Tracing sources of nutrients fueling *Microcystis* blooms in the Sacramento-San Joaquin Delta using a multi-fingerprinting approach

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Abstract

Twelve sites in the Sacramento-San Joaquin Delta which represented different habitats from shallow water brackish embayment to deep freshwater channel and experience regular *Microcystis* blooms were sampled biweekly in the summer of 2007, and 5 were again sampled biweekly in the summer of 2008. As part of a pilot study, samples were analyzed for the stable isotopic compositions of particulate organic matter (POM), nitrate (NO3), dissolved organic carbon (DOC), and water, in addition to the normal suite of chemical and biological parameters. DSM2 modeling output proved very useful in evaluating how much of the temporal variability was due to tides and flow, and allowed us to compare chemical and isotopic indicators of water sources with modeled percentages of water sources. The POM, NO3, and water isotopic measurements proved useful for identifying sources of organic matter, NO3, and water; there was insufficient DOC-$\delta^{13}C$ data to fully assess its usefulness. The main conclusions from this study are that (1) Sacramento River and San Joaquin River water and nutrients are isotopically distinguishable; (2) the dominant source of NO3 to the Delta sites studied is the San Joaquin River; (3) most of the NH4 at the study sites is derived from the Sacramento River; and (4) NH4, not NO3, is the dominant source of N fueling the *Microcystis* blooms in the Delta in the summers of 2007 and 2008.

Introduction

This report describes the data and findings from a small pilot study funded by the California DWR that was piggybacked onto the CALFED project "Biomass and toxicity of a newly established bloom of the cyanobacteria *Microcystis aeruginosa* in the Sacramento-San Joaquin Delta and its potential impact on beneficial use". The purpose of this low-budget project was to investigate whether the addition of source and process information from the analysis of POM samples for $\delta^{13}C$, $\delta^{15}N$, and C:N and the analysis of DOC samples for $\delta^{13}C$ would help identify (1) the source of the *Microcystis* biomass (internal island or external rivers), (2) the source of nitrogen utilized by *Microcystis*, and (3) if *Microcystis* affects the quality of the dissolved organic carbon available for the microbial food web at high and low frequency time scales. This report will focus on the first and second questions since many of the DOC sample bottles cracked and were lost in a refrigerator malfunction before they could be analyzed. As an attempt to make up for this unfortunate loss of DOC samples, all the archived water samples were analyzed for $\delta^{18}O$ and $\delta^{2}H$, and selected archived nitrate samples were analyzed for $\delta^{15}N$ and $\delta^{18}O$, to improve our ability to answer the first two questions.

Applications of natural abundance stable isotope techniques to tracing sources and processes in watersheds began in the 1970s and have increased dramatically over the last decades (Kendall and McDonnell, 1998). Good recent reviews chapters for using isotopes to trace sources and sinks of organic matter and nutrients include Finlay and Kendall (2007) and Kendall et al. (2007). In the last 20 years, there have been several isotopic studies of the sources and processes affecting NH4 and/or NO3 in estuaries (e.g., Cifuentes et al. 1989; Sebilo et al. 2006; York et al. 2007; Wankel et al., 2009), including ones conducted by the USGS in the San Joaquin River (Kratzer et al., 2004; Kendall et al., 2008a), San Francisco Bay and Delta (Wankel et al. 2006; Kendall et al., 2008b), and current studies in the Sacramento River and Delta (Kendall et al., 2010b). Applications of nitrate isotopes to coastal areas have proliferated since the early 2000s when an improved method was developed for analyzing nitrate isotopes (Sigman et al. (2001) and Casciotti et al. (2002).

The basic idea behind using isotopes for environmental forensic studies is that nutrient and organic matter sources and sinks can often be identified, traced, and semi-quantified because nutrients and organic matter derived from different sources and land uses often have distinctively different isotope compositions, and different kinds of sinks can sometimes cause distinctive shifts in isotopic compositions. In other words, different sources of nutrients and organic matter often have distinctive isotope "fingerprints" that can provide a better understanding of the system than just chemical data. Table 1 lists the interpretive values of the suite of "isotope fingerprinting tools" used in this report for determining sources and biogeochemical processes as part of habitat characterization.

Figure 1 is a typical N cycling model for the SFE, showing the main processes that convert one pool of N to another. If conservative mixing is the main process affecting the distribution of nutrients in the estuary, the $\delta^{15}N$ of NH4 (and similarly NO3) at a location in the estuary can be estimated from a simple mass balance equation: $NH4_{(total)} * \delta^{15}N_{(total)} = NH4_{(A)} * \delta^{15}N_{(A)} + NH4_{(B)} * \delta^{15}N_{(B)}$, where A and B are the two main sources of NH4 (e.g., the SR and SJR).

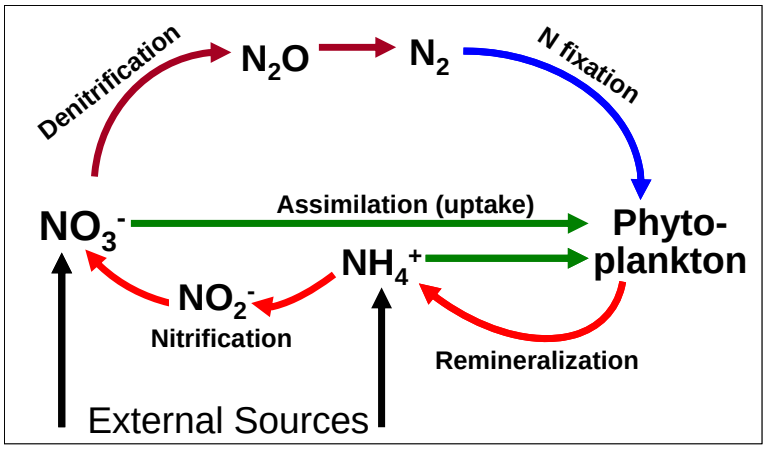

Figure 1. This cartoon shows the main sources of N and processes that cycle N in aquatic systems. Each of the N pools (constituents) probably has a different $\delta^{15}N$ value, and the processes (arrows) that convert one constituent to another often cause distinctive changes in $\delta^{15}N$. There are several significant external sources of NH4 to the San Francisco Bay estuary, including waste water treatment plants (WWTPs), agricultural drains, and wetlands.

Figure 2 shows how two common processes in the Sacramento River (nitrification of NH4 to NO3, and uptake of NO3 and/or NH4 by algae) result in significant changes in the $\delta^{15}N$ values of newly formed NO3, residual NH4, and new algae. For example, if isotopic fractionation during algal uptake involves a single-step unidirectional reaction in a closed system, the relationship between changes in $\delta^{15}N$ and NH4 concentration can be described by classical "Rayleigh" fractionation (Mariotti et al., 1981). The reaction favors the preferential incorporation of ^{14}N into algae, with the result that the $\delta^{15}N$ of the substrate (i.e., NH4) becomes exponentially higher as the reaction proceeds. If NO3 is the major source of N to phytoplankton, as is believed to be the case for the San Francisco Bay (Dugdale et al., 2007), the $\delta^{15}N$ of the new phytoplankton will be lower than the $\delta^{15}N$ of the residual NO3. A large range of isotope fractionations (-27 to 0‰) have been observed in field and laboratory experiments for assimilation of NO3 and NH4 by algae in aquatic environments (Fogel and Cifuentes, 1993). Typical isotope fractionations for NO3 uptake under non-nutrient-limited conditions in rivers are 4-6‰ (Battaglin et al., 2001; Kratzer et al., 2004; Finlay and Kendall, 2007). Fractionations are commonly lower when the system is nutrient limited, and can approach 0‰ for fast reactions.

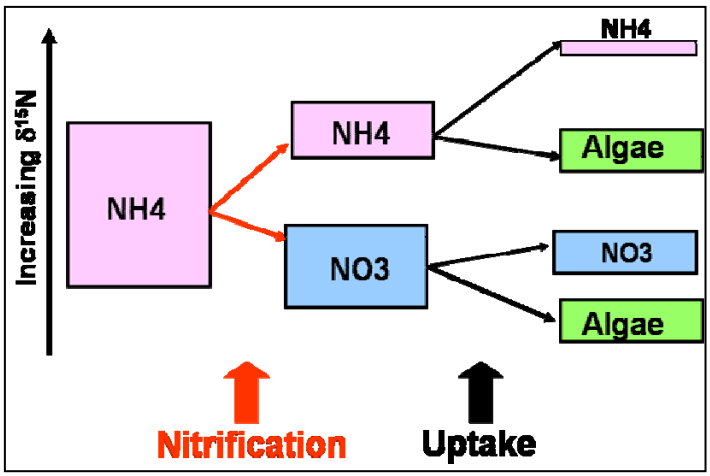

Figure 2. Conceptual model showing how biological processes (e.g., nitrification and uptake) can produce distinctive changes in $\delta^{15}N$. The different pools of N (boxes) have different colors; the box size reflects the size of the pool and the position of the box reflects its average $\delta^{15}N$. Note that the original pool of NH4 ultimately results in 6 pools with different $\delta^{15}N$ values.

