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Disinfection By-products

Effect of bromide

**RSSCTs predict
GAC control
of DBPs**

Removing BOM

**Evaluating DBP
surrogates**



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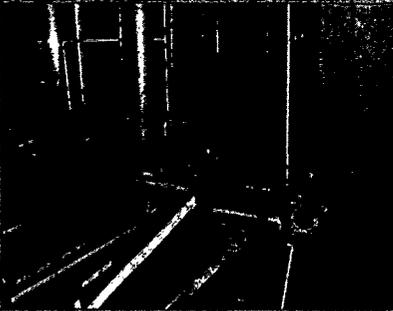
 American Water Works Association

Volume 86, No. 6 June 1994

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PERIODICAL SECTION



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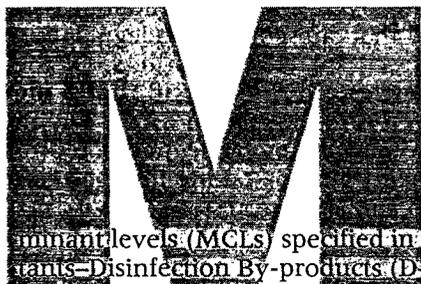
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Quality degradation: implications for DBP formation

The results of these studies of the Sacramento-San Joaquin River Delta demonstrate that DBP control strategies should include watershed management as well as treatment processes in other regions of the United States.

Stuart W. Krasner, Michael J. Scimenti, and Edward G. Means



Maximum contaminant levels (MCLs) specified in the draft Disinfectants-Disinfection By-products (D-DBP) Rule are 80 µg/L for total trihalomethanes (TTHMs), 60 µg/L for the sum of five haloacetic acids (HAA5), and 10 µg/L for bromate.¹ In addition, utilities that use surface waters will be required to remove DBP precursors through enhanced coagulation or softening. The removal of total organic carbon (TOC) is to be used as an indicator of treatment performance for compliance with the precursor

removal criteria. The rule will control individual TTHMs (and other individual DBPs) through the MCLs for TTHMs and HAA5 and the DBP precursor control requirement. (Because bromodichloromethane

During development of the draft Disinfectants-Disinfection By-products (D-DBP) Rule, the issue of watershed management for DBP precursor control was discussed but not included in the rule. This article focuses on a major California watershed, describing examples of the types of studies that utilities can use to determine precursor sources and develop solutions for control. In addition, a chlorination and ozonation study of a five-by-five matrix of total organic carbon and bromide levels—which spanned a wide range of concentrations that can be expected in many US waters—provided insights into the effects of organic and inorganic precursors and disinfectants in DBP formation.



Water in the Sacramento-San Joaquin River Delta meanders through tracts of agricultural land, which increases its TOC content and THM formation potential.

focuses on a major watershed in California as an example of the types of studies that can be performed to determine the source of precursors so that regional systems can be developed for DBP precursor control.

The delta

The San Francisco Bay and Sacramento-San Joaquin River Delta is a source of drinking

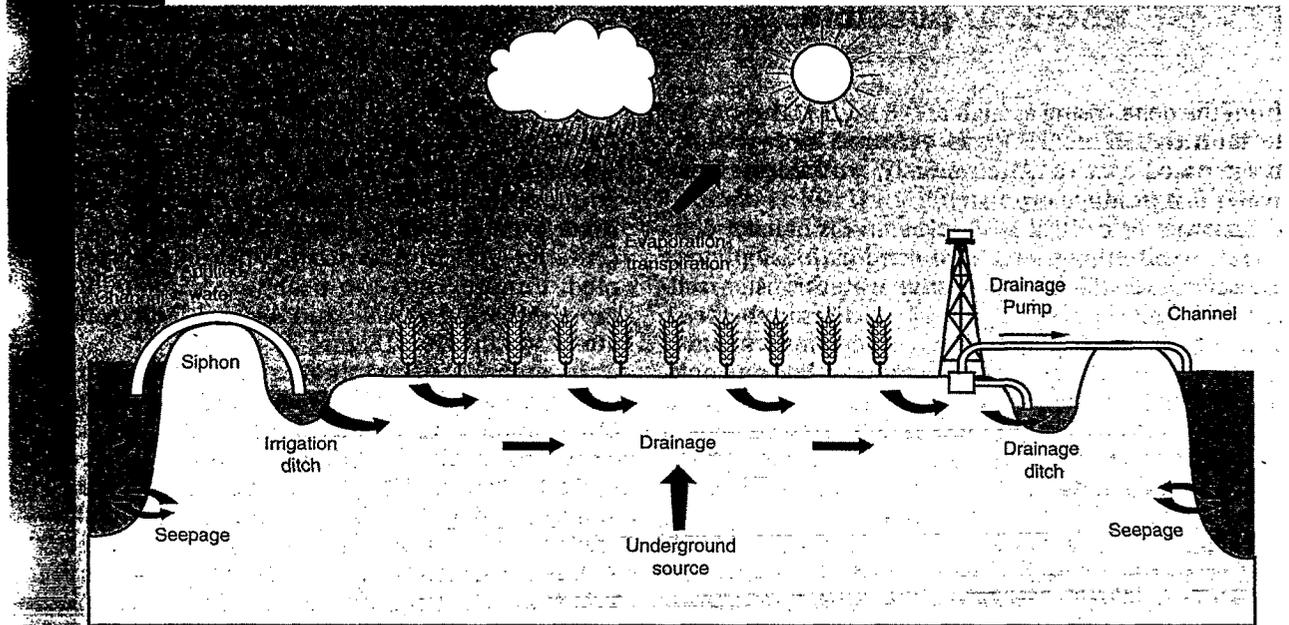
poses a greater potential cancer risk [Table 1] than chloroform, the US Environmental Protection Agency had considered regulating individual THMs.)

During development of the D-DBP Rule, the issue of watershed management for the control of DBP precursors was discussed. The draft rule, however, has no specific provisions for watershed controls because of statutory limitations as well as the lack of control that most utilities have over land use. However, watershed protection is highly desirable and should be pursued wherever possible. This article

water for 20 million Californians. Sacramento River water above the delta typically contains 1-2 mg/L TOC and ≤ 0.02 mg/L bromide (Br^-). However, water pumped from the delta to utilities in Northern and Southern California typically contains 3-7 mg/L TOC and 0.1-0.5 mg/L Br^- . This degradation in water quality presents users of delta water with several challenges in meeting disinfection and DBP regulations.

A significant source of TOC in delta water is the agricultural tracts of land that are composed of peat

Typical delta water exchange²



Individual
MCLs
for con-
methane

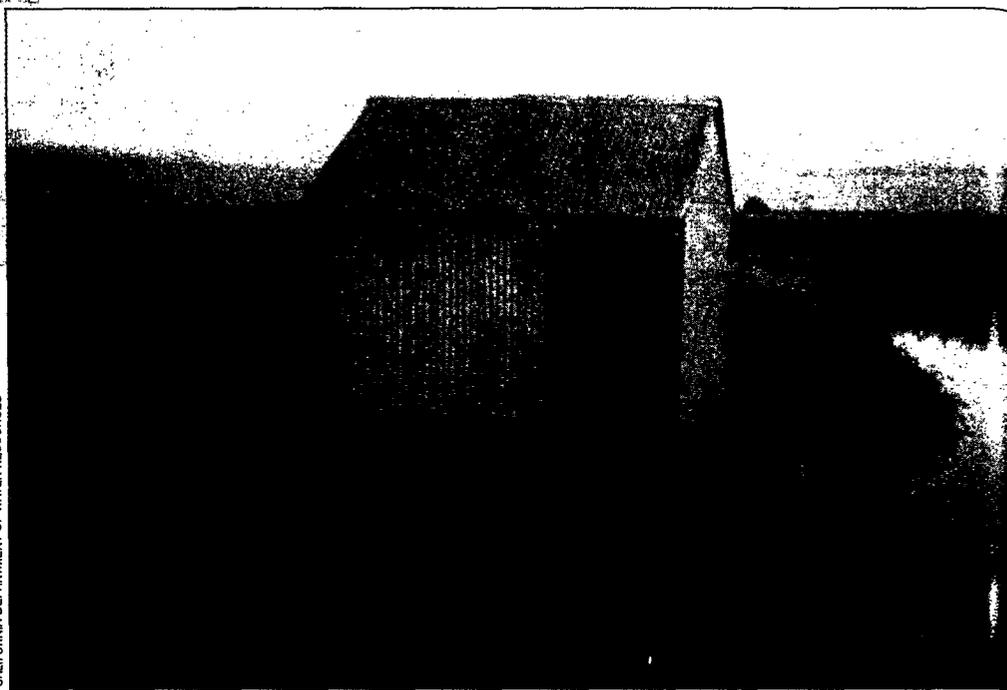
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Drainage water from agricultural land in the delta can account for almost half the THM formation potential in exported water.

