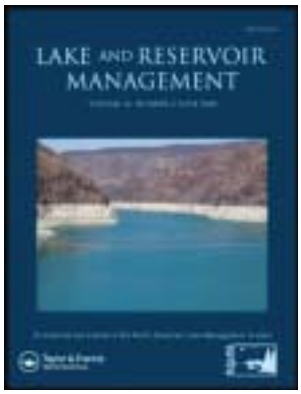

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How reservoirs alter drinking water quality: Organic matter sources, sinks, and transformations

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How reservoirs alter drinking water quality: Organic matter sources, sinks, and transformations

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Abstract

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Within reservoirs, production, transformation, and loss of dissolved organic matter (DOM) occur simultaneously. While the balance between production and loss determines whether a reservoir is a net sink or source of DOM, changes in chemical composition are also important because they affect DOM reactivity with respect to disinfection by-product (DBP) formation. The composition of the DOM pool also provides insight into DOM sources and processing, which can inform reservoir management. We examined the concentration and composition of DOM in San Luis Reservoir, a large off-stream impoundment of the California State Water Project. We used a wide array of DOM chemical tracers including dissolved organic carbon (DOC) concentration, trihalomethane and haloacetic acid formation potentials (THMFP and HAAFP, respectively), absorbance properties, isotopic composition, lignin phenol content, and structural groupings determined by ^{13}C nuclear magnetic resonance (NMR). There were periods when the reservoir was a net source of DOC due to the predominance of algal production (summer), a net sink due to the predominance of degradation (fall–winter), and balanced between production and consumption (spring). Despite only moderate variation in bulk DOC concentration (3.0–3.6 mg C/L), changes in DOM composition indicated that terrestrial-derived material entering the reservoir was being degraded and replaced by aquatic-derived DOM produced within the reservoir. Substantial changes in the propensity of the DOM pool to form THMs and HAAs illustrate that the DBP precursor pool was not directly coupled to bulk DOC concentration and indicate that algal production is an important source of DBP precursors. Results suggest reservoirs have the potential to attenuate DOM amount and reactivity with respect to DBP precursors via degradative processes; however, these benefits can be decreased or even negated by the production of algal-derived DOM.
[Supplemental materials are available for this article. Go to the publisher's online edition of Lake and Reservoir Management *to view the supplemental file.]*

Key words: algae, disinfection by-products, dissolved organic carbon, dissolved organic matter, haloacetic acids, trihalomethanes, water quality

Reservoirs are critical components of many drinking water supply systems; they can store water when supply exceeds demand, thereby allowing withdrawals during periods when demand exceeds supply. This allows water providers to meet peak demands and maximize supply yields and also provides both drought and flood protection. However, storage of water in reservoirs can also affect water quality. In particular, processes that affect the amount and composition of dissolved organic matter (DOM) in reservoirs can substantially alter the amount of disinfection by-products (DBPs) that form during drinking water treatment (Croue et al. 1999).

DBPs form when specific compounds within the DOM pool, commonly referred to as DBP precursors, react with

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disinfectants such as chlorine or ozone to form chlorinated or brominated compounds. Although disinfection is clearly beneficial and is required by federal and state regulations, some DBPs are carcinogenic or mutagenic and thus pose a significant health threat. Currently two classes of DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs), are regulated in many countries. With increasingly strict regulations on the concentrations of DBPs permissible in tap water, there is an increasing need to understand the sources of DBP precursors and particularly management actions that can reduce their occurrence (Cooke and Kennedy 2001). Despite the prevalence and importance of reservoirs to water supply worldwide, few studies have looked at the sources and processing of DBP precursors in these systems, and most of the studies used a mass balance approach to determine net changes in DBP precursor loads (Palmstrom et al. 1988, Stepczuck et al. 1998b, Nguyen et al. 2002, Bukavekas et al. 2007).

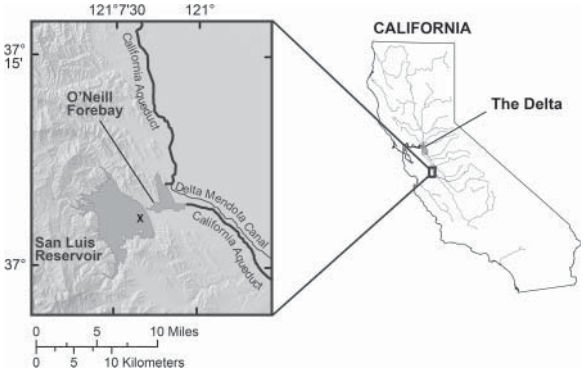

Figure 1.-Location of San Luis Reservoir, O'Neil Forebay, the California Aqueduct, and Delta Mendota Canal, CA, USA. X marks the reservoir sampling location.

DOM in reservoirs can be divided into 2 sources: (1) external (allochthonous) sources such as riverine inputs and catchment inflows, which comprise a myriad of terrestrial inputs, and (2) internally produced aquatic (autochthonous) sources, which comprise phytoplankton, periphyton, macrophyte and bacterial production, and DOM released from bottom sediments. In addition, processes such as microbial biodegradation and photolysis within the reservoir will lead to transformation and loss of DOM. Together, reservoir DOM production, transformation, and loss can alter both the overall concentration and composition of DOM, including the fraction of DOM that reacts to form DBPs.

Many chemical measurements are used to assess DOM composition and reactivity, and by examining these we can better discern DOM sources and processing and thereby identify primary factors affecting drinking water quality. For example, compared to terrestrial-derived organic material, aquatic-derived material tends to be lower in aromatic content and higher in aliphatic content, contains no lignin, and has a lower carbon to nitrogen ratio (C:N; Aiken et al. 1992, Mash et al. 2004, Rostad et al. 1997). Isotopic signatures of DOM can also be used to infer relative contributions of aquatic versus terrestrially derived materials (Finlay and Kendall 2007). Similarly, optical properties of DOM have been widely used to gain insight into microbial versus terrestrial sources (McKnight et al. 2001, Miller et al. 2009a), sediment release (Downing et al. 2008), and effects of biodegradation and photolysis (Spencer et al. 2009, Pellerin et al. 2010).

This study investigated changes in the amount and composition of DOM in San Luis Reservoir (SLR), an off-stream reservoir used to store excess winter and spring flows from the Sacramento–San Joaquin Delta (Delta) for both the California State Water Project (SWP) and the US Bureau of Reclamation's Central Valley Project (CVP). The main objectives were to (1) determine whether SLR was a net source or sink for DOC, (2) examine how DOM composition changed over time, (3) assess how the propensity of DOM to form DBPs changed over time, and (4) identify the dominant processes (aquatic production, biodegradation, photodegradation) affecting DOM concentration, composition, and reactivity. In addition to measuring DOC and DBP precursor concentrations, we used a suite of geochemical analyses to examine changes in DOM composition and reactivity and thereby identify sources and processes affecting the reservoir DOM pool. These analyses included determination of specific THM and HAA formation potentials; absorbance properties; lignin phenol content and composition; C and N stable isotopic compositions; XAD fractionation; and structural groupings determined using cross polarization, magic angle spinning (CPMAS) ^{13}C nuclear magnetic resonance (NMR).

