Watershed Sources of Disinfection Byproduct Precursors in the Sacramento and San Joaquin Rivers, California

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High levels of dissolved organic carbon (DOC) and bromide (Br) in the Sacramento and San Joaquin River waterways are of concern because DOC and Br are organic and inorganic precursors, respectively, of carcinogenic and mutagenic disinfection byproducts (DBPs). The Sacramento and San Joaquin Rivers are the two major rivers supplying water to the San Francisco Bay Delta, but sources and loads of DBP precursors into the Delta are still uncertain. The major objectives of this study were to evaluate both the quantity (DOC and Br fluxes) and the quality (reactivity in forming DBPs) of DBP precursors from the Sacramento and San Joaquin watersheds. Water samples were collected every 2 weeks at up to 35 locations along the Sacramento and San Joaquin Rivers and selected tributaries and analyzed for DOC (4 years), Br (1 year), and ultraviolet absorbance at 254 nm (1 year). Selected water samples were also tested for THM formation potential. Estimated fluxes for the Sacramento River were 39 000 ± 12 000 Mg DOC year^{-1} and 59 Mg of Br year^{-1} as compared to 9000 ± 5000 Mg of DOC year^{-1} and 1302 Mg of Br year^{-1} for the San Joaquin River. The THM formation potential was higher in the San Joaquin River (441 ± 49 μg L^{-1}) than the Sacramento River (176 ± 20 μg L^{-1}) because of higher concentrations of both organic (DOC = 3.62 ± 0.14 vs 1.92 ± 0.09 mg L^{-1}) and inorganic DBP (Br = 0.80 ± 0.07 vs <0.03 ± 0.01 mg L^{-1}) precursors. The Sacramento River's greater DOC load despite lower DOC concentrations is due to its discharge being about 5 times greater than the San Joaquin River (50 × 10^9 vs 10 × 10^9 L day^{-1}). The DOC concentration was significantly correlated with several land-cover types, including agriculture; however, no relationship was found between DOC quality and land-cover at the watershed scale.

Introduction

Natural water utilized for a municipal water supply must be disinfected to prevent transmission of waterborne disease and to destroy pathogens. A variety of carcinogenic and mutagenic disinfection byproducts (DBPs), such as trihalomethanes (THMs), are formed when disinfectants, such as chlorine, react with dissolved organic carbon (DOC) in source waters (*1*). The presence of bromide (Br) further enhances the formation of the more toxic bromated DBP species (*2*). Although various water treatment technologies, such as coagulation and filtration, may remove some precursors from source waters (*1*), controlling the precursors at their source could be a more effective and economical approach. Thus, studying the watershed sources of DBP precursors provides useful information for land and water management (*3*).

DBPs are of great concern in the Sacramento−San Joaquin Delta as it is a source of drinking water for 22 million people in California. High levels of DBP precursors have been recorded in Delta waters (*4*). For example, at the Banks Pumping Plant, which is the diversion station for the transfer of Delta water through the California Aqueduct to Southern California for the municipal water supply, the total organic carbon ranged from 2.2 to 7.5 mg L^{-1} with a median of 3.2 mg L^{-1}. The concentration of Br ranged from 0.11 to 0.22 mg L^{-1} with a median of 0.15 mg L^{-1} (*4*). Importantly, historical records indicated that DOC and Br in the Delta exceeded the safety guideline implemented by CALFED, suggesting <3 mg L^{-1} DOC and <0.05 mg L^{-1} Br in source water (*5*). High concentrations of organic carbon in Delta waters are partially attributable to agricultural drainage within the Delta; however, both the Sacramento and the San Joaquin Rivers are considered to be significant sources of organic carbon to the Delta as well (*6*, *7*). Agricultural return waters are believed to be the major sources of Br in the Delta, especially from waters draining Coast Range marine sediment deposits (*4*). While ecologists and hydrologists have explored the origin, transport, and fate of organic carbon and inorganic constituents in the inputs of the two rivers to the Delta (*4*, *7*, *8*), little has been done to understand the origins and characteristics of organic and inorganic DBP precursors at the watershed scale. The major objective of this study was to evaluate both the quantity (DOC and Br fluxes) and the quality (reactivity in forming DBPs) of DBP precursors in the Sacramento and San Joaquin watersheds. A goal of the research was to understand temporal and spatial variation of DBP precursors and to relate DOC concentrations to land-cover at the watershed scale.

Study Area. The Sacramento−San Joaquin Delta lies at the confluence of the Sacramento and San Joaquin Rivers upstream of the San Francisco Bay, CA (Figure 1). Water exported from the Delta is delivered for farmland irrigation and provides municipal drinking water to two-thirds of the state's population, about 22 million people (*4*). The Sacramento River is the largest river in California, and its basin covers an area of about 70 000 km^2 in the north-central part of California. It has an average annual discharge of 2.71 × 10^{10} m^3 and makes up 84% of the fresh water supply to the Delta. Land-cover of the Sacramento River basin is principally forest, rangeland, and agricultural lands. The San Joaquin River basin covers an area of 19 000 km^2 in central California. It has an average annual discharge of 4.20 × 10^9 m^3 and makes up 13% of the fresh water supply to the Delta. Because of upstream diversions, the San Joaquin River is generally dry during the summer above Highway (Hwy) 165 (site 31), and flow is initiated below this site due to irrigation return flows and subsurface drainage discharge. The major land use in the San Joaquin River basin includes forest, agricultural land, and rangeland (*8*, *9*).

