

Appendix 5: Characterizing nutrient sources and transformations in the SF Estuary using stable isotope techniques

Prepared by:

Carol Kendall, Megan B. Young, and Sara Peek

United States Geological Survey
Menlo Park, CA 94025

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Appendix 5.1. Introductory material about using isotopes as tracers of sources and processes

5.1.1 Abstract

The overall goal of this appendix is to use the isotope data from several previous studies to test and extend the interpretation of the seasonal and spatial variations in nutrient concentrations at the IEP sites that are the main focus of this SFEI-USGS-RMA project.

Appendix 5 consists of 3 sections that discuss the use of nutrient isotope data generated during earlier studies in the SFE, combined with chemical and hydrologic information, to improve our understanding of nutrient sources and sinks. The titles and brief summaries of the objectives of the different sections are listed below.

5.1 Introductory material about using isotopes as tracers of sources and processes

This section summarizes the objectives and scope of Appendix 5, and provides: an introduction to uses of isotopes, information about the different datasets discussed in this appendix, sample collection and analysis methods information, a summary of relevant recently published findings, and the references for the entire appendix.

5.2 Temporal and spatial changes in nutrients in the mainstem Sacramento River, Delta, and the northern San Francisco Bay

This section uses chemical and isotopic data in the Sacramento River, Delta, and northern SF Bay to provide insights about nutrient transformations at mainstem sites and at the nearby IEP sites used for N modeling in this report.

5.3 Combined use of stable isotopes and hydrologic modeling to better understand nutrient dynamics in the Stockton Deep Water Ship Channel, San Joaquin River and Delta

This section uses chemical and isotopic data with results from the DSM2-HYDRO model to investigate nutrient dynamics in the Stockton Deep Water Ship Channel and Sacramento-San Joaquin confluence region.

5.1.2 Introduction

We raised a number of nutrient-oriented questions in our proposal, including:

- How have nutrient concentrations varied spatially, seasonally, and over time throughout the Delta, and what are the major drivers of those changes?
- Are there regional, river reach-dependent, and temporal variations in nitrification rate or other rates of nutrient degradation? If so, what are the likely causes?
- What are the dominant processes affecting NH_4 concentrations, in particular with respect to thresholds hypothesized to inhibit NO_3 uptake?

- Are measured changes in isotope values between Delta sites consistent with nutrient loss or gain estimates produced by modeling and mass balance calculations?
- What is the Delta's ability to transform, remove, and assimilate nutrients and modulate nutrient loads to downstream systems? How do those processes vary spatially and seasonally, and what regulates their magnitudes?
- What additional monitoring or special studies are needed to address critical data gaps?

The purpose of this section of Appendix 5 is to provide, all in one place, basic information about the fundamentals of isotope biogeochemistry, conceptual models, locations of sampling sites, collection and analytical methods, data sources, etc. -- that might otherwise have to be repeated several times in the 2 subsequent sections of this appendix.

The purpose of the next 2 sections of Appendix 5 are to use various sets of isotope and chemical data from sites in the San Joaquin and Sacramento Rivers, their delta, and the northern San Francisco Bay to address the issues raised in the questions above.

Background about the use of isotopes¹

Isotopes are a popular tool for environmental studies because sources and sinks of various materials can often be identified using stable isotopes (Kendall and McDonnell, 1998). Isotopes provide "fingerprints" of different types and sources of nutrients (e.g., NO_3 and NH_4 , from waste water or agriculture) and organic matter (algae vs terrestrial organic matter), and of biological processes including the conversion of nitrate to ammonium (nitrification) uptake of nutrients into biomass (assimilation), and later degradation of biomass (rem mineralization). This information provides a better understanding of the system than standard chemical measurements alone can provide (Kendall et al., 2007; Finlay and Kendall, 2007). Furthermore, isotopes are a very cost-effective "add-on" to routine monitoring programs, requiring little additional effort by the field crews (Kendall et al., 2010). Compared with the costs associated with the field collections and basic chemical measurements, little additional resources are required to analyze selected constituents for isotopic composition. In other words, isotopes provide a "big bang for the bucks".

There are several significant N sources to the San Francisco Bay estuary, including waste water treatment plants (WWTPs), agricultural drains, minor tributaries, and wetlands. These different sources usually have a distinct range of $\delta^{15}\text{N}$ values, making $\delta^{15}\text{N}$ (combined with other isotopes of the constituent, e.g. $\delta^{18}\text{O}$ of NO_3 , $\delta^{15}\text{N}$ of NH_4 , or $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ of algae) useful tools for determining the source of the N at different sites and dates (Wankel et al, 2006). Furthermore, biogeochemical processes such as nitrification (the oxidation of NH_4 to NO_3) or assimilation (the uptake of NO_3 and/or NH_4 by phytoplankton) that convert one constituent to another often cause distinctive changes in $\delta^{15}\text{N}$ values. Hence, the magnitude and sign of a change in isotopic composition between pools (e.g., NO_3 - $\delta^{15}\text{N}$ and algae- $\delta^{15}\text{N}$), or between successive downstream samples of the same constituent, may be suggestive of one process or another, or may eliminate a process as implausible. For example, we were able to determine that the dominant N source to *Microcystis* blooms at a variety of sites in the Delta was NH_4

¹ This text is condensed from Kendall et al., 2015.

from the Sacramento River WWTP (Lehman et al., 2015). The estuary also has several significant sources of PO_4 with often distinctive differences in PO_4 - $\delta^{18}\text{O}$, which can also be used for determining the source of the PO_4 in samples (McLaughlin et al., 2006).

Processes which consume NO_3 (e.g., uptake and denitrification) cause a distinctive "coupled" shift in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values, with both the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of the residual NO_3 becoming increasingly higher as nitrate concentrations decrease because biological processes preferentially utilize the NO_3 with both lower $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values (because the bonds of the lower-mass isotopes require less energy to break), resulting in progressively higher $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values in the residual material. Hence, this preferential utilization of the lower mass ("lighter") isotopes can result in significant isotopic differences between the newly formed material (product) and the residual "reactant" or "substrate" material. This partitioning of the isotopes between compounds is called isotope fractionation.

Processes which consume NH_4 (e.g., uptake and nitrification) cause a relatively distinctive coupled increase in the $\delta^{15}\text{N}$ of the residual NH_4 as NH_4 concentrations decrease. If nitrification is the dominant NH_4 -consuming reaction, the influx of new NO_3 -- which very frequently has different $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values than the existing NO_3 in the water column -- causes distinctive downstream changes in chemical and isotopic compositions as NH_4 concentrations decrease, NO_3 concentrations increase, and the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of the bulk NO_3 change as the proportion of new NO_3 becomes a larger percent of the total NO_3 concentration.

Figure 5.1.1 shows a typical example of the effect of progressive downstream nitrification on the downstream variation in the $\delta^{15}\text{N}$ values and concentrations of NH_4 and NO_3 for samples collected along a transect in the Sacramento River and Delta. This downstream increase in the NH_4 - $\delta^{15}\text{N}$ is gradual while NH_4 concentrations are high, and then NH_4 - $\delta^{15}\text{N}$ increases rapidly as NH_4 concentrations drop downstream. The NO_3 - $\delta^{15}\text{N}$ values initially decrease downstream due to the addition of new NO_3 with a lower $\delta^{15}\text{N}$ than the original upstream NO_3 . However, as the $\delta^{15}\text{N}$ of residual NH_4 increases, the $\delta^{15}\text{N}$ of new NO_3 also increases. Eventually, as an increasing proportion of the NO_3 is derived from nitrification, the $\delta^{15}\text{N}$ of bulk NO_3 begins to reflect the $\delta^{15}\text{N}$ of the new NO_3 and NO_3 - $\delta^{15}\text{N}$ values start increasing downstream instead of decreasing. This inversion point typically occurs at or near the confluence of Cache/Yolo Slough with the Sacramento River, mainly because of the significant increase in NO_3 concentrations in this section of the transect. These same downstream changes in NH_4 - $\delta^{15}\text{N}$ and NO_3 - $\delta^{15}\text{N}$ due to progressive nitrification (Figure 5.1.2) are observed for Sacramento River and Delta samples collected during all the Dugdale and Foe transects (Kendall et al., 2015). Despite the strong downstream trends in NH_4 - $\delta^{15}\text{N}$ and NO_3 - $\delta^{15}\text{N}$ at sites, there is very little correlation of the $\delta^{15}\text{N}$ values of NH_4 and NO_3 from the same sample (Figure 5.1.3), mainly because the bulk NO_3 at most locations contains both original upstream NO_3 and newly formed NO_3 resulting from nitrification.

Nitrification followed by uptake of NH_4 and/or NO_3 by algae can cause shifts in the $\delta^{15}\text{N}$ of the resulting NH_4 , NO_3 , and algae pools, making it possible to determine if the dominant source of N to algae is NH_4 or NO_3 . Figure 5.1.4 shows a conceptual model for (1) how nitrification results in NH_4 and NO_3 pools with distinctive $\delta^{15}\text{N}$ values (with the $\delta^{15}\text{N}$ of the residual NH_4 higher than the $\delta^{15}\text{N}$ of the new NO_3), (2) how the $\delta^{15}\text{N}$ of the algae is always lower than the $\delta^{15}\text{N}$ of the dominant N source, and (3) how algae assimilating NH_4 should have distinctively higher $\delta^{15}\text{N}$ values than algae assimilating NO_3 (Kendall et al., 2015). The main principle is that biogeochemical processes preferentially utilize more of the lower-mass

isotopes (e.g., ^{14}N instead of ^{15}N), causing isotope fractionations that result in new NO_3 having a lower $\delta^{15}\text{N}$ than residual NH_4 , and algae having a lower $\delta^{15}\text{N}$ value than its N source (e.g., NO_3 or NH_4). Hence, analysis of the $\delta^{15}\text{N}$ values of NH_4 , NO_3 , and algae can be used to quantify the relative contributions of NH_4 and NO_3 to algal uptake (Kendall et al., 2015).

The studies described in the subsequent 2 sections of this appendix used a combined isotopic and chemical mass balance approach to characterize and differentiate various sources of nutrient and organic matter sources from different land uses to the SFE. The basic idea is that different sources of nutrients and organic materials, and different biogeochemical processes, frequently have characteristic isotopic signatures that, when used in conjunction with relevant chemical and hydrological data, allow these sources and processes to be quantified. For this report, we are going to focus mainly on the nutrient-oriented research in the previous studies.

During our first large nutrient-oriented study in the SFE in 2005-2007, we traced nitrate sources and biogeochemical processes from the upper San Joaquin River, through the Delta, to Angel Island (Figure 5.1.5). The large temporal and spatial changes in NO_3 concentrations across the estuary are shown in Figure 5.1.6b. This kind of plot is called a “chemoscape”, meaning chemical data presented at a landscape scale. If the variation in NO_3 concentrations on this plot was due to simply dilution, all the samples would have the same NO_3 isotopic compositions. The spatial and temporal variation in NO_3 concentrations is associated with a large 17 ‰ range of different $\delta^{15}\text{N}$ values (Figures 5.1.6a and b). The analytical precision of the $\delta^{15}\text{N}$ measurements is <0.5 ‰ hence, the spatial and temporal variations in $\delta^{15}\text{N}$ reflect a large range of N sources and biogeochemical processing of the nutrients in the estuary. Figure 5.1.7 compares the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate for samples from mainstem sites.

The main different sources of nitrate (fertilizer, animal/human waste, soil N, precipitation) generally have different ranges of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values (Figure 5.1.8). Different important N cycling processes (e.g., nitrification, uptake, denitrification) produce distinctive and often diagnostic shifts in isotopic compositions (as discussed above), as denoted by the line labeled with “denitrification” and “uptake.” Typical values for sites in the Sacramento River are shown in Figure 5.1.9.

5.1.3 Materials and Methods

Scope of work

We have had several large state-funded studies focusing on using stable isotopic techniques, combined with chemical and hydrological information, to investigate nutrient-algae linkages in the San Francisco Estuary (SFE) since 2005. However, this report only discusses data and results from 4 of them:

- (1) the “**San Joaquin River Up-Stream DO TMDL Project**” (ERP-02D-P63) funded by the San Joaquin Valley Drainage Authority, and headed by Will Stringfellow (Stringfellow et al., 2008; Kendall et al., 2008a);
- (2) the CALFED PIN700 project “**Determination of sources of organic matter and nutrients in the San Joaquin River**” headed by Carol Kendall (Kendall et al., 2008b);

(3) the SWC-funded Ammonium project “**Application of stable isotope techniques for determining NH₄ and NO₃ sources and cycling mechanisms related to POD-decline in the Sacramento River, Delta, and northern San Francisco Bay**” headed by Kendall (Kendall et al., 2015); and

(4) the IEP-funded Isotope Monitoring project “**Determination of the causes of seasonal and spatial variations in NH₄ sources, sinks, and contributions to algal productivity in the Sacramento River, Delta, and northern San Francisco Bay using a multi-isotope approach**” headed by Kendall (Kendall et al., 2015).

The **first** of these studies, the DO TMDL project, was focused on determining the sources of BOD in the upper San Joaquin River (Salt Slough downstream to Mossdale) by collecting samples from 6 mainstem and 15 tributary sites approximately twice a month 2005-2007 and analyzing them for a broad range of chemical parameters. As part of our Task #7 of this larger study, we analyzed particulate organic matter (POM) samples for stable isotopic composition, and archived splits of the samples for later analysis.

Our **second** study, the PIN700 project, piggybacked on the ongoing first study to obtain samples for a wider suite of isotopic analyses. In this study, we conducted a broader investigation of the usefulness of multi-isotopic techniques for assessment of temporal and seasonal changes in water, nutrient, and organic matter sources and sinks in the entire SJR-Delta-Bay system, by (1) piggybacking on the first study to obtain samples for a wider suite of isotopic analyses, (2) piggybacking on the approximately monthly sampling in 2006-2007 of the DWR DO Run project at 14 sites (Stockton Turning Basin to Prisoner’s Point) in the DWSC of the lower San Joaquin River to obtain isotope samples, and then (3) piggybacking on the USGS R/V *Polaris* program (<http://sfbay.wr.usgs.gov/access/wqdata/index.html>) at 19 sites (Rio Vista to Angel Island) in the Sacramento River, its Delta, and northern San Francisco Bay in 2006-2008 to obtain isotope samples.

The **third** large study, the Ammonium project, was aimed at a “proof of concept” of the potential usefulness of various multi-isotope approaches for answering questions about (1) sources and sinks of nutrients and organic matter, and (2) the relative importance of different nutrient sources to algal uptake in the Sacramento River and northern Delta. In specific, could isotopes help quantify the relative uptakes of NH₄ vs NO₃ at different sites and dates? This study also provided funding for (1) piggybacking on Chris Foe’s NH₄ monitoring project for the collection and archiving of samples from all his sites for future isotopic analysis, and (2) implementing our own “slough project” for the collection and archiving of samples from sites on Miner and Steamboat Sloughs, in addition to selected mainstem and tributary sites previously sampled by Chris Foe, to assess whether the 3 main channels of the Sacramento River were statistically significantly different.

The **fourth** large study, the Isotope Monitoring project, focused on applying a multi-isotope approach, combined with DSM2-derived modeling information, to address POD-related questions in the Sacramento River and northern Delta. The primary focus of the project was the isotopic analysis and interpretation of samples piggybacked on the approximately monthly sampling conducted by Chris Foe at 12 sites in the Sacramento River and northern Delta in 2009-2010.

Locations of sampling sites along different types of transects

Almost all our samples were piggybacked onto various federal, state, and university-organized water quality monitoring programs that established sets of sites in Sacramento River, the San Joaquin River, their Delta, and the northern San Francisco Bay to be sampled on a regular basis. Sets of samples collected along a section of the estuary over one to two days are referred to as **transects**.

All the sites discussed here except for SJR at Vernalis are impacted by tides. Since the monthly R/V *Polaris* cruises last 2 long days, it was impossible to sample all the sites at a consistent tide level. However, the shorter DWR DO Runs in the DWSC attempted to do most of their sampling in a 3 hour window of time over high slack (ebb) tide at Prisoner's Point. The Dugdale 2-day cruises started each day at an appropriate upstream Sacramento River site at low tide, and sampled downstream all day, regardless of tide changes; at the start of the second day, the last site of the previous day was resampled. In general, the 2-day Foe cruises collected samples at low tide each day, from upstream sites to downstream sites. The 1-day slough project cruises collected all samples at low tide, from upstream sites to downstream sites.

SJR transects: Land-based sampling of the upper San Joaquin River and tributaries was conducted between March 2005 and December 2007 as part of the Upstream DO TMDL Monitoring Project. Water quality and nutrient concentration data was also obtained from the Stockton Wastewater Treatment Plant for both the final effluent and upstream and downstream monitoring stations. The locations of these sites are shown on Figure 5.1.5. Table 1 provides a list of the sites and their latitudes and longitudes. The values for river miles (RM) in the tables are our best estimates; in the text, the RM values are usually reported as integers for ease in comparing site locations.

SJR DWSC transects: Boat-based sampling of the lower San Joaquin River was conducted at 14 stations (Figure 5.1.5) in the Stockton DWSC from the Stockton Turning Basin (STB) downstream to Prisoner's Point during the Department of Water Resources Dissolved Oxygen Runs (DWR DO Runs) between August 2006 and December 2007. Table 2 provides a list of the sites and their latitudes and longitudes. The DWR DO Runs were conducted biweekly starting around June of each year (depending upon the commencement of low DO conditions), and continued through November or December.

Polaris transects: Boat-based sampling of the lower Sacramento River, northern Delta, and north Bay was conducted at the USGS R/V *Polaris* Water Quality stations (Figures 5.1.5 and 5.1.10). Table 3 provides a list of the sites and their latitudes and longitudes. Samples were collected monthly at 19 stations (Rio Vista downstream to Angel Island) on the R/V *Polaris* from August 2006 through May 2008, except for some months during which the *Polaris* was in dry dock, and when storms prevented sampling.

Dugdale transects: Boat-based 2-day sampling of the Sacramento River, northern Delta, and north Bay was conducted at 23 stations (I-80 Bridge downstream to San Pablo Bay) during two transects in March and April 2009 (Figure 5.1.10). Table 4 provides a list of the sites and their latitudes and longitudes. We boarded their research vessel and collected our isotope samples at each site when they collected their chemistry samples.

Foe transects: Boat-based sampling of the Sacramento River, northern Delta, and north Bay was conducted at 12 stations (Tower Bridge downstream to Point Sacramento) during 11 2-day transects from March 2009 to February 2010 (Figure 5.1.10). Table 4 provides a list of the sites and their latitudes and longitudes. Foe collected isotope samples for our group from 11 transects July 2009-February 2010 at each site and date when he collected his water chemistry samples.

Slough transects: Boat-based sampling of ~14 sites on the Sacramento River and related waterways was conducted during 9 1-day transects conducted ~monthly April 2011 to December 2012 (Figure 5.1.10). The sites included 5 sites on the Sacramento River previously sampled during the Foe transects, two sites (one about a mile from the mouth and the other about halfway to the Sacramento River) on both Miner and Steamboat Sloughs, and the 4 tributary sites previously sampled during the Foe transects. Table 4 provides a list of the sites and their latitudes and longitudes. Some of these sites were also sampled during two “trial run” transects in winter and spring 2010. Except for a second October 2011 transect collected deliberately on flood tide to compare with samples collected at the same sites the previous day on ebb tide, all the other transects were collected on ebb tide.

Sample collection methods

Most of the samples discussed in this appendix were collected by the USGS Isotope Tracers Group working in conjunction with two long-term water quality monitoring programs conducted by the Department of Water Resources (DWR) and the U.S. Geological Survey (USGS). Samples were also collected in conjunction with 3 short-term monitoring programs conducted by Will Stringfellow (University of the Pacific, UoP), Dick Dugdale (San Francisco State University, SFSU), and Chris Foe (Central Valley Regional Water Quality Control Board, CVWQCB). Below is a brief discussion of the sample collection and sample analysis methods; for more details see Stringfellow et al. (2008), Kendall et al. (2008b), and Kendall et al. (2015).

Polaris and SJR DWSC transects: Samples were collected identically during the USGS *Polaris* and DWR DO Run cruises. Samples were collected at each station using the ship’s flow-through systems, both of which collect water from approximately 1 meter below the surface. Two one-liter Nalgene bottles were filled with water at each station, and were then kept chilled and in the dark for transportation to the laboratory and subsequent processing.

SJR transects: SJR samples at the Vernalis and Mossdale sites (and other SJR sites) were collected as part of the land-based DO TMDL sampling program. Field crews from Lawrence Berkeley National Laboratory (LBNL) and the University of the Pacific (UoP) collected all the samples from these sites, and performed initial sample processing prior to shipping the samples to the USGS Isotope Tracers Project. At each site, two splits of water were collected for isotopic analysis; one split was filtered upon return to the LBNL/UoP laboratory and the other remained unfiltered. The unfiltered sample splits were collected in 250 mL HDPE Trace-Clean wide mouth plastic bottles, and the samples for filtration were collected in 1L glass sampling bottles. All sample splits were stored in the dark at < 4° C until returned to the LBNL/UoP lab. The unfiltered samples were then placed in storage at -20° C prior to shipment.

The sample splits for filtration were filtered through precombusted Whatman GF/F 47mm filters (0.7 µm pore size) for POM collection within 24 hours of collection by the LBNL/UoP lab crews. The target volume filtered for POM analysis was either 1000 mL or less if four filters reached capacity prior to

1000mL. Total volume filtered was recorded for each sample, and all filters were kept at -20° C prior to shipment to the USGS Menlo Park Stable Isotope Laboratory (MPSIL). All water and filter samples were shipped overnight on dry ice, and immediately placed in -20° C storage at the MPSIL until preparation for isotope analysis.

Dugdale transects: Both of the Dugdale transects (March and April 2009) on the Sacramento River were sampled over two days. On the first day, 11 Sacramento River sites, from the I-80 Bridge (RM63) downstream to Rio Vista (RM12), plus 2 sites in the Cache/Yolo Slough Complex, were sampled; on the second day, 11-13 samples were collected from Rio Vista downstream into San Pablo Bay. Hence, for each transect there is a pair of samples from Rio Vista. Each day, sampling started just after high tide at the most upstream site and sites were sampled downstream on the outgoing tide. However, slack tide was encountered mid-day, resulting in the samples in the afternoon of each day being collected on rising (incoming) tides.

At each site, the boat stopped near the center of the channel and the Dugdale team collected water samples at ~1m depth using sets of Niskin bottles. These samples were analyzed in Dugdale's SFSU lab for concentrations of nutrients, organics, and chlorophyll; phytoplankton N and C uptake rates; and other parameters. See Parker et al. (2010, 2012) for more specifics about sampling protocols.

