Characterizing and quantifying nutrient sources, sinks and transformations in the Delta: synthesis, modeling, and recommendations for monitoring

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Contents

Figures

Tables

1. Introduction

The Sacramento-San Joaquin Delta (the Delta) receives high loads of the nutrients nitrogen (N) and phosphorous (P) from wastewater treatment effluent and agricultural runoff. Flows from the Sacramento River, San Joaquin River, and other tributaries transport these loads through a complex network of rivers, channels and flooded islands, before entering San Francisco Bay.

Excessive loads of N and P can adversely impact ecosystem health by causing excessive algal blooms and low dissolved (Valiela et al, 1992; Kamer and Stein 2003). Excessive nutrients may also contribute to the occurrence of harmful algal blooms (Bates et al, 1989) and overgrowth of nuisance aquatic macrophytes (Valiela et al, 1992). Major nutrient management decisions are being considered in both the Delta and San Francisco Bay, and those decisions require the best-available science to understand the factors that regulate ambient conditions, and the effects of loads and ambient conditions on ecosystem health. A mechanistic and quantitative understanding of nutrient cycling and fate in the Delta is essential both for informed decisions related to current conditions and also because of major anticipated changes in both loads to the Delta (upgrades at wastewater treatment facilities) and habitat function due to restoration efforts and water management.

We hypothesized that the Delta is an important biogeochemical reactor, and that transformations or losses strongly regulate ambient nutrient concentrations within the Delta and modulate nutrient loads to San Francisco Bay. Both N and P have complex cycles and require careful investigation. In this paper, we focus on nitrogen, including loads, cycling, and losses or transformations that influence its ultimate fate.

The specific goals of this study are:

1. Analyze seasonal and spatial variability in nitrogen forms and concentrations, as an indicator of potential transformation within the Delta
2. Quantify the capacity of the Delta to transform nitrogen using a one-box model and finer-scale mass balances
3. Use additional supporting water quality and isotope data to hypothesize what are the dominant processes controlling nutrient fate (transformation vs. uptake/burial)

This manuscript serves as a synthesis and distillation of the detailed data analysis and modeling modules of the project that are described in the accompanying appendices.

2. Methods

2.1 Seasonal and spatial trends in water quality

The CA Department of Water Resources Environmental Monitoring Program (DWR-EMP) has maintained a monitoring network for physical and chemical parameters, including nutrient concentrations, at fixed stations within the Delta 1-2x monthly the since 1975 (Figure 1). Data were downloaded from the DWR-EMP website (http://www.water.ca.gov/bdma/meta/Discrete/data.cfm; December 2013), and data processing, plotting, and statistical analyses performed using the statistical software R (https://www.r-project.org/), and the package wq (Jassby and Cloern, 2013). All parameters were measured by standard methods as described on DWR-EMP's website; we assumed the data received adequate QA/QC by DWR-EMP and therefore did not specifically asses data quality. The data and analyses presented are for the period 2000-2011 and focus on concentrations of N species (nitrate, NO3; ammonium, NH4; dissolved inorganic nitrogen, DIN = NO3 + NH4; total nitrogen, TN = DIN + organic nitrogen). Additional data analysis of this dataset, including for periods prior to 2000 and for other parameters, can be found in Appendix 2.

Seasonal and spatial variability were first explored through visual inspection of time-series data and by constructing boxplots of nitrogen concentrations by station and by month. In addition, empirical orthogonal functions (EOFs) were used to explore the seasonal, interannual, and spatial variability of NH4 and NO3 concentrations across Delta stations during the period 2000-2011 (Jassby and Cloern, 2013). EOFs are similar to other multivariate data analysis techniques (e.g., principal components analysis) but maintain the time-series nature of data and can be used to identify common modes of variability among multiple time series, and, in so doing, reveal similar underlying factor(s) contributing to that variability. Separate EOF analyses were conducted for NH4 and NO3 because initial tests indicated that, although some common patterns are evident across analytes, station-analyte combinations were more clearly explainable when analyzed separately. The EOF analysis yields several sets of information, including: the number of significant EOFs and the portion of the variability they explain; the strength of the relationship between an EOF and the individual station-analyte time series; and a time series of each EOF's response or amplitude. The EOF amplitude can be thought of as corresponding to the standardized response, or relative variability, at each station whose seasonal and interannual patterns are determined to be well-explained by that EOF. For example, the standardized NH4 time series at station X would be determined as:

$[NH4_{standardized}]_X = [(NH4(t)_X - NH4_{X,mean}) / NH4_{X,s.d.}]$

where $NH4(t)_X$ is the measured value for a given date at X; $NH4_{X,mean}$ and $NH4_{X,s.d}$. are the mean and standard deviations, respectively for the NH4 time series at X.

By targeting the standardized signals, the EOF analysis allows us to identify common patterns among stations whose absolute concentrations differ substantially but that deviate from their individual means in a similar manner over time.

"Volumetric fingerprints" for each DWR-EMP station were estimated using output of the hydrologic model Delta Simulation Model (DSM2); see Appendix 6 for more detail). The volumetric fingerprints estimate the relative contribution of various water sources to the ambient water at specified sites within the Delta, and are presented here on a daily-average basis from 2000-2011 for the DWR-EMP stations. Water sources include: Sacramento River; San Joaquin River; Estuarine water; Consumnes/Mokulumne Rivers; Agricultural return flows (pumped from the agriculturally managed islands); Yolo Bypass (a flood management bypass northeast of the Sacramento River); and several other minor sources.

Isotopic data ($\delta^{15}N$) for NO3 and NH4 in samples from around the Delta and San Francisco Bay are also presented. The available isotope data, relevant background, and interpretations are described in detail in Appendix 4 and 5. A subset of that data is used below to help interpret seasonal or spatial observations in N composition and as independent checks on mass balance observations.

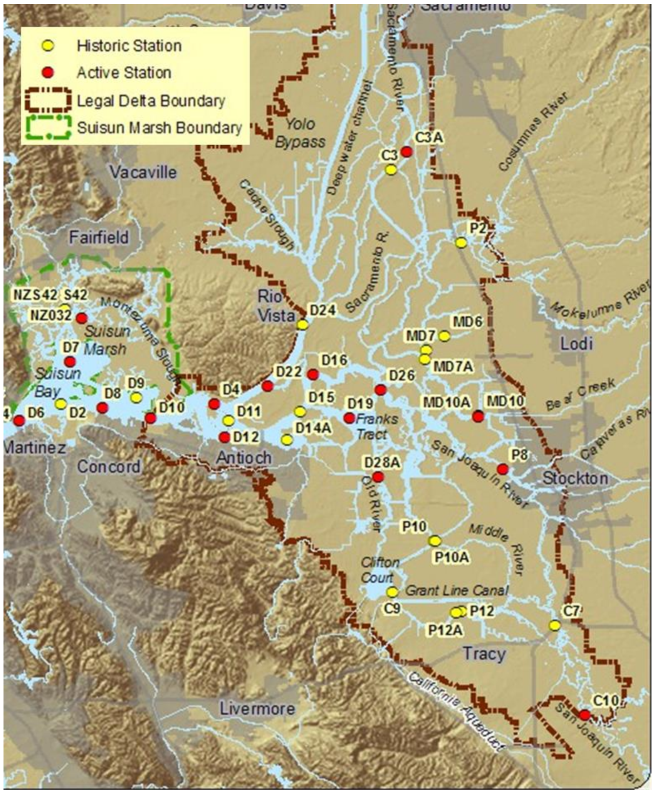

Figure 1 DWR-IEP water quality monitoring stations. In this report, we analyzed data from a subset of active stations. Appendix 2 presents a more detailed analysis of all active stations (Map courtesy of DWR-IEP)

2.2 Mass balance for the Delta

We first explored nutrient transformations/losses uptake in the Delta via a one-box mass balance for NH4, NO3, DIN and TN, adopting a method used previously to estimate organic matter loads into and out of the Delta (Jassby and Cloern, 2000). This method makes use of flow data from the DWR DAYFLOW program[1] and DWR-IEP monthly water quality data to estimate loads into the Delta, out of the Delta to water exports and out of the Delta to Suisun Bay (Figure 2). For the mass balance, we were primarily interested in the current state of the Delta, and therefore focused the analysis on the period 2006-2011 (rather than 2000-2011, the time for water quality data was analyzed), which also allowed us to maximize available data from wastewater treatment plant loadings (also known as publicly owned treatment works, POTWs). However, a number of the water quality stations used by Jassby and Cloern (2000) to estimate tributary loadings were discontinued in 1995. To bridge these data gaps, we used data from nearby on-going stations, adjusted based on the results of linear regressions performed for the time period when all stations existed, a discussion of which can be found in Appendix 3. In additional to tributary loadings, we included estimates of nutrients loads from several of the larger POTWs that discharge into the Delta (City of Stockton, City of Tracy); several smaller plants that were not considered here and whose loads are expected to be relatively small by comparison (Discovery Bay, Mountain House, Manteca, Lodi) are included in DSM2 (see Appendix 6). Loads from Sacramento Regional County Sanitation District (Regional San) were accounted for in the tributary loadings along Sacramento River, since water quality monitoring station C3 is downstream of the treatment outfall. Limited data existed to estimate internal agricultural loads, but estimates based on the Delta Simulation Model (DSM2) suggest that the loads of

[1] http://www.water.ca.gov/dayflow/output/

total N draining into the Delta from farmland were roughly equivalent to those being pumped out of the Delta to farmland (See Table 3.3 in Appendix 3). Therefore, internal agricultural loads were not expected to influence N budgets at the whole Delta scale, and were omitted from in the 1-box model. In addition, since internal agricultural activities would generally be expected to add nutrients to the system (as opposed to remove), their omission would lead to Delta losses being underestimated, and is thus a conservative assumption. We compared input loads and output loads of N in its various forms to estimate transformations or losses within the Delta. Because N undergoes complex cycling, including multiple potential forward and backward pathways between forms (e.g., see Figure 3), When NH4 inputs exceeded outputs, the difference was attributed to net transformations of NH4 through nitrification (to NO3) or assimilation (to organic N).