Particulate organic matter (POM) is composed of a mixture of algae, bacteria, aquatic macrophytes and terrestrial detritus. The C:N ratio of the POM can be used to estimate the relative proportions of mixtures of terrestrial plus aquatic plants vs algae plus bacteria because the C:N of mixtures of phytoplankton and bacteria have a low and narrow range of values (C:N ~5-7) whereas plants usually have C:N >15 (Finlay and Kendall, 2007). The contribution of bacteria to POM is very difficult to quantify. Since the C:N, $\delta^{13}C$, and $\delta^{15}N$ values are roughly similar (Finlay and Kendall, 2007), bacteria are lumped with algae in this report.

The $\delta^{13}C$ of aquatic plants (including algae, bacteria, and macrophytes) is controlled by the $\delta^{13}C$ of the dissolved inorganic carbon (DIC) in the water column assimilated by the plants. The isotopic composition of the DIC reflects both the isotopic compositions of the sources of the DIC (primarily bicarbonate in freshwaters) but also isotope fractionating processes like uptake and respiration. The $\delta^{13}C$ of marine DIC is higher than the typical DIC in freshwater systems; thus, marine algae generally have higher $\delta^{13}C$ than freshwater algae. Uptake of DIC during growth results in lower $\delta^{13}C$ values of new algae than the residual DIC because of isotope fractionation (Finlay and Kendall, 2007).

Table 1. The value of different "fingerprinting tools" for the determination of biogeochemical processes and sources of waters, nutrients, and organic matter as part of habitat characterizations.

Tool type	**Interpretive value for processes and sources**
Particulate organic matter (POM) $\delta^{15}N$, $\delta^{13}C$, and C:N	Information about the source of C and N, and the biogeochemical reactions that cycle them; Quantify algal *vs* terrestrial contributions to biomass; Evaluate role of algal-based foodwebs, contributions of marine sources of POM & nutrients; Quantify contributions of organic matter from different rivers or riverine vs marine to sites.
Nitrate $\delta^{18}O$ and $\delta^{15}N$	Quantify nitrate from different sources (fertilizer, wastewater, wetlands, etc); Role of algae and degree of recycling; Evidence for denitrification or assimilation; Evidence of nitrification of NH4 as a major NO3 source.
Water $\delta^{18}O$ and $\delta^{2}H$	Ideal conservative tracers of water sources and mixing; Useful for quantifying flow contributions from different sources (e.g., marine vs freshwater, rivers with different recharge areas.
Dissolved organic carbon (DOC) $\delta^{13}C$	Information on sources of DOC; Evidence for degradation of organic matter; Quantify algal vs terrestrial contributions to DOC.
DSM2-derived estimates of the volume % from different water sources	% of water at any site and date from the Bay, Sacramento River, San Joaquin River, major tributaries, WWTPs, etc.; % of water can be extrapolated to explain components dissolved in or transported by water; Useful for comparisons with the source percentages calculated using conservative tracers.

Site description

The San Francisco Estuary (SFE) consists of an inland delta that flows into a chain of downstream marine bays - Suisun, San Pablo and San Francisco - and creates one of the largest estuaries on the west coast of North America (Figure 3). The inland delta formed by the Sacramento River (SR) on the north and the San Joaquin River (SJR) on the south contains 200 km^2 of waterways. The SR is the largest of the rivers with an average discharge of 4795 m^3 s^{-1} compared with 400 m^3 s^{-1} for the SJR over the July through October period when *Microcystis* is most abundant. Other rivers influence streamflow in the Delta including the Mokelumne and Cosumnes Rivers with average discharge of 21 m^3 $s^{-1}$and 6 m^3 s^{-1}, respectively. An important feature of the delta is the large amount of water removed for agriculture that causes average reverse streamflow of 1578 m^3 s^{-1} in the Old River (OR) and 1339 m^3 s^{-1} in the SJR during August and September (www.waterdata.usgs.gov/nwis).

The delta has many kinds of habitats, from shallow flooded islands that are 2 m deep, to wide and deep river channels that are 13 m deep. Flow in the delta is influenced by tides that reach 2 m in depth, tidal velocities up to 30 cm s-1 and tidal excursions of up to 10 km. The delta is largely rural with a population of about 500,000 people within the cities of Sacramento, Stockton and West Sacramento. Most of the 1300 km of sloughs and 57 levied islands in the delta are used for agriculture and wildlife habitat. The sites included in this study were selected within this region which represented different habitats from shallow water brackish embayment to deep freshwater channel. This study combines data from two research studies, a large scale survey in 2007 when 12 sites were sampled weekly June through September, and a focused food web study in 2008 when only 5 sites were sampled weekly June through September (Figure 3).

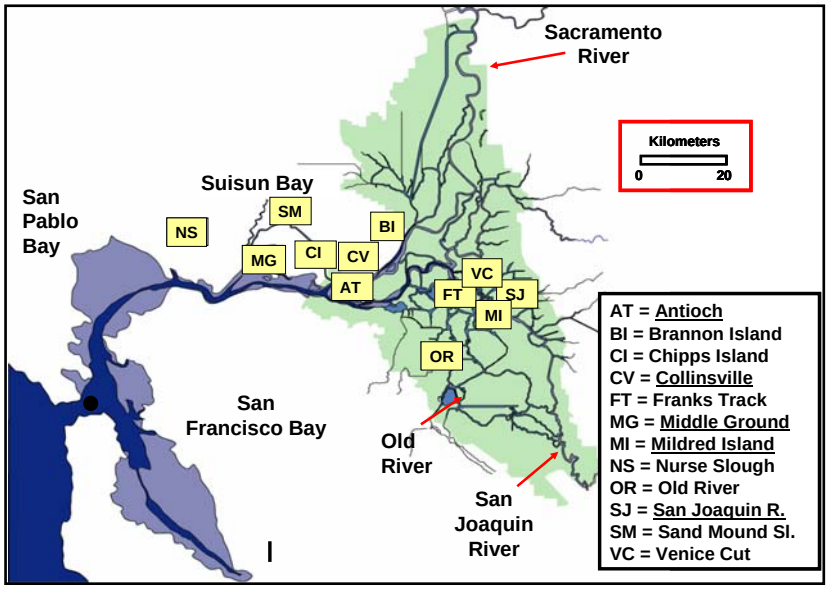

Figure 3. Twelve sites in the Delta were sampled every two weeks in summer 2007, 5 of which (underlined) were also sampled every two weeks in summer 2008. The site abbreviations in the legend are used throughout the report.

Methods

Field methods.
Particulate organic matter (POM) tissue was collected using a surface tow of a 0.5 m diameter plankton net fitted with a 75 µm mesh. A net tow was used for collection in order to get a representative sample. Colonies were visible, widely dispersed and reached 50,000 µm or more in diameter. A 75 µm mesh was used in order to prevent clogging due to heavy suspended sediments and cyanobacterial tissue. Surface water was collected by a van Dorn or diaphragm pump sampler 0.3 m below the surface.

Tissue samples were filtered through GF/F glass fiber filters. Filters for chlorophyll *a* analysis were treated with 1% magnesium carbonate solution to prevent acidity, immediately frozen on dry ice, and stored at -4°C until analysis for chlorophyll *a* and phaeophytin concentration. Pigments were extracted in 90% acetone and measured using spectrophotometry (American Public Health Association et al. 1998). Filters for microcystins analysis were immediately frozen on dry ice and maintained at -80°C until processing for total microcystins concentration using protein phosphate inhibition assay (PPIA; Lehman et al. 2010).

Chemical analysis.
Water samples for chloride, NH4-N, NO3-N plus NO2-N, and soluble reactive phosphorus were filtered through 0.45 µm nucleopore filters or maintained as whole water samples for total and volatile suspended solids and total organic carbon analysis, and kept at 4°C or frozen until analysis as appropriate (American Public Health Association et al., 1998; USEPA 1983; USGS 1985). Dissolved organic carbon (DOC) was filtered through pre-combusted GF/F filters and frozen at -4°C until analysis (American Public Health Association et al., 1998). Water temperature, pH, specific conductance, and dissolved oxygen were measured near the surface using a Yellow Springs Instrument (YSI) 6600 water quality sonde.

Water samples for *Microcystis* cell abundance analysis were preserved with Lugol's solution and identified and enumerated at 700 X using an inverted microscope technique (Utermöhl 1958) or Fluid Imaging Technologies FlowCAM digital flow cytometer (Sieracki et al., 1998).
For the microscope technique, cell carbon was calculated from cell volume computed from cell dimensions applied to simple geometrical shapes (Menden-Deuer & Lessard 2000).
For the FlowCAM, volume of colonies was measured directly and converted to carbon by equation (Menden-Deuer and Lessard 2000). Both methods allowed identification of *Microcystis* cells and colonies $\geq$6 µm in diameter.