Grab samples were collected by hand for isotopic analysis by USGS team members from the upper ~0.5m of the water column. Although we collected two 1L bottles of water for isotopic analysis at all locations where the Dugdale team collected their own chemistry samples, this report only presents the data for Sacramento River and Delta sites. The bottles were kept on ice in coolers and returned to the lab the evening of the second sampling day.

Foe transects: Between May 2009 and February 2010, 11 two-day Sacramento River and Delta transects were conducted by the Foe CVRWQCB team. Samples for each transect were collected from upstream to downstream, starting at high tide at Tower Bridge (RM59) on the first day and following the ebb (outgoing) tide down river to Rio Vista (RM12), collecting samples from 6 Sacramento River sites; samples were then collected from 4 Cache/Yolo Slough Complex sites. On the second day, samples were collected from any sites missed on the first day and then from 2 Sacramento River sites downstream of Rio Vista (at RM9 and RM-4); the boat then continued sampling on the San Joaquin River. If Foe was unable to get to a site before the tide turned, he would try to collect a sample from the ebb-tide water parcel.

At each site, grab samples were collected near the center of the channel at ~1m depth. Similar to the Dugdale transects, the Foe team collected samples to determine constituent concentrations (see Foe et al. 2010 for specifics about sampling protocols and analytical methods); in addition, the Foe team collected three 1L bottles of water for isotopic analysis. At the end of each day, samples for isotope analysis were packed with ice into coolers and express mailed to the USGS Menlo Park Stable Isotope Lab (MPSIL).

Slough transects: At each site, samples were collected by boat at the center of the channel at ~1m depth by USGS team members; five 1L bottles were filled at each site and the bottles were kept on ice in coolers. At the end of the day, two 1L bottles were delivered to Randy Dahlgren's lab at UC-Davis for the same suite of chemical analyses (nutrients, organics, chlorophyll) performed on Foe transect samples, and three 1L bottles were packed in ice and returned to the USGS MPSIL for processing for isotopic

analysis. The chemical data were graciously provided by Randy Dahlgren (UC Davis); sample processing and analysis followed the same procedures as those used for the Foe transects.

Isotope analysis methods

All water samples were packed with ice in coolers and express mailed or transported to the Menlo Park Stable Isotope Lab (MPSIL) either on the day of collection or within 24 hours of collection. Upon arrival at the MPSIL, the samples were kept chilled or frozen (depending on their status in the coolers they arrived in), and were immediately inventoried, filtered, and preserved as needed by freezing, chilling, or acidification.

All isotope samples were analyzed in the MPSIL, which is part of the USGS Isotope Tracers Project labs in Menlo Park, California. The isotope data are reported in permil (‰) relative to the usual international standards: Air for $\delta^{15}\text{N}$ and VSMOW for $\delta^{18}\text{O}$ and $\delta^2\text{H}$.

All NH_4 , NO_3 , and H_2O samples were prepared for isotopic analysis in duplicate (concentrations permitting). More replicates were later analyzed if the duplicates did not agree within acceptable limits, if the yields were abnormal, or if the isotope data were significantly different than spatially adjacent samples or otherwise suspicious. All isotopic analyses were conducted with blanks and multiple isotopic standards according to established methods. More specifics about these methods are given below. Only data for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3 , $\delta^{15}\text{N}$ of NH_4 , and $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of water will be discussed in this appendix (e.g., data for POM $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^{34}\text{S}$; DOC- $\delta^{13}\text{C}$; and DIC- $\delta^{13}\text{C}$ are omitted):

NO_3 - $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$: 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 "AutoScott" autosampler connected to an IsoPrime mass spectrometer. Samples where $[\text{NO}_2]$ is more than ~5% of the $[\text{NO}_2+\text{NO}_3]$ are analyzed after removal of the NO_2 , using the method of Granger and Sigman (2009). Unless otherwise noted, " NO_3 " is used in the text below to mean " NO_3+NO_2 ".

NH_4 - $\delta^{15}\text{N}$: Samples are analyzed using a minor modification of the Holmes et al. (1998) NH_4 micro-diffusion method. Samples are analyzed using an elemental analyzer connected to an Optima mass spectrometer.

H_2O - $\delta^{18}\text{O}$ and $\delta^2\text{H}$: Both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of water are measured by 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).

5.1.4 Results

Isotopic data

The isotopic data from the San Joaquin River 2005-07 and the Sacramento River, northern Delta, and northern San Francisco Bay 2006-2008 from the first two projects, and our preliminary interpretation of the data, are reported in Kendall et al. (2008b).

The isotopic data for Sacramento River and northern Delta 2009-2011, and our preliminary interpretation of the data, are reported in Kendall et al. (2015).

Chemical data

Chemical data for the upper San Joaquin River samples, and preliminary interpretation of the data, are reported in Stringfellow et al. (2008).

Splits of the isotope samples from both the DWR DO Run sites and the Polaris sites were analyzed for nitrate concentrations at the USGS Menlo Park Stable Isotope Lab using a standard single reagent colorimetric method (Doane and Horwath, 2003). Nutrient data (NO_3+NO_2 , NH_4 , PO_4 , SiO_2) and other water quality data (salinity, temperature, dissolved oxygen, and chlorophyll) for the R/V *Polaris* Water Quality sites were measured separately at a subset of the sites as part of the long-term San Francisco Bay Water Quality Monitoring Project, and we obtained this data from the website <http://sfbay.wr.usgs.gov/access/wqdata>.

The water chemistry samples were collected from the surface, in contrast to the 1 m depth of our samples. Water quality data (surface water and bottom water: dissolved oxygen, temperature, fluorimeter, nephelometer, secchi, specific conductance) for the DWR DO Run sites were collected as part of the DWR long-term DO monitoring program. Samples from some of these sites were also analyzed for nitrate and ammonium. These data were obtained directly from the Department of Water Resources (B. Noble, personal communication). Nutrient concentrations for the DO TMDL sites were analyzed in Randy Dahlgren's lab at UC Davis.

Chemical data for 2009-2011 samples come from 3 sources: (1) Analysis of samples collected as part of Richard Dugdale's cruises in 2009-2010; these samples were analyzed in Dugdale's SFSU lab (methods and data in Parker et al. 2010; 2012). (2) Analysis of samples collected as part of transects conducted by Chris Foe and colleagues from 3/2009 through 2/2010 as part of the CVRWQCB-organized NH_4 Monitoring Project; these samples were analyzed in Randy Dahlgren's UCD lab, and the data reported in Foe et al. (2010). (3) Analysis of samples collected as part of "slough project" transects conducted our USGS Isotope Tracers project colleagues; these samples were analyzed in Randy Dahlgren's UCD lab, and the data reported in Kendall et al. (2015).

In Appendix 5, [X] is used as a convenient notation for X concentration or concentrations. Thus, $[\text{NH}_4]$ means ammonium concentration(s). EC is used as an abbreviation for Electrical Conductivity.

5.1.5 Discussion

The overall goal of our part of this SFEI-RMA-USGS collaboration was to use existing isotopic and chemical data -- and interpretations of the data -- from several previous studies to test and extend the interpretation of the seasonal and spatial variations in nutrient concentrations at the IEP sites that are the main focus of this report.

In specific, this report builds on the interpretation in two reports: Kendall et al. (2008b) and Kendall et al. (2015). Below is copied the abstract from the 2015 report, summarizing these recent findings:

“The Kendall et al. (2015) online data release and report (<http://dx.doi.org/10.5066/F7QJ7FCM>) contains isotope and chemical data for samples collected during several overlapping studies in the Sacramento River and Delta conducted 2009-2011 to evaluate the potential usefulness of stable isotope techniques for testing hypotheses about sources of nutrients and algae, and biogeochemical processes in section of the San Francisco Estuary. One main focus of the studies was to provide an independent test of the hypothesis that ammonium derived primarily from waste-water treatment plants was inhibiting phytoplankton uptake of nitrate. Another main focus was to assess whether there were significant differences between the chemistry and isotopic compositions of mainstem Sacramento River samples and (1) samples from tributaries within the Cache/Yolo Slough Complex, and (2) samples from the main two distributaries of the Sacramento River downstream of the waste-water treatment plant: Miner Slough and Steamboat Slough.

The objectives of this report were to present (1) "proof of concept" of the usefulness of isotope techniques combined with water chemistry and hydrological modeling in this ecosystem, (2) key findings from some of the ongoing parts of the studies, and (3) downloadable Excel files of the relevant isotope and chemistry data to facilitate these data being useful for other investigations. The rationale was that if isotope techniques showed promise in identifying sources and processes in this ecosystem, a comprehensive multi-isotope approach would later be used for quantifying nutrient and organic matter sources and biogeochemical processes relevant to questions about causes of environmental problems.”

These more quantitative assessments are in progress.

5.1.6 Summary and Conclusions

The main objective of the Kendall et al. (2015) study was to investigate whether stable isotope techniques can:

- 1) Identify sources of ammonium (NH_4), nitrate (NO_3), and organic compounds (especially particulate organic matter (POM) as a proxy for algae) at key locations.
- 2) Determine relative biogeochemical reactions rates of NH_4 and NO_3 at key locations, especially the relative utilization of NH_4 and NO_3 by algae.
- 3) Identify the geographic sources of dissolved and particulate organic matter (especially of algal origin) found at key locations (e.g., major fish nursery areas).

We now can answer several questions, with text copied directly from the Kendall et al. (2015) report):

“1) Are nutrients and organic matter downstream of the WWTP isotopically distinguishable from upstream nutrients?

YES. Nitrification of SRWTP effluent causes the residual NH_4 and the bulk NO_3 to have distinctive isotopic signatures indicative of nitrification. The $\delta^{15}\text{N}$ values of NH_4 and NO_3 become progressively more distinctive downstream as more NH_4 is nitrified to NO_3 .

2) Do NH_4 and NO_3 have sufficiently distinctive isotopic compositions downstream of the WWTP to distinguish the source of nutrients to algal and bacteria?

YES, at many locations. As the $\delta^{15}\text{N}$ of NH_4 and NO_3 become more isotopically distinctive downstream, algae that assimilate mostly NH_4 have different $\delta^{15}\text{N}$ values than algae that assimilate mostly NO_3 .

3) Can we distinguish nutrients and organic matter derived from the Sacramento River from materials derived from the Cache/Yolo Complex sloughs?

YES. T-tests and paired t-tests of chemical and isotopic data from Isleton and all the main sloughs in the Cache/Yolo Complex area show that the waters are statistically significantly different.

Other key findings

- Analysis of archived *Microcystis* samples collected in 2007-2008 from Delta sites for $\delta^{15}\text{N}$ of NO_3 and POM (and other isotopes), combined with a detailed statistical analysis of chemical, isotopic, and hydrological data, conclusively demonstrated that the major source of N assimilated by the *Microcystis* was NH_4 derived from the Sacramento River downstream of SRWTP (Lehman et al., 2015).
- The fact that we could make the determination of the source of N to *Microcystis* without actually having any NH_4 - $\delta^{15}\text{N}$ data was illuminating! We are currently exploring the extent to which our having $\delta^{15}\text{N}$ data (or samples archived) for both NH_4 and NO_3 in all SFE samples collected since 2009 provides an over-determined system. We anticipate being able to use this information to estimate % NH_4 uptake for Bay-Delta samples collected 2005-2007 and previously NOT analyzed for NH_4 - $\delta^{15}\text{N}$. This should ultimately let us add the comparison of the relative amounts of NH_4 vs NO_3 uptake for the last two high-flow falls (2006 and 2011) to our ongoing investigation of factors affecting seasonal and spatial changes in habitat quality related to flow conditions.
- Our multi-isotope approach has demonstrated that many different isotope tracers are sensitive indicators of N-cycling mechanisms and sources, often providing unique information beyond what could be determined with just chemical data.
- Preliminary mass balance calculations using these isotopic differences between the tributaries and the mainstem Sacramento River at Isleton indicate little support for the Cache/Yolo Complex tributaries being significant sources of nutrients to downstream sites. Instead, this area appears to be a major sink of nutrients, and an important source of algae for local and downstream food webs. Now that we have solid statistical support for nutrients and organic matter from the Cache/Yolo Complex tributaries being usually isotopically distinctive from nutrients and organic matter from the Sacramento River at Isleton, our large datasets can be used for more sophisticated mass balance models evaluating the relations between nutrients

in the Sacramento River and algal growth in the Cache/Yolo Complex – and the contributions of this algae to Delta sites.

- The two major distributaries of the Sacramento River, Miner and Steamboat Sloughs, that have a combined flow often greater than the mainstem Sacramento River at Isleton, have chemical and isotopic compositions that show no statistically significant differences between them and the Sacramento River at Isleton for almost all of the chemical and isotopic parameters measured (11 out of 15), and only barely statistically significant differences for the other four parameters. This finding vastly simplifies the use of isotope and chemical data for mass balance calculations in this area.
- Detailed evaluation of the temporal and spatial changes in nutrient and total chlorophyll concentrations for March 2009 through March 2010 show that downstream changes in NH_4 concentrations are not mirrored in the downstream changes in NO_3 concentrations – although the trends in nutrient concentrations appear to mirror each other when averaged at each site (per Foe et al., 2010). This suggests that in some locations there is a sink for NH_4 besides nitrification, and in others there appear to be additional sources of NO_3 . The causes of these discrepancies are under investigation.
- Data from our detailed transects and continuous data from our USGS collaborators suggest that our efforts to conduct pseudo-Lagrangian transects by sampling carefully on ebb flow (i.e., trying to follow a parcel of water) on our transects were probably insufficient for accurate estimates of biogeochemical rates between successive downstream sites where we had chemical data -- unless we can make corrections using effluent data (or with DSM2-modeled effluent and travel-time data – which we have).
- We have found that $\text{POM-}\delta^{34}\text{S}$ is an extremely valuable tracer of organic matter (particulate and dissolved) derived from water sources that have distinctive $\text{SO}_4\text{-}\delta^{34}\text{S}$ values because of unique S sources and/or biogeochemical processes. In particular, algae growing in many of the Cache/Yolo Complex tributaries have an isotopically distinctive $\delta^{34}\text{S}$ value that provides a tracer for fish that are growing in these tributaries. Algae growing in the Bay also have a distinctive isotopic signature.
- Our realization that much of the site-to-site downstream changes in chemistry and isotopes observed in our transects was probably a function of spatio-temporal variations in effluent concentrations and travel times combined with tidal cycles directly led to the USGS 2013-2014 Lagrangian study; papers are in preparation. Our hope is that we will be able to derive equations for how effluent $[\text{NH}_4]$ varies with season and flow, that will allow us to better interpret the older transect datasets – and will make it easier to interpret further chemical and isotopic studies piggybacked onto state and federal monitoring programs in tidal rivers.“

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Appendix 5.1 Tables

Table 5.1.1. Locations of mainstem San Joaquin River sites.

Site Number	Site Name	Latitude-N	Longitude-W	River Mile
DO-01	Channel Point	37.95027	-121.33715	39.8
DO-02	SJR at Lathrop	37.83053	-121.31107	50.8
DO-03	SJR at Old River	37.81082	-121.32392	53.5
DO-04	SJR at Mossdale	37.78710	-121.30757	56.2
DO-05	SJR at Vernalis	37.67936	-121.26504	72.2
DO-06	SJR at Maze	37.64027	-121.22952	77.4
DO-07	SJR at Patterson	37.49415	-121.08071	99.4
DO-08	SJR at Crows Landing	37.43197	-121.01165	108.6
DO-09	SJR at Fremont Ford	37.30985	-120.93055	125.1
DO-10	SJR at Lander Avenue	37.29502	-120.85105	131.9

Table 5.1.2. Locations of DWR DO Run sampling sites in the Stockton DWSC.

Site Number	Site Name	Latitude - N	Longitude -W	River Mile
SC-57	Prisoner's Point/ Light 57	38.05967	-121.55600	24.4
SC-04	Light 4	38.05550	-121.52950	25.8
SC-06	Light 6	38.05383	-121.51517	27.0
SC-12	Light 12	38.04267	-121.49883	28.2
SC-14	Light 14	38.03400	-121.48367	29.2
SC-18	Light 18	38.02183	-121.46567	30.5
SC-19	Light 19	38.01067	-121.45667	31.4
SC-28	Light 28	37.99383	-121.43250	33.2
SC-34	Light 34	37.99400	-121.41367	34.3
SC-40	Light 40	37.97817	-121.38250	36.4
SC-41	Light 41	37.96867	-121.37150	37.4
SC-43	Light 43	37.95867	-121.35933	38.3
SC-48	Light 48	37.95217	-121.33783	39.6
SC-STB	Stockton Turning Basin	37.95233	-121.31733	40.7*

*The Turning Basin site is just upstream of where the SJR intersects with the DWSC.

Table 5.1.3. Locations of R/V *Polaris* Sampling Sites in the Delta and North Bay.

Site #	Site Name	Latitude - N	Longitude -W	River Mile
PO-18	Point Blunt (near Angel Island)	37.84667	-122.42167	-44.7
PO-17	Raccoon Strait	37.88167	-122.42667	-42.3
PO-16	Charlie Buoy	37.91500	-122.42667	-40.0
PO-15	Point San Pablo	37.97500	-122.43667	-35.7
PO-14	Echo Buoy	38.00667	-122.40500	-32.9
PO-13	N. of Pinole Point	38.02833	-122.37000	-30.5
PO-12	Pinole Shoal	38.05167	-122.31167	-26.9
PO-11	Mare Island	38.06167	-122.26333	-24.2
PO-10	Crockett	38.06000	-122.20833	-21.2
PO-09	Benicia	38.05000	-122.17333	-19.1
PO-08	Martinez	38.03000	-122.15167	-17.2
PO-07	Avon Pier	38.04833	-122.09667	-14.0
PO-06	Roe Island	38.06500	-122.03500	-10.3
PO-05	Middle Ground	38.06000	-121.98000	-7.3
PO-04	Delta (Simmons Point)	38.04833	-121.93500	-4.7
PO-03	Delta (Pittsburg)	38.05000	-121.87833	-1.5
PO-02	Delta- Chain Island	38.06333	-121.85500	0.0
PO-649	Sacramento River	38.06167	-121.80000	3.0**
PO-657	Rio Vista (Sacramento River)	38.14833	-121.68833	12.0**

**These are upstream in the Sacramento River, SJR river miles have been assigned so that these stations can be plotted.

Table 5.1.4. Locations of Sacramento River and Delta sites sampled during Dugdale, Foe, and Slough transects (modified from Kendall et al., 2015).

Project Name	Sampling Location	RM (SR)	RM (rel. SRWTP)	site type	Latitude	Longitude
Dugdale	SR @ I-80 Bridge	62.6	-16.6	mainstem	38.600	-121.553
Foe, Dugdale	SR @ Tower Bridge	59.0	-13.0	mainstem	38.580	-121.508
Dugdale	SR @ Oak Hall Bend	53.5	-7.5	mainstem	38.518	-121.529
Foe, Dugdale	SR @ Garcia Bend	49.4	-3.4	mainstem	38.478	-121.544
Dugdale	SR @ River Mile 44	43.8	2.3	mainstem	38.435	-121.524
Foe, Dugdale	SR @ Hood	38.3	7.7	mainstem	38.378	-121.525
Slough	SR @ Courtland	34.0	12.0	mainstem	38.327	-121.576
Slough	SR @ Steamboat Slough	32.4	13.6	mainstem	38.305	-121.573
Dugdale	SR @ Kenady Landing	31.3	14.7	mainstem	38.292	-121.562
Dugdale	SR @ Delta Cross Channel	27.0	19.0	mainstem	38.264	-121.511
Foe, Slough	SR @ Walnut Grove	26.8	19.2	mainstem	38.243	-121.514
Dugdale, Slough	SR @ L37	20.7	25.3	mainstem	38.194	-121.564
Foe, Dugdale, Slough	SR @ Isleton	16.6	29.4	mainstem	38.163	-121.610
Slough	Miner Sl. @ Hwy 84 Br.	14.1	17.9	tributary	38.291	-121.629
Slough	Steamboat Sl. @ Ryer Br.	14.1	19.2	tributary	38.238	-121.603
Foe, Slough	Miner Slough near mouth	14.1	23.2	tributary	38.234	-121.667
Foe, Slough	Steamboat Sl. near mouth	14.1	24.3	tributary	38.184	-121.650
Foe, Slough	Cache Slough @ DWSC	14.1	36.6	slough	38.237	-121.673
Foe, Slough	Liberty Island	14.1	38.0	slough	38.257	-121.680
Slough	Cache Sl. @ pumphouse	14.1	39.2	slough	38.269	-121.702
Foe, Slough	Lindsey Slough	14.1	40.1	slough	38.258	-121.726
Foe, Slough	Toe Drain @ Dredger	14.1	44.9	slough	38.354	-121.643
Dugdale	Cache Sl. @ Hastings Br.	14.1	38.2	slough	38.247	-121.702
Dugdale	Cache Sl. @ Ryer Island	14.1	38.0	slough	38.217	-121.670

Table 5.1.4. continued.

