Bay-Delta Drinking Water Quality: Bromide Ion (Br^-) and Formation of Brominated Disinfection By-Products (DBPs)

Gary Amy[1], Richard Bull[2], Kenneth Kerri[3],
Stig Regli[4], and Philip Singer[5]

FINAL DRAFT

[1]University of Colorado,
[2]Battelle Pacific Northwest Laboratory,
[3]California State University-Sacramento,
[4]U.S. Environmental Protection Agency, and
[5]University of North Carolina

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Summary

This report is an outgrowth of a meeting involving an expert panel on bromide ion (Br^-), convened by the CALFED Bay-Delta Program in Sacramento, California on September 8 – 9, 1998. Experts (the authors of this report) on water chemistry, drinking water treatment, health effects, drinking water regulations, and source assessment and management held a public meeting to exchange information with utility, government, and environmental representatives in the presence of CALFED staff. Panel members were provided background reports and unpublished data both before and after the meeting. The purpose of this report is to provide CALFED with input on controlling concentrations of bromide ion (Br^-) within regions of the Sacramento River Delta-San Francisco Bay (i.e., the *Bay-Delta*) used as a source for drinking water supply.

The Bay-Delta region is a complex, multi-use system comprised of two major freshwater inflows (the Sacramento and San Joaquin Rivers), San Francisco Bay, and transitional estuarine and Delta areas. The primary export facility for drinking water is the State Water Project (SWP), which originates in the southern reaches of the Delta; other export points include the North Bay Aqueduct (NBA), the South Bay Aqueduct (SBA), and the Contra Costa Canal (CCC). CALFED has proposed three alternatives for managing the flow of Sacramento River water through the Delta to points of drinking water export; each of these alternatives, embodying channel modifications, storage, and possibly a new conveyance channel, will have varying effects on Br^- levels in exported water.

It is well known that disinfection by-products (DBPs) are formed during water treatment disinfection/oxidation. The impetus for this report is that, in the presence of Br^- and natural organic matter (NOM, measured as total organic carbon (TOC)), various brominated DBPs are formed including: brominated trihalomethanes (THMs) and haloacetic acids (HAAs), formed upon chlorination; and bromate ion (BrO_3^-), formed upon ozonation.

The major source of Br^- within the Delta is seawater derived through tidal exchange with San Francisco Bay. The major incremental source of TOC (beyond that associated with inflows) are agricultural drains situated throughout the Delta.

There are major concerns about the public health (e.g., carcinogenic, mutagenic, or reproductive) effects of DBPs in drinking water. Brominated DBPs such as

bromodichloromethane (a THM species) and BrO_3^- may be of particular concern. The U.S. EPA intends to promulgate more stringent drinking water regulations in November of 1998, limiting the maximum contaminant levels of THMs (sum of four species), HAAs (sum of five species), and BrO_3^-. EPA is also considering further DBP regulation and more stringent disinfection regulations (e.g., Cryptosporidium inactivation) which could further influence changes in disinfection practice and create a potential conflict between minimizing chemical (DBPs) and microbial risk.

There are very limited treatment options (i.e., membranes) for removing Br^-. Conversely, there are both conventional (coagulation, sedimentation, filtration) and advanced (granular activated carbon, membranes) processes for effective removal of TOC; however, these processes increase the ratio of Br^-/TOC and may not proportionally reduce chemical risk to public health. Options exist for minimizing bromate formation during ozonation (e.g., low-pH ozonation), or for removing BrO_3^- after its formation (e.g., chemical reduction with ferrous salts); however, there are water quality and technology-development constraints to their implementation (e.g., low pH ozonation for high-alkalinity source waters; substitution of ferrous salts for traditional coagulants). Management of Br^- may be best realized through a combination of treatment and source control, with the three CALFED alternatives reflecting different options for managing the intermixing of seawater with freshwater as it is conveyed through the Delta. Given the synergistic behavior of Br^- and TOC in forming DBPs, the co-occurrence within the Delta and the fate through treatment of both Br^- and TOC are of importance. Similarly, the co-occurrence of fecal contamination with these parameters can exacerbate the control options for DBPs because of potentially higher disinfection levels needed to control pathogens.

There must be both a short-term (before implementation of an alternative) and a long-term (after alternative implementation) strategy for drinking water utilities using Delta water. In the short-term, more emphasis should be placed on treatment with some possibilities for source control (e.g., treatment or rerouting of agricultural drainage or storage (external to Delta) for dampening variations in Br^-, possibly also lowering TOC, and limiting fecal contamination); in the long-term, more substantial source management options are possible with implementation of an alternative for conveying water through the Delta.

1.0 Introduction and Background

1.1 Significance of Bromide (Br^-) in Drinking Water Sources

Bromide ion (Br^-) occurs ubiquitously in natural waters, ranging from < 5 ug/L in some freshwaters to 65 mg/L (65,000 ug/L) in seawater. While it is considered a trace contaminant in drinking water supplies (i.e., usually < 1 mg/L or < 1,000 ug/L), Br^- can have a significant impact on drinking water quality. Bromide itself is harmless; however, it reacts with water-treatment chemical disinfectants and oxidants (e.g., chlorine and ozone) to form potentially harmful disinfection by-products (DBPs). Chemical disinfection reduces microbial risk from pathogenic microorganisms (e.g., Giardia and Cryptosporidium); however, the formation of DBPs (e.g., bromodichloromethane and bromate) poses a chemical risk to public health. While Br^- serves as the inorganic DBP precursor, it interacts with natural organic matter (NOM), measured as total organic carbon (TOC), playing the role of the organic DBP precursor, which contributes to the formation of organic DBPs.

1.2 General Sources and National Occurrence of Br^- and TOC

Both natural sources of bromide in water (e.g., geochemical weathering, connate seawater, seawater intrusion) and anthropogenic sources (e.g., industrial and oil field brine discharges) exist. A nation-wide survey (Amy, et al., 1994) reported that the average drinking water source in the U.S. contains 62 ug/L of bromide, with a range from 5 to 430 ug/L observed for 88 randomly-sampled sources; the 90-percentile concentration was estimated to be about 300 ug/L. The average Br^- concentration in 12 targeted (known high Br^- levels) sources was 210 ug/L (Bay-Delta water exported through the State Water Project (SWP) was included in this grouping).

Amy et al. (1994) reported a nation-wide average TOC concentration in 100 drinking water sources to be 2.7 mg/L, a finding consistent with other studies; the range of TOC concentrations was <0.2 to 21 mg/L. The co-occurrence of TOC with Br^- can be represented by a Br^-/TOC ratio; the average ratio reported by Amy et al. (1994) was 28 ug Br^-/mg TOC; no significant correlation was observed between Br^- and TOC occurrence.

1.3 Formation and Chemistry of Brominated Disinfection By-Products (DBPs)

The traditional chemical disinfectant, chlorine (Cl_2), as well as alternative disinfectants, ozone (O_3), chlorine dioxide (ClO_2), and chloramines (NH_2Cl, monochloramine), all form their own suite of DBPs. The following discussion will emphasize chlorination and ozonation DBPs because of the importance of Br^- in their formation. In contrast, the major chlorine-dioxide DBP is chlorite ion (ClO_2^-), a non-brominated DBP. When chloramine practice involves free chlorine followed by ammonia addition, lesser amounts of chlorination DBPs are formed; however, observations of enhanced formation of cyanogen chloride have raised concerns about a possible bromine analog, cyanogen bromide.

1.3.1 Trihalomethanes (THMs) and Haloacetic Acids (HAAs)

Bromide (Br^-) ion is itself harmless; however, through interaction with chemical disinfectants and oxidants, it can become incorporated into disinfection by-products (DBP). Br^- is oxidized by chlorine (Cl_2) to bromine (Br_2), more specifically hypobromous acid in equilibrium with hypobromite ($HOBr \leftrightarrow H^+ + OBr^-$). Cl_2 and Br_2 collectively react with natural organic matter (NOM), measured as total organic carbon (TOC), to form halogenated (chlorinated and/or brominated) organic DBPs that can be represented by organic-halogen (TOX) including organic-chlorine (TOCl) and organic-bromine (TOBr) components. Less than 50 % of the TOX pool has been identified as specific compounds/compound classes such as trihalomethanes (THMs) and haloacetic acids (HAAs). Of the four THM species, one is fully chlorinated (chloroform, $CHCl_3$), one is fully brominated (bromoform, $CHBr_3$), and two are mixed species (bromodichloromethane and dibromochloromethane). Of the nine HAA species, three are fully chlorinated (tri-, di-, and mono-chloroacetic acid), three are fully brominated (tri-, di-, and mono-bromoacetic acid), and three are mixed species (bromodichloro-, dibromochloro-, and bromochloro- acetic acid). The relevant chemistry is summarized below:

$$2\,Br^- + Cl_2 \rightarrow Br_2 + 2\,Cl^-$$

$$NOM + Cl_2 \rightarrow TOCl \qquad \text{(e.g., } CHCl_3\text{)}$$

$$NOM + Br_2 \rightarrow TOBr \qquad \text{(e.g., } CHBr_3\text{)}$$

$$NOM + Cl_2 + Br_2 \rightarrow TOCl + TOBr$$

The formation of total THMs (TTHM) is positively (+) influenced by temperature, pH, Cl_2 dose, Br^- concentration, TOC, and reaction time. The formation of total HAAs (THAA) is similarly influenced by the same parameters except for pH; pH has a significant inverse (-) effect on certain HAA species (e.g., trichloroacetic acid). The relative amounts of Br^- and TOC affect the species distribution of both TTHM and THAA, with a higher Br^-/TOC ratio driving the mixture toward greater bromination. NOM properties, as indicated by measurements of UV absorbance at 254 nm (UVA_{254}) and specific UV absorbance (SUVA = UVA_{254}/TOC), also affect TTHM and THAA formation. UVA_{254} and SUVA are indicative of the aromatic (non-polar) character of NOM. A positive correlation have been observed between TTHM and SUVA. Polar NOM has been shown to be more influential in THAA than TTHM formation. Higher bromination (THM-Br and HAA-Br) has been observed for polar NOM. It is important to note that Br has a molecular weight of 80 versus 35.5 for Cl; thus, because of weight-based (ug/L) standards, Br^- exacerbates TTHM and THAA formation. Another important observation is that brominated DBPs form more rapidly that chlorinated DBPs, a factor that may affect control strategies such as chloramination involving free-chlorine contact subsequently followed by ammonia addition.

1.3.2 Bromate (BrO_3^-) and Organic-Bromine (TOBr)

Br^- is also oxidized by ozone (O_3) to $HOBr/OBr^-$ (Br_2); OBr^- serves as an important reaction intermediate to formation of bromate (BrO_3^-), an inorganic DBP. BrO_3^- can form through two potential pathways: a molecular ozone (O_3) and a hydroxyl radical ($OH^\bullet$) pathway. The molecular ozone pathway is summarized below:

$$Br^- + O_3 \rightarrow OBr^- + O_2$$
$$OBr^- + 2\,O_3 \rightarrow BrO_3^- + 2\,O_2$$

The $OH^\bullet$ pathway is represented below, in a simplified (unbalanced) format:

$$Br^- + OH^\bullet \rightarrow BrO_3^-$$

Bromate is positively (+) affected by temperature, pH, O_3 dose, and Br^- concentration. The radical pathway is more dominant under higher pH conditions and in the presence of NOM.

TOBr may also form during ozonation in the presence of Br^-, with an inverse (-) pH effect, through the reaction of NOM with the HOBr intermediate:

$$NOM + HOBr \rightarrow TOBr$$

1.3.3 Co-Occurrence of Br- and TOC, DBP Mixtures, and Balancing Risk

The above discussion shows the linkage between Br^-, the inorganic DBP precursor, and NOM (TOC), the organic precursor. Thus, their co-occurrence in Delta water and their relative removals during water treatment are of concern. As regulations drive practice toward use of multiple disinfectants/oxidants, a DBP mixture will result. From a risk perspective, there is a need to balance chemical risk to public health, associated with the resultant DBP mixture created by a disinfectant/oxidant or combinations thereof, with microbial risk posed by pathogenic microorganisms.

Another important consideration is the co-occurrence of Br^- and TOC with microbes (e.g., fecal coliforms); the co-occurrence of Br^- and Cryptosporidium creates a dilemma between effective inactivation by ozone versus bromate formation.

1.4 National Occurrence of Brominated DBPs

Krasner et al. (1989) reported the results of a 35-utility DBP survey. All four THM species and five HAA species (HAA_5) were measured prior to point of entry into the distribution system. Median values for chloroform, bromodichloromethane, dibromochloromethane, and bromoform were reported to be 13, 6.6, 3.4, and 0.6 ug/L, respectively; median values for trichloracetic acid, dichloroacetic acid, monochloroacetic acid, dibromoacetic acid, and monobromoacetic acid were reported to be 5.4, 6.4, 1.1, 1.2, and <0.5 ug/L, respectively. Recent work by Zhu (1994) has shown that, because of the concentration of bromochloroacetic acid (a sixth species), HAA_6 on average is about 10 % greater than HAA_5. Little is known about the occurrence of the remaining three HAA species. Krasner et al. (1993) found bromate levels ranging from < 5 ug/L to 60 ug/L in pilot studies and at operating ozonation facilities.

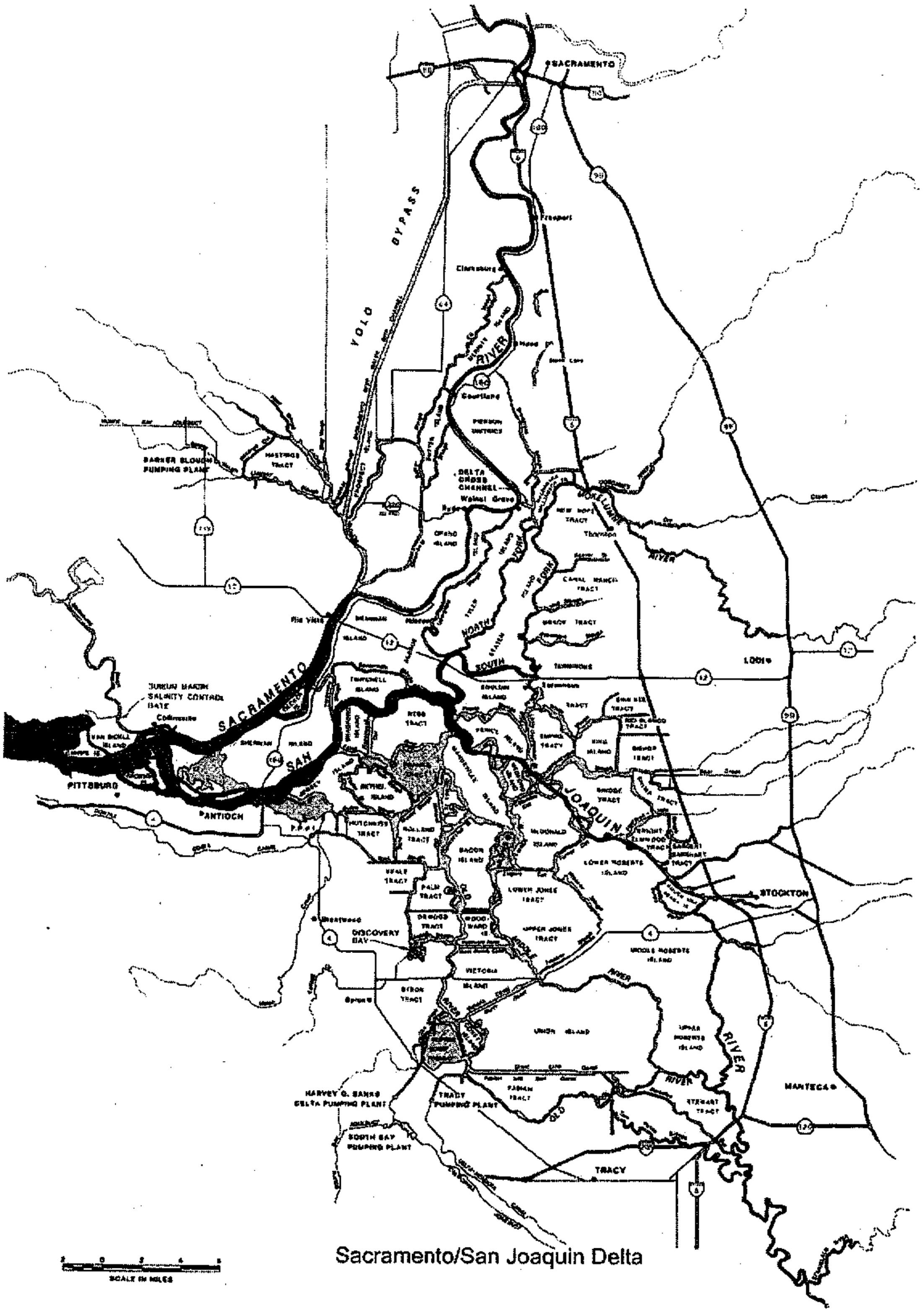
1.5 The Bay-Delta System as a Drinking Water Source

The Bay-Delta system is a region encompassing the confluence of the Sacramento and San Joaquin Rivers, San Francisco Bay, and the transitional estuarine and Delta areas (Figures 1 and 2). CALFED is charged with developing a consensus on potentially conflicting beneficial uses of the Bay-Delta, with drinking water supply identified as one important beneficial use. CALFED has articulated three alternatives to reconcile Bay-Delta issues. These three alternatives, summarized below, would have varying impacts on drinking water quality in general, and levels of bromide ion (Br^-) in particular:

- Alternative 1 (Figure 3) "proposes existing Delta channels, with some modifications for water conveyance and various storage options";
- Alternative 2 (Figure 4) "proposes significant modifications of Delta channels to increase water conveyance across the Delta combined with various storage options"; and
- Alternative 3 (Figure 5) "includes Delta channel modifications coupled with a conveyance channel that takes water around the Delta with various storage options". (This alternative will include an isolated conveyance facility with a capacity of 8,000 to 12,000 cfs, connecting the Sacramento River to drinking water export facilities).