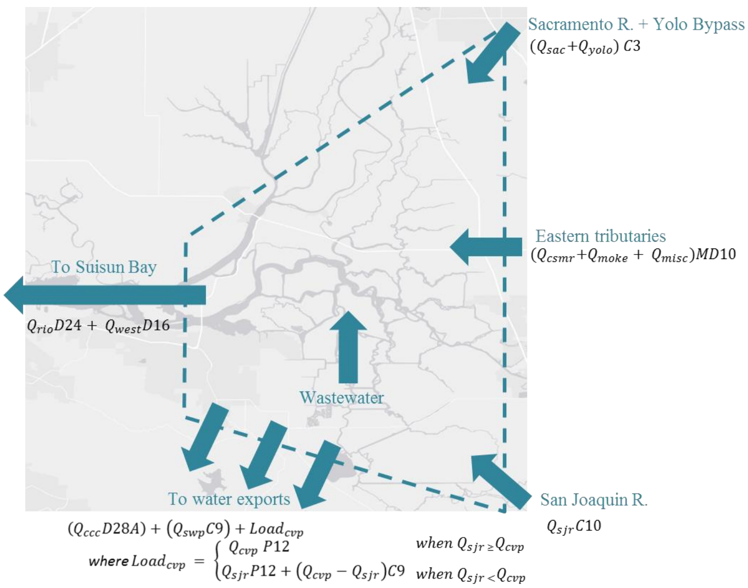

Figure 2 Schematic for 1-box mass balance for the Delta, adapted from an approach used by Jassby and Cloern (2000). We included large Delta POTWs (City of Stockton and City of Tracy). Loads from Sacramento Regional Sanitation District were accounted for by water quality monitoring at station C3, downstream of the treatment outfall. Some of the water quality stations used in this model were discontinued in 1995. For the 2006-2011 model, new stations were substituted for the discontinued stations (see Table A.3.1 for details). There was insufficient data to include agricultural withdrawals and returns in the mass balances, but output from the Delta Simulation Model (DSM2) suggests that withdrawals and returns are comparable across all N species considered and therefore do not affect the net balance (see Table A.3.2). We focused our analysis on the period June-October because we suspected transformations would be greatest during this time. A mass balance for Suisun Bay was also performed, the results of which are included in Appendix 3.

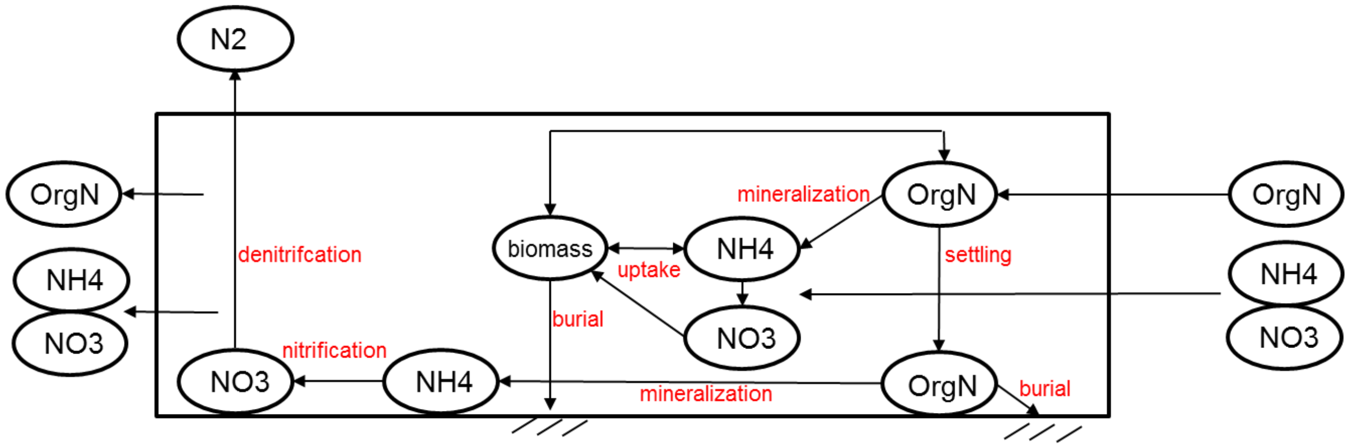

Figure 3 Conceptual model of TN loss pathways. TN can be lost via denitrification of NO3 at the sediment/water interface or through burial/storage of TN in organic matter. Organic matter can be import into the system as particular organic matter and buried within, or can come from internal production (via phytoplankton, benthic algae or aquatic plants) and stored/buried in the system.

We applied an existing a 1-D hydrodynamic and water quality model for the Delta (DSM2-QUAL) to quantify transformations/losses on finer spatial-scales related to NH4 and TN and identify zones of greatest and least transformation/losses. Details of the DSM2 suite of models and the QUAL nutrient model, in particular, can be found in Appendix 6. Output from the model, which has more than 100 nodes, was aggregated to the whole Delta for comparison with the 1-box model results, and also into 6 regions, and inputs, exports, and transformations/losses were quantified within each of those zones.

The DSM2-HYDRO hydrodynamic model is well-calibrated for flow, originating water source, and flow routing, because one of its applications is as a water resource management decision-support tool for the Delta[2]. The water quality module includes boundary condition inputs (constituent concentrations.) at each flow boundary, and within the model domain is calibrated to nitrogen and phosphorous concentrations (as well as other modeled constituents) at a number of locations within the Delta (see Appendix 6).

Although QUAL nutrient model has some limitations, it was the best available model and its capabilities are suitable for our goals of obtaining higher spatial and temporal resolution estimates of NH4 and TN budgets within the Delta and export to San Francisco Bay. Nitrification is well-parameterized, and the model calibration for NH4 concentrations is well-calibrated throughout the system. The water quality data used to calibrate and validate the model were generally monthly, although at some locations they were more frequent. The measurement stations used for calibration and validation are located throughout the Delta at hydrologically-important locations that experience diverse of nutrient conditions, and thus provide sufficient data resolution and diversity to support the regionally-aggregated estimates of transformation and loss rates. Model skill was assessed for each modeled constituent at each location and also as a Delta-wide average with three statistical parameters (see Appendix 6 for details). For the purposes of this study, the most important model skill was Model Bias. On a Delta-wide basis, model bias was rated as very good for TN, and good for NH3. Most stations had generally good Model Skill, although a couple of stations (P8 and MD10) had generally poor results for all statistical measures.

[2] http://baydeltaoffice.water.ca.gov/modeling/deltamodeling/models/dsm2/dsm2.cfm

For both the 1-box model and DSM2 mass balance approaches, results allowed us to estimate overall nitrogen loss from the system, but did not shed light on the dominant processes that could explain this loss (transformation vs. uptake/burial). We used additional lines of evidence, such as isotope data or productivity estimates, to explore the relative importance of these various loss processes.

3. Results and Discussion

3.1 Multi-year records of NH4, NO3, DIN, and TN

Concentrations of NH4, NO3, DIN and TN varied with strongly-periodic signals that generally correspond with the wet/dry and warm/cool Mediterranean climate of Bay-Delta region (Figures 4-7). Those seasonal variations are superposed upon substantial spatial differences in concentrations, in addition to both interannual variability (e.g., occasional concentration jumps) and apparently increasing or decreasing trends for some parameters and stations. Seasonal and spatial variability and long term trends in these and other water quality parameters, over the periods 2000-2011 and 1975-2011 are explored in more detail in Appendix 2.

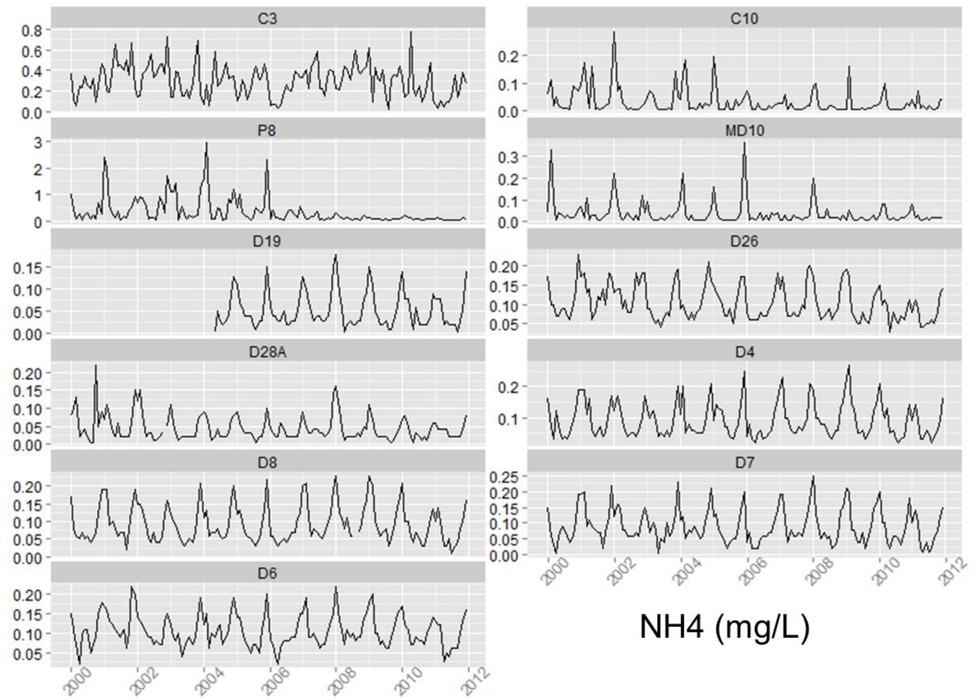

Figure 4 Time-series of NH4 (mg N/L) at select DWR-IEP water quality monitoring stations, 2000-2011. Note varying y-axis scales