Materials and methods

Site description

Jointly owned and operated by the California Department of Water Resources and the US Bureau of Reclamation, SLR is located near Los Banos, California (USA) at kilometer 113 (mile 70) of the California SWP (Fig. 1). With a storage capacity of 2.5×10^9 m^3 (2,027,835 ac-ft), SLR is the largest off-stream reservoir in the United States and a critical component of the state's water supply system. While the maximum depth of the reservoir is 63 m (280 ft), levels typically drop as low as 36 m (120 ft) during the summer, reducing its storage capacity to below 5.4×10^8 m^3 (440,000 ac-ft).

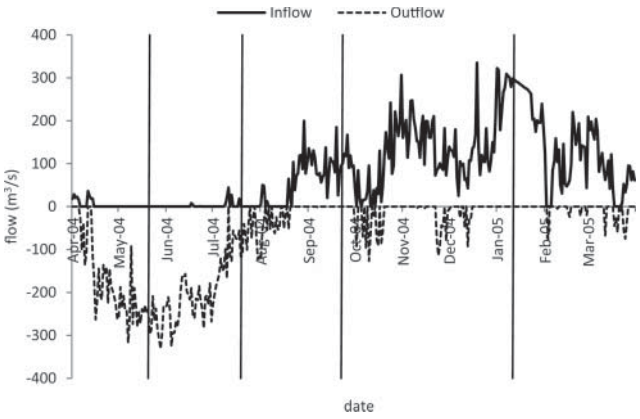

Figure 2.-Inflow and outflow water volumes for San Luis Reservoir during the period of study. Vertical black lines indicate sampling dates.

Inflows to SLR come predominantly from water pumped out of the Sacramento–San Joaquin Delta. Natural inflows from the reservoir's 220 km^2 (85 mi^2) watershed are insignificant relative to the reservoir's total capacity, accounting for $<1\%$ of total annual inflows (DWR 2001). SLR both receives water from and releases water to O'Neil Forebay via the Gianelli Pumping-Generation Plant located on the east side of the reservoir. In addition to receiving water releases from SLR, O'Neill Forebay receives Delta water from the H.O. Banks Pumping Plant via a 107 km (66.7 mi) stretch of the California Aqueduct (part of the SWP), and from the C.W. Jones Pumping Plant via the Delta Mendota Canal and the O'Neill Pump-Generation Plant (part of the CVP) located at the north eastern corner of the forebay (Fig. 1).

The Delta receives its water from the 140,000 km^2 (54,000 mi^2) watershed of the Sacramento and San Joaquin rivers. Total organic carbon (TOC) concentrations exiting the Delta typically range between 2 and 7 mg C/L, with highest concentrations occurring during the winter (http://cdec.water.ca.gov, Supplementary Information Figure S1). SLR is filled primarily during the fall and winter (Sep–May) when water and conveyance capacity are available. Average daily releases from SLR are highest in the spring and summer when water demands are the greatest (Fig. 2). Starting in April or May, water from SLR is released into O'Neill Forebay to meet water demands of users located south of the Delta. SLR also supplies water to the Santa Clara Valley Water District and the San Benito County Water District through the CVP's San Felipe Division on the west side of the reservoir. To generate energy, water can also be released from SLR to O'Neil Forebay during the day and then pumped back into the reservoir at night when energy is cheaper; however, this is not a frequent occurrence.

Table 1.-Sample dates and depths from which samples were composited.

Date	Composite	Depths (m)
20 May 2004	Upper	5 + 10 + 25
	Lower	40 + 60
19 Jul 2004	Upper	1.5 + 7.5 + 15
	Lower	33.5 + 23
22 Sep 2004	Upper	1 + 10 + 15
	Lower	25 + 35
11 Jan 2005	Upper	1 + 10 + 15
	Lower	30 + 40

Water sampling and processing

Sampling was conducted at SLR on 20 May, 19 July, and 22 September 2004 and 11 January 2005. Water samples were collected by boat near the dam about 1 km (0.62 mi) from the inlet–outlet structure (37°03′15″N, 121°05′24″W; Fig. 1). For each sampling date, water was collected from 5 discrete depths. Because some analyses were extremely time-intensive and costly, water was also composited across depths to reduce the number of samples; however, water samples collected from the upper and lower depths were kept separate to examine differences in DOM (Table 1, Supplementary Information Table S1).

Both filtered and unfiltered water samples were collected using submersible centrifugal pumps and high purity, plasticizer-free 0.5 inch Tygon tubing. Filtered water samples were passed through 10 μm and 0.2 μm membrane filters (Osmonics Memtrex, 0.25 m). Samples were collected into precombusted amber glass bottles or acid-washed Teflon containers with the following exceptions: dissolved inorganic carbon (DIC) samples were collected in 40 mL clear Environmental Protection Agency volatile organic compound (EPA VOC) vials containing several milligrams of copper sulfate to ensure there was no further biological activity, and δ^{13}C-DOC samples were collected and stored in precombusted 40 mL amber EPA VOC vials containing approximately 40 μL of 85% phosphoric acid. All VOC vials were filled until a positive meniscus formed, then tightly capped so that no headspace remained.

Samples for particulate organic material (POM) and chlorophyll were collected using a Go-Flow sampler and filtered within 4 h of collection using precombusted 0.3 μm glass fiber filters; the filters were placed on dry ice in the field and kept frozen until analysis. Large volume ($\sim$200 L) samples collected for DOM fractionation were stored in stainless steel soda kegs (19 L capacity), acidified to pH 2 with concentrated reagent-grade hydrochloric acid (HCl), and transported back to the lab where they were processed within 48 h. All other samples were immediately placed on ice and

transported back to the lab where they were refrigerated at 4 C until analysis.

Analytical methods

Upon arrival in the lab, samples for DOC concentration and ultraviolet absorbance (UVA) were acidified to pH 2 using reagent-grade concentrated HCl and analyzed within 3 d of collection. DOC concentration was measured using high temperature catalytic oxidation with a Shimadzu TOC-5000A TOC analyzer measuring nonpurgeable organic carbon (Bird et al. 2003). Each analysis represents the mean of 3 or more injections. Accuracy and precision for this method were within 3% of the measured value. Optical absorbance was measured between 200 and 800 nm at constant temperature (25 C) with a Cary 300 UV/VIS spectrophotometer using a quartz cell with 1.0 cm path length and distilled water as a blank (Saraceno et al. 2009). Specific UVA (SUVA) was calculated by dividing the absorbance at 254 nm by DOC concentration. Spectral Slope (S) was calculated using a nonlinear least squares curve-fitting technique on spectral ranges 275–295, 290–350, and 350–400 nm (Boss and Zaneveld 2003). The spectral slope ratio ($S_R = S_{275\text{-}295}{:}S_{350\text{-}400}$) was also calculated (Helms et al. 2008).

DBP formation potentials for THMs (THMFP) and HAAs (HAAFP) were determined for both filtered (0.2 μm) and unfiltered samples at the Metropolitan Water District of Southern California laboratory following US EPA Methods 551.1 and 552.2. Briefly, chlorine-dosing conditions involved a 48 h reaction time, pH buffered at 8.2, temperature held at 25 C, and final residual-free chlorine concentrations restricted to not less than 0.5 mg/L. THMFP included measurement of all 4 THM species (Cl_3CH, Br_3CH, $ClBr_2CH$, Cl_2BrCH), and HAAFP included a measurement of all 9 HAA species (ClAA, Cl_2AA, Cl_3AA, BrAA, Br_2AA, Br_3AA, BrClAA, $BrCl_2AA$, Br_2ClAA). Specific THMFP and HAAFP (STHMFP and SHAAFP, respectively) were calculated for filtered water by dividing by the sample DOC concentration determined just before DBPFP analysis with a Sievers 800 TOC analyzer, and are reported as mmol-DBP/mol-C. DOC measurements were consistently higher on the Seviers instrument compared to the Shimadzu (on average 0.4 mg C/L higher); however, this does not impact relative differences between STHMFP and SHAAFP within this dataset.