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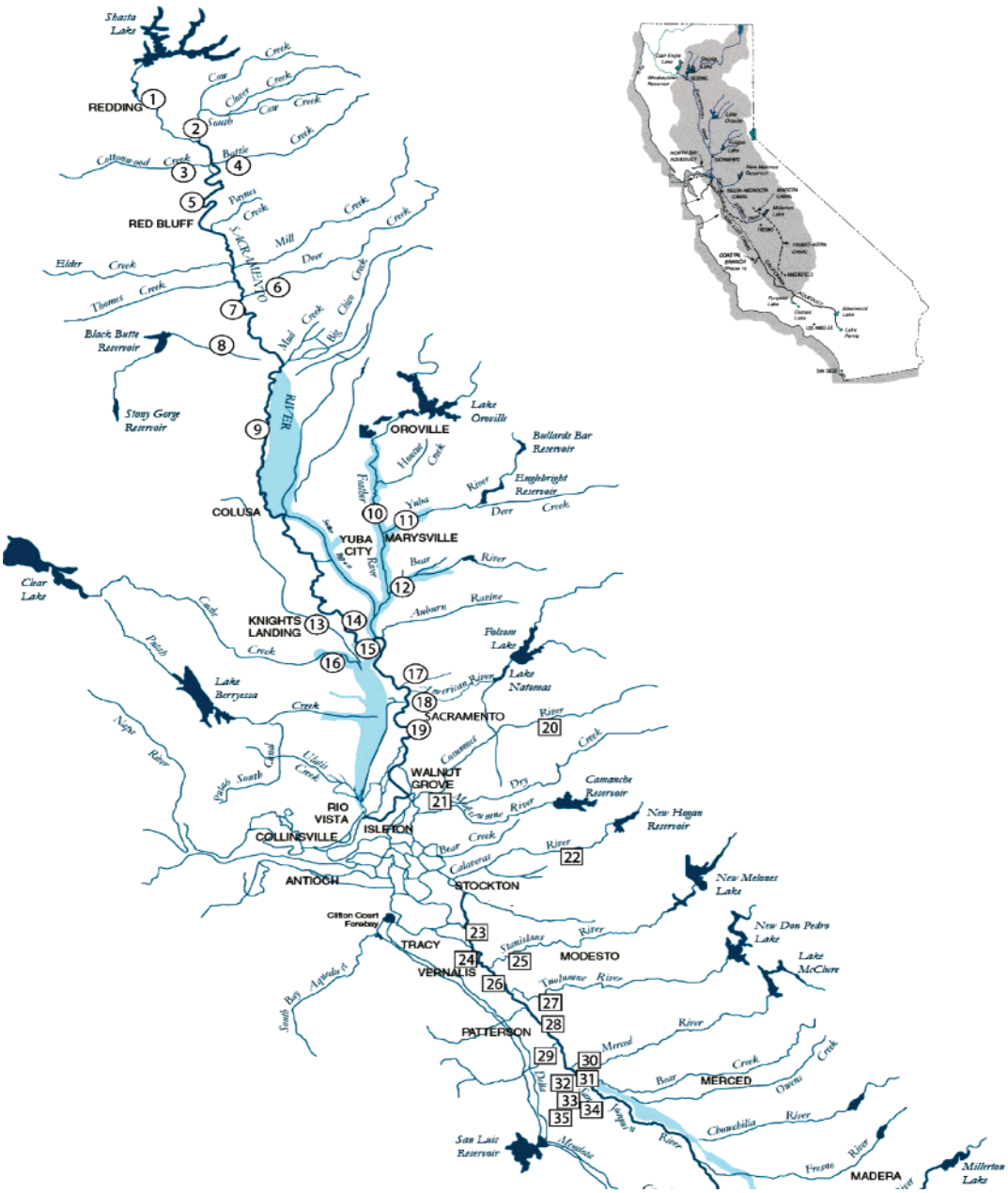

FIGURE 1. Map showing mainstream and tributaries of Sacramento and San Joaquin Rivers. Numbers in circles and squares indicate the sampling sites in the Sacramento River and San Joaquin River, respectively. Gray area in the small map shows the drainage area of Sacramento and San Joaquin Rivers.

Materials and Methods

There were five sampling sites on the mainstream and 16 sampling sites on tributaries of the Sacramento River. In the San Joaquin River, there was a total of 14 sampling sites with four mainstream sites (Figure 1 and Tables 1and 2). Sampling sites were selected such that major tributaries, agricultural drains, and several mainstream locations were represented. At each site, water flow measurements were available or estimated from a nearby gauging station. Sampling sites were labeled consecutively from north to south such that sites 1−21 and 22−35 were located on the Sacramento and San Joaquin Rivers, respectively.

Two liter grab samples were collected from the upper 50−75% of the water column at mid-channel from up to 35 sites every 2 weeks from October 1, 1999 to September 30, 2003 (the water year is defined as October 1 through September 30). The sampling design resulted in 26 samples per site per year. Water samples were stored on ice and filtered through a pre-rinsed 0.2 μm polycarbonate membrane (Millipore) within 24 h of collection. Filtered samples were stored at 4 °C through completion of analyses.

DOC was measured using a Dohrmann UV enhanced-persulfate TOC analyzer (Phoenix 8000) with a detection limit of 0.05 mg L^{-1}. Ultraviolet absorbance at 254 nm (UVA) was determined using a diode array spectrophotometer (Hewlett-Packard P8452A). Br was measured by ion chromatography (Dionex 500x; AS4A anions) with a detection limit of 0.03 mg L^{-1}. Solute fluxes were calculated by multiplying the mean daily flow by the average solute concentration between sequential sampling dates (period-weighting method (*10*)). If a site had no water flow, or the solute concentration was below the detection limit, a zero value was assigned for that time period. Specific ultraviolet absorbance at 254 nm (SUVA) was determined by normalizing UVA with the concentration of DOC. SUVA is correlated with the aromaticity of DOC and