soil. Agricultural drainage waters from these tracts are high in both TOC (up to 30–50 mg/L) and THM formation potential (THMFP) (up to 5,000 µg/L). (Figure 1 illustrates agricultural water usage in the delta.) Whereas water entering the delta can have a THMFP of ~150 µg/L, water exported to municipalities can have a THMFP of ~400 µg/L. Studies have indicated that the agricultural drainage in the delta during the summer irrigation months—as well as in the winter, when channel waters are used to leach out salts that have built up in the soil during the year—can account for up to approximately half the THMFP of exported water.^{2,3}

During drought, high-tide, or low-river-flow conditions, saltwater intrusion from San Francisco Bay has resulted in higher Br⁻ levels in water exported

CALIFORNIA DEPARTMENT OF WATER RESOURCES



This article presents (1) the results of investigations into the effects of seawater intrusion, agricultural drainage, and wetlands management on delta water quality; and (2) their implications for compliance with pending DBP regulations. Furthermore, the more global implications associated with the effects of Br⁻ and TOC on DBP formation and control are discussed.

Watershed protection is highly desirable and should be pursued wherever possible.

from the delta (rising as high as 0.8 mg/L). This has led to an increase in TTHMs as well as a shift to more brominated species. Alternatively, ozonation of this water can produce bromate.

In order to control DBP levels in disinfected delta waters, Californians have examined various options.⁴ These include utilizing alternative water transfer facilities; changing land management practices in the delta; building raw-water storage reservoirs; and implementing alternative treatment plant operations. For example, one alternative land management practice under consideration involves switching agricultural tracts of land to seasonal wetlands to provide needed wetland habitats. A series of tests has been performed to evaluate the sources of DBP precursors in the delta as well as the effect on water quality of converting agricultural lands into wetlands. These tests are providing insights into which option will provide the best solution for controlling DBPs of health and regulatory concern.

Experimental methods

Sample sites. The Sacramento and San Joaquin rivers upstream of the delta were sampled at Greene's Landing and Vernalis, respectively (Figure 2). Delta outflow was sampled at the H.O. Banks pumping plant (Figure 2).

Greene's Landing is approximately 10 mi downstream from the city of Sacramento and has variable levels of ammonia as a result of wastewater discharges. Therefore, for one study in which ammonia-free water was required, the Sacramento River was sampled upstream of the city. Three representative agricultural drains in the delta were sampled: Empire Tract (on peat soil), Upper Jones (on more mineralized soil), and Bacon Island (intermediate in soil quality) (Figure 2).

In a parallel delta salinity study, 20 locations were typically sampled. These sites were sampled periodically—as often as weekly. Sample sites included channel waters in the western delta that were affected by saltwater intrusion, fresh waters upstream of the delta, and a sampling site within the estuary (Mallard Island; see Figure 2).

State project water (SPW) travels 444 mi (715 km) from the delta through the California Aqueduct to Southern California, where the aqueduct splits

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into the east and west branches—i.e., EBSPW and WBSPW, respectively (Figure 3). EBSPW is stored in Silverwood Lake (0.2-year retention time) and flows through the Devil Canyon Afterbay. WBSPW is stored in Pyramid and Castaic lakes; this lake system has a holding time of approximately 2.1 years. Devil Canyon Afterbay and Castaic Lake effluents were sampled to represent the inputs from the two SPW branches to the Metropolitan Water District of Southern California's (MWD's) conventional treatment plants.

Sources of DBP precursors. DBP formation potential (DBPFP) tests—for both THMs and HAAs—determined the relative contributions of DBP precursors in the delta. Samples tested included drainage from agricultural tracts of land, river water, delta outflow, and wetlands experimental samples.

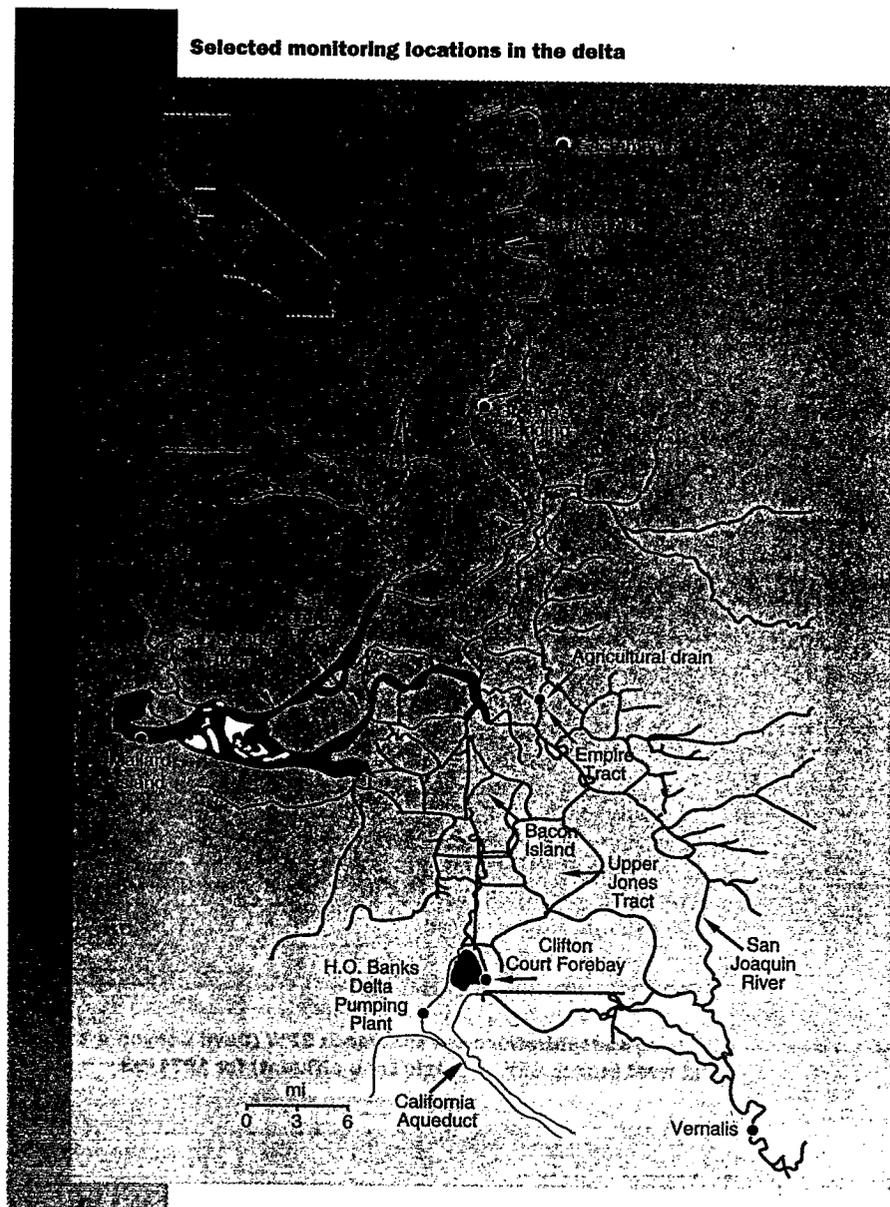
DBPFP tests were conducted at 25°C and pH 8.2 for seven days. These conditions were chosen to represent the effect of summer temperatures, when DBP formation can be the highest, as well as a typical pH level that MWD uses for distributed water to meet the requirements of the Lead and Copper Rule. A boric acid-sodium hydroxide buffer solution was used to maintain the pH.⁵ For samples with an acidic pH, sodium hydroxide was initially added to raise the pH before applying the buffer solution.

Samples were chlorinated with a dose based on organic and inorganic demand:

$$\text{Cl}_2 \text{ (mg/L)} = 3 \times \text{TOC} + 7.6 \times \text{NH}_3\text{-N} \quad (1)$$

When ammonia was present in the raw water, the sample required breakpoint chlorination before a free-chlorine residual could be achieved. In addition, some wetlands samples contained hydrogen sulfide, which also has a high chlorine demand. Because the wetlands samples were filtered through a 0.45- μm filter to remove turbidity prior to chlorination, the hydrogen sulfide was removed—based on olfactory assessment—during the vacuum filtration step.