Concentration and carbon isotopic composition ($\delta^{13}C$) of DIC were obtained using an OI Analytical 1010 TOC analyzer interfaced with a Micromass IsoPrime continuous flow mass spectrometer according to a method modified after that of St. Jean (2003). Elemental and isotopic compositions of the POM isolates were determined using a Carlo Erba NA 1500 NCS Elemental Analyzer interfaced with a Micromass Optima mass spectrometer (Kendall et al. 2001), and C to N ratios (C:N) are reported on an atomic basis (mol-C/mol-N). Chlorophyll *a*, pheophytin *a*, cation, anion, and electrical conductivity data were measured using standard water quality analyses (Kratzer et al. 2004).

Column chromatography using Amberlite XAD-8 and XAD-4 adsorbent resins (Aiken et al. 1992) was employed to characterize the DOM as well as to provide sufficient amounts of solid organic material for isotopic, lignin, and solid state ^{13}C NMR analyses. The XAD-8 isolated material is commonly referred to as the hydrophobic acid fraction (HPOA), the XAD-4 material as the transphillic acid fraction (TPIA), and the unretained material as the hydrophilic fraction (HPIA; Croue et al. 1999). Elemental and isotopic compositions of C and N were determined on both the XAD-8 and XAD-4 fractions as described above for POM. Elemental and sulfur isotopic compositions were analyzed from a separate aliquot using reagents as described in Fry et al. (2002) and a standard sulfur column. Lignin phenol analysis was determined as described by Eckard et al. (2007). Previous analyses of XAD-8 and XAD-4 isolated DOM has shown that most of the lignin is isolated in the XAD-8 fraction (90% on average); thus, only XAD-8 was analyzed for lignin phenols (Eckard et al. 2007, Spencer et al. 2010). Solid state CPMAS ^{13}C NMR spectra were obtained for the XAD-8 isolates as described by Kraus et al. (2008).

Conservatively modeled vs. measured DOC concentrations

To determine if changes in DOC concentration were due to in-reservoir processes or due to the addition of new water from O'Neil Forebay, we compared measured reservoir DOC concentrations to concentrations calculated assuming conservative behavior. Conservative reservoir DOC concentrations were calculated each day (24 h time step) as

$$C_{x+1} = (V_x C_x \pm V_{in} C_{in} - V_{out} C_{out})/V_{x+1} \quad (1)$$

where V_x = initial reservoir volume, V_{in} = inflow water volume for the day, V_{out} = outflow water volume for the day, V_{x+1} = reservoir volume at the end of the day, C_x = the initial reservoir DOC concentration, and C_{x+1} = modeled DOC concentration at the end of the day.

The model was run for the 3 intervals between sampling dates: (1) 20 May–19 July, (2) 19 July–22 September, and (3) 22 September–1 January. Daily reservoir storage (V_x and V_{x+1}) and inflow (V_{in}) and outflow (V_{out}) volumes were obtained from the California Department of Water Resources (DWR) Division of Operations and Maintenance Operations Control Office (http://wwwoco.water.ca.gov). The starting reservoir DOC concentration for each model run was input

as the depth-weighted average DOC concentration measured within the reservoir itself. Inflow water DOC concentrations (C_{in}) were assumed to be the same as that measured at the Harvey O. Banks Pumping Station (Banks), located 106 km (66 mi) upstream of O'Neil Forebay. This assumption was based on the strong correlation between UVA at Banks and the O'Neil Forebay outflow when water was entering SLR from O'Neil between August 2005 and January 2006 ($R^2 = 0.92$). Daily DOC concentration data for Banks were obtained from the DWR California Data Exchange Center (http://cdec.water.ca.gov). Because the reservoir was well mixed, outflows were assumed to have no effect on reservoir DOC concentrations, and thus outflow DOC concentrations were input as the daily reservoir concentration (i.e., $C_{out} = C_x$).

Differences between the conservatively modeled (C_{mod}) and measured (C_{mes}) reservoir DOC concentrations were attributed to in-reservoir processes (i.e., $C_{mod} > C_{mes}$, net sink; $C_{mod} < C_{mes}$, net source; $C_{mod} = C_{mes}$, net balance).

Results and discussion

Water flow

Between the first 2 sampling dates, May 20 and July 19, there were virtually no water inputs to SLR (Fig. 2). Instead, this was a period of high outflow during which reservoir storage dropped 61%. Therefore, any changes in DOC concentration and composition that occurred during this period can be attributed to in-reservoir processes. Starting in mid-August there were substantial reservoir inflows. Between July 19 and September 22, storage first dropped to 5.5×10^8 m^3 (441,711 ac-ft) then increased to 7.6×10^8 m^3 (615,415 ac-ft); thus, at the time of the September sampling, about 28% of the reservoir water was from recent O'Neil inflows. Between September 22 and Jan 11, an additional 10.8×10^8 m^3 (873,149 ac-ft) were added to the reservoir, more than doubling reservoir storage. Taking into account outflows during this period, approximately 60% of the water in SLR at the time of the January sampling was added after the September sampling.

Stratification

Differences in DOM amount, composition, or reactivity by depth and/or date can indicate whether production, transformation, or consumption was occurring at specific locations within the water column or over time. However, frequent mixing and lack of stratification can obscure processes occurring at specific depths. At SLR, strong westerly winds commonly push water from the shallow west end to the deepest portion of the reservoir toward the east side near the dam. Gravity then pushes this water down, mixing surface water with water at great depth and preventing the formation of a thermocline (DWR 2001). Temperature and conductivity (Supplementary Information Figure S2) depth profile data confirmed the reservoir was not highly stratified during any of the sampling events. During the May and July samplings, there was some deep thermal structure in the lake, indicating it was not well mixed all the way to the bottom. During the September and January sampling events, both temperature and conductivity were constant with depth, indicating the reservoir was well mixed.

Chlorophyll a and nutrient data

Surface water (5 m) chlorophyll *a* and pheophytin *a* concentrations demonstrate that phytoplankton concentration was much greater in September compared to the other sampling dates (~30–50 vs. 0–10 μg/L, respectively; Supplementary Information Figure S3). Chlorophyll *a* concentrations were also higher in July (~10 μg/L) compared to March (~2 μg/L) and January (~0.6 μg/L). There was a notable decrease in reservoir nitrate concentrations (~0.15 mg NO_3-N/L per month during the spring and summer, indicative of algal and/or bacterial consumption. Decreases in reservoir N and phosphorus (P) at SLR accompanied by higher pH values in the summer are linked to algal blooms, typically dominated by cyanobacteria, in the reservoir (DWR 2001).