TABLE 1. Water Samples Collected from 21 Sites of Sacramento River Every 2 Weeks from October 1, 2002 to September 30, 2003 for DOC, SUVA, and Br Analyses[a]

site ID	location	DOC (mg L^{-1})	SUVA (L mg^{-1} m^{-1})	Br (mg L^{-1})	THMFP (μg L^{-1})
1[b]	Sacramento River at Court Rd.	0.96 ± 0.01	3.70 ± 0.28	ND	NA
2	Cow Creek at Dersch Rd.	1.70 ± 0.03	3.78 ± 0.23	ND	NA
3	Cottonwood Creek at Cottonwood	1.57 ± 0.04	3.13 ± 0.20	ND	NA
4	Battle Creek at Grover Rd.	1.17 ± 0.02	3.60 ± 0.25	ND	77 ± 12$^{(4)}$
5[b]	Sacramento River at Bend Ferry Rd.	1.08 ± 0.02	3.72 ± 0.18	ND	116 ± 17$^{(4)}$
6	Deer Creek at Leiniger Rd.	1.40 ± 0.04	3.62 ± 0.23	ND	NA
7[b]	Sacramento River at A9	1.31 ± 0.02	3.55 ± 0.32	ND	NA
8	Stony Creek at Orland	2.05 ± 0.05	2.64 ± 0.13	ND	NA
9[b]	Sacramento River at Butte City	1.48 ± 0.04	3.12 ± 0.18	ND	NA
10	Feather River at Yuba City–Marysville Bridge	1.67 ± 0.06[c]	3.18 ± 0.22	0.000 ± 0.000$^{(1)}$	NA
11	Yuba River at Simpson Lane	1.16 ± 0.05[c]	2.93 ± 0.19	ND	NA
12	Bear River at Forty Mile Rd.	1.95 ± 0.10[c]	2.89 ± 0.11	ND	NA
13	Colusa Basin Drainage at Knights Landing	4.74 ± 0.19[c]	3.28 ± 0.17	0.057 ± 0.020$^{(10)}$	315 ± 57$^{(5)}$
14[b]	Sacramento River at Knights Landing	1.57 ± 0.09[c]	3.61 ± 0.27	0.006 ± 0.002$^{(7)}$	NA
15	Sacramento Slough at Karnack	3.48 ± 0.05	3.21 ± 0.09	0.009 ± 0.009 $^{(1)}$	301 ± 42$^{(4)}$
16	Cache Creek at Hwy 102	2.80 ± 0.12[c]	2.56 ± 0.12	0.176 ± 0.033$^{(17)}$	NA
17	main drainage at El Camino	5.48 ± 0.19[c]	2.89 ± 0.08	0.023 ± 0.017$^{(7)}$	NA
18	American River at Discovery Park	1.58 ± 0.05[c]	2.94 ± 0.10	ND	160 ± 26$^{(4)}$
19[b]	Sacramento River at Freeport	1.92 ± 0.07[c]	3.17 ± 0.21	0.005 ± 0.002$^{(5)}$	176 ± 20$^{(4)}$
20	Consume River at Michigan Bar	1.53 ± 0.16[c]	3.45 ± 0.27	0.006 ± 0.006$^{(1)}$	NA
21	Mokelumne River at New Hope Rd.	1.91 ± 0.06[c]	2.58 ± 0.11	ND	NA

[a] Total sample size is 26 unless specified. Values are expressed as mean ± standard error. Sample size of site 13 for THMFP was 5. ND: not detectable for all 26 water samples with a detection limit of 0.03 mg L^{-1}. NA: not available. Only selected samples were tested for THMFP. Superscript number in parentheses next to the bromide concentration indicates the number of detectable (≥0.03 mg L^{-1}) observations. There was a total of 26 sampling events in 2002–2003. If any positive samples were observed, the average was taken for 26 samples, and values of zero were assigned for nondetectable samples. Superscript number in parentheses next to THMFP indicates the sample size of the measurement. Water samples were collected October to December 2002 from selected sites. [b] Sampling site is the mainstream of the Sacramento/San Joaquin Rivers. [c] Mean and standard error of DOC was calculated based on 4 years of data, from October 1, 1999 to September 30, 2003. Total sample size is 104: 26 samples for 4 years.

TABLE 2. Water Samples Collected from 14 Sites of San Joaquin River Every 2 Weeks from October 1, 2002 to September 30, 2003 for DOC, SUVA, and Br Analyses[a]

site ID	location	DOC (mg L^{-1})	SUVA (L mg^{-1} m^{-1})	Br (mg L^{-1})	THMFP (μg L^{-1})
22	Calaveras at Hwy 26	3.13 ± 0.16 [c]	2.72 ± 0.08	ND	NA
23[b]	San Joaquin River at Hwy 120	3.62 ± 0.14 [c]	3.01 ± 0.05	0.796 ± 0.067$^{(26)}$	441 ± 49$^{(5)}$
24[b]	San Joaquin River at Vernalis	3.30 ± 0.11 [c]	2.89 ± 0.08	0.718 ± 0.053$^{(26)}$	NA
25	Stanislaus River at Caswell Park	1.95 ± 0.10 [c]	3.17 ± 0.14	0.001 ± 0.001$^{(1)}$	NA
26[b]	San Joaquin River at Hwy 132 (Maze)	3.80 ± 0.14 [c]	3.15 ± 0.11	0.921 ± 0.069$^{(26)}$	NA
27	Tuolumne River at Shiloh Rd.	2.21 ± 0.09 [c]	3.45 ± 0.17	0.024 ± 0.005$^{(14)}$	265 ± 36$^{(5)}$
28[b]	San Joaquin River at Patterson	4.80 ± 0.18 [c]	3.20 ± 0.09	1.224 ± 0.079$^{(26)}$	600 ± 29$^{(5)}$
29	Orestimba Creek at River Rd.	4.03 ± 0.18 [c]	3.40 ± 0.16	0.415 ± 0.060$^{(24)}$	NA
30	Merced River at River Rd. (J18)	2.24 ± 0.10 [c]	3.06 ± 0.12	0.085 ± 0.021$^{(21)}$	NA
31	San Joaquin River at Hwy 165	6.27 ± 0.21 [c]	2.84 ± 0.10	2.282 ± 0.297$^{(26)}$	NA
32	Los Banos Creek at Hwy 140	10.63 ± 0.61[c]	3.23 ± 0.10	1.115 ± 0.136$^{(26)}$	1444 ± 178$^{(5)}$
33	Salt Slough at Hwy 165	6.23 ± 0.22 [c]	3.22 ± 0.05	1.063 ± 0.074$^{(26)}$	NA
34	San Luis Drain Terminus	5.32 ± 0.22 [c]	3.14 ± 0.11	4.049 ± 0.223$^{(26)}$	854 ± 92$^{(5)}$
35	Mud Slough at Kesterson	7.95 ± 0.37[c]	3.11 ± 0.10	2.537 ± 0.184$^{(26)}$	NA

