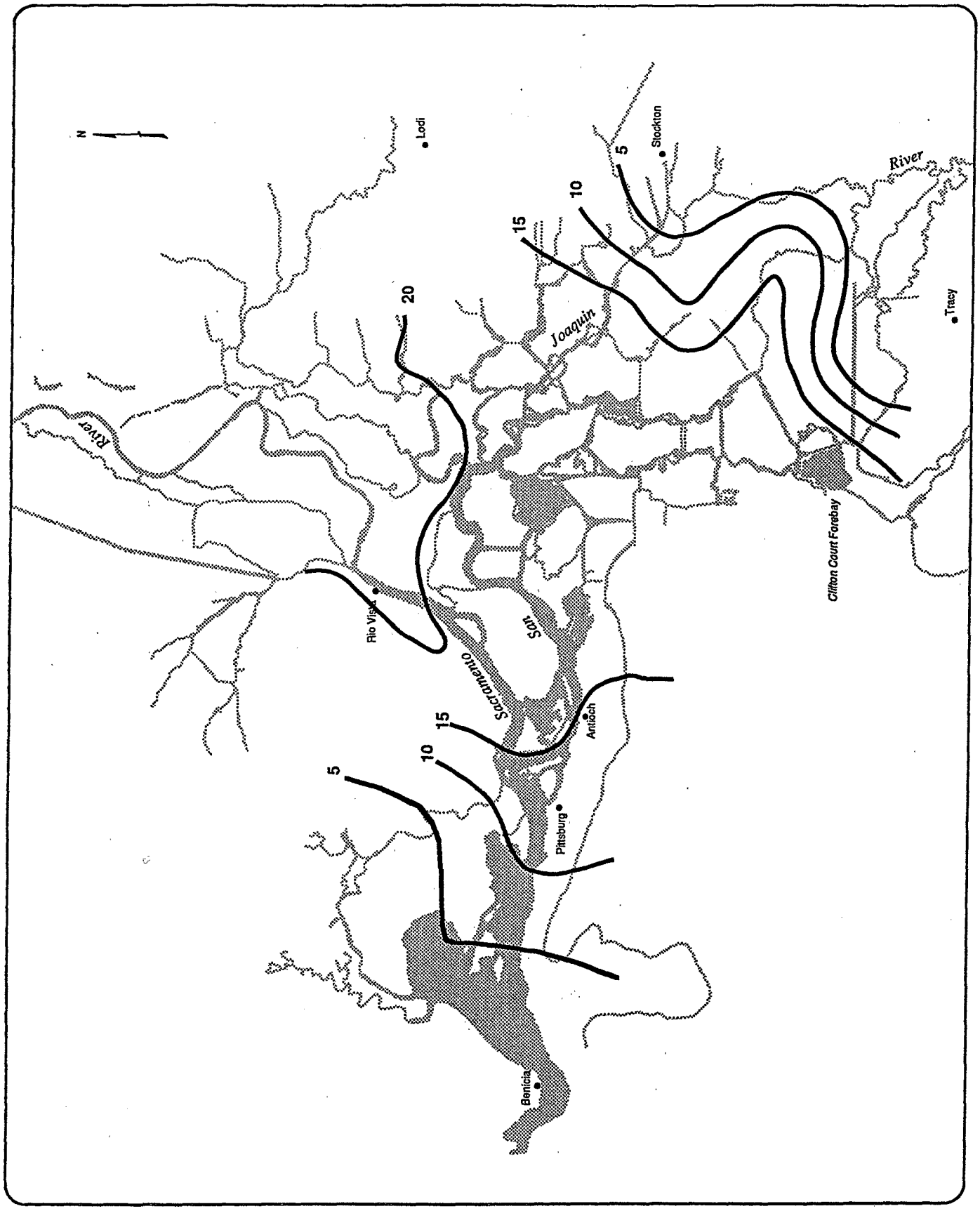

Figure 20. Sacramento River TFPC Impact: Scenario 1 (TFPC in μg/L)

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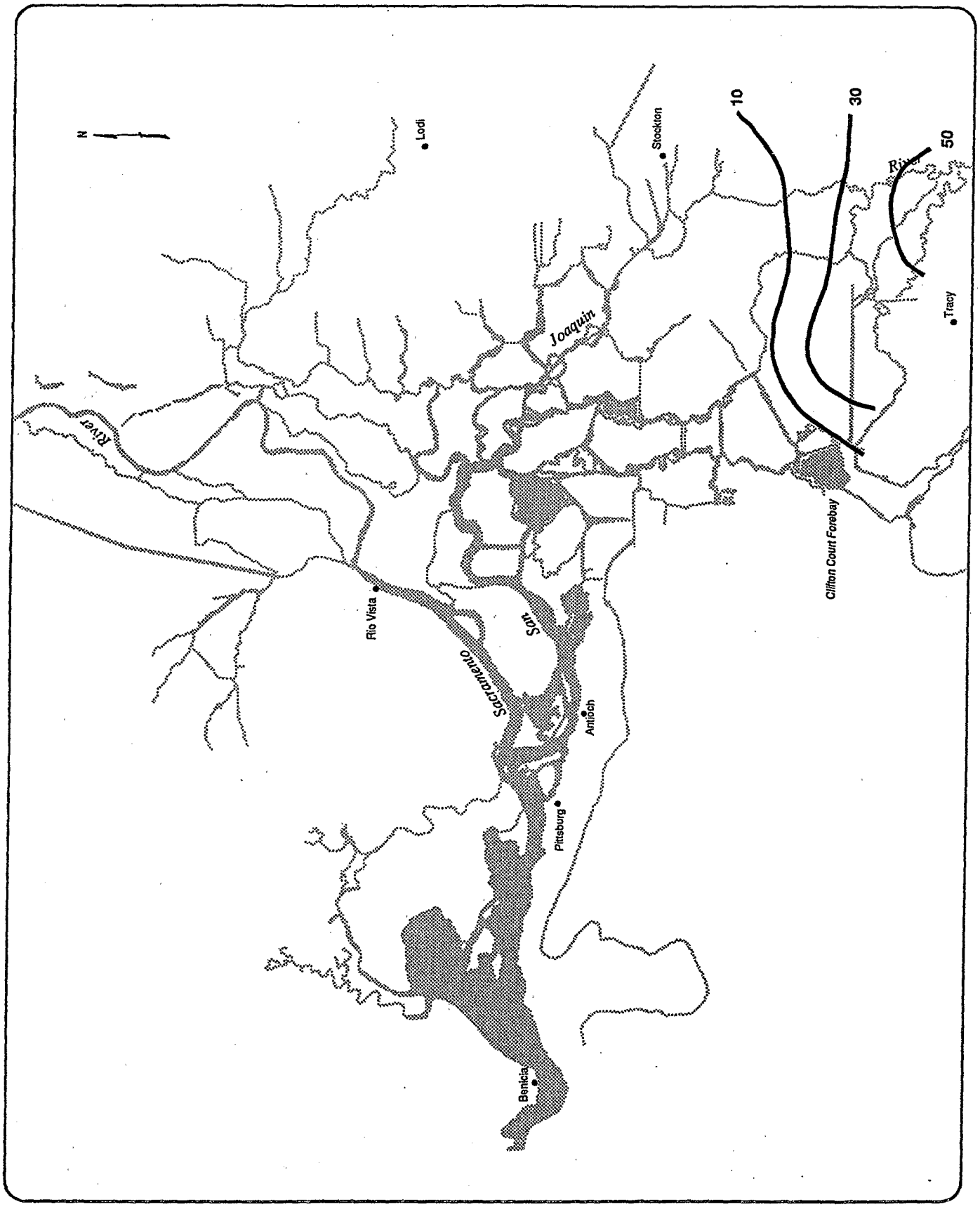

Figure 21. San Joaquin River TFPC Impact: Scenario 2 (TFPC in μg/L)

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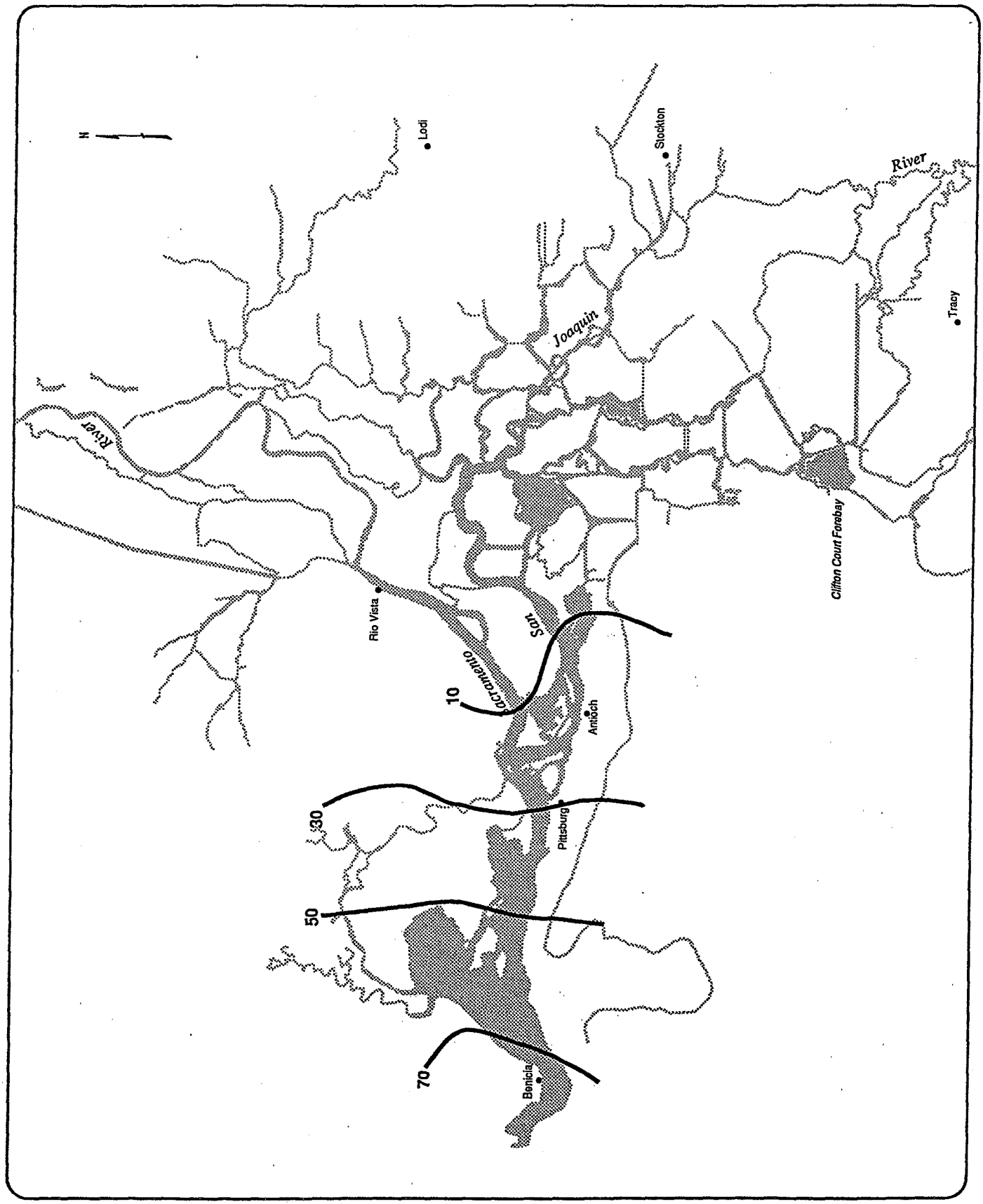

Figure 22. Bay TFPC Impact: Scenario 3 (TFPC in μg/L)

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The boundary condition was estimated from the following mass balance relationship:

TFPC at Mallard = Benicia influence + freshwater influence + agricultural drain influence ..... (8-1)

where freshwater influence was determined from Scenarios 1 and 2, and agricultural drain influence was determined from Scenarios 4 and 5. These influences comprise the total Delta influence at Mallard Island. Sacramento River was the only significant Delta influence identified, contributing about 20 percent of the TFPC at Mallard Island. (Delta influences are more substantial under wetter hydrologies when outflow to San Francisco Bay is greater.) When the sum of Delta TFPC influences is estimated to be less than the total TFPC concentration at Mallard Island, the difference is assumed to originate from the Bay-Delta interface at Benicia.

Even under the low net Delta outflow conditions assumed, Scenario 3 predicts a small Bay-Delta TFPC influence at Clifton Court Forebay (2 μg/L). When net Delta outflow increases under wetter hydrologies, the Bay-Delta influence at Clifton Court Forebay should be expected to be even smaller. Therefore, a lack of data at Benicia does not appear to be critical in modeling TFPC transport in the Delta. DWRDSM reached steady state in approximately 120 days of simulation.

Scenario 4

Fig. 23 shows the influence of island drainage from peat soils is concentrated in the central and southern Delta. Model results indicate that peat island drainage contributes 6 μg/L TFPC at Clifton Court Forebay under steady state conditions. DWRDSM reached steady state in approximately 120 days of simulation.

Scenario 5

Fig. 24 shows the influence of island drainage from mineral/intermediate organic soils is concentrated in the central and southern Delta. Although not shown in the figure, Lindsey Slough in the northern Delta is also strongly influenced by mineral island drainage. Model results indicate that drainage from mineral/intermediate organic islands contributes 3 μg/L TFPC at Clifton Court Forebay under steady state conditions. DWRDSM reached steady state in approximately 120 days of simulation.

Scenario 6

Fig. 25 illustrates the cumulative impact of fresh water inflows, Bay-Delta influences, and agricultural drainage on TFPC concentrations throughout the Delta. Model results indicate a cumulative contribution of 30 μg/L TFPC at Clifton Court Forebay under steady state conditions. DWRDSM reached steady state in approximately 200 days of simulation.

The model estimate of 30 μg/L TFPC at Clifton Court Forebay compares reasonably well with an August 9, 1988 field measurement of 38 μg/L at the same location. In previous data analysis of TFPC, a one month time lag between estimates and field data was found to compensate for inconsistent measuring dates.[1]

Scenarios 1-6 illustrate an important application of the THMFP model formulation: quantifying individual and cumulative impacts of source waters on Delta export water quality. A pie diagram in Fig. 26 summarizes individual TFPC contributions at Clifton Court Forebay from Scenarios 1-6. The diagram shows the Sacramento River to be the largest contributor of TFPC at 63 percent. Agricultural drainage (peat and mineral soils) is shown to contribute 30 percent of the total TFPC load. This estimate is similar to a simple mass balance performed by Amy et al.[5] Based on limited data, their analysis suggested that agricultural drainage may contribute as much as 20 percent of the THMFP found in SWP water. For irrigation months (April-August), DWR[1] has estimated that drainage contributes approximately 40 to 45 percent of the total Delta TFPC load. Fig. 27 shows pie diagrams similar to Fig. 26 at eight MWQI monitoring stations located throughout the Delta. As expected, TFPC source contributions vary significantly from station to station. Agricultural drains contributes the lowest fraction at Mallard Island (2 percent) and the highest fraction at Lindsey Slough (53 percent).