Isotope analysis.
Samples were also collected for POM, DOC, water, and NO3 stable isotopic composition from most collection dates. All available samples were analyzed for POM, DOC, and water isotopes. Only a subset of samples was analyzed for NO3 isotopes. Two separate samples of POM were collected as above at each site, and were kept frozen until analysis. The samples were prepared and analyzed separately, and the results averaged. Splits of water collected and filtered through 0.45 µm filters for chemical measurements were further split into separate bottles for DOC,

water, and NO3 isotopes. NO3 isotope samples were kept frozen until analyzed. DOC samples were preserved with a droplet of 85% phosphoric acid and kept chilled until analyzed.

All samples were analyzed for isotopic composition in the USGS Isotope Tracers Project labs in Menlo Park, CA. All NO3 and water samples were prepared in duplicate (concentrations permitting). 10-15% of DOC and POM samples were prepared in duplicate. All isotopic analyses were conducted with blanks and multiple isotopic standards according to established methods. More specifics about the methods are given below.

Isotopic compositions are reported in the standard notation, in units of parts per thousand (‰):

$$\delta(‰) = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 1000$$

where R represents the ratio of the heavy to light isotope (e.g., $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{18}O/^{16}O$, or $^{3}H/^{2}H$) in either the sample or standard. The data are reported relative to the usual international standards (e.g., PDB for $\delta^{13}C$, Air for $\delta^{15}N$, V-SMOW for $\delta^{18}O$ and $\delta^{2}H$). Analytical precisions for replicate analyses of the same sample are method and isotope dependent, with observed precisions of: <0.3 ‰ for $\delta^{13}C$ and <0.5‰ for $\delta^{15}N$ of POM; <0.3‰ for DOC-$\delta^{13}C$; <0.2 ‰ for $\delta^{18}O$ and <1.0‰ for $\delta^{2}H$ of water; and 0.2‰ for $\delta^{15}N$ and 1.5‰ for $\delta^{18}O$ of NO3.

POM-$\delta^{13}C$, $\delta^{15}N$, and C:N: The samples were prepared and analyzed following the method described in Kendall et al. (2001), using an Optima mass spectrometer. Ground samples were vapor acidified to remove any carbonate prior to preparation and analysis for $\delta^{13}C$ and $\delta^{15}N$. C:N values are reported as atomic (at) ratios.

DOC-$\delta^{13}C$**:** Samples were prepared and analyzed using an automated OI TOC analyzer connected to an IsoPrime mass spectrometer using a modification of the method described in St. Jean (2003). This method first acidifies water samples to remove DIC, and then analyzes the concentration and $\delta^{13}C$ value of CO_2 obtained from persulfate oxidation of DOC.

H2O-$\delta^{18}O$ and $\delta^{2}H$: Both $\delta^{18}O$ and $\delta^{2}H$ of water were measured using laser spectroscopy on a Los Gatos Research DLT-100 Liquid-Water Isotope Analyzer, using a modification of the method described in Lis et al. (2008).

NO3-$\delta^{15}N$ and $\delta^{18}O$: Samples are analyzed using a minor modification of the Sigman et al. (2001) and Casciotti et al. (2002) microbial denitrifier method, using a custom-designed autosampler connected to an IsoPrime mass spectrometer. This method uses bacteria to convert the nitrate quantitatively to N_2O, which is purified and analyzed for $\delta^{15}N$ and $\delta^{18}O$.

DSM2 analysis.

Hydrological model output used in the statistical analysis of the chemical and isotopic data were generated using DSM2, a one-dimensional hydrodynamic and water quality simulation model used to represent conditions in the Sacramento-San Joaquin Delta. The hydrodynamics module (HYDRO) in DSM2 was developed from the USGS FOURPT model (Nader, 1993). The water quality and transport module (QUAL) in DSM2 is based on the Branched Lagrangian Transport Model (Jobson, 1997), also developed by the USGS. QUAL uses the hydrodynamics simulated in HYDRO as the basis for its transport calculations. DSM2 Version 8.0.6 was used for this project, and documentation on the calibration and validation of the modules used in the current implementation of the Historical model is available at: http://baydeltaoffice.water.ca.gov/modeling/deltamodeling/models/dsm2/dsm2.cfm . HYDRO was used to calculate stage, flow, and net flow at 15-minute intervals. QUAL was used to calculate volumes of water from different water sources (e.g., the Sacramento River vs the San Joaquin River) at 15 minute intervals, which were averaged to produce daily average values.

Nitrate concentrations and isotopes

Median NO3 concentrations at SR sites were ~20% higher than at SJR sites during the sampling dates. However, the strong correlations of NO3-δ^{15}N and other chemical measurements with flow from different water sources indicate that the SJR was the primary source of NO3 in the Delta. Nitrate δ^{15}N values ranged from +5.5 to +11.2‰ throughout the Delta and differed among sites ($p < 0.01$, ANOSIM), with a mean of +7.7‰. Median values (Figure 4) were greater at SJR sites (SJ and SM) than sites in the SR and Suisun Bay (BI, CI, CV, NS and MG), or at the Middle and Old River sites (MI and OR; $p < 0.05$). NO3-δ^{15}N values were correlated with the DSM2-calculated percent of the flow derived from the SJR ($r=0.39$, $p < 0.01$). This association was supported by the stronger correlations between NO3-δ^{15}N and the percentage of SJR flow on ebb and slack tide ($r=0.49$, $p < 0.01$ and $r=0.68$, $p < 0.01$, respectively), when more SJR water is in the Delta, than on flood tides when SR water dominates. The correlation varied with water year, and was greater during 2008 when flows were lower than in 2007 when flows were higher (2008 $r=0.60$, $p < 0.01$ and 2007 $r=0.26$, $p < 0.05$).

The influence of the SJR on NO3 in the Delta was further supported by significant correlations between NO3-δ^{15}N values and environmental variables. For example, NO3-δ^{15}N was negatively correlated with chloride, silica, total suspended solids and NH4, and was positively correlated with water temperature ($r =- 0.26$, $r = -0.25$, $r = -0.21$, $r = -0.28$ and $r = 0.24$, $p < 0.05$). These water quality conditions are characteristic of the SJR sites where chloride, silica, total suspended solids and NH4 are relatively low compared with SR sites (Table 2). The percentage of SJR flow was also positively correlated with NO3, and negatively correlated with chloride and silica. While NO3-δ^{15}N values were correlated with SJR flow, NO3-δ^{18}O was correlated with the

percentage of Sacramento River flow and had similar correlations in both 2007 and 2008 (-0.31, $p < 0.05$ in 2007 and -0.36, $p < 0.05$ in 2008).

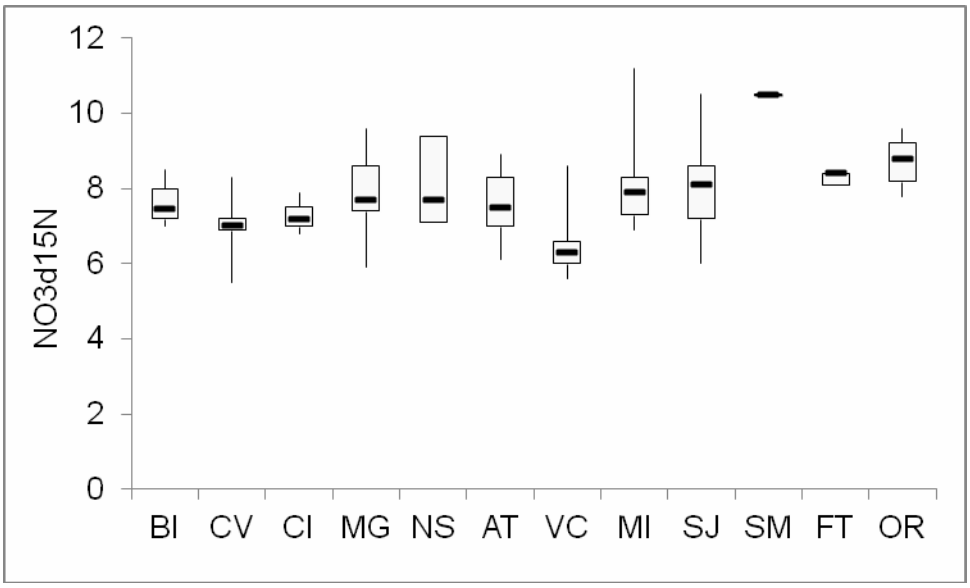

Figure 4. Median NO3-δ^{15}N values measured at sites (abbreviated per the legend in Figure 3) throughout the Delta in the summer of 2007 and 2008.