The average annual freshwater inflow into the Delta is about 27 MAF/yr (million acre-feet/year), 62 % derived from the Sacramento River. This inflow, however, is volumetrically small in comparison to tidal exchange with San Francisco Bay. On average, about 5.9 MAF/yr are exported via the major drinking water aqueduct, the State Water Project (SWP, 3.6 MAF/yr); and the major agricultural water aqueduct, the Central Valley Project (CVP, 2.3 MAF/yr). On a much smaller scale, drinking water is exported via the North Bay Aqueduct (NBA, 25,000 acre-feet/year), the South Bay Aqueduct (SBA, 160,000 acre-feet/year), and the Contra Costa Canal (CCC, 100,000 acre-feet/year). Flow patterns throughout the Delta are influenced by tidal actions and export operations. There is a clear seasonality to inflow, lowest in the summer and highest in the winter; this is in contrast to variations in water demand which are highest in summer. Variations in inflow versus demand can be dampened by storage in the form of surface reservoirs or groundwater basins; presently, there are 30 reservoirs with a combined capacity of 25 MAF.

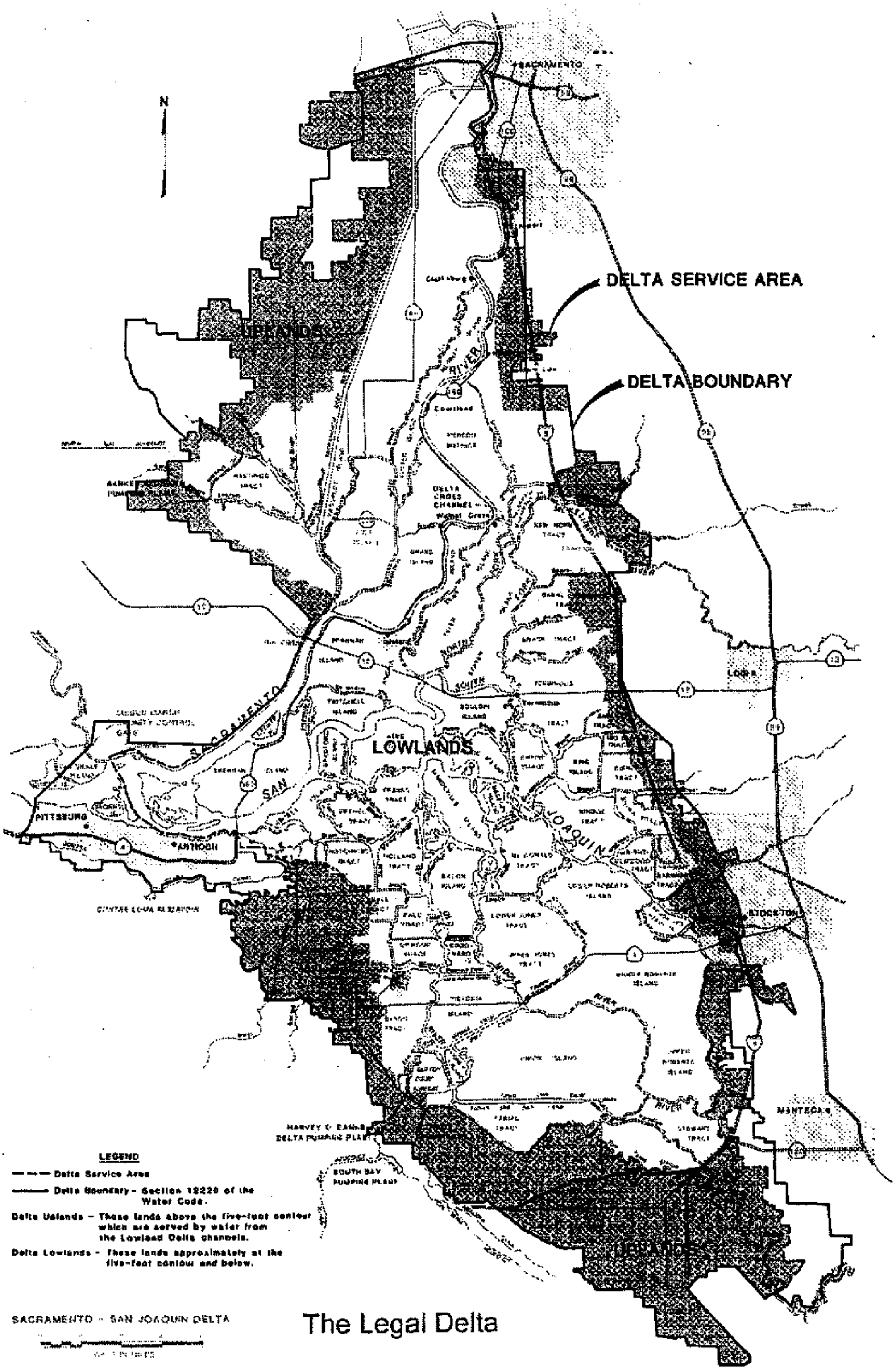
FIGURE 1



Sacramento/San Joaquin Delta

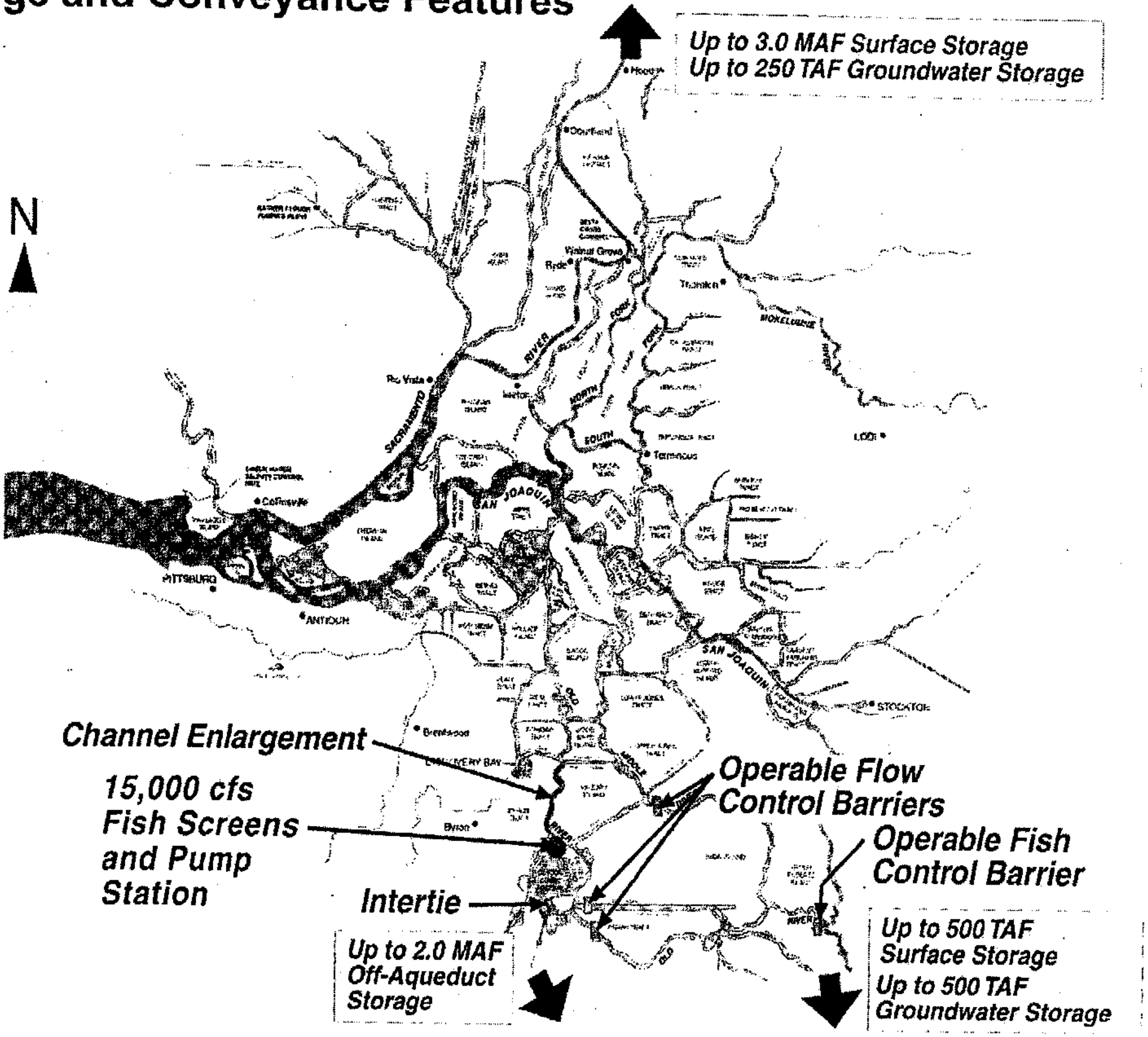
FIGURE 2

The Legal Sacramento/ San Joaquin Delta



Alternative 1

Storage and Conveyance Features



Up to 3.0 MAF Surface Storage
Up to 250 TAF Groundwater Storage

Channel Enlargement

15,000 cfs
Fish Screens
and Pump
Station

Intertie

Up to 2.0 MAF
Off-Aqueduct
Storage

Operable Flow
Control Barriers

Operable Fish
Control Barrier

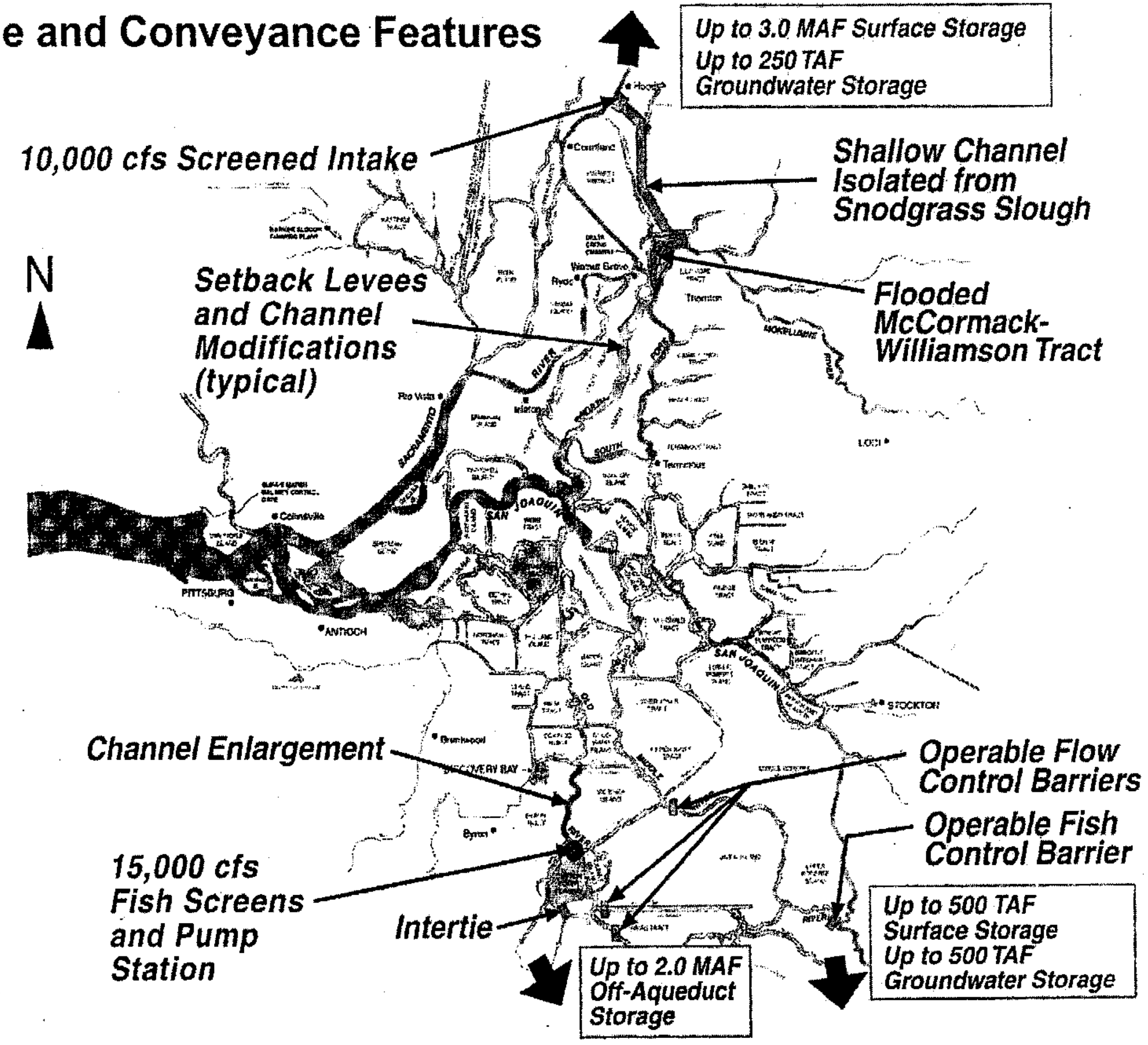
Up to 500 TAF
Surface Storage
Up to 500 TAF
Groundwater Storage

Alternative 1

FIGURE 3

Alternative 2

Storage and Conveyance Features



Up to 3.0 MAF Surface Storage
Up to 250 TAF
Groundwater Storage

10,000 cfs Screened Intake

Shallow Channel Isolated from Snodgrass Slough

Setback Levees and Channel Modifications (typical)

Flooded McCormack-Williamson Tract

Channel Enlargement

Operable Flow Control Barriers

Operable Fish Control Barrier

15,000 cfs Fish Screens and Pump Station

Intertie

Up to 2.0 MAF Off-Aqueduct Storage

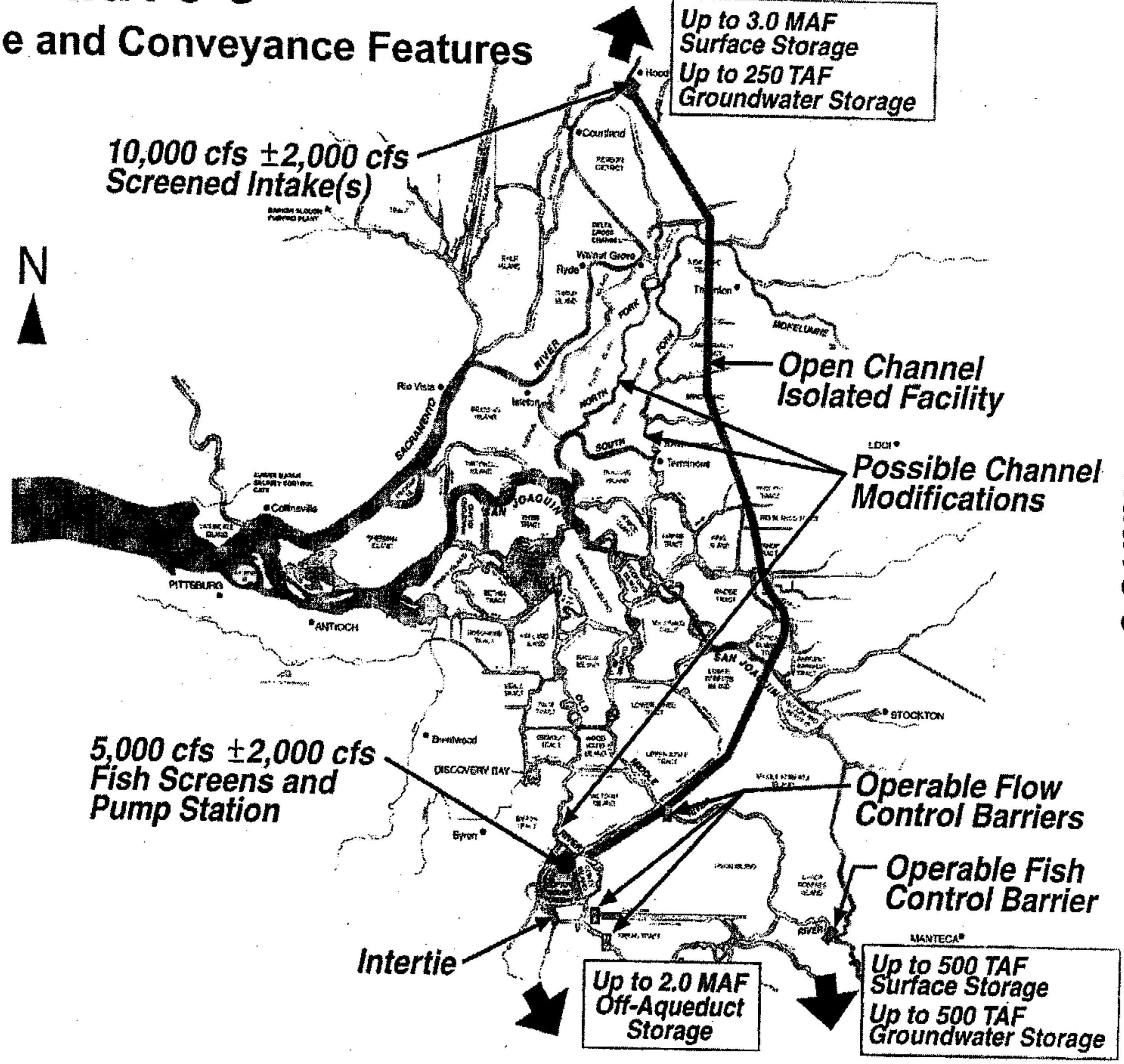
Up to 500 TAF
Surface Storage
Up to 500 TAF
Groundwater Storage

Alternative 2

FIGURE 4

Alternative 3

Storage and Conveyance Features



Up to 3.0 MAF Surface Storage

Up to 250 TAF Groundwater Storage

10,000 cfs ±2,000 cfs Screened Intake(s)

Open Channel Isolated Facility

Possible Channel Modifications

5,000 cfs ±2,000 cfs Fish Screens and Pump Station

Operable Flow Control Barriers

Operable Fish Control Barrier

Intertie

Up to 2.0 MAF Off-Aqueduct Storage

Up to 500 TAF Surface Storage

Up to 500 TAF Groundwater Storage

There is presently a permit-based export limitation restricting the pumping rate to 6,680 cfs (cubic feet per second) of SWP and 4,600 cfs of CVP; the various CALFED alternatives will increase the permitted pumping rate of SWP to 10,300 cfs (14,900 CFS for combined SWP and CVP), with new storage reservoirs of up to 6 MAF.