DOC concentration, THMFP and HAAFP

Depth-averaged DOC concentrations for May and July were similar at 3.1 mg/L, increased to 3.5 mg/L in September, and showed a slight decrease to 3.4 mg/L in January. There were no clear trends in DOC concentration by depth with the exception of September when concentrations were greater near the surface than at depth (Table 2, Supplementary Information Figure S4). This increase suggests algal production in surface waters contributed DOC during the summer.

Unfiltered DBP formation potential data were available for May, July, and January, and comparison of these data to the filtered water data showed that the particulate fraction was usually responsible for <5% of the unfiltered water THMFP and HAAFP. Exceptions to this were seen in July near surface (>15 m) samples for which POM accounted for about 15% of THM and 35% of HAA precursors, and in January where POM accounted for 18% of THM precursors in the deepest water sample (40 m). Unfiltered DBPFP data were not available for September. Subsequent discussion of DBPs pertains to the filtered water samples.

In contrast to DOC concentration, there were marked changes in THMFP and HAAFP by sampling date (Table 2, Supplementary Information Figure S4). Even with no substantial inflows and no measurable change in reservoir

Table 2.-San Luis reservoir DOC, DBP formation potentials, SUVA, spectral slopes, slope ratios, and isotopic composition of the dissolved and particulate pools by date and depth.*

Date	Depth (m)	DOC (mg/L)	THMFP (μmol/L)	HAAFP (μmol/L)	STHMFP (mmol-THM/mol-C)	SHAAFP (mmol-HAA/mol-C)	SUVA (L/mg-C m)	$S_{275–295}$ (1/10^{-3}nm)	$S_{290–350}$ (1/10^{-3}nm)	$S_{350–400}$ (1/10^{-3}nm)	S_R	DOC δ^{13}C (‰)	DIC conc. (mg/L)	DIC δ^{13}C (‰)	POM δ^{13}C (‰)	POM δ^{15}N (‰)	POM C:N (at.)
20 May 2004	5	3.28	nd	nd	nd	nd	3.13	18.11	18.48	17.94	1.01	−25.7	19.0	−7.5	−25.3	7.3	9.2
	10	3.34	1.36	0.41	4.53	1.35	3.09	18.08	18.46	18.14	1.00	−25.5	19.6	−8.1	−25.6	4.6	8.2
	25	3.19	1.23	0.38	4.09	1.26	3.17	16.89	17.83	17.71	0.95	−26.1	22.7	−8.9	−22.2	nd	14.0
	40	3.15	1.33	0.52	4.66	1.83	3.20	16.58	17.86	18.55	0.89	−25.8	21.7	−9.9	−26.2	nd	
	60	3.06	nd	nd	nd	nd	3.34	16.05	17.14	17.70	0.91	−26.1	24.2	−9.9	−26.7	nd	24.5
19 Jul 2004	1.5	3.16	1.63	0.97	5.46	3.23	2.96	19.55	19.27	18.86	1.04	−25.7	22.9	−7.9	−27.3	8.3	15.3
	7.5	3.16	1.59	1.04	5.41	3.53	3.00	19.58	19.44	19.23	1.03	−25.7	22.8	−8.0	−27.5	7.8	9.9
	15	3.20	1.68	0.96	5.81	3.31	2.93	18.77	18.96	18.69	1.01	−26.1	20.8	−8.3	−27.2	6.2	11.1
	23	3.15	1.58	1.15	5.44	3.96	2.95	18.86	19.16	19.18	0.98	−26.3	19.1	−7.1	−28.3	nd	9.9
	33.5	3.04	1.57	1.06	5.40	3.62	3.12	18.58	19.14	18.92	0.99	−25.4	17.5	−7.3	−27.0	nd	11.1
22 Sep 2004	1	3.61	1.86	1.79	6.25	6.00	2.48	20.59	19.90	21.71	0.95	−24.7	11.2	−3.5	−17.8	9.8	6.6
	10	3.62	1.79	1.60	6.29	5.61	2.46	19.07	19.25	21.00	0.91	−24.9	12.5	−4.8	−19.6	9.8	6.4
	15	3.42	2.04	1.81	7.41	6.55	2.60	19.93	19.40	21.19	0.94	−24.3	13.4	−4.5	−21.4	2.5	7.2
	25	3.34	1.88	1.49	6.88	5.46	2.67	19.63	19.48	21.28	0.92	−24.4	14.7	−5.8	−20.1	8.2	5.7
	35	3.34	1.85	1.55	6.62	5.53	2.25	19.69	19.51	21.25	0.93	−25.5	15.8	−6.1	−20.1	8.6	6.3
11 Jan 2005	1	3.40	1.75	0.89	5.96	3.04	3.16	18.03	18.06	19.55	0.92	−26.9	16.4	−10.9	−26.7	26.2	4.9
	10	3.29	1.86	0.93	6.32	3.14	3.18	17.61	18.12	20.50	0.86	−27.1	16.8	−11.6	−28.6	14.8	6.5
	15	3.26	1.65	0.88	5.64	3.00	3.16	17.77	18.34	20.16	0.88	−27.5	16.8	−11.3	−28.5	14.9	6.8
	30	3.37	1.59	0.89	5.40	3.00	3.02	17.10	18.06	20.10	0.85	−25.3	17.1	−11.7	−28.0	13.2	6.0
	40	3.47	1.63	0.89	5.58	3.05	2.96	18.01	18.66	21.56	0.84	−26.3	17.2	−11.7	−25.6	8.3	5.6

*nd: no data.

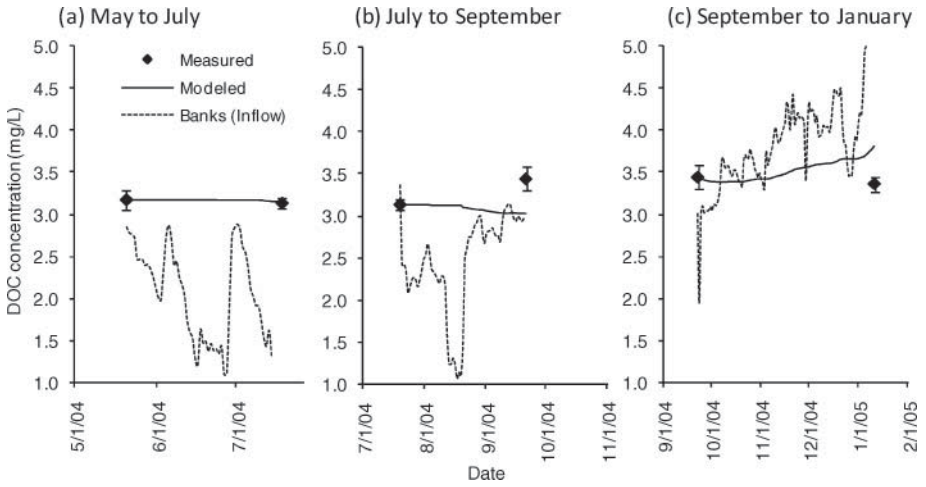

Figure 3.-Measured vs. modeled DOC concentrations at San Luis reservoir for the periods between sampling dates. Dashed line represents DOC concentrations of the inflow water as measured at the H.R.O. Banks Pumping Plant. Error bars indicate standard error associated with depth averaged DOC concentrations ($n = 5$).

DOC concentration, THMFP increased 23% from May to July and HAAFP increased 137%. By September, both THMFP and HAAFP increased an additional 17% and 60%, respectively, while DOC concentration increased only 10%. There were no clear trends in DBPFP by depth, although the highest HAAFP was measured near the surface (5 m) in September.