[a] Total sample size is 26 unless specified. Values are expressed as mean ± standard error. Sample size of site 13 for THMFP was 5. ND: not detectable for all 26 water samples with a detection limit of 0.03 mg L^{-1}. NA: not available. Only selected samples were tested for THMFP. Superscript number in parentheses next to the bromide concentration indicates the number of detectable (≥0.03 mg L^{-1}) observations. There was a total of 26 sampling events in 2002–2003. If any positive samples were observed, the average was taken for 26 samples, and values of zero were assigned for nondetectable samples. Superscript number in parentheses next to THMFP indicates the sample size of the measurement. Water samples were collected October to December 2002 from selected sites. [b] Sampling site is the mainstream of the Sacramento/San Joaquin Rivers. [c] Mean and standard error of DOC was calculated based on 4 years of data, from October 1, 1999 to September 30, 2003. Total sample size is 104: 26 samples for 4 years.

has been widely used as a surrogate for DBP precursors (*11*, *12*).

A total of 50 samples (25 from each river basin) from 11 sites was selected to determine the THM formation potential (THMFP) during the 2002–2003 water year (Tables 1 and 2). These samples had DOC concentrations ranging from 0.7 to 11.6 mg L^{-1} and Br concentrations ranging from <0.03 to 4.0 mg L^{-1} and included mainstream, tributaries, and agricultural drains. In addition, water samples from the Sacramento River at Freeport (site 19) and Mud Slough at Kesterson (site 35) were spiked with NaBr to evaluate the influence of bromide on THM formation. A stock bromide solution was spiked into water samples to increase the ambient Br concentrations by 0.25, 1.0, and 2.5 mg L^{-1}; samples were run in duplicate.

The dose-based THMFP method developed by Bryte Laboratory at the California Department of Water Resources was used in this study (*4*). Briefly, samples were chlorinated with freshly prepared $NaOCl/H_3BO_3$ buffered at pH 8.3 ± 0.1. Each sample was diluted to a DOC value less than 10 mg L^{-1} and treated with a constant chlorine dosage (120 mg L^{-1}). The vials were incubated for 7 days at room temperature (20 ± 1 °C). Following incubation, 0.15 mL of 10% sodium sulfite solution was added to quench the residual chlorine. Quantification of THM was accomplished using a Hewlett-

Packard 5890 II gas chromatograph fitted with a capillary split−splitless inlet, a ^{63}Ni electron capture detector, and a RESTEK Rtx-502.2 column (105 m × 0.53 mm × 3 μm). THMFP was calculated as the sum of four THM species: trichloromethane, bromodichloromethane, dibromochloromethane, and tribromomethane. Specific THMFP (STHMFP), which is determined by normalizing THMFP with the concentration of DOC, represents the reactivity of DOC in forming DBPs.

The bromine substitution factor (BSF) was calculated for representing the yield of brominated species in THM formation (*13*). BSF is equal to zero if pure chloroform is formed and is equal to 100% if pure bromoform is produced.

$$\mathrm{BSDF} = \frac{\sum_{n=0}^{3} n[\mathrm{CHCl}_{(3-n)}\mathrm{Br}_n]}{3\sum_{n=0}^{3} \mathrm{CHCl}_{(3-n)}\mathrm{Br}_n} \times 100\% \quad 0 \le \mathrm{BSF} \le 100$$

ArcGIS 9.1 Desktop GIS software was used to determine the composition of land-cover characteristics within the Sacramento and San Joaquin River subwatersheds. All datasets were converted to a common digital format, using a common coordinate system (Albers Equal Area). Multisource land-cover data (*14*) were reclassified into eight groups, including urban, agricultural lands, hardwood forest, coniferous forest, wetland, grassland, chaparral, and other. Land-cover data were intersected with previously derived watershed boundaries (*15*). GIS tools were used to calculate the area of each land-cover type within each subwatershed. The category termed other was calculated as the difference between 100% and the sum of the percent cover by all other land-cover types and never exceeded 13%.

Results and Discussion

Spatial and Temporal Variation in DOC. Tables 1 and 2 summarize the concentrations of DOC and Br, the two major DBP precursors, and SUVA, a surrogate for DBP precursors, for the 35 sampling sites. Overall, the San Joaquin River had a higher concentration and a greater variation in DOC concentrations along the river. The annual average DOC concentration for the five San Joaquin River mainstream sites was 4.03 ± 0.11 mg of C L^{-1} (mean ± standard error), and it was significantly ($p < 0.05$) higher than mainstream sites of the Sacramento River (2.02 ± 0.06 mg of C L^{-1}). The DOC in the mainstream, tributaries, and agricultural drains of the San Joaquin River ranged from 1.95 to 10.63 mg of C L^{-1}. The range is almost twice that of the Sacramento River and its tributaries, which was 0.96−5.48 mg of C L^{-1}. The ranges and average of DOC concentrations in our studies are comparable to Saleh et al.'s study (*8*), which used the U.S. Geological Survey National Water Information System, EPA Storage and Retrieval System, and the California Interagency Ecological Program database.