From a drinking water perspective, the Sacramento River is a high quality source with low to moderate levels of various inorganic and organic constituents. The San Joaquin River exhibits lower water quality largely due to agricultural runoff within its watershed (its relatively high Br^- concentrations are largely attributed to "recycling" of high-Br^- water from the Delta). There are numerous "islands" within the Delta that are used for agricultural purposes; agricultural drainage from these peat-soil islands further degrades Delta water. The primary impact of agricultural drainage is an increase in organic matter as measured by TOC (total organic carbon), with greater impacts observed during winter when leaching activities are more intensive. The Sacramento River contains moderate TOC ($\approx$ 2 mg/L), relatively low TDS (total dissolved salts, $\approx$ 100 mg/L), and little Br^- ($\approx$ 20 ug/L); the primary impact of seawater interchange is an increase in TDS (seawater contains 35,000 mg/L of TDS) and, in particular, Br^- (seawater contains 65 mg/L of Br^-). The impact of seawater on Delta water quality has been corroborated by tracking the extent of tidal exchange through the ratio of Br^-/Cl^- in seawater. Seawater contains little TOC ($\approx$ 0.5 mg/L).

The location of the major drinking water export facility (Figure 1) is near Clifton Court, which feeds into the H.O. Banks Delta Pumping Plant. Other major export facilities are Rock Slough (the origin of the Contra Costa Canal intake), Barker Slough/North Bay Pumping Plant (the origin of the North Bay Aqueduct), and California Aqueduct/South Bay Pumping Plant (the origin of the South Bay Aqueduct). Thus, these locations represent points of primary concern for drinking water quality.

1.6 Present Drinking Water Treatment Practice for Bay-Delta Water

There are presently over 40 water treatment plants that use Delta water exported through the SWP; a number of other plants use North Bay Aqueduct water, several plants use South Bay Aqueduct water, and several plants use Contra Costa Water District Aqueduct water. While conventional water treatment is widely practiced, there are some direct filtration facilities. Some of the conventional facilities are being modified or have been modified to implement enhanced coagulation for improved TOC removal; others are being modified to incorporate ozonation.

The Alameda County Water District (ACWD) operates two conventional plants: the first employs pre-ozonation, biofiltration, and free chlorine addition followed by ammonia addition (chloramination); because BrO_3^- levels are highly variable with instantaneous levels as high as 30 ug/L, acid-addition capabilities are presently being installed to permit low-pH ozonation. The second ACWD plant has the same chloramination practice but no ozonation; TTHM and HAA_5 levels range from about 60 to 100 ug/L and 30 to 60 ug/L, respectively. The Santa Clara Valley Water District operates three conventional plants, and is presently designing for intermediate (settled-water) ozonation. The Metropolitan Water District (MWD) operates 5 conventional or direct filtration plants which use SWP or combinations of SWP and Colorado River Water; MWD practices chloramination in the mode of free chlorine contact followed by ammonia addition (typical TTHM levels are 40 to 50 ug/L), and is designing for pre-ozonation and biologically active filters (biofiltration). MWD has done extensive demonstration-scale testing of low-pH ozonation; while BrO_3^- levels can be reduced significantly, acid costs are high and TDS increases (because of acid and subsequent base addition) are significant. The Contra Costa Water District (CCWD) operates two plants: the first is a conventional plant with intermediate ozonation that typically forms <5 to 10 ug/L of BrO_3^-, while the second is an unusual plant that includes GAC with both pre- and post-ozonation. CCWD has built an external storage reservoir to dampen variations in Delta-water Br^-. The Los Angeles Department of Water and Power (LADWP) operates a direct filtration facility with pre-ozonation that occasionally treats a mixture of SWP with Los Angeles Aqueduct water.

In summary, SWP treatment practice largely consists of conventional treatment and includes fairly widespread ozonation and chloramination, but there is little advanced treatment practice involving GAC and membranes. One CCWD facility uses GAC and some pilot testing of membranes has taken place at CCWD, MWD, and ACWD.

1.7 Objectives of Report

The objectives of this report are summarized below:

- Define the sources and occurrence of Br^- (present and projected) in the Delta, and articulate source management options;

- Summarize present drinking water regulations, and project future trends;
- Describe the health effects of Br^- in disinfected drinking water, and identify ongoing/future studies;
- Identify and compare drinking water treatment options for controlling brominated DBPs;
- Contrast treatment versus source management approaches; and
- Make recommendations on short-term and long-term treatment practice and source management, and identify information/research needs.

2.0 Sources and Occurrence of Bromide, and Source Management Options

2.1 Occurrence of Bromide in the Delta

Concentrations of bromide in Delta waters are summarized in Figure 6 (California Department of Water Resources, 1998a); this figure lists bromide concentrations in micrograms per liter (ug/L) for mean measurements and also mean plus or minus one standard deviation at the following monitoring locations: (i) Sacramento River at Greenes Landing; (ii) North Bay Pumping Plant (SWP); (iii) Sacramento River at Mallard Island; (iv) Rock Slough at Old River; (v) H.O. Banks Pumping Plant (SWP); (vi) Delta Mendota Canal at Lindemann Road (CVP); and (vii) San Joaquin River near Vernalis.

Figure 7 (California Department of Water Resources, 1998a) shows bromide concentrations in Delta channels from October 1994 through September 1997 and Figure 8 (California Department of Water Resources, 1998b) shows bromide concentrations in Delta agricultural drains for the same time period.

2.2 Sources of Bromide in the Delta

The sources of bromide in Delta waters include: (i) sea water intrusion, (ii) recycling of agricultural drain waters from the Delta, (iii) methyl bromide used for soil, commodity and structural fumigation, (iv) discharges from olive processing facilities, (v) discharges from municipal wastewater treatment plants, and (vi) disinfectants used in spas. Apparently, sources of bromide from olive processing facilities, municipal wastewater treatment plants, and disinfectants used in spas contribute minimal amounts of bromide to Delta waters. This statement is based on the fact that Sacramento River water above the Delta typically contains

FIGURE 6

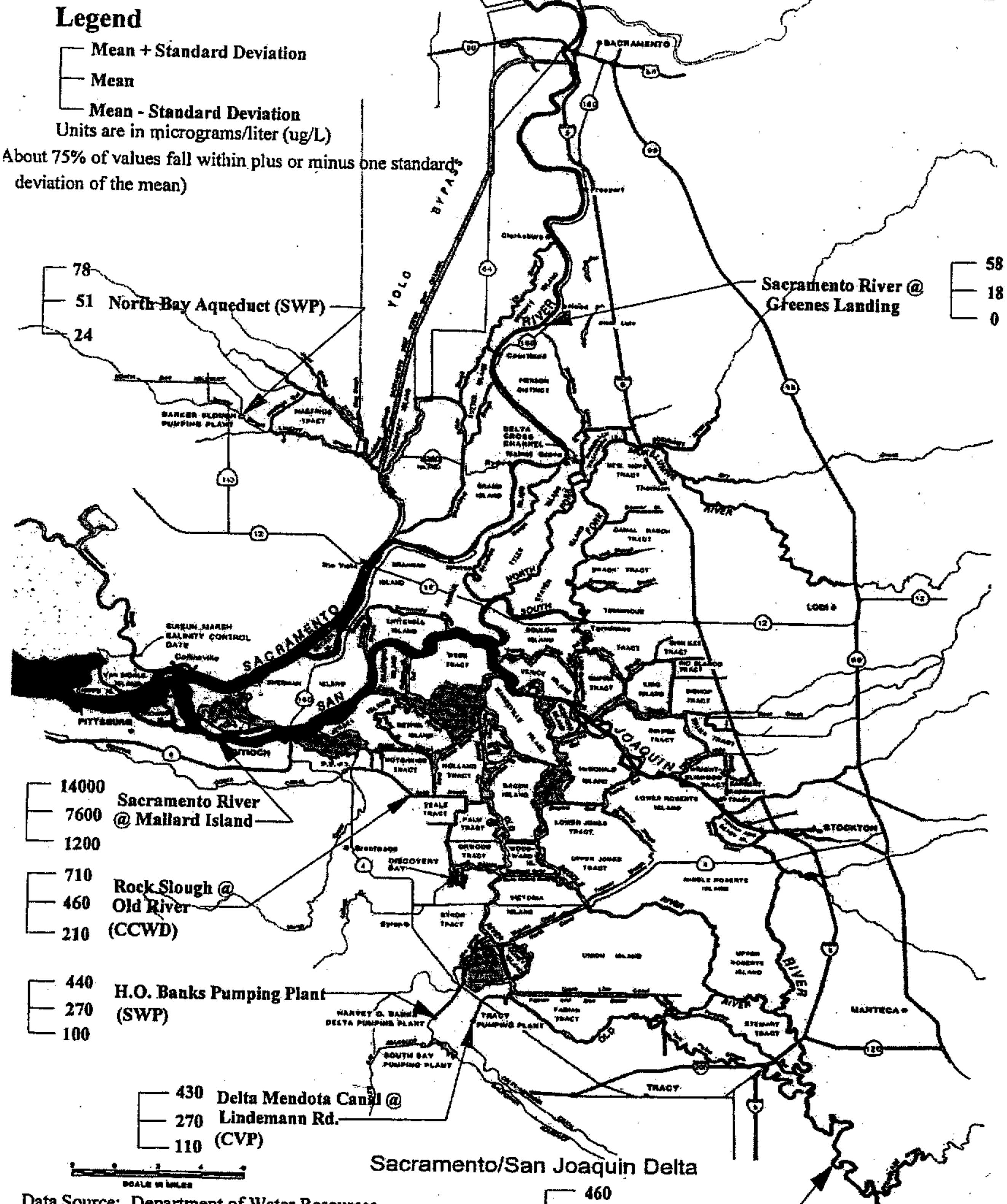
Sources of Bromide and Levels at Diversion Points

Legend

- Mean + Standard Deviation
- Mean
- Mean - Standard Deviation

Units are in micrograms/liter (ug/L)

About 75% of values fall within plus or minus one standard deviation of the mean)



North Bay Aqueduct (SWP): 78 / 51 / 24

Sacramento River @ Greenes Landing: 58 / 18 / 0

Sacramento River @ Mallard Island: 14000 / 7600 / 1200

Rock Slough @ Old River (CCWD): 710 / 460 / 210

H.O. Banks Pumping Plant (SWP): 440 / 270 / 100

Delta Mendota Canal @ Lindemann Rd. (CVP): 430 / 270 / 110

San Joaquin River near Vernalis: 460 / 310 / 160

Sacramento/San Joaquin Delta

Data Source: Department of Water Resources
Municipal Water Quality Investigations Program

FIGURE 7

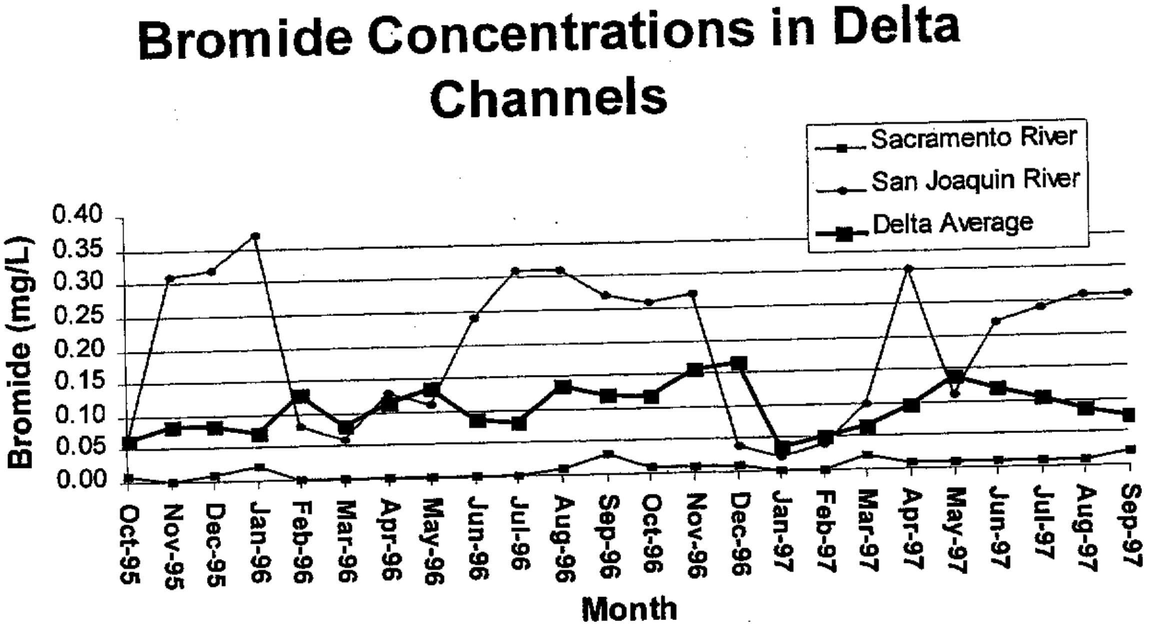
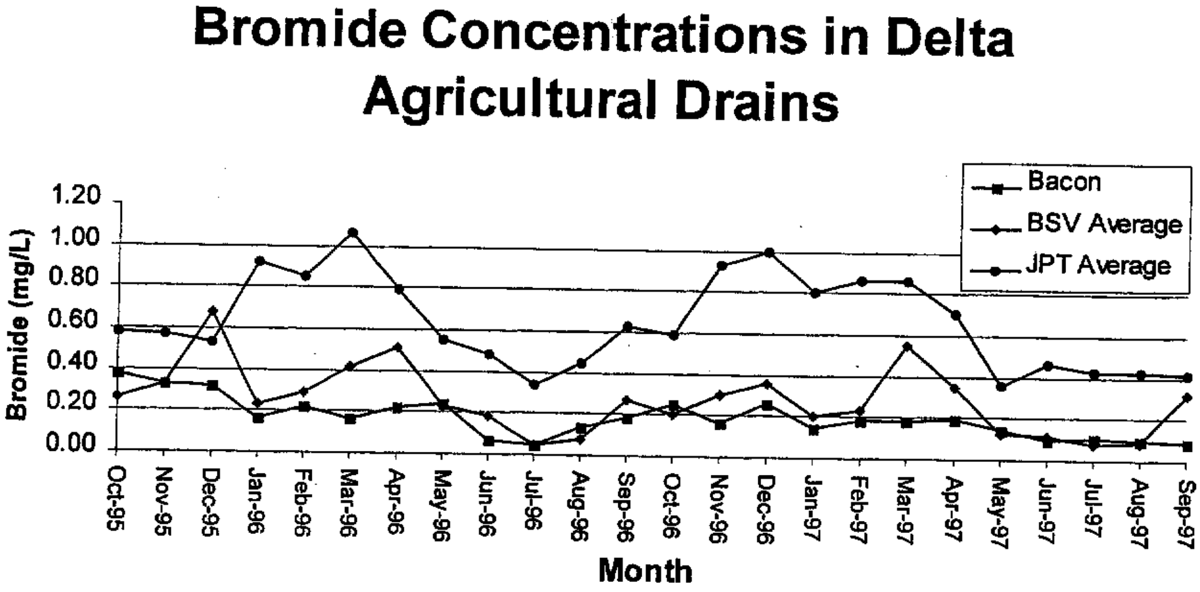

Bromide Concentrations in Delta Channels
Sacramento River
San Joaquin River
Delta Average
Bromide (mg/L)
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Oct-95
Nov-95
Dec-95
Jan-96
Feb-96
Mar-96
Apr-96
May-96
Jun-96
Jul-96
Aug-96
Sep-96
Oct-96
Nov-96
Dec-96
Jan-97
Feb-97
Mar-97
Apr-97
May-97
Jun-97
Jul-97
Aug-97
Sep-97
Month

FIGURE 8



Bromide Concentrations in Delta Agricultural Drains
Bacon
BSV Average
JPT Average
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Bromide (mg/L)
Oct-95
Nov-95
Dec-95
Jan-96
Feb-96
Mar-96
Apr-96
May-96
Jun-96
Jul-96
Aug-96
Sep-96
Oct-96
Nov-96
Dec-96
Jan-97
Feb-97
Mar-97
Apr-97
May-97
Jun-97
Jul-97
Aug-97
Sep-97
Month

less than 20 micrograms per liter (μg/*L*) of bromide (California Department of Water Resources, 1998b).