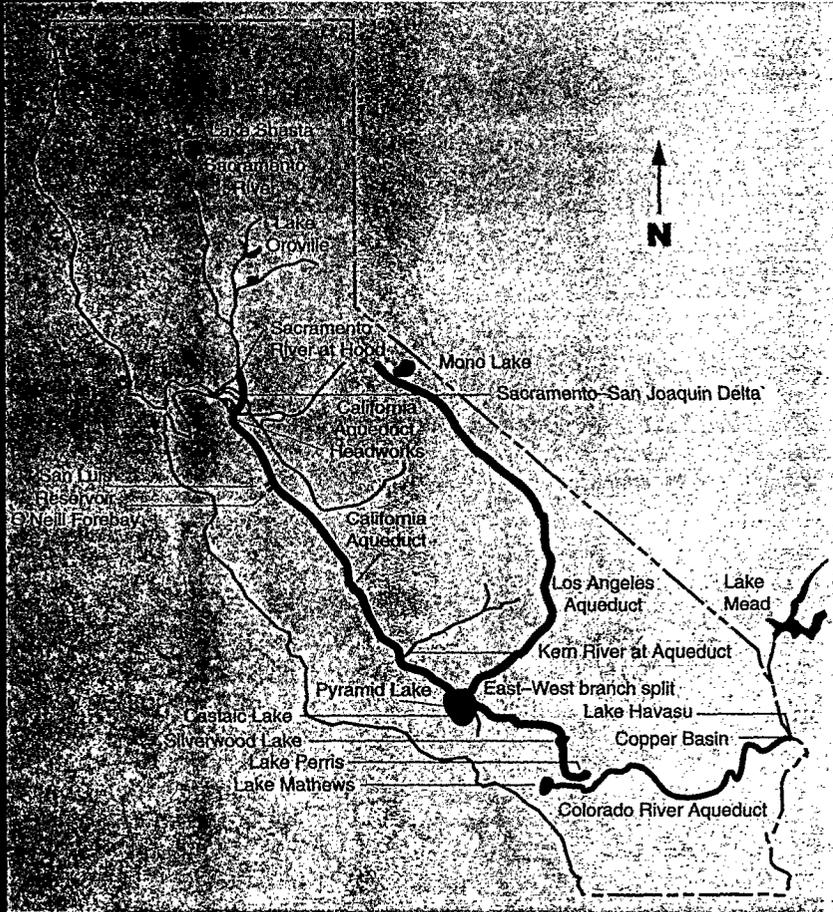
Selected monitoring locations in the delta



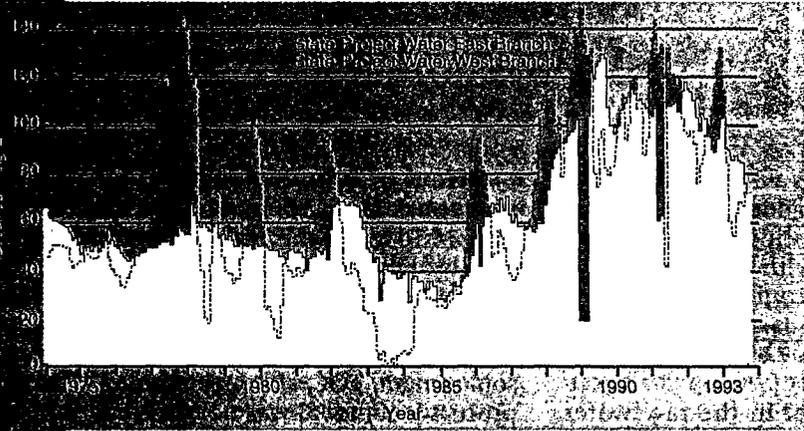
Effect of bromide and TOC on THM formation and speciation. Simulated distribution system evaluation. To assess the amount and speciation of THMs that could be formed in actual full-scale operations, simulated distribution system (SDS) testing was performed.^{5,6} In this testing, samples were jar-treated with alum (20 mg/L) to remove turbidity (and, to some extent, TOC, although optimized coagulation for precursor removal was not utilized). Settled-filtered waters were chlorinated at 25°C at pH 8.2 for 3 h, a typical detention time within MWD's treatment plants. Chlorine doses were adjusted to achieve a target chlorine residual of 0.5–1.5 mg/L, a residual that is typical in MWD's full-scale operations before postchlorination.

SDS testing was performed on Sacramento River water and different sites downstream from the delta; in this article, however, data from only the Greene's

General area of studies



Chloride concentrations in east branch SPW (Devil Canyon Afterbay) and west branch SPW (Castaic Lake effluent) for 1974-93



Landing and H.O. Banks sites are reported. This testing has been performed monthly or quarterly since August 1990, but data from only the initial program are shown to illustrate the effect of the monitoring. These data made it possible to assess the effects of water quality degradation in the delta, as well as the benefits that could be derived from an isolated delta

during prechlorination, as MWD's plants currently utilize postammoniation to stop THM production.

Effect of bromide and TOC on bromate formation. The samples from the five-by-five matrix were also ozonated to assess the impact of Br⁻ and TOC parameters on bromate formation. A continuously stirred, flow-through reactor with a mean hydraulic

transfer facility (e.g., a peripheral canal around the delta).

Bromide and TOC matrix. Some facilities under consideration will attempt to improve the transfer of water through the delta. To assess the possible combinations of TOC and Br⁻ that could emanate from such facilities, a five-by-five matrix of waters spanning a wide range of TOC and Br⁻ levels—as well as bromide-to-TOC ratios—was evaluated. Sacramento River water above the city of Sacramento was used as the baseline water (1.1 mg/L TOC and ≤0.01 mg/L Br⁻). A TOC spike was prepared from agricultural drainage water (35 mg/L TOC) sampled from a peat-soil tract of land. Thus, the TOC spike represented the actual type of natural organic matter present in the delta. Sodium bromide was used to augment Br⁻ levels.

Five TOC levels, from ambient to 4 mg/L, and five bromide levels, from ambient to 0.8 mg/L, were tested. These 25 unique water qualities were chlorinated under SDS-type conditions. Instead of being jar-treated, these samples were filtered through a 0.45-μm filter to remove turbidity but not TOC. They were then chlorinated at various temperatures and reaction times at pH 8.2 and were analyzed for THMs, HAAs, and haloacetonitriles.⁷ Data on the effect of TOC and bromide on THM speciation for the 3-h, 25°C tests are presented in this article. Again, all samples were chlorinated to achieve a target chlorine residual of 0.5–1.5 mg/L at the end of the incubation period. In this instance, these tests correspond to THM formation

retention, hydraulic apparatuses.⁹ The hydraulic apparatus was tank reaction

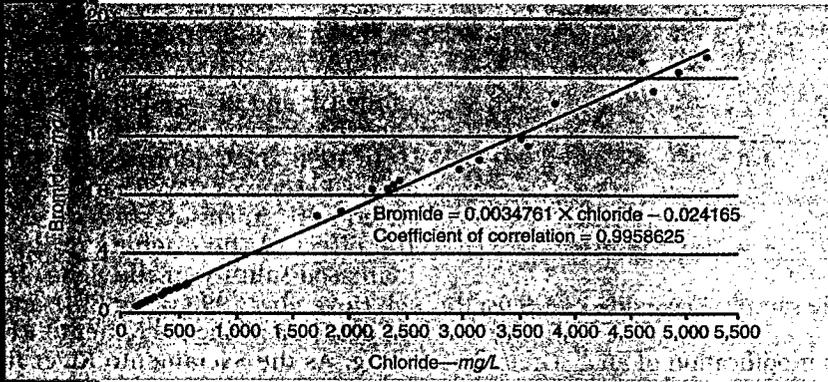
All samples were chlorinated at 20°C (0.2 pH unit) under similar disinfection conditions × T is the reaction × C = 0.35 ± 0 formation-stratification-inactivated mg/L lead, however, a significant residual was chlorinated. Prechlorination and