In spite of a higher DOC concentration in the San Joaquin River, the Sacramento River contributed a significantly greater amount of DOC to the Delta. At the outflow of the Sacramento River into the Delta, including the flows of the Sacramento Freeport (site 19), Cosumnes River (site 20), and Mokelumne River (site 21), the Sacramento River carried an annual DOC load of 39 000 ± 12 000 Mg year^{-1} (mean ± standard error) in water years 1999−2003. In contrast, the San Joaquin River, including the Calaveras River (site 22), contributed a load of 9000 ± 5000 Mg of DOC year^{-1}. Such large variations in the annual DOC in both rivers are due to the huge differences in the annual water discharge between wet and dry years. The water fluxes in the driest year were 40% less than in the wettest year. Notably, results matched the calculations from Saleh et al. (*8*), who used data from before 2000, and showed that the Sacramento and San Joauqin Rivers contributed 33 000 and 11 000 Mg of DOC year^{-1} for the wet years, respectively. The Sacramento's greater DOC load despite a lower DOC concentration is due to the Sacramento River's discharge being about 5 times greater than the San Joaquin River (50 × 109 vs 10 × 109 L day^{-1}; Figure 2). Moreover, the carbon flux was strongly correlated with the water flux in both rivers. High discharges in February to April due to the rainy season and snowmelt carried elevated amounts of organic carbon into the Delta. The greatest DOC contribution to the Delta was found in winter. At other times of the year, both rivers usually remained at base flow, and both water and carbon fluxes were relatively stable (*8*, *16*)

DOC Sources and Quality. The average DOC concentration increased downstream along the Sacramento River mainstream from Court Road to Freeport (sites 1, 5, 7, 9, 14, and 19) from 0.96, 1.08, 1.31, 1.48, and 1.57 to 1.92 mg of C L^{-1}, respectively (Table 1). A mass balance calculation suggests that the majority of mainstream DOC is autochthonous. Autochthonous organic carbon that arises from instream processes may include dead organisms, phytoplankton, exudates, etc., whereas allochthonous carbon sources result from external sources, such as leachate from surrounding soils and terrestrial vegetation. Considering the DOC loads in the Sacramento River for 2002−2003 (the only year with complete data for all sites), the summation of loads from measured tributaries and drains (Figure 3a) was equal to 22 000 Mg and was less than 50% of the downstream load at Freeport (site 19). Although not all tributaries were included in the study (all major tributaries were included), there is no reason to believe that the unsampled small tributaries with similar land uses would behave differently from sampled tributaries and contribute a large amount of DOC to the mainstream. This suggests that a significant portion of DOC was produced within the river rather than from allochthonous organic carbon from the tributaries.

In contrast to the Sacramento River, there were no obvious trends in DOC concentration along the mainstream of the San Joaquin River (Table 2). The fluctuation in DOC along the river was probably due to its relatively smaller water volume, large inputs of agricultural drainage in the upstream portion, and dilution from the east-side tributaries. Downstream tributaries (sites 25, 27, and 30) contributed about 50% of the summer flow and have lower DOC concentrations (2.0−2.2 mg L^{-1}) than the mainstream. Summation of loads from the sampled tributaries and drains (Figure 3b) accounted for 75% of the DOC load at Hwy 120 (site 23), indicating a greater importance of allochthonous sources in the San Joaquin River.

Allochthonous sources of DOC to the Sacramento and San Joaquin Rivers were different due to differences in land-cover between the two watersheds. For example, agricultural land-cover in the San Joaquin Basin (22%) is roughly twice as high as agricultural land-cover in the Sacramento Basin (13%). Of the land-cover classes examined, DOC concentrations correlated significantly ($p < 0.01$) and positively with agricultural land, wetland, and grassland ($r^2 = 0.30$, 0.27, and 0.63, respectively). Conversely, DOC concentrations were strongly negatively correlated with forest cover ($p < 0.001$, $r^2 = 0.67$). There was no significant relationship between DOC concentration and urban area, chaparral, or other categories. These results suggest that lowland land-cover types (e.g., agricultural land and wetlands) contribute more DOC on a per-area basis than upland land-cover types (e.g., forests).

In spite of different organic carbon sources, DOC in both the Sacramento and the San Joaquin River watersheds had similar chemical characteristics in terms of SUVA (Figure 4). If data from all sites are used, a strong correlation between