A report prepared by the Department of Water Resources (California Department of Water Resources, 1998b) articulated the following points regarding the sources of bromide in Delta waters. The Delta has one major source of bromide, sea water that enters the western Delta from tidal excursions and mixes with Sacramento River water flowing through the Delta to the export facilities in the southern Delta. Bromide levels at Clifton Court Forebay and at the Contra Costa Canal intake are attributed to sea water intrusion. Another source of bromide may be the San Joaquin River; however, the primary source of bromide in the San Joaquin River is probably from agricultural return water which contains bromide and is exported from the Delta, so this may simply be a "recycling" of bromide from sea water intrusion. Another source of bromide is connate water beneath some Delta islands (e.g., Empire Tract) (California Department of Water Resources, 1994). Overall, the primary source of bromide in Delta waters is the result of sea water intrusion (Krasner et al., 1994).

Figures 9 and 10 (California Department of Water Resources, 1998a) show average bromide concentrations in ug/L and percentage of total respectively for (1) CCC (Contra Costa Canal) Intake, (2) H.O. Banks Intake, and (3) DMC (Delta Mendota Canal) Intake for baseline 1922-92, with sources of bromide from sea water, agricultural drainage, east sources, San Joaquin River and Sacramento River.

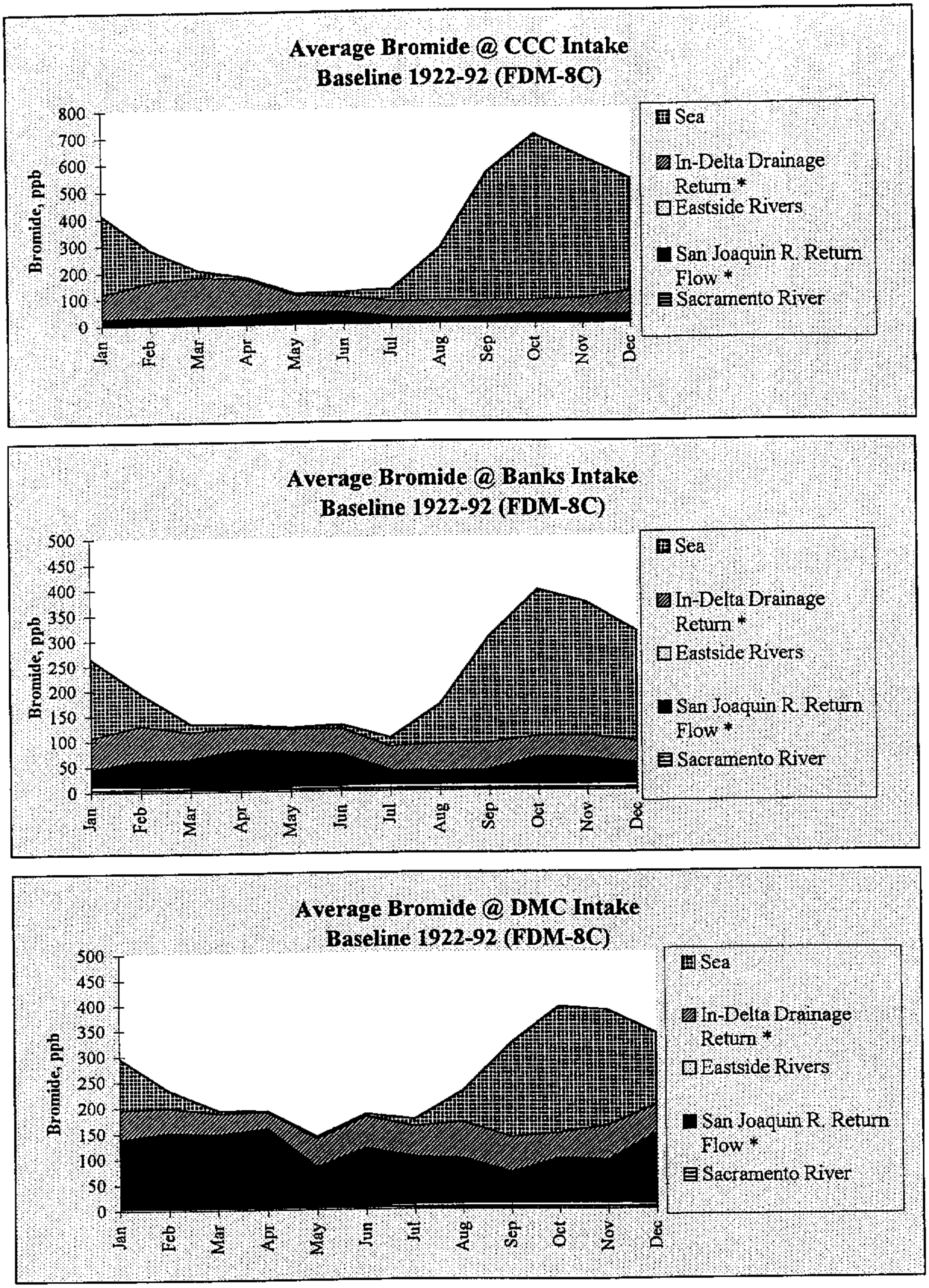
Figures 6 through 10 contain information on the magnitude of sources of bromide at points of diversion for drinking water supply and at other locations in the Delta. The magnitude of bromide in the Deltas is near the upper 90th to 95th percentile, based on the nationwide bromide survey by Amy et al. (1994), suggesting that the bromide problem facing CalFed is more of a regional than national one.

A concern was expressed during the Bromide Panel meetings in Sacramento held on September 8 and 9, 1998, that some of the "recycled" bromide in the San Joaquin agricultural drain waters could come from agricultural applications of methyl bromide.

2.3 Management Options for Bromide Sources

Identification of sources of bromide from: (i) methyl bromide fumigation applications, (ii) olive processing facilities, (iii) municipal wastewater treatment plants, and (iv) disinfectants

FIGURE 9



* Past studies indicated that seawater intrusion is the primary source of bromide in the Delta, hence bromide in San Joaquin River return flows and in-Delta drainage returns primarily originated from the ocean.

Source: Metropolitan Water District of Southern California

FIGURE 9

UNDER DEVELOPMENT

FIGURE 10

UNDER DEVELOPMENT

used in spas; will allow for management and control of these sources. Information on methyl bromide fumigation applications could be obtained from the Department of Pesticide Regulation. Regional water quality control boards could provide information on potential bromide discharges from municipal wastewater treatment plants and olive processing facilities. Merchants selling disinfectants for spas could indicate whether or not bromine is used as a disinfectant, how much is used, and its ultimate fate (as bromide) in the environment.

Considerable modeling has been performed by various agencies to forecast the effectiveness of various combinations of storage and conveyance features for Alternatives 1, 2 and 3.

The predicted effectiveness of these three alternatives for changing water quality concentrations of bromide are shown in Figure 11 (Clifton Court) and Figure 12 (Rock Slough) (California Department of Water Resources, 1998a). The figures show average predicted bromide concentrations as well as the upper and lower 95 percent bromide confidence limits. Projected TOC levels at the H. O. Banks Pumping Plant are 3.2, 3.1, 3.1, and 2.5 mg/L for no action, Alternative 1, Alternative 2, and Alternative 3, respectively.

Figures 13 and 14 (California Department of Water Resources, 1998a) illustrate the predicted monthly average bromide concentrations in ug/L at Clifton Court and the Contra Costa intake for Alternatives 1, 2 and 3 for the water year. It is evident that Alternative 3 has the most impact on Br^- levels at Clifton Court, whereas Alternative 2 provides lower Br^- levels at the Contra Costa intake; thus, there is no single alternative that provides lowest Br^- levels for all drinking-water export points.

2.4 Additional Information Needed

CalFed should assemble information on the monthly variations of bromide concentrations for key locations (Clifton Court, Contra Costa Intake) for each alternative (1, 2, 3). CalFed should perform a sensitivity analysis by estimating how much effort, cost, benefit and environmental impact would result if each alternative (1, 2, 3) were modified for both an incremental increase and decrease of bromide at key locations (Clifton Court, Contra Costa Intake). CalFed should assemble and analyze additional TOC occurrence data, particularly co-occurrence of TOC with Br^-.