Measured vs. modeled DOC concentrations

Comparison between conservatively modeled and measured reservoir DOC concentrations indicated whether the reservoir was a net sink or source for DOC. During the 60 d between 20 May and 19 July, there were virtually no inflows to SLR (Fig. 2). Thus, based on the assumption that outflows have no effect on reservoir DOC pools, the conservative model showed no changes in DOC concentration for this period (Fig. 3). Measured DOC concentration within the reservoir also did not change significantly between these 2 dates, indicating that during this period the reservoir was neither a net sink nor a net source for DOC.

Starting in late August, there were substantial inflows to SLR. Measured reservoir DOC concentrations for the 65 d period between 19 July and 22 September started at 3.1 mg/L and increased to 3.5 mg/L. During this time, DOC concentrations at Banks generally ranged between 1 and 3 mg/L (Supplementary Information Figure S2); therefore, addition of this water with lower DOC can not account for the measured increase in reservoir DOC concentration. Modeled DOC concentrations showed a steady decline during this period to 3.0 mg/L (Fig. 3). Thus, in-reservoir processes during this period seem to have caused the net increase in DOC concentration, indicating the reservoir was a net source for DOC.

Between 22 September and 11 January, SLR was being refilled, leading to a ~2.5-fold increase in reservoir storage. During this 111 d period, the model predicted an increase in reservoir DOC concentration from 3.5 to 3.8 mg/L due to inflow of water containing higher DOC concentrations (Fig. 3). However, measured SLR DOC concentrations on 11 January were 3.4 mg/L, significantly lower than the predicted 3.8 mg/L, indicating that in-reservoir processes were a net sink for DOC.

DOM composition

Absorbance data: SUVA, spectral slope (S) and slope ratio (S_R)

SUVA values, obtained by normalizing absorbance at 254 nm to DOC concentration, provide a relative index for the capacity of bulk DOC to absorb light at this wavelength. SUVA values have been shown to strongly correlate with aromatic content (Weishaar et al. 2003 and references therein). Differences in S values are also sensitive to changes in DOM composition; higher values are associated with lower aromaticity and lower molecular weight, while lower values are associated with higher aromaticity and higher molecular weight (Blough and Del Vecchio 2002). Because recently produced DOM derived from algae and bacteria has lower aromatic content and molecular weight than vascular plant-derived DOM that has undergone degradation, differences in SUVA and S can be used to infer DOM source (Mash et al. 2004, Helms et al. 2008). However, studies have

also shown that photoexposure can affect SUVA, S, and S_R values (Miller et al. 2009b, Spencer et al. 2009), confounding interpretation.

At SLR, SUVA values decreased slightly between May (3.2 $\pm$ 0.1 L/mg-C m) and July (3.0 $\pm$ 0.1 L/mg-C m), followed by a substantial decrease in September (2.6 $\pm$ 0.1 L/mg-C m; Table 2). Values for $S_{290\text{-}350}$ throughout the water column were higher in July and September (19.0–19.9 $\times$ 10^{-3} nm) compared to May and January (17.1–18.7 $\times$ 10^{-3} nm). These trends point toward a greater contribution from autochthonous production of lower aromatic, lower molecular weight material during the summer. In September, lower SUVA values and higher S values measured in the surface samples compared to depth suggest production of authochthonous, low aromatic DOM in the photic zone. By January, SUVA values increased to 3.1 $\pm$ 0.1 L/mg-C m and $S_{290\text{-}350}$ decreased to 18.2 $\times$ 10^{-3} nm. These changes likely reflect the addition of Delta-derived DOM from the California aqueduct, in which SUVA values ranging between 3–6 L/mg-C m have been measured (Kraus et al. 2008).

Irradiation can decrease SUVA due to oxidative cleavage of covalent bonds; however, $S_{275\text{-}295}$ values generally increase while $S_{350\text{-}400}$ decrease, leading to higher S_R values upon photoexposure (Helms et al. 2008, Spencer et al. 2009). Here, S_R values showed little variation (0.8–1.0) while $S_{350\text{-}400}$ values increased over the summer, suggesting that changes in the chromophoric DOM pool due to photoexposure were masked by production of new DOM.

Specific disinfection by-product formation

Normalizing THMFP and HAAFP to DOC concentration (STHMFP and SHAAFP, respectively) provides an indication of DOC reactivity on a molar basis with respect to the formation of these 2 classes of DBPs. Both STHMFP and SHAAFP were significantly lower in May (4.4 $\pm$ 0.3 mmol-THM/mol-C and 1.5 $\pm$ 0.3 mmol-HAA/mol-C) and higher in September (6.7 $\pm$ 0.5 mmol-THM/mol-C and 5.8 $\pm$ 0.5 mmol-HAA/mol-C) compared to the samples collected in July (5.5 $\pm$ 0.2 mmol-THM/mol-C and 3.5 $\pm$ 0.3 mmol-HAA/mol-C) and January (5.8 $\pm$ 0.5 mmol-THM/mol-C and 3.0 $\pm$ 0.1 mmol-HAA/mol-C; Table 2, Supplementary Information Figure S5). Thus, during spring and summer there was a substantial increase in the DBP precursor content of the DOM pool, which can be attributed, at least in part, to in-reservoir processes. The subsequent drop in both STHMFP and SHAAFP in January was likely due predominantly to mixing of the reservoir DOM pool with inflow water DOM because biodegradation can lead to an increase in STHMFP and SHAAFP (Pellerin et al. 2010).

XAD fractionation and characterization

The percent of the bulk DOC pool isolated by the XAD-8 (HPOA) and XAD-4 (TPIA) resins ranged from 37 to 53% and from 16 to 26%, respectively (Table 3). The total DOM fraction isolated by both resins (67 $\pm$ 7%, n = 8) was considerably higher than has been reported for aquatic systems with substantial autochthonous inputs (~30%) and closer to those reported for rivers dominated by terrestrial-derived or highly processed DOM (~80%; Aiken et al. 1996, Mash et al. 2004, Nguyen et al. 2005).

The fraction of XAD-8 and XAD-4 isolated material in September (~55% of DOM) was considerably lower compared to the other 3 sampling dates (~70% of DOM), which indicates a higher proportion of hydrophilic, unretained material (HPIA). Similarly, the upper depth composites showed a greater proportion of unretained HPIA in May, July, and September compared to the lower depths (Table 3). These differences are likely a reflection of the production of algal-derived DOM in surface waters during the summer, which caused an increase in the nonhumic fraction with a concomitant decline in the fraction of humic-like DOM.

Both the XAD-8 and XAD-4 isolated fractions were analyzed for %C,%N,%S, C:N, δ^{13}C, δ^{15}N, and δ^{34}S (Table 3, Supplementary Information Table S2). Little variability was observed in these parameters with the exception of the September δ^{13}C values for both fractions, which were significantly higher (~1.1‰) than the other 3 sampling dates. This increase most likely reflects release of aquatic-derived DOM produced from the δ^{13}C enriched DIC pool. However, photo-oxidation of DOM has also been shown to increase δ^{13}C-DOC values and may contribute to the observed enrichment in this study (Opsahl and Zepp 2001, Spencer et al. 2009).