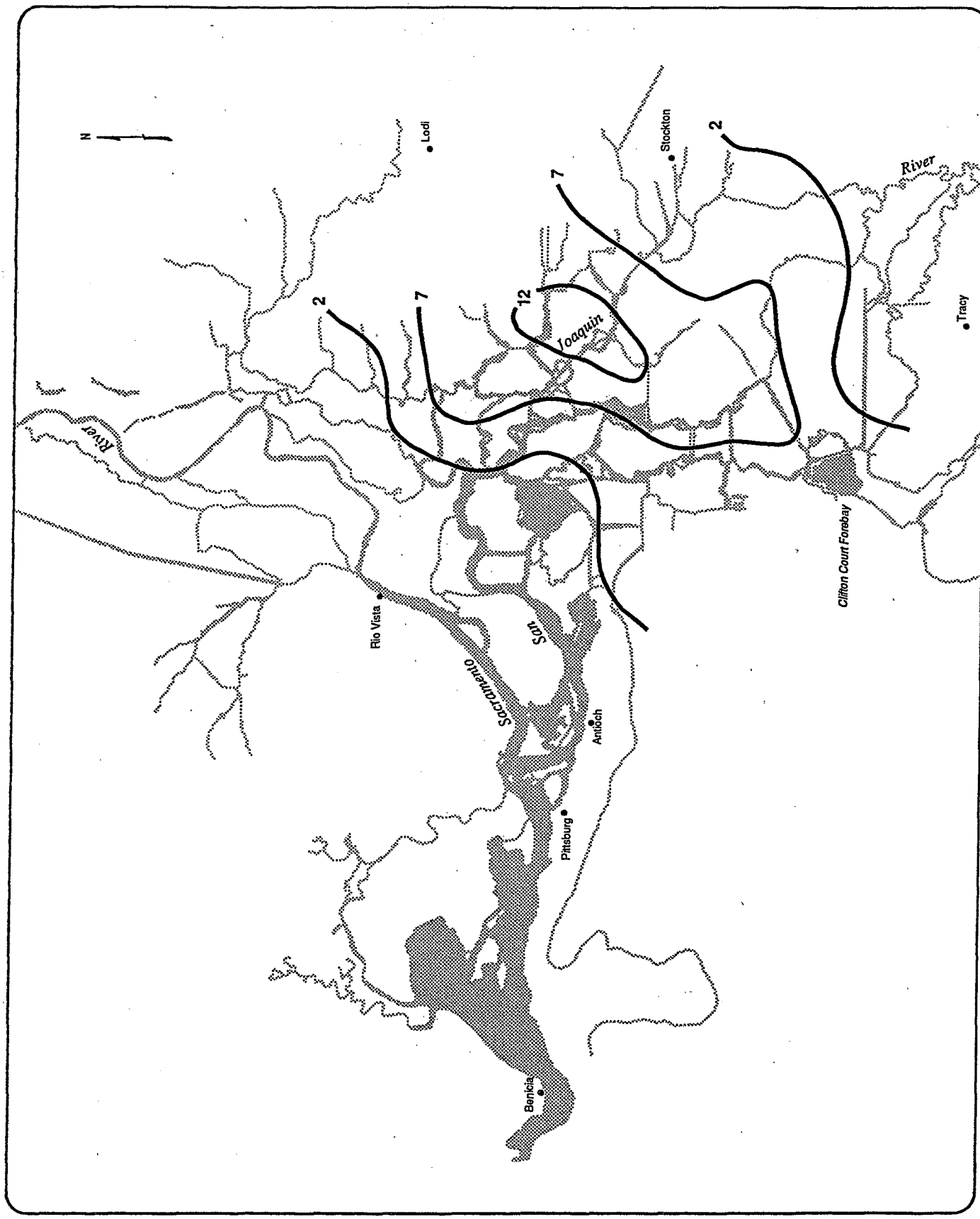

Figure 23. Peat Drainage TFPC Impact: Scenario 4 (TFPC in μg/L)

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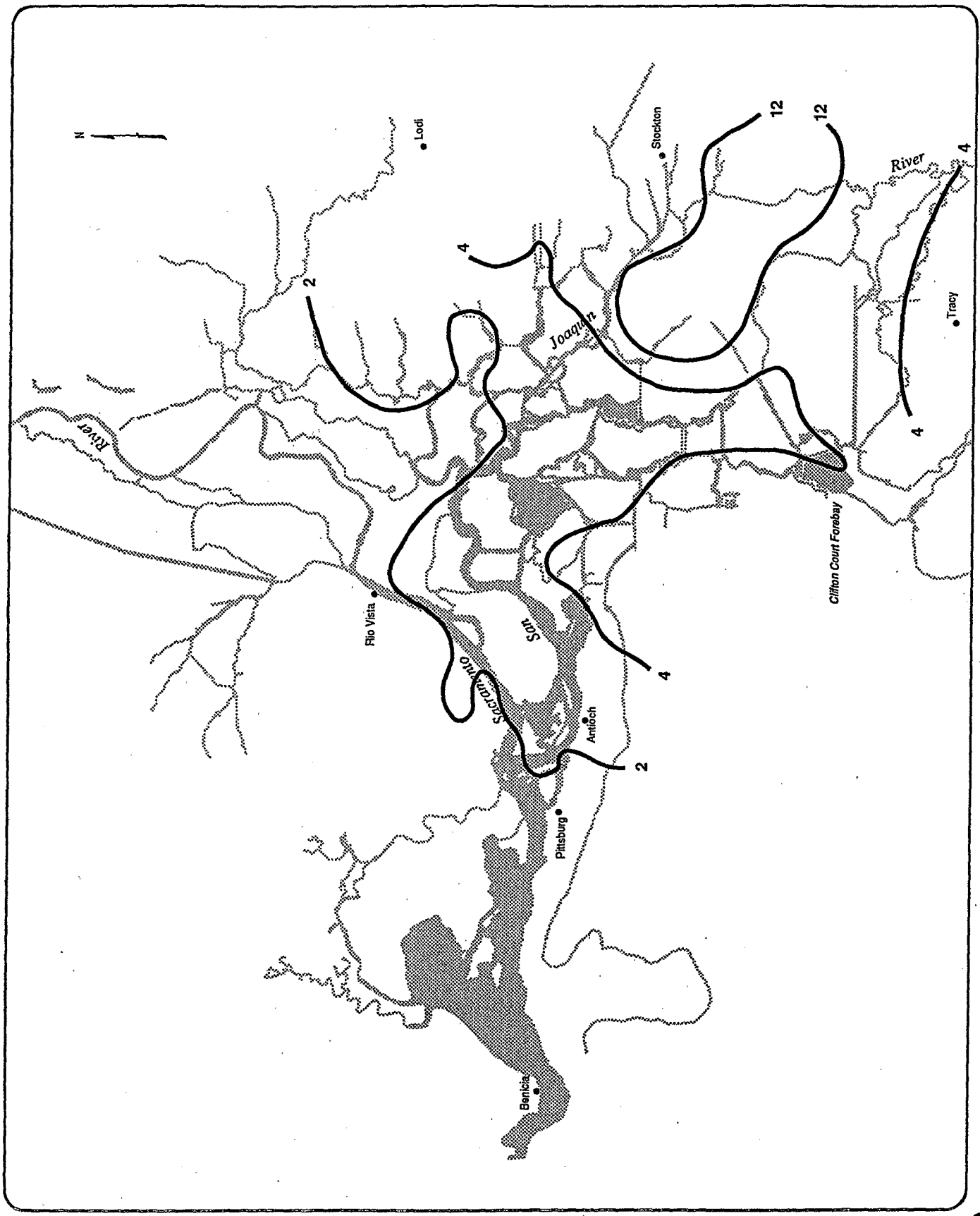

Figure 24. Mineral Drainage TFPC Impact: Scenario 5 (TFPC in μg/L)

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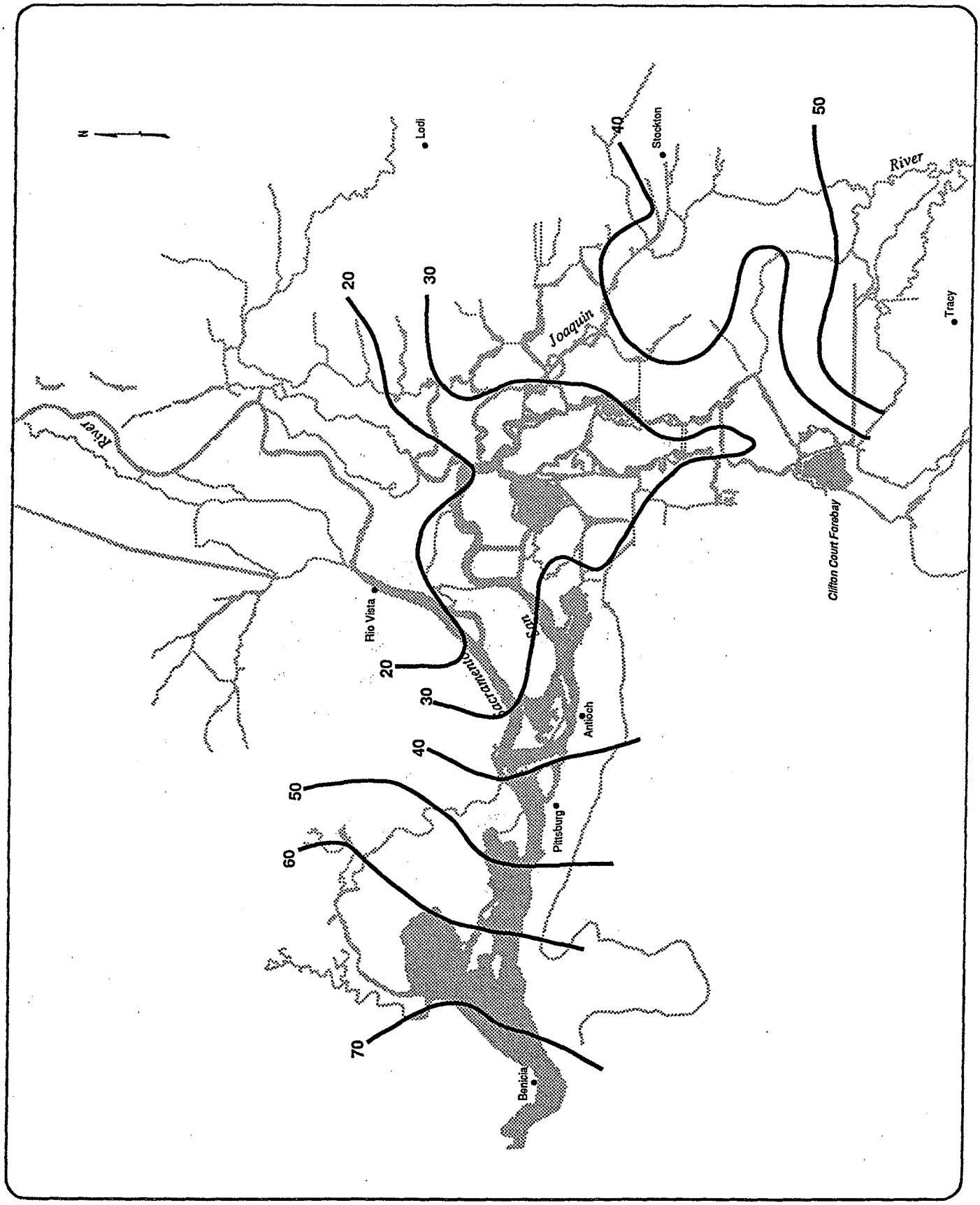

Figure 25. Cumulative Source TFPC Impact: Scenario 6 (TFPC in μg/L)

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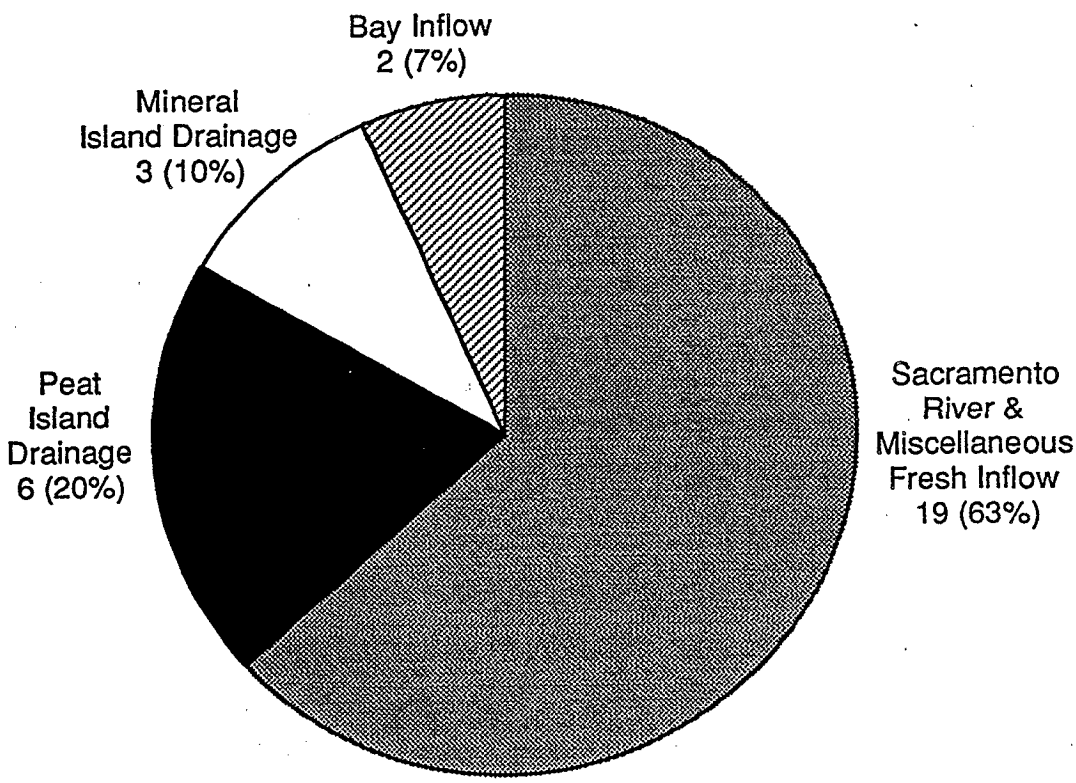

Figure 26. TFPC at Clifton Court Forebay: Scenario 6 (in μg/L)

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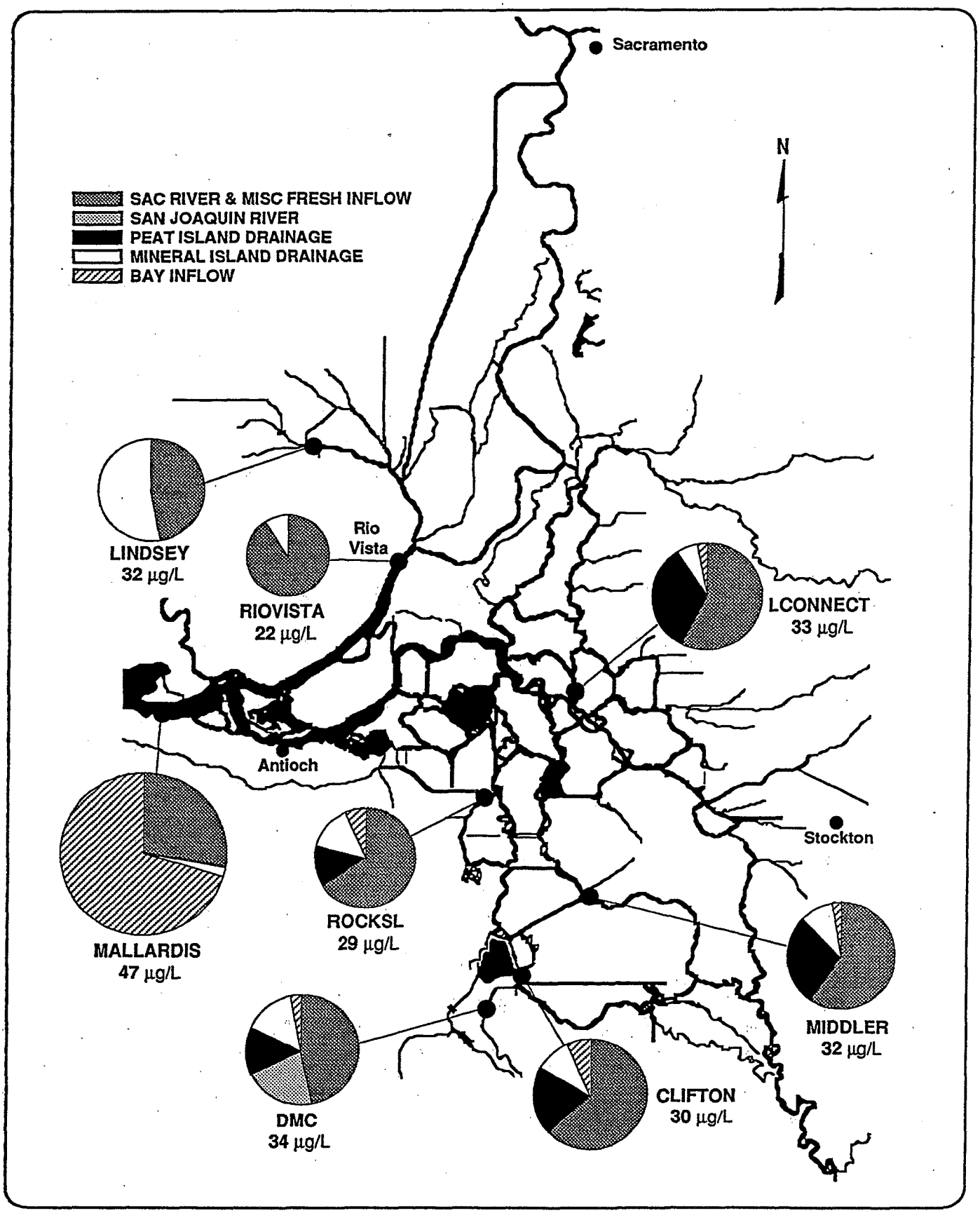

Figure 27. TFPC at Selected MWQI Monitoring Stations: Scenario 6

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Scenario 7

To illustrate another important THMFP model application (simulating bromide effects from the Bromine Incorporation Factor and Bromine Distribution Factors submodels), Delta-wide salinity transport was simulated in Scenario 7. Fig. 28 shows steady state salinity values as measured by TDS. A TDS concentration of 473 mg/L, which translates into a chloride concentration of approximately 180 mg/L, is predicted at Clifton Court Forebay. TDS salinities represent proportional chloride (and thus bromide) concentrations throughout the Delta.