Project Name	Sampling Location	RM (SR)	RM (rel. SRWTP)	site type	Latitude	Longitude
Foe, Dugdale	SR @ Rio Vista	12.0	34.0	mainstem	38.157	-121.685
Dugdale	USGS 655	9.8	36.2	mainstem	38.122	-121.701
Foe	SR @ Three Mile Slough	9.4	36.6	mainstem	38.106	-121.700
Dugdale	USGS 653	8.4	37.6	mainstem	38.106	-121.720
Dugdale	Sacramento River	3.0	43.0	mainstem	38.045	-121.799
Dugdale	SR @ Chain Island	0.0	46.0	mainstem	38.063	-121.855
Foe	SR @ Pt. Sacramento	-0.3	46.3	mainstem	38.062	-121.857
Dugdale	Pittsburg	-1.5	47.5	mainstem	38.055	-121.875
Foe	Chipps Island	-3.9	49.9	mainstem	38.046	-121.919
Dugdale	Simmons Point	-4.7	50.7	mainstem	38.049	-121.930
Dugdale	Middle Ground	-7.3	53.3	mainstem	38.060	-121.979
Dugdale	Roe Island	-10.3	56.3	mainstem	38.065	-122.040
Dugdale	Avon Pier	-14.0	60.0	mainstem	38.032	-122.098
Dugdale	North of Pinole Point	-30.5	76.5	mainstem	38.029	-122.369
Dugdale	Paradise Cay	-35.7	81.7	mainstem	37.934	-122.459

Appendix 5.1 Figures

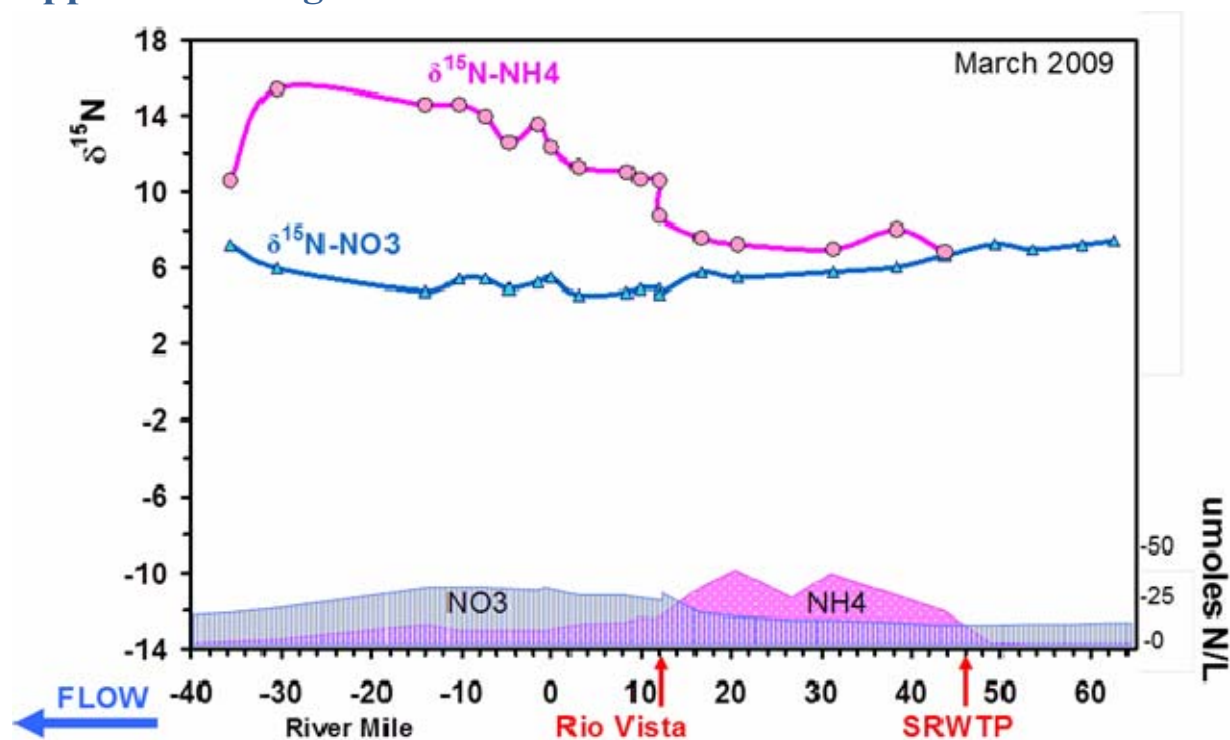


Figure 5.1.1. Downstream variation in the $\delta^{15}\text{N}$ values and concentrations of NH_4 and NO_3 for the March 2009 transect of the Sacramento River. SRWTP: indicates where treated effluent from the Sacramento Regional Wastewater Treatment Plant enters the River. Chemical data from Parker et al. (2010). Modified from Kendall et al. (2015).

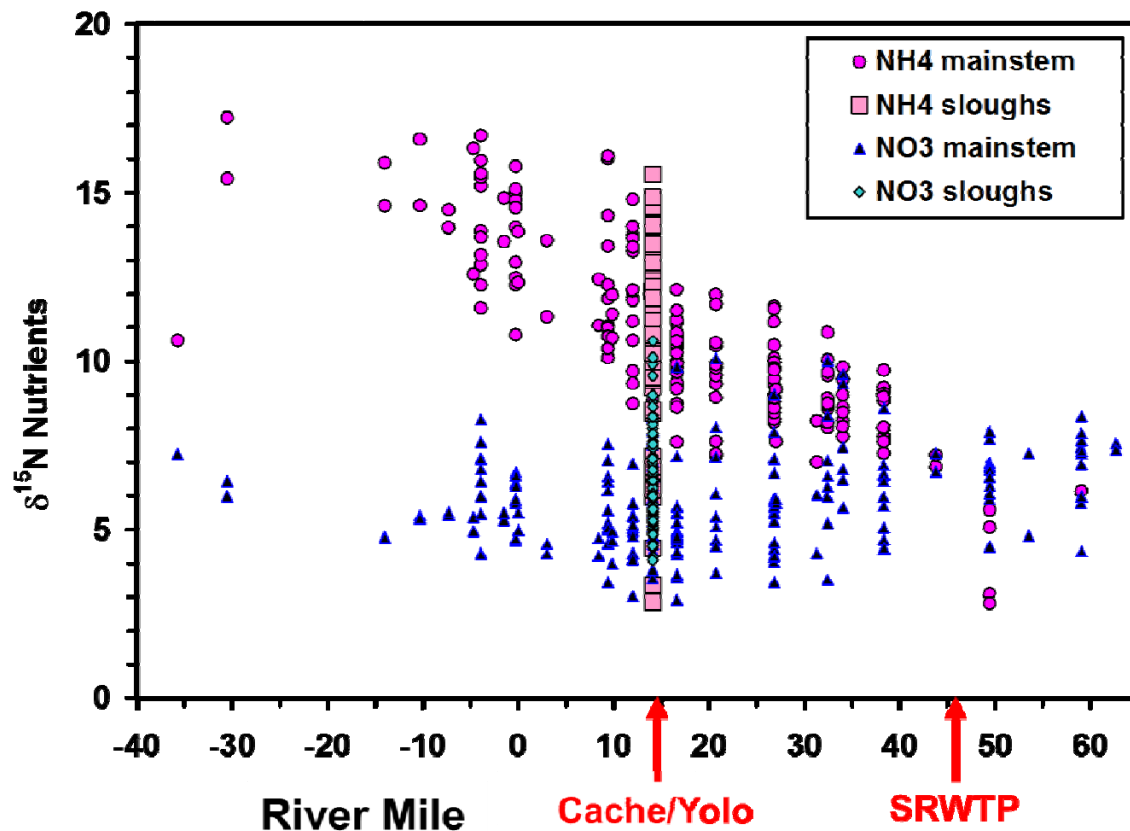


Figure 5.1.2. Downstream variation in the $\delta^{15}\text{N}$ values of NO_3 (pink/violet) and of NH_4 (blue/aqua) for all the samples collected during the Dugdale and Foe transects of the Sacramento River in 2009-2010. Symbol shape identifies mainstem versus slough samples. The entry points of SRWTP effluent and water from the Cache/Yolo Complex sloughs into the Sacramento River are shown with red arrows. All the slough samples (actually samples from 4 tributary sites) are plotted at RM14.1 because the various sloughs (tributaries) sampled all drain into Cache Slough and this RM value is where Cache Slough converges with the mainstem Sacramento River. From Kendall et al. (2015).

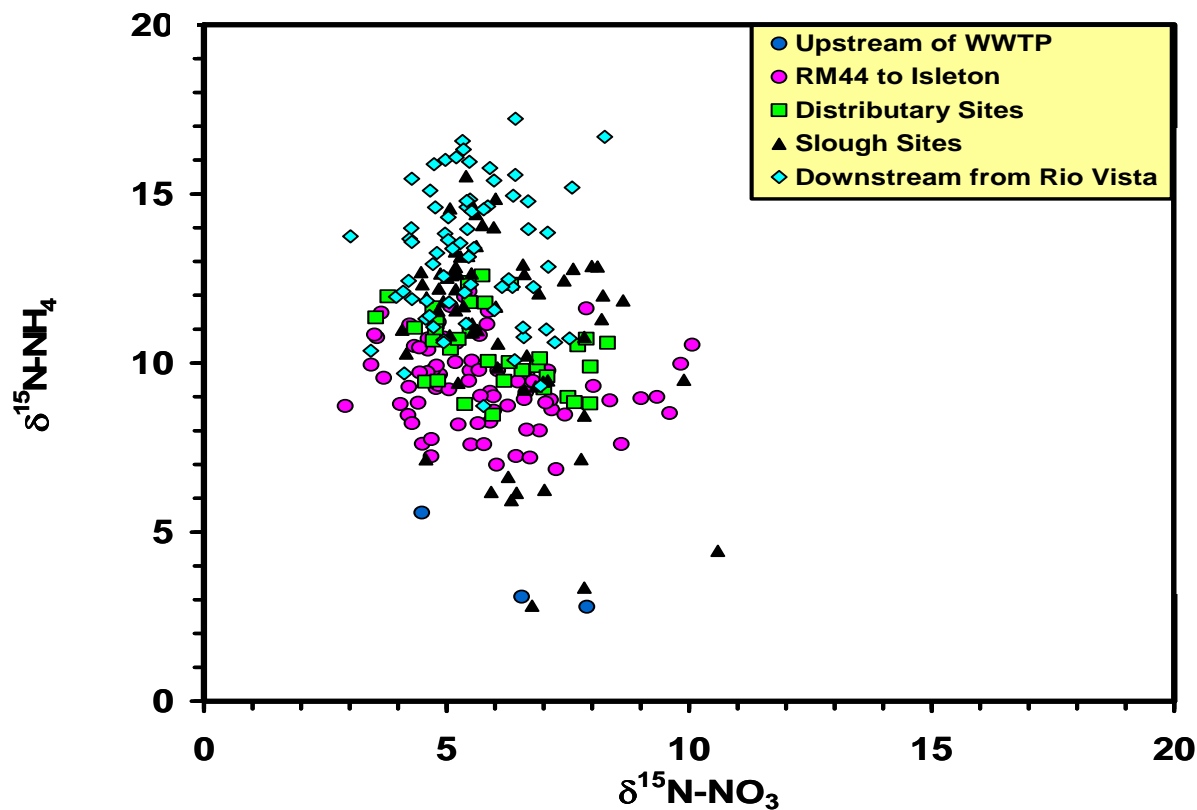


Figure 5.1.3. Despite intense nitrification, the $\delta^{15}\text{N}$ of NH_4 and NO_3 are poorly correlated for the entire dataset. Comparison of the $\delta^{15}\text{N}$ values of NO_3 and NH_4 for all sites sampled on all Sacramento River transects. Different symbol shapes and colors indicate sample types (e.g., distributary and slough sites) and section of the river for mainstem sites. From Kendall et al. (2015).

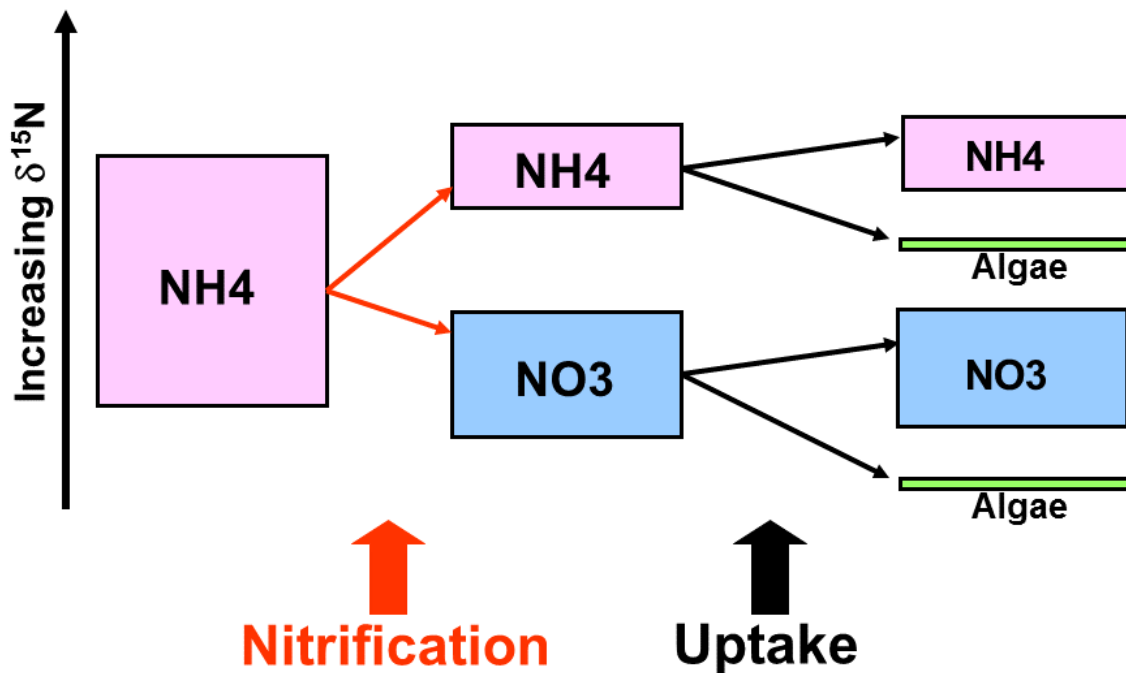


Figure 5.1.4. This cartoon shows how nitrification and uptake can cause shifts in the $\delta^{15}\text{N}$ of the resulting NH_4 , NO_3 , and algae pools. The relative uptakes of N sources to algae can often be quantified because algae always have a lower $\delta^{15}\text{N}$ than their N source. The sizes of the boxes APPROXIMATE the relative amounts of N in algae and nutrients during NH_4 and NO_3 uptake, and the relative vertical positions of the boxes APPROXIMATE their relative $\delta^{15}\text{N}$ values. These boxes are not to scale in that the uptake rate of NH_4 is about an order of magnitude higher than that of NO_3 (Parker et al., 2012). From Kendall et al. (2015).

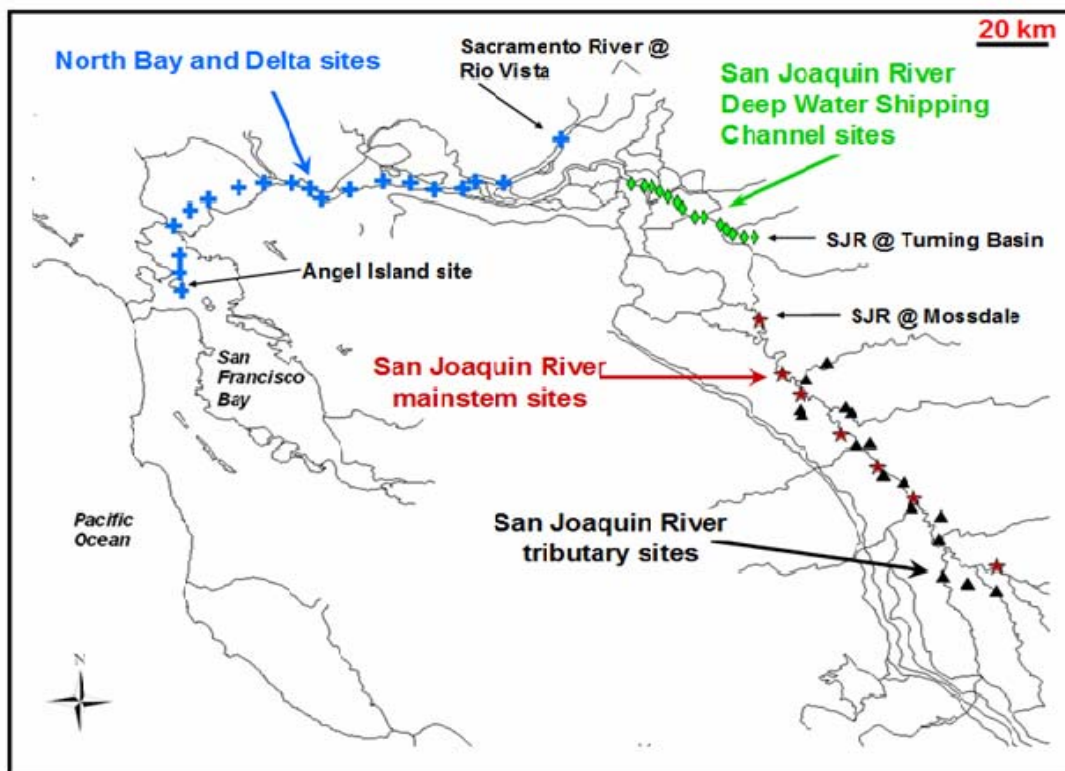


Figure 5.1.5. This map shows the locations of sites sampled as part of several studies 2005-2007. Only data from the mainstem sites were used to prepare the next 2 figures. The mainstem samples include sites on the main channel of the San Joaquin River (RM109 to RM56), on the main channel of the upper (deltaic) San Joaquin River (RM41 to RM24), and then on the main channel of the lower (deltaic) Sacramento River (RM12 to RM-45).

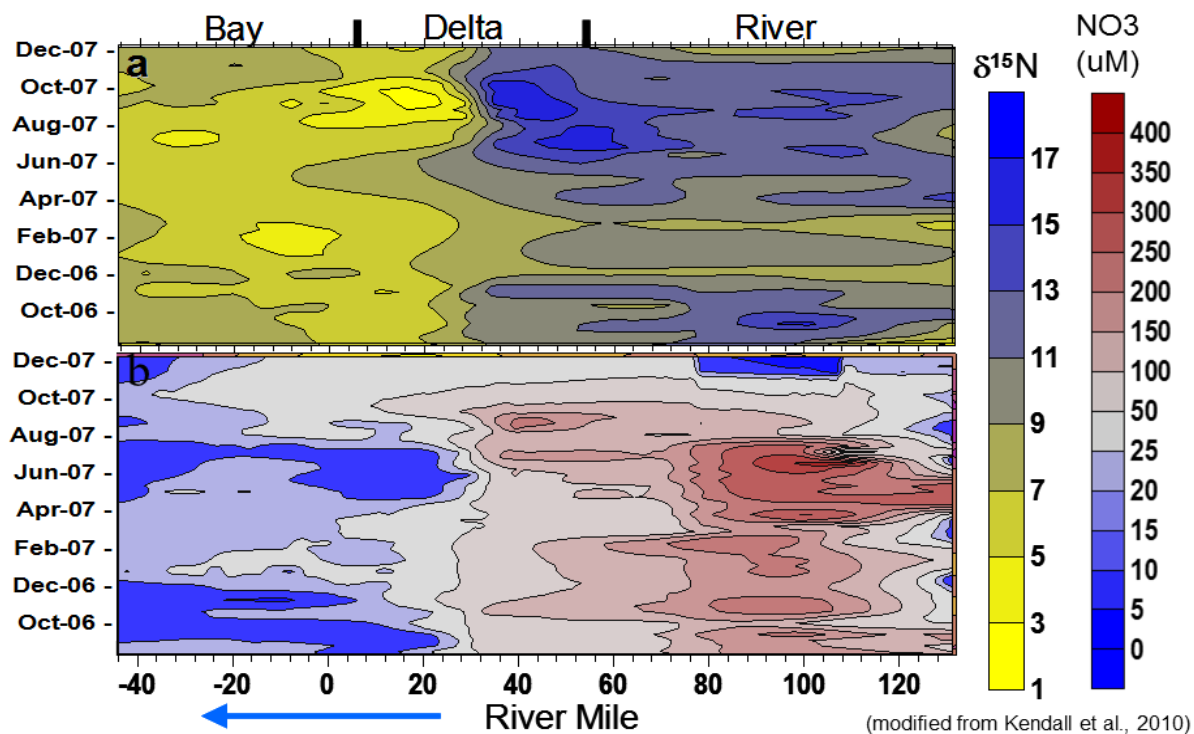


Figure 5.1.6. Spatial and temporal distribution of nitrate- $\delta^{15}\text{N}$ values (a) and nitrate concentrations (b) along 170 miles of river, extending from the upper San Joaquin River (“River”), through the Deep Water Shipping Channel on the lower San Joaquin River and Delta (“Delta”), and across the northern San Francisco Bay (“Bay”) to where the estuary drains into the Pacific Ocean. River miles are measured from where the San Joaquin River converges with the larger Sacramento River (RM0), with positive RM values representing upstream locations and negative values representing downstream locations. This plot reflects data from ~1200 samples collected August 2006–December 2007. Figure modified from Kendall et al. (2010).

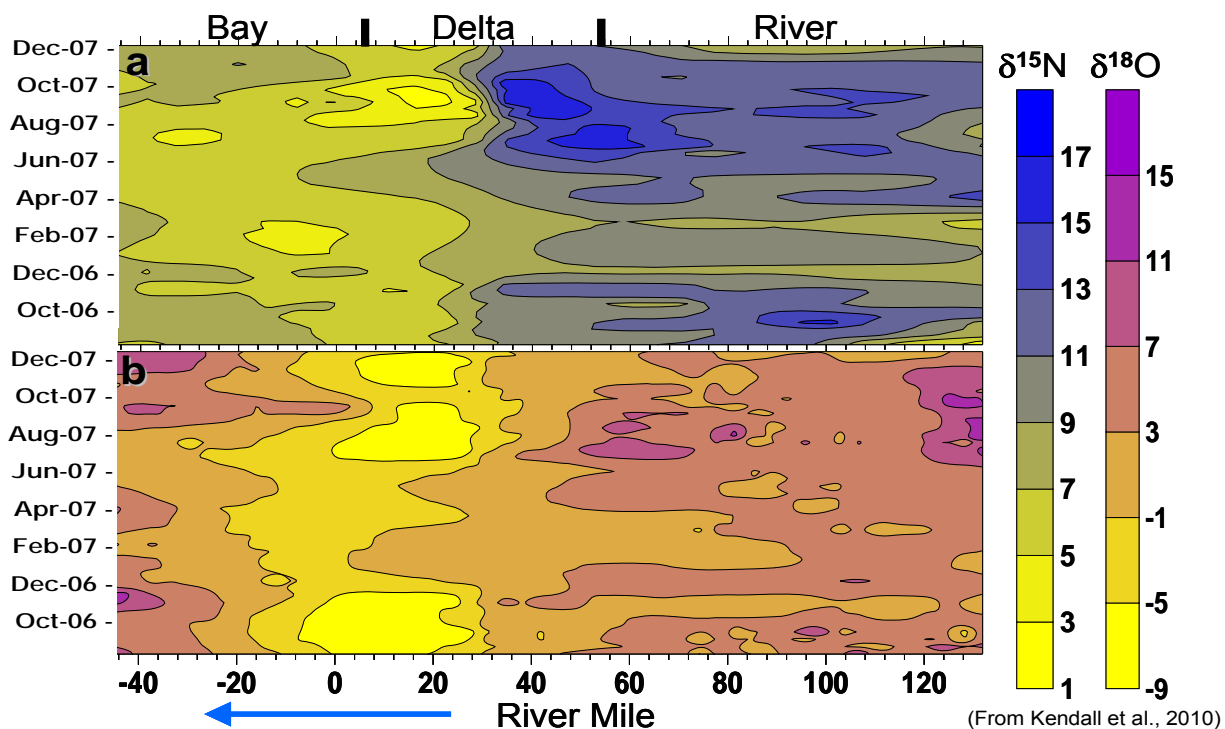


Figure 5.1.7. Spatial and temporal distribution of nitrate- $\delta^{15}\text{N}$ values (a) and nitrate- $\delta^{18}\text{O}$ values (b) along 170 miles of river, extending from the upper San Joaquin River (“River”), through the Deep Water Shipping Channel on the lower San Joaquin River and Delta (“Delta”), and across the northern San Francisco Bay (“Bay”) to where the estuary drains into the Pacific Ocean. Figure from Kendall et al. (2010).