FIGURE 11

Bromide Water Quality
Predicted Bromide at Clifton Court

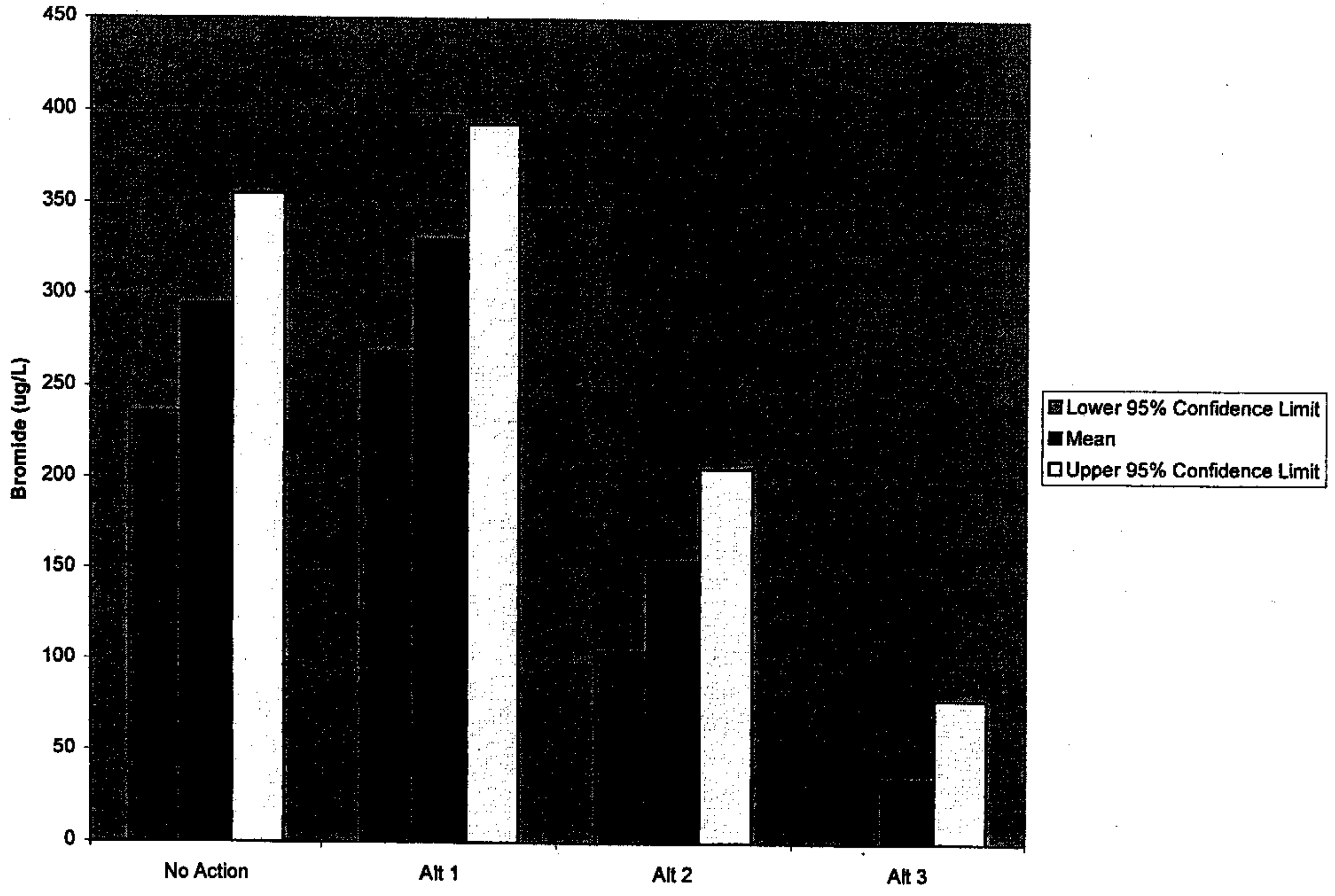


FIGURE 12

Bromide Water Quality

Predicted Bromide - Contra Costa Intake at Rock Slough

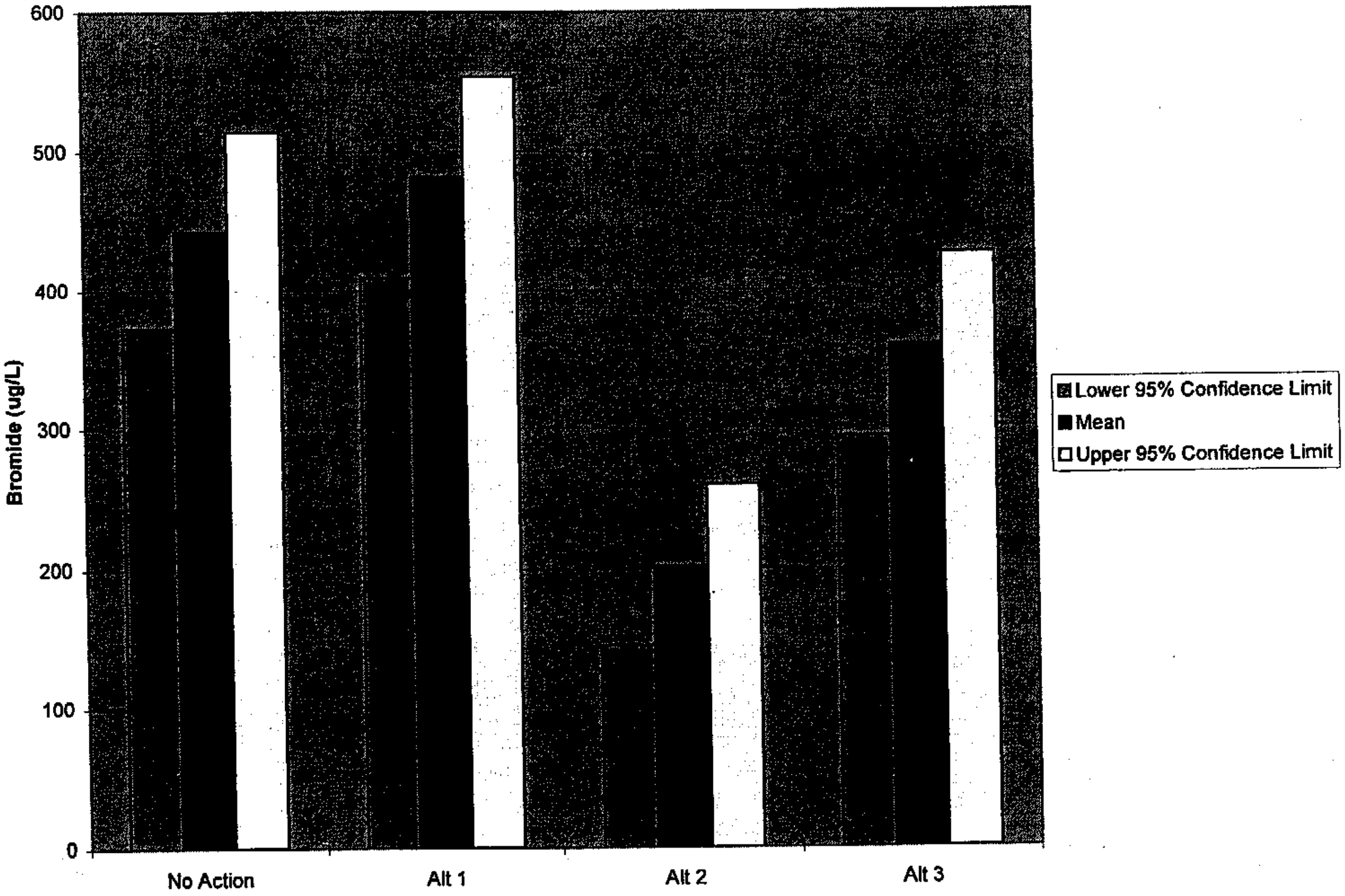
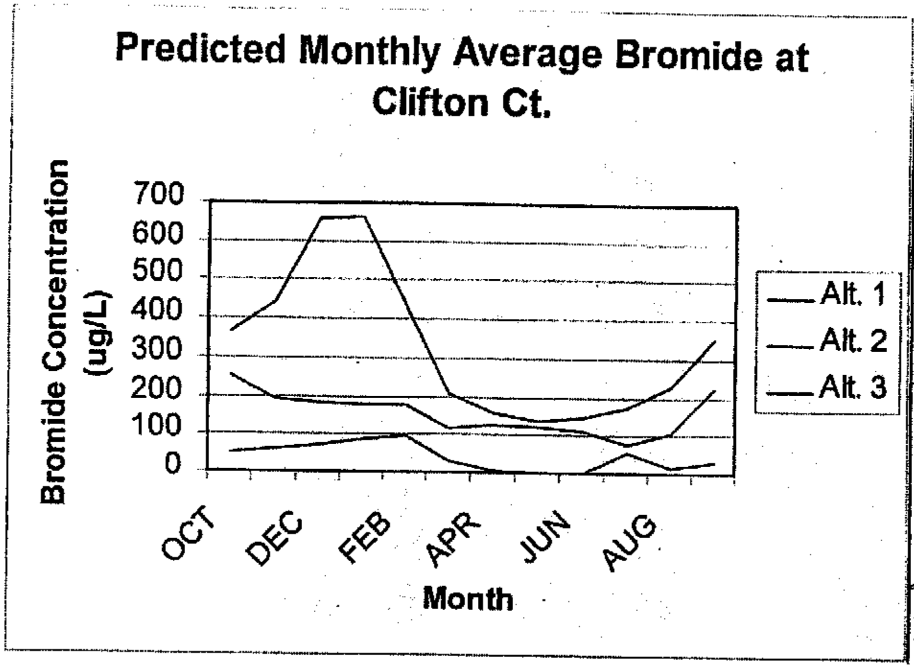
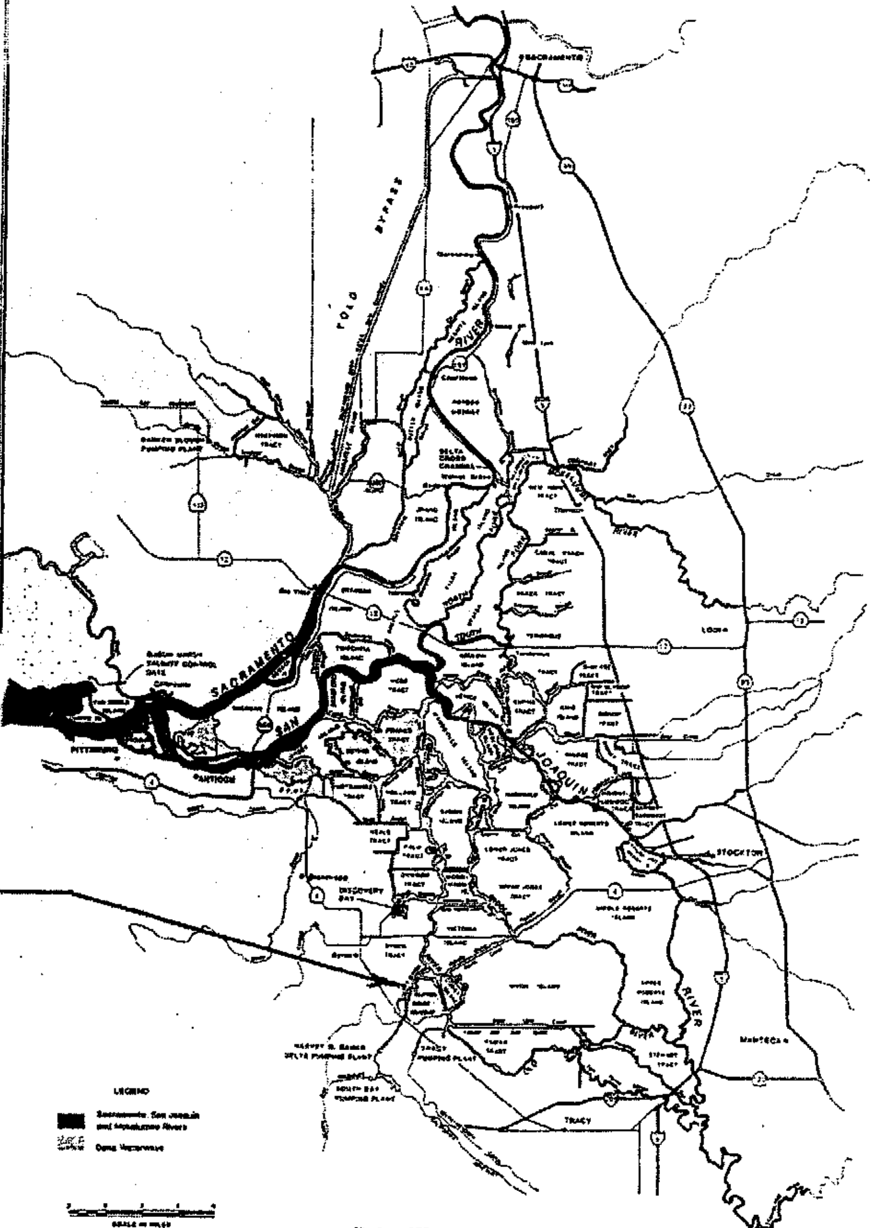


FIGURE 13



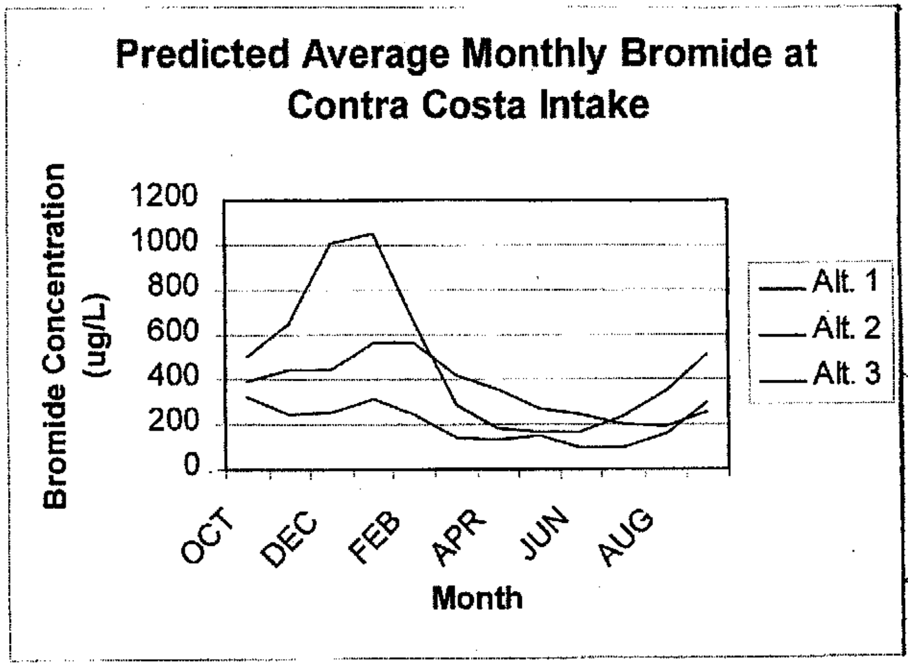
Based on CALFED model results for 1976-1991 hydrology

Clifton Court Forebay
Combined Point of Diversion
for State Water Project
and Fed. Central Valley Project

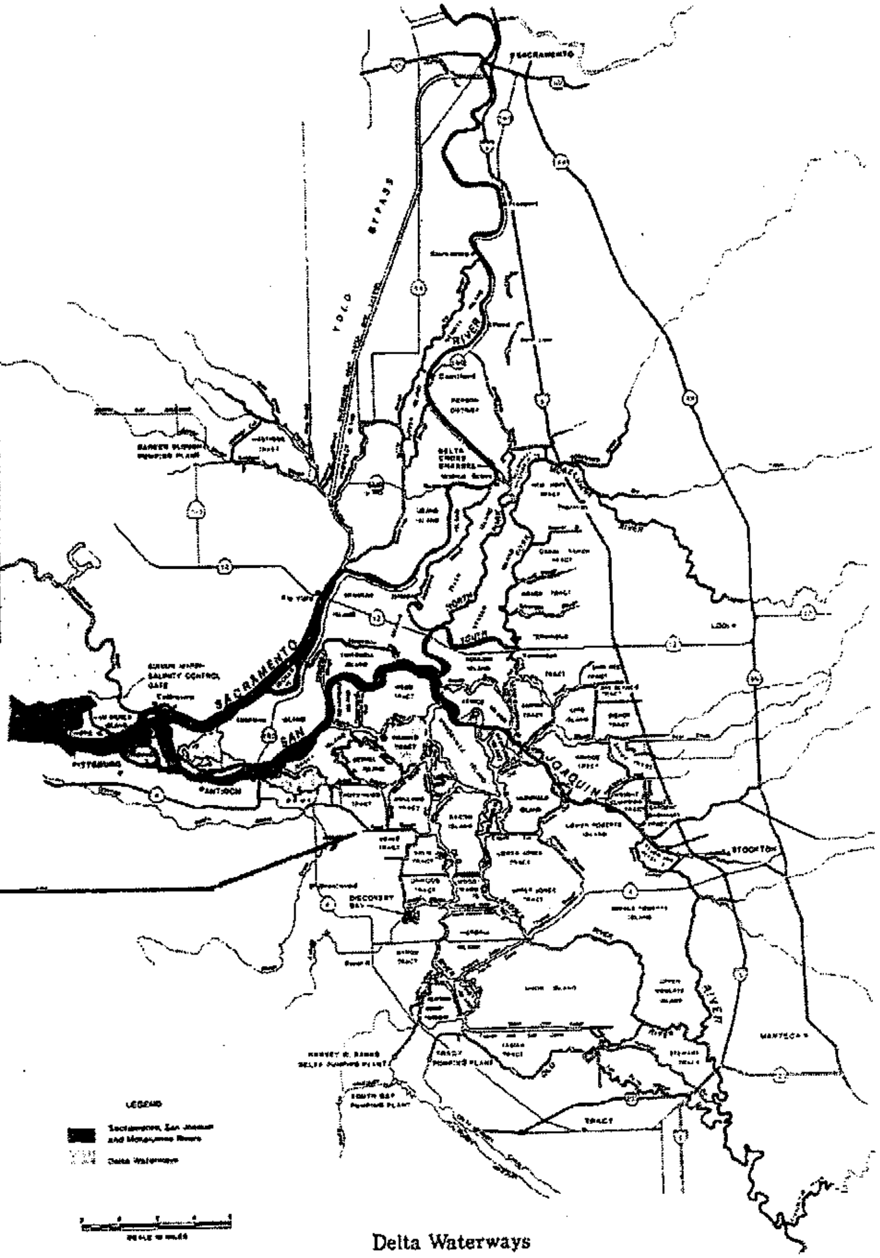


Delta Waterways

FIGURE 14


Predicted Average Monthly Bromide at Contra Costa Intake

Based on CALFED model results for 1976-1991 hydrology



Contra Costa Canal Intake
at Rock Slough
Point of Diversion for
Contra Costa Water District

Delta Waterways

2.5 Recommendations

CalFed should resolve concern regarding whether or not (or how much) of "recycled" bromide from agricultural return drains is actually "recycled" or is from agricultural fumigation activities using methyl bromide. CalFed should investigate options for immediate opportunities to enhance source controls of bromide. These options could include identification and control of all possible sources of bromide. Another option could be alternative means of managing storage and flows through the Delta. Potential short-term solutions/options should be implemented as soon as possible. CalFed should study the potential for using alternative sources of high quality water for drinking purposes and using lower quality waters to meet agricultural water supply demand.

3.0 Health Concerns Posed by Bromide in Source Waters Used for Drinking Water

High concentrations of bromide in source water are of little direct health concern. However, bromide serves as a precursor for the formation of a wide variety of organic by-products when chlorine or chloramines are used in disinfection. With the use of ozone, bromate becomes a major concern. A number of these by-products are carcinogenic, produce reproductive and developmental toxicities, and have other toxicological properties that would be of concern if produced at sufficient concentrations. The major focus of this section is to provide some basis for appreciating the reasons one might be more concerned about brominated by-products than their chlorinated analogs.

3.1 Epidemiology Suggests Different and Greater Hazards than Available Toxicological Data.

It is difficult to gauge the actual magnitude of risks from disinfection by-products in drinking water. Epidemiological data has associated increases in bladder and colorectal cancer with the use of chlorine as a disinfectant. Meta analyses have been applied to these data that suggest that the attributable risk could be thousands of cases of cancer in the U.S. annually (Morris et al., 1992). It must be noted that the utilization of meta analyses in this case has been seriously questioned (Poole, 1997). However, *if the epidemiological results are actually valid, these are the levels of risk that would be derived from the positive studies.* If these estimates are real, risks of this magnitude may warrant significantly more stringent control of chlorinated

DBPs than anticiapated under the Stage 1 DBP rule. However, proof of causality has been elusive (Poole et al., 1997; USEPA, 1998a). Many scientists in the area believe it to be premature for precipitous action based on available epidemiological data.

Toxicological studies have identified chemicals that can produce cancer in rodents, but the target organs most frequently identified are the liver and kidney. Two by-products have been shown capable of producing colon cancer in rats (bromodichloromethane and bromoform), but their activities are much too weak to account for the incidence seen in the epidemiology studies. To date, no bladder carcinogen has been identified. There are a number of reasons to explain both the quantitative and qualitative discrepancies between the epidemiological and toxicological data. The possible risks suggested by epidemiology studies may simply not be correct. On the other hand, the experimental animals used may simply be poor models for human susceptibilities to these disinfection by-products. The fact is that a very large fraction of disinfectant by-products have not actually been subjected to cancer bioassays. Brominated by-products are very underrepresented in the untested compounds. Moreover, the National Toxicology Program (NTP) noted that induction of colon cancer was a rare event in bioassays. However, this site was targeted by three other brominated compounds in the experience of NTP (Melnick et al., 1994). Therefore, one must consider the problem that is stated in Table 1.

The same type of problem of interpreting possible cancer risks from chlorinated DBPs pertains to understanding possible reproductive and developmental risks from chlorinated DBPs. There has been a single, well conducted epidemiology study associating disinfection by-products as a potential cause of spontaneous abortion (Waller et al., 1998); it is noteworthy that this study was performed in California, involved brominated THMs, and possibly some Delta water. Toxicological studies have identified a number of chemicals that have effects on male reproduction and new experiments are exploring other reproductive hazards. The most potent DBP found to affect male reproductive function is dibromoacetic acid (Linder et al., 1995) suggesting that brominated species may be the most likely group of chemicals to produce these effects. Still the potency of dibromoacetic acid is too low to account for the epidemiological results and the studies focused on different endpoints. However, if other short-chained chlorinated hydrocarbons are examined, the substitution of bromine for chlorine significantly increases the probability of adversely affecting male reproductive function (Lag et al., 1991).

Therefore, the issues identified in Table 1 are even more important for developmental and reproductive toxicities that might be associated with DBPs.

Table 1. Potential explanations for the discrepancy between epidemiological studies of chlorinated water and toxicological studies of disinfection by-products.

1. Chlorinated by-products have been the most thoroughly studied.
2. Concerns about major chlorinated by-products (chloroform, dichloroacetate and trichloroacetate) are fading at the low levels produced in drinking water based upon new toxicodynamic data. These by-products are the major liver and kidney carcinogens.
3. The majority of by-products produced from chlorination have not been subjected to toxicological testing.
4. Brominated by-products comprise a major portion of the untested compounds.

3.2 Brominated By-products – Reasons for Concern.

As should be appreciated from the above discussion, the data available at this time are too sparse to raise alarms about brominated DBPs. However, relatively large investments are being considered to improve environmental conditions in the Bay-Delta system. These improvements are being viewed to an end point that is 25-30 years in the future. As some of the alternatives could potentially change bromide levels present in drinking water sources, it is necessary to consider the potential impacts of the resulting by-products on human health. Aside from the limited data on brominated by-products referenced above, there are several theoretical reasons why bromine containing disinfection by-products could become a serious problem over this time horizon. Anticipation of these potential problems should help avoid commitment to alternatives that could be untenable in the long-term.

3.2.1 Direct and Indirect Effects of DBPs

Chemicals may exert their toxic effects as the parent compound or they may require metabolism to become active. Examples of both types are found with disinfection by-products. Dichloroacetic acid and trichloroacetic acid appear to act directly (i.e. do not require metabolism to be active) to produce liver cancer. It is likely that these chemicals bind through reversible hydrophobic and electrostatic interactions to proteins. The trihalomethanes can act directly at very high doses to produce anesthesia. However, their more severe toxicities are produced by being metabolized oxidatively to phosgene, reductively to a free radical, or reacting with glutathione to produce a third reactive intermediate. These reactive intermediates interact covalently with proteins and nucleic acids to produce toxicity and induce mutation, respectively. Oxidants can also produce damage by inducing oxidative stress. Generation of hydrogen peroxide, superoxide radical, and hydroxyl radical can produce damage to cell membranes and produce oxidative damage to purine and pyrmidine bases in DNA *in vivo*. Such reactions may occur spontaneously, but in some cases various enzymes that are present in the body accelerate them.