Table 2. Median and interquartile range for environmental variables measured at the Sacramento, San Joaquin and Old River sites during the summer of 2007 and 2008.

variable	**Sacramento River**	**San Joaquin River**	**Old River**
ammonium (mg N l^{-1})	0.05 $\pm$ 0.01	0.03 $\pm$ 0.02	0.03 $\pm$ 0.01
nitrate (mg N l^{-1})	0.35 $\pm$ 0.05	0.3 $\pm$ 0.1	0.2 $\pm$ 0.1
soluble reactive P (mg P l^{-1})	0.06 $\pm$ 0.02	0.06 $\pm$ 0.01	0.06 $\pm$ 0.01
silica (mg l^{-1})	14 $\pm$ 0.85	14.15 $\pm$ 1.25	13.25 $\pm$ 1.5
chloride (mg l^{-1})	1570 $\pm$ 960	46 $\pm$ 94	116 $\pm$ 50
specific conductance	4778 $\pm$ 3621	309 $\pm$ 127	514 $\pm$ 202

dissolved oxygen (mg O_2 l^{-1})	8.8 ± 0.25	8.6 ± 0.5	8.55 ± 0.65
pH	7.9 ± 0.2	8.1 ± 0.25	8.05 ± 0.25
Secchi disk depth (m)	60 ± 18	108 ± 40	104 ± 40
water temperature (°C)	21.3 ± 0.75	23.15 ± 1.2	23.5 ± 0.9
total organic carbon (mg C l^{-1})	2.1 ± 0.5	2.3 ± 0.3	2.5 ± 0.25
total suspended solids (mg l^{-1})	16.5 ± 7	5 ± 3	6 ± 2
volatile suspended solids (mg l^{-1})	3 ± 1.5	1 ± 0.5	1 ± 0.5

Ammonium concentrations

The Sacramento River was the dominant source of the NH4 to the Delta. Median NH4 concentrations (Table 2) were greater in the SR than in the SJR by a factor of 1.5 ($p < 0.01$). NH4 concentrations are positively correlated with chloride and total suspended solids but negatively correlated with water temperature (r=0.39, r=0.50, r=-0.42, for chloride, total suspended solids, and water temperature, respectively). These conditions characterize the SR. In addition, concentrations were more elevated when flow was low in both rivers (r = -0.33 and r = -0.20 for the SR and SJR). Unfortunately, we did not archive water samples for NH4-$\delta^{15}N$ analysis so we cannot directly fingerprint NH4 sources like we can for NO3 sources.

Particulate organic matter concentrations and isotopes

Suspended solids.
Median concentrations of total suspended solids (TSS) were >3x higher in the SR than in the SJR or OR; volatile suspended solids were also 3x higher in the SR (Table 2). The measurement of C:N ratios of POM samples provides a mechanism for determining how much of the TSS is from different kinds of particles.

C:N.
The average POM-C:N value was 7.0, only slightly higher than the Redfield Ratio (6.7). Median POM-C:N values for different sites ranged from 5.9 to 9.7. Most sites had median C:N values ≤7.0 (NS, MG, MI, FT, AT, CI, SJ, and VC). If the C:N of plants is assumed to be 15 and 6.7 is used as the C:N of algae, >95% of the POM at these sites is algae (plus bacteria). Thus, the median isotopic composition of the POM is a good proxy for the isotopic composition for algae

plus bacteria at these sites. However, 2 sites had C:N values in the range of 7.9 to 8.1 (CV and SM), indicating ~10% terrestrial detritus and/or macrophytes; and 2 sites had C:N values in the range of 9.2-9.7 (BI and OR), indicating >20% terrestrial detritus and/or macrophytes.

For these 4 sites, interpretation of the $\delta^{15}N$ and $\delta^{13}C$ values is potentially complicated by the presence of plant detritus of unknown source and isotopic composition (Cloern et al., 2002). The presence of terrestrial or macrophytes probably has more of an effect on the interpretation of $\delta^{13}C$ values than $\delta^{15}N$ values because of C4 terrestrial plants (corn and grasses are the main C4 plants in the watershed) have much lower $\delta^{13}C$ values (~ -13‰) compared to the more common C3 plants (~ -27‰). The presence of macrophytes has much less effect on $\delta^{13}C$ because they generally have $\delta^{13}C$ values similar to co-existing algae (Finlay and Kendall, 2007). POM-$\delta^{15}N$ values are relatively unaffected by the presence of modest amounts of terrestrial detritus because typical detritus has $\delta^{15}N$ values similar to the POM-$\delta^{15}N$ values of algae-dominated sites, and macrophytes generally have $\delta^{15}N$ values similar to co-existing algae (Finlay and Kendall, 2007). Therefore, the average $\delta^{13}C$ and $\delta^{15}N$ values of POM are reasonable proxies for the average $\delta^{13}C$ and $\delta^{15}N$ of algae plus bacteria for the sites in this study.

The measured C:N values for individual samples (n=57) ranged from 4.5 to 14.8, with ~10% of the samples having C:N > 9.7. Thus, if the C:N of plant detritus is assumed to ~15, then the % of plant material in these samples ranges from 20-100%. For these samples, estimates of the isotopic compositions of the algal component (if any) are more complicated and have high error bars.

$\delta^{13}C$.

Median POM-$\delta^{13}C$ values ranged from -30.7 to -25.9‰, with higher (less negative) values associated with a higher percentage of SJ flow. Most SJR sites (i.e., AT, SM, VC, MI, OR and FT) had higher median POM-$\delta^{13}C$ values ($p < 0.05$) than most of those in the SR and Suisun Bay sites (i.e., BI, CI, CV and MG) (Figure 5). The two outlier sites were the farthest upstream site in the SJR (SJ), which had a low (-28.85‰) value more similar to POM-$\delta^{13}C$ values in the SR, and the most seaward site in northern Suisun Bay at NS that had the lowest median $\delta^{13}C$ value (-30.7‰). Relatively high $\delta^{13}C$ values were positively correlated with the percentage of SR flow ($r = 0.32$, $p < 0.01$) and negatively correlated with net flow ($r = -0.31$, $p < 0.01$; Figure 6). There is a strong negative correlation between POM-$\delta^{13}C$ values and chloride ($r = -0.61$, $p < 0.01$) for sites with a wide range of brackish conditions; but the freshwater sites with low chloride show little correlation of $\delta^{13}C$ values and chloride (Figure 7). Chloride was negatively correlated with both the percentage of SR and SJR flow ($r = -0.48$, $p < 0.01$ and $r = -0.46$, $p < 0.01$, respectively), as would be expected if most of the chloride was marine in origin.

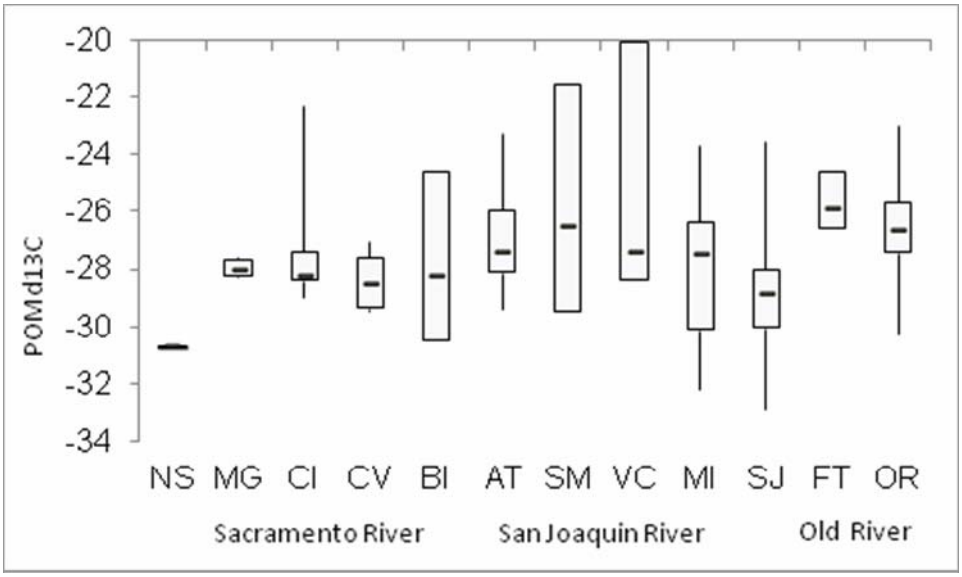

Figure 5. Median POM-δ^{13}C values for sites throughout the Delta in the summer of 2007 and 2008.

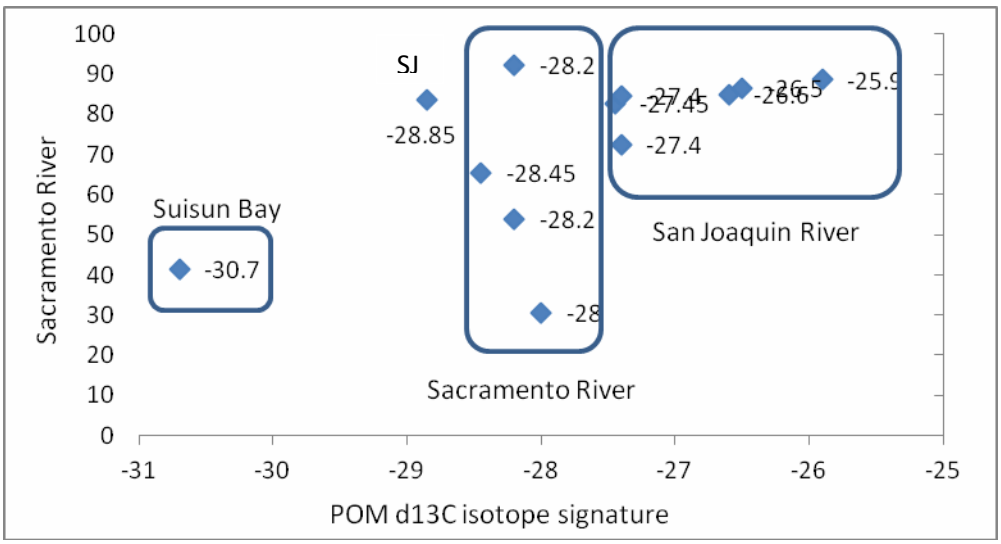

Figure 6. POM-δ^{13}C values in relation to the percentage of Sacramento River flow for summer 2007 and 2008.