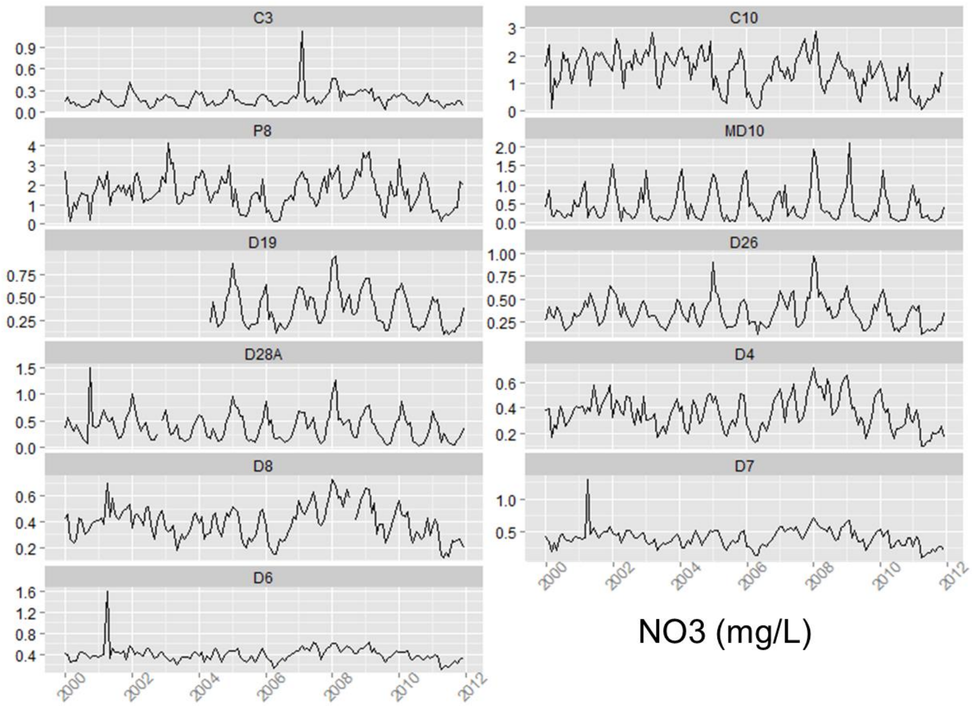

Figure 5 Time-series of NO3 (mg N/L) at select DWR-IEP water quality monitoring stations, 2000-2011. Note varying y-axis scales

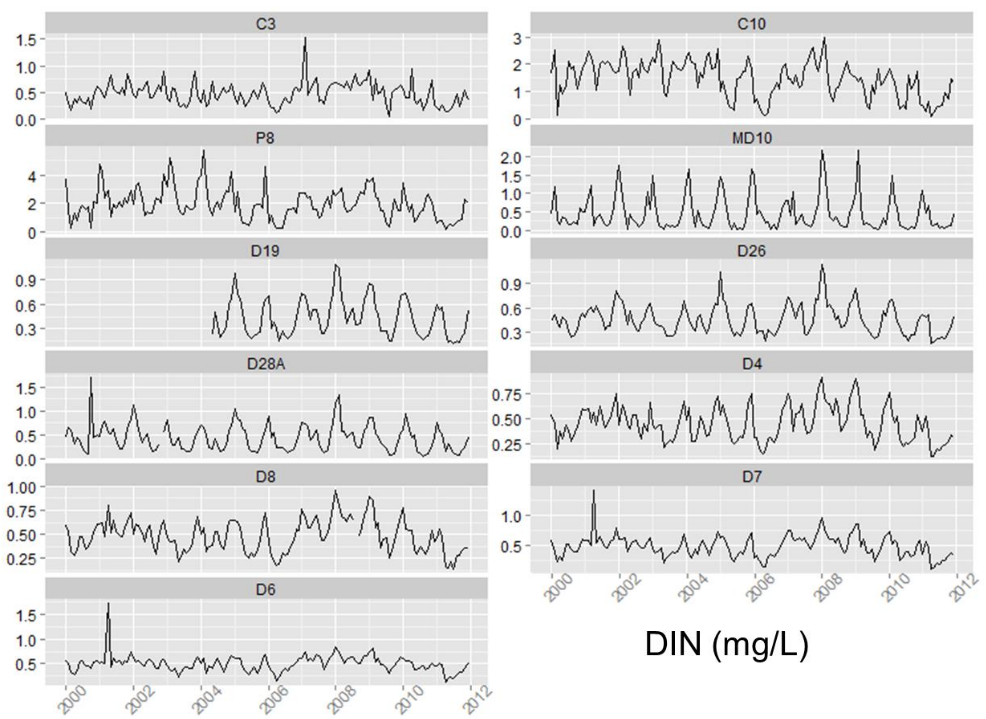

Figure 6 Time-series of DIN (mg N/L) at select DWR-IEP water quality monitoring stations, 2000-2011. Note varying y-axis scales

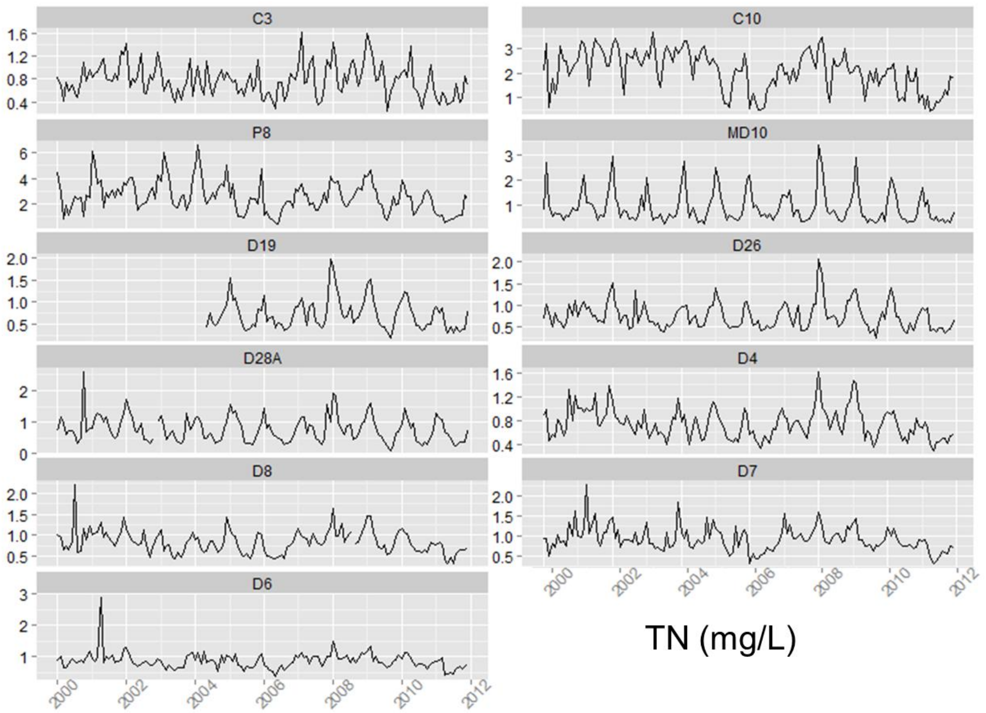

Figure 7 Time-series of TN (mg N/L) at select DWR-IEP water quality monitoring stations, 2000-2011. Note varying y-axis scales

The majority of TN was present as DIN, with DIN generally comprising 50-75% of the total (Figure 8). By visual inspection, the ratio of TN:DIN varied both spatially and seasonally, with greater TN:DIN at lower DIN concentrations.

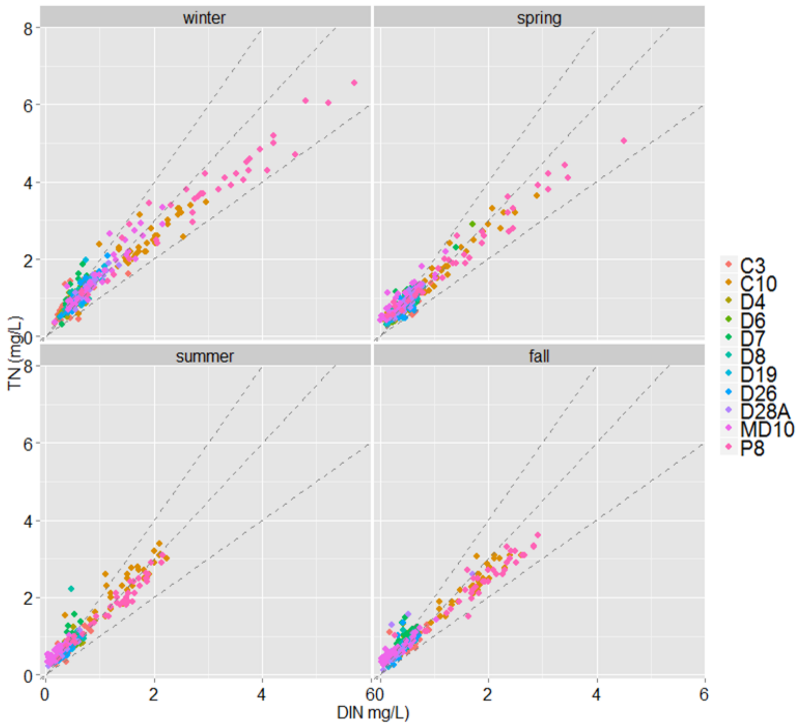

Figure 8 DIN (mg N/L) vs. TN (mg N/L), grouped by season and colored by stations

The spatially- and temporally-varying patterns in N concentrations throughout the Delta (Figures 4-7) are shaped by numerous factors, including (see conceptual model, Figure 9): the relative contributions of source waters and the chemical composition of those source waters; seasonal and temporal variability in loads; N transformations and losses within the system, with seasonally-varying rates; flow rates (dilution, residence time) and flow routing (withdrawals); climate variability (wet vs. dry years); and habitat-specific (local) factors. To better understand the factors influencing observed N concentrations at stations throughout the Delta, we explored the spatial and temporal variations in nutrient concentrations; how water sources varied among stations; and seasonal variability of key parameters at several diverse and hydrologically-important sites; Although some long-term trends in N concentrations are evident in the longer time series record (Appendix 2), the analysis presented here was aimed at improved understanding of current conditions, and therefore focuses on a recent era (2000-2011).