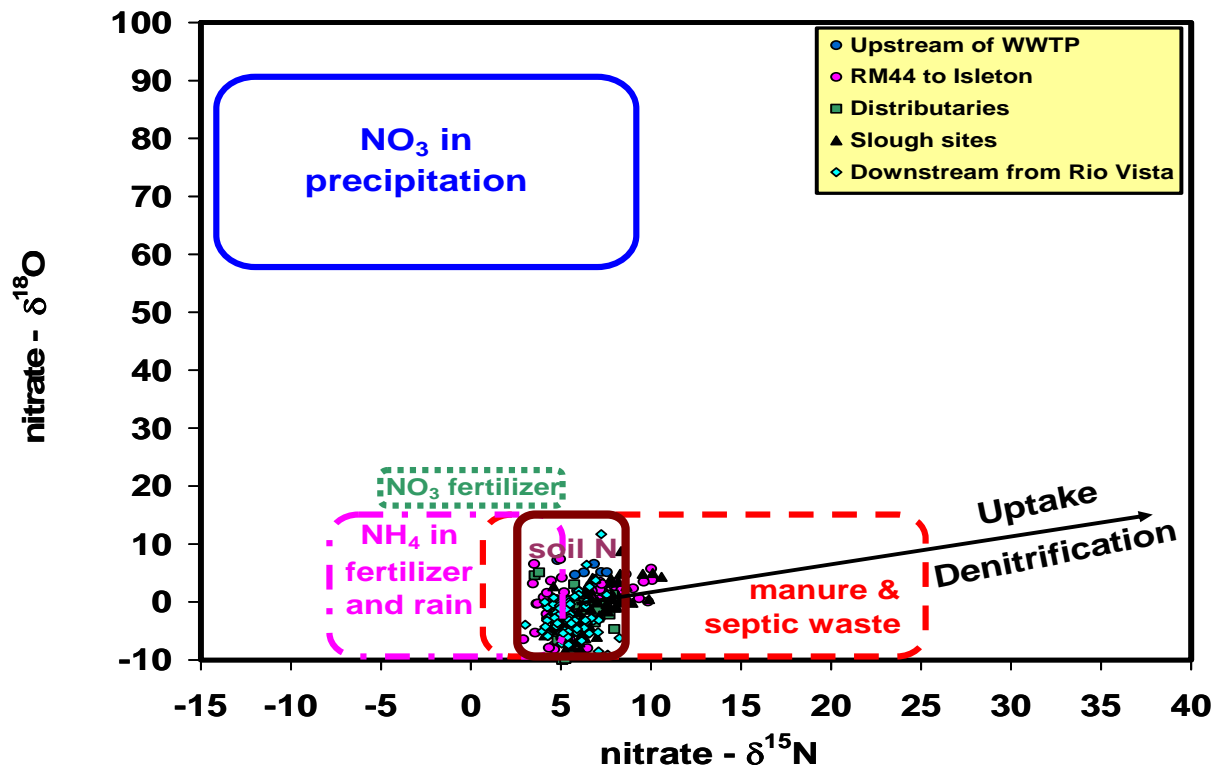


Figure 5.1.8. Nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values for all sites and dates are plotted on a dual isotope plot (Kendall et al., 2007). Samples from different types and locations of sites are denoted by different symbol colors and shapes. The expected trend for uptake (and denitrification) is shown as a thin black arrow. Despite all the N-cycling in the ecosystem, the isotopic compositions of NO_3 have not changed very much from what would be considered “typical” NO_3 derived from a mixture of soil, agricultural, and septic waste sources. From Kendall et al. (2015).

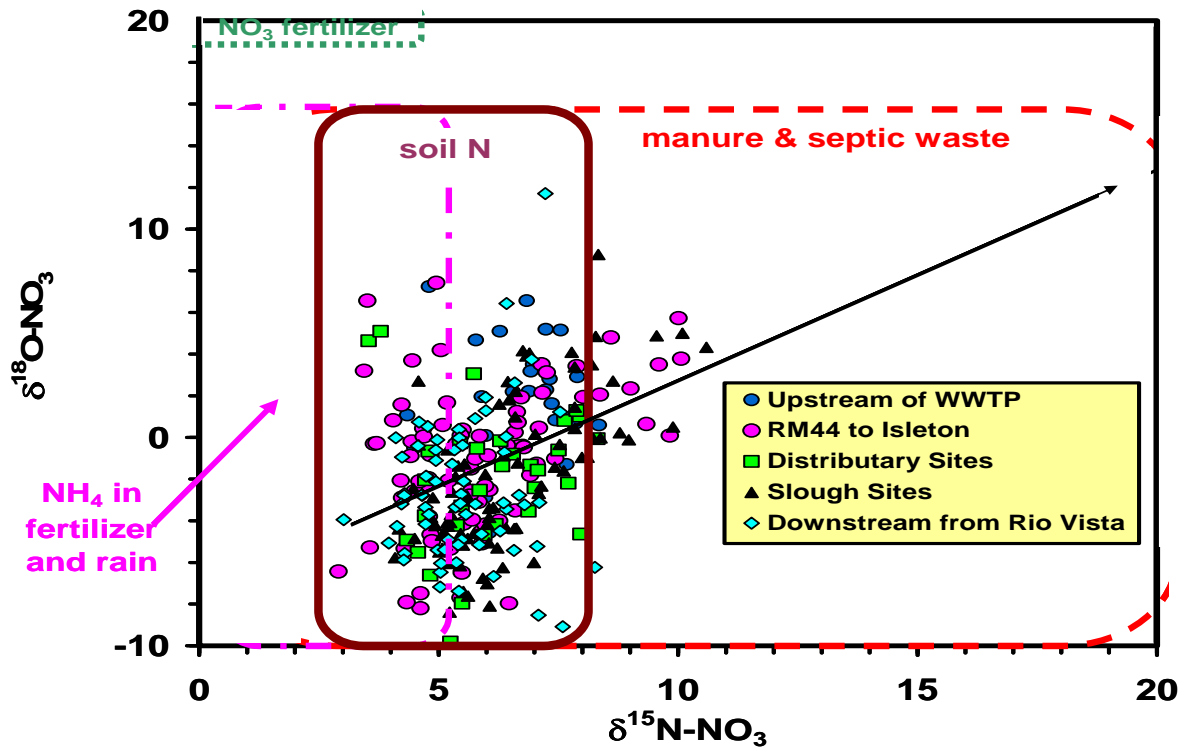


Figure 5.1.9. This plot expands the scale of the previous plot to show that samples collected upstream of the WWTP tend to have slightly higher NO_3 - $\delta^{18}\text{O}$ values compared to other sites. The samples with the highest $\delta^{15}\text{N}$ values seem to be plotting along the uptake fractionation line. Also, there is some indication that uptake may be causing $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values from some “RM44 to Isleton” and “Slough” samples to increase along the theoretical “uptake line” indicated by the black arrow. However, this very slight trend might also be explained by temporal and spatial variation in the original nitrate sources to different sites, later augmented by the effects of mixing with newly formed nitrate. From Kendall et al. (2015).

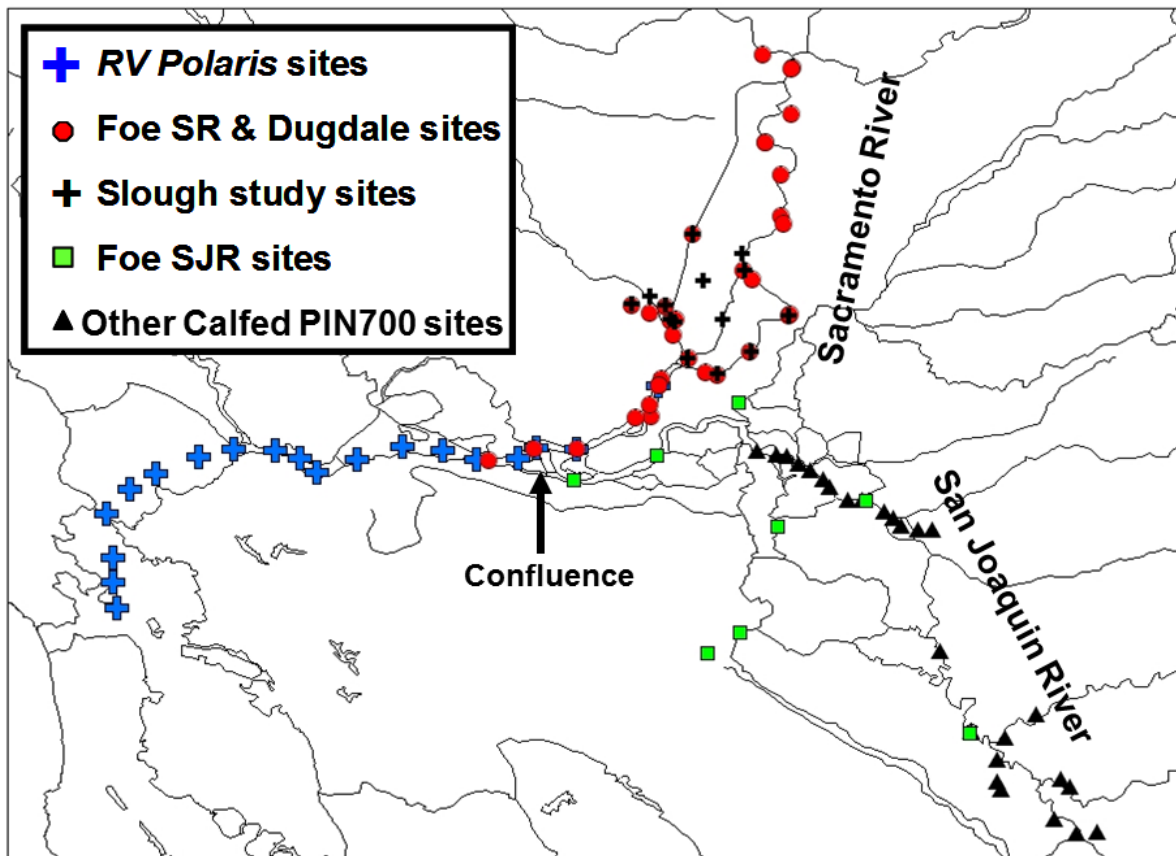


Figure 5.1.10. Map showing the sites sampled as part of the different transects listed in Tables 5.1.1 to 5.1.4.

Appendix 5.2. Temporal and spatial changes in nutrients in the mainstem Sacramento River, Delta, and the northern San Francisco Bay

5.2.1 Abstract

Nitrification of ammonium from the SRWTP and the consequent mixing of newly formed nitrate with nitrate derived from upstream of SRWTP are the main processes affecting the temporal and spatial variation in nutrients and their isotopic compositions in the Sacramento River and Delta. Kendall et al. (2015) provided “proof of concept” of the usefulness of isotope techniques combined with water chemistry and hydrological modeling for identifying sources and processes in the Sacramento River and Delta. This report section takes the next step of providing a detailed qualitative interpretation of the temporal and spatial variations in nutrient concentrations, nutrient isotopes, and a few other constituents at 25 main-channel sites from Tower Bridge downstream to Angel Island, sites near the mouths of the 2 main distributaries of the Sacramento River, and sites on the 4 main tributaries in the Cache/Yolo Slough Complex. Each site was sampled approximately monthly for 1-3 years during the period 2006-2011.

A main goal of this study was to evaluate whether the seasonal trends in this limited set of data for sites sampled during our transect studies were similar to the historic trends in nutrient concentrations at the nearby IEP sites. Since the seasonal trends in the 2 datasets are similar, the isotope and chemical data for our intensively studied sites were used to (1) provide interpretations of the causes of the seasonal patterns at the nearby IEP sites and adjacent sections of the estuary, (2) suggest hypotheses that could be tested with the existing data using simple mass balance and isotope fractionation models, and (3) make recommendations about the adequacy of the current IEP sites.

Among the several important findings from this detailed interpretation of temporal and spatial trends is that the temporal variation in effluent-derived NH_4 leaves a characteristic and persistent temporal “signature” which can be traced >40 miles down the estuary, and can probably be used to estimate seasonality in nitrification rates at different sites. Temporal variations in NO_3 concentrations derived from upstream of SRWTP also provide a useful signature that persists for >40 miles and can be used to identify new inputs and changes in downstream sites. In some instances, isotopes plus nutrient chemistry indicated whether nitrification probably occurred in adjacent marshes vs in the main river channel, or whether a suspected local source of nutrients was probably a distributed source vs a point source. This multi-tracer approach also identified several “hot spots” of nutrient inputs and N transformations, and determined that most of the nitrification in the Cache/Yolo Slough Complex probably occurs in the tributaries, not in the wider parts of the Slough. Formulating hypotheses based on qualitative descriptions of patterns is a necessary prerequisite for deciding how to test hypotheses with a more quantitative approach involving mass balance and isotope fractionation models -- to determine how much of the variation in time and space is due to inputs of local nutrient sources and how much to nitrification, uptake, or other N transforming reactions.

Recommendations for the IEP monitoring program include (1) the addition and/or activation of historic but currently inactive IEP monitoring sites at Isleton and Rio Vista and near one or two hot spots of

nutrient inputs and algal productivity; and (2) replacing current DIN measurements at critical sites with separate analyses of NH_4 , NO_3 , and NO_2 . With just DIN data, movement between different N species cannot be determined; and the movement of N from NH_4 to NO_3 , from hot spots of N into the main channel and from different sources of N into algae, cannot be adequately assessed. Managers also might want to consider collecting and archiving a complete suite of isotope samples -- during the next couple years while the estuary recovers from the recent drought -- to better evaluate the usefulness of a multi-isotope approach, combined chemical and hydrologic data, for quantifying nutrient and organic matter sources and biogeochemical processes at selected IEP sites. Other suggestions for possible future studies are listed in the conclusions.

5.2.2 Introduction

This appendix section focuses on the spatial and temporal variation in NO_3 and NH_4 concentrations, NO_3 and NH_4 isotopes, and other relevant isotopic, chemical, and hydrologic data from samples collected for various periods 2006-2011 during four different water quality monitoring programs that routinely collected samples along specific transects. A variety of plots were prepared with the chemical and isotopic data to (1) evaluate whether the seasonal trends in this limited set of data for sites sampled during our transect studies match the seasonal trends in nutrients and chlorophyll observed at 5 nearby IEP nearby sites in the Sacramento River and Delta that have been extensively discussed in this report; and (2) if so, to use some of the isotope and chemical data for our intensively studied sites to provide interpretations of the causes of the seasonal patterns at the nearby IEP sites and adjacent sections of the estuary.

These data are interpreted to (1) provide qualitative insights about nutrient sources and transformations at these transect sites in the Sacramento River, Delta, and northern San Francisco Bay; (2) discuss the adequacy of the existing IEP monitoring sites discussed in this report; (3) make recommendations for improvements to the IEP network and monitoring program; and (5) suggest potential future work.

The results and discussion section is divided into 4 main sections. Each section contains sets of plots showing the temporal and/or spatial variations in the chemical and isotopic compositions of samples collected along transects. The 4 sections are:

- Chemoscapes for mainstem sites
- Spatial changes in chemical and isotopic compositions at mainstem sites
- Temporal changes in chemical and isotopic compositions at mainstem sites
- Spatial and temporal changes at tributary and distributary sites in the Cache/Yolo Slough Complex

The spatial changes are illustrated by “transect” box plots showing the average chemical and isotopic compositions (EC, water- $\delta^{18}\text{O}$, water- $\delta^2\text{H}$, NH_4 , $\text{NO}_3 + \text{NO}_2$, NO_2 , NH_4 - $\delta^{15}\text{N}$, NO_3 - $\delta^{18}\text{O}$, NO_3 - $\delta^{15}\text{N}$, chlorophyll-a, and chlorophyll ratio) for 25 sites along the mainstem Sacramento River, Delta, and Bay from Tower Bridge (RM59) to near Angel Island (RM-45), using data from the Polaris, Foe, Dugdale, and Slough transects described in Appendix 5.1. These transect plots are useful for making a general assessment of the locations where major changes (transitions) in water or nutrient sources – and/or biogeochemical processes – significantly affect the compositions at subsequent downstream locations. This allows the mainstem sections to be divided into regions with similar characteristics (e.g.,

compositions are decreasing downstream, increasing downstream, or approximately constant) bounded by transitional sites.

The temporal changes are illustrated by “monthly” box plots showing the average monthly compositions at 17 sites along the mainstem Sacramento River, Delta, and Bay from Tower Bridge (RM59) to near Angel Island (RM-45), using data from the Polaris, Foe, Dugdale, and Slough transects described in Appendix 5.1. Monthly box plots were not prepared for all 25 mainstem sites plotted on the transect plots because some sites did not have sufficient nutrient and/or chlorophyll data to show reliable monthly patterns.

Transect and monthly box plots are also provided for several non-mainstem sites on sloughs that are significant contributors of water and/or solutes to the Sacramento River, including sites near the mouths of the two main Sacramento River distributaries: Miner and Steamboat Sloughs; and four tributary sites in the Cache/Yolo Slough Complex.

5.2.3 Materials and Methods

The isotope and chemical data discussed in this appendix section are from samples collected during four different water quality monitoring programs that routinely collected samples along specific transects: the USGS “Polaris transects” in 2006-2008, the Dugdale “transects” in March and April 2009, the “Foe transects” in 2009-2010, and the “Slough transects” in 2010-2012. The locations of these sites are shown on Figures 5.2.1-5.2.6.

Lists of the names and sites where samples were collected, additional maps, and details about (1) how samples were collected and analyzed for chemical and isotopic compositions, and (2) where the data can be found are provided in Appendix 5.1.

5.2.4 Results and Discussion

Chemoscapes for mainstem sites

Spatial and temporal changes in the Delta and northern SFB, 1990-2010.

Figures 5.2.7-5.2.16 show several kinds of “chemoscapes” (chemical data plotted at a landscape scale as a color-contour diagram to show temporal and spatial variations of different chemical constituents). On all plots, the x-axis is river miles (RM) upstream or downstream of RM0 where the San Joaquin River converges with the larger Sacramento River, and the y-axis is the date. Positive RM numbers indicate sites upstream of RM0, and negative RM numbers indicate sites downstream of RM0. The RM numbers are usually rounded to integers in the text; however, the actual RM values are reported in Tables 5.1.1-5.1.4. For reference, the temporal changes in Sacramento River flow measured at Freeport are shown on the right side of each chemoscape. In general, chemical data were available at monthly intervals for each plot. See Appendix 5.1 for maps, names of different sampling transects, lists of site names and locations, sources of the chemical and isotopic data, etc.

Figures 5.2.7-5.2.12 show 20 years of ~monthly data from USGS R/V *Polaris* transects, for samples collected from Rio Vista (RM12) downstream to Angel Island (RM-45). These plots were included to

provide a larger temporal context for the discussion of seasonal and spatial variations of selected nutrient concentrations and isotopic compositions for ~monthly samples from these sites 2006-2008 discussed

The salinity data (Figure 5.2.7) show that ocean-derived water with salinity of ≥ 30 psu extends 10-20 miles upstream of Angel Island (RM-45) for several months each fall, and salinities at Angel Island drop to 5-20 psu for weeks to months each spring. As expected, the higher the flow of the Sacramento River, the farther downstream low salinity, river-derived water extends into the Bay.

During most years, the $[\text{NH}_4]$ was $\geq 6 \mu\text{M}$ at Rio Vista almost all year (Figure 5.2.8). For example, NH_4 concentrations were consistently high 1999-2005, and these high concentrations extended to Angel Island for about half of the monthly transects. In contrast, from 1995-1998, NH_4 concentrations at Rio Vista were rarely ≥ 6 and low concentrations extended to Angel Island. Regular seasonal changes in $[\text{NH}_4]$ are not apparent on this plot.

Correlations of flow and $[\text{NH}_4]$ are subtle. Most periods with relatively low flow all year long (e.g., 2000-2003) have high $[\text{NH}_4]$. In years with very high flow for a few months, the maximum flows are sometimes associated with very low $[\text{NH}_4]$. In general, wedges (fingers) of high concentrations of NH_4 extend downstream from Rio Vista, and wedges of low concentrations of NH_4 extend upstream from Angel Island. Comparison of the temporal and spatial changes in salinity and $[\text{NH}_4]$ suggest that upstream tidal sloshing of marine-derived saline water explains a large part of the spatial variation in $[\text{NH}_4]$ at Delta sites. However, low $[\text{NH}_4]$ at Rio Vista and downstream sites for some high flow periods (e.g., spring of 2006 when low salinity water extended far into the Bay) can be better explained by low $[\text{NH}_4]$ derived from sites upstream of Rio Vista.

NO_3 concentrations (Figure 5.2.9) showed more gradual (and less oscillating) temporal changes than salinity and NH_4 , making it easier to see the wedges of persistently high $[\text{NO}_3]$ extending downstream from Rio Vista and wedges of low $[\text{NO}_3]$ extending upstream from Angel Island. In general, periods with low flow (e.g., 2007-2010) had higher $[\text{NO}_3]$ than periods with high flow (e.g., 1995-2000).

PO_4 concentrations (Figure 5.2.10) appear to be highly correlated with flow, with higher concentrations in dry years (e.g., 2007-2010 and especially in 1990-93) than in the wet years 1995-2002. PO_4 is always higher in the summer than winter.

Chlorophyll-a concentrations (Figure 5.2.11) are generally $< 4 \text{ mg/m}^3$, with lenses of higher values mostly occurring during a couple months in the late spring. Concentrations appear to be generally higher 2002-10 than in most previous years, especially at downstream sites, where the high values were found for several months in the spring in fall. The longest period of high ($> 16 \text{ mg/m}^3$) concentrations on this plot is in spring 1998. It is clear from this plot that chlorophyll concentrations (and hence blooms) are generally higher at Bay sites than in the Sacramento River. Lenses of higher chlorophyll concentrations extending downstream from upstream sites generally occur shortly after the first period of high flow in the spring.

Chlorophyll ratios (Figure 5.2.12) appear to be generally higher (more fresh) in 2001-2010 than in many previous years, especially at downstream sites; these high values correlate with the locations and times of slightly higher chlorophyll concentrations (Figure 5.2.11). There are many years (e.g., 2000-2001) when almost all the algae appear to be “old”. In contrast, from 1995-2001, lenses of alternating low and high ratios can extend from upstream to downstream sites for multiple months.