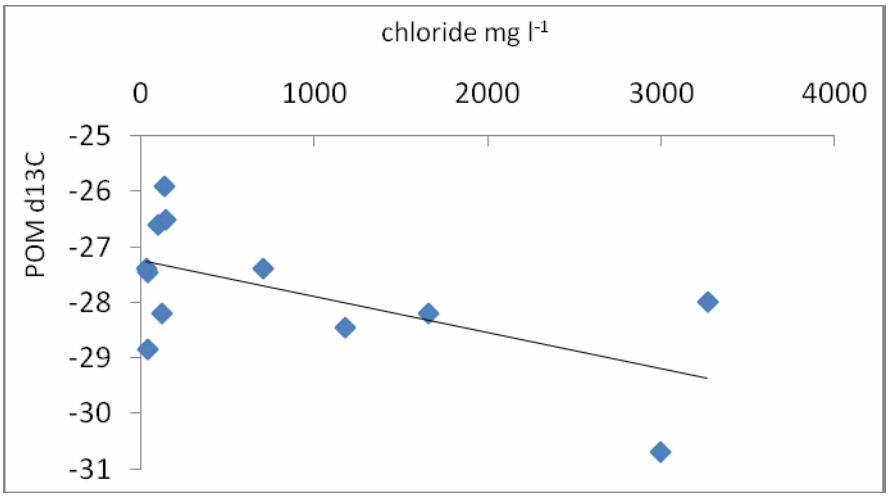

Figure 7. Variation of median POM-$\delta^{13}C$ values with chloride at sites in the Delta during the summer of 2007 and 2008.

The source of the POM was influenced by tide. Higher (less negative) POM-$\delta^{13}C$ values occurred on ebb tide when the percentage of SR flow at sites was high ($r = 0.40$, $p < 0.01$) and the percentage of SJR flow at sites was low ($r = -0.30$, $p < 0.05$), and also on slack tide when the percentage of SR flow was also high ($r = 0.82$, $p < 0.05$). The negative correlation between the percent flow from the SR and SJR ($r = -0.29$) supported the opposite flow pattern in these two rivers. DOC-$\delta^{13}C$ values followed the same pattern as POM-$\delta^{13}C$, with more positive values associated with a greater percent flow from the SR ($r = 0.21$, $p < 0.05$) and lower percent flow from the SJR ($r = -0.40$, $p < 0.01$).

$\delta^{15}N$.

The median POM-$\delta^{15}N$ was similar among sites (Figure 8) and was correlated with NH4 and NO3 concentrations. Median $\delta^{15}N$ values ranged from +8.1 to +10.7 among sites, with a mean of +9.9‰ for samples analyzed for NO3-$\delta^{15}N$. SR and SJR sites had higher POM-$\delta^{15}N$ values than Old River sites in the center of the Delta. POM-$\delta^{15}N$ values were directly correlated with NH4 and NO3 concentrations in the water column ($r = 0.28$, $p < 0.01$ and $r = 0.29$, $p < 0.01$, respectively). These positive correlations with NO3 and NH4 concentration varied with tide and were larger on flood and slack tides ($r = 0.42$, $p < 0.05$ and $r = 0.40$, $p < 0.05$ on flood; and $r = 0.84$, $p < 0.05$ and $r = 0.79$, $p < 0.05$ on slack tide for NH4 and NO3, respectively) than on ebb tides. The positive correlation between NO3 or total dissolved nitrogen and the percent SJR flow ($r = 0.45$, $p < 0.01$ and $r = 0.37$, $p < 0.01$) but negative correlations with the percent SR flow ($r = -0.61$, $p < 0.01$ and $r = 0.-63$, $p < 0.01$), suggest that the SJR was the source of most of the nitrate and dissolved nitrogen at these sites. In contrast, NH4 was elevated in the Delta when the percent of both the SR and SJR flows were low ($r = -0.33$, $p < 0.01$ and $r = -0.20$, $p < 0.05$).

POM-δ^{15}N was negatively correlated with POM-δ^{13}C ($r = -0.24$, $p < 0.05$). The negative correlation suggests that the more positive POM-δ^{15}N values were associated with POM production at sites in the SR or Suisun Bay where POM-δ^{13}C values were more negative. This correlation was slightly stronger on ebb and slack tide ($r = -0.31$, $p < 0.05$ and $r = -0.78$, $p < 0.05$).

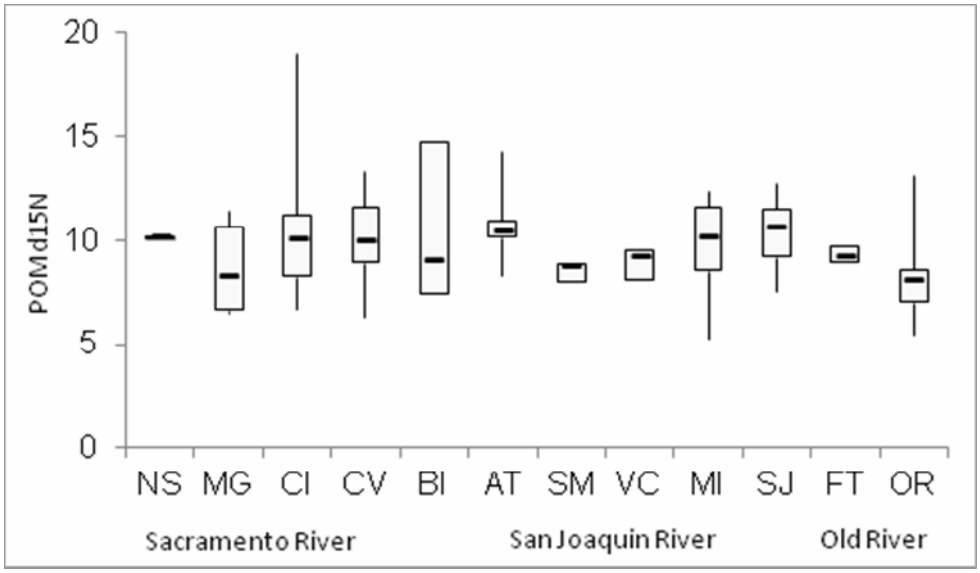

Figure 8. Median POM-δ^{15}N values measured at sites throughout the Delta in the summer of 2007 and 2008.

Water isotopes

Both the δ^{18}O and δ^{2}H values of water were significantly greater ($p < 0.01$) in the SR than in the SJR or Old River (Figs. 9 and 10). Since marine waters have δ^{18}O and δ^{2}H values near 0‰, much higher than the δ^{18}O and δ^{2}H of freshwaters, the higher δ^{18}O and δ^{2}H values of the SR sites are partially caused by the higher amounts of marine water in the SR. The SR site closest to the ocean (NS) has higher δ^{18}O and δ^{2}H values than sites further upstream. Water δ^{18}O and δ^{2}H values are negatively correlated with the percent SR water ($r = -0.57$ and $r = -0.53$, $p < 0.01$), but there is no correlation with the percent SJR water. The positive correlations of water isotopes with both chloride and total suspended solids ($r = 0.50$ and $r = 0.51$, $p < 0.01$ and $r = 0.47$ and $r = 0.57$, $p < 0.01$ for δ^{18}O and δ^{2}H, respectively) further support the association of more positive water isotope values with greater contributions of marine water.

Although this is not readily apparent at the scale of Figures 9 and 10, both the δ^{18}O and δ^{2}H values of SR water are higher than the δ^{18}O and δ^{2}H of SJR and Old River water (Figure 10). The SR and SJR sites are listed in order of their distance from the ocean (from left to right).

Each set shows increasing $\delta^{18}O$ and $\delta^{2}H$ values towards the left. Hence, the increase in $\delta^{18}O$ and $\delta^{2}H$ values for SR sites can be explained by increasing contributions of marine water downstream. In contrast, the increasing $\delta^{18}O$ and $\delta^{2}H$ values downstream for SJR sites reflects both increasing marine water and increasing contributions of SR water.

The positive correlations between both $\delta^{18}O$ and $\delta^{2}H$ and NH4 ($r = 0.42$ and $r = 0.26$, $p < 0.01$) also suggest the SR is the main source of NH4 to the estuary. Similarly, the positive correlation ($r = 0.35$, $p < 0.01$) between water-$\delta^{18}O$ and NO3-$\delta^{18}O$ suggests that NO3 concentrations were a function of source flow, with NO3 moving into the Delta from the SJR where concentrations were elevated.