Comparison with Historic Data

DWRDSM steady state results for TFPC and TDS at the eight MWQI monitoring stations located in Fig. 27 were used to predict chloride, Bromine Incorporation Factor (η) and THMFP values ($CHCl_3$, $CHCl_2Br$, $CHClBr_2$, $CHBr_3$) at each location. These values, in addition to TFPC, are compared with historic data in Fig. 29. THMFP estimates compare very well with historic data at Clifton Court Forebay, Delta-Mendota Canal, Rock Slough and Mallard Island. Although historic data were not available at Rio Vista, model values were reported to show that the model correctly reflects low THMFP concentrations at fresh water stations. The close agreement between predicted and observed values at these stations makes the model formulation appear quite promising.

Deviations between predicted and observed values of THMFP are greatest at stations LCONNECT, LINDSEY, and MIDDLER. All three stations are shown in Fig. 27. THMFP at these stations appears to be heavily influenced by agricultural drainage, highlighting the need to develop relationships that more accurately describe agricultural drainage quality in the Delta.

Although predicted and observed TFPC values are similar at LCONNECT, the chloride estimate of 76 mg/L is substantially greater than the observed value of 10 mg/L. This deviation results in much higher Bromine Incorporation Factor (0.37 instead of 0.17) and thus higher bromomethane concentrations. Because of a good TFPC prediction, the chloroform estimate is similar to the observed value.

The high deviation in chloride values at LCONNECT is partially attributed to DWRDSM and partially to an apparent anomaly in the TDS:Cl^- conversion. DWRDSM overpredicted TDS by a factor of two, predicting a value of 232 mg/L while a nearby station (Little Potato Slough) was observed at 103 mg/L.[48] TDS was not measured at LCONNECT during July 1988. However, by converting the predicted value of TDS to chloride with a relationship developed for another nearby station (South Fork Mokelumne River below Sycamore Slough),[47] the overprediction was magnified to a factor of eight.

LINDSEY suffers from the opposite problem described at LCONNECT. The 32 µg/L TFPC prediction deviates from the historic value (63 µg/L), but chloride values agree quite well. The TFPC deviation results in a low prediction of chloroform concentration (291 µg/L instead of 590 µg/L). The good chloride prediction results in similar observed and predicted bromomethane concentrations.

The high deviation in TFPC values at LINDSEY may be related to the boundary condition assumed for Yolo Bypass. Yolo Bypass was assigned a TFPC concentration equal to the Sacramento River (21 µg/L), even though it acts as an agricultural drainage channel in the summer. Yolo Bypass contributed 7 µg/L (22 percent) of the 32 µg/L TFPC at LINDSEY under simulated conditions. A better assumption may be that Yolo Bypass water quality is similar to Natomas Main Drain. With this assumption, the July 1988 boundary condition would be 104 µg/L TFPC[2] and the contribution at LINDSEY would be 35 µg/L. This revised assumption results in a total TFPC concentration of 60 µg/L, a Bromine Incorporation Factor of 0.05, and a chloroform concentration of 570 µg/L—predictions nearly identical to historically observed values. Percent TFPC contributions change accordingly, with 58 percent from Yolo Bypass, 13 percent from Sacramento River, and 29 percent from mineral island drainage.

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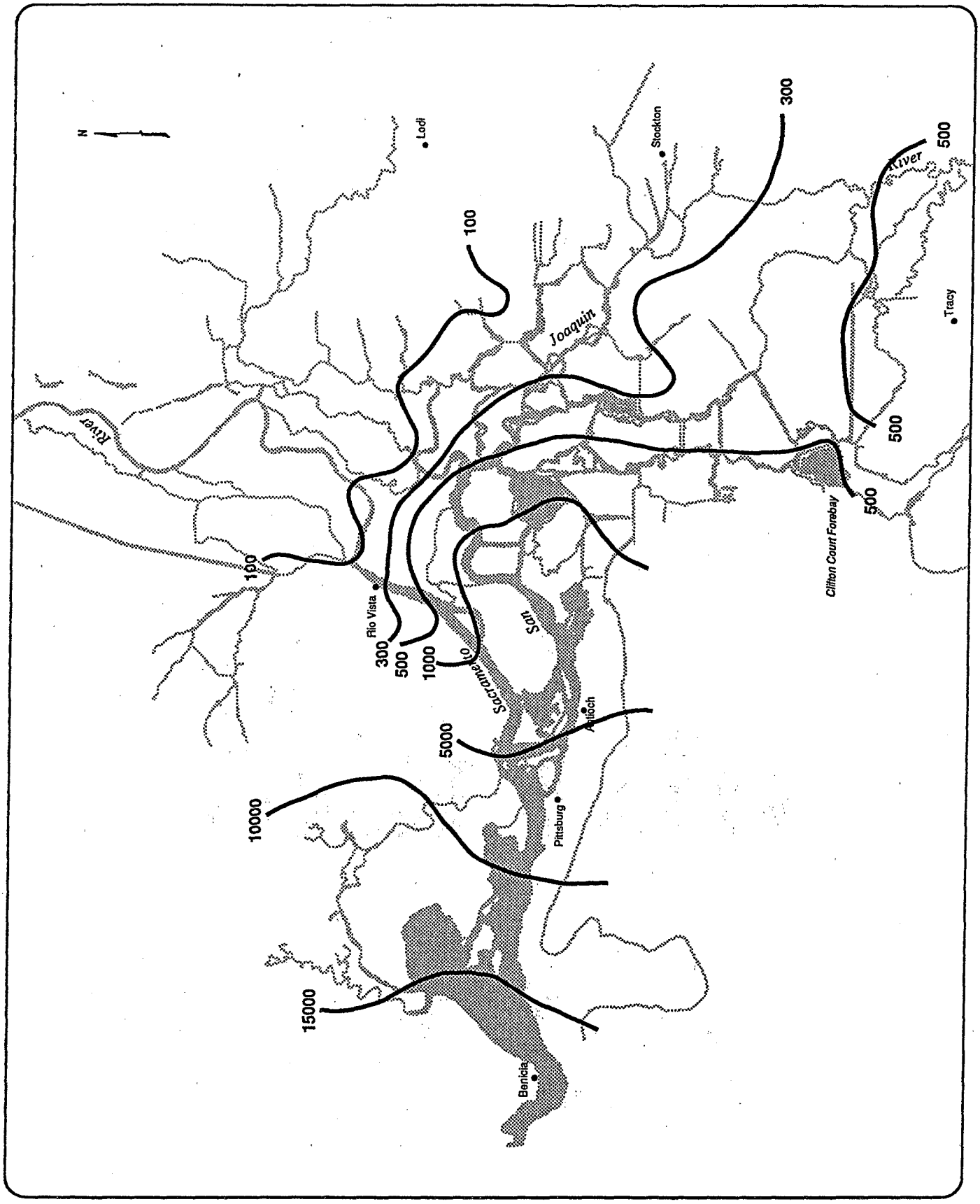

Figure 28. Cumulative Source Salinity Impact: Scenario 7 (TDS in mg/L)

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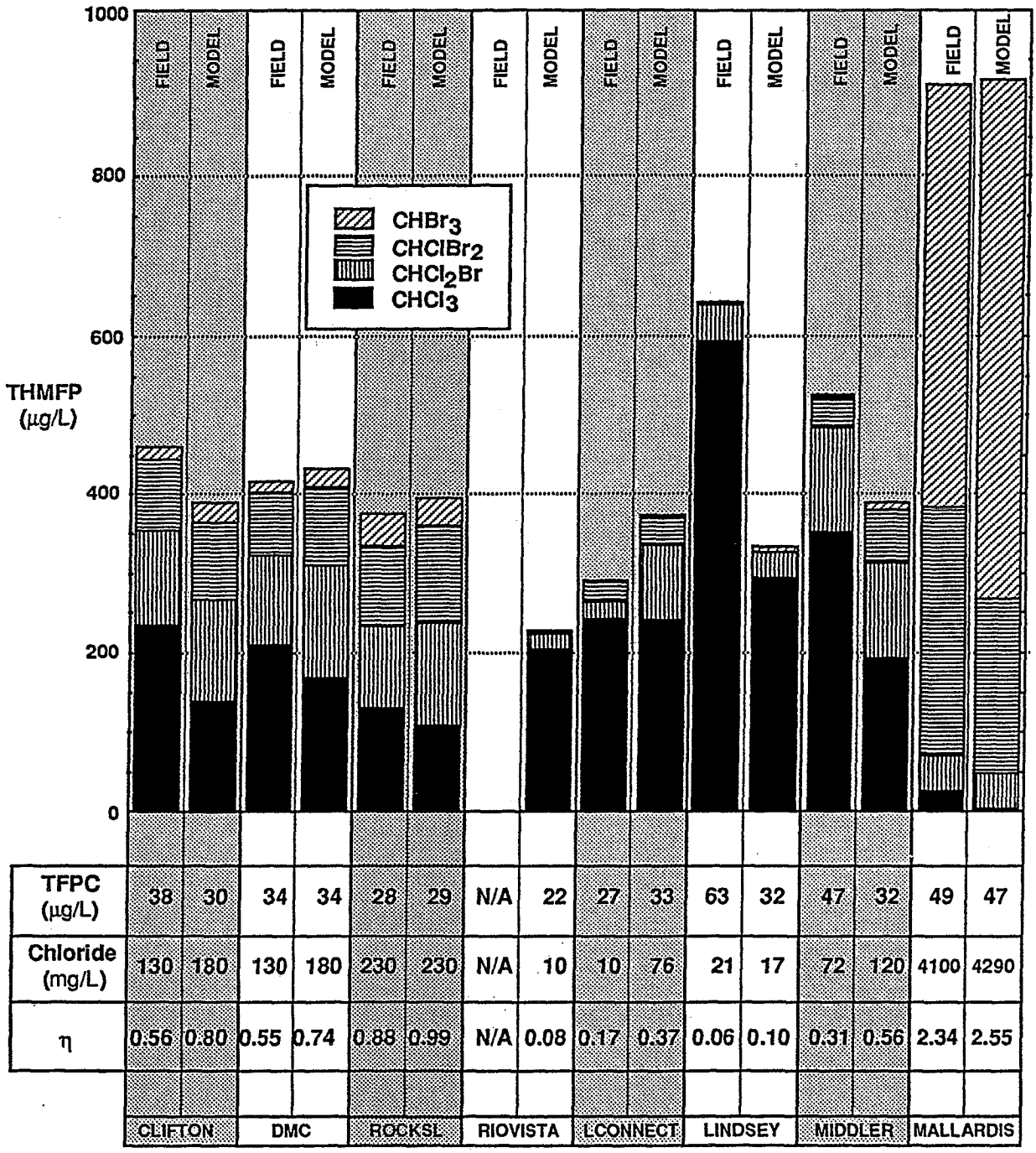

	CLIFTON		DMC		ROCKSL		RIOVISTA		LCONNECT		LINDSEY		MIDDLER		MALLARDIS	
	FIELD	MODEL	FIELD	MODEL	FIELD	MODEL	FIELD	MODEL	FIELD	MODEL	FIELD	MODEL	FIELD	MODEL	FIELD	MODEL
TFPC (µg/L)	38	30	34	34	28	29	N/A	22	27	33	63	32	47	32	49	47
Chloride (mg/L)	130	180	130	180	230	230	N/A	10	10	76	21	17	72	120	4100	4290
η	0.56	0.80	0.55	0.74	0.88	0.99	N/A	0.08	0.17	0.37	0.06	0.10	0.31	0.56	2.34	2.55

Figure 29. Field and Model Values: THMFP Steady State Analysis

Both TFPC and chloride predictions compare poorly with observed values at MIDDLER. However, THMFP estimates appear to be more sensitive to the deviation in TFPC than in chloride, as shown by the relatively poor agreement between chloroform concentrations and relatively good agreement between bromomethane concentrations. The overprediction of chloride at MIDDLER is attributable to DWRDSM, as the TDS to chloride relationships was valid for this observation. Because TFPC is underpredicted rather than overpredicted, this deviation is probably a result of incomplete agricultural drainage description rather than a problem with DWRDSM.

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CHAPTER 9. FUTURE DIRECTIONS

The THMFP model framework, as presented in Chapter 5 and developed in Chapters 6 and 7, was applied to seven simulation scenarios in Chapter 8. This exercise illustrated the model's ability to quantify relative contributions of THM precursors from various Delta inflows and also illustrated the model's ability to simulate bromide effects in the Delta. The exercise also revealed a number of directions that can be taken in the future to enhance the model framework.

Enhanced Boundary Conditions

Boundary conditions required by the Sacramento–San Joaquin THMFP model depend on the selected mode of analysis. For example, to simulate historic THM precursor transport in steady state or time series modes, chloride and TFPC boundary conditions should be based on observed data for the period of interest. The problem presented in Chapter 8 is an example of simulating historic THM precursor transport in a steady state mode. To simulate THM precursor transport in a planning mode, "base" hydrologic and water quality conditions can be developed from historic records to represent various year types and seasons.

Simulating THM precursor transport in a predictive or real–time mode with the existing model formulation is problematic in regard to establishing boundary conditions. As discussed in Chapter 5, TFPC (the model parameter representing precursor effects) cannot be estimated a priori but must be calculated from observed THMFP measurements. But by establishing relationships between TFPC and directly measurable water quality and hydrologic parameters at the boundaries, the model can potentially be used in a predictive mode. In the past, DWRDSM has not typically been run in a predictive mode because of uncertainties associated with prototype geometry, boundary conditions, and mixing characteristics. Potential refinements in the descriptions of agricultural drains and other boundary conditions are proposed below.

Agricultural Drain Boundary Conditions

The simulation results presented in Chapter 8 highlight the need for a better description of precursor contributions from agricultural drains. Deviations between predicted and observed values of THMFP were greatest at stations heavily influenced by agricultural drainage. A lack of drain water quality and flow data is considered to be a critical limitation of the current THMFP model formulation. In addition to expanding the MWQI monitoring program to include a larger number of agricultural drains, an effective model enhancement would be to develop a mathematical description of precursor movement on Delta islands.

THMFP from agricultural drains appears to be related to soil type and degree of water saturation of the soil.[1] These factors are also considered to be important in predicting agricultural drain salinity. Therefore, an existing DWRDSM drainage salinity submodel[50] could be modified to simulate TFPC formation and transport from Delta islands. A preliminary revision to the numerical formulation is presented in Eq. 9–1 of Fig. 30.

In Eq. 9–1, the impact of soil type on drainage quality is primarily represented by a term CS_i, the maximum TFPC concentration for a particular island soil. The DWRDSM drainage salinity submodel defines CS_i as an average salinity for a particular island soil, a value that varies by the mechanisms of salt accumulation and leaching. When describing TFPC, CS_i values should be higher for peat soils and lower for mineral soils. CS_i could be utilized as a calibration factor in a drainage TFPC submodel.

Soil type is also represented by the term f_1, the leaching efficiency factor. This factor is assumed to vary between 0.2 for clay soils and 0.6 for sandy soils in the DWRDSM drainage salinity submodel. The impact of soil saturation on drainage quality is primarily represented by the term f_2, the drainage activity factor. This term is a calibration factor in the DWRDSM drainage salinity module and is correlated with precipitation. The product of the leaching efficiency factor and the drainage activity factor is defined by the term f in Eq. 9–1. As f approaches its maximum value of 1, drainage quality is influenced mainly by soil type and approaches a maximum value of CS_i. As f approaches its minimum value of 0, drainage quality is influenced mainly by irrigation quality and approaches a minimum value of C_i.