The C:N values in the XAD-8 (32 $\pm$ 3) and XAD-4 (19 $\pm$ 2) isolates were very similar to measurements in Arizona reservoirs (Mash et al. 2004) and fall between allochthonous and autochthonous endmembers (Aiken et al. 1996). The consistency in XAD C:N ratios even in September suggests that DOM production by algae may not significantly affect the hydrophobic fraction isolated on the columns. Much of the recently produced DOM from authochthonous production comprises the unrecovered hydrophilic fraction (Nguyen et al. 2005), and this was seen in the increase in this unretained pool.

The XAD-8 material was analyzed by ^{13}C NMR to look more closely at structural changes in the DOM pool (Table 3). As was seen with many of the other compositional parameters, similar structural distributions were found across all 4 sampling dates, with the exception of September when there was a higher heteroaliphatic and anomeric content

Table 3.-Percent DOC isolated on XAD-8 and XAD-4 resins and elemental composition, isotopic composition, and structural groupings determined by ^{13}C NMR and lignin data for the XAD-8 isolate.*

Date	Depth	XAD-8 (%*C*)	XAD-4 (%*C*)	C (%)	N (%)	S (%)	C:N (at.)	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	$\delta^{34}S$ (‰)	Aliphatic (%)	Hetero-aliphatic (%)	Anomeric (%)	Aromatic (%)	Carboxyl (%)	Carbonyl (%)	Lignin Σ (mg/L)	lignin λ (mg/100 mg-OC)
20 May 2004	Upper	46	22	50.1	2.2	1.6	26.6	−26.9	2.9	−4.2	47.6	15.6	4.5	19.4	11.4	1.6	6.97	0.20
	Lower	51	22	52.5	1.9	1.8	32.7	−27.1	2.3	−4.2	47.4	15.9	4.7	19.8	10.7	1.5	8.95	0.29
19 Jul 2004	Upper	45	23	53.3	1.9	1.9	32.5	−26.9	2.7	−4.1	48.8	15.7	4.4	18.8	10.8	1.5	4.22	0.13
	Lower	45	26	53.2	1.9	1.6	32.6	−27.1	2.7	−3.3	49.0	15.2	4.2	18.9	11.2	1.5	4.27	0.14
22 Sep 2004	Upper	37	16	51.8	1.8	1.3	33.8	−26.2	3.4	−1.1	46.7	18.9	4.8	17.3	10.9	1.3	4.10	0.12
	Lower	43	18	52.1	1.8	1.5	33.8	−26.5	3.0	−3.1	47.3	18.6	5.2	18.3	9.2	1.5	3.55	0.11
11 Jan 2005	Upper	46	26	53.4	1.8	2.0	34.4	−27.0	2.2	−4.3	46.4	15.9	5.1	20.9	10.0	1.7	5.89	0.17
	Lower	46	25	54.9	2.0	2.0	31.8	−26.9	2.4	−3.8	44.3	15.7	5.0	20.8	11.8	2.3	7.02	0.20

*For elemental and isotopic composition of the XAD4 material see supplementary information.

(23.8 ± 0.1%, $n = 2$) compared to the other 3 sampling dates (20.3 ± 0.6%, $n = 6$), in addition to a decline in aromatic content (17.8 ± 0.7% vs. 19.8 ± 0.9%). A higher proportion of heteroaliphatic and anomeric moieties is primarily associated with production of carbohydrates, lipids, and proteins, which in September likely are contributed from aquatic-derived DOM that has undergone little biochemical transformation.

Because lignin is produced only by vascular plants, differences in the total concentration (Σ_8, sum of 8 lignin monomers in μg/L) as well as C-normalized content (Λ_8, mg/100 mg OC) can distinguish between vascular plant-dominated sources versus phytoplankton-derived sources for DOM (Hernes and Benner 2003). SLR has a steep shoreline, and rapid changes in reservoir water levels discourage macrophyte growth at the reservoir margins; thus, in-reservoir lignin production can be assumed to be negligible. Between May and July, when there were minimal inflows to SLR and no change in DOC concentration, the decrease in Σ_8 from ~8 to 4 μg/L signifies that approximately half of the lignin phenol pool was degraded over this 2 month period. The simultaneous decrease in carbon-normalized lignin phenol yields (Λ_8) indicates that either there was preferential loss of lignin phenols relative to the bulk DOC pool or that any loss of the total DOC pool due to degradation was balanced by production of nonlignin containing algal-derived DOM (Table 3). Photooxidation is known to lead to oxidation of aromatic compounds, including lignin (Spencer et al. 2009).

Between July and September there was only a small decrease in both Σ_8 and Λ_8 (Table 3), possibly explained by the 28% increase in reservoir storage capacity that added water from the Delta containing higher Σ_8 and Λ_8 (Eckard et al. 2007). Similarly, between September and January the increase in reservoir water Σ_8 (4–6.5 μg/L) and Λ_8 (0.1–0.2 mg/100 mg OC) reflects reservoir inflows of Delta-derived water that increased reservoir storage capacity more than 2-fold.

Isotopic data

The stable isotope composition of DIC (δ^{13}C-DIC), DOC (δ^{13}C-DOC), and POM (δ^{13}C-POM, δ^{15}N-POM) were determined to provide additional information about DOM processing (Table 2). In surface waters, the concentration and composition of DIC is primarily controlled by addition or removal of dissolved CO_2 by biological processes and mixing of water sources. Simultaneous measurement of DIC concentration and δ^{13}C-DIC reduces the ambiguity associated with interpreting changes in DIC concentration. For example, the conversion of DOC and POC with a low δ^{13}C composition (−25 to −30‰) to CO_2 by decomposition will cause a decrease in δ^{13}C-DIC values with a concomitant increase in DIC concentration. Photosynthesis will have an opposite effect; DIC concentrations will decrease as aqueous CO_2 is utilized for primary production, and δ^{13}C-DIC should increase as lower-mass $^{12}CO_2$ is preferentially taken up relative to $^{13}CO_2$ (Finlay and Kendall 2007). Therefore, changes in DIC concentration and δ^{13}C can indicate the net balance between photosynthesis and respiration; however, the amount and δ^{13}C of DIC can also be affected by mixing between waters of different composition.

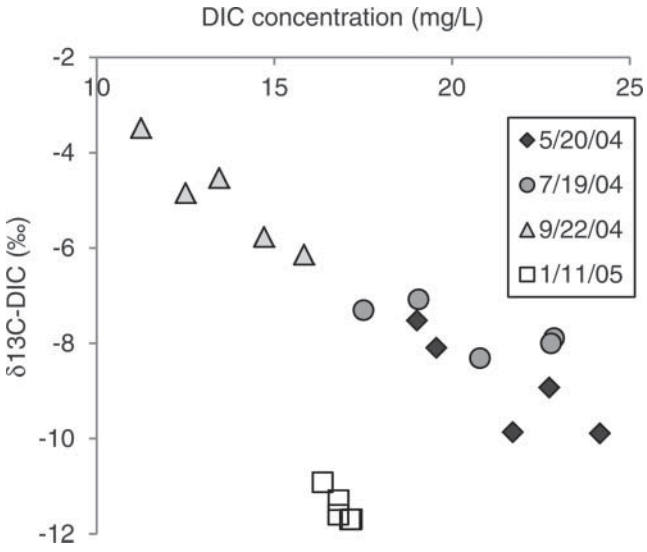

Figure 4.-Dissolved inorganic carbon (DIC) concentrations vs. δ^{13}C-DIC values. For data by depth see Table 3.