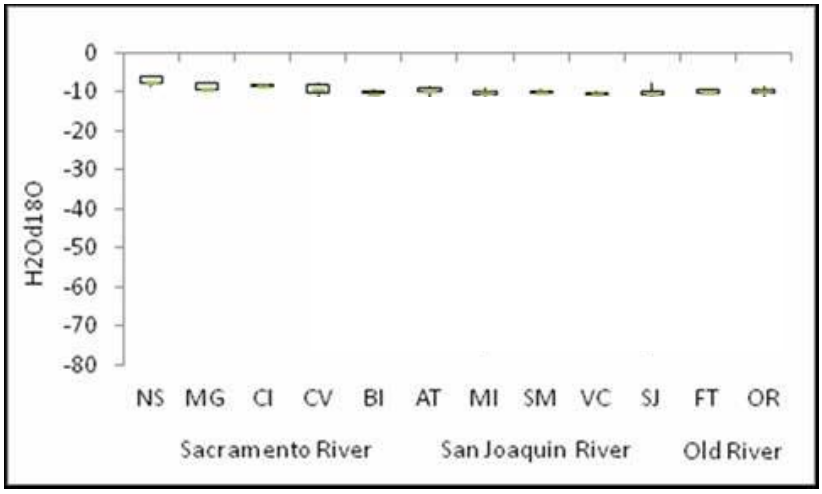

Figure 9. Water-$\delta^{18}O$ for sites in the San Francisco estuary in the summer of 2007 and 2008

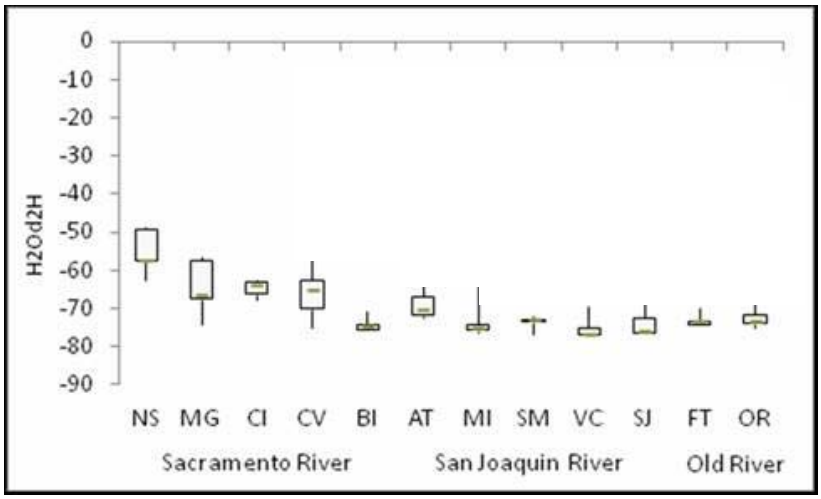

Figure 10. Water-$\delta^{2}H$ for sites in the San Francisco Estuary in the summer of 2007 and 2008.

Phytoplankton and cyanobacteria

Median chlorophyll-*a* concentration ranged from 0.01 to 0.28 ng l^{-1} among sites and was greater ($p < 0.01$) in the SJR and Old River sites than the SR sites (Figure 11). Chlorophyll-*a* concentration was strongly correlated with *Microcystis* abundance ($r = 0.77$, $p < 0.01$). *Microcystis* occurred throughout the Delta and was also more abundant ($p < 0.01$) in the SRJ and Old River than the SR (Figure 12). Most of the difference among the rivers was due to the lower *Microcystis* abundance seaward in the lower SR at sites NS, MG, CI and CV. *Microcystis* abundance reached an average median value of 5115 cells ml^{-1} in the SJR and Old River. These elevated *Microcystis* abundance values were associated with elevated concentrations of the *Microcystis* toxin, total microcystins ($r = 0.77$, $p < 0.01$; Figures 12 and 13).

Chlorophyll-*a* and total microcystins concentration as well as *Microcystis* abundance varied directly with the POM-$\delta^{13}C$ values ($r = 0.70$, $r = 0.63$ and $r = 0.50$, $p < 0.01$), which were higher in the SJR and Old River. The strong correlations between both water $\delta^{18}O$ and $\delta^{2}H$ and the measurements of chlorophyll-*a* , total microcystins concentration, and *Microcystis* abundance support the different contribution of each river to the bloom dynamics in the summer (for water-$\delta^{18}O$: $r = -0.37$, $r = -0.40$ and $r = -0.34$, $p < 0.01$; and for water-$\delta^{2}H$: $r = -.26$, $r = -.26$ and $r = -.36$, $p < 0.01$ for chlorophyll-*a*, total microcystins and *Microcystis* abundance, respectively).

Chlorophyll-*a* concentration and *Microcystis* abundance were negatively correlated with low chloride and total suspended solids concentration and high water temperature ($r = -0.35$, $r = -0.32$ and $r = 0.34$, $p < 0.01$ for chloride, total suspended solids and water temperature). San Joaquin River water typically has a lower chloride and suspended solid concentration and a higher temperature than the Sacramento River, and lower NH4, NO3 and soluble phosphorus concentrations compared with the SR (Table 2). Chlorophyll-*a* concentration and *Microcystis* abundance were both negatively correlated with NH4, NO3, and soluble phosphorus concentration (for chlorophyll-*a*: $r = -0.25$, $r = -0.52$ and $r = -0.38$, $p < 0.01$; and for *Microcystis*: $r = -0.27$, $r = -0.58$ and $r = -0.36$, $p < 0.01$ for NH4, NO3 and soluble phosphorus, respectively). Elevated chlorophyll-*a* concentration and *Microcystis* abundance were also more abundant when the net flow and the percent of SJR flow were low.

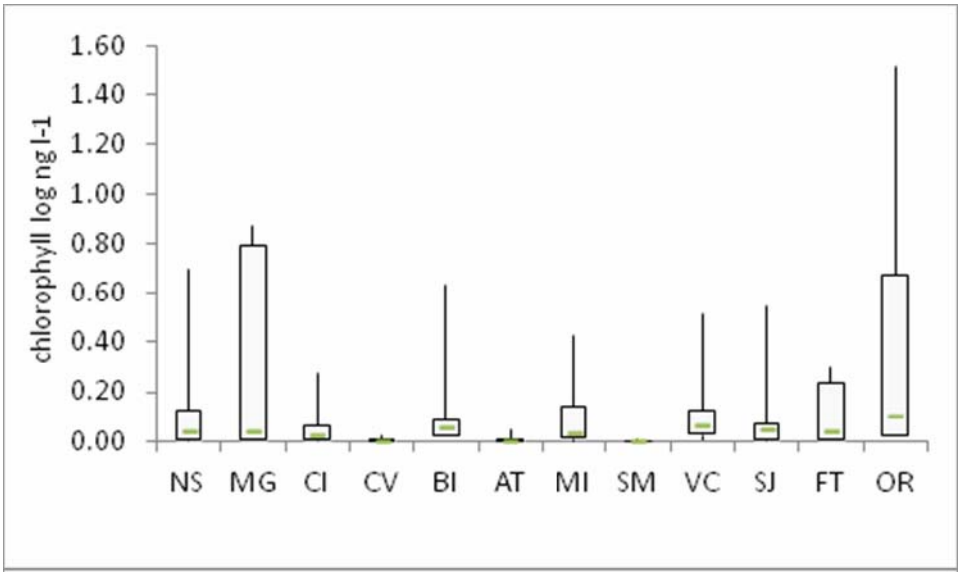

Figure 11. Maximum, minimum, median and the 25th and 75th percentiles for log chlorophyll *a* concentration in net tows collected during the summer of 2007 and 2008.

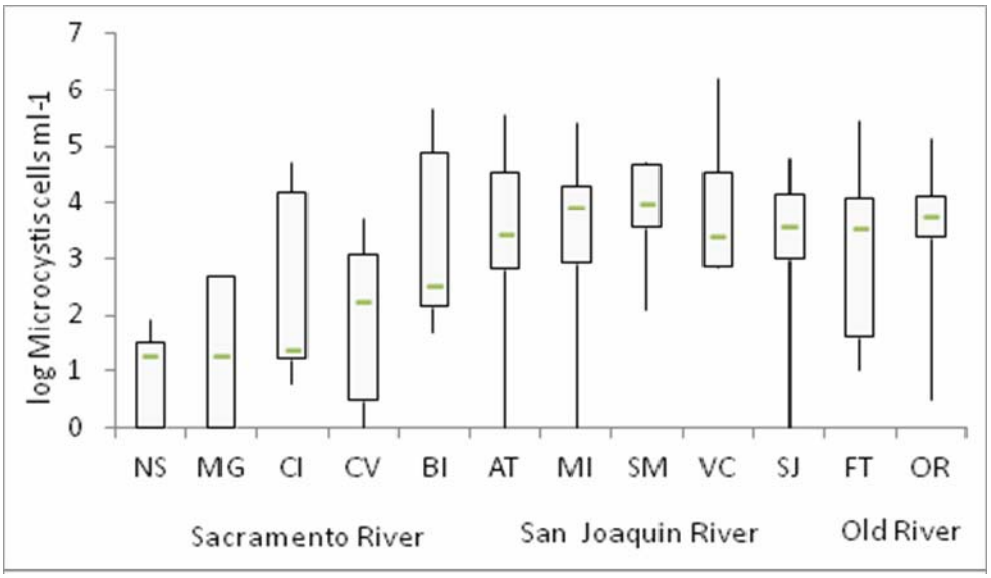

Figure12. Maximum, minimum, median and the 25th and 75th percentiles for log *Microcystis* abundance in net tows collected during the summer of 2007 and 2008.