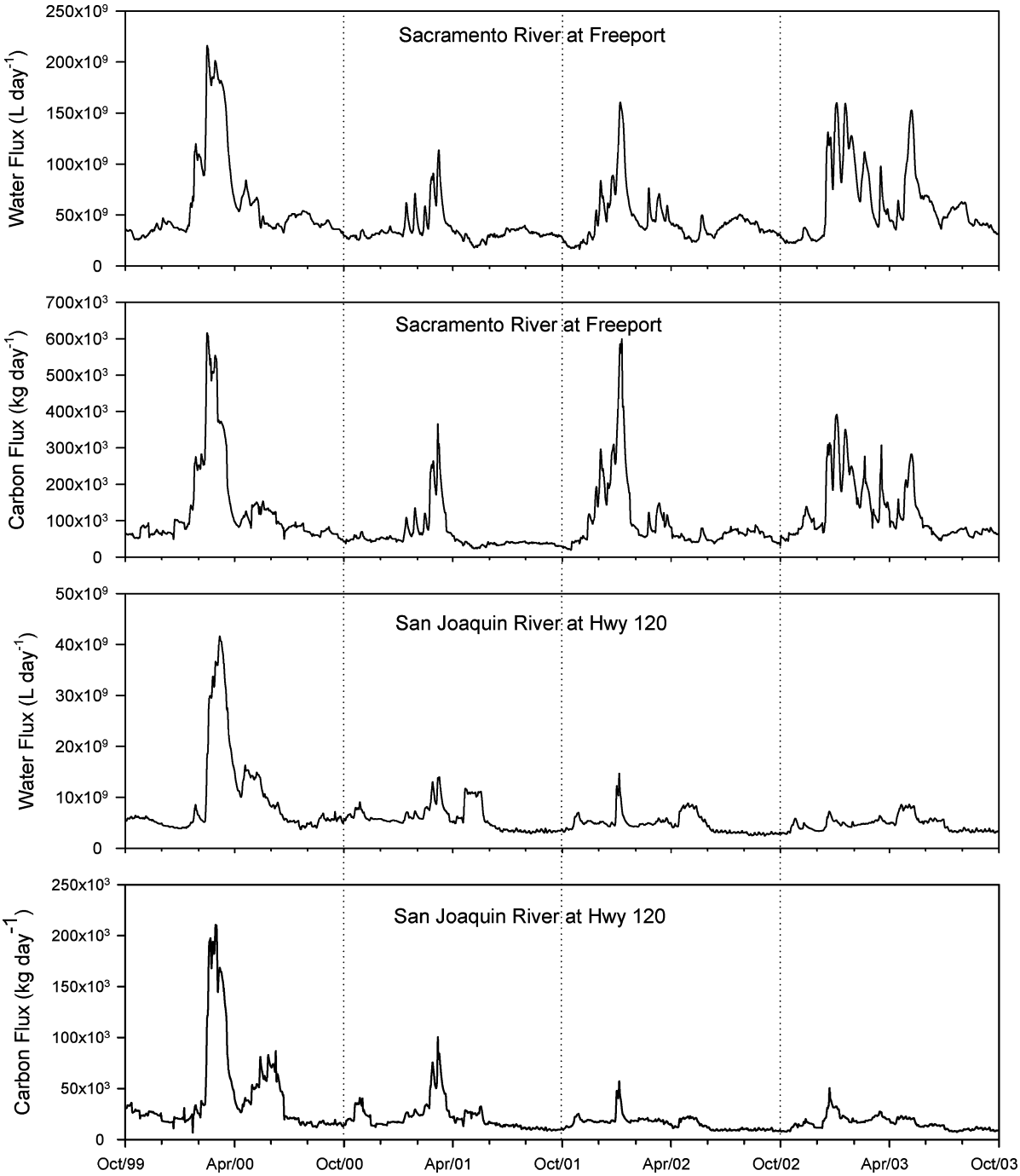

FIGURE 2. Water discharge and DOC fluxes of the Sacramento River at Freeport (site 19) and San Joaquin River at Hwy 120 (site 23) in water years 1999−2003. Water flows for the Hwy 120 site are estimated from the San Joaquin at Vernalis site immediately upstream.

DOC and UVA is obtained with a slope of 30.37 mg cm L^{-1} ($r^2 = 0.92$). The slope is the inverse of SUVA and is equivalent to 3.29 L mg^{-1} m^{-1}. SUVA has been used as a surrogate for DBP precursors and is strongly correlated with the aromatic carbon content of DOC (*12*, *17*). The average SUVA of waters from the Sacramento River (3.25 ± 0.09 L mg of C^{-1} m^{-1}; average ± standard error) was not statistically different ($p > 0.05$) from that of the San Joaquin River (3.10 ± 0.06 L mg of C^{-1} m^{-1}). The similarity in SUVA suggests that measuring the aromaticity alone is insufficient to distinguish the sources and the chemical characteristics of DOC.

Spatial and Temporal Variation in Bromide. In addition to the high DOC concentrations, high Br concentrations were observed in the San Joaquin River, particularly in the upper reaches (Table 2). At sampling sites 34 (San Luis Drain Terminus) and 35 (Mud Slough), average Br concentrations were 4.05 ± 0.22 and 2.54 ± 0.22 mg L^{-1} (average ± standard error), respectively. Similar to DOC, San Joaquin River Br concentrations decreased downstream, indicating dilution by low Br concentrations entering from Sierra Nevada tributaries. At mainstream sites 28 (Patterson), 26 (Hwy 132), and 24 (Vernalis), Br concentrations were 1.22, 0.92, and 0.72 mg L^{-1}, respectively. Results suggested that agricultural drainage from the upstream portion of the San Joaquin River is the major source of Br. Studies (*18*, *19*) suggest that Br in the lower San Joaquin River originates primarily from seawater entrained at the Delta pumps and distributed for upstream irrigation by way of the Delta Mendota Canal. Bromide becomes evapoconcentrated through irrigation and managed wetlands and finally makes its way back to the San