Spatial and temporal changes in the Sacramento River, Delta, and northern SFB, 2009-2010.

Figures 5.2.13-5.2.16 show 1 year of ~monthly data (March 2009-March 2010) from sites sampled during the Polaris, Foe, Dugdale, and Slough transects, from the I-80 Bridge on the Sacramento River (RM62) downstream to Angel Island (RM-45). Dots indicate where chemical concentration data are available. The locations of water inputs from SRWTP and the Cache/Yolo Sloughs are denoted by colored vertical lines; the other main source of water along this section of the river is at RM0 where the San Joaquin River converges with the Sacramento River. The flow at Freeport is shown on each plot; flows were high in early March 2009 and mid January to March 2010. These plots were included to provide a different perspective for the discussion below of temporal and spatial variations of selected nutrient concentrations and isotopic compositions for these sites. The plots and discussion below about these plots are slightly modified from Kendall et al. (2015).

NH_4 concentrations (Figure 5.2.13) are low upstream of SRWTP (RM46) and maximum NH_4 concentrations are seen at RM32 to RM38. This gradual increase in $[\text{NH}_4]$ suggests slow downstream mixing of the effluent plume and/or degradation of effluent to form NH_4 . Downstream of about RM32, the $[\text{NH}_4]$ start declining and become much lower at sites downstream of where the Cache/Yolo Slough merges with the Sacramento River. For sites upstream of Rio Vista, the negative correlation of low $[\text{NH}_4]$ with period of high flow is very apparent; downstream of Rio Vista, the correlations of flow and $[\text{NH}_4]$ are much reduced, as was noted for Figure 5.2.8.

The sum of NO_3 and NO_2 (referred to as NO_3) concentrations upstream of SRWTP are significantly higher during periods of high flow (Figure 5.2.14), especially ones with abrupt increases in flow, than during low flow. This positive correlation with flow (or season) persists downstream of Rio Vista. During these high-flow periods, $[\text{NO}_3]$ show little increase downstream until about RM32 and then $[\text{NO}_3]$ increase gradually downstream of Isleton (RM17) where NH_4 concentrations begin to drop. Between Isleton (RM17) and Rio Vista, $[\text{NO}_3]$ often increase abruptly, probably in part from contributions of NO_3 from the Cache/Yolo Slough Complex. During lower-flow periods, $[\text{NO}_3]$ also show little increase downstream until about RM32 and then increase gradually downstream; however, $[\text{NO}_3]$ at sites downstream of Rio Vista never reach the high $[\text{NO}_3]$ in the Delta observed during higher flows. It is interesting that the small but steady increase in flow starting in late June, which continued for about a month before slowly declining through September, resulted in an extended period of very low $[\text{NO}_3]$ – and $[\text{NH}_4]$ -- that persisted downstream to Angel Island.

The temporal and spatial variations in NO_2 concentration (Figure 5.2.15) are very similar to those of NO_3 . $[\text{NO}_2]$ gradually increase downstream the SRWTP for ~ 20 miles. Concentrations then either level off across the delta and Bay, or reach maximum values near or downstream of Rio Vista at dates where NO_3 concentrations are also high. Some of the variation is an artifact of the sampling density, but the NO_2 maxima near or downstream of Rio Vista are well-supported by data. The steepest downstream increases in $[\text{NO}_2]$ are usually found between Isleton (RM17) and Rio Vista (RM12); hence, it is likely that a significant amount of the NO_2 observed at Rio Vista is derived from Cache/Yolo Slough. As was seen with NO_3 (Figure 5.2.14), NO_2 concentrations upstream of SRWTP are higher during high flow. However, unlike with NO_3 , during very high-flow periods in early March 2009 and mid-January to March 2010, $[\text{NO}_2]$ remained relatively constant downstream.

The ratios of chlorophyll-a to total chlorophyll concentrations (Figure 5.2.16) are useful for indicating the relative “freshness” of algae; a higher ratio suggests a higher fraction of fresh (dominated by chlorophyll-a) algae. Higher ratios are found at upstream Sacramento sites during times of higher flow, especially in the early spring (e.g., March 2009 and February 2010). Algae freshness generally increases downstream of RM10 as $[\text{NH}_4]$ decrease. Downstream sites in May 2009 and September 2009 appear to have abundant fresh, marine-derived (or marine-influenced) algae.

Spatial changes in chemical and isotopic compositions at mainstem sites

Introduction.

Figures 5.2.17-5.2.27 are box plots showing the average chemical and isotopic compositions (EC, water- $\delta^{18}\text{O}$, water- $\delta^2\text{H}$, NH_4 , $\text{NO}_3 + \text{NO}_2$, NO_2 , NH_4 - $\delta^{15}\text{N}$, NO_3 - $\delta^{18}\text{O}$, NO_3 - $\delta^{15}\text{N}$, chlorophyll-a, and chlorophyll ratio) for 25 sites along the mainstem Sacramento River, Delta, and Bay from Tower Bridge (RM59) to near Angel Island (RM-45), using data from the Polaris, Foe, Dugdale, and Slough transects described in Appendix 5.1.

These plots are useful for making a general assessment of the locations where major changes (transitions) in water or nutrient sources – and/or biogeochemical processes – significantly affect the compositions at subsequent downstream locations. This allows the mainstem sections to be divided into regions with similar characteristics (e.g., compositions are decreasing downstream, increasing downstream, or approximately constant) bounded by transitional sites. The plots of this report were compared with similar plots over a longer time span to ensure that the locations of the transitional zones were not biased by insufficient data.

The locations of transitional sites were qualitatively determined and may be different for different constituents, and some transition locations may move up or downstream depending on temporal differences in flow, biogeochemical reaction rates, variations in the compositions of point sources, and other factors. The determination of transition locations using these plots may have been affected by having the sites plotted as though they were equidistant. In hindsight, it probably would have been better to arrange the site information in the box plots in terms of river miles since some of the transitions between regions were defined by a change in the apparent “gradient” of a downstream change in composition.

These plots also provide a useful way to visualize whether the IEP sites (e.g., C3, D4, D8, D7, D6) are located appropriately within the regions of the most important constituents and hence are likely to provide adequate data for mass balance calculations in the different regions -- especially regions that show important differences in nutrient sources and chlorophyll concentrations or differences in major nutrient transformation processes.

Figure 5.2.28 provides a compilation of the locations of the transitions between regions defined by the different constituents, to facilitate comparisons of transition locations for different constituents. This figure should also make it easier to keep track of the relative locations of the different transect sites (that are variably referenced in the text and figure titles using site name, site number, or RM number) and the IEP sites discussed in this section. The regions for each constituent are color-coded to indicate

downstream trends: increasing, decreasing, or constant – and whether the gradients were steeper or higher than in adjacent regions.

EC. Electrical conductivity increases downstream because of tidal mixing of fresh water from the Sacramento River with ocean water. In terms of EC, the mainstem sites can be divided into four major regions (Figure 5.2.17). The Sacramento River sites (Tower Bridge downstream to Isleton) have extremely low EC (generally $< 250 \mu\text{S/cm}$). Sites within the relatively narrow channel extending from Rio Vista downstream to about Chipps Island (RM-4) show that EC increases downstream in steps (instead of gradually) as marine-derived waters (and salts) are tidally mixed with waters derived from the Sacramento and San Joaquin Rivers.

As the channel widens downstream of Chipps Island, EC increases steadily downstream to about PO-14 (RM-33), upstream of the mouth of San Pablo Bay. Beyond PO-14, the EC values for the next sites show some oscillation while generally increasing downstream to Angel Island (RM-45). Within this last region, EC values for the next downstream site, PO-15 at the narrow mouth of San Pablo Bay, are significantly lower than at PO-14, suggesting major local river water inputs to this narrow channel location that are not well-mixed. However, downstream of PO-15, the next 3 sites show increasing EC in the northern Bay but the region has a different “gradient” of increasing salinity than the upstream region because of the higher proportion of fresh water being tidally mixed with marine-derived water.

Water $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Water isotopes increase downstream because of tidal mixing of water from the Sacramento River with low $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values with ocean water with $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of 0 ‰. These two plots show very similar downstream trends (Figures 5.2.18 and 5.2.19). Like EC, water isotopes are a reliable conservative tracer of mixing of fresh and saline water sources. The water isotopes divide the mainstem sites into the same 4 major regions as EC. However, the 2nd downstream region (Rio Vista to Chipps Island) shows that the mixing in this section is less gradational and occurs more “in steps” than with EC data, and the region could be divided into two smaller sub-regions. If so, the two upstream sites (Rio Vista and the Three Mile Slough site (RM9), have water with essentially identical $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values. The two next two downstream sites, Point Sacramento and Chain Island, have water with distinctively higher $\delta^{18}\text{O}$ and $\delta^2\text{H}$ than at the 2 upstream sites, probably due to significant and not well-mixed inputs of San Joaquin River water. From Middle Ground (PO-5) to PO-14 in region 3, water isotopes show a steady increase, indicating progressive mixing with marine water. Water isotopes, like EC, indicate a significant local source of fresh water to PO-15, thus defining a 4th region.

NH_4 . Ammonium concentrations (Figure 5.2.20) show a huge range because of 1 major source of NH_4 (SRWTP effluent) and 3 minor sources of NH_4 (Sacramento River upstream of SRWTP, Suisun Bay, and Bay/marine) that define 5 main regions. Sites upstream of SRWTP in the first region have low $[\text{NH}_4]$, with values usually $< 4 \mu\text{M}$. Between SRWTP and PO-18, $[\text{NH}_4]$ drop by a factor of 10, with the data generally plotting along an exponential-looking curve with a high degree of temporal variability at the upstream sites. At first glance, this entire section could be viewed as region 2 because of the strong curving trend. However, comparison of the data in Figure 5.2.20 with data from subsequent years suggests that this section should be divided into 4 regions, for a total of 5 regions for $[\text{NH}_4]$.

The second region extends from SRWTP to Isleton; the 3 sites in this region are characterized by a wide range of generally high (10-50 μM) NH_4 concentrations, reflecting a high degree of temporal variability at these sites. Walnut Grove usually has lower $[\text{NH}_4]$ than sites on either side, which is probably an artifact

of sampling this site on low tides (Kendall et al., 2015). There is a huge drop in $[\text{NH}_4]$ between Isleton and Rio Vista due to nitrification and uptake in the Cache/Yolo Complex (Kendall et al., 2015).

In the third region, which extends from Rio Vista downstream to PO-5 (Middle Ground), $[\text{NH}_4]$ gradually decrease downstream. Sites in this region show a much narrower range of concentrations than upstream of Rio Vista. Downstream of PO-5 in region 4, NH_4 concentrations show a small step increase of at least 4 μM , and concentrations remain relative constant for 4 sites in Suisun Bay, from Roe Island (PO-6) downstream to Benicia (PO-9). Given the lack of NH_4 data between PO-9 and PO-13, it is unclear whether $[\text{NH}_4]$ continue to gradually decline downstream of Suisun Bay to PO-13, or abruptly drop $\sim 3 \mu\text{M}$ to about the concentration observed at PO-13. Given the abrupt increase in $[\text{NH}_4]$ at the upstream end of this region, indicative of a poorly mixed continuous local source, an abrupt decrease at the lower end of Suisun Bay seems plausible.

While conservative tracers like EC and water isotopes indicate a relatively consistent downstream gradient of mixing with marine-derived water, the leveling off of $[\text{NH}_4]$ between PO-13 and PO-18 in region 5 suggests that the $[\text{NH}_4]$ reflect steady-state mixing with a local San Pablo Bay or marine source of NH_4 . Since the water isotope data indicate a significant input of fresh water to PO-15 (Figures 5.2.18 and 5.2.19), the local source of NH_4 may be associated with that fresh water input. However, given the fresh water appears as a point source at PO-15 (i.e., because it is poorly mixed with water at adjacent sites) and the constant $[\text{NH}_4]$ at sites PO-13 to PO-18, it is more likely that most of the NH_4 in this region is not associated with the local fresh water source at PO-15. Therefore, the relatively constant $[\text{NH}_4]$ in this region probably reflects a more distributed local NH_4 source, perhaps from local marshes (and/or from human activities adjacent to the marshes), as was observed in Suisun Bay – not a marine point source. Given the trends in this section of the Bay seen in $\text{NH}_4\text{-}\delta^{15}\text{N}$ (Figure 5.2.23) and other constituents, it is likely that the transition between region 4 and 5 occurs upstream of PO-13.

$\text{NH}_4\text{-}\delta^{15}\text{N}$. Although the $\text{NH}_4\text{-}\delta^{15}\text{N}$ values at Hood and Garcia Bend plot approximately on the same rapidly increasing line as data downstream of SRWTP, given the differences in $[\text{NH}_4]$ at sites upstream and downstream of SRWTP, defining a transition zone between Garcia Bend and Hood seems reasonable. The average $\delta^{15}\text{N}$ values of NH_4 (Figure 5.2.23) increase by 10 ‰ between Garcia Bend (RM49) and PO-13 (RM-31), with data plotting along a slightly oscillating exponential-appearing curve, while concentrations decrease by a factor of >5 . An exponential relation of $[\text{NH}_4]$ and $\text{NH}_4\text{-}\delta^{15}\text{N}$ values is characteristic of nitrification (Kendall et al., 2007; 2015). Figure 5.1.1 provides a typical example of the downstream changes in $\text{NH}_4\text{-}\delta^{15}\text{N}$ due to nitrification in the Sacramento River in 2009.

There is a slight dip in $\text{NH}_4\text{-}\delta^{15}\text{N}$ at PO-649 (Point Sacramento), near where the San Joaquin River converges with the Sacramento River. At this same site, NH_4 concentrations are slightly higher than at adjacent sites. These data could mean a small local point source of NH_4 with a much lower $\delta^{15}\text{N}$ than the riverine NH_4 . Alternatively, this NH_4 might come from the San Joaquin River. Given the that much of the water in the deltaic part of the San Joaquin River is actually Sacramento River diverged south via the Delta Cross Channel (DCC) and Georgiana Slough (see Appendix 5.3), it is plausible that much of the NH_4 at PO-649 appears less nitrified than adjacent sites (i.e., has a lower $\text{NH}_4\text{-}\delta^{15}\text{N}$) because this water parcel – and its NH_4 -- reached this site via the DCC and the San Joaquin River faster than similar parcels that traveled down the mainstem Sacramento River and/or its two distributaries, sloshed back and forth in

Cache Slough, and then flowed past Rio Vista (see animations in Kendall et al. (2015) at: <http://water.usgs.gov/nrp/isotope-tracers/animation-overview.html>).

The small oscillations in region 2 may indicate a variety of point sources of NH_4 ; whether these oscillations reflect point sources or natural variability will become clearer when/if we are eventually able to analyze archived samples from Polaris transects 2007-2010 for $\text{NH}_4\text{-}\delta^{15}\text{N}$. Given the paucity of data downstream of PO-7 (RM-14) and the slightly oscillating semi-exponential curve of the data, the data for all the sites from Hood to Angel Island could be viewed as all in region 2.

However, comparison with $\text{NH}_4\text{-}\delta^{15}\text{N}$ data from subsequent years (data not shown) shows a small step increase between PO-12 and PO-13, thus defining a break between region 2 and region 3. $\text{NH}_4\text{-}\delta^{15}\text{N}$ values then gradually decrease downstream from PO-13 to PO-18. These trends are denoted with a dashed line on Figure 5.2.23. The drop in $\text{NH}_4\text{-}\delta^{15}\text{N}$ values at the downstream end of the transect is shown in Figure 5.1.1.

NO_3 . Nitrate ($\text{NO}_3 + \text{NO}_2$) concentrations (Figure 5.2.21) at each site are highly variable, with temporal ranges varying from 15-40 μM , and average values that only show steady downstream trends in the upper Sacramento River (upstream of Rio Vista) where there is less temporal variability at each site. The average NO_3 concentrations define 3 main regions. From Tower Bridge downstream to Isleton, average $[\text{NO}_3]$ steadily increase from 4 to 16 (or 23) μM . While the data in Figure 5.2.21 are not clear whether Isleton or Rio Vista is the more appropriate choice for the downstream end of the first region, longer-term data show that Rio Vista is clearly in the next region.

Sites in the second region (Rio Vista to Martinez) are characterized by high temporal variability and average $[\text{NO}_3]$ that oscillate between about 23 and 28 μM but show no obvious downstream trend. For lack of a consistent downstream pattern, the $[\text{NO}_3]$ can be viewed as being approximately constant – or perhaps the oscillations reflect some small point sources. For example, the small dip in $[\text{NO}_3]$ at PO-649 (RM0) probably is “real” and reflects water from the San Joaquin River that has a slightly lower $[\text{NO}_3]$. The lower $[\text{NO}_3]$ at this site is consistent with the interpretation presented above (based on the slightly higher $[\text{NH}_4]$ and slightly lower $\text{NH}_4\text{-}\delta^{15}\text{N}$ at this site) that the San Joaquin water at this site has experienced less nitrification than at adjacent transect sites.

From about Benicia (PO-9, RM-19) downstream to Angel Island, concentrations show an oscillating general decrease to about 15 μM , with a slight indication that $[\text{NO}_3]$ level off for the last 3 sites. However, more data are needed before these oscillations are interpreted as possible point sources.

NO_2 . NO_2 concentrations (Figure 5.2.22) define 4 different regions. In region 1, NO_2 concentrations steadily increase from Tower Bridge to Isleton. In general, places with significant $[\text{NO}_2]$ are sites ongoing active nitrification; hence, appreciable nitrification is occurring upstream of SRWTP. There is a large increase in $[\text{NO}_2]$ between Isleton and Rio Vista. Rio Vista shows an extremely wide range of concentrations, probably due to large temporal variations in processing of nutrients in the Cache/Yolo Slough, which converges with the mainstem Sacramento River between Isleton and Rio Vista.

Downstream of Rio Vista, the limited NO_2 concentration data in region 2 (including data for other years not plotted here) appear to remain approximately constant downstream (with an average of 0.9 μM) to upstream of PO-5. The third region consists of 4 sites near Suisun Bay (PO-5 downstream to PO-8) where

[NO₂] increase to about 1.5 μM; these sites also have higher [NH₄] than adjacent sites (Figure 5.2.20). The higher [NO₂] at these sites suggest enhanced nitrification, perhaps in the marshes lining the Bay.

There are limited NO₂ concentration data downstream of Suisun Bay in region 4. However, comparison of the data in Figure 5.2.22 with data from subsequent years (not shown here except as dashes) suggests that [NO₂] downstream of PO-8 are slightly higher than 1 μM and remain approximately constant downstream to Angel Island. Hence, nitrification continues downstream. It is interesting that [NO₂] and [NH₄] appear to be approximately constant in this region -- whereas [NO₃], like EC, shows a steady decline due to mixing with marine sources of water. One plausible explanation for these observations is that there are many small local sources of NH₄ and sites of local partial nitrification to NO₂ in this region, that continuously mix into the river water column faster than these constituents can be tidally homogenized into the normal mixing gradient.

NO₃-δ¹⁸O. In estuarine systems with active nitrification, it is often easier to use the δ¹⁸O values of NO₃ (Figure 5.2.24) to partition the system into regions than to use the δ¹⁵N values (Figure 5.2.25). This is because (1) new nitrate formed by nitrification has NO₃-δ¹⁸O values that are strongly affected by water-δ¹⁸O values (2/3 of the O in the new NO₃ is generally derived from the O in H₂O), and (2) estuarine systems show a systematic downstream increase in water-δ¹⁸O as salinity increases (because ocean water has a δ¹⁸O of 0 ‰). Since water-δ¹⁸O changes downstream from -11 to -1 ‰ (Figure 5.2.18), the NO₃-δ¹⁸O changes similarly as the proportion of new NO₃ becomes a progressively larger component of the total NO₃.

The average NO₃-δ¹⁸O values at each downstream site define 3 different regions. In the first region, Tower Bridge downstream to Rio Vista, the δ¹⁸O values decrease downstream as [NO₃] increases from 4 to 23 μM. The steady decrease in NO₃-δ¹⁸O as [NO₃] increases by a factor of ~6 reflects the dilution of the old nitrate with new NO₃ formed by nitrification in water with a water-δ¹⁸O averaging -11 ‰. With data from a longer time period (not shown), the first region of decreasing NO₃-δ¹⁸O values ends at Isleton and the second region starts with Rio Vista.

In the second region, defined in this report as Three Mile Slough (≈ PO-655) downstream to Chippis Island (PO-4), the [NO₃], the [NO₂], and the NO₃-δ¹⁸O remain approximately constant while the water-δ¹⁸O increases by only 1 ‰ and the EC shows a gradual increase downstream. The continued relatively high [NO₂] suggests ongoing nitrification. A plausible explanation for the active nitrification combined with constant [NO₃] and NO₃-δ¹⁸O is nitrification and removal of NO₃ by tidal mixing in this narrow and restricted channel of the Delta have achieved a steady-state, balanced condition. Comparison with data for a longer time period (not shown) suggests that this “balanced condition” is transitory and this section of the estuary, over longer time scales, behaves the same as the next downstream region.

In the third region, Middle Ground (PO-5) downstream to PO-18, [NO₃] oscillates around 25 μM and NO₃-δ¹⁸O gradually increases downstream until Benicia, and then [NO₃] steadily decreases downstream to PO-18. It is intriguing that NO₃-δ¹⁸O steadily increases downstream all the way to Angel Island, indicating a progressively larger proportion of the bulk NO₃ is composed of new NO₃ formed in contact with water of a steadily increasing water-δ¹⁸O (Figure 5.2.18), first while [NO₃] initially remains approximately constant from Three Mile Slough (RM9) to Martinez (RM-17), and then when [NO₃] steadily declines from Martinez to Angel Island. These patterns suggest that two different steady-state environments were established in this region. In the first of these hypothetical environments, production

of new nitrate and removal of NO_3 were balanced while the NO_3 - $\delta^{18}\text{O}$ continued to increase downstream. In the second, nitrification continues to produce new NO_3 with NO_3 - $\delta^{18}\text{O}$ values that increase downstream while there is a progressive downstream removal of NO_3 by tidal mixing.

It remains to be seen whether most nitrification takes place in the outgoing tide using NH_4 ultimately derived from SRWTP, or if a significant amount of nitrification might occur in incoming tides using NH_4 derived from sources in Suisun and San Pablo Bay – or from the ocean. The slightly elevated but steady $[\text{NH}_4]$ and the decreasing NH_4 - $\delta^{15}\text{N}$ at sites downstream of PO-13 suggests a local NH_4 source. If so, then the steadily increasing NO_3 - $\delta^{18}\text{O}$ values downstream could reflect another steady-state condition, one between downstream movement of NO_3 with a lower $\delta^{18}\text{O}$ (formed upstream of the sampling location) with upstream movement of NO_3 with a higher $\delta^{18}\text{O}$ (formed downstream of the sampling location). All in all, the different isotopic and chemical patterns and relationships described above suggest that simple mass balance models might provide considerable illumination about the interplay of nitrification, hydrology, and steady-state vs non-steady-state mixing in this complex environment.