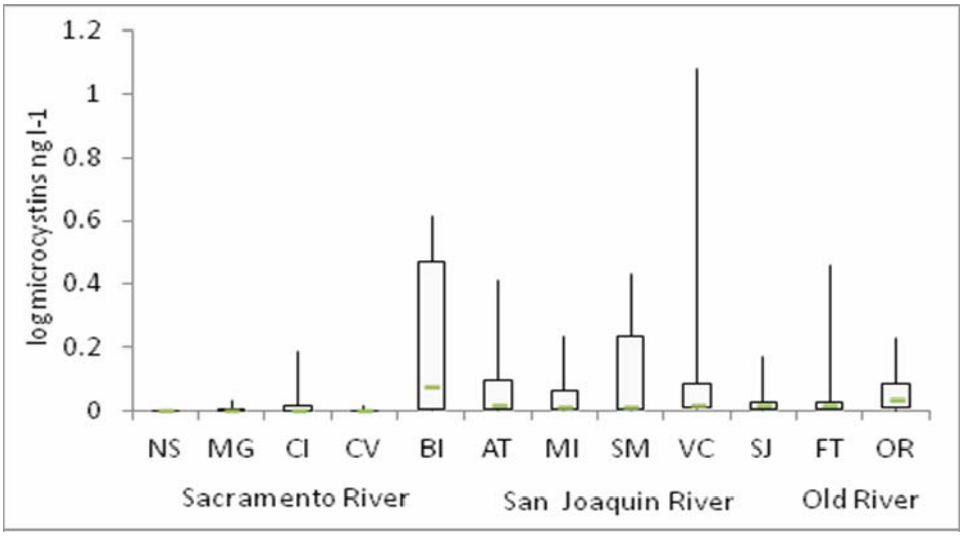

Figure 13. Maximum, minimum, median and the 25th and 75th percentiles for log microcystins concentration ng l^{-1} in net tows collected during the summer of 2007 and 2008.

Discussion

Most of the statistics in this report are for all data for all sites combined together, with some instances when the data are divided by year, tide status, etc. for separate statistics Many sites show a wide range of compositions (e.g., Figures 5, 8, 11-13) indicative of temporal changes in sources and/or biogeochemical processes. The site-specific hydrological and biogeochemical controls on nutrients and organic matter will be explored in a future document. This paper is focused on identifying the dominant source of the nutrients fueling *Microcystis* blooms.

This study confirms that the SJR and SR have distinctively different NO3 isotopic compositions (Kendall et al., 2008b). The average NO3-δ^{15}N and δ^{18}O values for 67 SJR samples collected at Vernalis 3/05 to 12/07 are +10.7‰ (±1.9‰) and +4.2‰ (±1.8‰), respectively; the average δ^{15}N and δ^{18}O for 16 SR samples collected 8/06 to 5/08 at Rio Vista are +5.3‰ (±1.0‰) and -3.7‰ (±3.6‰), respectively (Kendall et al., 2008b). The higher NO3-δ^{15}N value of SJR water probably reflects significant contributions of NO3 from dairies in the SJR Basin (Kratzer et al., 2004), whereas the lower δ^{15}N of SR water is partially a result of extensive downstream nitrification of effluent from SRWTP (Kendall et al., 2010b). Water from these two rivers are also distinguishable by their differences in chemical characteristics, with the high temperature and low chloride, silica, total suspended solids, and NH4 concentrations typical of the SJR correlated with high NO3-δ^{15}N values and high calculated % of SJR at the sites. The correlations of high NO3-δ^{15}N and high % SJR water were also stronger during ebb and slack tides, and when flows were lower, all conditions when less SR water would be in the Delta. Hence, multiple lines of evidence confirm that the dominant source of NO3 at the Delta sites studied can be identified using NO3-δ^{15}N, and it is the SJR.

The NO3-$\delta^{18}O$ values of SR and SJR sites are also distinguishable. However, the NO3-$\delta^{18}O$ was correlated with the % SR water, whereas the NO3-$\delta^{15}N$ was correlated with the % SJR water. This "decoupling" of the $\delta^{15}N$ and $\delta^{18}O$ of NO3 in the SFE was first observed by Wankel et al. (2006) and was explained by nitrification. During nitrification, the NO3-$\delta^{15}N$ reflects the $\delta^{15}N$ of the NH4 source (plus isotope fractionation) whereas the NO3-$\delta^{18}O$ reflects the $\delta^{18}O$ of the water source (also plus isotope fractionation). The low NO3-$\delta^{18}O$ values in the SR are the result of high nitrification rates downstream of SRWTP, which caused a 10‰ increase in NH4-$\delta^{15}N$ and a 5-10‰ decrease in the NO3-$\delta^{18}O$ (Kendall et al., 2010b). The downstream decrease in NO3-$\delta^{18}O$ in the SR upstream of Rio Vista (located at RM12) reflects the addition of new NO3 with lower $\delta^{18}O$ values produced in the SR. This new NO3 has lower $\delta^{18}O$ values because the SR, where some of O in the new NO3 is derived during nitrification, has a lower water-$\delta^{18}O$ value than the environment where the original SR NO3 obtained its NO3-$\delta^{18}O$. Besides the low value of NO3-$\delta^{18}O$, another distinctive characteristic of SR water is high NH4 concentrations. The NH4 concentrations are positively correlated with the high chloride and total suspended solid concentrations and low temperature typical of the SR. Hence, several lines of evidence indicate that SR water had a distinctive signature.

Interpretation of the POM-$\delta^{13}C$ data as a potential tracer of the geographic source of the POM (e.g., is the POM derived from one location and perhaps wind-driven to another prior to being sampled) and of biogeochemical processes related to *Microcystis* blooms is complicated by the overlapping $\delta^{13}C$ values of POM from the SJR and SR. The average POM-$\delta^{13}C$ and $\delta^{15}N$ values for 67 SJR samples collected at Vernalis 3/05 to 12/07 are -27.9‰ (±0.9‰) and +7.2‰ (±1.7‰), respectively; the average $\delta^{15}N$ and $\delta^{18}O$ for 16 SR samples collected 8/06 to 5/08 at Rio Vista are -28.1‰ (±0.6‰) and 5.4‰ (±1.9‰), respectively (Kendall et al., 2008b). These data contradict the apparent separation of POM-$\delta^{13}C$ values for most SJR and SR sites shown in Figures 5 and 6.

The contradiction can be partially explained by the fact that these datasets do not overlap in time. However, a more likely explanation is that the earlier study collected mid-channel samples from mainstem SJR sites where phytoplankton was the major source of POM, whereas most of the sites in the current study are from Delta channel margins exhibiting major *Microcystis* blooms. At channel margin sites, flow is likely to be slower, water depths less, and residence times longer; these factors would allow in-situ biogeochemical processes such as uptake and respiration to have a larger effect on the $\delta^{13}C$ of DIC.

Large algal blooms typically have low POM-$\delta^{13}C$ values because of isotope fractionation during uptake of low-$\delta^{13}C$ DIC as the algae grow. Progressive uptake of DIC eventually causes the $\delta^{13}C$ of the remaining pool of DIC to increase; respiration generally has the opposite effect, with the $\delta^{13}C$ of DIC decreasing as DIC concentrations increase (Finlay and Kendall, 2007). The strong positive correlations of POM-$\delta^{13}C$ with chlorophyll-*a,* microcystin concentration, and *Microcystis* abundance indicate that cyanobacteria blooms and algal blooms have similar environmental effects on aquatic carbon biogeochemistry.

Superimposed on the seasonal rise and fall in POM-$\delta^{13}C$, chlorophyll-*a,* microcystin concentration, and *Microcystis* abundance during the peak bloom at most sites are several small in-phase oscillations in POM-$\delta^{13}C$, POM-$\delta^{15}N$, NO3-$\delta^{15}N$, NO3-$\delta^{18}O$, and DOC-$\delta^{13}C$. The correlations of higher POM-$\delta^{13}C$ values and tidal fluctuations indicate that these oscillations at least partially reflect small changes in the relative percentages of SR and SJR water to the sites, not just biogeochemical processes.

Another complication for interpreting the POM-$\delta^{13}C$ values at sites with high chloride (Figure 7) is that marine DIC has a significantly higher $\delta^{13}C$ than most freshwater sites. The average DIC-$\delta^{13}C$ and POM-$\delta^{13}C$ values from the USGS *RV Polaris* site #18 near Angel Island are -3.7‰ (±1.6‰, n=7) and -23.5‰ (±1.5‰, n=16) for samples collected 8/06 to 5/08 (Kendall et al., 2008b). Hence, Bay-derived algae should have a high $\delta^{13}C$ value. In contrast, the NS site in Suisun Bay has a very low POM-$\delta^{13}C$ value. Given these ranges of $\delta^{13}C$ values for different POM sources and different biogeochemical processes, definitive explanations for the site-specific POM-$\delta^{13}C$ values are complicated and beyond the scope of this paper.