Comparing SLR samples collected in May, July, and September, DIC concentrations decreased and δ^{13}C-DIC values increased over time, indicative of net photosynthesis, particularly during July to September (Fig. 4). The strong negative correlation ($R^2 = 0.89$, $P < 0.001$, $n = 15$) between DIC concentration and δ^{13}C-DIC across these 3 months suggests biological processes rather than inputs account for the observed changes. September measurements yielded notably high δ^{13}C-DIC indicative of high net rates of photosynthesis compared to respiration. In contrast, January measurements were distinctly different, which likely reflects the addition of new inflow waters that had a more negative δ^{13}C-DIC and greater DIC concentration associated with the decomposition of DOM (Finlay and Kendall 2007). However, the shift in the January δ^{13}C-DIC values also may be attributed to net in-reservoir decomposition of DOM between September and January. In September, DIC concentrations were lower and δ^{13}C -DIC values were higher near the surface compared to depth, further evidence of significant algal production in the photic zone. In contrast, elevated DIC concentrations in July surface waters suggest that production of DIC by respiration was greater than its

uptake by photosynthesis. The absence of higher δ^{13}C-DIC near the surface in July supports the hypothesis that any increase in δ^{13}C-DIC due to photosynthesis at this time was largely balanced by the release of DIC with a lower δ^{13}C from decomposition.

Higher δ^{13}C-DOC values in the September surface waters (<30 m) compared to depth and compared to May and July support the addition of DOC from autochthonous production over the late summer (Table 2). The addition of new DOC from photosynthesis occurring within the water column would be expected to have higher δ^{13}C values reflective of the ^{13}C-enriched DIC pool (-5 to -10‰). However, photodegradation can also contribute to increasing δ^{13}C-DOC values (Opsahl and Zepp 2001, Spencer et al. 2009). In January, lower δ^{13}C-DOC values were likely due to the addition of allochthonous DOM in inflow waters, while the higher values at depth likely reflect release of DOM from bottom sediments.

In SLR, sources of POM can be categorized into autochthonous- (plankton, bacterial, and detritus) and terrestrial- (soil organic matter and terrestrial plant) derived material, which can be distinguished by C:N ratio and C and N isotopic compositions. The C:N ratio of plankton and bacteria falls between 5 and 8 while that of terrestrial plants is generally >15 (Finlay and Kendall 2007). Although δ^{13}C-POM values from all sources are largely overlapping, δ^{13}C values of phytoplankton are often somewhat higher compared to materials from terrestrial and bacterial sources because they reflect photosynthetic uptake up of the ^{13}C-enriched DIC pool contained in natural waters (Finlay and Kendall 2007). In SLR, δ^{13}C-DIC values were about 16‰ higher than δ^{13}C-DOC values. For nitrogen, the δ^{15}N values of terrestrial POM sources usually fall into a restricted range between 0 and 7‰ while the δ^{15}N of aquatic POM sources may range between -15 and $+20$‰ (Finlay and Kendall 2007).

For most samples, POM C:N values were low (<10; Table 2), indicating the reservoir POM pool was made up predominantly of phytoplankton and bacteria rather than terrestrial-derived particulates. In July, lower δ^{13}C-POM values compared to May suggests the presence of heterotrophic bacteria that obtain their C from the DOC pool (about -25‰) as opposed to algae that obtain their C from the DIC pool (about -10‰). In September, the low POM C:N ratio (5–7) accompanied by higher δ^{13}C-POM values (-17 to -20‰) supports other data, indicating there are significant algal populations in the reservoir. In particular, there were notably low C:N values and high δ^{13}C-POM values near the surface, another indication of algal POM that has derived its C from the more ^{13}C-enriched DIC pool (-5 to -10‰).

Reservoir DOM production versus consumption

Reservoirs are complex biogeochemical systems in which production, transformation, and loss of organic matter occur simultaneously. The net effects of these processes are determined by a number of factors, including inflow DOM quantity and composition, algal and bacterial activity, nutrient availability, temperature, and solar radiation. Because many of these factors vary by season, temporal differences in reservoir DOM processing are expected.

Examination of DOM amount and composition in SLR demonstrated that although there was only moderate variation in bulk DOM concentration (3.0–3.6 mg C/L), there were significant changes in its composition. Furthermore, changes in DOM composition greatly affected its reactivity with respect to DBPFP, demonstrating that the DBP precursor pool is not necessarily coupled to the bulk DOM pool. The decoupling of these pools is a consequence of the substantial loss of terrestrial-derived DOM entering the reservoir from the Delta, concurrent with substantial production of new DOM by aquatic sources. In addition, transformation of existing DOM by both biodegradation and photodegradation was occurring.

Previous studies that have examined fluxes of DOC and DBP precursors in reservoirs and lakes have also found that reservoirs can act as either a source (Palmstrom et al. 1988, Karimi and Singer 1991, Stepczuck et al. 1998b) or sink (Nguyen et al. 2002, Garvey and Tobiason 2003, Bukavekas et al. 2007). The time frame over which a study is conducted greatly impacts findings due to both seasonal and hydrologic controls on DOM budgets. Our finding that SLR seems to be a source of DOC and DBP precursors during the summer due to high phytoplankton activity, and a sink during the winter when degradative processes predominate, is similar to findings by Stepczuck et al. (1998b) for a reservoir in New York. Below, we discuss the balance between DOM degradation and production for 3 different periods.

Spring (May-Jul): Changes in DOM composition between May and July can be attributed solely to in-reservoir processes because there were virtually no inflows to SLR during this period. Although there was no net change in reservoir DOC concentration, data indicate simultaneous degradation and production of DOM, resulting in a marked increase in the DBP precursor pool: THMFP increased 23% while HAAFP increased 137%.

The almost 50% loss of lignin phenols during this period was one of the key indicators that degradation of allochthonous DOM occurred. Lignin is produced exclusively by vascular plants, and thus its decrease reflects loss of DOM entering the reservoir from upstream sources. The decline in the

total amount of lignin during a period when there was no change in DOC concentration translated into a decrease in carbon-normalized lignin yields, Λ_8 (Table 3). The decrease in lignin amount and content can be attributed to microbial and photodegradation combined with the addition of autochthonous, nonlignin-containing DOM from phytoplankton during this period.

Further evidence for the occurrence of bacterial respiration and degradation of allochthonous DOM during the spring include high DIC concentrations in surface waters and a decrease in δ^{13}C-POM. Evidence for simultaneous contributions of algal-derived material to the DOM pool between May and July includes increasing chlorophyll *a* and pheophytin *a* concentrations, decline in SUVA, and an increase in *S* values. Previous studies have demonstrated that these trends are associated with autochthonous production of DOM (McKnight et al. 2001, Mash et al. 2004).

Summer (Jul-Sep): Measured versus modeled DOC concentrations show that between July and September, SLR was a net source for DOC, and other data suggest a shift toward a greater proportion of algal-derived material. There was a greater increase in THMFP (17%) and HAAFP (60%) compared to DOC concentration (10%), indicating that in-reservoir processes increased the propensity of the DOC pool to form DBPs. Because reservoir storage increased about 30% during this period, some of the changes in DOM composition may be attributed to and/or offset by the addition of new material in inflow waters; however, changes in DOM composition along with ancillary data point to the addition of algal-derived DOM within the reservoir itself.