NO_3 - $\delta^{15}\text{N}$. During nitrification, the $\delta^{15}\text{N}$ of the newly formed NO_3 is a function of the $\delta^{15}\text{N}$ of ambient NH_4 and always has a lower $\delta^{15}\text{N}$ than the NH_4 - $\delta^{15}\text{N}$. If the only two significant sources of NO_3 to the estuary are upstream Sacramento River NO_3 and newly formed NO_3 resulting from nitrification, and the only significant source of NH_4 to the estuary is the SRWTP effluent, the NO_3 - $\delta^{15}\text{N}$ values should progressively increase or decrease downstream for some distance, depending on the $\delta^{15}\text{N}$ of the original upstream NO_3 and the evolving (increasing) $\delta^{15}\text{N}$ of the newly formed NO_3 . However, as the pool of residual NH_4 becomes smaller and its $\delta^{15}\text{N}$ continues to increase due to nitrification, eventually there will be an inversion point when the $\delta^{15}\text{N}$ of the bulk NO_3 will also start to increase. Hence, in this simple theoretical system, one would expect two regions. Figure 5.1.1 provides a typical example of the downstream changes in NO_3 - $\delta^{15}\text{N}$ due to nitrification, showing the transition between decreasing $\delta^{15}\text{N}$ values to increasing $\delta^{15}\text{N}$ values between RM0 and RM-10. The average downstream trend of $\delta^{15}\text{N}$ values (Figure 5.2.24) clearly show these two main expected regions, defined by the transition at Isleton between an upstream region where NO_3 - $\delta^{15}\text{N}$ values decrease downstream -- to a downstream region where NO_3 - $\delta^{15}\text{N}$ values increase downstream.

However, superimposed on this simple 2-region model are other minor “subregions” within the theoretical region 2, including: (a) the rapid increase in $\delta^{15}\text{N}$ from Rio Vista to upstream of PO-3 (RM-2), (b) a trend of decreasing $\delta^{15}\text{N}$ to PO-7 (RM-14) correlating with sites in Suisun Bay, (c) a sharp increase in $\delta^{15}\text{N}$ to PO-9, (d) relatively constant $\delta^{15}\text{N}$ values to PO-14, and then (e) slightly increasing $\delta^{15}\text{N}$ to PO-18. Hence, NO_3 - $\delta^{15}\text{N}$ values are divided into a total of 5 regions. Examination of data from a longer time span (data not shown) shows that NO_3 - $\delta^{15}\text{N}$ values generally increase downstream from Rio Vista to PO-9. This pattern correlates with moderately constant $[\text{NO}_3]$ in this region -- except for a small drop in $\delta^{15}\text{N}$ values at sites near Suisun Bay. The minor regions d and e are combined to define a region of approximately constant NO_3 - $\delta^{15}\text{N}$ values that match up with decreasing $[\text{NO}_3]$ from PO-9 (Benicia) downstream to PO-18.

The ~1 ‰ drop in NO_3 - $\delta^{15}\text{N}$ at the 4 Suisun Bay sites (PO-3 to PO-7) probably reflects the nitrification of a small amount of local source of NH_4 with a much lower NH_4 - $\delta^{15}\text{N}$ than the ambient (or “riverine”) NH_4 . These sites had slightly higher $[\text{NH}_4]$ than adjacent sites (Figure 5.2.20), no obvious difference in NH_4 - $\delta^{15}\text{N}$ compared to adjacent sites, and the highest $[\text{NO}_2]$ values (Figure 5.2.22) observed at any other

mainstem sites. The lack of any significant differences in $[\text{NO}_3]$ and $\text{NO}_3\text{-}\delta^{18}\text{O}$ values for the 4 Suisun Bay sites compared to adjacent sites supports an interpretation that the amount of new NO_3 was small compared to the existing NO_3 in the river water column, and that the nitrification at the 4 sites was in contact with water of about the same $\delta^{18}\text{O}$.

Chlorophyll-a. The average chlorophyll concentrations (Figure 5.2.26) range from about 1 to 5 mg/L, with occasional blooms causing outliers over 10. The data define 4 main regions: declining values downstream to Isleton, significantly higher and relatively constant values from Rio Vista downstream to Benicia (PO-9), gradually increasing values downstream to PO-15, and then a significant drop in concentrations for the last 3 sites. Comparison with data from a longer time span (not shown) suggests 3 regions are sufficient to describe the data, with a general pattern of gradually increasing values from PO-9 to PO-18 with fewer oscillations than observed in the smaller dataset described in this report. Average chlorophyll-a concentrations are highest at downstream sites, from PO-10 downstream to PO-18, and that the algae here is “fresher” (i.e., has a higher average ratio of chlorophyll-a to total chlorophyll) than elsewhere (Figure 5.2.27).

Temporal changes in chemical and isotopic compositions at mainstem sites

Introduction.

Figures 5.2.29-5.2.45 show the average monthly compositions at 17 sites along the mainstem Sacramento River, Delta, and Bay from Tower Bridge (RM59) to near Angel Island (RM-45), using data from the Polaris, Foe, Dugdale, and Slough transects described in Appendix 5.1. Monthly box plots were not prepared for all 25 mainstem sites plotted on the transect plots (Figures 5.2.17-5.2.27) because some sites did not have sufficient nutrient and/or chlorophyll data to show reliable monthly patterns.

Several non-mainstem sites on waterways that are significant contributors of water and/or solutes to the Sacramento River have been sampled for various lengths of time in 2009-2011. Figures 5.2.46 and 5.2.47 are box plots showing the average monthly compositions near the mouths of the two main distributaries to the Sacramento River: Miner and Steamboat Sloughs. A third important distributary is the San Joaquin River, which usually contains 80-95% Sacramento River water and significant amounts of NO_3 when it merges with the Sacramento River near Chain Island (see Appendix 5.3).

Each plot contains 8 smaller box plots with monthly data for EC (or salinity), water- $\delta^{18}\text{O}$, $[\text{NH}_4]$, $\text{NH}_4\text{-}\delta^{15}\text{N}$, $[\text{NO}_3 + \text{NO}_2]$, $\text{NO}_3\text{-}\delta^{15}\text{N}$, $\text{NO}_3\text{-}\delta^{18}\text{O}$, and [chlorophyll-a]. In the discussion below, the $\text{NO}_3 + \text{NO}_2$ concentrations are referred to as NO_3 concentrations. These plots combine data from Polaris transects 2006-2008, Dugdale transect data from 2009, and Foe transect data from 2009-2010. Although the monthly values are plotted January to December, the actual sampling period for sites sampled from Tower downstream to Rio Vista was from March 2009 through February 2010, Polaris sampling started in July 2006, and there are missing months each year. Hence, the monthly patterns may be biased by the irregular sampling.

The seasonal variations in flow at Freeport are shown in Figure 5.2.13. Flows were briefly high in mid-March 2009 and then even higher and for an extended period of time in mid-January to March 2010. Flows in early 2010 were so high that the waters rose over the banks of the Yolo Bypass and flooded adjacent areas, thus potentially transporting a lot of material washed from flooded agricultural areas into

the river. The anomalously high and low values of many upstream Sacramento River samples collected in January and February are probably related to this flood event.

These plots were prepared to (1) evaluate whether the seasonal trends in this set of data for sites sampled for only a few years during our transect studies match the seasonal trends in nutrients and chlorophyll observed at the 5 IEP sites in the Sacramento River and Delta (Figures 15-20 from Appendix 2) during a longer but overlapping time span (e.g., the green boxes for data from 1998-2013); and (2) if so, to use some of the isotope and chemical data for these intensively studied sites to provide interpretations of the causes of the seasonal patterns at the nearby IEP sites. Although box plots have been provided for all the transect sites with sufficient data, the discussion below will focus mostly on the sites closest to the IEP sites.

To make it easier to compare these monthly plots with the monthly box plots for the IEP sites, the $[\text{NO}_3]$ and $[\text{NH}_4]$ plots from the box plots in Appendix 2 have been copied into Figures 5.2.71 and 5.2.72. The site names and site numbers of USGS Polaris transect sites are shown in Figure 5.2.5. Figure 5.2.57 shows the relative positions of the Polaris transect sites and the IEP sites from Rio Vista downstream to Angel Island, and their site numbers. To make it easier to compare the downstream changes in $[\text{NO}_3]$ and $[\text{NH}_4]$ of adjacent transect sites, the relevant box plots were copied from Figures 5.2.29-5.2.47 into Figures 5.2.48-5.2.54. To make the temporal trends easier to see, colored lines were added to connect the average monthly values.

Sites upstream of SRWTP.

The two transect sites upstream of SRWTP and the IEP site C3 at Hood (RM38), Tower Bridge (RM59) and Garcia Bend (RM49), have similar chemical and isotopic compositions (Figures 5.2.29 and 5.2.30), as expected since they are both downstream of where the American River intersects the Sacramento River and there are no other significant water inputs to the river until SRWTP at RM46.

The EC data and water- $\delta^{18}\text{O}$ values, both good conservative tracers of water sources, show moderately similar trends at both sites, with generally low values in the spring and summer and higher values in the fall and winter “rainy season” months, with very similar monthly oscillations. The pattern of higher water- $\delta^{18}\text{O}$ values in the late fall and winter and low values in the summer is opposite to the trend expected in local rain but is typical for a river dominated by reservoir releases of snowmelt-derived water in the spring and summer (Kendall and Coplen, 2001).

The EC and water- $\delta^{18}\text{O}$ data show a distinctive “W-shaped” monthly trend, with the middle arm of the “W” lower than the two adjacent arms and typically occurring in June. There is no major change in flow at Freeport during June of 2009 (Figure 5.2.13) but the changes in EC and water- $\delta^{18}\text{O}$ indicate a significant change in water source -- to one with high EC and water- $\delta^{18}\text{O}$ -- took place in June. As will be discussed below, many constituents show a prominent local maximum in June. This phenomenon is seen at many different sites but not all adjacent sites, suggesting that the phenomenon is of short duration. Therefore, samples collected at some sites along June transects, which necessarily are not true Lagrangians, may not sample the parcel or parcels with the unusual source of water.

NO_3 concentrations at both sites (Figure 5.2.48) show the same very artificial-looking “asymmetrical U-shape” pattern of steadily declining $[\text{NO}_3]$ from December through August, a sharp increase September

through October that reaches a maximum $[\text{NO}_3]$ of about half the value seen in December, and then a small decrease in $[\text{NO}_3]$ through the end of the year. Superimposed on the U-shapes of NO_3 at both sites is a slight increase in $[\text{NO}_3]$ in June. As a result, the trend from December to October looks vaguely W-shaped – and thus is similar to the W-shaped trends in EC and water- $\delta^{18}\text{O}$. The increase in $[\text{NO}_3]$ starting after August correlates with the fall increase in EC, suggesting leaching of soil waters during early fall rains.

NO_3 - $\delta^{15}\text{N}$ values of the two sites show similar seasonal patterns, with a small decreasing trend in $\delta^{15}\text{N}$ in February through October associated with the generally decreasing $[\text{NO}_3]$. NO_3 - $\delta^{18}\text{O}$ values of the two sites are also similar, with similar temporal oscillations and general patterns, including relatively constant values January through July before a sharp drop in values in October, correlating with the minor $[\text{NO}_3]$ peak in October. The correspondence in the temporal trends of $[\text{NO}_3]$, $\delta^{15}\text{N}$, and $\delta^{18}\text{O}$ suggest seasonal changes in dominant NO_3 sources to the Sacramento River are the same at both sites, with a source with lower $\delta^{15}\text{N}$ (more soil or fertilizer N?) dominating during low $[\text{NO}_3]$ in the summer, and other sources with oscillating higher and lower $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values contributing in increasing amounts in the fall and winter as EC increases.

NH_4 concentrations are low and variable at both sites, with no simple seasonal trend besides the high values in January and February (that are probably related to the high flows and flooding at that time) and many minor $[\text{NH}_4]$ oscillations that occur at the same times at both sites (Figure 5.2.48). The consistency of the oscillations makes it likely that the variations reflect real temporal changes in NH_4 sources to the river from upstream of Tower Bridge. For example, both sites show a small increase in $[\text{NH}_4]$ in June and a trend from December to September that is vaguely W-shaped. The few NH_4 samples with sufficiently high $[\text{NH}_4]$ that we were able to analyze for $\delta^{15}\text{N}$ showed a range of relatively low $\delta^{15}\text{N}$ values (-2 to +6 ‰), significantly lower than the NH_4 - $\delta^{15}\text{N}$ values observed downstream of SRWTP at Hood.

The NH_4 - $\delta^{15}\text{N}$ values showed a positive correlation with $[\text{NH}_4]$, which is inconsistent with nitrification being the likely cause of the variability in $[\text{NH}_4]$ since nitrification would cause increases in NH_4 - $\delta^{15}\text{N}$ as $[\text{NH}_4]$ decreased (Kendall et al., 2015). Instead this pattern is consistent with the variability in $\delta^{15}\text{N}$ being related to temporal oscillations in $[\text{NH}_4]$ due to temporal variations in the amounts of NH_4 sources from low- $\delta^{15}\text{N}$ fertilizer sources to higher- $\delta^{15}\text{N}$ sources likely related to human/animal waste sources. A good check on this hypothesis would be to see if there is any seasonal pattern in $[\text{NO}_2]$ at these 2 sites, since the average $[\text{NO}_2]$ at these sites are probably high enough to suggest active nitrification. If there is, then perhaps part of the correspondence in seasonal variations in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ at these sites is due to appreciable new nitrate.

Hood.

The chemistry and isotopic compositions (Figure 5.2.31) at Hood (RM38), ~8 miles downstream of SRWTP, are very similar to the upstream data described above, with the chlorophyll-a concentrations being perhaps the most different constituent. EC and water- $\delta^{18}\text{O}$ data show similar broad patterns (lower in the summer and higher in the winter), with most monthly oscillations in phase. However, the W-shaped trends seen at the 2 upstream sites, which included a small maximum in June, are less well-defined at Hood. Chlorophyll concentrations at Tower and Garcia increase January through March and April, and then drop to low levels in the fall. In contrast, chlorophyll-a concentrations at Hood are lower,

show minor monthly oscillations while decreasing December through November, and show no peak in the spring as seen upstream.

The temporal trend in $[\text{NO}_3]$ at Hood is almost identical to the trends observed upstream, with all sites showing a local $[\text{NO}_3]$ maximum in October (Figure 5.2.48). The oscillations in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ at Hood are generally consistent with those observed at upstream sites, suggesting small seasonal variations in sources are the main causes of seasonality in $[\text{NO}_3]$. But whatever is causing the October $[\text{NO}_3]$ maximum and its associated abrupt shifts in $\delta^{18}\text{O}$ and to a lesser extent $\delta^{15}\text{N}$ to very low values in October at all 3 sites, followed by abrupt increases in $\delta^{18}\text{O}$ in November, is not a small change to the system. The normal pattern expected for nitrification in the upstream Sacramento River is for new NO_3 to have lower $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values (Figures 5.2.24 and 5.2.25) than the original NO_3 , so an abrupt input of NO_3 from newly nitrified NH_4 from upstream of Tower could explain the similar fall patterns in all 3 sites.

All 3 sites show very low NO_3 - $\delta^{15}\text{N}$ values in January. These were the lowest NO_3 - $\delta^{15}\text{N}$ values observed at the Tower and Garcia sites, whereas the Hood site had similarly low values three times during the year. These low $\delta^{15}\text{N}$ values were not associated with anomalous $\delta^{18}\text{O}$ values. However, these 3 low NO_3 - $\delta^{15}\text{N}$ values at Hood are associated with 3 drops in $[\text{NH}_4]$, although neither of the January low NO_3 - $\delta^{15}\text{N}$ values at the other 2 sites is associated with drops in $[\text{NH}_4]$. Two of these dips in $[\text{NH}_4]$ at Hood, the ones in January and November, are approximately correlated with increases in NH_4 - $\delta^{15}\text{N}$, consistent with nitrification; and the 2 low NO_3 - $\delta^{15}\text{N}$ values at closely matching dates are also consistent with nitrification being responsible for the dips in NO_3 - $\delta^{15}\text{N}$ at these dates. Hence, these data are contributing valuable information about seasonal changes in nitrification at Hood.

The main downstream change between Garcia and Hood is the huge 10-50 times higher $[\text{NH}_4]$ observed at Hood. Hence, it is not surprising that the temporal trends in $[\text{NH}_4]$ at Hood show little similarity to upstream trends. For example, $[\text{NH}_4]$ at Hood increases January through May whereas it decreases through the winter at the 2 upstream sites (Figure 5.2.48). But there are two oscillations that are seen at all 3 sites: low values in July and high values in September. In general, $[\text{NH}_4]$ at Hood increase January through late fall, but with a prominent several-month decrease in June through August, and another shorter duration dip in November.

There is some correspondence of seasonal changes in NH_4 - $\delta^{15}\text{N}$ with $[\text{NH}_4]$ at Hood. For example, $\delta^{15}\text{N}$ shows a sharp decrease in July, corresponding to the very prominent drop in $[\text{NH}_4]$ in July, and both $[\text{NH}_4]$ and $\delta^{15}\text{N}$ steadily increase February to May or June, and decrease in the fall. The NH_4 - $\delta^{15}\text{N}$ values for Hood are also much higher than at upstream sites, with values ranging from about +8 to +10 ‰ at Hood but much lower at upstream sites. However, as seen at the upstream sites, the general positive (in-phase) relation between several temporal oscillations in $[\text{NH}_4]$ and in NH_4 - $\delta^{15}\text{N}$ at Hood precludes seasonal differences in the extent of nitrification from being a probable explanation for seasonal changes in concentration and $\delta^{15}\text{N}$ for these dates. Alternative explanations for the strong positive correlation of low $[\text{NH}_4]$ and low NH_4 - $\delta^{15}\text{N}$, especially in July, are seasonal differences in the relative amounts of major NH_4 sources (ones with different NH_4 - $\delta^{15}\text{N}$ values) to the WWTP and/or seasonal differences in degradation processes during treatment that preferentially degrade different kinds of organics that have different $\delta^{15}\text{N}$ values.

Effluent is a major source of DOM to the water column. Data from Foe et al. (2010) show seasonal changes in nutrients and DOM concentrations downstream of SRWTP in 2009 that are apparently a result

of significant changes in effluent composition (Kendall et al., 2015). Analysis of archived samples from Foe transect samples for $\delta^{15}\text{N}$ (and $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$) of DOM could be an appropriate test of whether there were seasonal changes in the isotopic composition of the DOM from effluent. We have developed a new method that allows us to easily extract and analyze DOM from new and archived water samples for C-N-S isotopes (Silva et al., 2014; Tirumalesh et al., 2015; with an article draft in co-author review). We have archived suitable samples from all our Sacramento River, Delta, and Bay samples since 2006 in hopes of being able to add data on the C-N-S isotopes of DOM to our existing data on C-N-S isotopes of POM for the purpose of better tracing interactions between nutrients and organic matter in the estuary.

Are the seasonal patterns observed in our limited set of transect data (2009-2010) at Hood similar to the longer-term patterns observed at the IEP C3 site at Hood in 1998-2013? In general: yes. The NO_3 concentrations at C3 (Figure 5.2.55) show a prominent seasonal cycle with lowest values in August and highest in January, as is seen in Figure 5.2.48. However, the data at C3 do not show the local maximum at October seen at our transect sites, both upstream and downstream of Hood (Figure 5.2.48). Hence, this October maximum appears to be an isolated event not consistently repeated in other years. In contrast, $[\text{NO}_3]$ data at C3 show the W-shape with the prominent June maximum seen at Tower and Garcia, but no prominent June peak is apparent at the Hood transect site (Figure 5.2.48). Hence, the June 2009 transect sample may not have sampled the water parcel(s) with the short-duration change in water source. It is noteworthy that the June maximum is apparent in the average $[\text{NO}_3]$ data for C3 for 1998-2013 but not for earlier time spans (Figure 5.2.55), suggesting a change in watershed management practices,.

NH_4 concentrations at C3, like at our transect Hood site, do not show any simple or clear seasonal pattern except for the consistent drop in concentration in July. The averages at C3 for most months, but not July, show high variability. July had the lowest average $[\text{NH}_4]$ at C3 for 1976-86 and 1998-2013, and July had almost the lowest $[\text{NH}_4]$ in 1987-97 (the average in June was slightly lower). Hence, there is probably some watershed-wide event that has been regularly occurring for many decades that causes the summer maximum in $[\text{NO}_3]$ at C3 from 1976-2013 (Figure 5.2.31). One plausible explanation for the short-duration input of high- NO_3 waters into the Sacramento River would be a regular June release of water from reservoirs that flushes NO_3 from agricultural fields.

Average chlorophyll concentrations at C3 are slightly higher February through May than during the rest of the year, with occasional higher values in February and April. In contrast, only the chlorophyll levels at the Tower site seem similar to the C3 pattern.

Relevance to IEP site C3. In summary, monthly trends in $[\text{NO}_3]$ and $[\text{NH}_4]$ at C3 (Figure 5.2.55) are probably similar enough to those seen at the transect data at Hood (Figure 5.2.31) for us to extrapolate our interpretations (above) of the chemical and isotope data in Figure 5.2.31 to the longer record at the C3 site.

In specific, the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of NO_3 at Hood suggest that the relatively smooth seasonal variation in $[\text{NO}_3]$ at C3 camouflage a much more complicated story of seasonality in different sources of NO_3 to the site. The large and small oscillations in EC and water- $\delta^{18}\text{O}$ are better indicators of different sources of water (and nitrate) to the site than the smooth gradational changes in $[\text{NO}_3]$ for all months but June. Some of these oscillations in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3 could be explained by nitrification adding new nitrate of variable $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ that mixes with old nitrate, but most of the oscillations are more likely due to differences in NO_3 sources from upstream sources. All of the $[\text{NH}_4]$ data for C3 are higher than at

upstream sites. Hence, most of the NH_4 and most of the seasonal oscillations in $[\text{NH}_4]$ at C3 are probably due to seasonality in amounts of effluent NH_4 in the river.

Hood to Isleton.

Are the seasonal trends at Hood (or C3) representative of the patterns seen at the next two downstream sites, Walnut Grove (WNG, RM27) and Isleton (RM17)? If not, should the IEP add a site at Isleton to better reflect the Sacramento River water compositions that mix with Cache/Yolo Slough Complex waters to form the waters at Rio Vista?