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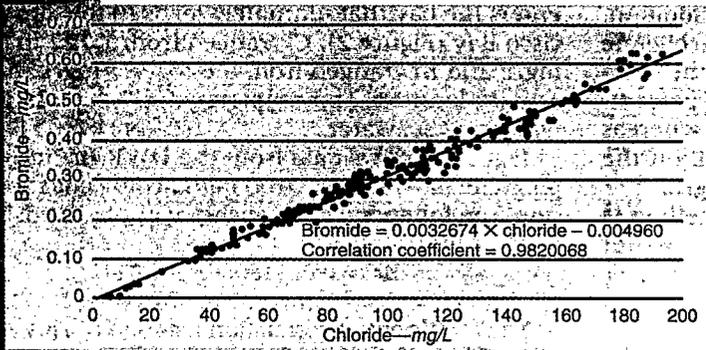
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Data from DWR delta salinity study, Aug. 6, 1990-Jan. 2, 1991, showing the relationship of chloride and bromide when chloride is >100 mg/L



Data from DWR delta salinity study, Aug. 6, 1990-Jan. 2, 1991, showing the relationship of chloride and bromide when electroconductivity is <900 µmho/cm and chloride is <200 mg/L



retention time of 8 min was used.⁸ The effects of hydraulic flow rate, gas flow rate, and water temperature on the residence time distribution in the apparatus have been investigated using tracer studies.⁹ The results of the tracer studies indicated that the hydraulic behavior exhibited by the bench-scale apparatus was more characteristic of a continuously stirred tank reactor than of a full-scale system.

All samples were ozonated at the ambient pH (~8) at 20°C (the range of pH levels typically varied within 0.2 pH unit). Each water was ozonated to meet similar disinfection criteria, or $C \times T$ values (in which $C \times T$ is the product of disinfectant residual concentration \times contact time), with an ozone residual goal of 0.35 ± 0.05 mg/L. MWD is also evaluating bromate formation in a countercurrent, over-under demonstration-scale contactor.¹⁰ $C \times T$ credit for a 0.5-log *Giardia* inactivation would require a residual of ≥ 0.3 mg/L leaving the first chamber of the contactor. However, a staged ozone application with a lower ozone residual leaving the first chamber could also be utilized. Previous experiments in which delta water was split and ozonated in both the bench-scale apparatus

and a countercurrent pilot-scale contactor (in use prior to the construction of the demonstration-scale facility) yielded similar bromate levels when both systems were ozonated to yield an ozone residual of approximately 0.4 mg/L.¹¹ In a sense, this bench-scale testing was an attempt at producing a simulated treatment plant bromate value.

Effect of precursor loading from a wetlands. Studies are currently being conducted to investigate the effect of changing land management practices on TOC-

DBPFP inputs into the delta. An experiment evaluated the yield of DBP precursors from plant biomass decomposition over time.¹² The experimental protocol involved the following:

- Vegetation biomass samples (dominated by smartweed, watergrass, and swamp timothy) were collected from demonstration wetlands in the delta. Biomass samples averaged ~435 g/m², with an average lignin content of 9.5 percent.
- Five 30-gal (114-L) containers were filled with water from the delta. Barrels 1 and 2 received biomass clippings loaded to the natural density. Barrels 3 and 4 were loaded with a higher density of biomass. The fifth barrel did not receive any of the biomass clippings and was used as a control.

- The barrels were sampled every two weeks for a total of 10 weeks.

In addition, a soil experiment was performed:¹²

- Soil samples were collected from the surface and from the bottom of a 3-ft- (91-cm-) deep hole at two locations in the demonstration wetlands and from two locations in an adjacent agricultural field (both located on peat soils).

- Each soil sample was split into three aliquots in order to perform three water extraction procedures each. Just enough deionized water was added to each aliquot to saturate the soil sample. The pastes were allowed to stand for durations of $\leq 1-2, 7,$ and 30 days before the soil-water samples were filtered.

Chemical analyses. HAA analysis was performed for five species (monochloro-, dichloro-, trichloro-, monobromo-, and dibromoacetic acid).¹³ At the time of these studies, a commercial standard was unavailable for the bromochloroacetic acid. Accuracy for HAA samples has been between 80 and 125 percent, whereas replicate samples have differed by <19 percent. THM analyses¹⁴ included all four species. Accuracy for THM samples has usually been between 87

Health effects of individual THMs

THM	Maximum Contaminant Level Goal µg/L	Theoretical Excess Cancer Risk Level—µg/L		
		10 ⁻⁴	10 ⁻⁵	10 ⁻⁶
CHCl ₃	0	600	60	6
CHCl ₂ Br	0	60	6	0.6
CHClBr ₂	60	NA*	NA	NA
CHBr ₃	0	400	40	4

*NA—not available

and 123 percent, whereas replicate samples have differed by <12 percent.

Bromate was analyzed using a modification of an ion chromatography (IC) method developed by Kuo and colleagues.¹⁵ Diethylamine was added to quench active oxidant residuals (e.g., ozone, hypobromite ion). The minimum reporting level (MRL) for bromate during this study was 3 µg/L. The MRL was lowered from its original value of 10 µg/L by increasing the sample loop volume from 50 to 200 µL. In addition, the anion micromembrane suppressor had to operate in perfect condition. For bromate accuracy, the average recovery of spiked samples was 100.1 percent, with a standard deviation of 8.7 percent, whereas replicate samples agreed to within 1.7 µg/L on the average, with a standard deviation of 2.7 µg/L.

Bromide was analyzed by a different IC method.¹³ TOC samples were analyzed by the ultraviolet (UV)-persulfate oxidation method.¹³

Results and discussion

Saltwater intrusion and bromide levels. As a result of saltwater intrusion, varying chloride (Cl⁻) levels are detected in delta water. Saltwater intrusion also increases Br⁻ levels. Drought conditions in recent years have resulted in an increase in the Cl⁻ (Figure 4) and Br⁻ levels in the delta. Because of the relatively short holding time in Silverwood Lake, higher Cl⁻ (and Br⁻) levels were experienced in EBSPW. Because of the longer holding time in the Pyramid-Castaic lake system, changes in delta water were blended out in the WBSPW (Figure 2). However, the extended drought of the later 1980s and early 1990s resulted in a rise in the salinity of the WBSPW to as high a level as in the EBSPW.

Because of the stoichiometric relationship between Cl⁻ and Br⁻ in seawater, Br⁻ levels can be predicted based on measured Cl⁻ levels (provided that no other confounding sources of Br⁻ or Cl⁻ are present). The concentration of Cl⁻ and Br⁻ in seawater is 18,980 and 65 mg/L, respectively.¹⁶ If Br⁻ and Cl⁻ in delta water were only from seawater diluted with unsalty freshwater, then the following equation could be used to predict Br⁻ levels, given a measured Cl⁻ level:

$$\text{Br}^- = 0.00342 \times \text{Cl}^- \quad (2)$$

MWD empirically developed a Br⁻ to Cl⁻ relationship in SPW, based on data collected from 1987 through 1989:¹⁷

$$\text{Br}^- = 0.00289 \times \text{Cl}^- + 0.00671 \quad (3)$$

These limited data suggested that most of the Cl⁻ and Br⁻ present in delta water could be explained by seawater intrusion.

In 1990, the California Department of Water Resources (DWR) and MWD initiated a Br⁻ intrusion study to evaluate the effect of the ongoing drought on increased salinity in the delta. During

August through November 1990, 7 mg Cl⁻/L and 0.01 mg Br⁻/L were detected in the Sacramento River at Greene's Landing. As the Sacramento River flowed through the delta, however, saltwater intrusion significantly affected the salinity levels. During August 1990 through January 1991, Cl⁻ levels in delta outflow increased from 81 to 192 mg/L, and Br⁻ levels increased from 0.27 to 0.61 mg/L. At the Mallard Island sampling site, where the Sacramento River enters the bay that ultimately leads to the San Francisco Bay (Figure 2), Cl⁻ ranged from 1,722 to 5,200 mg/L and Br⁻ ranged from 6.6 to 17.7 mg/L. At this estuary location, approximately 9–27 percent of the water was seawater.

Figure 5 shows data from the DWR Br⁻ intrusion program, in which Cl⁻ >100 mg/L. Using linear regression, the following relationship was obtained:

$$\text{Br}^- = 0.00348 \times \text{Cl}^- - 0.0242 \quad (4)$$

The coefficient of correlation was 0.996. This empirical relationship exactly matches the relationship derived from pure seawater as the only source of salinity (Eq 2).