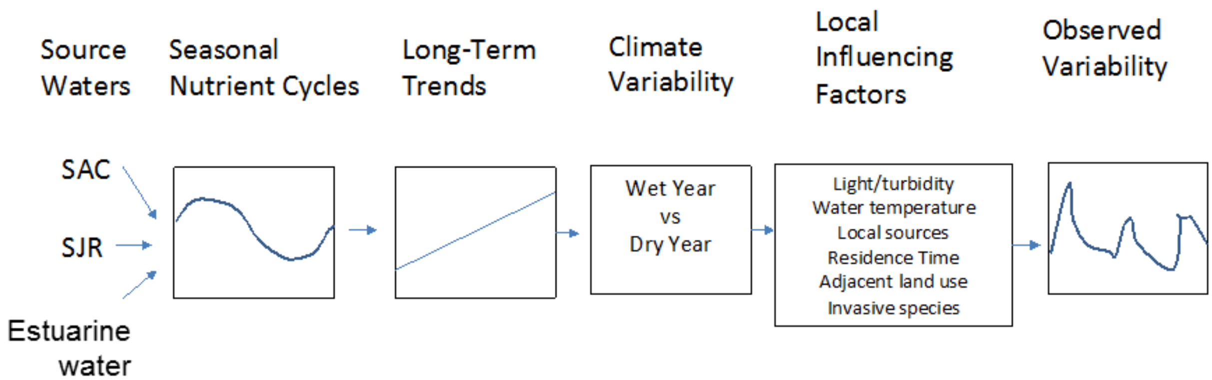

Figure 9 Basic conceptual model of factors regulating ambient water quality. The Delta's multiple hydrologic inputs (Figure 1) transport externally-sourced N into the system, with temporally-varying magnitudes and different N compositions. Internal sources contribute additional N (wastewater, agriculture).

3.2 Source water 'fingerprint'

The Delta receives multiple hydrologic inputs that have diverse water quality characteristics, including different concentrations and forms of N. The Sacramento River and San Joaquin River are the two largest freshwater sources, followed by the Consumnes and Mokulumne Rivers entering from the east. Estuarine waters from San Francisco Bay, transported by tides and estuarine circulation, are another important water source, especially for stations in Suisun Bay and, to a lesser degree, stations in the western Delta. Water exports from the Delta for agriculture and domestic consumption account for ~25% of annual flow, and during summer (low inflow) months commonly exceed 75% of instantaneous flows. During low flow periods, the water exports, centered in the southwest Delta, can substantially alter flow routing within the Delta.

Substantial spatial, seasonal, and interannual variability in water sources is evident in the volumetric fingerprint time series, derived from hydrologic model output, over the period 2000-2011(Figure 10). Stations C3 and C10 were clear hydrologic end-members, comprised entirely of Sacramento and San Joaquin Rivers, respectively. Waters at all other stations were mixtures of multiple sources in proportions that varied seasonally and interannually:

- D26, D19, and D28: Water composition is similar at these stations, both on average and in their seasonal and interannual shifts. The Sacramento River is the dominant source throughout most of the year. There are brief spring pulses during which San Joaquin and Cosumnes/Mokelumne Rivers account for non-trivial amounts of source water. The San Joaquin River is the dominant water source for extended periods in 2006 and 2011, the two wettest years during this period, and to a lesser extent during 2005, which was also a wet year. There are also minor contributions from agricultural return flows. In addition, D19 and D26 received minor contributions from estuary waters and the Yolo Bypass.
- Suisun Bay stations (D4, D6, D7, D8): Water composition is characterized primarily by seasonally-varying proportions of Sacramento and estuarine sources, with the estuarine influence greatest during low flow periods, and a pronounced east-west gradient from mostly Sacramento (D4) to Sacramento-estuarine (D8, D7), and mostly estuarine sources (D6). Flows from the Yolo

Bypass contributed to Suisun stations at low levels (<10%, except for short spikes) during winter/spring.

- MD10: MD10 MD10 exhibited the greatest diversity in its volumetric fingerprint. San Joaquin flows water contributed substantially during late-winter/early-spring, with the broadest peaks occurring during the wettest years (2005, 2006, 2011) and fall peaks during some years. Sacramento waters became dominant, on average, during summer and fall. Cosumnes/Mokelumne Rivers were also an important source during short periods, typically at its greatest in winter (January/February). Compared to all other sites, agricultural return flows contributed to the greatest extent at MD10. The peak seasonal contribution from the Sacramento River may be driven in part by water exports inducing the southward movement of Sacramento River water during summer.
- P8: San Joaquin was the dominant water source at P8. Contributions from the Sacramento and Calaveras rivers peaked in summer, and were most pronounced during three of the driest years of the decade (2007, 2008, 2009). Agricultural return flows contributed seasonally (up to ~15%), following a similar pattern as contributions from the Sacramento and Calaveras rivers.

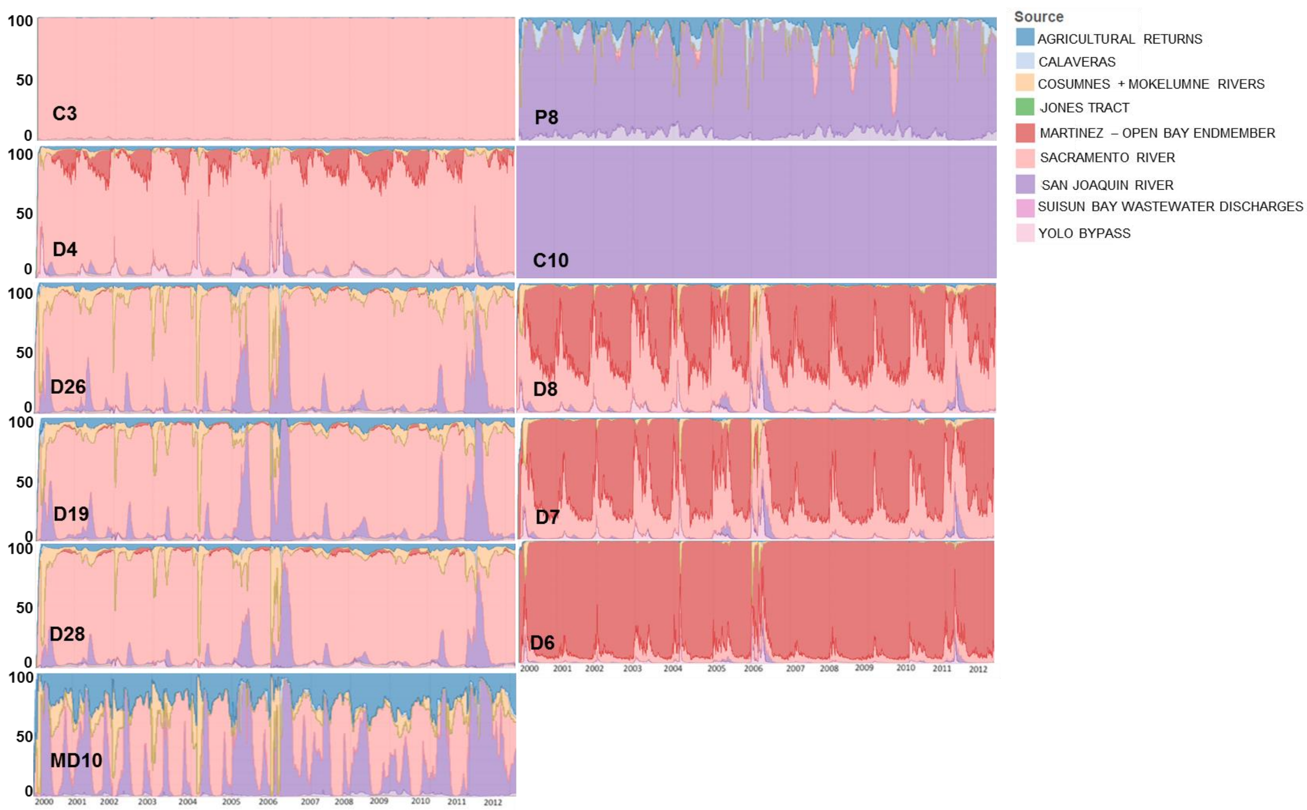

Figure 10 Percent contribution of each end member to water volume at DWR-IEP water quality stations. Data: DSM2 Model output

3.3 Seasonal, spatial, and interannual variability in N species

Monthly NH4, NO3, DIN and TN concentrations were examined over the period 2001-2011 for a subset of stations to identify typical seasonal patterns and to develop hypotheses to explain seasonal variability (Figure 11). The station subset was selected based on a combination of geographic location and volumetric fingerprints: C3 to represent the Sacramento River endmember, C10 to represent the San Joaquin River endmember, D28A to represent the interior Delta group (D19, D26, D28), and D4 to represent the Suisun stations. Plots of monthly data for other stations are included in Appendix 2.

NH4 concentrations were greatest along the Sacramento River (station C3; Figure 11), consistent with a strong influence from Regional San's treated wastewater effluent, which discharges N primarily as NH4 to the river. NH4 concentrations at C3 showed limited seasonality, except for slightly lower concentrations in January and February (Figure 10), likely caused by dilution during seasonally-higher flows. NH4 concentrations at C3 do not, on average, decrease during summer months, which is not surprising given the short distance between Regional San's input and C3's location approximately 15km downsteam, and limited time for nitrification or NH4 uptake to influence concentration. NO3 at C3 exhibited some seasonal variability, with winter median concentrations that were ~2x higher than other times of year. Little seasonality is evident for DIN at C3 (Figure 11), in part because the seasonal highs and lows of NH4 and NO3 offset each other. The modest seasonal variation in TN concentration at C3 exceeds any changes in DIN, and therefore resulted from seasonal changes in organic N concentration.

The highest median concentrations for NO3, DIN, and TN were observed along the San Joaquin River (station C10, Figure 11), and likely resulted from intensive agricultural activity in the San Joaquin River watershed. At station C10, NO3 was the dominant form of inorganic nitrogen in all months, accounting for more than 95% of DIN on average. NO3, DIN, and TN concentrations reached minimum values in May and June, and then gradually rose throughout the summer/fall. C10 had the lowest peak NH4 concentrations of all stations, observed during winter months, and reached the lowest NH4 levels of all stations in spring, summer, and early fall.