In general, the seasonality of conservative tracers like EC and water- $\delta^{18}\text{O}$ for Hood and the next two downstream sites (Figures 5.2.32 and 5.2.33) are moderately similar, meaning that the major oscillations are in phase and the W-shape with a small maximum in June can still be detected. The similarity of patterns downstream of Hood is reasonable since there are no major water inputs in this river section. The oscillations in chlorophyll are also very similar to those at Hood, with all 3 sites having high values in January (a high flow period) that were not seen at upstream sites.

The prominent asymmetrical, U-shaped seasonal $[\text{NO}_3]$ cycle observed at sites from Tower to Hood has evolved downstream to now show a more prominent local maximum in June at Walnut Grove and Isleton and hence has now evolved to be distinctly W-shaped. All sites still show a small rise in values around October. Average $[\text{NO}_3]$ increased downstream from Tower to Isleton due to nitrification, with $[\text{NO}_3]$ at Isleton about 8 μM higher than at Hood. While this increase is clear on the spatial plot (Figure 5.2.21), it is very difficult to see an increase in $[\text{NO}_3]$ downstream when comparing the monthly box plots (Figures 5.2.48 and 5.2.49). However, it appears that most of the increase in $[\text{NO}_3]$ at downstream sites is occurring in the summer and fall.

The increases in $[\text{NO}_3]$ and decreases in $[\text{NH}_4]$ downstream of Tower Bridge (Figures 5.2.48 and 5.2.49) are associated with very large decreases in the NO_3 - $\delta^{15}\text{N}$ and NO_3 - $\delta^{18}\text{O}$, and increases in NH_4 - $\delta^{15}\text{N}$ (Figures 5.2.24-5.2.25) because of nitrification. The monthly trends in NO_3 - $\delta^{15}\text{N}$ and NO_3 - $\delta^{18}\text{O}$ trends at Hood, WNG, and Isleton are hard to describe. However, with some imagination, a vague W-shape can be detected, with the middle arm in August. This local August maximum in both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ at Hood to Isleton corresponds with the August minimum in $[\text{NO}_3]$ seen in the asymmetrical U-shape at Tower that evolved downstream to become the August minimum at the second leg of the W-shaped $[\text{NO}_3]$ at Walnut Grove and Isleton (Figures 5.2.29-5.2.33).

With this visual connection made between the monthly patterns in $[\text{NO}_3]$, $\delta^{15}\text{N}$, and $\delta^{18}\text{O}$ – it is now easier to see the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values are generally in phase with each other but are sometimes out of phase with the oscillations in $[\text{NO}_3]$. Nitrification rates are likely to be higher in months where the isotope values decrease while $[\text{NO}_3]$ increase, than in months when isotope values decrease while $[\text{NO}_3]$ decreases or when isotope values increase. With the data available, we can eventually calculate the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of new NO_3 to each sample and ultimately use the isotope data (which are less susceptible to problems caused by non-Lagrangian sampling than nutrient concentration measurements) to detangle seasonal changes in sources from seasonal changes in nitrification. But these calculations are beyond the current scope of this appendix.

NH_4 concentrations decrease downstream from Hood to Isleton (e.g., maximum $[\text{NH}_4]$ at Hood is about 10 μM higher than at Isleton). There are some consistent seasonal $[\text{NH}_4]$ trends that are seen from Tower

to Isleton (Figures 5.2.48 and 5.2.49). The main similarity is that all 5 sites show relatively constant, mid-range concentrations in July and August. In addition, the $[\text{NH}_4]$ maxima in September and November at Tower and Garcia are present at Walnut and Isleton (but only partially at Hood); and all 5 sites show some kind of $[\text{NH}_4]$ peak in January through March. If the NH_4 losses to nitrification at each site were the same each month, regardless of original concentrations for each month at upstream sites, the seasonal patterns should be dampened downstream but the main oscillations should persist downstream. The persistence of many oscillations at downstream sites shows that seasonal changes in nitrification, if present, were insufficient to erase original seasonal patterns.

The 3 sites show more similarity in the seasonal variations in $\text{NH}_4\text{-}\delta^{15}\text{N}$ than in $[\text{NH}_4]$. Besides the dip in $\text{NH}_4\text{-}\delta^{15}\text{N}$ in June, the 3 sites also have small peaks in June and August, with steady decreases in $\delta^{15}\text{N}$ from August to December, and steady increases in $\delta^{15}\text{N}$ from February, March, or April. These oscillations produce a rounded “M-shaped” trend at all 3 sites in the spring through winter months. The high $\text{NH}_4\text{-}\delta^{15}\text{N}$ values of the first leg of the M are associated with low $[\text{NH}_4]$, consistent with nitrification being the main cause of the dip in $[\text{NH}_4]$ and associated increase in the $\delta^{15}\text{N}$ of the residual NH_4 . It is more difficult to decide if the $\text{NH}_4\text{-}\delta^{15}\text{N}$ values of second leg of the M are associated with an increase in $[\text{NH}_4]$, consistent with nitrification, or not. This is because the $[\text{NH}_4]$ values for September through December for both sites oscillate while the $\delta^{15}\text{N}$ values show a steady decrease for September through December. However, since the changes in $[\text{NO}_3]$, $\text{NO}_3\text{-}\delta^{15}\text{N}$, and $\text{NO}_3\text{-}\delta^{18}\text{O}$ at Isleton for October through December, as well as the changes in $[\text{NH}_4]$ and $\text{NH}_4\text{-}\delta^{15}\text{N}$, are consistent with nitrification, a plausible interpretation is that much of the nutrient changes in the second leg of the M also reflect nitrification.

The statistical analysis of more than a year years of ~ monthly chemical and isotopic data from Isleton and from near the mouths of the two main Sacramento River distributaries, Miner Slough and Steamboat Sloughs -- that combined carry flows equivalent to that at Isleton – show no significant differences between these 3 sites on these 3 channels of the Sacramento River (Kendall et al., 2015). Hence these data can be used, combined with data from Rio Vista, to estimate transformations of nutrients in Cache Slough. However, Hood is **not** a suitable endmember for such nutrient transformation calculations because of the significant downstream changes in $[\text{NO}_3]$, $\text{NH}_4\text{-}\delta^{15}\text{N}$, $\text{NO}_3\text{-}\delta^{15}\text{N}$, and $\text{NO}_3\text{-}\delta^{18}\text{O}$ between Hood and Isleton discussed above, that are indicative of extensive nitrification. Therefore, an additional IEP monitoring site at or near Isleton seems warranted. Walnut Grove is not a good candidate for a monitoring site intended for sampling at or before ebb tide because samples collected there often have anomalously low $[\text{NH}_4]$, suggesting that the water parcel sampled there contains a tidally biased reduced fraction of effluent (Kendall et al., 2015).

Isleton to Rio Vista.

This section of the Sacramento River contains the transition between the upstream Sacramento River, which ends at Isleton, and the downstream Sacramento River, which starts somewhere between Isleton and Rio Vista (depending on perspective). Many important transitions in chemical and isotopic compositions occur between Isleton and Rio Vista. In specific, of all the constituents summarized in Figure 5.2.28, only $\text{NH}_4\text{-}\delta^{15}\text{N}$ and $\text{NO}_3\text{-}\delta^{18}\text{O}$ do not show transitions here. The $\text{NH}_4\text{-}\delta^{15}\text{N}$ values continue to show a semi-exponential increase downstream to San Pablo Bay because there continues to be NH_4 to nitrify and the $\delta^{15}\text{N}$ value is a more sensitive indicator of changes in the size and sources of the NH_4 pool than NH_4 concentration measurements. The $\text{NO}_3\text{-}\delta^{18}\text{O}$ values show a major transition a couple miles downstream of Rio Vista, apparently because this is the location where there has finally been enough new

NO₃ formed by nitrification -- under conditions where the water-δ¹⁸O is significantly higher than the upstream Sacramento River -- that the δ¹⁸O of the new NO₃ overwhelmed the δ¹⁸O signature of the original upstream NO₃.

For some of the constituents that show a transition here, the transition is subtle (e.g., EC, water isotopes) and for some the change is very prominent ([NO₃], [NO₂], NO₃-δ¹⁵N, chlorophyll-a). For EC and water isotopes, the change was between constant compositions from Tower Bridge downstream to Isleton, followed by rapid increases from Rio Vista downstream. These constituents were constant upstream of Rio Vista because there was only a minor addition of water from SWRTP, which did not have appreciably different water isotopes or EC. The constituents increased rapidly downstream of Isleton partly because of salts and evaporated water from the tributaries, but also because of mixing with marine-derived water from tidal sloshing. For nutrients, the changes reflected the transition between the rapid downstream increases in [NO₃] and [NO₂] and the corresponding rapid decreases in [NH₄] due to nitrification – to a region where the compositions showed less downstream change.

There are huge changes to the Sacramento River between Isleton and Rio Vista. The most notable change is probably that there is an approximate doubling of the flow between RM17 and RM12. This is because Miner and Steamboat Sloughs (actually distributaries) empty into Cache/Yolo Slough, which merges with the mainstem at about RM14. There are additional sources of flow to this section of the Sacramento River, including minor amounts of flow from the tributaries in the Cache/Yolo Slough Complex. During the collection dates of our 2009-2010 samples, DSM2 estimates of the % of flow at Rio Vista derived from the Cache/Yolo Slough Complex tributary sites (e.g., “Yolo + Ag”) range from 3 to 54% (personal communication, Marianne Guerin, 2015). Estimates of main peak travel time between Isleton and Rio Vista are 16 hrs +/- 10 hours (N=29) for 3/09 to 7/09; for a tidally averaged flow, the travel times were longer: 31 hrs +/- 10 hours (N=8) (personal communication Marianne Guerin, 2010). Hence, there is ample time for variable mixing of mainstem, distributary, and tributary waters – and additional biogeochemical processing of nutrients in the wide section of the Cache Slough – prior to the arrival of the water at Rio Vista.

To better understand how water from Isleton changes (evolves) downstream to become the water at Rio Vista, temporal and spatial changes in chemistry and isotopes at sites near the mouths of the two main distributaries (Miner and Steamboat Sloughs) and at sites in the 4 main tributaries (Cache Slough @ DWSC, Liberty Island, Lindsey Slough, and Toe Drain @ Dredger) are discussed below. The obvious next step, mass balance calculations to estimate the seasonal changes in contributions of water and solutes from these different waterways to Rio Vista are in progress but were beyond the scope of this report. However, our recent report (Kendall et al., 2015) provides proof of concept of the validity of doing these kinds of mass balance calculations. In specific, (1) the composition of Sacramento River water at Isleton was statistically indistinguishable from water from sites near the mouths of Miner and Steamboat Sloughs, and (2) waters from the 4 main tributaries in the Cache/Yolo Slough Complex were determined to be statistically significantly different from water at Isleton.

Delta sites near the confluence with the San Joaquin River.

We have data from 3 transect sites (Figures 5.2.34-5.2.36) upstream of the IEP site D4 (Figures 5.2.56 and 5.2.57): Rio Vista (PO-657 at RM12), PO-655 (RM10), and PO-649 (RM3); and from one site just downstream of D4: PO-2 (RM0). The 2 upstream sites, only 2 miles apart, have similar ranges of water-

$\delta^{18}\text{O}$ but not similar seasonal trends, with no correlation of the oscillations in water- $\delta^{18}\text{O}$ and EC. However, the seasonal trends in water- $\delta^{18}\text{O}$ at Rio Vista closely resemble the trends at Isleton.

The two downstream sites (PO-649 and PO-2), only 3 miles apart, have higher water- $\delta^{18}\text{O}$ values than the 2 upstream sites. They also have very similar, vaguely W-shaped, seasonal $\delta^{18}\text{O}$ trends -- including the significant June maxima observed at Tower down to Hood. These sites also show the W-shaped seasonal trend in salinity observed at all the sites upstream of Rio Vista, also with significant maxima in June; at these sites, the highest salinities occur in December and January when flows are highest. The persistence of the small June maxima downstream continues to be surprising, especially at sites downstream of Rio Vista. EC data from near the mouths of Miner and Steamboat Sloughs, which are distributaries of the Sacramento River and carry about half of the Sacramento River reaching Rio Vista, do not show the W-shaped pattern, nor do data from the 4 Cache/Yolo Slough tributary sites (Kendall et al., 2015). One explanation is that water from the San Joaquin River also has these monthly patterns, and these patterns are re-introduced in the Sacramento River from the confluence and perhaps via Three Mile Slough. Chlorophyll levels are higher in the spring and summer at all sites but otherwise there is no consistency in which months have higher levels.

Seasonal changes in NO_3 concentrations of these 4 sites are roughly similar, keeping in mind that site PO-655 (with combines data from the actual PO-655 (RM9.8) site plus data from the nearby Three Mile Slough site (RM9.4) sampled during Foe transects) was sampled less often than the other two sites routinely sampled by the Polaris program. NO_3 concentrations are highest in the late fall and winter and lowest in the late spring and summer, with concentrations lowest in July and August at all sites. However, all 4 sites show a maximum in $[\text{NO}_3]$ in June (that at some sites starts in May) that divides the mid-year low $[\text{NO}_3]$ values into two time periods. However, only 3 of the sites (Rio Vista, PO-655, and PO-649) show a well-defined W-shaped trend (Figure 5.2.49). The W-shaped seasonal $[\text{NO}_3]$ pattern for PO-655 closely resembles the W-shaped pattern seen at Isleton and WNG (Figures 5.2.48 and 5.2.49), sites that were also as part of the Foe and Dugdale transect studies. IEP site D4 has the same W-shaped seasonal $[\text{NO}_3]$ pattern, with a small peak in June.

A possible explanation for the strong seasonal pattern of low $[\text{NO}_3]$ in the summer and early fall, and high $[\text{NO}_3]$ in the winter and spring, that is so noticeable in the monthly plots of many sites (e.g., Figures 5.2.48 and 5.2.49) can be deduced from the $[\text{NO}_3]$ chemoscape presented earlier (Figure 5.2.14). The high winter and spring $[\text{NO}_3]$ values are correlated with periods of high flow during winter storms. The local small increase in $[\text{NO}_3]$ also seen at many sites in June is perhaps related to the small flow peak that also occurred in June. However, the water at these sites in the summer, based on the low water- $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values (Figure 5.2.19), appears to be largely derived from winter and/or high elevation precipitation and thus is probably snowmelt stored in reservoirs and released later in the year, probably for agricultural needs and/or to flood wetlands used by migratory birds.

NH_4 concentrations at all 4 transect sites also show a strong seasonal pattern, with low values in mid-summer and highest values in February to March; the pattern at D4 is the same. NH_4 concentrations at Rio Vista were higher than at the 3 downstream sites. NH_4 concentrations at site PO-649 -- and to a lesser extent, Rio Vista -- showed a well-defined U-shaped trend, with the bottom of the U centered around July and August. However, the monthly trends of $[\text{NH}_4]$ at the intermediate site (PO-655) and the site downstream of PO-649 (PO-2) were similar to each other but not very U-shaped and instead the

seasonal changes at the beginning and end of the summer low $[\text{NH}_4]$ values were much more abrupt. There are other odd differences among these 4 sites. For example, the average $[\text{NH}_4]$ in the summer months for 3 of the sites (PO-655, PO-649, and PO-2) was $\sim 3 \mu\text{M}$, whereas it was $9 \mu\text{M}$ at Rio Vista. And 3 of the sites (Rio Vista, PO-655, and PO-649) all had maximum $[\text{NH}_4]$ of $\sim 17 \mu\text{M}$ in the winter months, whereas it was $9 \mu\text{M}$ at PO-2. Hence, the upstream site (Rio Vista) has higher summer $[\text{NH}_4]$ and the downstream site (PO-2) has lower winter $[\text{NH}_4]$ than the two intermediate sites. Since the general downstream trend is for decreasing $[\text{NH}_4]$ due to nitrification, it makes sense that Rio Vista would have a higher $[\text{NH}_4]$ than PO-2.

It is difficult to imagine hydrological conditions that would cause the monthly average $[\text{NH}_4]$ in pairs of non-adjacent sites to be so similar to each other but so different from the other pair of non-adjacent but intermediate sites. The sites with the oddly shaped NH_4 trends are usually sites with fewer NH_4 measurements (e.g., no data box, just a bar) than the sites with nice U-shaped curves. Hence, a plausible explanation is that since PO-655 and PO-2 were sampled less often than the adjacent sites, the temporal trends were biased by one slightly atypical year. Another possibility is that the two odd sites might have different depths or degrees of mixing than the other sites that, depending on tidal mixing conditions when the samples are collected, produce data that are significantly different from adjacent sites. Comparing the seasonal trends for data for different years at these sites should help clarify the situation.

Temporal trends in $[\text{NH}_4]$ from Hood to Isleton (Figure 5.2.48) were mainly ascribed to small drops in $[\text{NH}_4]$ caused by nitrification superimposed on temporal variations in effluent-derived NH_4 . Comparison of the temporal $[\text{NH}_4]$ patterns at Isleton with those at Rio Vista and sites downstream (Figures 5.2.48-5.2.49) shows that temporal trends in $[\text{NH}_4]$ continue to be similar downstream, despite the decreases in $[\text{NH}_4]$ caused by nitrification. The similarity in seasonal trends from Isleton to PO-2 indicates that effluent-induced variations continue to be the main cause of temporal variations at all these sites, despite the significant downstream decreases in $[\text{NH}_4]$ and increases in $\text{NH}_4\text{-}\delta^{15}\text{N}$ due to continued nitrification.

The temporal trends in $\text{NH}_4\text{-}\delta^{15}\text{N}$ at Rio Vista are quite similar to those at PO-655 (Figures 5.2.34 and 5.2.35), with both sites having low $\delta^{15}\text{N}$ values February to April, high values in June, low values in July and September, high values in October, and then declining values to February. These oscillations show some resemblance to the temporal patterns upstream at Isleton, which has low $\text{NH}_4\text{-}\delta^{15}\text{N}$ values in March, high values in June, low in July, high in October, and generally declining values to March. The oscillations at the two downstream sites, PO-649 and PO-2 (Figures 5.2.36 and 5.2.37), are also similar to those at Rio Vista, with PO-649 having low $\text{NH}_4\text{-}\delta^{15}\text{N}$ values in March and April, high values in October, and then declining values through December; and PO-2 having low values in February, high values in May and June, low in August and September, and high in October. Hence, it is clear that effluent-induced temporal variations can be traced for at least 40 miles downstream.

There is a “dampening” of the maximum and minimum values of the temporal oscillations in $[\text{NH}_4]$ and $\text{NH}_4\text{-}\delta^{15}\text{N}$ from Isleton downstream (Figure 5.2.33). If the relative changes in $[\text{NH}_4]$ and $\delta^{15}\text{N}$ are estimated using $\Delta[\text{NH}_4] / \Delta\delta^{15}\text{N}$, then the values from Isleton to Rio Vista changed from 5.8 to 2.7, and then the values continued to decrease downstream to 2.4 at PO-655, 2.3 at PO-649, and 1.5 at PO-2. These changes suggest the possibility of estimating seasonality in the extent of nitrification by comparing the downstream changes in $[\text{NH}_4]$ and $\text{NH}_4\text{-}\delta^{15}\text{N}$ of traceable oscillations in effluent-derived NH_4 .

The $\text{NO}_3\text{-}\delta^{15}\text{N}$ values of these 4 sites define a region (Figures 5.2.24 and 5.2.28) with steadily increasing $\delta^{15}\text{N}$ values, located just upstream of the transition to the Suisun Bay region; in Suisun Bay, the $\text{NO}_3\text{-}\delta^{15}\text{N}$ values decrease for several sites. The seasonal $\text{NO}_3\text{-}\delta^{15}\text{N}$ trends at PO-655 show little resemblance to the $\delta^{15}\text{N}$ trends seen at the adjacent sites. The $\text{NO}_3\text{-}\delta^{18}\text{O}$ for PO-655 are very similar to the $\delta^{15}\text{N}$ trends at this site, with the oscillations in compositions usually in phase; hence, these seasonal variations show strong evidence for nitrification being the main cause of temporal variation. During 2009-2010 when these sites were intensively sampled, this PO-655 site (actually data from 2 adjacent sites combined) usually had higher $[\text{NO}_3]$ than any other site (Figure 5.2.21), consistent with nitrification being a more significant contributor to total NO_3 at this site than at adjacent sites (i.e., a local hot spot).

Rio Vista shows the greatest temporal variability in $[\text{NO}_2]$ of any of our transect sites (Figure 5.2.22), suggesting that this site (and/or the tributary sites in the Cache/Yolo Slough plus Miner and Steamboat Sloughs that contribute about half of the Sacramento River water that reaches Rio Vista) may have the highest seasonal range in local nitrification. Given the good correlations of downstream trends and relations among constituents during the summer discussed above, it appears that there is less nitrification in the summer (July-September) than at other seasons at Rio Vista – or at the sites in the Cache/Yolo Slough Complex that contribute NO_2 to the “integrator” site at Rio Vista. The much lower $[\text{NO}_2]$ concentrations at Rio Vista in July-September 2009 (Figure 5.2.15) supports this interpretation, which was derived solely from the data in Figures 5.2.22 and 5.2.34.

Rio Vista shows a very well-defined U-shaped seasonal pattern in $\text{NO}_3\text{-}\delta^{18}\text{O}$ (Figure 5.2.25), with low but slightly oscillating values June through November, and highest values in February; this pattern is similar to the seasonal variation in water- $\delta^{18}\text{O}$. The period of low $\text{NO}_3\text{-}\delta^{18}\text{O}$ values overlaps with multi-month periods of low values of most other constituents: $[\text{NO}_3]$ for July-September, $\text{NO}_3\text{-}\delta^{15}\text{N}$ for September-November, $[\text{NH}_4]$ for July-September, and $\text{NH}_4\text{-}\delta^{15}\text{N}$ for July-September, EC for May-July, and water- $\delta^{18}\text{O}$ for June-July.

In contrast, the trends of most constituents in this region (Figure 5.2.28) are to increase downstream: $\text{NO}_3\text{-}\delta^{18}\text{O}$, $\text{NO}_3\text{-}\delta^{15}\text{N}$, $\text{NH}_4\text{-}\delta^{15}\text{N}$, EC, and water- $\delta^{18}\text{O}$. $[\text{NH}_4]$ decreases downstream and 2 constituents stay approximately constant: $[\text{NO}_3]$ and $[\text{NO}_2]$. For the 5 constituents that increase downstream in this region, the first 3 are tracers of nitrification and their increases downstream mean continued nitrification downstream; the decrease in $[\text{NH}_4]$ downstream supports this interpretation. The other two constituents are tracers of downstream mixing with marine water. As for the relative consistency in $[\text{NO}_3]$ and $[\text{NO}_2]$ in this region, this is typical of this section of the estuary downstream to about Benicia and is interpreted as an indicator of a steady-state condition where production of new nitrate is balanced with bulk nitrate losses to tidal mixing.