Because linear regression equations can be driven by extreme values, DWR study data for only those sampling stations where Cl⁻ was ≤200 mg/L and electroconductivity was <900 µmho/cm were plotted (Figure 6). A relationship with a correlation coefficient of 0.982 was obtained:

$$\text{Br}^- = 0.00327 \times \text{Cl}^- - 0.00496 \quad (5)$$

This equation falls between the pure seawater relationship in Eq 2 and the relationship derived by MWD for SPW in Eq 3. It is clear from these figures and equations that seawater is by far the major source of salinity in the delta. When saltwater intrusion is left unchecked, salinity—which includes Br⁻—increases in delta water exported to municipal users.

Two nationwide studies have attempted to characterize the occurrence of Br⁻ throughout the United States and to determine the relationship of Br⁻ to Cl⁻. In a 35-utility study performed in 1988–89, the median and maximum Br⁻ occurrences were 0.08 and 3.0 mg/L, respectively.¹⁸ There was a good correlation between Cl⁻ and Br⁻ in this study. When the

Br⁻ values were yielded coefficient

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Testing of delta waters for THMFP*

	Channel Waters			Agricultural Drains		
	Greene's Landing	Vernalis	H.O. Banks	Upper Jones	Bacon Island	Empire Tract
TOC (mg/L)	3.65	0.36	0.14	6.63	10.95	30.89
UV ₂₅₄ (1/L)	0.64	0.07	0.48	0.24	0.454	2.574
THMFP (µg/L)	0.02	0.07	0.051	0.037	0.042	0.044
CHCl ₃ (µg/L)	34	36	70	37	38	40
CHClBr ₂ (µg/L)	67	70	38	36	40	40
CHBr ₃ (µg/L)	37	38	40	36	40	40
THMs (µg/L)	150	157	157	157	157	157
24-h SDS THM (µg/L)	34	34	34	34	34	34
CHCl ₃ (µg/L)	65	73	117	102	117	117
CHClBr ₂ (µg/L)	102	117	117	102	117	117
CHBr ₃ (µg/L)	36	40	40	36	40	40
THMs (µg/L)	237	263	263	237	263	263

Comparison of synthetic delta sample* with one from H.O. Banks pumping plant

	H.O. Banks Sample	Synthetic Sample
TOC (mg/L)	3.65	3.53
UV ₂₅₄ (1/L)	0.122	0.126
THMFP (µg/L)	0.48	0.48
CHCl ₃ (µg/L)	12	13
CHClBr ₂ (µg/L)	34	36
CHBr ₃ (µg/L)	67	70
THMs (µg/L)	37	38
24-h SDS THM (µg/L)	150	157
CHCl ₃ (µg/L)	34	34
CHClBr ₂ (µg/L)	65	73
CHBr ₃ (µg/L)	102	117
THMs (µg/L)	36	40
THMs (µg/L)	237	263

*Synthetic water = 90 percent Greene's Landing + 10 percent agricultural drainage + bromide spike sample

Br⁻ values for the utility with atypically high Br⁻ levels were excluded (i.e., 3.0 mg/L), linear regression yielded the following equation (with a correlation coefficient *r* of 0.86):

$$\text{Br}^- = 0.0034 \times \text{Cl}^- - 0.0071 \quad (6)$$

It is significant that high Br⁻ levels were detected not only at utilities affected by saltwater intrusion, but at inland utilities as well. Thus, the Br⁻ to Cl⁻ relationship tended to be similar to that in seawater (Eq 2).

More recently, a nationwide Br⁻ study was conducted at 100 utilities.¹⁹ The median Br⁻ occurrences for 68 large and 20 small utilities (based on a population cutoff of 50,000) were 0.042 and 0.029 mg/L, respectively, whereas the median Br⁻ level for 12 targeted utilities with known Br⁻ problems was 0.190 mg/L. In this study, there was no clear common Br⁻ to-Cl⁻ relationship, although the median ratio was similar to that of seawater. When surface water (river

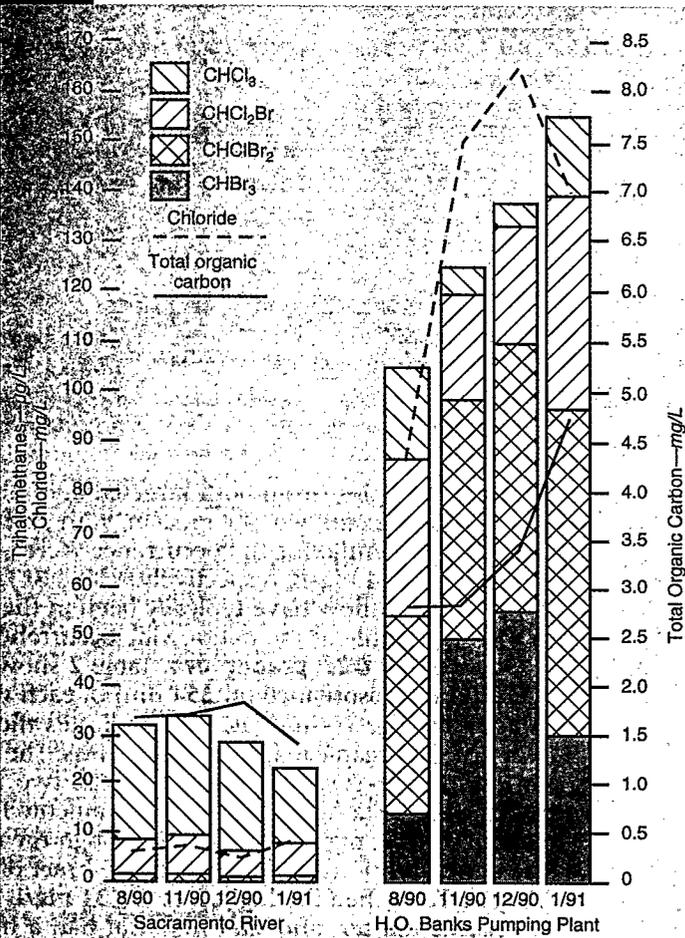
and lake) samples (from both targeted and random utilities) were examined, the median, 90th percentile and 95th percentile for Br⁻ occurrence were ~0.03, ~0.14, and ~0.4 mg/L, respectively.²⁰ The Br⁻ levels in the delta outflow have typically been in the 90th to 95th percentile of the nationwide occurrence.

Sources of DBP precursors. Table 2 shows the TOC and UV absorbance (at 254 nm) of each water. In addition, the UV-to-TOC ratio indicates the tendency of the organic matter to form THMs. The TOC, UV, and UV-to-TOC data show that the two rivers entering the delta (particularly the Sacramento River) pick up organic matter in passing through the delta. The agricultural drain on the peat-soil tract of land (Empire Tract) had the highest level (31 mg/L TOC) of organic matter, and that material had a higher reactivity based on the UV-to-TOC ratio.

Chlorinated channel waters produced THMFPs of 144–421 µg/L (1.2–3.2 µmol/L), whereas the agricultural drains contained 731–4,526 µg/L (5.4–31 µmol/L) THMFP. As Sacramento River water passed through the delta, the THMFP (on a molar basis) increased almost threefold in traversing the distance from Greene's Landing to the H.O. Banks pumping plant. Empire Tract had 27 times more THMFP than Greene's Landing, so the significant contribution of peat-soil agricultural drainage is clear. The molar yield of THMs per unit of TOC was 0.75–1.2 percent; this yield tended to increase with increasing UV-to-TOC ratio. However, samples high in Br⁻ will tend—even on a molar basis—to have a higher yield of THMs. This may explain the higher yield for Vernalis (0.36 mg Br⁻/L) than for H.O. Banks (0.14 mg Br⁻/L) and the very high yield for Empire Tract (3.1 mg Br⁻/L).

The HAA5 formation potential (HAA5FP) was 77–215 µg/L for channel waters and 316–1,872 µg/L for agricultural drains. Although HAA5 does not represent total HAAs (because not all of the nine HAA species were measured), comparisons can be made between di- or trichloroacetic acid (DCAA or TCAA) and chloroform (CHCl₃): the DCAA-to-CHCl₃ weight

SDS trihalomethane speciation for Sacramento River at Greene's Landing and H.O. Banks pumping plant



Effect of bromide and TOC on THM formation and speciation. As shown in Figure 7, 23–33 µg/L TTHMs were realized in the SDS testing of the Greene's Landing samples (upstream of the delta). During this testing period, SDS TTHM levels for the H.O. Banks samples (outflow from the delta) increased from 104 to 155 µg/L. The initial increase in TTHMs (from 104 to 124 µg/L) was caused by an increase in salinity (both the Cl⁻ and Br⁻ increased, but the increase was caused by the Br⁻); the TOC levels were initially unchanged. This increase in TTHMs resulted, in part, from the greater formation of bromoform (CHBr₃), the heaviest THM molecule. Subsequent H.O. Banks samples reflect increases in both salinity and TOC. The relatively high organics level at Banks in the January sample may have been partially a result of agricultural drainage from leaching.