Although station D28 (and D19 and D26) is dominated by Sacramento water, the seasonal variations and dominant forms of N differ substantially from those observed upstream at C3. Maximum NH4 concentrations at D28 were >2x lower than at C3, and, unlike C3, exhibited strong seasonal variations, with 4-5 fold lower NH4 concentrations in summer than winter. In addition, despite the dominance of Sacramento water at D28, NO3 was the dominant form of DIN in all months, requiring that substantial transformations occurred as the NH4-rich Sacramento water at C3 traveled to D28. NO3, DIN, and TN concentrations also by 3-4 fold between winter and summer, suggesting that substantial N loss occurred.

Further downstream at station D4, which was comprised of approximately 80% Sacramento River water on average, seasonal patterns in N concentrations were comparable to those observed upstream at D28. Similar to D28, NO3 was the dominant form of DIN year-round, suggesting that nitrification was an important process. The substantial decreases in DIN and TN between C3 and D4 are consistent with substantial losses of N occurring along the water's flow path. .

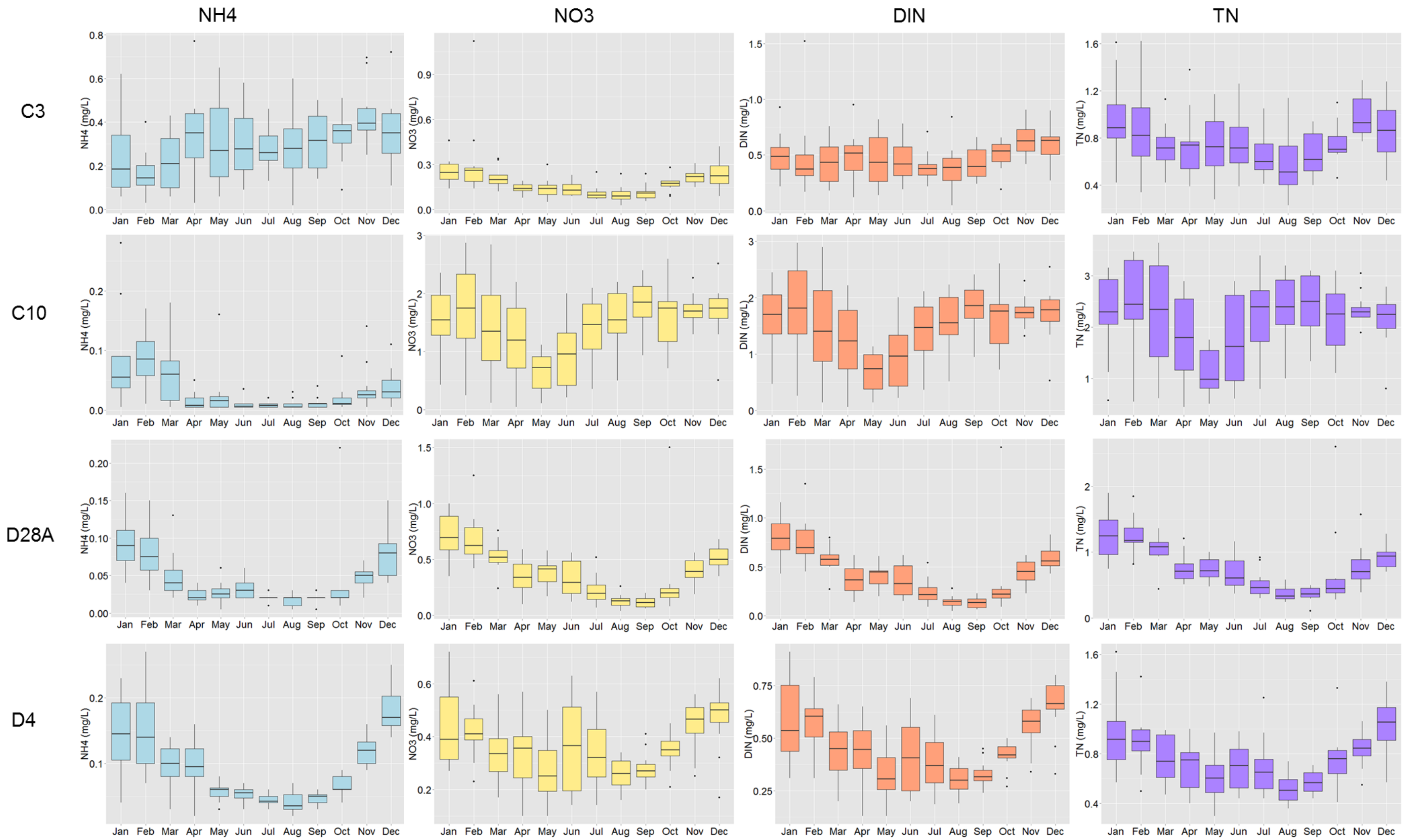

Figure 11 Boxplots on NH4, NO3, DIN and TN concentrations at a subset of DWR-IEP stations for the period 2000-2011. The boxes show median concentration and 25th/75th percentiles, and the whiskers extend to 1.5x the interquartile range. Anything beyond that are considered outliers and shown with dots. Note the varying y-axis scales.

EOFs were used to further examine the seasonal, interannual, and spatial variability in N concentrations across the Delta. The EOF analyses determined that the 20 time series for NH4 and NO3 (one for each of the 10 stations) can be reasonably well-explained by 4 modes of variability, suggesting that a common set of dominant underlying processes influence N cycling, helping to simplify the explanation of what is otherwise a large and complex system.

Analysis of the 10 NH4 time series identified 2 significant EOFs that explained 73% of the variability over time and space (Figure 12A; see Appendix 2 for more information). NH4 concentrations at the Suisun Bay stations (D4, D6, D7, and D8) and at D26 varied in a manner captured by NH4-EOF1. The substantial and consistently-timed peaks in October-December/January are an important feature of NH4-EOF1. Those peaks pre-date the timing of large changes in flow rates; it is therefore unlikely that they resulted from changing NH4 loads or concentrations in runoff; instead, they are likely result from the system-wide slow-down in either nitrification (conversion of NH4 → NO3) or NH4 assimilation during primary production. In 2006 and 2011, the NH4-EOF peaks are followed by sharp and sustained decreases, suggesting that NH4 concentrations at Suisun stations and D26 were similarly-influenced by high-flow dilution, in particular during the wettest years. The moderately negative amplitude of NH4-EOF1's during spring and summer of other years captures the seasonal NH4 decreases at these sites, due to either nitrification or uptake.

The EOF analysis for NH4 also identified NH4-EOF2, which explained a large portion of the variability at MD10, C10, and P8. The timing of the NH4-EOF2 peaks lag those from NH4-EOF1 by 1-2 months in most years. For stations MD10, C10, and P8, this may be due to a slightly lagged temperature response due to warmer conditions and longer residence within the Delta prior to the wet season, compared to the Suisun stations and D26. While P8's NH4 time series (Figure 4) is well-explained by NH4-EOF1 prior to 2006, peak NH4 concentration at P8 decrease sharply after 2006, which corresponds to the timing of an upgrade to nitrification at Stockton's wastewater treatment plant that discharges near P8. D28 was only marginally explained by NH4-EOF2; however this suggests that NH4 concentrations at D28 were regulated by a combination of factors more similar to the central/southern Delta stations than to Suisun stations and D26. The decreasing NH4 concentrations at P8 after 2006 are likely a main driver of the decreasing amplitude for NH4-EOF2, although NH4 concentrations at MD10 also appear to decline after 2006. C3's NH4 time series is also well-explained by NH4-EOF2; however, the coefficient for C3 was negative (i.e., peaks in Figure 11 are aligned with troughs in C3's NH4 time series). The sharp decreases in NH4 may be due to the beginning of higher flows in January-February, an effect that only becomes evident at downstream sites 1-2 months later (i.e., minima in NH4-EOF1). Thus, although the underlying mechanisms were different, the timing and the relative influence on NH4 concentrations detected by the EOF analysis were similar for C3 and MD10, C10, and P8.

Analysis of the 10 NO3 time series also identified 2 significant EOFs that explained 75% of the variability (Figure 12B), with some interesting differences from from the EOFs for NH4. NO3-EOF1 captures much of the variability in NO3 concentrations at the Suisun stations. Interestingly, NO3 concentrations at P8 and C10 are also well-aligned with NO3-EOF1, despite the substantial distance between them and the Suisun stations, and the fact that they are hydrologically distinct. NO3-EOF1 exhibits less of the clear seasonal variability of NH4-EOF1, but captures the large drops in winter 2006 and winter 2011; NH4-EOF1 may therefore be capturing major event-driven responses. NO3-EOF2 identifies more of the strong seasonal responses than NO3-EOF1, showing the similar patterns of strong seasonality for NO3 at stations MD10, D28, and D26, including late fall/early-winter peaks in NO3 and spring and summer minima.