Impact of Bromine Substitution on Metabolism Leading to Reactive Intermediates. Halogen substitution on organic molecules provides an electronegative point of attack for either oxidative or reductive metabolism. In reductive dehalogenation reactions, free radicals are generated that lead to oxidative stress or to direct damage by the halogen radical. As halogens become larger, they become more electronegative and are more easily removed. Chlorine is a better leaving group than fluorine and bromine is better than chlorine. Therefore, toxicities that are the result of interactions of reactive metabolites are generally greater if bromine is substituted on a carbon instead of chlorine. To the extent that these metabolites can reach the DNA in the cell, they are frequently mutagenic.

The limited comparisons of toxic and carcinogenic effects of the relatively small numbers of brominated disinfection by-products are consistent with this hypothesis. The weight of evidence (induction of tumors in multiple species, multiple sites, and sites of relatively low incidence) of bromodichloromethane is much stronger than for chloroform. Moreover, the carcinogenic potency of bromodichloromethane is approximately 10-times that of chloroform using the linearized multistage model for comparisons at low doses (Bull and Kopfler, 1991).

Mutagenicity as a Major Determinant for Using Linear Approaches to Low-dose Extrapolation. The mutagenic activity of a chemical is a major determinant of whether linear methods are to be used for low dose extrapolation (USEPA, 1996). Within the THM and haloacetic acid groups of DBPs that have been investigated, the chlorinated members of the group are very inconsistently active in mutagenesis assays. There are three different pathways for metabolizing the THMs to reactive metabolites. In the two of the three pathways that have been investigated, substitution of bromine increases the mutagenic activity significantly above that seen with the chlorinated analogs (Zieger, 1990; Pegram et al., 1997). Dichloroacetic acid and trichloroacetic acid are very weak mutagens, requiring greater than millimolar concentrations to product modest responses (Harrington-Brock et al., 1998; Giller et al., 1997). Dibromoacetic acid and tribromoacetic acid are at least an order of magnitude more potent as mutagens in the Salmonella fluctuation assay (Giller et al., 1997).

Mutagenic activity of a compound assumes this importance based on the assumption that mutagenic events are cumulative with dose. Mutations are essentially irreversible events to the extent that the mutated cell and its progeny survive.

Based on the relative lack of data implicating a mutagenic mechanism for chloroform, an MCLG (maximum contaminant level goal) of 300 μg/L was recommended by the USEPA in a Notice of Data Availability (USEPA, 1998b). However, it is highly improbable that bromodichloromethane would be treated in the same way. In all probability, an MCLG = 0 will be maintained for bromodichloromethane because of its mutagenic activity and because of its more robust activity as a carcinogen. It is also improbable that dichloroacetic acid and trichloroacetic acid will be treated with linear-low dose extrapolation. As with bromodichloromethane, the mutagenic activity associated with the brominated haloacetic acids may also be used to rationalize linear low-dose extrapolation for these chemicals. In addition, the brominated haloacetic acids have been shown to produce a sustained elevation of oxidatively damaged DNA in the liver of chronically treated mice (Parrish et al., 1996), an effect not observed with dichloroacetic acid and trichloroacetic acid. As a result, the MCLGs proposed for the chlorinated vs. the brominated haloacetic acids could vary widely even though they have approximately the same carcinogenic potency in animal studies (Bull, unpublished data).

3.2.2 Bromate

When ozone is used in the disinfection of water containing significant amounts of bromide, the formation of bromate will result. When the concentrations of bromate produced in these circumstances are compared to those which induce cancer in rats (Kurokawa et al., 1986), the margin of safety is significantly lower than for disinfectant by-products that are produced with chlorination.

Estimated Cancer Risk. Applying the linearized multistage model to data obtained in cancer bioassays in rats, the concentrations of bromate associated with the 1 in a million additional lifetime risk is 0.05 μg/L (Bull and Kopfler, 1991). The 1 in 10,000 added risk is estimated at 5 μg/L which approximates the practical quantitation limit (PQL) in water.

Lack of Toxicokinetic and Toxicodynamic Data. The risk that bromate represents as a cancer hazard in humans may not be accurately reflected by the linearized multistage model. Unlike chlorination, no epidemiological studies have been conducted to suggest that ozonation of water carries a cancer risk for humans. Available data, however, suggest a relationship with oxidative damage to DNA in the induction of renal tumors (Umemura et al., 1993). The actual mechanisms involved are somewhat controversial. *In vitro* studies of bromate-induced DNA damage suggest that the process requires glutathione and produces a damage more consistent with the generation of bromide radicals than reactive oxygen species (Ballmaier and Epe, 1995). Conversely, Chipman et al., (1998) found little dependence upon glutathione *in vivo*, but indirect methods (i.e. glutathione depletion) were used to investigate glutathione dependence. On the other hand, these investigators did find evidence of lipid peroxidation in the kidney of rats following 100 mg/kg dose of potassium bromate, but not at 20 mg/kg. Neither case provided a rationale for why these effects were observed in the kidney and not other organs like the liver (Cho et al., 1993; Lee et al., 1996). The oxidative damage to DNA is also produced at very high rates by the normal energy metabolism of the body. The repair mechanisms for this type of damage are very rapid and efficient (Lee et al., 1996). At low doses, the amount of oxidative damage anticipated from bromate would be very small compared to the damage induced by normal metabolism. Consequently, it is likely that cancer risk would be low at the concentrations of bromate that might be anticipated in ozonated drinking water. Irrespective of a detailed mechanism, however, it will be necessary to obtain a much clearer and quantitative model of the toxicokinetics and toxicodynamic nature of bromate-induced cancer. The research of Lee et al. (1996) provides an excellent start by identifying a critical biomarker for kidney cancer, but has yet to be coupled with biological responses in a quantitative way. Thus, detailed toxicokinetic and toxicodynamic data appear necessary to provide evidence that non-linear extrapolation is appropriate for bromate-induced cancer.

3.3 Variations in sensitivity in the human population.

It is important to acknowledge that the differences in epidemiological and toxicological studies of disinfection by-products could be that rodents are a poor representation of the distribution of human sensitivities to toxic chemicals. In general rodents used in toxicological tests are inbred strains. Frequently, these strains are chosen because they are sensitive models for certain types of toxic effects. While this may be generally true, it does not always hold true in particular cases. The factors that influence sensitivities to toxic chemicals frequently have a very specific basis that is not necessarily reflected by so-called "sensitive experimental animal models". It is beyond the scope of this report to cover this subject in a comprehensive way. However, there are two types of interaction that need to be identified and discussed in an illustrative way. Once the mechanisms involved in these two general processes are identified, the identification of traits that characterize sensitive populations can be done rationally in a chemical-specific way.

3.3.1 Enzymes involved in metabolism of disinfection by-products.

Several types of metabolic processes are involved in the toxicology of disinfection by-products. However, a broad class of enzymes, glutathione-S-transferases, have been implicated in the toxicities of the trihalomethanes, the haloacetic acids, and the haloacetonitriles. In the case of the THMs, the theta isoform appears to be capable of producing a mutagenic metabolite (Pegram et al., 1997). This isoform is not expressed by approximately 40% of the U.S. population. Therefore, the sensitive population may be only 60% of the human population. Conversely, evidence has been gathered that demonstrates that a new glutathione-S-transferase, the zeta isoform, acts to detoxify dichloroacetic acid (Tong and Anders, 1998). If there is a significant fraction of the population that did not express this enzyme, that fraction of the population could be extremely sensitive to this disinfection by-product.

3.3.2 Susceptibility to effects of DBPs.

Other host-related factors that could be the basis for higher sensitivity of humans to disinfection by-products are more difficult to identify, but may be more important than variations in enzymes involved in the metabolism of DBPs. Broad examples can be provided, however. If a disinfection by-product acts through damaging DNA, lack of the enzymes that recognize and repair those lesions could make an individual much more sensitive. Some disinfection by-products (e.g. the haloacetic acids) appear to act by interfering with cellular signaling systems that are activated by insulin and related growth factors. Diabetics are much more prone to the development of liver cancer than the rest of the population. Consequently, if epidemiological studies had focused on this subpopulation, a risk of liver cancer may have been identified.

3.4 Summary

From the health effects standpoint, there are issues that surround bromide and brominated by-products that can be resolved in the next 5-10 years, but others that will require decades to solve. Properly directed toxicological screening studies and mechanistic studies could provide much better perspective on the actual risks associated with disinfection by-products in the shorter time frame. Without specific and detailed knowledge of the mechanisms by which disinfection by-product toxicity is induced, it is very difficult to identify those variables that would affect the distribution of human sensitivities to these chemicals that could be applied in a meaningful way in epidemiological studies.

The importance of establishing the mode of action by which chemicals induce toxicity, particularly in carcinogenesis, cannot be overstated. Nowhere is this more apparent than when considering the potential differences in risk that may exist between chlorinated and brominated by-products. Clearly, these molecules will share some aspect of their mechanism of action. As bromine substitution increases, however, multiple mechanisms are likely to become apparent. The non-genotoxic mechanism found with the corresponding chlorinated DBP will undoubtedly still be represented, but the brominated analogs are significantly more likely to add mechanisms of carcinogenesis involving mutagenesis. Thus, not only will the mechanisms contributing to the adverse response become more diverse, but they will also require linear extrapolation. In some cases, the mechanism responsible for the effect induced by the chlorinated analogs may actually disappear as the degree of bromine substitution increases. The permission from one mechanism to another could lead to some complex structure-activity relationships that might have to be resolved before the relative impact at concentrations found in drinking water can be estimated with confidence.

4.0 Regulatory Background

The purpose of this section is to provide a perspective on possible regulatory criteria that may influence treatment and associated cost impacts on public drinking water drinking systems using the Bay-Delta as their source water.

4.1 Overview of 1996 SDWA Amendments as they Pertain to DBPs/Microbes

In 1996, Congress issued amendments to the Safe Drinking Water Act requiring EPA to develop regulations within a specified time. These include promulgation of the Interim Enhanced Surface Water Treatment Rule (IESWTR) and Stage 1 Disinfectants and Disinfection By-Products Rule (DBPR1) by November 1998, a Long Term Enhanced Surface Water Treatment Rule (LT1ESWTR) by November 2000, and a Stage 2 Disinfectants and Disinfection By-Products Rule (DBPR2) by May 2002. As part of the 1996 amendments, Congress also requires EPA to consider risk from contaminants that might be indirectly affected by regulation. In this regard, EPA intends to propose and promulgate a Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) concurrently with the DBPR2.

4.2 Overview of DBPR1/IESWTR/LT1ESWTR

The purpose of the DBPR1 is to reduce risks from disinfectants and DBPs in public water systems which disinfect. Unlike the Maximum Contaminant Level (MCL) of 100 ug/l for total trihalomethanes (TTHMs), which only pertains to systems serving 10,000 people or more, the DBPR1 will apply to all system sizes. The purpose of the IESWTR is to reduce risks from pathogens, especially *Cryptosporidium*, and to prevent increases in microbial risk while systems comply with the DBPR1. With the exception of sanitary survey requirements (which will pertain to all system sizes), the IESWTR will pertain to systems serving 10,000 or more people. In November 1997, EPA issued two Notices of Data Availability in the Federal Register indicating the rationale supporting the criteria intended for promulgation in the DBPR1 and the IESWTR.

Criteria under consideration for the final DBPR1 include: (i) MCLs for TTHMs (0.080 mg/L = 80 ug/L), the sum total of 5 haloacetic acid concentrations otherwise known as HAA_5 (0.060 mg/L = 60 ug/L), bromate/BrO_3^- (0.01 mg/L = 10 ug/L), and chlorite/ClO_2^- (1.0 mg/L = 1,000 ug/L); (ii) maximum residual disinfectant levels for chlorine (4.0 mg/L), chloramines (4.0 mg/L), and chlorine dioxide (0.8 mg/L); and (iii) enhanced coagulation requirements for systems using conventional treatment or softening to remove DBP precursors (measured as percent reductions of total organic carbon (TOC)).

Criteria under consideration for the final IESWTR include: (i) tightening the combined filter turbidity performance criteria for systems using rapid sand filtration to less than 0.3 NTU in at least 95% of turbidity measurements taken each month; (ii) continuous turbidity monitoring requirements for individual filters and reporting of results to States depending upon individual filter performance; (iii) a provision that would not allow systems to lower existing levels of inactivation to comply with the Stage 1 DBPR MCLs without first consulting with the responsible State officials; and (iv) provisions that would require the responsible State agencies to conduct sanitary surveys of all surface water systems (including those serving <10,000 persons), and for systems to implement remedial action if problems are identified by State agencies. A sanitary survey incorporates not only an inspection of the treatment plant, but examination of a wider range of factors that influence the quality of drinking water, including the watershed and the distribution and storage system.

EPA envisions similar requirements to the IESWTR being issued for systems serving fewer than 10,000 persons in the LT1ESWTR scheduled for proposal in November 1999, and for promulgation in November 2000.

EPA intends to set compliance dates for the DBPR1 that will coincide with compliance dates for the IESWTR (November 2001 for systems serving 10,000 or more people) and the LT1ESWTR (November 2003 for systems serving less than 10,000 people).

EPA is planning to conduct stakeholder meetings beginning in December 1998 to discuss information and the process to support the development of the DBPR2 and LT2ESWTR. Major issues related to these rules are discussed below.

4.3 DBPR2 Issues

Major issues with developing the DBPR2 include: interpretation of cancer, developmental, and reproductive risk associated with DBPs from limited toxicological and epidemiological data; assessing the feasibility and costs of using various treatment technologies to reduce DBP concentration levels; and assessing the potential changes in microbial risk that might result from treatment changes to control for DBPs. Addressing the above issues will help determine the extent to which additional regulation may be appropriate such as whether to set

MCLs for DBP groups, individual DBPs, or treatment technique requirements (e.g., limits for total organic halides (TOX), or TOC removal requirements). Another issue may be whether MCLs should be set based on a running annual average as is currently the case, or on maximum single event concentration levels. MCLs based on maximum values within a distribution system would prevent all people from being exposed above a certain level. Such a strategy could become important if developmental or reproductive effects from exposure to DBPs are determined to be of concern.

Several specific issues relative to the broad generic issues discussed above may have particular significance for utilities using the Bay Delta as their source water. These include: (i) the risk associated with brominated DBP species versus the risks from the complete mixture of chlorinated DBPs; and (ii) if the risks from brominated species are deemed substantially more significant than those from the chlorinated species, the extent to which brominated species formed primarily through chlorination (e.g., bromodichloromethane or bromochloroacetic acid) or ozonation (e.g., bromate) can be controlled.

The setting of any new MCLs or treatment technique requirements will consider potential exposures (and associated risks) able to be avoided, and the technical feasibility and costs for reducing exposures on a national level. In considering this type of analysis, it becomes important to understand the national distribution of source water quality parameters (e.g., bromide, TOC, UVA_{254}) that most significantly affect the treatability of the water. Systems using the Bay-Delta as their source water (primarily because of the high bromide content), may have greater difficulty than the average utility in the U.S. in meeting a particular regulatory endpoint; another important consideration is the character of the TOC in Bay-Delta water. This regional consideration is also relevant to the national standard-setting provision that treatment must be affordable for large systems. The significance of this issue may also be largely influenced by the co-occurrence of pathogens (particularly *Cryptosporidium*) and DBP precursors. Depending upon the requirements of the LT2ESWTR, the level of inactivation required to control microbial risks could make it more difficult for systems to comply with the DBPR2 criteria. For example, a system with high levels of *Cryptosporidium* and DBP precursors (bromide and TOC) in their source water may have greater difficulty in complying with the DBPR2 and LT2ESWTR than systems with average source water quality. Each rule will have to consider and appropriately address the factors of affordability and availability of treatment raised by compliance with the other rule.

4.4 LT2ESWTR Issues

Major issues with developing the LT2ESWTR include: estimating the microbial risk likely to remain after implementation of the IESWTR and LT1ESWTR, given limitations of data; determining appropriate risk goals (e.g., EPA's 1994 proposed 10^{-4} annual risk goal for *Giardia* or *Cryposporidium*); and determining the appropriate regulatory framework and target organism(s). Several regulatory frameworks were considered under the 1994 proposed IESWTR and are likely to be revisited under the development of the LT2ESWTR. These include: a proportional treatment requirement, (where systems might be required to achieve at all times a minimum level of total removal/inactivation for *Cryptosporidium*, depending upon an estimated reasonable worst case pathogen occurrence in the source water); and a fixed level treatment requirement (where all systems would be required to achieve at least the same minimum level of treatment, with exceptions allowed, depending upon site specific characteristics).

Major constraints with developing the IESWTR included: lack of available methods for adequately measuring *Giardia* or *Cryptosporidium* in the source water, and limitations by which treatment efficiencies (physical removal and chemical inactivation) for these organisms could be practically determined. The extent to which these issues can be resolved may largely influence criteria to be included in the LT2ESWTR.