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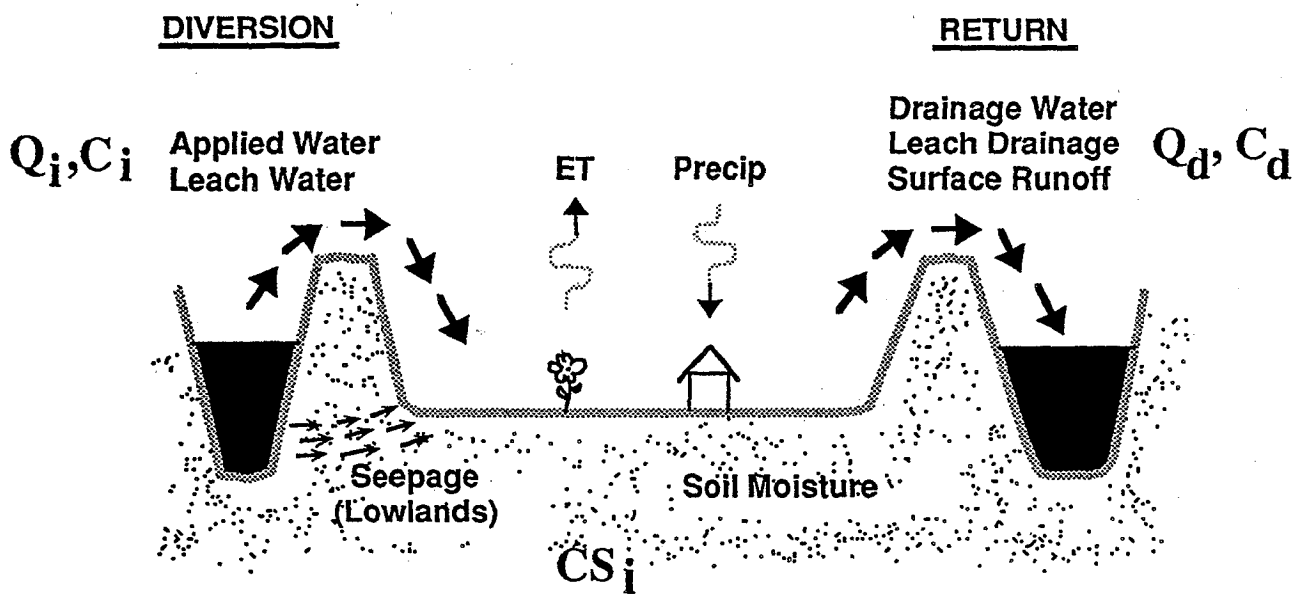

MATHEMATICAL FORMULATION

$$C_d^{t+1} = f \times CS_i + (1-f) \times C_i^t \quad \text{..... (9-1)}$$

WHERE:

C_d = Average TFPC concentration in return water

CS_i = Maximum TFPC concentration in soil

C_i = Average TFPC concentration in diversion water

$f = f_1 \times f_2 < 1$

f_1 = Leaching efficiency factor

f_2 = Drainage activity factor

Figure 30. TFPC Contributions from Agricultural Drainage

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Other Boundary Conditions

Ideally, TFPC boundary conditions could be specified as a multivariate function similar to Eq. 5-3 developed by Amy et al.[29] Given DWR's fixed reaction conditions (chlorine dose, time, temperature) and reported insensitivity to bromide,[29] modified relationships could be developed as functions of UVA, TOC, pH, and chlorine residual. This latter term may include inorganic as well as organic demands. Unfortunately, the existing MWQI data base is not adequate to develop such correlations. Instead, a simplified formulation was developed to estimate TFPC as a function of TOC and average hydrology at key boundaries. This preliminary procedure is outlined below (see Fig. 31) using the San Joaquin River at Vernalis as an example boundary:

1. Specify a flow rate and TOC concentration at the boundary. Historic daily monthly average flow values are readily available from DAYFLOW.[49]

2. Predict molar chloride concentration at the boundary from an established flow–salinity relationship:

$$\ln [Cl^-] = 6.69 - 0.758 \ln Q \qquad (9\text{–}2)$$

where chloride concentration is in mM and flow is in cfs.

3. Calculate Bromine Incorporation Factor from the following location–specific empirical relationship:

$$\eta = \frac{3[Cl^-]}{19.98 + [Cl^-]} \qquad (9\text{–}3)$$

4. Calculate the THMFP concentration of one THM compound as a function of TOC and chloride. At Vernalis, the best functional relationship was found with the compound $CHCl_2Br$:

$$[CHCl_2Br] = 0.228\ TOC^{0.340}\ [Cl^-]^{0.659} \qquad (9\text{–}4)$$

where:

$CHCl_2Br$ and TOC concentrations are in μM and mg/L, respectively.

5. Calculate the distribution factor associated with the THMFP concentration determined in Step 4. Empirical relationships were developed in Chapter 7. For $CHCl_2Br$,

$$s_1 = \frac{-.0446\eta^3 - .1888\eta^2 + .8659\eta}{\eta + 1} \qquad (9\text{–}5)$$

6. Divide the THMFP concentration calculated in Step 4 by the distribution factor calculated in Step 5 to arrive at the TFPC concentration. For the Vernalis example,

$$[TFPC] = \frac{[CHCl_2Br]}{s_1} \qquad (9\text{–}6)$$

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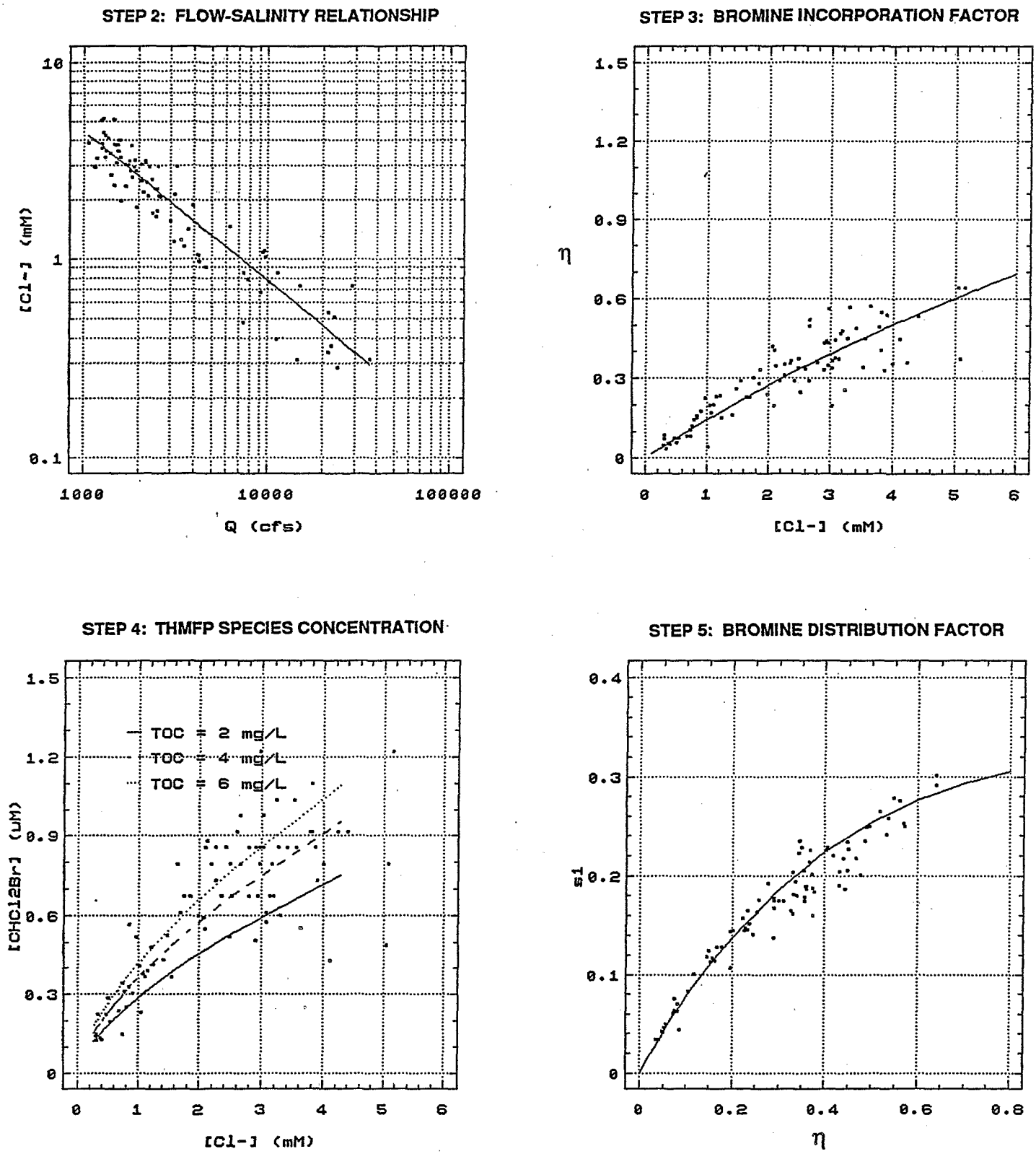

Figure 31. Boundary Conditions at Vernalis

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Fig. 32 shows the relationship between TFPC and flow as derived from Eqs. 9–2 through 9–6. Observed data is also plotted in Fig. 32. Development of preliminary TFPC boundary conditions at Greene's Landing and Benicia is documented in Appendix B.

Correlations Between THMFP and Actual THM Formation

Developing correlations between raw water THMFP and finished water THMs was previously identified as an important area of future research.[1,38] The lack of an established correlation was identified in Chapter 5 as a limitation of the THMFP model's applicability, because DWR's test produces neither the total nor the distribution of THMs produced under actual treatment conditions. The test's tendency to produce higher total THMs and lower bromomethane fractions has been attributed to the exceptionally high chlorine dose utilized by DWR. Although not an absolute requirement in evaluating source water management alternatives, a correlation would be necessary to evaluate treatment alternatives. One approach to establishing a correlation between THMFP and actual THM formation was investigated and is discussed below.

MWD Southern California performed six parallel THMFP and "Simulated Distribution System" (SDS) tests on Banks Pumping Plant water during July and August of 1987.[46] MWD's SDS test is designed to simulate actual THM formation during water treatment and distribution. A comparison of the SDS and THMFP data indicated that molar THM values from the SDS test were 15 to 25 percent of the TFPC values from the THMFP test. Less carbon is oxidized under SDS conditions than under THMFP conditions because of lower chlorine doses and shorter reaction times. Furthermore, values of Bromine Incorporation Factor measured under SDS conditions were 15 to 30 percent higher than predicted by the regression equation developed in Chapter 7. Fig. 33, which plots both observed and predicted SDS values of η, demonstrates that the regression equation reflects a correct sensitivity to chloride concentration in spite of its low predictions.

From the following observed relationship between THMFP and SDS data:

η (from SDS test) = 1.2 η (from THMFP test)

Molar THM (from SDS test) = 0.20 TFPC

data collected at Rock Slough and Banks Pumping Plant under the MWQI program were adjusted to reflect SDS conditions. Adjusted values of η are plotted against chloride concentration in Fig. 34. The adjusted Banks data compares very favorably with THM values observed by MWD Southern California at their Jensen Treatment Plant between 1979 and 1990.[51]

Of course, a useable correlation between THMFP and actual THM formation must be based on more than six parallel observations. Also, it is important to note that a chlorine residual was not maintained in some of MWD's parallel tests, indicating that the THM values were minimum concentrations that could be formed.[46] In spite of these limitations, the comparison presented in this section is a possible first step in developing a correlation between THMFP data and THM formation in treated drinking water. To continue development of such a relationship, the following recommendations are offered:

- A number of parallel THMFP and SDS tests should be performed to quantify the relationship between TFPC and molar THMs produced in the SDS test.
- Regression analysis should be performed on existing SDS data to determine best-fit coefficients for the Bromine Incorporation Factor submodel. The Bromine Distribution Factors submodel was applied successfully to SDS data collected by MWD;[51] therefore, new best-fit coefficients for this submodel do not appear to be necessary. Observed and predicted SDS THM values are compared in Figs. 33, 35, and 36. Estimated values of η were increased by a factor of 1.2 to compare observed and predicted THMs.

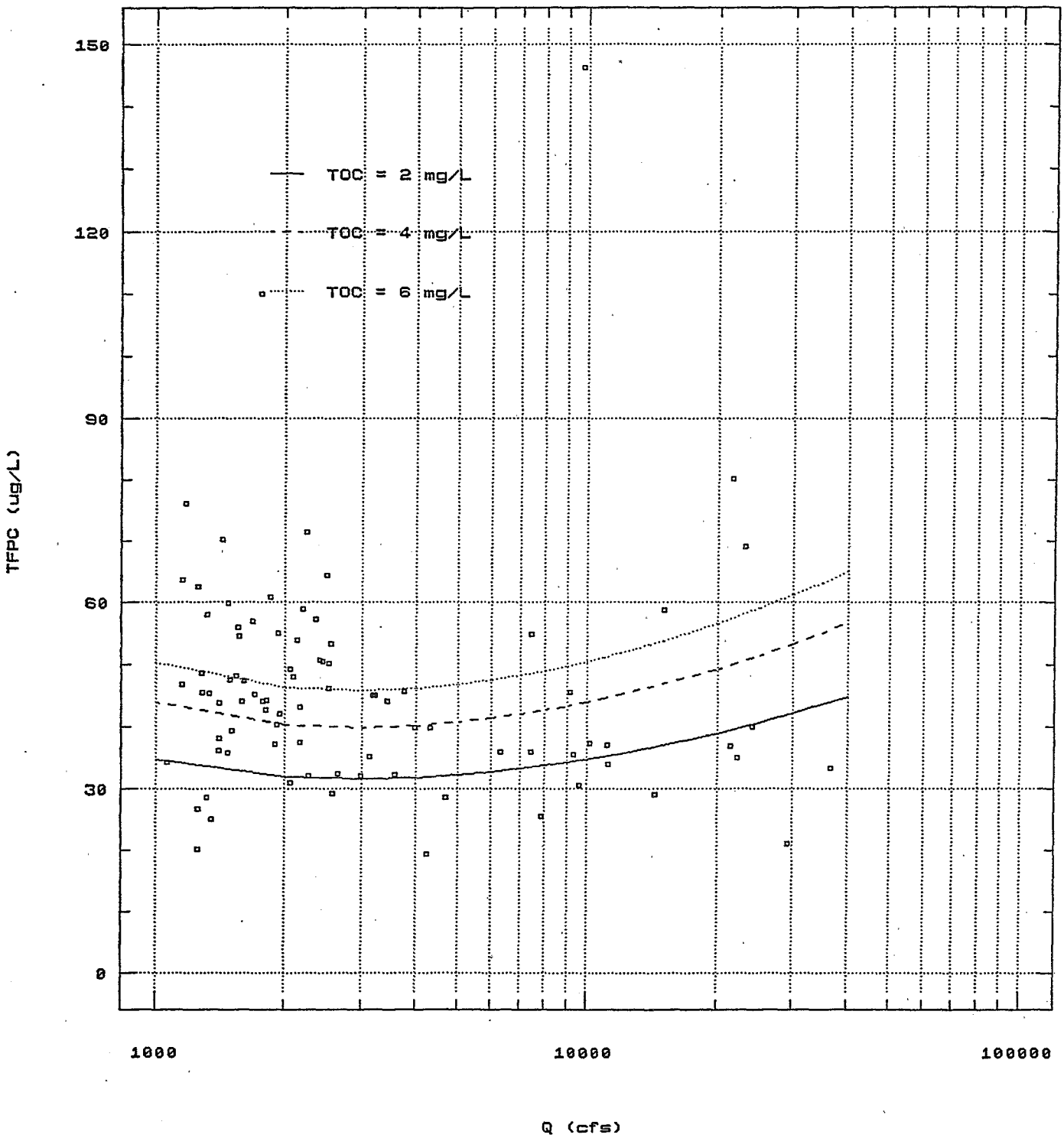

Figure 32. Flow–TFPC Relationship at Vernalis

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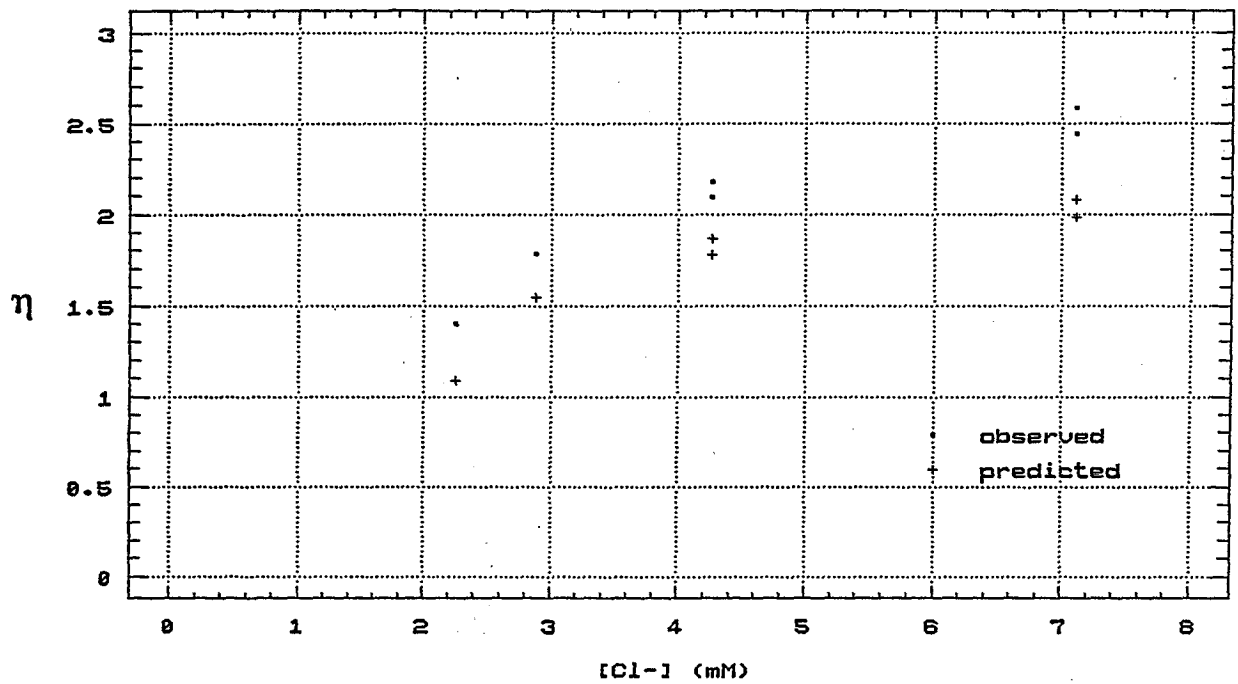