Previous studies in major rivers have shown that comparison of the $\delta^{15}N$ values of POM and NO3 is useful for determining whether NO3 is the main source of N to algae (Finlay and Kendall, 2007). This relationship is only valid if the $\delta^{15}N$ of POM is a reasonable proxy for the $\delta^{15}N$ of algae, which can be determined by checking if the C:N of POM is close to the Redfield Ratio (6.7). As described above, if NO3 is the dominant N source to algae then the $\delta^{15}N$ of algae should be ~ 4‰ lower than the $\delta^{15}N$ of the co-existing NO3.

In the upper San Joaquin River (i.e., between Lander and Mossdale), where the POM is predominantly algal in origin (Kratzer et al., 2004), the $\delta^{15}N$ of POM is typically 4‰ lower than the $\delta^{15}N$ of the associated NO3 (Kendall et al., 2008b). Data from two transects of the Sacramento River and Delta from March and April 2009, where uptake rate calculations indicate that NO3 is the dominant source of N to phytoplankton (Dugdale et al., 2007), show that the average difference between the $\delta^{15}N$ of NO3 and the corresponding $\delta^{15}N$ of POM is 3.5‰ in the upper SR from Freeport to Isleton (Kendall et al., 2010b). The average C:N value of POM in this reach is 7.9, consistent with algae being the predominant organic matter source to POM, and supports the assumption that the $\delta^{15}N$ of POM is a reasonable proxy for the $\delta^{15}N$ of phytoplankton in this part of the ecosystem.

In contrast with phytoplankton-dominated sites in the upper SJR and upper SR, the average difference between the $\delta^{15}N$ values of NO3 and POM for the *Microcystis*-dominated sites in this study is -2.2‰, with values ranging from 3.3 to -12.4‰. This difference in δ values is sometimes referred to as the $\Delta\delta$ value. Despite an average C:N of 7.6, indicating that the $\delta^{15}N$ of POM should be a good proxy for the $\delta^{15}N$ of algae, there is little correlation between NO3-$\delta^{15}N$ and POM-$\delta^{15}N$ values ($r = 0.04$).

Plotting NO3-δ^{15}N values relative to POM-δ^{15}N values provides a useful means for evaluating whether NO3 uptake could be significant for various sites since the δ^{15}N of algae should always be equal or lower than the δ^{15}N of the N source. As shown in Figure 14, no sites show $\Delta\delta^{15}$N differences as high as 4‰ (i.e., no sites plot above the upper diagonal line defined by NO3-δ^{15}N minus POM-δ^{15}N = 4‰). Only a few sites plot between the diagonal lines, consistent with minor uptake of local nitrate. And most of the δ^{15}N data plot below the lower diagonal line defined by POM-δ^{15}N = NO3-δ^{15}N, indicating insignificant uptake of NO3. Therefore, NO3 was of minor importance as an N source to *Microcystis*-dominated sites, and NH4 was the primary source of nitrogen to phytoplankton and cyanobacteria in the Delta.

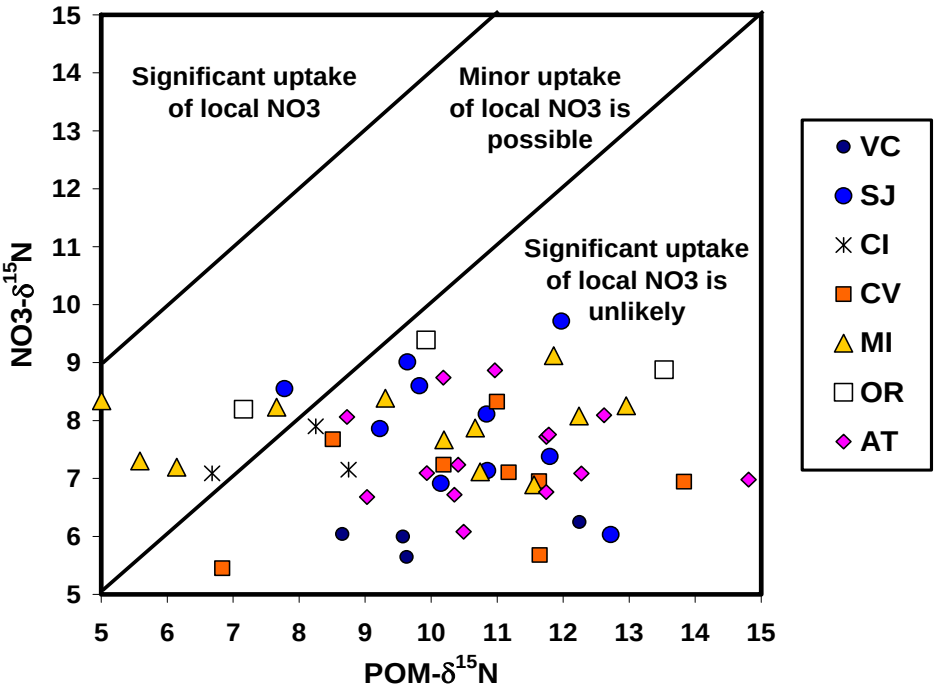

Figure 14. All available NO3-δ^{15}N values and the corresponding POM-δ^{15}N values are plotted here. The diagonal lines indicate the expected δ^{15}N values if there was no isotopic fractionation during uptake (lower line), and the expected δ^{15}N values if the fractionation was 4‰ (upper line), a typical fraction for uptake of NO3 (Finlay and Kendall, 2007). The further the data plot below the lower line, the less likely it is that algae and bacteria used NO3.

If archived samples from 2007-08 had been suitable for analysis for NH4-δ^{15}N, we would have been able to compare these NH4-δ^{15}N values with the POM-δ^{15}N and NO3-δ^{15}N values. If NH4 was the main N source to *Microcystis*, NH4-δ^{15}N values would have been equal to or a few ‰ higher than the corresponding POM-δ^{15}N values. If the isotopic fractionation was ~4‰ (i.e., the

same as for NO3), the NH4-δ^{15}N values would have ranged from +9 to +19‰ for POM-δ^{15}N values ranging from +5 to +15 (Figure 14), in good agreement with the observed range of +6 to +18‰ for NH4-δ^{15}N in the Sacramento River and Delta (Kendall et al., 2010b).

The greater the $\Delta\delta$ value (i.e., the further the data plot to the lower right of the lower line on Figure 14), the less likely NO3 is being utilized by algae and the more likely that NH4 is the dominant N source. The average $\Delta\delta$ values for the 7 different sites indicate that OR, SJ, and MI were more likely to have minor amounts of NO3 uptake than VC, CV, AT, or CI. Several parameters show small correlations with $\Delta\delta$ values. For example, DOC concentration and POM-C:N are positively correlated with $\Delta\delta$ values ($r= 0.21$ and $r=0.15$, respectively; $p<0.01$), and NO3-δ^{18}O is negatively correlated with $\Delta\delta$ values ($r= -0.13$, $p<0.01$). NO3 shows no correlation with $\Delta\delta$ but NH4 shows a diffuse negative correlation ($r = -0.37$, $p= 0.48$). It appears that the explanation for the wide variation in $\Delta\delta$ values is complex, with no single parameter explaining a significant portion of the variance. A wide range in $\Delta\delta$ values was also observed in the San Joaquin River (Kendall et al., 2008b), and could not be readily explained either.

A number of processes could explain the variations in $\Delta\delta$. We have no information about the actual isotope fractionations associated with uptake of NH4 by cyanobacteria in the Delta, and how they might vary with environmental conditions. All we know for sure is that the δ^{15}N of the cyanobacteria will be equal or lower than the δ^{15}N of the main N source. Wind-driven *Microcystis* blooms could create a situation where the POM at the sampling time may not be in contact with the nutrients used during growth. Thus, the δ^{15}N values of the nutrients might have little relation to the POM-δ^{15}N. Also, if the environmental conditions during growth, including the δ^{15}N of NH4, are highly variable, the POM-δ^{15}N (because of its longer residence time) would integrate that environmental variability whereas the NH4-δ^{15}N is an instantaneous measurement. Future isotopic studies that incorporate measurement of POM-δ^{15}N and the δ^{15}N of both NO3 and NH4 would help resolve many of these puzzles.

Conclusions

The POM, NO3, and water isotopic measurements proved useful for identifying sources of organic matter, nitrate, and water; there was insufficient DOC-δ^{13}C data to fully assess its usefulness. The main conclusions from this study are that (1) Sacramento River and San Joaquin River water and nutrients are isotopically distinguishable; (2) the dominant source of NO3 to the Delta sites studied is the San Joaquin River; (3) most of the NH4 at the study sites is derived from the Sacramento River; and (4) NH4, not NO3, is the dominant source of N fueling the *Microcystis* blooms in the Delta in the summers of 2007 and 2008.

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