Although LT2ESWTR criteria will not become apparent for quite some time, factors which could significantly influence the impact of this rule on a particular utility include the magnitude and variability of *Cryptosporidium* in the source water, physical removal efficiencies for *Cryptosporidium*, and the feasibility of inactivating *Cryptosporidium* while also meeting new regulations for DBPs (as discussed above under DBPR2 issues). Systems with low pathogen loadings in their source water and/or high physical removal efficiencies are likely to be less affected by any inactivation requirements that might be specified for *Cryptosporidium*.

4.5 Recommendation

The CALFED program should strive to deliver the highest possible raw-water quality to the sources used for drinking water supply. This effort will minimize treatment costs and the threat to public health from drinking water.

5.0 Treatment Considerations

5.1 Overview of Treatment Considerations

A variety of treatment technologies are available for the disinfection of water. A number of these (e.g. chlorination, ozonation) produce potentially harmful disinfection by-products (e.g. trihalomethanes, haloacetic acids, bromate). The incorporation of bromine into these disinfection by-products increases as the bromide concentration in the water being treated increases. For example, the speciation of THMs shifts away from chloroform and toward bromodichloromethane, dibromochloromethane, and bromoform, respectively, as the concentration of bromide increases. Likewise, the speciation of haloacetic acids shifts away from di- and trichloroacetic acid towards bromochloroacetic acid and bromodichloroacetic acid, respectively, with increasing bromide concentrations. In the case of ozonation, bromate formation increases with increasing bromide concentrations. If disinfection requirements become more stringent with future regulations, greater concentrations of disinfectants may need to be applied, resulting in greater concentrations of disinfection by-products unless there is a shift toward higher quality source water or greater degrees of pretreatment prior to disinfection.

To control the formation of these potentially harmful disinfection by-products, several treatment strategies can be employed:

(a) removal of the organic precursors with which the disinfectant reacts prior to the application of the disinfectant;
(b) removal of the bromide prior to disinfection;
(c) removal of the disinfection by-products after they are formed;
(d) modification of treatment conditions to limit the formation of specific DBPs; or
(e) use of alternative disinfectants which do not produce DBPs of health concern.

Processes that can be used for the removal of organic precursors (TOC) include enhanced coagulation, granular activated carbon adsorption (GAC), membrane filtration, and chemical oxidation coupled with biofiltration. The only practical process that has been demonstrated to be applicable for the removal of bromide is membrane treatment (i.e. reverse osmosis, and to a lesser extent nanofiltration). The removal of disinfection by-products after they are formed is difficult, primarily because of the wide array of DBPs with their very different physical-chemical properties. An exception is bromate, where several technologies have been examined for its removal. Treatment conditions which can be modified to minimize bromate include decreasing the pH of ozonation to lower the formation of bromate. Disinfectant options include the use of ozone, chloramines, chlorine dioxide, ultraviolet (UV) irradiation, and membrane filtration to partially or fully offset the use of free chlorine.

5.2 Disinfection Practice

The most common chemical disinfectants for the treatment of drinking water are chlorine, ozone and chlorine dioxide. All are capable of inactivating viruses and Giardia cysts, at reasonable doses and contact times, in accordance with specifications of the Surface Water Treatment Rule. However, the LT2ESWTR may require greater removal and/or inactivation of Cryptosporidium oocysts. Ozone, and to a lesser extent, chlorine dioxide, appear to be the only chemical disinfectants capable of inactivating Cryptosporidium oocysts, although disinfectant combinations (e.g. free chlorine and chloramines) have been reported to be moderately effective as well. Because of this relationship, the waterworks industry has been moving toward ozonation in place of chlorination for primary disinfection, and many utilities in California that use Delta water have adopted ozonation for primary disinfection and for taste and odor control; ozone is also one of the more effective agents, along with activated carbon, for removing taste and odor-causing organic substances from water. Depending upon criteria developed under the LT2ESWTR, many more utilities may consider ozonation. A major limitation to more widespread practice of ozonation, however, is the fact that ozonation of bromide-containing waters produces bromate. A number of water systems that currently ozonate Delta water experience levels of bromate in excess of the proposed Stage 1 maximum contaminant level for bromate at certain times of the year, and many are investigating techniques to limit bromate formation or to remove bromate after it is formed.

Other non-chemical or physical options for achieving the Giardia and virus removal/inactivation requirements of the Surface Water Treatment Rule and possible Cryptosporidium removal/inactivation requirements include UV-disinfection and membrane filtration. UV-disinfection for cyst inactivation has yet to be demonstrated on a practical, full-scale level, but a number of promising new technologies are under development. The next several years will determine whether or not these new technologies will be practical, and the type of pre-treatment requirements that will be necessary to allow them to function effectively. In contrast, microfiltration has already been demonstrated to be an effective technology for the "absolute" removal of Giardia cysts and Cryptosporidium oocysts. Microfiltration will not remove viruses, but tighter membranes, such as nanofiltration or ultrafiltration membranes, can be employed for this purpose. Alternatively, post-treatment of micro-filtered water with free chlorine for only a short contact time can achieve virus inactivation, but in some cases, excessive levels of halogenated disinfection by-products can still be formed, especially in bromide-enriched waters. Two major limitations of membrane filtration processes, particularly nanofiltration and ultrafiltration, are their relatively high costs compared to the more conventional processes, and the fact that they have a product recovery of only about 80% (somewhat greater for ultrafiltration); i.e. a significant amount of the influent water must be wasted, a particularly troublesome limitation for a water-short region like California.

5.3 Removal of Bromide

Bromide occurs as a dissolved species in water and cannot be readily removed by precipitation. It is also not readily removed by coagulation and associated solid-liquid separation processes and tends to pass conservatively through conventional treatment processes. It can be removed by ion exchange, but most resins available today are not very selective for bromide and therefore the process is not very practical for this application. The only processes available at this time for the removal of bromide are reverse osmosis and nanofiltration; bromide rejections of about 90 % and 50 % have been reported, respectively, for these membrane processes. These membrane processes, however, are the most costly of the membrane processes, require the use of conventional treatment (coagulation, clarification, filtration) prior to their use, and have the lowest recovery, making them relatively impractical for applications in California.

5.4 Removal of Organic Precursors

The most widely studied and demonstrated approach for controlling the formation of disinfection by-products is removal of the organic precursors prior to disinfectant addition. The rationale is that, with lower levels of precursors in the water, the disinfectant demand of the water decreases and lower doses of disinfectants can be applied to achieve the desired level of disinfection, thereby lowering the formation of DBP's. In order of increasing cost and effectiveness, the most viable processes are enhanced coagulation, granular activated carbon adsorption, and membrane filtration. The success of these processes depends significantly upon the nature of the organic material in the water, i.e. whether it is hydrophobic or hydrophilic organic material. Generally, the organic material is characterized in terms of its total organic carbon (TOC) concentration, its ultraviolet (UV) absorbance at 254 nm, or a composite of the two parameters, its specific UV absorbance (SUVA).

Enhanced coagulation involves adding sufficient amounts of coagulant, often more than is typically used for turbidity (particle) removal, to achieve specific TOC removal requirements specified in the proposed Disinfectants/Disinfection By-Products Rule. Given the typical alkalinity and TOC concentration of Delta water, these requirements range from 15 to 40%. SUVA values at exports points are generally in the range of 3 to 4 $m^{-1}/(mg\ C/L)$. These values indicate that the water likely contains a mixture of non-polar and higher MW versus and polar and lower MW NOM. The water is moderately amenable to coagulation and GAC; membranes would provide the most effective NOM removal. Limitations of practicing enhanced coagulation on Delta water are: the relatively large doses of coagulant required to remove the organic DBP precursors; the corresponding larger amount of sludge that is generated and must be disposed of; the possible need for relatively large amounts of acid to lower the pH in this relatively high alkalinity water to a level where coagulation of organic material is more effective; and the corresponding need for high levels of base to be added to bring the pH back up to acceptable distribution system levels for corrosion control. It should be noted that enhanced coagulation will not remove bromide from the water.

The effectiveness of granular activated carbon (GAC) adsorption for removal of DBP precursors depends upon the empty bed contact time (EBCT) of the carbon bed. Typically, EBCT's in excess of 15-20 minutes are needed for this particular objective. GAC can be used either in a filter-adsorber mode, in which the GAC is added to the conventional filter bed in place of the anthracite and/or sand media, or in a post-filter adsorber, in which a separate GAC adsorption bed is installed. The former approach, because of the relatively low EBCT's in conventional filter beds (5-10 min), is not very effective for precursor removal. Post-filter adsorbers can be designed and operated at any target EBCT, but the cost increases with increasing EBCT. Additionally, the GAC must be regenerated when its adsorptive capacity is reached. The frequency of regeneration ranges from about 3 to 6 months, depending upon the TOC concentration of the water. The cost of GAC increases with increasing frequency of regeneration. GAC will not remove bromide from the water.

A variety of membrane processes are available for water treatment practice, including, in order of increasing relative cost, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). The effectiveness of these processes for the removal of organic precursors depends on the size of the pores of the membranes, or more precisely, their molecular weight cutoff (MWCO). MWCO's of 200-500 Daltons are required for effective TOC removal, indicating that NF or RO must be used, although some modest removal can be realized with UF. While microfiltration is effective for the removal of particulate material (e.g. protozoan cysts), it is not fine enough for the removal of TOC, although it can be combined with some powdered activated carbon or coagulant addition to achieve some modest levels of TOC removal. Membrane elements that come in a spiral wound as opposed to a hollow fiber configuration (RO, most NF, some UF) require a substantial degree of pre-treatment to remove particulate material that can cause membrane fouling problems. As noted above, these processes have recoveries on the order of 80% (somewhat higher for NF and UF), making them of dubious practicality for a water-short region like California. Also, as noted above, only reverse osmosis has the ability to reject (remove) bromide.

A number of the larger utilities in California, some of which use Delta water, are currently running bench-scale and pilot-scale studies of GAC adsorption and membrane filtration as part of the EPA's Information Collection Rule to evaluate the effectiveness of these processes for TOC removal and DBP control.

The fact that the majority of these TOC removal processes do not remove bromide means that the bromide/TOC ratio will increase after treatment. As a result, although overall formation of DBPs will be reduced because of the reduced disinfectant requirements, the speciation of the DBPs will shift toward the bromine-containing species such as bromodichloromethane, bromochloroacetic acid, and bromodichloroacetic acid.

One additional treatment approach for removing organic DBP precursors is chemical oxidation and biofiltration. Ozone or advanced oxidation processes involving some combination of ozone, hydrogen peroxide, and UV irradiation, can be employed for this purpose. While these processes do not reduce the TOC concentration appreciably, i.e. they do not convert much of the organic carbon to carbon dioxide, they do alter the nature of the organic material. The oxidation by-products, consisting of aldehydes, organic acids, and other lower molecular weight more oxygenated compounds, are generally more biodegradable than the parent material. Passage of the oxidized water through a biologically acclimatized bed of filter media, e.g. granular activated carbon, anthracite, and/or sand, results in the biological removal of many of these by-products, producing a water with a lower DBP formation potential than the untreated water. Many of the water systems currently using ozone to treat Delta water also employ biological filtration. The effluent from the filters, however, must be treated with a disinfectant such as free chlorine or UV irradiation to inactivate heterotrophic bacteria that are sheared off the filter media. If free chlorine is used for this purpose and the residual precursor concentration in the filter effluent is still significant, appreciable concentrations of DBPs can still be produced, even if the chlorination contact time is relatively short, i.e. on the order of 15 min. This is because the kinetics of DBP formation are more rapid in the presence of bromide. Oxidation coupled with biofiltration is effective only when the water temperature is reasonably warm, e.g. above 10°C. During colder temperatures, the kinetics of microbial degradation are much slower and biofiltration is not as effective. Additionally, if the raw water contains bromide and ozone is the oxidant, bromate formation will occur. Biodegradation of bromate does not occur, except under anoxic conditions which are typically not desirable in water treatment.

5.5. Removal of DBPs

A number of the halogenated organic disinfection by-products produced from chlorination can be removed from the treated water after they have been formed. The trihalomethanes are volatile compounds, i.e. they have low vapor pressures, and can be removed by air stripping. The effectiveness of stripping decreases in the order chloroform, bromodichloromethane, dibromochloromethane, bromoform. These, however, are the only volatile species among the halogenated DBPs and therefore the only ones that can be removed by air stripping. A number of the haloacetic acids have been shown to be biodegradable under aerobic conditions and, accordingly, can be removed by passing, for example, pre-chlorinated water through a biologically active filter bed. The trihalomethanes, however, are biologically stable under aerobic conditions. They can be biodegraded anaerobically, but anoxic treatment is undesirable in water treatment. The haloacetonitriles have been shown to be unstable under elevated pH conditions, undergoing alkaline hydrolysis. Such conditions, however, promote THM formation. The DBP species all have different physical, chemical, and biological properties, hence there is no single treatment process that can be employed to remove them all. Removal of the halogenated organic DBPs after they are formed is therefore not practical; it is a more prudent strategy to try to control their formation by the techniques described above.

Bromate removal, however, may be an effective treatment strategy for controlling bromate levels following its formation by ozonation. Three strategies have been suggested: the use of ferrous iron salts, granular activated carbon adsorption, or UV irradiation. Ferrous iron can chemically reduce bromate to bromide; a ferric hydroxide precipitate is produced that must be removed by subsequent clarification and filtration processes. Hence, such treatment must occur early in the treatment train. pH control is critical to prevent the added ferrous iron from being initially oxidized by dissolved oxygen in the water, although eventual oxidation to ferric hydroxide allows it to function as an iron coagulant. Granular activated carbon can adsorb bromate, but its capacity for doing so is limited, leading to short effective lifetimes for this application of GAC. UV irradiation decomposes BrO_3^- to Br^-, with medium-pressure lamps being more effective than low-pressure lamps. RO and NF membranes can also remove BrO_3^-, but suffer from the same limitation described for Br^- removal. Of these processes, bromate reduction by ferrous iron appears to be most attractive, but more research and demonstration of this technique needs to be conducted before it can be reliably implemented on a full-scale basis.

5.6 Control of Bromate Formation

A final option for controlling bromate levels in finished drinking water is to minimize its formation in the first place. For example, the extent of bromate formation increases with increasing pH. Hence, pH adjustment to values below 6.5-7.0 prior to ozonation can reduce the formation of bromate. However, as in the case of enhanced coagulation, pH depression requires significant the addition of acid to high-alkalinity waters (Delta water exhibit medium-levels of alkalinity). Additionally, it has been demonstrated that splitting the application of ozone between several of the stages in a multi-stage ozone contactor produces lower levels of bromate than if all of the ozone is applied in the first stage. The judicious use of hydrogen peroxide and ammonia have also been shown to be potentially effective methods for limiting the formation of bromate. Whether or not such modifications can maintain bromate levels below the proposed and potential future MCLs for bromate in waters with elevated bromide levels such as those found in the Delta remains to be demonstrated. Most work to date has focused on the 10 ug/L proposed standard; the efficacy of bromate minimization approaches for a significantly lower MCL has not been studied.

5.7 Matching Treatment to Regulatory Options for Various Source Water Qualities

The national average of Br^- in drinking water sources is significantly less than 100 ug/L. Water exported from the Delta and intended for drinking water has Br^- at levels that are at least the 90th percentile on a national basis. It is noteworthy that BrO_3^- is 63 % Br by weight; this suggests that exceeding the 10 ug/L MCL for BrO_3^- requires only 6.3 ug/L of incorporated Br^-. Br^- is efficiently converted into THM and HAA species, with THM-Br $\approx$ 20 % and HAA_5-Br $\approx$ 10%.

One general approach to examining treatment options to meet various future regulatory objectives is to determine source water quality characteristics in terms of bromide and TOC concentrations that would allow Delta water users to meet these regulations using existing or future water treatment technologies. DBP prediction models; e.g., $BrO_3^- = f(Br^-, \text{etc.})$ or TTHM

= f(Br^-, etc.); can be used to predict a *limiting* value of Br^-; e.g., $Br^-_{LIMIT} = f(BrO^-_{3\,MCL})$ or $Br^-_{LIMIT} = f(TTHM_{MCL})$; to meet a MCL under a given set of water quality (e.g., temperature or pH) and treatment (e.g., O_3 or Cl_2 dose) conditions. Such an exercise was performed by Owen et al. (1998) in assessing potential compliance of Delta water to Stage 1 MCLs for TTHM, HAA_5, and BrO_3^- as well as SWTR disinfection requirements by considering coagulation, ozonation, GAC, and membranes. Their conclusion was that TOC and Br^- would be contrained to < 3 mg/L and < 50 ug/L, respectively, for utilities incorporating either enhanced coagulation or ozone disinfection; < 5 mg/L and < 50 –100 ug/L for GAC; and < 7 mg/L and < 300 ug/L for (NF) membranes. While Br^- and TOC are inter-related, it is Br^- that is the limiting factor; since the analysis by Owen et al. (1998) did not consider low-pH ozonation, it would be reasonable to stipulate an upper Br^- constraint of 100 ug/L for present SWP treatment practice (conventional treatment with movement toward implementing ozonation and enhanced coagulation). The most flexible treatment approach is membrane treatment, but brine disposal and associated water loss (up to 20 %), as well as cost are serious constraints. It is noteworthy that the models used by Owen et al. (1998) have limitations: the BrO_3^- model used is only applicable to pre-O_3 and the Cl_2 models used do not account for HAA formation nor the reduction in NOM reactivity with treatment.