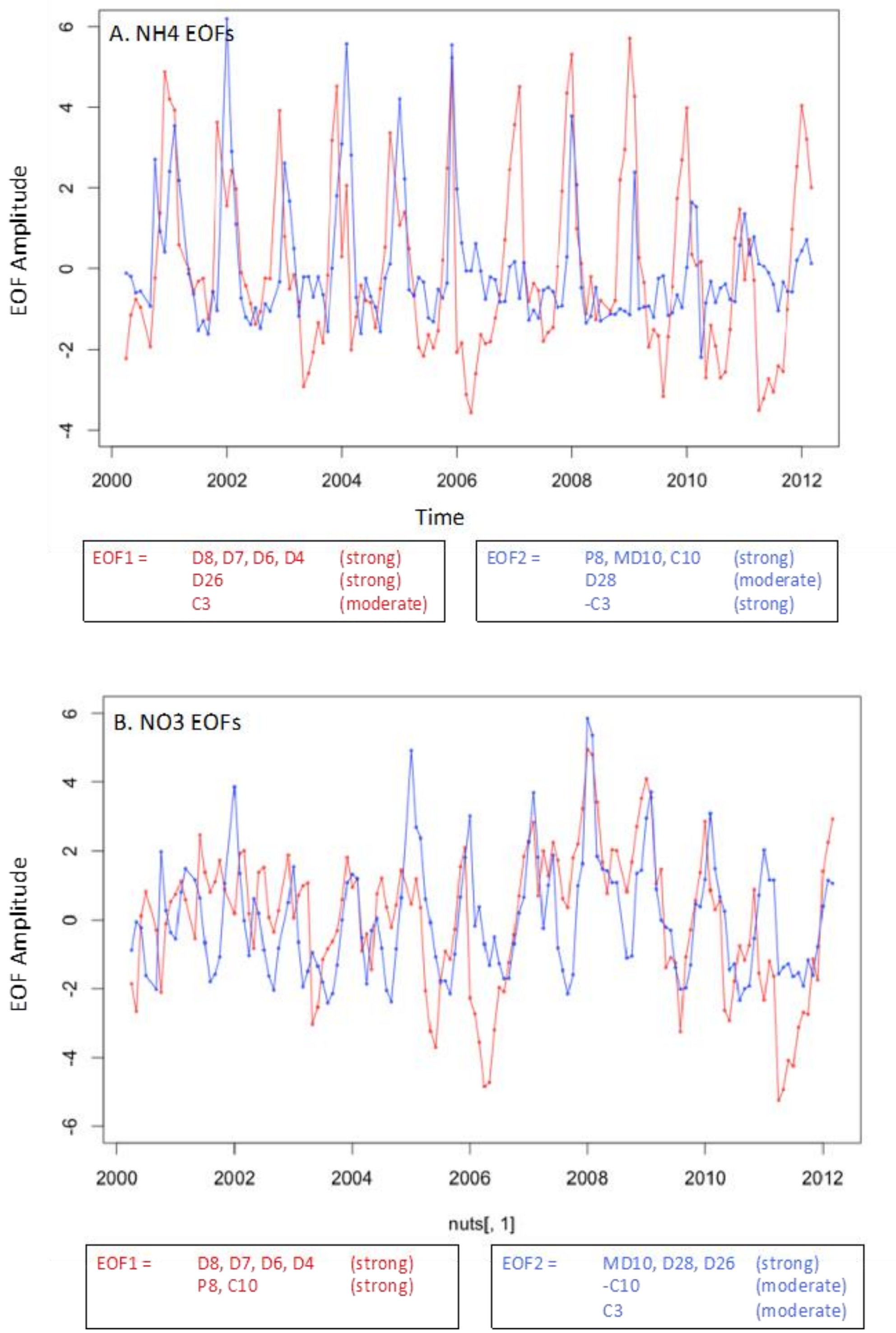

Figure 12 Results of empirical orthogonal function (EOF) analysis, by N species, for A. NH4 and B. NO3 the period 2000-2011.

3.2 Mass balance

The seasonal patterns of NH4, NO3, DIN and TN concentrations, combined with the volumetric fingerprint estimates, strongly suggest that N transformations and losses play an important role in regulating N levels within the Delta, and that the Delta is an important biogeochemical reactor that modulates the magnitude and composition of N loads to San Francisco Bay. To quantify nitrogen transformations and losses, we used two mass balance approaches at different spatial resolutions.

First, we applied a 1-box model to quantify transformations and losses at the whole-Delta scale, adapting an approach developed by Jassby and Cloern (2000) for the Delta to quantify organic carbon loadings (we extended this approach into Suisun Bay as well, results presented in Appendix 3). The discussion below focuses on mass balance results from summer months (June-October), when hydraulic residence times were longest and biologically-mediated chemical transformations (i.e., nitrification, assimilation, denitrification) occur most rapidly due to higher temperatures), allowing those transformations to be greatest and most readily detected relative to inputs. The majority of NH4, DIN and TN entering the Delta during summer months arrived via the Sacramento River (95%, 65% and 65%, respectively; Figure 13A). Although the San Joaquin River's summer flow rate is roughly 1/5th the flow of the Sacramento River, the San Joaquin contributes ~50% of the NO3 loads to the Delta despite (Kratzer et al 2011) . The City of Stockton discharges wastewater containing N primarily as NO3 to the same region of the Delta, but those loads are small relative to tributary loads from the San Joaquin River. During summer months, on average 65% of the NH4 that entered the Delta did not exit as NH4, and was therefore transformed (nitrification, assimilation) as it traveled through the system (Figure 13). Approximately 30% and 25% of DIN and TN input loads, respectively, were lost during transport through the Delta. NO3 inputs and outputs were approximately equal: although some transformation or loss of NO3 undoubtedly occurred within the Delta, that loss was apparently offset by NO3 produced through nitrification (Figure 13).

The period 2006-2011 consisted of two years of above-average flows (WY 2007 and WY 2011). We hypothesized that both the mass and the percent of transformations and losses in the Delta would be lower during these high flow years as compared to average or below average flow years due to decreased residence time. The average loads into and out of the Delta during these different flow conditions are summarized in Table 1. The results support the hypothesis that less transformation occurs on a mass basis during high flow years.

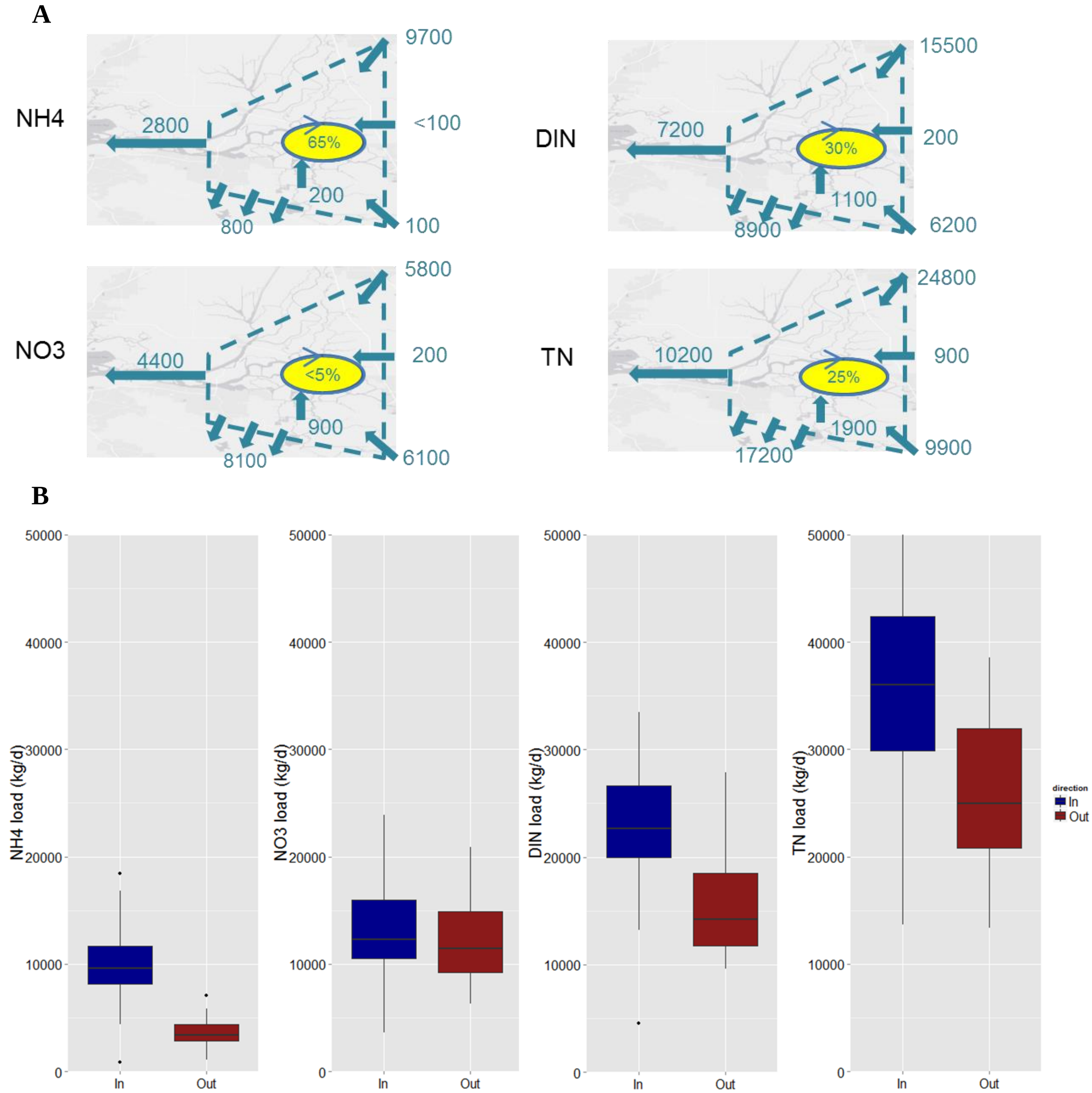

Figure 13 A. Average Summer (Jun-Oct) Delta-scale mass balance results for NH4, NO3, DIN and TN for the period 2006-2011, by component **B.** Boxplots of 1-box model results (loads into and out of the Delta) for NH4, NO3, DIN and TN for the period 2006-2011. Boxplots show the median and 25th/75th percentile, and the whiskers extend to 1.5x the interquartile range. Mass balance calculations for Suisun Bay were performed and are included in Appendix 3. All units are kg N-day

Table 1 Comparison of nitrogen losses in the Delta between high flow years (WY2007, WY 2011) and low flow years (WY2006, WY2008, WY2009, WY2010), based on our 1-box model. All loads are in units of kg-N/d. Loads in and loads out of the Delta are averages for the years indicated.

	High flow years				Average/low flow years			
	Loads in	Loads out	Mass loss	% loss	Loads in	Loads out	Mass loss	% loss
NH4	10700	4700	6000	55%	9600	3100	6500	70%
NO3	14900	15100	-200 (gain)	-1% (gain)	11900	11300	600	5%
DIN	25600	19900	5700	20%	21500	14400	6200	35%
TN	39700	32700	7000	15%	36200	24800	11400	30%

In reality, nutrient transformations or losses do not happen uniformly throughout the Delta. Instead specific areas are likely responsible for greater amounts of transformations or losses due site-specific or system characteristics. The 1-box model was a useful tool for an initial whole-Delta estimate; however, that approach (or a several-box model) is not well-suited for the spatially-resolved question because of the system's complex hydrology and limited nutrient data.