From a health perspective, it is not only the increase in TTHMs that is of concern, but also the shift in speciation from primarily CHCl₃ in the Greene's Landing samples to the brominated THMs in the H.O. Banks samples. The latest data suggest that bromodichloromethane (CHCl₂Br) may be the THM of greatest toxicological concern (Table 1).²¹ Even when an increase in salinity shifted the formation from CHCl₂Br to dibromochloromethane (CHClBr₂) and CHBr₃, concentrations of the latter THM exceeded its 10⁻⁵ risk level of 40 µg/L.

Because Greene's Landing and H.O. Banks represent two extremes (i.e., low TOC and Br⁻ versus moderate amounts of both), the five-by-five matrix was used to address all possible combinations of TOC and Br⁻ that might be experienced with alternative delta transfer facilities. Furthermore, this matrix may encompass the range of water qualities in a high percentage of the sources in the United States—if not in the raw water, at least

ratios were 32–39 percent, and the TCAA-to-CHCl₃ weight ratios were 21–35 percent. All the water had comparable relative yields of DCAA, but the agricultural drains appeared to have a somewhat higher relative yield of TCAA. Future tests on these waters will include the sixth HAA, bromochloroacetic acid.

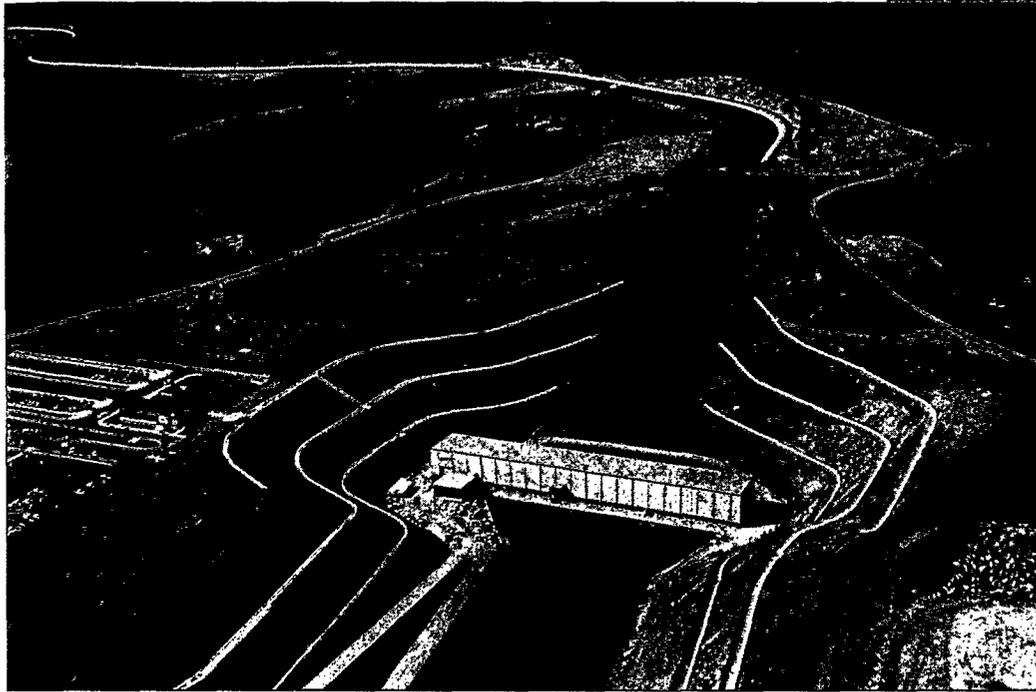
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Effect of TOC-bromide on THM speciation in the five-by-five matrix*

	Br-TOC—mg/mg					Br-Cl ⁻ —µmol/µmol†				
	0.3 mg Br/L	0.4 mg Br/L	0.8 mg Br/L	0.01 mg Br/L	0.1 mg Br/L	0.2 mg Br/L	0.4 mg Br/L	0.8 mg Br/L		
0.3 mg TOC/L	0.13	0.36	0.73	0.003	0.05	0.10	0.19	0.38		
0.4 mg TOC/L	0.16	0.29	0.58	0.002	0.05	0.10	0.17	0.33		
0.8 mg TOC/L	0.10	0.20	0.40	0.002	0.05	0.07	0.14	0.27		
0.01 mg Br/L	0.07	0.14	0.26	0.002	0.04	0.08	0.14	0.27		
0.1 mg Br/L	0.06	0.10	0.21	0.002	0.04	0.08	0.13	0.26		

*0.4 mg/L; however, a value of 0.005 mg/L was used in estimating the bromide level in the relationships in this table.

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To ensure that an agricultural drain sample could be used as a TOC spike, a preliminary test compared a sample from H.O. Banks with a synthetic sample consisting of 90 percent Greene's Landing and 10 percent agricultural drainage, with an appropriate Br⁻ spike (Table 3). The synthetic sample matched the H.O. Banks sample in TOC, UV, and Br⁻ levels, and similar amounts of individual and total THMs were produced.

Table 4 and Figure 8 show the effect of Br⁻ and TOC on THM speciation for the five-by-five matrix. As TOC increased or Br⁻ decreased, CHCl₃ formation increased. As Br⁻ increased, CHBr₃ increased. However, as TOC increased, CHBr₃ formation increased, reached a max-

(e.g., CHBr₃) were formed. CHCl₂Br₂, like CHBr₃, increased with increasing TOC up to a point, and then its concentration decreased. CHCl₂Br, at least under these test conditions, increased with increasing TOC. Although minimizing TOC minimizes the formation of CHCl₂Br, control of the latter through precursor removal is best realized at high Br⁻ levels (≥0.2 mg/L). At 0.1 mg Br⁻/L, decreasing TOC decreased the concentration of CHCl₂Br, but not as significantly as at the higher Br⁻ levels.

Changes in DBP speciation are attributable to several parameters. Amy and colleagues²³ found that increasing the Br⁻-to-TOC ratio yielded a higher percentage of brominated THMs. One means of evaluating THM speciation is the use of the bromine incorporation factor *n*, in which *n* is the molar amount of bromine in the THMs (TTHM-Br) divided by the molar TTHM concentration.²⁴ The value of *n* can vary between 0 and 3, with 0 corresponding to all CHCl₃

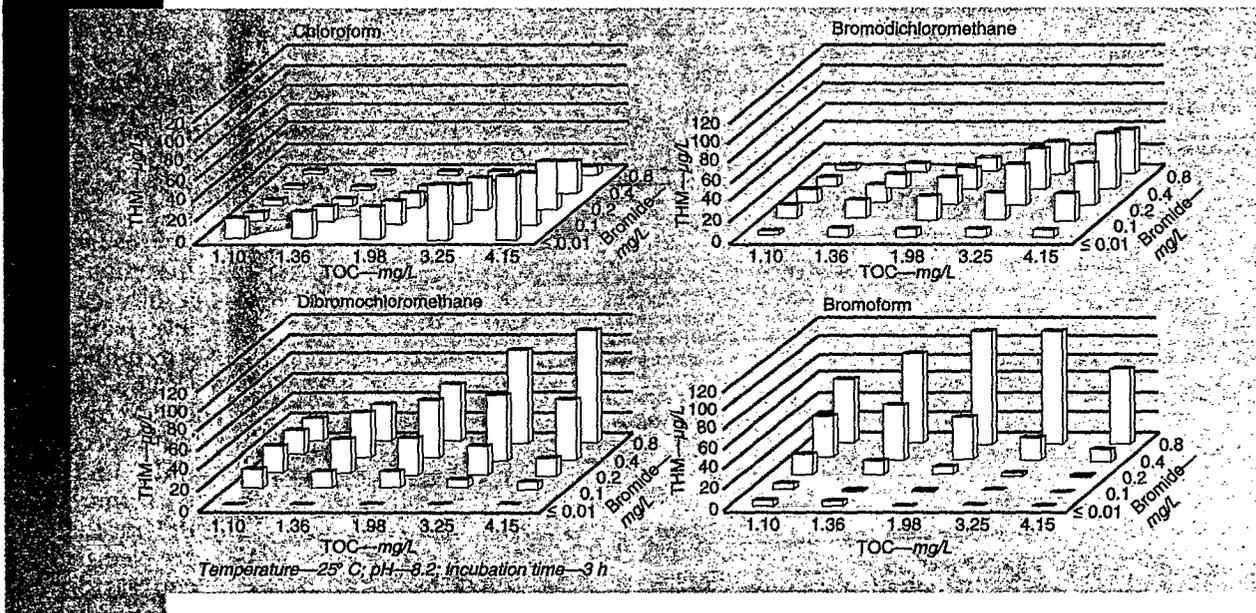
Effect of TOC-bromide on THM speciation in the five-by-five matrix* (continued)