Krasner (CALFED, 1998) performed bench-scale tests of “synthetic” Delta water (agricultural-drain water diluted with Milli-Q water and spiked with Br^-) under SDS-chlorination conditions (target Cl_2 residual of 0.5 – 1.5 mg/L, incubation time of 3 hours, pH 8.2, 25°C) and bromate formation potential conditions (O_3/TOC ≈ 2 mg/mg, pH 8.0, 20 °C). These results are summarized in Tables 2 and 3, portraying potential Br^- and/or TOC constraints to chlorination and ozonation.

5.8 Summary

Table 4 summarizes the various treatment technologies and their relevance to disinfection and disinfection by-product control in Delta water.

Based on the previous summary, Table 5 matches potential approaches for the treatment of Delta water to meet various possible regulatory options. The approaches may depend significantly on the bromide, organic carbon content, and the level of fecal contamination in the Delta water.

Table 2. SDS-THM Results Portraying Potential Br^- and TOC Constraints.

Br^- (ug/L)	TOC (mg/L)				
	1.1	1.4	2.0	3.3	4.2
<10	24	31	38	64	78
100	43	51	60	80	91
200	60	75	83	103	113
400	75	113	128	142	159
800	88	137	182	241	243

Table 3. BrO_3^- (ug/L) Formations Results Portraying Potential Br^- and TOC Constraints.

Br^- (ug/L)	TOC (mg/L)				
	1.2	1.6	2.2	2.9	3.7
<10	<3	<3	4	<3	7
100	6	7	11	12	19
200	11	12	19	25	27
400 - 500	25	23	36	39	49
700 - 900	29	40	53	57	65

Table 4. Matrix of Treatment Processes: Advantages, Disadvantages, Additional Considerations, and Costs.

PROCESS	ADVANTAGES	DISADVANTAGES	ADDITIONAL CONSIDERATIONS	RELATIVE COST*
Chlorination	Effective primary disinfectant for Giardia, viruses; good secondary disinfectant	Produces halogenated DBPs (THMs, HAAs); ineffective for inactivation of Cryptosporidium	May be effective for Cryptosporidium inactivation when coupled with chloramines	+
Ozonation	Most effective chemical disinfectant for Cryptosporidium; does not produce chlorinated organic DBPs; can be coupled with biofiltration to limit formation of overall organic DBP formation	Produces bromate; can produce brominated organic DBPs; primary disinfectant only; must be coupled with secondary disinfectant such as chlorine or chloramine	Bromate formation can be controlled to some degree by pH adjustment, method of ozone addition; bromate removal possible but requires study	++
Chloramination	Does not produce appreciable THMs or HAAs; good secondary disinfectant for distribution system	Poor primary disinfectant, must be used with free chlorine or ozone as primary disinfectant; does produce unidentified halogenated organic material (TOX) but at lower levels than free chlorine		+
Chlorine Dioxide	Effective primary disinfectant for Giardia, viruses; does not produce halogenated DBPs; also inactivates Crypto but not as effectively as ozone	By-product chlorite exhibits acute toxicity; proposed MCL for chlorite of 1.0 mg/L limits use	Chlorite removal may be possible but requires study	+
UV Irradiation	Effective primary disinfectant for viruses; new emerging UV technologies for inactivation of cysts, but not yet demonstrated; does not produce DBPs	Requires use of secondary disinfectant for distribution system	Emerging new UV technologies being evaluated/demonstrated on plant-scale	++

Enhanced Coagulation	Useful for removal of organic DBP precursors	TOC in Delta water not very amenable to coagulation; does not remove bromide		+
Granular Activated Carbon Adsorption	Useful for removal of organic DBP precursors	Requires EBCT in excess of 15-20 min; does not remove bromide; limited usefulness for bromate removal	Requires regeneration at 3-6 mos. frequency	+++
Microfiltration	Effective for Giardia, Cryptosporidium cyst removal	Ineffective for virus removal but can be coupled with post-chlorination for virus inactivation; ineffective for TOC removal but can be coupled with powdered carbon or coagulant for partial TOC removal; will not remove bromide; waste stream needs to be disposed of	Membrane process technology undergoing rapid changes, becoming more practical and less expensive	+++
Nanofiltration And Ultrafiltration	Effective for Giardia, Cryptosporidium cyst removal and virus removal; NF effective for TOC removal at MWCO less than 200-500 Daltons; NF provides some bromide removal	UF will not remove bromide; requires pre-treatment to prevent membrane fouling; relatively low product recovery; waste stream needs to be disposed of	Membrane process technology undergoing rapid changes, becoming more practical and less expensive	++++
Reverse Osmosis	Effective for Giardia, Cryptosporidium cyst removal and virus removal; effective for removal of TOC and bromide	Requires pre-treatment to prevent membrane fouling; relatively low product recovery; waste stream needs to be disposed of	Membrane process technology undergoing rapid changes, becoming more practical and less expensive	+++++

* Relative costs are indicated by number of + entries

Table 5. Possible Treatment Options for Meeting Proposed or Future Rules.

PROPOSED OR FUTURE RULE	POSSIBLE TREATMENT OPTIONS
Interim Enhanced Surface Water Treatment Rule	No change in disinfection practice
LT2ESWTR	Treatment may depend on level of fecal contamination in source water: Ozonation; Chlorine Dioxide, Microfiltration; Possibly Emerging UV Disinfection
Stage 1 D/DBP Rule, with 10 ug/L bromate MCL	Chlorination with secondary chloramination; ozonation with/without biofiltration coupled with secondary chloramination with need for bromate control
Stage 2 D/DBP Rule (as proposed in 1994), with 5 ug/l bromate MCL. Stage 2 will be reproposed and these criteria may differ significantly from 1994 proposed criteria. .	Ozonation with/without biofiltration coupled with secondary chloramination with need for bromate control; nanofiltration with post-chloramination; microfiltration with chlorine and chloramines; and possibly emerging UV disinfection with post-chloramination

In summary, treatment processes are available to treat Delta water that will produce safe drinking water and minimize the risks to public health, although treatment costs may significantly increase with implementation of advanced treatment.

6.0 Treatment versus Source Control

General source control options for Br^- are largely limited to segregation of Delta water intended for export from saltwater intrusion. Another course of action is represented by storage intended to dampen seasonal variations in Br^-. Of course, within this general approach are many specific options that are largely embodied within the CALFED alternatives. Source control options for NOM include (on-site) treatment or diversion of agricultural drainage (or modified drainage practice) and algae control.

Even with selection of a CALFED alternative, there will still need to be a short-term strategy for utilities to meet Stage 1 and Stage 2 DBP regulations before alternative implementation. Much will depend on differences between the Stage 1 versus Stage 2 MCLs, and the Cryptosporidium-based disinfection requirements that will evolve through the ESWTR. During this same time period, additional health effects data will be forthcoming on HAA species and BrO_3^-, which may lead to either a relaxation or further restriction of current MCLs.

Enhanced coagulation, low-pH ozonation, and optimal use of multiple disinfectants will likely be the minimum technology required. Given that ozonation presently appears to be the only viable inactivation option for Cryptosporidium, it is likely that ozone use will continue to increase. Finally, there are exciting new developments in membrane and UV technology that may play a role in Delta-water treatment in the area of selective membranes (e.g., UF) that are less prone to fouling, capable of physical removal of microbes, and provide high (> 90 %) water recoveries.

7.0 Recommendations and Research Needs

7.1 Recommendations

The Cal-Fed program must examine issues as they are likely to develop over a 20 to 30 year horizon. The problems in the Delta are immense and will require a very large reliance on research that involves many disciplines. Short-term decisions will have to be geared toward meeting regulations that should be largely anticipated from stage II of the M/DBP rule. However, as the program develops its research agenda, its short-term research agenda must be consistent with providing more definition for decisions that impact water quality 20 to 30 years from now.

It is recommended that CALFED articulate a clear, short-term plan, comprised of both treatment and source control approaches, to deal with bromide-related drinking water issues before and during implementation of the various CALFED alternatives. It is not the charge of the expert panel to make an unqualified recommendation to CALFED on an alternative; however, considering *only* drinking water quality, it is clear that Alternative 3 would provide the most benefit with regard to the beneficial use of Delta water for drinking water supply, although Alternative 2 would provide more benefit at certain export points (e.g., CCC). Other hydraulic management options not included in the three Alternatives might also provide improvement in source water quality over that currently obtainable from the Delta. While it is not in the charge of this panel to identify such options, CALFED may wish to develop and consider such options within the phased process now under consideration for the CALFED long-term plan.

7.2 Research Needs

The panel recommends that a) CALFED follow and promote important health effects research that is ongoing/planned to focus on brominated DBPs, b) source-specific (e.g., SWP) DBP models be developed to assess various treatment and source control options, and c) given the importance of NOM, a NOM inventory of Delta water be performed to elucidate the spatial and seasonal distribution of NOM, both amount (TOC) and properties (e.g., UVA_{254}, DBP formation potential), followed by development of a model to predict TOC concentrations throughout the Delta.

Given that co-occurrence of pathogens and DBP precursors may significantly influence the feasibility of simultaneously controlling for both DBPs and pathogens under future drinking water regulations, the panel also recommends that CALFED a) obtain information indicating the level and variability of fecal contamination (including measurement of *Cryptosporidium* and *Giardia* [using best available methods] and *E. coli)* in source waters, b) obtain information on the co-occurrence of bromide, TOC, UVA_{254}, and microbes in source waters, and c) determine the extent to which pathogens and DBP precursors can feasibly be reduced in source waters of utilities.

Given the potential for membrane technology, it is recommended that NF and UF membrane processes be assessed for their collective ability to remove Br^-, TOC, and microbes from Delta water. Given the potential constraint of bromate formation, CalFed should evaluate BrO_3^- control strategies to meet a range of potentially more restrictive MCLs.

CALFED should resolve the concern regarding whether or not (or how much of) "recycled bromide from agricultural return drains is actually "recycled" or is from agricultural fumigation activities using methyl bromide.

CALFED should encourage and cooperate with epidemiological investigations of cancer, reproductive and developmental toxicities that may be associated with disinfectant by-products. This cooperation should focus on adding bromide to established studies that have been conducted on a national scale rather than trying to initiate new epidemiological studies that focus only on the Bay-Delta area. It is important to pursue reproductive and developmental toxicity issues as well as carcinogenic effects of disinfectant by-products in any research program. The low-dose carcinogenic risk of bromate is a critical issue if bromide-containing waters are to be ozonated. Investment in careful studies of the type that have been done for chloroform, dichloroacetate and trichloroacetate, but following hypotheses more appropriate for bromate induced tumorigenesis, could possibly raise the MCL.

8.0 References

Amy, G., et al., (1994) "Survey of Bromide in Drinking Water and Impacts on DBP Formation".

Ballmaier, D. and Epe, B. (1995) Oxidative DNA damage induced by potassium bromate under cell-free conditions and in mammalian cells. Carcinogenesis 16:335-342.

Bull, R.J. and Kopfler, F.C. (1991) Health Effects of Disinfectants and Disinfection By-Products. AWWA Research Foundation and American Water Works Association, Denver, CO

CALFED (1998) Phase II Interim Report.

CALFED (1998) Bromide Expert Panel Meeting Package.

CALFED (1998) Bromide Expert Panel Meeting Package Addendum.

California Department of Water Resources (1994) "Five-Year Report of the Municipal Water Quality Investigations Program".

California Department of Water Resources (1998a) Unpublished Data.

California Department of Water Resources (1998b) "The Significance of Bromide on the Drinking Water Quality of Sacramento-San Joaquin Delta Waters".

Chipman, J.K., Davies, J.E., Parsons, J.L., Nair, J., O'Neill, G.O. and Fawell, J.K. (1998) DNA oxidation by potassium bromate; a direct mechanism or linked to lipid peroxidation? Toxicology 126:93-102.

Cho, D.H., Hong, J.T., Chin, K., Cho, T.S. and Lee, B.M. (1993) Organotropic formation and disappearance of 8-hydroxydeoxyguanosine in the kidney of Sprague-Dawley rats exposed to Adriamycin and $KbrO_3$. Cancer Lett. 74:141-145.

Fox, A.W., Yang, X., Murli, H., Lawlor, T.E., Cifone, M.A. and Reno, F.E. (1996) Absence of mutagenic effects of sodium dichloroacetate. Fundam. Appl. Toxicol. 32:87-95.

Giller, S., LeCurieux, F., Erb, F. and Marzin, D. (1997) Comparative genotoxicity of halogenated acetic acids found in drinking water. Mutagenesis 12:321-328.

Harrington-Brock, K., Doerr, C.L. and Moore, M.M. (1998) Mutagenicity of three disinfection by-products: di- and trichloroacetic acid and chloral hydrate in L5178Y/TK+/--3,7,2C mouse lymphoma cells. Mutation Res. 413:265-276

Krasner, S. et. al, (1994) "Quality Degradation: Implications of DBP Formation," Jour. AWWA, 86:6:34.

Krasner, S., et al., (1993) "Formation and Control of Bromate During Ozonation of Waters Containing Bromide", Journal AWWA 85:1:73.

Kurokawa, Y., Takayama, S., Konishi, Y., Hiasa, Y., Asahina, S. Takahashi, M., Maekawa, A. and Hayashi, Y. (1986b) Long-term in vivo carcinogenicity tests of potassium bromate, sodium hypochlorite, and sodium chlorite conducted in Japan. Environ. Health Persp. 69:221-235.

Lag, M., Soderlund, E.J., Omichinski, J.G., Brunborg, G., Holme, J.A., Dahl, J.E., Nelson, S.D., and Dybing, E. (1991) Effect of bromine and chlorine positioning in the induction of renal and testicular toxicity by halogenated propanes. Chem. Res. Toxicol. 4:528-534.

Lee, Y.S., Choi, J.-Y., Park, M.-K., Choi, E-M., Kasai, H. and Chung, M.-H. (1996) Induction of oh^{8}Gua glycosylase in rat kidneys by potassium bromate (KbrO_3), a renal oxidative carcinogen. Mutation Res. 364:227-233.

Linder, R.E, Klinefelter, G.R., Strader, L.F., Narotosky, M.G., Suarez, J.D., Roberts, N.L., and Perreault, S.D. (1995) Dibromoacetic acid affects reproductive competence and sperm quality in the male rat. Fundam. Appl. Toxicol. 28:9-17.

Melnick, R.L., Dunnick, J.K., Sandler, D.P., Elwell, M.R., and Barrett, J.C. (1994) Trihalomethanes and other environmental factors that contribute to colorectal cancer. Environ. Health Persp. 102:586-588.

Morris, R.D., Audet, A.-.M., Angelillo, I.F., Chalmers, T.C., and Mosteller, F. (1992) Chlorination, chlorination by-products, and cancer: A meta-analysis. Am. J. Publ. Health 82:955-963.

Owen, D., et al. (1998) Bay-Delta Water Quality Evaluation, California Urban Water Agencies (1998).

Parrish, J. M., Austin, E.W., Stevens, D.K., Kinder, D.H. and Bull, R.J. (1996) Haloacetate-induced oxidative damage to DNA in the liver of male B6C3F1 mice. Toxicology 110:103-111.

Pegram, R.A., Andersen, M.E., Warren, S.H., Ross, T.M., and Claxton, L.D. (1997) Glutathione-S-transferase-mediated mutagenicity of trihalomethanes in Salmonella typhimurium: contrasting results with bromodichloromethane and chloroform. Toxicol. Appl. Pharmacol. 144:183-188.

Poole, C. (1997) Analytical meta-analysis of epidemiological studies of chlorinated drinking water and cancer: Quantitative review and reanalysis of the work published by Morris et al., Am. J. Public Health 1992;82:955-963.

Tong, Z., Board, P.G. and Anders, M.W. (1998) Glutathione transferase zeta catalyzes the oxygenation of the carcinogen dichloroacetic acid to glyoxylic acid. Biochem. J. 331:371-374.

Umemura, T., Sai, K., Takagi, A., Hasegawa, R., and Kurokawa, Y. (1993) A possible role for cell proliferation in potassium bromate ($KBrO_3$). J. Cancer Res. Clin. Oncol. 119:463-469.

USEPA (1996) U.S. Environmental Protection Agency: Proposed Guidelines for carcinogen risk assessment; notice. Fed. Reg. 61:17960-10811.

USEPA (1998a) Synthesis of the peer review of meta-analysis of epidemiological data on risks of cancer from chlorinated water. National Center for Environmental Assessment, contract no. 68-C6-0041.

USEPA (1998b) U.S. Environmental Protection Agency: National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts Notice of Data Availability: Proposed Rule. Fed . Reg. 63:15674-15692,

Waller, K., Swan, S.H., DeLorenze, G., and Hopkins, B. (1998) Trihalomethanes in drinking water and spontaneous abortion. Epidemiology 9:134-140.

Zeiger, E. (1990) Mutagenicity of 42 chemicals in Salmonella. Environ. Mol. Mutagen. 16(Suppl 18):32-54.