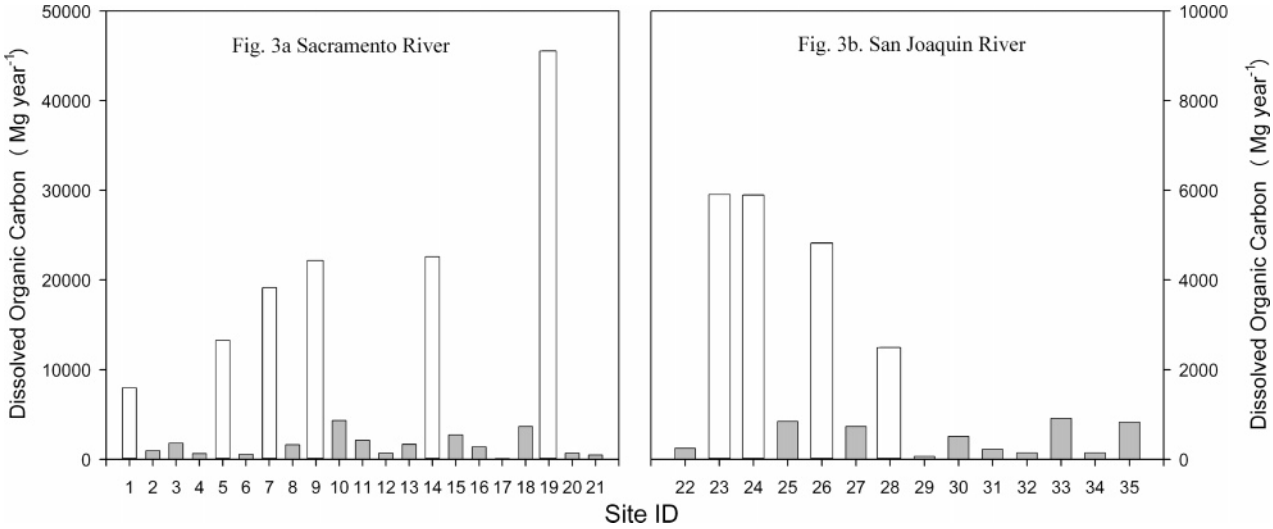

FIGURE 3. Annual carbon load in water year 2002−2003 at each sampling site. Empty bar represents the mainstream of the rivers, and gray bar represents the tributaries. Water flows from site 1 to 19 in the Sacramento River. Sites 20 and 21 are tributaries of the Sacramento River downstream from Freeport. Water flows from site 35 to 23 in the San Joaquin River. Site 22 is a tributary of the San Joaquin River downstream of the Hwy 120 site.

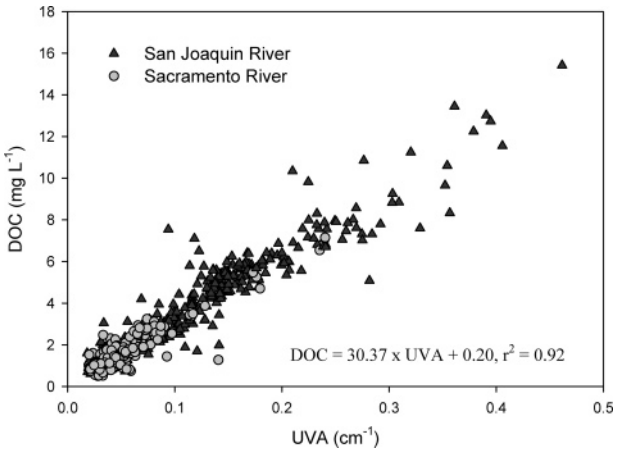

FIGURE 4. Correlation of DOC and UVA from the Sacramento and San Joaquin Rivers and their tributaries in water year 2002−2003. Total sample size is 910, with 546 and 364 samples from the Sacramento and San Joaquin Rivers, respectively.

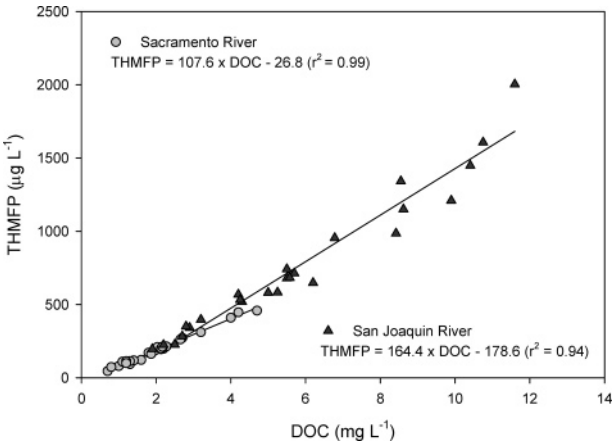

FIGURE 5. Correlation of THMFP and DOC from Sacramento and San Joaquin River sampling sites (see Tables 1 and 2 for specific sites used in this study).

Joaquin River. The Br flux calculated for water year 2002−2003 showed higher Br fluxes, ranging from 4000 to 8000 kg day^{-1}, during the rainy season (January to May). The Br flux during summer baseflow conditions was about 2000 kg day^{-1}, and the annual load was about 1302 Mg. In contrast, Br was rarely detected (<0.03 mg L^{-1}) in the 21 Sacramento River sites, except for sites 13 (Colusa Basin Drainage) and 16 (Cache Creek), which have watersheds with parent materials derived from the marine sediments in the Coast Ranges. The Sacramento River delivered about 59 Mg of Br to the Delta in 2002−2003, which was significantly lower than the San Joaquin River (1302 Mg). As a more conservative estimate, if the nondetectable values for Br were replaced by 0.015 mg L^{-1} (1/2 the detection limit), the Sacramento River could contribute about 370 Mg of Br annually. In either case, there is no doubt that the San Joaquin River is the dominant source of Br to the Delta.

Reactivity in Forming DBPs. On the basis of the analysis of 50 selected samples from 11 sites, the average THMFP in the Sacramento River watershed was 191 ± 29 μg L^{-1} (mean ± standard error, $n = 25$) and was significantly lower ($p < 0.01$) than sites in the San Joaquin River watershed (743 ± 97 μg L^{-1}, $n = 25$). THMFP values at the furthest downstream sites were somewhat lower, 135 ± 31 and 346 ± 10 μg L^{-1}, for the Sacramento River at the Freeport (site 19) and San Joaquin at Hwy 120 (site 23) sites, respectively (mean ± standard error, $n = 5$). Lower THMFP in outflows was likely due to dilution from the Sierra Nevada tributaries that have low DOC and Br waters originating from high elevation forests. In contrast, high THMFP values were mainly collected from the agricultural sites, which typically contained higher levels of DOC and Br.