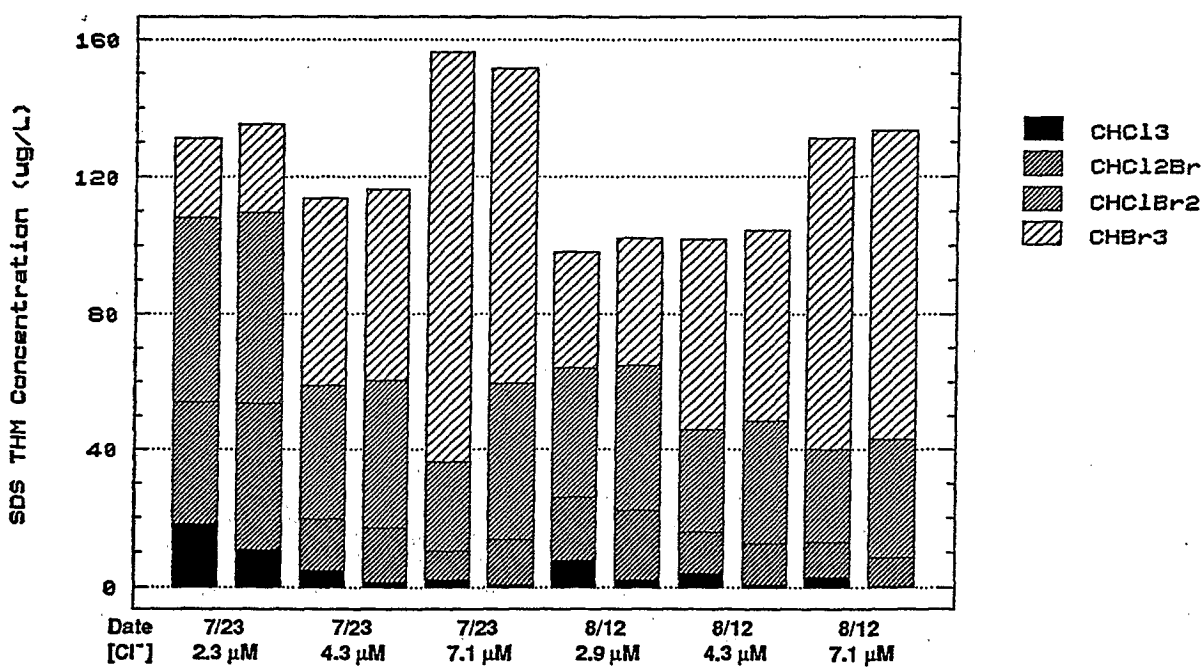

Figure 33. Banks Pumping Plant SDS Tests

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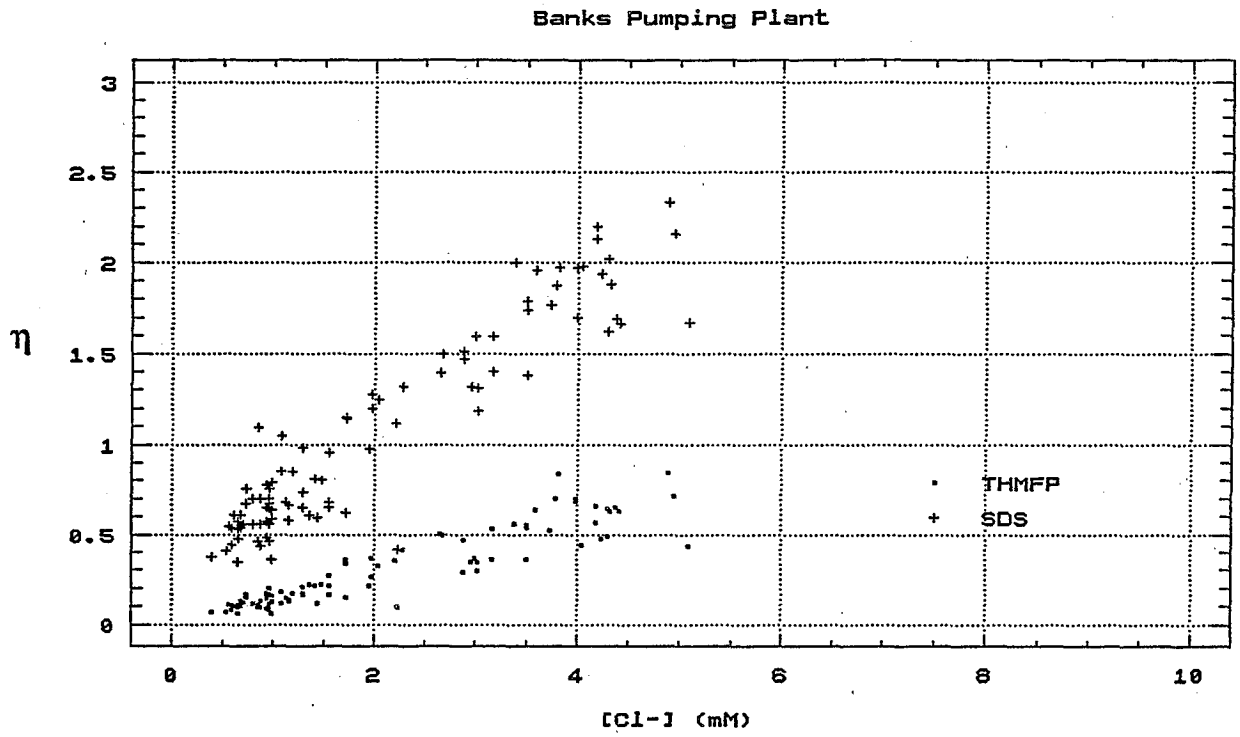

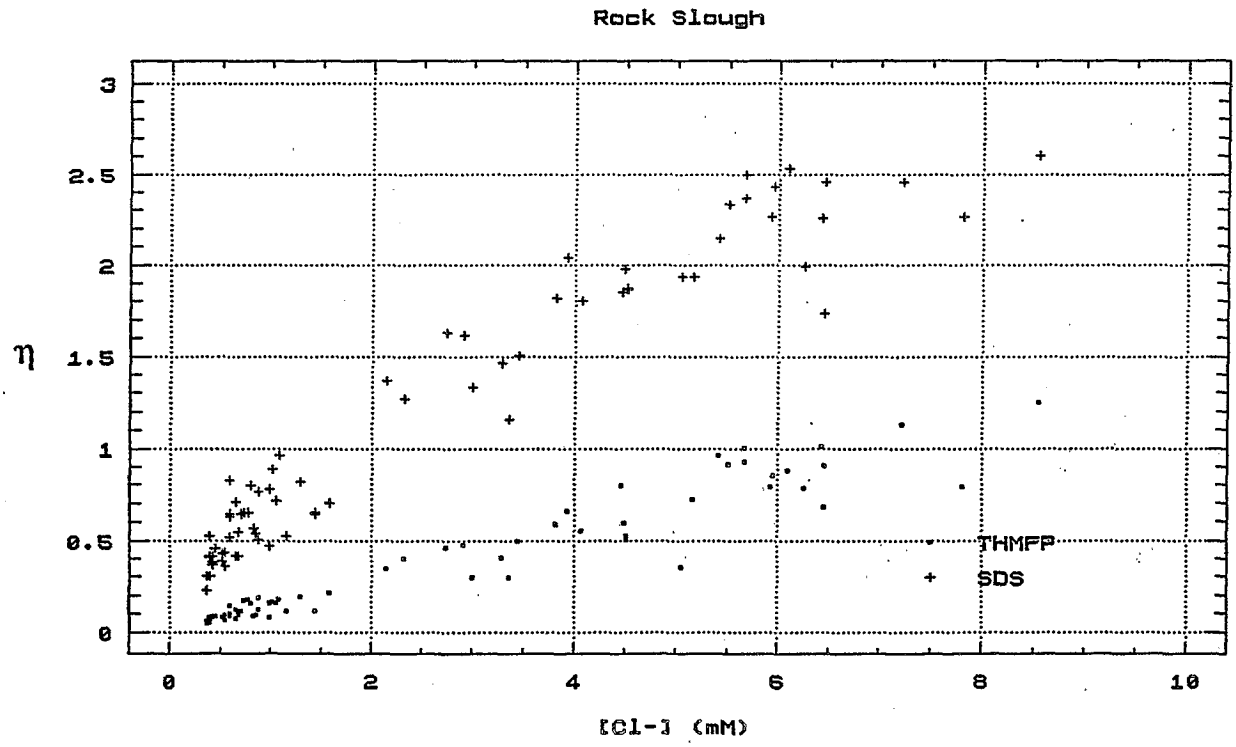

Figure 34. THMFP Data Adjusted to SDS Conditions

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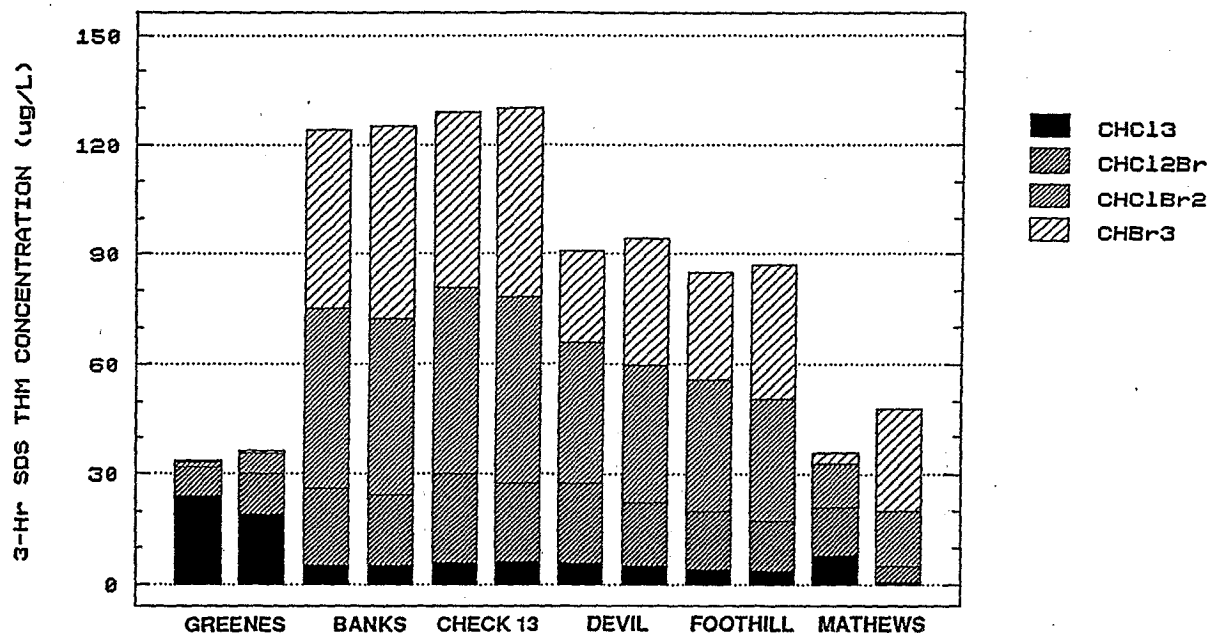


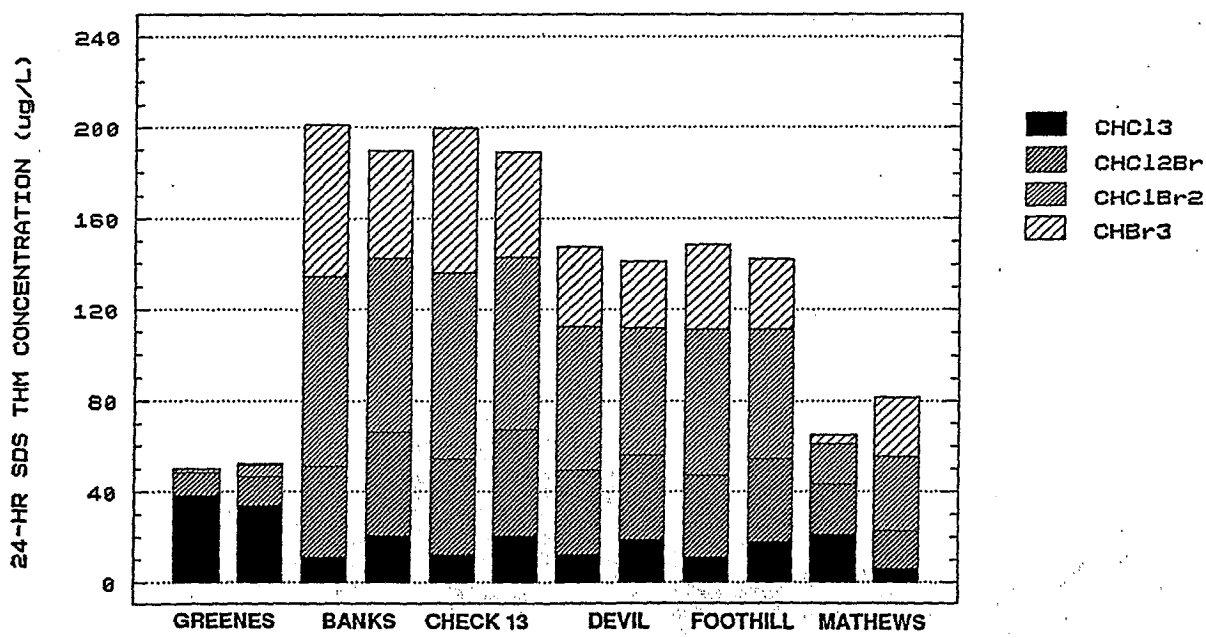
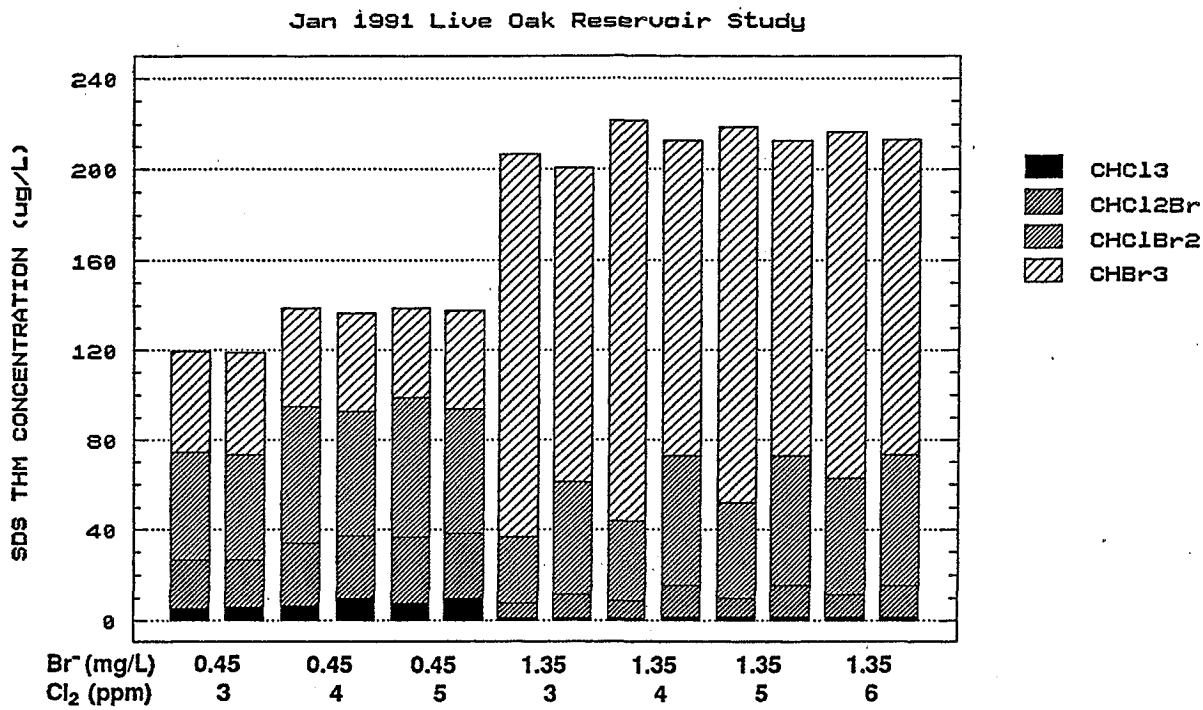