To examine N transformations and losses at higher spatial resolution, we used DSM2 and QUAL model output, and estimated losses of NH4 and TN in 6 sub-regions of the Delta (Table 2, Figure 14). We first compared the results from the 1-box model to DSM2 model output over the whole Delta (same years), and found that the losses were of similar magnitude: 85% loss of NH4 with DSM2, compared to 65% loss with 1-box model; 25% loss of TN estimated with both methods (more details in Appendix 3). The 6 regions had markedly different NH4 and TN losses, both in terms of actual mass lost and proportional loss (relative to input to that region). In 4 of the 6 Delta regions >50% of the NH4 that entered the region was lost; losses were ~20% and 40% in the South and the Confluence regions, respectively. The greatest NH4 loss (mass and percentage) occurred in the North region, followed by the East. TN losses were greatest in the North (2900 kg/d; 10%), Central (5500 kg/d; 25%) and South regions (2600 kg/d; 15%), and smaller in the East, San Joaquin and Confluence regions. A similar set of mass balances for Suisun Bay also yielded substantial losses on a mass basis of all N species compared to the Delta regions, and greater percent-losses than within the Delta (see Appendix 3 for more details).

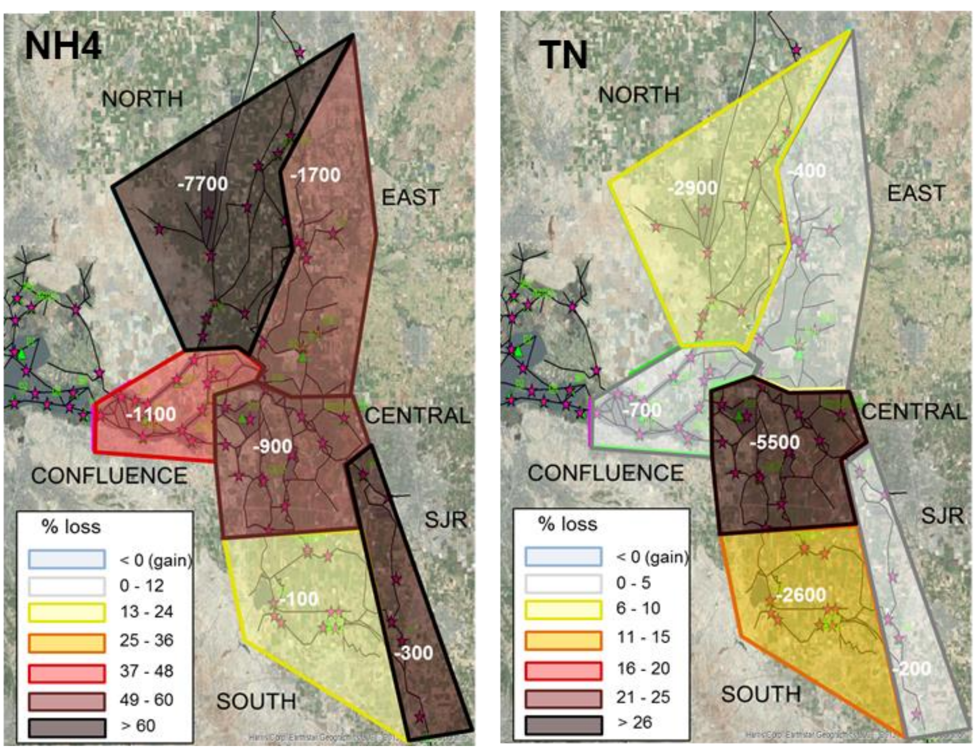

Figure 14 Nitrogen loss within each Delta sub-region, on average, for June-October of 2006-2011. Color indicates % loss in each region (note different scale for NH4). Mass losses are indicated in text, in units of kg N/day

Table 2 Nitrogen loads in/out of each Delta sub-region, on average, and for the entire Delta for June-October of 2006-2011, as well as % loss within each region. Total loads into/out of the Delta are not the sum of the loads in each region, because some load exchanges within regions are internal to the model domain. Units are kg N/day

	NH4			TN		
	In	Out	Loss	In	Out	Loss
North	12700	5000	61%	28500	25600	10%
East	3400	1700	50%	11700	11300	3%
Central	1600	700	56%	20800	15300	26%
Confluence	2800	1700	39%	23700	23000	3%
South	900	800	11%	20400	17800	13%
San Joaquin	500	200	60%	13700	13500	1%
Total Delta	**13900**	**2300**	**85%**	**48800**	**36400**	**25%**

3.3 Isotopic evidence for transformations

Seasonal transformations in nutrient concentrations and mass balance results indicate that substantial (>50%) NH4 loss occurs in most regions of the Delta. Isotopic data confirm that nitrification is occurring throughout the Delta, particularly along the Sacramento River corridor (Figure 15). In addition, a comparison of δ^{15}N-NO3 and δ^{15}N-NH4 values between high flow and low periods indicates that less nitrification occurred during high flow periods, consistent with seasonally-higher NH4 concentrations being observed at downstream stations (Suisun, D19, D26, D28). Preliminary isotopic evidence also suggests that in some parts of the Delta, uptake by phytoplankton may be the dominate fate of nitrogen in the system, although a full mass balance to test this theory is still underway.

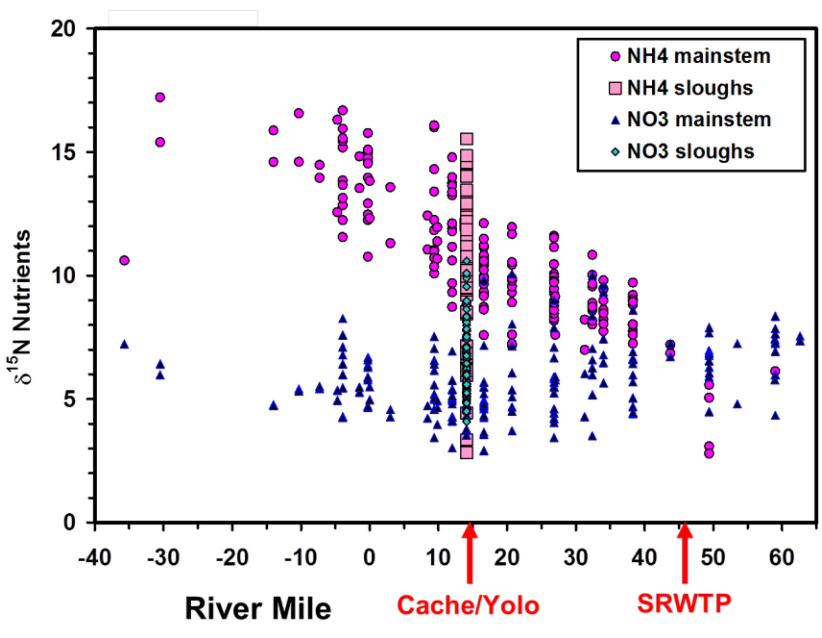

Figure 15 Comparison of δ^{15}N values of NO_3 (pink/violet) and NH_4 (blue/aqua) plotted against River Mile for samples collected at mainstem and slough locations of the Sacramento River for all transects 2009-2011. Symbol shape identifies mainstem versus slough locations. The entry points of SRWTP effluent and water from the Cache/Yolo Complex sloughs are shown with red arrows. All the slough samples are plotted at RM14.1 because the various sloughs sampled all drain into Cache Slough and this RM value is where Cache Slough converges with the mainstem Sacramento River. The data show the overall downstream trend of increasing NH_4-δ^{15}N as an isotopically light fraction of the ammonium pool is preferentially converted to nitrate (nitrification). (Figure from Kendall et al, 2015)

Along the San Joaquin River in the Stockton Deep Water Ship Channel, however, in-situ biological processes do not appear to be the dominant control on nitrogen concentrations. In this region, DIN is present mostly as NO3, and mixing between San Joaquin River water and Sacramento River water strongly influences nitrate concentrations and distributions (Figure 16). The San Joaquin River water is characterized by higher nitrate concentrations in comparison to the Sacramento River water, and the nitrate from the two rivers is isotopically distinct, providing a useful tracer for the different nitrate sources (Appendix 5.3). Most of the NO3 in Sacramento River water during summer months must have originated as NH4

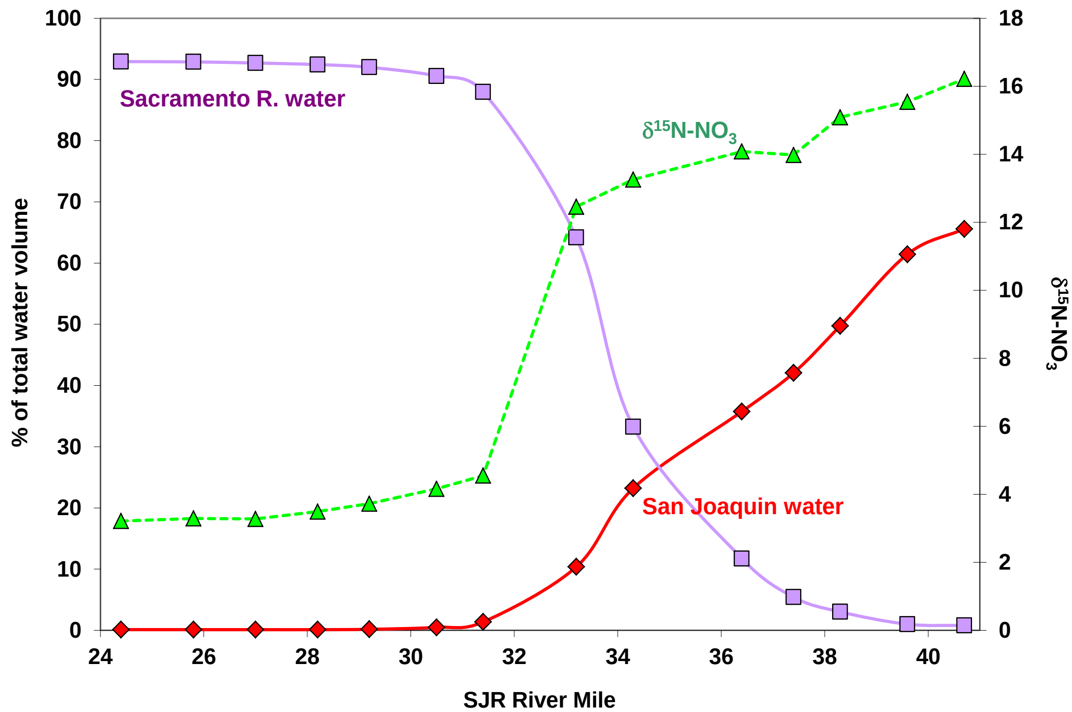

Figure 16 Water and nitrate isotope dynamics along the DWR DO transect in the Stockton Deep Water Ship Channel on August 23, 2007. The percentages of San Joaquin and Sacramento River water at each location were calculated using the DSM2 model, while the δ^{15}N-NO$_3$ was measured in water samples collected at each station. These results show the abrupt physical transition between the high-δ^{15}N nitrate carried by the San Joaquin River, and the isotopically distinct (and lower concentration and lower δ^{15}N) nitrate in the Sacramento River water.