0.8 mg Br ⁻ /L	TOC mg/L	TTHM-Br-Br ⁻ — μmol:μmol†					<i>n</i>				
		0.01 mg Br ⁻ /L	0.1 mg Br ⁻ /L	0.2 mg Br ⁻ /L	0.4 mg Br ⁻ /L	0.8 mg Br ⁻ /L	≤0.01 mg Br ⁻ /L	0.1 mg Br ⁻ /L	0.2 mg Br ⁻ /L	0.4 mg Br ⁻ /L	0.8 mg Br ⁻ /L
0.38	1.1	0.49	0.24	0.22	0.16	0.10	0.17	1.22	1.80	2.26	2.56
0.33	1.4	0.47	0.22	0.22	0.22	0.15	0.12	0.93	1.52	2.13	2.50
0.27	2.0	0.58	0.22	0.24	0.24	0.20	0.12	0.76	1.27	1.89	2.41
0.27	3.2	0.67	0.18	0.19	0.20	0.22	0.08	0.47	0.85	1.44	2.17
0.26	4.2	0.78	0.17	0.14	0.20	0.21	0.08	0.38	0.57	1.13	1.92

*25°C, 3 h, pH 8.2

†The ambient bromide level was <0.01 mg/L; however, a value of 0.005 mg/L was used in estimating the bromide level in the relationships in this table.

Effect of TOC and bromide on concentration and distribution of trihalomethane species in the five-by-five matrix



and 3 corresponding to all CHBr_3 . In the five-by-five matrix, for a particular TOC level, an increase in the Br^- -to-TOC ratio (i.e., caused by an increase in Br^-) yielded a higher value of n . For a particular Br^- concentration, an increase in the Br^- -to-TOC ratio (i.e., from a decrease in TOC) also yielded a larger n .

In addition, as TOC increases, the chlorine demand increases. Therefore, the chlorine-to-bromide ratio increases as TOC increases for a fixed chlorine residual goal. Although hypobromous acid (HOBr) is a better halogenation agent than hypochlorous acid (HOCl), if sufficient chlorine is added, HOCl can start to compete more effectively with HOBr .⁶ Symons and colleagues⁶ utilized the fraction Br^- to Cl^+ (in which Br^- represented the initial bromide concentration and Cl^+ was the average free available chlorine during the reaction time, both in molar units) to examine the HOBr - HOCl interplay. In the five-by-five matrix, for a particular Br^- level, an increase in TOC resulted in a higher chlorine demand (i.e., a higher chlorine dosage was required to meet the target residual); thus, the Br^- -to- Cl^+ ratio and n decreased.

Symons and colleagues also observed that bromine utilization (expressed as the fraction TTHM-Br to Br^- on a molar basis) decreases with increasing Br^- concentration, because the precursor sites are becoming limiting.⁶ In the five-by-five matrix, at the lowest TOC concentration (1.1 mg/L)—at which the organic precursor material was the most limited—the bromine utilization decreased with increasing Br^- level. However, as the TOC level increased, increases or decreases in bromine utilization approximately paralleled the trends observed for CHBr_3 and CHCl_2Br formation. For example, at the highest Br^- level (0.8 mg/L), as organic precursor sites became less limiting, bromine

utilization increased with increasing TOC up to a point. At the same time that organic precursor sites became more plentiful—which increased bromine utilization—more chlorine was added, and the Br^- -to- Cl^+ ratio was simultaneously decreasing. Clearly, there was a point at which the HOCl became more competitive with the HOBr .

Figure 9 shows TTHM formation in the five-by-five matrix for the 3-h prechlorination scenario. With postchloramination, delta water could meet the draft TTHM MCL of 80 µg/L, with up to 4 mg/L TOC, if Br^- were not present. As Br^- increases, however, the range of TOC levels that would enable compliance with an 80-µg/L TTHM standard shrinks, even with enhanced coagulation (which removes TOC, but not Br^-). Thus, to control the potential carcinogenic risk from TTHMs, both TOC and Br^- must be controlled. Ozonation of delta waters, followed by chloramination, presents another option for compliance with TTHM standards.

Effect of bromide and TOC on bromate formation. Table 5 shows the conditions for the ozonation experiments. To achieve the target ozone residual of 0.35 ± 0.05 mg/L, an ozone-to-TOC ratio of approximately 2 mg/mg was utilized. In a nationwide Br^- study, Amy and co-workers¹⁹ utilized a similar applied ozone-to-TOC ratio in bench-scale tests, which resulted in an average residual of 0.43 mg/L.

Table 6 shows bromate formation as a function of TOC and Br^- under the given ozonation conditions. For a different ozone contactor configuration or ozone residual goal, different bromate results could be expected. These sets of conditions, however, provide a basis for the relative effects of TOC and Br^- on bromate formation. For a particular TOC level, bromate

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production increased with increasing Br⁻ levels. Bromate formation appeared to be more sensitive to increasing Br⁻ at low Br⁻ levels. For a specific Br⁻ concentration, increasing the TOC level increased bromate formation. Because a higher ozone dosage was required to achieve the target ozone residual of 0.35 mg/L in high-TOC samples, more ozone was available to oxidize the Br⁻ to bromate. Because natural organic matter may also scavenge the hydroxyl radical,²⁵ the addition of TOC may have other effects on bromate formation.

More research is needed to better understand the kinetics of bromate formation. However, under these test conditions (e.g., ozonation at pH ~8 and a target ozone residual of ~0.35 mg/L), delta water with 2 mg/L TOC and 0.1 mg/L Br⁻ may be capable of achieving the draft bromate MCL of 10/L µg, whereas an increase in either TOC or Br⁻ may yield >10 µg/L bromate. Thus, MWD and other utilities are exploring bromate control options for the ozonation of delta waters.

Effect of wetlands on DBPFP. Vegetation testing.

Table 7 shows the results of the first sampling of the vegetative biomass experiment. In general, levels stayed approximately the same over the remainder of the 10-week testing period. The control had a TOC level of 4.3–4.9 mg/L, whereas the vegetative biomass barrels contained 12–17 mg/L and 30–40 mg/L TOC for the natural and elevated biomass densities, respectively. Upon chlorination, the control yielded 480–570 µg/L THMs. The chlorinated samples for the natural and elevated biomass yielded 1,100–1,500 µg/L and 2,300–2,900 µg/L THMs, respectively. The

Conditions for ozonation experiments

TOC (mg/L)	Br ⁻ (mg/L)	Average Ozone Residual (mg/L)
2.0	0.1	0.36
2.0	0.2	0.34
2.0	0.38	0.38
2.0	0.40	0.40
2.0	0.36	0.36

control (delta water) had a 0.8–1.0 percent THM yield per unit of TOC (on a molar basis). The natural and elevated-density biomass THM yields were 0.8–1.1 and 0.7–0.9 percent, respectively. The vegetative biomass was also a source of HAA precursors.

Because decaying vegetation is a source of humic material, these results are not surprising. Even the upstream channel waters can potentially pick up TOC and DBPFP from decaying vegetation in the delta. These data demonstrate that the wetlands vegetation can contribute DBP precursors to the delta.