Figure 35. Source Water DBP Study



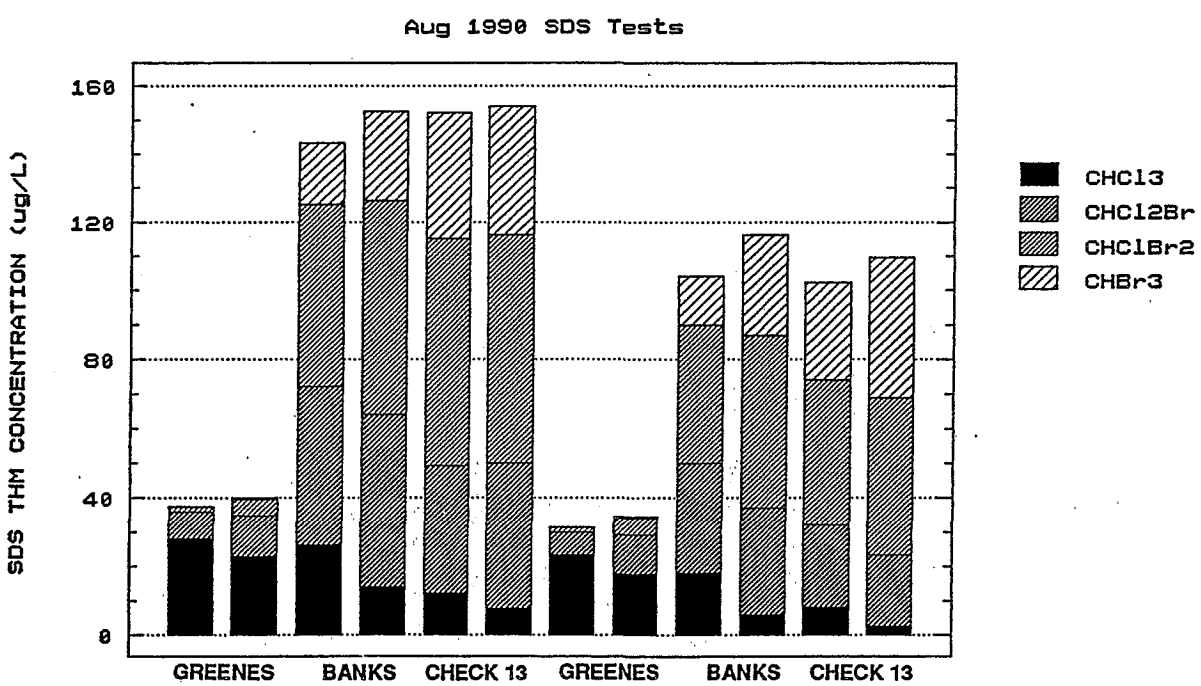


Figure 36. Other SDS Studies

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Multi–Constituent Transport

Seven DWRDSM runs were made to illustrate the model methodology in Chapter 8. Of these seven runs, five simulated the transport of TFPC from different boundaries, one simulated the cumulative effect of TFPC from all boundaries, and one simulated the cumulative effect of chloride from all boundaries. The information from these seven DWRDSM runs could be reproduced in one run by modifying the model to route several conservative constituents simultaneously. For the analysis of THMFP in the Delta, conservative constituents would include chloride and TFPC from five major independent sources (Sacramento River, San Joaquin River, Benicia, Peat Island drainage, and Mineral/Intermediate Organic Island drainage). Multi–constituent transport would save considerable model analysis time.

Coordinated Data Collection and Analyses

The preliminary modeling efforts have emphasized the importance of coordination between the Division of Local Assistance and the Division of Planning. As the model is refined and calibrated with additional data, it will continue to provide better guidance in planning the MWQI monitoring program. Model sensitivity analysis can play a key role in establishing data collection priorities. This link between model analysis and data collection will require an even closer coordination between the two Divisions in the future.

Management Alternatives Evaluation

When further confidence is gained with the THMFP model calibration, a variety of water quality management alternatives can be evaluated. For example, benefits of new tidal barriers, variable pumping schedules, and regulated agricultural drainage can be evaluated and quantified.

To illustrate the evaluation of management alternatives, a simple problem is presented below. The problem was defined so that no DWRDSM runs were required. No conclusions should be drawn from this illustration.

Hypothetical Problem Definition

Due to concerns with THMs in treated water from the Delta, salinity barriers are strategically placed so that reverse flow into the Delta from the Bay is greatly reduced. The resulting water quality impact is as follows: bromide concentration is reduced from 0.51 mg/L (150 mg/L chloride) to 0.17 mg/L (50 mg/L chloride). How much is THMFP reduced at Clifton Court Forebay by this action?

Hypothetical Problem Assumption

The intent of the management alternative is to minimize reverse flow into the Delta from the Bay. It is assumed that this alternative impacts the bromide load but has little impact on the organic precursor load at Clifton Court Forebay. This assumption is based on the DWRDSM model results (Scenario 3) presented in Chapter 8, which shows that Bay influences on TFPC transport are limited to the western Delta.

Marginal Benefit Calculations

Figs. 37a–37b show the marginal effects of controlling bromide on THMFP production, assuming TFPC concentrations typically observed at Delta export stations. These curves were derived from the empirical relationships Bromide Incorporation Factor and Bromine Distribution Factors.

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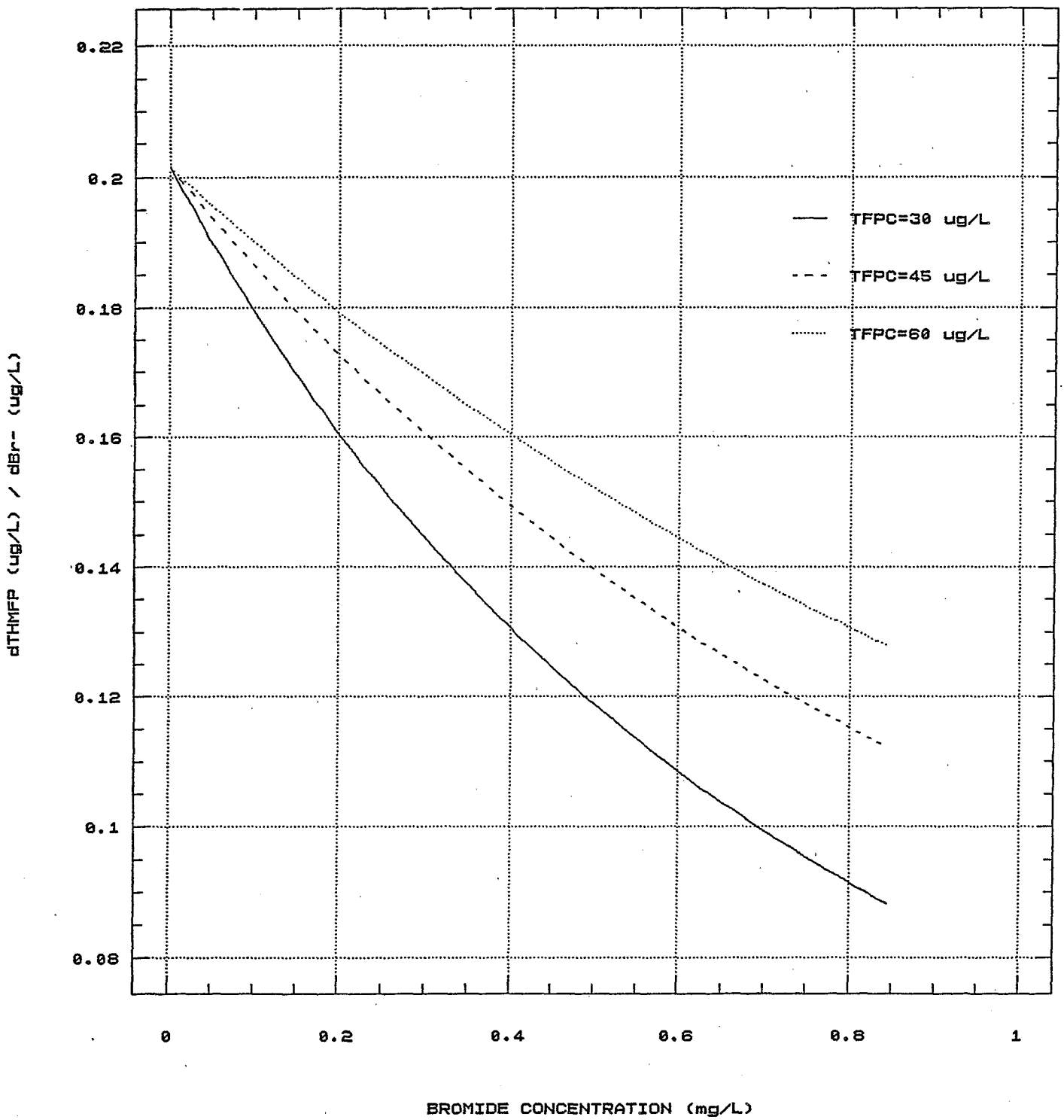

Figure 37a. Marginal Benefits of Bromide Control

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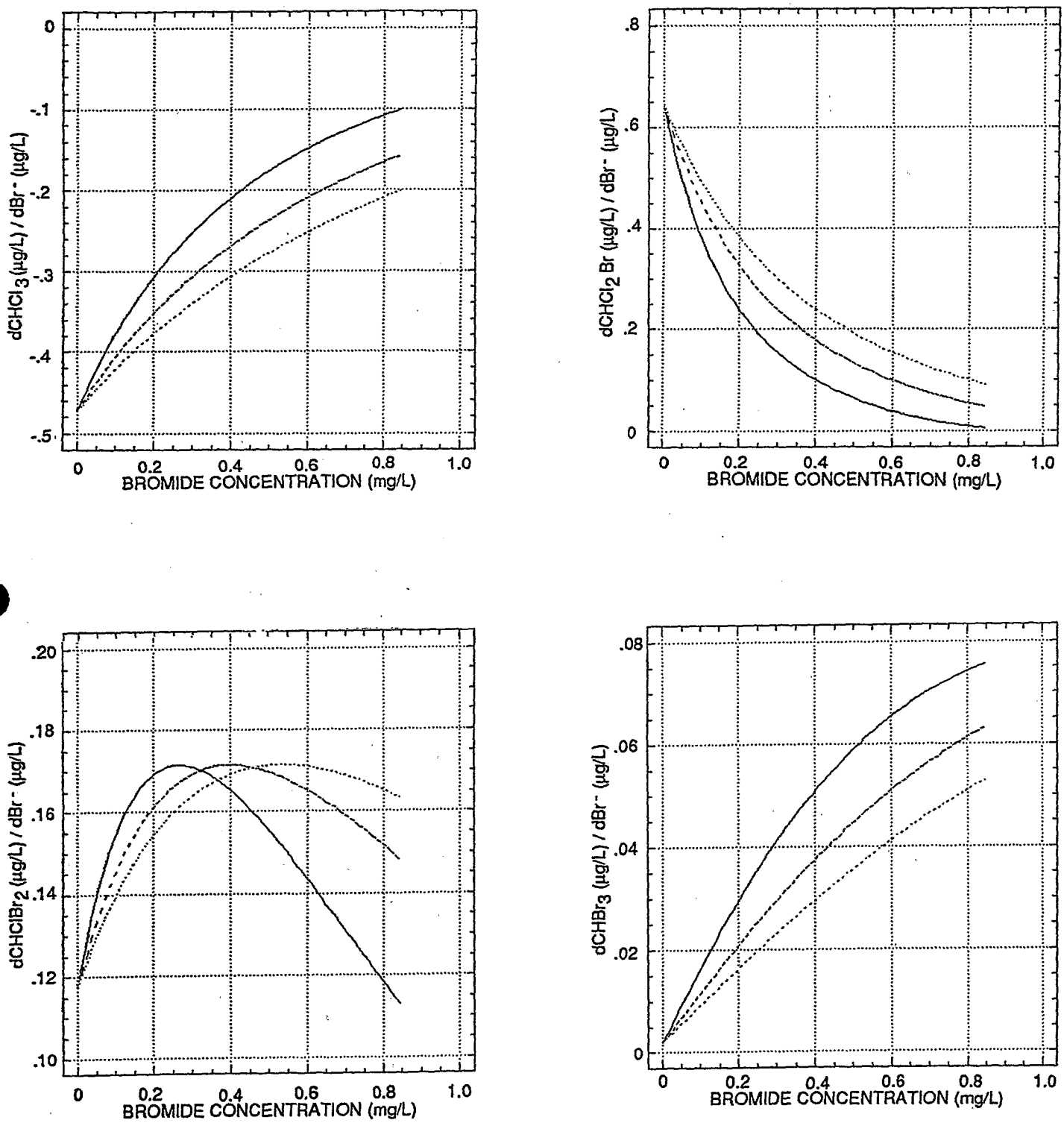

Figure 37 b. Marginal Benefits of Bromide Control

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Total THMFP. The following linear relationship exists between average molecular weight (AMW) and Bromine Incorporation Factor (η) for the four THM species:

$$\text{AMW } (\mu g/\mu mole) = 119.4 + 44.4\eta \quad (9\text{–}7)$$

THMFP mass concentration is equal to the product of TFPC and AMW, yielding:

$$\text{THMFP } (\mu g/L) = 119.4[\text{TFPC}] + 44.4\eta[\text{TFPC}] \quad (9\text{–}8)$$

The partial derivative of THMFP with respect to $[Cl^-]$ is the product of the partials:

$$\frac{\partial\, THMFP}{\partial\, [Cl^-]} = \frac{\partial\, THMFP}{\partial \eta}\,\frac{\partial \eta}{\partial\, [Cl^-]} \quad (9\text{–}9)$$

where:

$$\frac{\partial\, THMFP}{\partial \eta} = 44.4\ [TFPC] \quad (9\text{–}10)$$

$$\frac{\partial \eta}{\partial\, [Cl^-]} = \frac{3b\ [TFPC]}{(b\ [TFPC] + [Cl^-])^2} \quad (9\text{–}11)$$

Fig. 37a plots the partial derivative given in Eq. 9–9, modified to reflect mass bromide concentration instead of molar chloride concentration. The modification assumes a bromide to chloride mass ratio of 0.0034. This figure suggests that in a typical Delta export salinity range of 0.17–0.85 mg/L bromide (50–250 mg/L chloride), the marginal benefit of reducing bromide by 1 µg/L corresponds to a reduction in THMFP by approximately 0.1–0.2 µg/L.

$CHCl_3$. By modifying Eq. 7–5, the mass concentration of $CHCl_3$ can be defined as the product of s_0, TFPC molar concentration, and $CHCl_3$ molecular weight, or:

$$CHCl_3\ (\mu g/L) = 119.4[\text{TFPC}](c\eta^3 + d\eta^2 + e\eta + 1) \quad (9\text{–}12)$$

where c,d, and e represent the regression coefficients in Eq. 7–9. The partial derivative of $CHCl_3$ with respect to $[Cl^-]$ is the product of the partials:

$$\frac{\partial\, CHCl_3}{\partial\, [Cl^-]} = \frac{\partial\, CHCl_3}{\partial \eta}\,\frac{\partial \eta}{\partial\, [Cl^-]} \quad (9\text{–}13)$$

where:

$$\frac{\partial\, CHCl_3}{\partial \eta} = 119.4\ [TFPC]\ (3c\eta^2 + 2d\eta + e) \quad (9\text{–}14)$$

and $\dfrac{\partial \eta}{\partial\, [Cl^-]}$ is defined in Eq. 9–11.