3.4 Potential loss pathways

The pronounced seasonal decreases in DIN and TN concentrations (Figures 4-7; Figure 11), combined with volumetric fingerprint estimates, offer strong anecdotal evidence for substantial summertime N losses in the Delta. The two mass balance approaches, which estimate that TN loss in the Delta occurred at a rate of 10,000 – 12,000 kg N/day, provide independent quantitative evidence that losses occurred and that the losses were substantial relative to inputs (~30%). While N loss from a system such as the Delta is not surprising, the important role that these losses play in regulating ambient nutrient concentrations within the Delta and modulating N loads to San Francisco Bay had not previously been quantified. The estimated losses must have occurred along one, or both, of two broad pathways (see also Figure 3):

1. N was lost from the system through denitrification (conversion of NO3 to N2 by heterotrophic microorganisms during metabolism of organic matter), or possibly through anamox (carried out by chemosynthetic $NO_3^- + NH_4^+ \rightarrow N_2$);
2. TN was lost from the system through storage (in viable plants, or by initial settling of particulate N) and eventually permanent burial of organic matter within the system. The organic matter lost within the Delta could have been produced internally (e.g.,phytoplankton; benthic algae; aquatic vegetation); or was loaded into the system as particulate N) by upstream tributaries and buried within the Delta.

There are few direct measurements within the Delta that would allow direct estimates of the N losses along these pathways. Therefore, we used data from a range of freshwater and estuarine ecosystems, in addition to Delta-specific data when available, to quantify potential losses, or estimates of related processes from other Delta studies.

In oxic waterways like most of the Delta, the majority of denitrification would be expected take place in low oxygen environments, such as the sediment water interface, because denitrifying organisms require low oxygen conditions (< 5 µM). Cornwell et al (2014) performed sediment incubation experiments to estimate rates for a number of processes flux estimates, including denitrification, at 8 locations within Suisun Bay and the Delta (within the Confluence and Central regions in Figure 14). They estimated that denitrification occurred at rates on the order of 10-12 mg N/m2-d, which fall within an intermediate range for denitrification rates estimated for a number of estuaries (Cornwell et al 2014). As a first approximation, if those rates are extrapolated to the entire area of Delta waterways (2.7×10^8 m^2; Jassby and Cloern 2000), denitrification losses amount to 3000 kg N/d, or 25-30% of the estimated TN lost in the Delta. Therefore, while denitrification may be one of several factors contributing to N loss, these initial estimates do not indicate that denitrification can alone explain the majority of the loss.

Burial or long-term storage of organic matter is another pathway along which N could leave the aqueous system. A nontrivial amount of N that enters the Delta arrives as organic N (allochthonous organic N), and most of that organic N is found in the dissolved phase (DON ~67%, PON ~ 33%; Jassby and Cloern). In order for that allochthonous DON to settle and be stored or buried in the Delta, it must first be incorporated into the particulate phase through assimilation by the microbial community. We estimate that ~40% of allochthonous DON can be incorporated into microbial (particulate) biomass. (using an approach similar to the one used by Jassby and Cloern (2000) estimate allochthonous dissolved organic carbon assimilation by microbes). When this assimilable-DON fraction is combined with the portion of allochthonous total organic N (TON) that was already in the particulate phase (30%), ~70% of the allochthonous TON load, or about 10,000 kg/d, has the potential to settle and be stored within the Delta (either direct settling, or grazing by primary consumers and subsequent settling). Organic N is also produced within the Delta (autochthonous organic N) by phytoplankton, benthic algae and aquatic plants. Delta-wide, Jassby and Cloern (2000) estimated that average summertime net phytoplankton productivity in the Delta was approximately 55 t C/day or ~9,000 kg N/day (assuming C:N ~ 6). This value serves as an upper bound on autochthonous organic N burial. Some of this autochthonous organic N will be flushed downstream to San Francisco Bay in the form of viable or decomposing phytoplankton. In addition, the autochtonous organic N that does settle within the Delta will be labile; a sizable portion of it will be mineralized to NH4, some of which may undergo denitrification (after conversion to NO3) and the rest of which will (eventually) be transported back to the water column. .

Nitrogen could also be stored and eventually permanently buried in aquatic plants. Jassby and Cloern (2000) estimated production from two major species of aquatic macrophytes in the Delta: the submerged macrophyte *Egeria densa* was estimated to contribute 5 t C/day (annual average) and the free-floating macrophytre *Eichhornia crassipes* contributed approximately at approximately 7 t C/day annual average, but this was based on an areal extent of macrophyte coverage of approximately 800 and 300 hectares, respectively. However, the areal coverage of both species has grown to approximately 2,000 ha for *Egeria* (Santos 2009) and 800 ha for *Eichhornia* (Boyer and Sutula 2015), which would scale up to approximately 12.5 and 18.5 t C/day (respectively), or approximately 5,000 kg N/day combined. A greater proportion of the organic matter produced by macrophytes tends to be refractory compared to phytoplankton, and therefore has a greater likelihood of being efficiently buried with less re-mineralization. Benthic microalgae productivity from Jassby and Cloern (2000) are trivial compared to these other two sources, and while it is possible that the extent of benthic microalgae has increased since the time of this earlier study, we will assume it remains small by comparison.

When all of these PON-related mass transfer terms – either transporting PON into the system or converting dissolved N into PON - are combined (24,000 kg/d), they reach a number that roughly equals 2/3 of the summertime TN loads to the Delta. In other words, it is feasible that most of the TN loads that the Delta receives are (eventually) susceptible to settling and burial. This serves as an upper bound of the mass that could ultimately be stored within the Delta. If only a minor fraction (e.g., 20-30%; 5000-8,000 kg/d) of that combined PON experienced burial as its ultimate fate, it can, in combination with denitrification, readily explain the mass balance loss term.

Through our sub-region mass balances, we identified three regions in which TN losses were highest:
1. The "North" region which includes the Yolo Bypass and the Cache Slough complex
2. The "Central" region which includes several flooded islands
3. The "South" region, which includes a flooded island and water withdrawals

We hypothesize that hydrologic features within these regions contribute to greater TN removal. Flooded islands may act to promote TN removal by increasing residence time, which would in turn increase nutrient uptake, settling and burial in the sediments, and TN loss by denitrification. An initial particle-tracking analysis using an additional RMA 2D model for the Delta (the RMA2 model) suggests that water in flooded islands is not flushed as rapidly as water along the main rivers and channels (M Guerin, personal communication). Lastly, flooded islands could be an area of greater density of aquatic vegetation, particularly *Egeria* (Santos et al, 2009), which would also contribute to larger TN removal through uptake/storage. The San Joaquin River region (SJR, as defined in Figure 14) serves as an interesting counter example of our hypothesis. This region does not have any flooded islands and residence times are lower in this region than in many other locations in the Delta. DSM2 results suggest that there is very little TN lost from this portion of the Delta, and in fact, isotope data confirms that physical processes (i.e. mixing) dominate over biological processes in determining the fate of nitrogen in this region (see Figure 16).

4. Summary

Multiple lines of evidence demonstrate that the Delta acts as an important biogeochemical reactor for N. Seasonal trends in N speciation and concentration indicate that nitrification (NH4 → NO3) and other transformations or losses (assimilation, denitrification, burial) strongly regulate ambient NH4 and NO3 concentrations in the Delta. Seasonally-varying concentrations throughout the Delta suggest that transformations and losses were most pronounced during warmer, low-flow periods, with both the resulting faster biologically-mediated reactions rates (at higher temperatures) and longer residence times lending themselves toward maximizing the observable effects in concentration data. Evidence from nitrogen isotopes (δ^{15}N-NO3 and δ^{15}N-NH4) along transects through the northern and confluence regions of the Delta also pointed to an important role for nitrification.

Mass balance estimates using two independent approaches provide quantitative evidence that the Delta is an important biogeochemical reactor. The majority (65-85%) of NH4 that entered the Delta during summer months did not leave system as NH4, and must therefore have undergone nitrification or been assimilated. In addition, 25% of TN loads to the Delta were lost during summer months. Realistic estimates of denitrification and accumulation/burial within the Delta can combined readily explain these losses.

Both the Delta and downstream San Francisco Bay are embarking on major science and monitoring programs to inform important nutrient management decisions. The biogeochemical transformations and losses of N in the Delta play important roles in shaping ambient water quality conditions within the Delta, and also in modulating the N loads that ultimately enter San Francisco Bay from the Delta. While the available evidence consistently points toward substantial N transformations and losses, there are large uncertainties related to transformation rates, physical and biogeochemical factors influencing rates and mass removal, and the ultimate fate of N. For example, there are limited data from direct measurements to quantitatively validate the potential loss terms such of denitrification and burial. In addition, more targeted modeling work is needed to identify areas where the greatest losses occur, and to understand the relative importance of factors contributing to those losses, such as flow routing, residence time, and temperature. Lastly, major changes in the Delta system are expected in the relatively near future, including: planned upgrades at Sacramento's wastewater treatment facility (upgrade to nitrification; 30% decrease in TN); large-scale habitat restoration efforts within the Delta; and changes in water conveyance. These fundamental changes will undoubtedly influence ambient N concentrations and speciation within the Delta and loads to San Francisco Bay. Well-informed nutrient management decisions need reliable forecasts of ambient conditions under these imminent future scenarios, which in turn require well-calibrated biogeochemical models that can accurately account for losses and transformations under current conditions and respond in realistic ways to changes in physical and chemical forcings.

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