Consistent with previous studies (*4*, *20*), our results found a strong correlation between DOC and THMFP for the Sacramento ($r^2 = 0.99$) and San Joaquin ($r^2 = 0.92$) Rivers, respectively (Figure 5). However, the slopes of the two linear regressions were significantly different ($p < 0.05$) and suggest an impact of the water sources in THM formation. The slopes of the lines, which are equal to THMFP divided by DOC, can be considered to be the reactivity of THM formation per unit carbon with units of μg of THM per mg of C. As discussed in the previous section, DOC from the two rivers had similar chemical characteristics in terms of SUVA; therefore, the difference in reactivity was attributed to the higher concentrations of Br, which enhanced the formation of brominated species and increased the total THMFP on a mass basis. We further examined this hypothesis by spiking selected samples with bromide (Table 3). The total THM formation increased with a decrease in the DOC/Br molar ratio. The

TABLE 3. Water Samples from Sacramento River at Freeport (Site 19) (1.2 mg of DOC L^{-1}) and Mud Slough at Kesterson (Site 35) (5.5 mg of DOC L^{-1}) Spiked with NaBr to Evaluate the Br Effect on THM Formation[a]

level of Br (mg L^{-1})	DOC/Br (mol mol^{-1})	TTHM (μg L^{-1})	TTHM (μmol L^{-1})	STHMFP (mmol mol^{-1})	BSF (%)
		Sacramento River at Freeport			
0.01 ± 0.00[b]	799	115 ± 4	0.95 ± 0.03	9.45 ± 0.31	1.6 ± 0.2
0.26 ± 0.02	33	159 ± 3	1.07 ± 0.01	9.88 ± 0.11	21.8 ± 0.8
1.02 ± 0.01	9	183 ± 2	1.23 ± 0.01	10.57 ± 0.07	21.7 ± 0.5
2.55 ± 0.04	3	254 ± 3	1.32 ± 0.03	12.17 ± 0.27	54.7 ± 1.5
		San Joaquin River at Mud Slough			
1.79 ± 0.02[b]	20	740 ± 5	4.31 ± 0.03	9.40 ± 0.07	39.1 ± 0.0
2.04 ± 0.03	18	797 ± 6	4.58 ± 0.04	9.99 ± 0.08	40.9 ± 0.1
2.81 ± 0.05	13	848 ± 2	4.58 ± 0.02	9.99 ± 0.05	49.4 ± 0.4
4.39 ± 0.04	8	888 ± 6	4.50 ± 0.04	10.01 ± 0.10	58.3 ± 0.4

[a] Duplicates were run for each sample (av ± range). [b] Original sample.

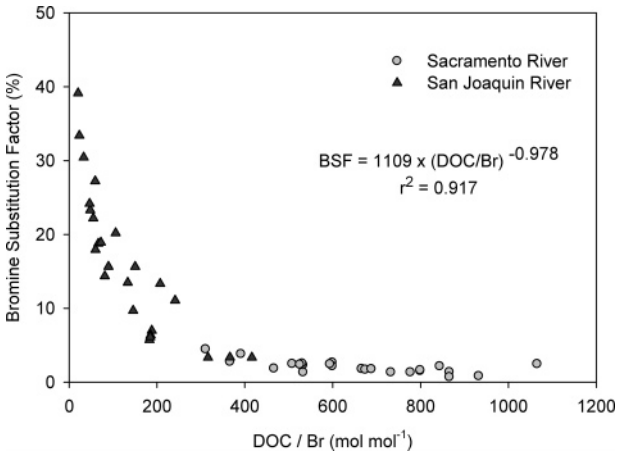

FIGURE 6. Bromine substitution factor increases exponentially with a decrease of the DOC/Br ratio.

increase in THM formation was mainly due to the changes in THM speciation, switching from chlorinated to brominated forms and increasing substitution from mono- to di- or tri-brominated species. The extra bromide in solution did not extensively increase the number of THM molecules in chlorinated waters. Considering the Br spiking test for water from the Sacramento River at Freeport (site 19), THMFP and BSF were significantly increased from 115 to 254 μg L^{-1} and from 2 to 55%, respectively, when the DOC/Br molar ratio decreased from 799 to 3. However, the molar basis STHMFP increased from 9.45 to 12.17 mmol mol^{-1}, indicating that only an extra three carbon atoms were active in forming THM per 1000 carbon atoms in solution. Similar results were obtained using waters from Mud Slough at Kesterson (site 35), but to a lesser extent.

Many studies have shown that Br increases DBP yields in treated waters (*13*). With DOC/Br molar ratios greater than 300, less than 5% of available sites (three sites in each THM molecule) is occupied by bromine atoms. When the DOC/Br molar ratio drops below 200, the incorporation increases exponentially with up to 40% of available sites occupied by bromine at a ratio around 20 (Figure 6). As the Br concentration increases, brominated THM species are formed preferentially over chloroform. Importantly, brominated species are generally considered to be more toxic than chlorinated species (*2*).

As compared to other studies using the same THMFP assay, the Sacramento River has a similar reactivity when compared to other sources, such as soil humic substances and agricultural drainage waters in the central Delta, which ranged from 75 −to 111 μg of THM per mg of C (*4*, *11*). Results suggested that different sources of DOC had a similar reactivity and that Br played a more important role in DBP formation. Our data indicated that the DOC/Br ratio at the San Joaquin River at Hwy 120 (site 23), the outflow of the San Joaquin River, had an average ratio of 30 ± 3, which favors the formation of more highly brominated species. Thus, special attention should be implemented to practices that control Br in the San Joaquin River.

Supporting Information Available

Tables of land uses of the 35 sampling sites in Sacramento and San Joaquin Rivers. This material is available free of charge via the Internet at http://pubs.acs.org.

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