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$CHCl_2Br$, $CHClBr_2$ & $CHBr_3$. The partial derivatives of the THMFP bromomethane species with respect to [Cl^-] can be developed in a manner similar to that presented for $CHCl_3$, resulting in the following partials:

$$\frac{\partial\, CHCl_2Br}{\partial \eta} = \frac{163.8\ [TFPC]\ (2c\eta^3 + d\eta^2 + 3c\eta^2 + 2\,d\eta + e)}{(\eta + 1)^2} \qquad \text{(9–15)}$$

$$\frac{\partial\, CHClBr_2}{\partial \eta} = 208.3\ [TFPC]\ (3c\eta^2 + 2d\eta + e) \qquad \text{(9–16)}$$

$$\frac{\partial\, CHBr_3}{\partial \eta} = 252.7\ [TFPC]\ (3c\eta^2 + 2d\eta + e) \qquad \text{(9–17)}$$

Fig. 37b plots the partial derivatives for each THMFP species with respect to [Cl^-], again modified to reflect mass bromide concentration instead of molar chloride concentration. The figures suggest that in a typical Delta export salinity range of 0.17–0.85 mg/L bromide (50–250 mg/L chloride), the marginal effect of reducing bromide by 1 µg/L corresponds to the following change in THMFP species distribution:

0.1–0.4 µg/L increase in $CHCl_3$

0.0–0.4 µg/L decrease in $CHCl_2Br$

0.1–0.2 µg/L decrease in $CHClBr_2$

0.0–0.1 µg/L decrease in $CHBr_3$

The marginal benefit analysis presented in this example problem suggests that controlling bromide intrusion into the Delta results in a net reduction in THMFP. The net reduction in THMFP is accomplished through a redistribution of THMFP species, with more chloroform and fewer bromomethanes produced.

THMFP Reduction Calculations

Table 6 summarizes the calculated THMFP values under base and plan conditions defined above. The management alternative results in a reduction of total THMFP mass concentration by approximately 8 to 12 percent. An even more important result is the change in THMFP species distribution between the base and plan conditions. While chloroform increased by 26 to 50 percent, all bromomethane species decreased dramatically: $CHCl_2Br$ was reduced by 41 to 53 percent, $CHClBr_2$ was reduced by 70 to 71 percent, and $CHBr_3$ was reduced by 85 to 90 percent. As discussed throughout this report, THMFP data must be interpreted with an awareness that the test inherently produces higher total THMs and lower bromomethane fractions than produced under actual water treatment conditions.

Table 6. THMFP: Base versus Plan Conditions

	30 µg/L TFPC		45 µg/L TFPC		60 µg/L TFPC	
	base	plan	base	plan	base	plan
$CHCl_3$	153	230	279	374	413	520
$CHCl_2Br$	123	72	159	81	184	87
$CHClBr_2$	83	25	82	24	79	23
$CHBr_2$	18	2	13	2	10	1
THMFP	376	330	532	481	686	631

Base Condition: Br– = 0.51 mg/L (Cl– = 150 mg/L)
Plan Condition: Br– = 0.17 mg/L (Cl– = 50 mg/L)

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APPENDIX A

REVIEW OF DWR'S THMFP MODEL – G. AMY

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REVIEW OF DWR'S "TRIHALOMETHANE FORMATION POTENTIAL IN THE SACRAMENTO-SAN JOAQUIN DELTA: A MATHEMATICAL MODEL"

Gary L. Amy, Professor of Environmental Engineering
University of Colorado at Boulder

Synopsis

The overall modeling effort is conceptually impressive in simulating existing data; it addresses both total THM formation as well as speciation issues. However, as acknowledged by the author, the model is not, in its present configuration, capable of making THM predictions based on measurements of surrogate parameters and water quality data.

In THM modeling, it is important to couple precursor effects (total THM formation) and bromide effects (THM speciation). In DWR's model, the former is handled through the total formation potential carbon, TFPC, parameter; the latter through the bromide incorporation factor, n. The parameter n has a true predictive capability if one knows the concentration of bromide (or a surrogate such as chloride) and TFPC. The TFPC parameter, however, is based on historical THM data at a point (and time) of interest. It is thus merely a simulation parameter and cannot be predicted via DWR's model. Thus, the author concedes that the main utility of the model is for planning/management purposes. If this is the acceptable endpoint of the model, there is little for this reviewer to criticize (see below). However, if the goal is for the model to evolve into a predictive tool, there are opportunities which require additional and/or modified analytical measurements to be integrated into DWR's Delta monitoring program. The present model can function as the framework for a predictive model.

Critique of Existing Model

The concerns raised in my previous review regarding the TFPC parameter (TFPC cannot be used a priori to predict THMFP) have been addressed in this new version of the report. While the model's predictive capabilities have been deemphasized, the author has done an excellent job in showing (through examples) the use of the model as a planning/management tool. The following points need clarification.

- The author states that poor correlations were found between THMFP and TOC; however, the correlation coefficients (or

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coefficients of determination) associated with Figures 2 and 3 are not reported. With the elimination of a few outliers, these correlations seem fair. I would maintain that a r^2 of, for example, 0.8 would be reasonable as a predictive tool for obtaining approximations.

- The correlation coefficient (or coefficient of determination) for Equation 4-4, showing bromide as a function of chloride, should be indicated.

- Equation 7-1 in Figure 6 is misnumbered.

- For the relationships shown in Table 1, the linearization technique and the linear forms should be indicated. Since r^2 values pertain to linearized forms, it should be noted that, in the case of transformed variables, r^2 requires careful interpretation.

- As indicated by the author, submodel # 3 in Table 1 mimicks the mathematical definition of n. However, it provides the poorest correlation of data. Since n does not vary linearly with Cl^- (Br^-), there is clearly an asymptotic behavior as n approaches 3.0 at high Cl^- (Br^-). The relationship selected, submodel # 5, makes theoretical sense because it indicates the importance of the Br^-/TOC ratio in influencing THM speciation.

- The example shown on page 35 is somewhat curious. The problem statement includes an assumed TFPC of 30 ug/L, based on some historical THM data. The problem then proceeds to "predict" THM species. How do the predictions compare with the data used to estimate TFPC in the first place? I realize that bromide (n) is also influential but it would be interesting to compare the two sets of THM values.

Future Directions

The TFPC parameter represents a measure of the organic carbon which becomes incorporated into THM species; thus, a measurement of the four species along with molecular weight relationships permits its calculation. Since on a molar basis, TFPC carbon and THMFP are equal; it might be less confusing and more appropriate to simply use the latter terminology (i.e., molar-THMFP) within the model. The TFPC parameter really gives no insight into precursor character but rather merely describes observations of molar-THM formation without any measurements of the amount and character of organic-precursor present in that sample. If THM

data for its calculation did not exist, one would expect TFPC (or molar-THMFP) to be a function of the total amount of organic matter (TOC), the character of the organic matter (e.g., humic content), and water quality conditions (e.g., pH).

DWR should strive to develop a means of predicting (as opposed to measuring) TFPC (or molar-THMFP). The necessary independent parameters should reflect organic-precuror characteristics and bromide, as well as influential water quality parameters such as pH.

The best opportunities for developing predictive relationships for TFPC are for source-specific correlations (e.g., Sacramento River, San Joaquin River, agricultural drains). The hydrodynamic features of the present model configuration would allow assessment of the transport of different-character precursors through the Delta.

Whereas TOC alone may not be an adequate surrogate parameter for TFPC (or molar-THMFP), multiplicative parameters (e.g., a multiplicative function of TOC and UV absorbance) may provide more accuracy. Another easy-to-measure surrogate parameter is fluorescence.

DWR should reexamine the way it performs THMFP tests. There are two alternative approaches: (i) based on a specified chlorine/total organic carbon (Cl_2/TOC) ratio (e.g., 3mg/1mg) or (ii) based on the chlorine dose required to provide a target residual (e.g., 0.5 to 1.0 mg/L) at the end of the designated reaction time frame. The use of an arbitrarily high chlorine dose (120 mg/L) causes two problems: (i) it provides an unequal "driving force" for low versus high precursor samples and (ii) it understates the magnitude of brominated THMs. DWR's test also uses ambient pH; differences of +/- one pH unit can significantly affect THM formation. Also, my understanding is that DWR does not quantitatively measure chlorine residual which, if done, would permit a determination of chlorine utilization/demand. Beyond FP tests, there is much merit to simulated distribution system (SDS) tests, based on lower chlorine doses (e.g., Cl_2/TOC = 1:1) and shorter reaction times (e.g., 24 hours). The merits of these tests are two-fold: (i) they are more representative of actual water distribution systems and (ii) the magnitude of brominated species is more accurately represented. Some utilities have developed good relationships between either SDS-THMs or actual distribution-system THMs and THMFP; typically, the former has

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been found to be about 25 to 50 % of the latter. This endeavor, however, has been limited to utility-specific correlations.

The large amount of chlorine used in DWR's THMFP tests favors more chloroform formation; also, the long reaction time frame provides for more chloroform formation since the formation kinetics for bromoform and brominated species are more rapid than those for chloroform.

THM speciation is important for two reasons: (i) recent health evidence suggests that bromodichloromethane may represent a higher risk than other THM species and (ii) brominated species make it more difficult to meet a weight-based (ug/L) MCL. (Expressing concentrations as molar-based dampens the "chemical" role of bromide).

Future Data Needs

Through its Delta monitoring program, DWR could develop an inventory of precuror and actual bromide levels throughout the Delta. Sample locations should include major inflows, outflows, relevant transects between inflows and outflows, and agricultural drains. Precursor parameters could include DOC, UV absorbance, fluorescence, THMFP, and SDS-THMs. Other water quality parameters such as pH should be included. If quantitative measurements of chlorine residual are made, this would provide a means of calculating chlorine utilization/demand. The resultant data base would permit identification of: (i) multivariate correlations for TFPC (molar-THMFP) and (ii) correlations between THMFP and SDS-THMs which would provide insight into actual distribution-system THMs.

In any future modeling (reformulation, recalibration), the relationships involving n may have to be modified. The n factor is based on TFPC results derived from the present THMFP protocol.

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APPENDIX B

ESTIMATING TFPC AND CHLORIDE BOUNDARY CONDITIONS

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APPENDIX B. ESTIMATING TFPC AND CHLORIDE BOUNDARY CONDITIONS

The THMFP model formulation presented in this report utilizes TFPC as a measure of precursor effects. Chapter 5 discusses the main limitation of this assumption: TFPC cannot be measured directly but must be calculated from historical THM measurements. Consequently, the model formulation cannot be used to simulate real time conditions in a predictive fashion, but is limited to simulating historic or plan conditions.

To expand the THMFP model's potential application, Chapter 9 highlights the need for TFPC model boundary conditions to be based on directly measurable water quality parameters. The existing data base appears inadequate to develop multivariate relationships similar to Eq. 5–3 developed by Amy et al.[29] Therefore, Chapter 9 develops and presents a methodology to estimate TFPC boundary conditions as functions of TOC and flow–salinity relationships, relationships based on available data at San Joaquin River at Vernalis. This appendix documents similar boundary conditions developed for Sacramento River at Greene's Landing and the Bay–Delta interface at Benicia. Some of the relationships presented in this appendix have limited significance by statistical measures, but are reported to provide a complete methodology.

Sacramento River at Greene's Landing

Water quality at Greene's Landing can be determined from known or assumed values of Sacramento River flow and TOC. The procedure outlined below is similar to that presented in Chapter 9 for Vernalis.

1. Specify a flow rate and TOC concentration at the boundary. Historic daily and monthly average flow values are readily available from DAYFLOW.[49]

2. The DWR Delta Modeling Section has typically assumed a constant chloride value of 8 mg/L[47] to represent the boundary water quality condition of the Sacramento River, as the variation in measured chloride values at Greene's Landing tends to be small.

An an alternative to the above assumption, a flow–salinity relationship was developed from DWR's THMFP data base:

$$\ln [Cl^-] = 3.89 - 0.578 \ln Q \qquad \text{(B–1)}$$

where chloride concentration is in mM and flow is in cfs. This relationship is shown in Fig. B–1.

3. Calculate Bromine Incorporation Factor from the following location–specific empirical relationship:

$$\eta = \frac{3[Cl^-]}{13.32 + [Cl^-]} \qquad \text{(B–2)}$$

4. Calculate the THMFP concentration of one THM compound as a function of TOC and chloride. At Greene's Landing, the best functional relationship was found with the compound $CHCl_2Br$:

$$[CHCl_2Br] = 0.172\, TOC^{0.191}\, [Cl^-]^{0.529} \qquad \text{(B–3)}$$

where $CHCl_2Br$ and TOC concentrations are in μM and mg/L, respectively.

5. Calculate the distribution factor associated with the THMFP concentration determined in Step 4. Empirical relationships were developed in Chapter 7. For $CHCl_2Br$,

$$s_1 = \frac{-.0446\eta^3 - .1888\eta^2 + .8659\eta}{\eta + 1} \qquad \text{(B–4)}$$

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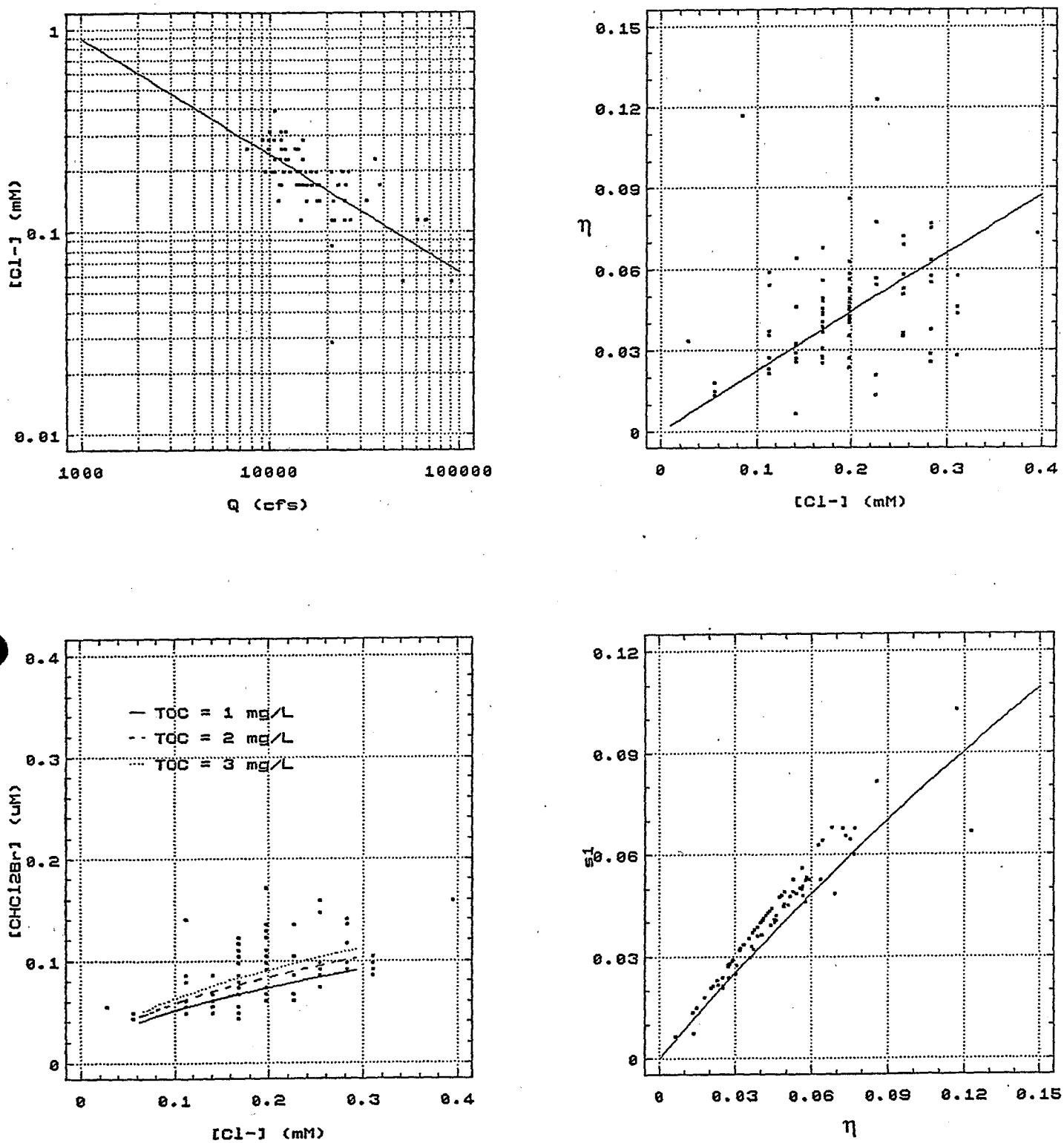

Figure B–1. Boundary Conditions at Greene's Landing

6. Divide the THMFP concentration calculated in Step 4 by the distribution factor calculated in Step 5 to arrive at the TFPC concentration. For Greene's Landing,

$$[TFPC] = \frac{[CHCl_2Br]}{s_1} \quad \text{(B-5)}$$

Fig. B-2 shows the relationship between TFPC and flow as derived from Eqs. B-1 through B-5. Observed data is also plotted in Fig. B-2.