At SLR, the summer is a period of warm temperatures and high solar radiation that promotes algal and microbial activity as well as photooxidation (Mash et al. 2004). As in the spring, the decline in lignin phenol concentration, Σ_8, during this period again indicates loss of allochthonous DOM, and the concomitant decline in Λ_8 points toward the contribution of aquatic-derived, nonlignin-containing DOM. Previous work has shown that Σ_8 in water exported from the Delta range between 4 and 20 μg/L (Eckard et al. 2007); thus, reservoir inflows would be expected to increase reservoir Σ_8.

The shift from terrestrial-derived DOM toward more aquatic-derived DOM is corroborated by decreases in SUVA, aromatic content, and XAD-8 fractions, along with increases in $S_{350\text{-}400}$, δ^{13}C-DOC, and heteroaliphatic and anomeric content. There were low DIC concentrations and high δ^{13}C-DIC values in the September samples, as would be expected during a period of elevated algal production. Furthermore, in-reservoir algal DOM contributions were indicated by higher DOC concentrations, lower SUVA, lower DIC concentrations, higher δ^{13}C-DIC, higher δ^{13}C-POM, decreased XAD-8 fraction, and lower aromatic content in surface waters compared to those at depth, although the reservoir was not stratified at this time. High algal production over the summer is also supported by greater chlorophyll *a* and pheophytin *a* concentrations in surface waters in July and September. Additionally, higher δ^{13}C-POM and lower POM C:N values indicate an increase in the algal fraction of the POM pool.

Fall–Winter (Sep-Jan-May): Measured versus modeled DOC concentrations between September and January indicate that SLR was a net sink for DOC in the fall and winter. Because reservoir storage capacity more than doubled during this period, it can be inferred that changes in DOM composition were substantially affected by the inflow of a new pool of DOM. However, the addition of inflow waters cannot explain the observed changes. For example, the decrease in SHAAFP (48%) can only be partially attributed to the addition of DOM from O'Neil Forebay, which had SHAAFP values of about 4 mmol-HAA/mol C (T. Kraus, unpublished data). Most likely there was degradation of both existing in-reservoir DOM and newly added DOM during this period, particularly considering that some of the DOM added during the summer from algal production likely was highly labile.

The composition of reservoir DOM in May compared to other sampling periods suggests that reservoir processes occurring over the winter reduce the DBP precursor pool. In particular, both STHMFP and SHAAFP were notably lower in May compared to January. Nguyen et al. (2002) also reported losses of THM and HAA precursors during reservoir residence time. Similarly, the Ohio River was found to be a net sink for THM precursors due to the predominance of bacterial respiration over photosynthesis (Jack et al. 2002). At SLR during winter, cooler temperatures and lower solar radiation are less favorable to photoplankton activity, as was reflected by the lower chlorophyll *a* concentrations measured in January.

Algae as a source of DBP precursors

While there is conflicting evidence regarding whether DOM produced by algae is more or less prone to forming DBPs per unit C versus terrestrial sources, it is well-established that algae are a source of DOM containing DBP precursors (Wardlaw et al. 1991, Plummer and Edzwald 2001). Differences in DBP precursor content of algal-derived DOM arise from a combination of factors, including algal species, growth stage, release of extracellular material versus particulate cellular material, and environmental processing of algal-derived compounds (Jack et al. 2002, Nguyen et al. 2005, Huang et al. 2009). Many lines of evidence indicate that algal production contributed significantly to DOM in SLR,

particularly over the summer. Higher STHMFP and SHAAFP found in summer suggest that DOM recently contributed by phytoplankton production has a higher propensity to form DBPs, particularly HAAs, than allochthonous inputs. This notion is supported by previous studies that showed algal production, algal senescence, and possibly photolysis all play a role in increasing DBPFP (Jack et al. 2002).

Results from this and other studies clearly illustrate that DOM derived from phytoplankton production contributes significantly to the DBP precursor pool (Jack et al. 2002). Furthermore, algal growth in lakes and reservoirs is also an issue because it can impact taste, odor, and toxicity as well as treatment efficacy (Cooke and Kennedy 2001). However, little is known about the fate of *in situ* production. Fresh algal-derived DOC and POC are highly bioavailable (Nguyen et al. 2005) and thus can be rapidly degraded in the environment; therefore, the impact of DOM from algal production may depend on travel time to water intakes. If travel time to drinking water intakes is long, then environmental processes may moderate affects on drinking water quality. Future studies that take into account algal and bacterial species composition and characterize how they change both over time, and with depth, will further advance our understanding of how phytoplankton impacts drinking water quality.

Conclusions and implications

A more complete understanding of how reservoirs influence water quality needs to consider variability in DOM composition related to sources and processing. This is highlighted in SLR, where despite moderate variation in DOM concentration (3.0–3.6 mg/L), significant changes in DOM composition and DBP formation occurred. These changes resulted from appreciable degradation of Delta-derived DOM entering the reservoir and its replacement by autochthonous sources.

In California, the Sacramento San Joaquin Delta is a major source of drinking water, which is a major impetus toward identifying management actions that will lower DOC concentrations to improve the quality of water entering the SWP and local utilities. This study demonstrates that reservoir storage has the potential to attenuate Delta-derived DOM and DBP precursors via degradative processes over a period of a few months or less; however, these benefits can be negated, particularly during the summer, by the production of algal-derived DOM. Moreover, increases in the propensity of the DOM pool to form THMs and HAAs appear to be linked to the addition of algal-derived material.

The strong link between algal production and increases in both DOM amount and reactivity points to the need for reducing nutrient loadings to diminish algal growth, (Stepczuck et al. 1998a, 1998b, Bukavekas et al. 2007). Other factors that clearly will affect reservoir DOM cycling include temperature, solar radiation, and residence time (Nguyen et al. 2002, Mash et al. 2004). For example, longer water residence times during periods where respiration exceeds photosynthesis may provide an opportunity for environmental processing of DOM, which may reduce the DBP precursor pool (Jack et al. 2002).

This study also highlights the disconnect between bulk DOC concentration and the potential for this material to form DBPs found in other studies (Stepczuk et al. 1998b). Furthermore, our results are consistent with other studies that found that precursor sources and processing differ for THMs and HAAs (Kraus et al. 2008). Specifically, this study and others (Chen et al. 2008, Hong et al. 2008) provide evidence that DOM produced by algae is particularly reactive with respect to HAAs. This emphasizes the need to incorporate determination of HAAs and other types of DBPs along with THMs in future studies of watershed DBP precursor sources.

Incorporating *in situ* measurements of DOM amount, quality, source, and propensity for DBP formation (as is now possible) into real-time reservoir monitoring programs may permit active management appropriate for maximizing drinking water quality. For example, recent studies have demonstrated the promising use of absorbance and fluorescence to monitor both DOM amount and composition (Downing et al. 2008, Kraus et al. 2010, Pellerin et al. 2011). Similar tools have been developed that can determine algal biomass and pigment group (a surrogate for speciation). These data can be used to identify effective management actions such as selective withdrawal, water diversions, nutrient control, and algaecide applications. Continuous data of this type are also useful for identifying seasonal and long-term changes in reservoir water quality.

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