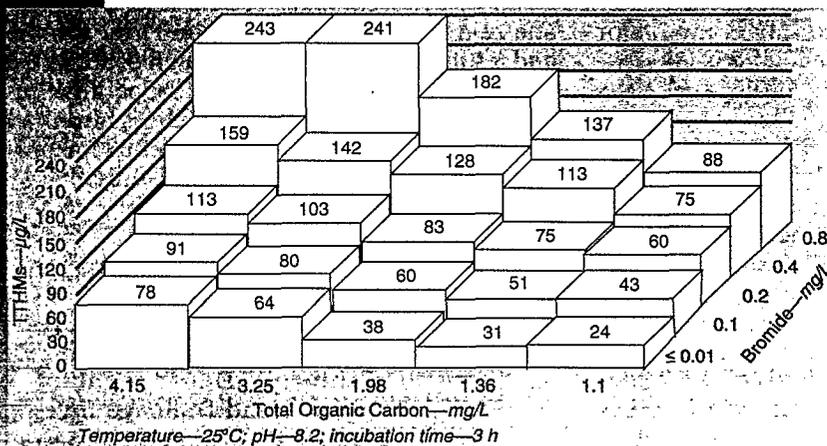
The use of wetlands as a source of water is not unique to California. Other areas in the United States are examining wetlands to address water quantity concerns; however, these results for the delta wetlands suggest that water quality is a consideration as well.

Soil testing. Water-paste saturation tests of peat soils from adjacent tracts of land indicate that more TOC and THMFP can be extracted from the soil of an agricultural tract than from that of a wetlands. In addition, there was more TOC and THMFP in the agricultural field surface samples (~100–190 mg/L TOC and ~8,200–14,000 µg/L THMFP) than in the agricultural field bottom samples (~40–100 mg/L TOC

and ~2,800–5,000 µg/L THMFP); there was a smaller difference in the wetlands surface samples (~30–70 mg/L TOC and ~2,100–5,000 µg/L THMFP) and bottom samples (~20–70 mg/L TOC and ~1,400–2,700 µg/L THMFP). This may result, in part, from the constant exposure of soil to oxidative conditions during agricultural operations.

When the soil data are evaluated for a molar yield of THMFP per unit of TOC, these samples give relatively comparable values (median value, 0.63 percent; 25th- and 75th-percentile values, 0.56 and 0.72 percent, respectively). In general, these lev-

Effect of TOC and bromide on the formation of total trihalomethanes in the five-by-five matrix



Temperature—25°C; pH—8.2; incubation time—3 h

Bromate formation as a function of TOC and bromide

TOC mg/L	Bromate—µg/L				
	0.01 mg Br/L	0.1 mg Br/L	0.2 mg Br/L	0.4-0.5 mg Br/L	0.7-0.9 mg Br/L
1	3	6	11	25	29
2	3	7	12	23	40
3	4	11	19	36	53
4	3	12	25	39	57
5	7	19	27	49	65

Results of first sampling of delta wetlands vegetative biomass experiment*

Barrel	Barrel 1	Barrel 2	Barrel 3	Barrel 4
1	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00
7	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00
11	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00
13	0.00	0.00	0.00	0.00
14	0.00	0.00	0.00	0.00
15	0.00	0.00	0.00	0.00
16	0.00	0.00	0.00	0.00
17	0.00	0.00	0.00	0.00
18	0.00	0.00	0.00	0.00
19	0.00	0.00	0.00	0.00
20	0.00	0.00	0.00	0.00
21	0.00	0.00	0.00	0.00
22	0.00	0.00	0.00	0.00
23	0.00	0.00	0.00	0.00
24	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00
28	0.00	0.00	0.00	0.00
29	0.00	0.00	0.00	0.00
30	0.00	0.00	0.00	0.00
31	0.00	0.00	0.00	0.00
32	0.00	0.00	0.00	0.00
33	0.00	0.00	0.00	0.00
34	0.00	0.00	0.00	0.00
35	0.00	0.00	0.00	0.00
36	0.00	0.00	0.00	0.00
37	0.00	0.00	0.00	0.00
38	0.00	0.00	0.00	0.00
39	0.00	0.00	0.00	0.00
40	0.00	0.00	0.00	0.00
41	0.00	0.00	0.00	0.00
42	0.00	0.00	0.00	0.00
43	0.00	0.00	0.00	0.00
44	0.00	0.00	0.00	0.00
45	0.00	0.00	0.00	0.00
46	0.00	0.00	0.00	0.00
47	0.00	0.00	0.00	0.00
48	0.00	0.00	0.00	0.00
49	0.00	0.00	0.00	0.00
50	0.00	0.00	0.00	0.00
51	0.00	0.00	0.00	0.00
52	0.00	0.00	0.00	0.00
53	0.00	0.00	0.00	0.00
54	0.00	0.00	0.00	0.00
55	0.00	0.00	0.00	0.00
56	0.00	0.00	0.00	0.00
57	0.00	0.00	0.00	0.00
58	0.00	0.00	0.00	0.00
59	0.00	0.00	0.00	0.00
60	0.00	0.00	0.00	0.00
61	0.00	0.00	0.00	0.00
62	0.00	0.00	0.00	0.00
63	0.00	0.00	0.00	0.00
64	0.00	0.00	0.00	0.00
65	0.00	0.00	0.00	0.00
66	0.00	0.00	0.00	0.00
67	0.00	0.00	0.00	0.00
68	0.00	0.00	0.00	0.00
69	0.00	0.00	0.00	0.00
70	0.00	0.00	0.00	0.00
71	0.00	0.00	0.00	0.00
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75	0.00	0.00	0.00	0.00
76	0.00	0.00	0.00	0.00
77	0.00	0.00	0.00	0.00
78	0.00	0.00	0.00	0.00
79	0.00	0.00	0.00	0.00
80	0.00	0.00	0.00	0.00
81	0.00	0.00	0.00	0.00
82	0.00	0.00	0.00	0.00
83	0.00	0.00	0.00	0.00
84	0.00	0.00	0.00	0.00
85	0.00	0.00	0.00	0.00
86	0.00	0.00	0.00	0.00
87	0.00	0.00	0.00	0.00
88	0.00	0.00	0.00	0.00
89	0.00	0.00	0.00	0.00
90	0.00	0.00	0.00	0.00
91	0.00	0.00	0.00	0.00
92	0.00	0.00	0.00	0.00
93	0.00	0.00	0.00	0.00
94	0.00	0.00	0.00	0.00
95	0.00	0.00	0.00	0.00
96	0.00	0.00	0.00	0.00
97	0.00	0.00	0.00	0.00
98	0.00	0.00	0.00	0.00
99	0.00	0.00	0.00	0.00
100	0.00	0.00	0.00	0.00

*Dose = 25 mg Br/L in 100 L of water. Chlorine dose = 3 x TOC + 8 x NH₄-N (mg/L)

els were the same regardless of the saturation period tested. These limited data indicate that the volumes of discharge water (from either the drainage of seasonal wetlands or agricultural operations) must be factored into the analysis of the effect of changing land management practices in the delta.

Summary and conclusions

The relationships among (1) chloride and bromide from seawater intrusion into the delta, (2) TOC loading in the delta, and (3) DBPs formed upon disinfection of delta waters have been studied. The main findings include:

- The ratio of chloride to bromide in delta waters is essentially the same as in pure seawater. Saltwater intrusion from the San Francisco Bay is the major source of bromide ions in exported delta waters.
- Agricultural drainage, particularly from tracts of land that are high in peat soil, is a major source of TOC and DBP precursors.
- Wetlands can also contribute TOC and DBPFP, both from vegetative biomass and from leaching of underlying peat soils. Although an agricultural operation may yield more TOC-DBPFP than an adjacent seasonal wetlands, the volumes of discharge water must be factored into the analysis of the relative contributions of each to the delta channel waters.
- There is a pressing need to limit all DBP precursors (both TOC and bromide) at municipal intakes because of the potential health effects of individual DBPs (e.g., CHCl₂Br and bromate) and the cost to

remove precursors once they are present in the water. In order to minimize health risks, bromide ion and TOC must be minimized wherever possible.

Finally, these experiments in the delta have resulted in (1) a better methodology to evaluate the source and effects of DBP precursors in the delta and (2) a better understanding of how different control measures—either in the delta or at the treatment plant—will affect the production of DBPs of health and regulatory concern. The data demonstrate that DBP control strategies should include watershed management as well as treatment plant processes. If California utilities are to meet future DBP standards, a way must be found to minimize water quality degradation in the delta.

This article should provide insights into the source and control of DBP precursors in other watersheds in the United States. Furthermore, the chlorination and ozonation study of a five-by-five matrix of TOC and bromide levels should provide for other utilities insights into the interplay of organic and inorganic precursors and disinfectants in DBP formation.

Acknowledgment

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