Bay-Delta Interface at Benicia

Chapter 8 describes a trial and error procedure used to estimate TFPC boundary conditions at Benicia. A trial and error procedure is required as data is not available at that location. The procedure attempts to determine TFPC values at Benicia that produce comparable observed and predicted values at Mallard Island. Mallard Island is the THMFP monitoring station most representative of the Bay-Delta interface. The iterative procedure detailed below determines boundary condition water quality with a combination of regression relationships and DWRDSM model runs.

1. The DWR Delta Modeling Section typically utilizes a program called SALDIF to determine "plan" salinity conditions at the Benicia model boundary. SALDIF estimates this boundary condition as a function of a) salinity at Golden Gate Bridge and b) net Delta outflow. Once boundary conditions are established, DWRDSM can be run to determine a chloride concentration at Mallard Island.

2. Calculate Bromine Incorporation Factor at Mallard Island from the following location-specific empirical relationship (see Fig. B-3):

$$\eta = \frac{3[Cl^-]}{18.99 + [Cl^-]} \quad \text{(B-6)}$$

3. Calculate the THMFP concentration of one THM compound as a function of TOC and chloride. At Mallard Island, the best functional relationship was found with the compound $CHCl_2Br$:

$$[CHCl_2Br] = 0.366\ TOC^{0.009}\ [Cl^-]^{0.662} \quad \text{for } [Cl^-] < 10\ \text{mM} \quad \text{(B-7)}$$

$$[CHCl_2Br] = 13.7\ TOC^{0.169}\ [Cl^-]^{-0.850} \quad \text{for } [Cl^-] \geq 10\ \text{mM} \quad \text{(B-8)}$$

where $CHCl_2Br$ and TOC concentration are in μM and mg/L, respectively.

4. Calculate the distribution factor associated with the THMFP concentration determined in Step 3. Empirical relationships were developed in Chapter 7. For $CHCl_2Br$,

$$s_1 = \frac{-.0446\eta^3 - .1888\eta^2 + .8659\eta}{\eta + 1} \quad \text{(B-9)}$$

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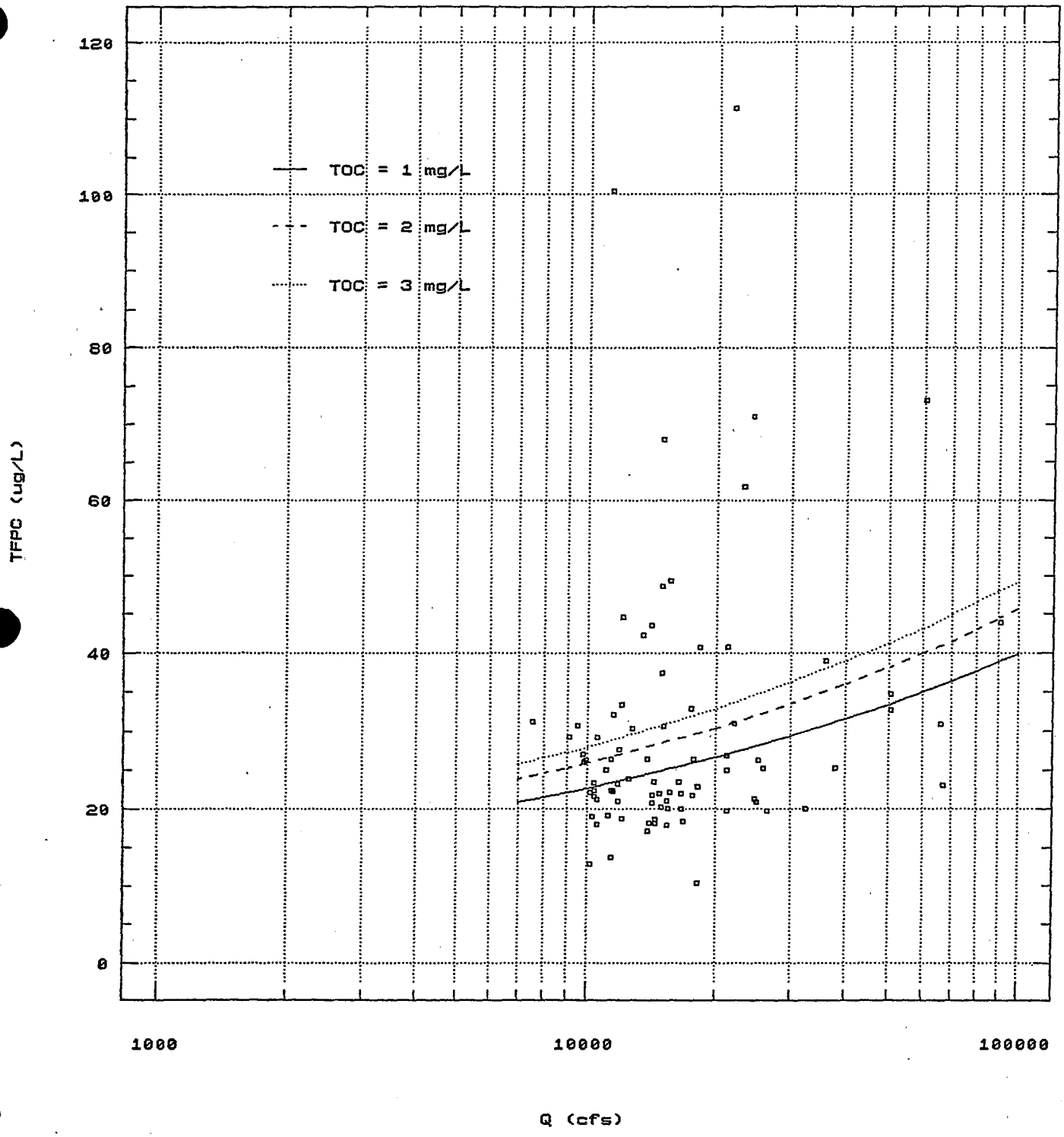

Figure B–2. Flow–TFPC Relationship at Greene's Landing

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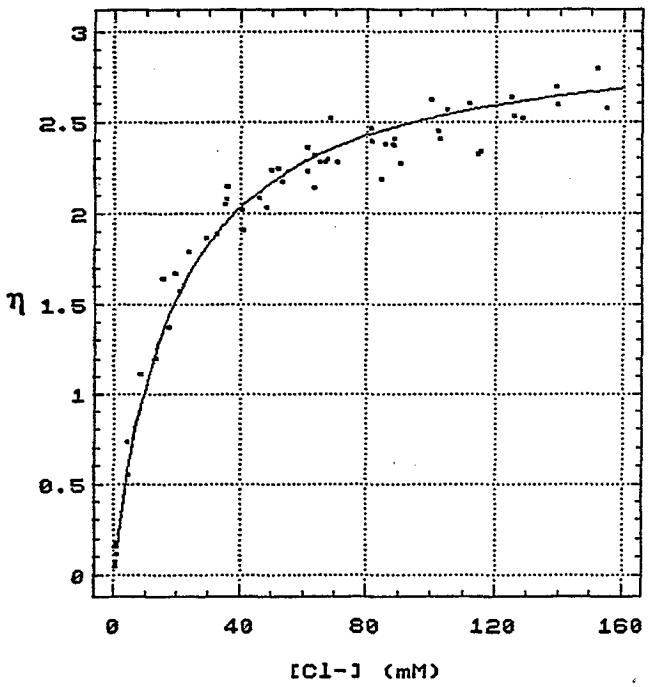

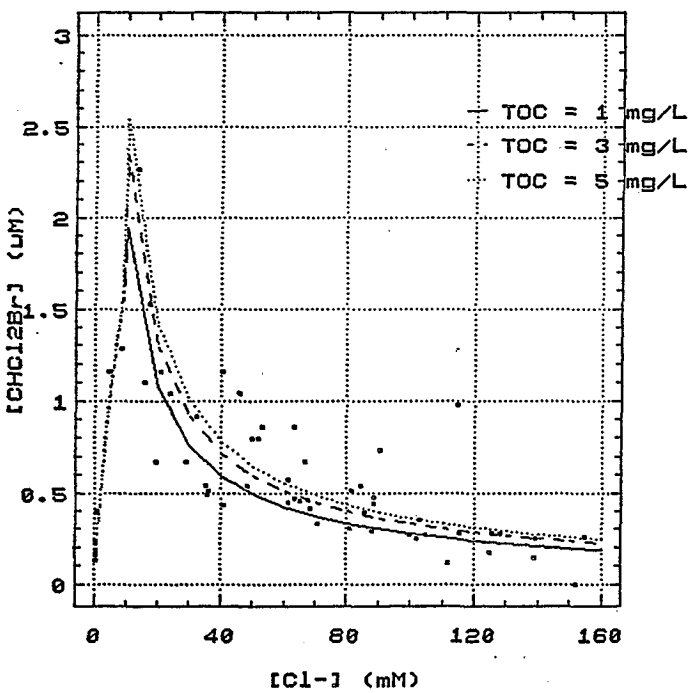

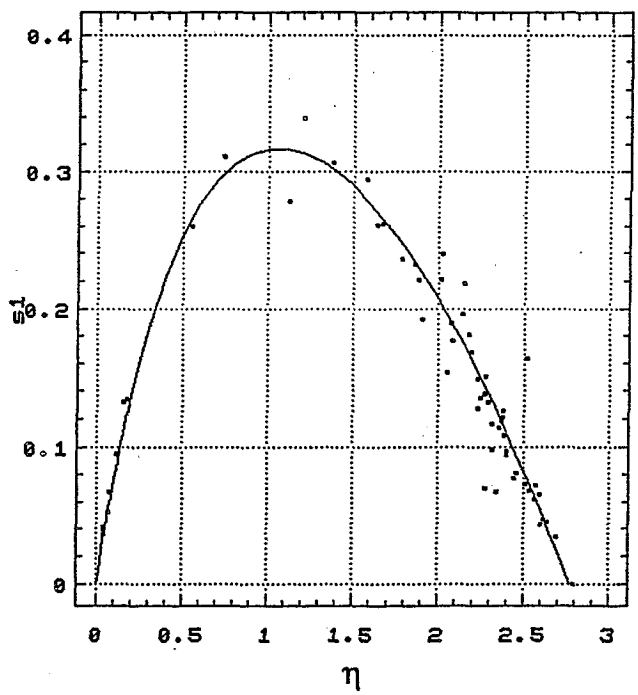

Figure B–3. Boundary Conditions at Mallard Island

5. Divide the THMFP concentration calculated in Step 3 by the distribution factor calculated in Step 4 to arrive at the TFPC concentration. For Mallard Island,

$$[TFPC] = \frac{[CHCl_2Br]}{s_1} \qquad \text{(B–10)}$$

Fig. B–4 shows the relationship between TFPC and chloride as derived from Eqs. B–6 through B–10. Observed data is also plotted in Fig. B–4.

After a TFPC value is determined at Mallard Island, the trial and error procedure outlined in Chapter 8 should be followed to arrive at a Benicia boundary condition. DWRDSM runs should be made until TFPC model estimates at Mallard Island are consistent with values determined by the regression equations presented above.

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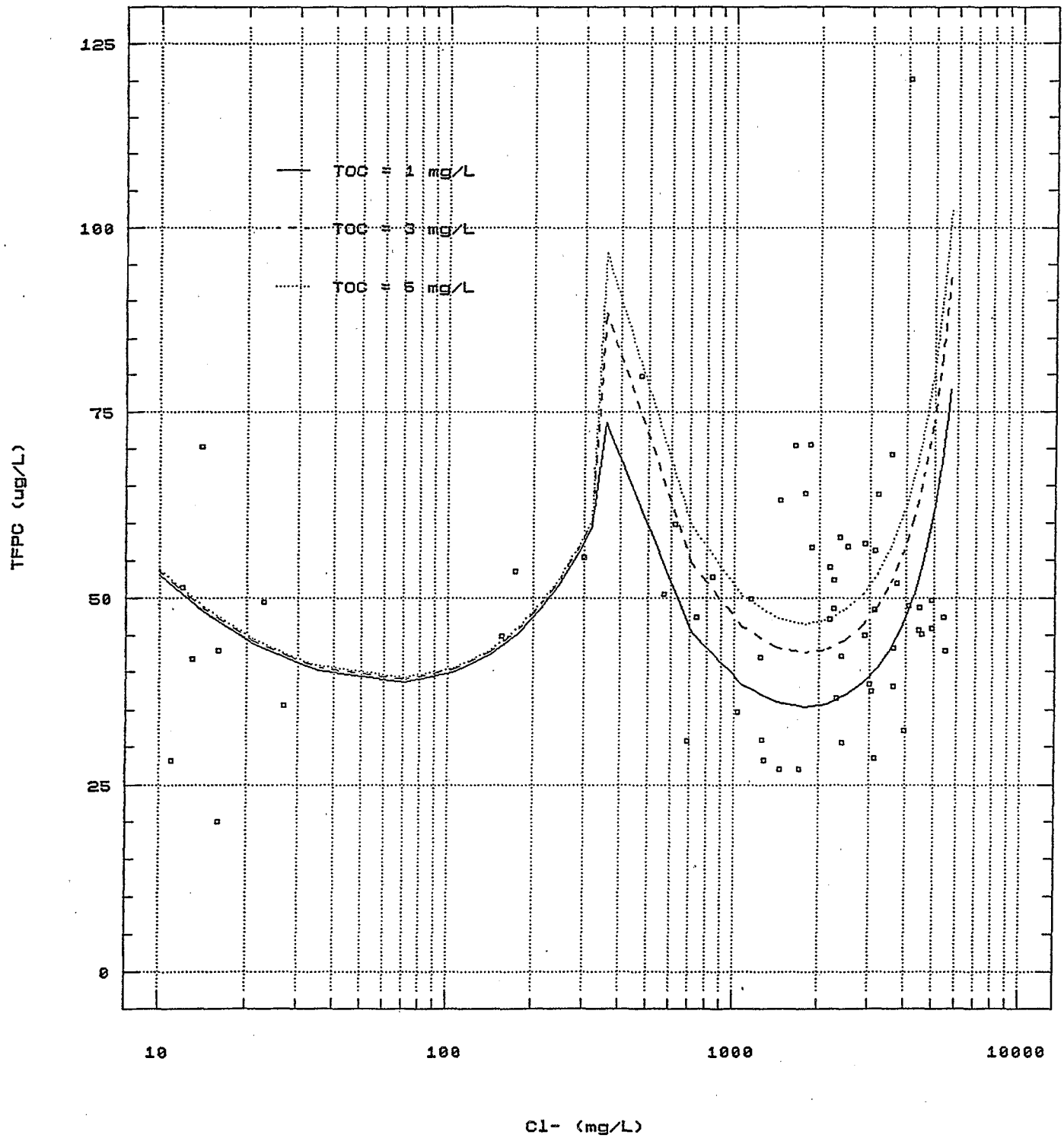

Figure B–4. Chloride–TFPC Relationship at Mallard Island

APPENDIX C

NOTATION

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APPENDIX C: NOTATION

The following symbols are used in this report:

[ ]	=	molar concentration
a,b,c,d,e	=	regression model coefficients
AMW	=	average molecular weight
Br^-	=	bromide ion
$CHCl_3$	=	chloroform
$CHCl_2Br$	=	dichlorobromomethane
$CHClBr_2$	=	dibromochloromethane
$CHBr_3$	=	bromoform
CVP	=	Central Valley Project
DIDI	=	Delta Island Drainage Investigation
DOC	=	dissolved organic carbon
DWR	=	California Department of Water Resources
Cl^-	=	chloride ion
Cl_2	=	chlorine
DWRDSM	=	DWR Delta Simulation Model
EC	=	electrical conductivity
H^+	=	hydrogen ion
H_2O	=	water
HOBr	=	hypobromous acid
HOCl	=	hypochlorous acid (free chlorine)
IDHAMP	=	Interagency Delta Health Aspects Monitoring Program
MCL	=	maximum contaminant level
MWQI	=	Municipal Water Quality Investigations
n	=	sample number
N	=	number of bromide ions in THM species
OCl^-	=	hypochlorite ion
RMS	=	root mean square
r^2	=	coefficient of determination
SDS	=	simulated distribution system
SEE	=	standard error of estimate
SSE	=	sum-of-squares error
s_N	=	Bromine Distribution Factor
s_0	=	$CHCl_3$ Distribution Factor
s_1	=	$CHCl_2Br$ Distribution Factor
s_2	=	$CHClBr_2$ Distribution Factor
s_3	=	$CHBr_3$ Distribution Factor
SWP	=	State Water Project
TBFP	=	total bromomethane formation potential
TDS	=	total dissolved solids
TFPC	=	total formulation potential carbon
THM	=	trihalomethane
THMFP	=	THM formation potential
THMFP-Br	=	bromide ion in THMFP species
TOC	=	total organic carbon
UVA	=	absorbance of ultraviolet light at a wavelength of 254 nm, cm^{-1}
η	=	Bromine Incorporation Factor

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