Samples collected from Rio Vista show a $>10\text{‰}$ range in $\text{NO}_3\text{-}\delta^{18}\text{O}$ values (Figure 5.2.34, 5.2.25). The lowest $\text{NO}_3\text{-}\delta^{18}\text{O}$ values (about -7‰) occur in the summer when water- $\delta^{18}\text{O}$ values at Rio Vista are also lowest (-11‰). The average $\text{NO}_3\text{-}\delta^{18}\text{O}$ at Tower Bridge was $\sim 0\text{‰}$. Average $[\text{NO}_3]$ increased by over a factor of 4 between Tower Bridge and Rio Vista, and the $[\text{NO}_3]$ at Rio Vista is about $5\text{ }\mu\text{M}$ higher than at Isleton. Hence, the NO_3 at Rio Vista should be mostly new NO_3 produced by nitrification.

But where was most of this $5\text{ }\mu\text{M}$ of new NO_3 produced? Comparison of the small difference between summer and winter water- $\delta^{18}\text{O}$ values ($\sim 2\text{‰}$) at Rio Vista with the $>10\text{‰}$ seasonal difference in $\text{NO}_3\text{-}\delta^{18}\text{O}$ values indicates that nitrification at Rio Vista is insufficient to explain the $\sim 10\text{‰}$ difference in

summer and winter $\text{NO}_3\text{-}\delta^{18}\text{O}$ values. Hence, part of the seasonal differences is likely due to differences in NO_3 sources. Since the average water- $\delta^{18}\text{O}$ of tributary sites in Cache Slough is 1-3 ‰ higher than the water- $\delta^{18}\text{O}$ values at Isleton and Rio Vista, this is a likely production area for most of the new nitrate. Nitrification in the tributaries will be discussed below.

PO-2 (Figure 5.2.37), the site just downstream of D4, shows seasonal variations in chemical compositions that are very similar to PO-649 (Figure 5.2.36), the site just upstream of D4. In particular, both have a prominent change in EC or salinity in June, and strong seasonality in $[\text{NO}_3]$ and $[\text{NH}_4]$ -- with low values in the summer and fall, and high values in the late fall and early winter. The asymmetrical U-shaped seasonal trend in $[\text{NH}_4]$ at D4 more closely matches the trend in $[\text{NH}_4]$ at PO-649 than at PO-2. The seasonal chlorophyll-a trends of these two sites are also very similar to the trends seen at D4 (Figure 5.2.55). PO-2 shows a much more subtle inversion point in $[\text{NO}_3]$ in June than at PO-649; both sites show small chlorophyll peaks in April and August.

The downstream persistence of the maxima in June at PO-2 for a conservative parameter like EC and a non-conservative constituent like NO_3 is fascinating. Interestingly, even the prominent $[\text{NO}_3]$ maximum seen in June is present at D4. Given the proximity of PO-2 to the confluence with the San Joaquin River (SJR), a plausible explanation of the persistent $[\text{NO}_3]$ peak could be NO_3 from the SJR (see Appendix 5.3). Based on data in appendix 5.3, the average $\delta^{15}\text{N}$ for the SJR at Prisoner's Point (RM24) in June was +8 ‰, with a seasonal range from about +3 ‰ in September to +8 ‰ in June. The $\text{NO}_3\text{-}\delta^{15}\text{N}$ at PO-649, immediately upstream from PO-2 is +4.5 ‰. Hence, a small contribution of NO_3 from the SJR to PO-2 in June is a plausible explanation of the change in $\text{NO}_3\text{-}\delta^{15}\text{N}$ values between these sites. The $\text{NO}_3\text{-}\delta^{15}\text{N}$ in September at both PO-2 and PO-649 is +7 ‰ when the $\text{NO}_3\text{-}\delta^{15}\text{N}$ in the SJR is +3 ‰; hence, significant contributions of NO_3 from the SJR in September are implausible. These estimates could be tested with $\text{NO}_3\text{-}\delta^{18}\text{O}$ values and other constituent concentrations.

Relevance to D4. In summary, monthly trends in $[\text{NO}_3]$ and $[\text{NH}_4]$ at D4 (Figure 5.2.55) are probably similar enough to those seen at the transect data at PO-649 and PO-2 (Figures 5.2.36 and 5.2.37) for us to apply our interpretations (above) of the chemical and isotope data in Figures 5.2.36 and 5.2.37 to explaining the seasonal trends in the longer record at the D4 site.

Comparison of the location of D4 with Figure 5.2.28 shows that this site lies approximately in the middle of several regions defined by various downstream trends of important constituents. Conservative constituents like EC, water- $\delta^{18}\text{O}$, and water- $\delta^2\text{H}$ show this site to be in the middle of regions extending from Rio Vista to Chipps Island (PO-4) where the proportion of marine-derived water is increasing downstream. Several non-conservative constituents have approximately constant compositions in this region, including NO_2 , NO_3 , $\text{NO}_3\text{-}\delta^{18}\text{O}$, and chlorophyll-a. In contrast, $[\text{NH}_4]$ are slowly decreasing downstream, and $\text{NH}_4\text{-}\delta^{15}\text{N}$ and $\text{NO}_3\text{-}\delta^{15}\text{N}$ are both increasing downstream – consistent with progressive nitrification. It appears that tidally-induced mixing, combined with nitrification, allows some constituents to maintain what seem to be steady-state constant compositions over the region, while other constituents show strong downstream trends.

Suisun Bay sites.

We have data from 3 transect sites (Figures 5.2.40-5.2.42) that bracket the locations of the 3 IEP sites in Suisun Bay (see map Figure 5.2.6): PO-5 (Middle Ground) that is upstream of D8, PO-6 (Roe Island)

that is downstream of D8 and directly south of D7 (which is located further into the wide part of Suisun Bay), and PO-9 (Benicia) that is downstream from D6. There are other USGS Polaris sites near these IEP sites (e.g., PO-7 and PO-8), but consistent nutrient data are apparently not available for these sites.

The three transect sites show very similar monthly trends in salinity, with the typical “W-shape” seen at many other sites (e.g., at PO-2: Figure 5.2.37) with low values in March and August, a local maximum in June, and highest values in October through January (depending on site). Although the seasonal patterns are almost identical, the average monthly values for the 3 sites increases downstream, showing a higher percent of marine salt at sites closer to the ocean. The seasonal water- $\delta^{18}\text{O}$ patterns of PO-6 and PO-9 are very similar, but the patterns at PO-6 are only similar in September-December. The average monthly values for the 3 sites increase downstream, showing a higher percent of marine water closer to the ocean.

All three sites (PO-5, PO-6, and PO-9) show very similar monthly trends in $[\text{NO}_3]$, with the typical “W-shape” seen at many other sites (e.g., at PO-649: Figure 5.2.36) with the first low values in March, April, or May (depending on site) and the second low values in October, a local maximum in June, and highest values in February or March (depending on site). The seasonal trends in $[\text{NH}_4]$ for PO-6 and PO-9 are almost identical, with more symmetrical “U-shaped” trends than seen at upstream sites (e.g., Figure 5.2.38). The 3 IEP sites show very similar seasonal changes in nutrients (Figure 5.2.56) as the 3 transect sites (Figures 5.2.40-5.2.42). The IEP sites also show W-shaped seasonal trends in $[\text{NO}_3]$, but with the local $[\text{NO}_3]$ maxima in June at the transect sites now transmuted into a broader maximum during both June through July for the IEP sites. The IEP sites show a more symmetrical U-shaped seasonal trend in $[\text{NH}_4]$ at D6, while D7 and D8 have less symmetrical U-shaped seasonal trends. Hence, there are some very slight differences in the seasonal trends at the IEP and transect sites.

Comparison of the locations of IEP sites D8, D7, and D6 (Figure 5.2.57) with the transect sites included in Figure 5.2.28 shows that these sites are all located together within the same region, and that the sites are at the upstream, middle, or downstream ends of the regions for various constituents. Conservative constituents like EC, water- $\delta^{18}\text{O}$, and water- $\delta^2\text{H}$ show these sites to be located near the upstream ends of regions extending from Middle Ground (PO-5) downstream to PO-14 where the proportion of marine derived water is increasing downstream. Several non-conservative constituents have approximately constant compositions in this region, including NH_4 , NO_2 , NO_3 , and chlorophyll-a. However, the concentrations of NH_4 and NO_2 are both higher in Suisun Bay than in the adjacent upstream and downstream regions, indicative of a local NH_4 source and more active nitrification than in adjacent regions. In contrast, NH_4 - $\delta^{15}\text{N}$ and NO_3 - $\delta^{18}\text{O}$ do not have constant compositions in this region but instead are both increasing downstream, and NO_3 - $\delta^{15}\text{N}$ is decreasing downstream; these trends are consistent with progressive downstream nitrification.

The changes in chemical and isotopic trends at the sites in Suisun Bay provide a lot of information about the nitrification process in Suisun Bay. The increasing NO_3 - $\delta^{18}\text{O}$ indicates that the newly formed NO_3 is deriving its O from water which is increasing in $\delta^{18}\text{O}$ downstream due to mixing with marine water, a trend that remains the same in Suisun Bay and downstream to PO-18. Since the NH_4 - $\delta^{15}\text{N}$ values at sites in Suisun Bay show the same semi-exponential trend as the rest of this region, this suggests that the $\delta^{15}\text{N}$ of the local NH_4 source that mixed with normal riverine NH_4 (i.e., NH_4 derived from upstream, ultimately mainly from SRWTP effluent) and caused a significant increase in the $[\text{NH}_4]$ at Suisun sites was roughly similar to the $\delta^{15}\text{N}$ of the riverine NH_4 . The decreasing NO_3 - $\delta^{15}\text{N}$ values downstream in this region, when

$\text{NO}_3\text{-}\delta^{15}\text{N}$ values had been increasing in the adjacent upstream region, indicates that the new NO_3 formed in Suisun Bay has a significantly lower $\delta^{15}\text{N}$ than new NO_3 formed at sites in the upstream region.

The most plausible explanation for the decreasing $\text{NO}_3\text{-}\delta^{15}\text{N}$ values in this region (and the other nutrient and isotope trends described above) is that most of the new NO_3 was formed by nitrification of the local NH_4 source (i.e., local nitrification) that took place elsewhere in Suisun Bay, perhaps in the shallow marshes, NOT in the main channel. The local NH_4 source must have originally had a much lower $\delta^{15}\text{N}$ than riverine NH_4 , resulting in new NO_3 produced by local nitrification with a significantly lower $\delta^{15}\text{N}$ than the riverine NO_3 . Given the high NO_2 concentrations, it is reasonable to assume that the extent of local nitrification resulted in a large drop in $[\text{NH}_4]$ and a correspondingly large increase in $\text{NH}_4\text{-}\delta^{15}\text{N}$ of the residual local NH_4 , now giving the local NH_4 a $\delta^{15}\text{N}$ value not too different from that of riverine NH_4 . The residual NH_4 from local nitrification in the marshes, plus the newly formed NO_3 , then tidally mix with the riverine NH_4 and NO_3 to produce the observed chemical and isotopic compositions and downstream trends at the transect sites – and presumably at the IEP sites.

Relevance to D8, D7, and D6. In summary, monthly trends in $[\text{NO}_3]$ and $[\text{NH}_4]$ at the 3 IEP sites (Figure 5.2.56) are probably similar enough to those seen at the transect data at PO-5, PO-6, and PO-9 (Figures 5.2.40-5.2.42) for us to apply our interpretations (above) of the chemical and isotope data in Figures 5.2.40-5.2.42 to explaining the seasonal trends in the longer record at the IEP sites.

Sites downstream of Suisun Bay.

We show data from 3 transect sites (Figures 5.2.43-5.2.45) downstream of the IEP sites discussed in this report (see map Figure 5.2.6): PO-13 (North of Pinole Point in San Pablo Bay), PO-15 (Point San Pablo, at the mouth of San Pablo Bay), and PO-18 (near Angel Island). There are other USGS Polaris sites downstream of Suisun Bay, but consistent nutrient data are apparently not available for these sites. For many constituents (NH_4 , $\text{NH}_4\text{-}\delta^{15}\text{N}$, NO_2 , NO_3 , and $\text{NO}_3\text{-}\delta^{18}\text{O}$), all 3 sites are together in the same region. In this region, $[\text{NH}_4]$ and $[\text{NO}_2]$ are approximately constant, $\text{NH}_4\text{-}\delta^{15}\text{N}$ and $[\text{NO}_3]$ are decreasing downstream, and $\text{NO}_3\text{-}\delta^{18}\text{O}$ is increasing downstream.

For the 3 conservative tracers (EC, water- $\delta^{18}\text{O}$, and water- $\delta^2\text{H}$), PO-13 is in a slightly different region than PO-15 and PO-18. For $\text{NO}_3\text{-}\delta^{15}\text{N}$, PO-13 is in a region with approximately constant composition whereas PO-15 and PO-18 are in a different region with downstream increasing values. For chlorophyll, PO-13 and PO-15 are in a region with higher concentrations than the region containing PO-18. But the important point is that average chlorophyll-a concentrations from PO-10 downstream to PO-18 are higher than anywhere else at mainstem sites (Figure 5.2.26), and that the algae here is “fresher” (i.e., has a higher average ratio of chlorophyll-a to total chlorophyll) than elsewhere (Figure 5.2.27).

The most interesting downstream changes in this part of the Bay are that $\text{NH}_4\text{-}\delta^{15}\text{N}$ and $[\text{NO}_3]$ decrease while $\text{NO}_3\text{-}\delta^{15}\text{N}$ and $\text{NO}_3\text{-}\delta^{18}\text{O}$ increase. These are the only mainstem sites where $\text{NH}_4\text{-}\delta^{15}\text{N}$ decreases downstream. Such a large decrease in $\text{NH}_4\text{-}\delta^{15}\text{N}$ can only happen when there are significant inputs of local NH_4 with a significantly lower $\delta^{15}\text{N}$ than the riverine NH_4 ; uptake of NH_4 would have caused an increase in $\text{NH}_4\text{-}\delta^{15}\text{N}$ (Figure 5.1.4). While the $[\text{NH}_4]$ remains approximately constant in this region, the concentration is significantly higher than upstream of the Suisun Bay where the $[\text{NH}_4]$ had decreased to a relatively constant level. It is very difficult to envision how the increases in $\text{NO}_3\text{-}\delta^{15}\text{N}$ and $\text{NO}_3\text{-}\delta^{18}\text{O}$ in this region could have been caused by nitrification, given that both $[\text{NO}_3]$ and $\text{NH}_4\text{-}\delta^{15}\text{N}$ are decreasing

downstream. It seems unlikely but not impossible that the increases in $\text{NO}_3\text{-}\delta^{15}\text{N}$ and $\text{NO}_3\text{-}\delta^{18}\text{O}$ could be caused by the addition of substantial amount of new local NO_3 (with a significantly higher $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values than riverine NO_3) – all while the $[\text{NO}_3]$ is decreasing by dilution with marine water.

Simultaneous increases in $\text{NO}_3\text{-}\delta^{15}\text{N}$ and $\text{NO}_3\text{-}\delta^{18}\text{O}$ with decreasing $[\text{NO}_3]$ could also be caused by denitrification or uptake (Figure 5.1.8). Three different plausible mechanisms come to mind. First, the riverine NO_3 could undergo denitrification as the waters are tidally flushed through reducing marsh environments around the margins of San Pablo and the Central Bay. Second, there could be denitrification of local nitrate in adjacent marshes, resulting in a local source of new NO_3 with significantly higher $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values than riverine NO_3 , which then mixes with riverine NO_3 while the total $[\text{NO}_3]$ is decreasing by dilution with marine water. Third, the NO_3 might be the main N source for the active algae growth that characterizes this region (Figures 5.2.26 and 5.2.27), which would explain the decrease in NO_3 and associated increases in $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$.

Given the intriguing puzzles in the region (e.g., possible additional local sources of NH_4 and NO_3 with unusual but informative isotopic compositions in this part of the estuary, a local environment that might be providing a significant sink for N, or algae growth significantly decreasing NO_3 concentrations) additional IEP monitoring sites seem warranted. In addition, this region has the highest chlorophyll concentrations and the highest chlorophyll ratios of any sites in the SFE, producing algae that might be an important contributor to foodwebs in the Bay and Delta.

Spatial and temporal changes at tributary and distributary sites in the Cache/Yolo Slough Complex

Introduction.

This section provides a brief evaluation of the importance of Cache/Yolo Slough Complex (CYSC) tributaries and distributaries as sources and sinks of nutrients and sources of organic matter to Rio Vista and sites downstream. The site locations and site names are shown on maps Figure 5.2.57 and Figure 5.2.4, respectively), and the site names, river mile numbers, latitudes, and longitudes are shown in Table 5.1.4

To help with this evaluation, this section (1) compares the average chemical and isotopic compositions for sites on 4 Cache/Yolo Slough tributaries that drain into the CYSC, with the average compositions at nearby upstream and downstream Sacramento River sites; (2) compares the average monthly chemical and isotopic compositions for the 4 tributary sites; and (3) compares the average monthly chemical and isotopic compositions for 2 distributary sites, Miner and Steamboat Sloughs, with average compositions at Isleton and Rio Vista. Our original goal of using mass balance calculations in this report to evaluate how nutrients from the upper Sacramento River are transformed in the Cache/Yolo Slough Complex to produce the chemical and isotopic compositions observed at Rio Vista, was postponed for lack of time and resources.

Figures 5.2.58-5.2.68 are transect box plots showing the EC, water $\delta^{18}\text{O}$, $[\text{NH}_4]$, $[\text{NO}_3 + \text{NO}_2]$, $[\text{NO}_2]$, $\text{NH}_4\ \delta^{15}\text{N}$, $\text{NO}_3\ \delta^{15}\text{N}$ and $\delta^{18}\text{O}$, and [chlorophyll-a] for 13 sites arranged in downstream order (relative to SRWTP) from Hood to Isleton, the 4 tributary sites, and from Rio Vista to Chipps Island. The addition of the data from upstream and downstream mainstem sites to the transect plots of the tributaries makes it

easier to compare: (1) how the Sacramento River water evolves downstream of SRWTP, from Hood to Isleton (RM17); (2) how Sacramento River water derived from Isleton (and the two distributaries) continues to evolve while the water is being tidally mixed with tributary water to produce the water sampled at the 4 tributary sites; (3) how all these various water sources to Cache Slough continue to mix and evolve to produce the water sampled at Rio Vista; and, (4) how the water at Rio Vista (RM12) continues to evolve downstream to the compositions observed at Chipps Island (RM-4).

Like the mainstem sites, the tributaries are organized in order of river mile on the transect plots. However, the order of the tributaries is based on the river miles downstream of SRWTP via Miner Slough since this is the shortest and probably fastest flowpath from SRWTP on the mainstem Sacramento River to the tributary sites. These RM values (relative to SRWTP) for these and other sites are shown in Table 5.2.4. In terms of RM relative to SRWTP, the 4 sites are located at 36.6 (DWSC), 38.0 (Liberty), 40.1 (Lindsey), and 44.9 (Toe). Therefore, the DWSC site is positioned immediately “downstream” of Isleton and the Toe Drain (Toe) site is positioned just “upstream” of Rio Vista on these plots.

Although the ordering of the sites on the plots does reflect increases in distances along the direct path of water flowing from SRWTP via Miner Slough to the mouth of Miner Slough (~24 miles) sites, the water then is subject to considerable tidal mixing before it gets to the closest of the tributary sites, DWSC at RM36.6 relative to SRWTP. And the waters that reach the further “downstream” sites have experienced more mixing and longer travel times (e.g., Toe at RM44.9). Hence, while the 4 tributary sites are presented in these transects plots as though they were typical transect sites, the temporal and spatial relations among samples collected from the tributary sites are necessarily different from relations for samples collected from sites along the mainstem river channel. Therefore, since the use of the word “downstream” for trends among tributary sites is different from the typical usage at mainstem sites, when locations and trends for the tributary sites are compared in terms of “upstream” and “downstream”, these words will be put in quotes.

Due to tidal influences, most of the water at the tributary sites is Sacramento River water (which includes the Sacramento River water derived from the distributaries), with the proportion of water from “Yolo + Ag” sources <30% of the total water. However, for the collection dates of the tributary samples discussed here, the proportion of “Yolo + Ag” water was usually <10% of the water at the tributary sites (DSM2 information from M. Guerin). The two “upstream” tributaries (DWSC and Liberty) provide most of the “Yolo + Ag” flow from the CYSC, according to DSM2 model; the relative proportions of net flow from the 4 tributaries are 29% DWSC, 69% Liberty, and 2% Lindsey (DSM2 and net flow data from M. Guerin). There is essentially no net flow from the most “downstream” site, Toe Drain.

Figures 5.2.69-5.2.72 are box plots showing monthly compositions at the 4 tributary sites in Cache/Yolo Slough Complex (CYSC): Cache Slough @ DWSC, Liberty Island, Lindsey Slough, and Toe Drain @ Dredger, and Figures 5.2.55 and 5.2.56 show the compositions at Miner and Steamboat Sloughs. Figure 5.2.53 compares the monthly trends of $[\text{NO}_3]$ and $[\text{NH}_4]$ at the 4 tributary sites, and Figure 5.2.54 compares the monthly trends of $[\text{NO}_3]$ and $[\text{NH}_4]$ at Miner and Steamboat Sloughs with trends at Isleton and Rio Vista.

Spatial changes in composition.

Most constituents show a major transitional in downstream trends between Isleton and Rio Vista (Figure 5.2.28). Since most (> 90%) of the water at the tributary sites is derived from the Sacramento River, there must be significant inputs of nutrients and water from the upstream parts of the tributaries and/or significant nutrient transformations in the tributaries or the wide parts of CYSC to produce the compositions observed at Rio Vista.

The average EC and water isotope values (Figures 5.2.58-5.2.60) increase from Isleton “downstream” to Toe. Hence, these conservative tracers of water sources show that the longer the flowpath from SRWTP downstream to a tributary site, the more the compositions at that site diverge from the compositions at Isleton. However, this trend is somewhat illusory. A closer look reveals that the average values at the two “upstream” sites (DWSC and Liberty) are almost identical for EC and water isotopes, the values at Lindsey significantly higher, and the values at Toe **MUCH** higher. Hence, it is arguable whether the 4 sites should be viewed as gradational in terms of the processes that change EC and water isotopes (e.g., evaporation and mixing); or should the two “upstream” sites be viewed as in one category, Toe in another category, and perhaps Lindsey as slightly gradational between the two categories.

Average EC values for Toe are similar to those of Rio Vista and Three Mile Slough (TMS \approx PO-655). However, the water isotopes show that the water at Toe is very different from the water at Rio Vista – or any of the tributary sites. The water isotope data for the tributary sites plot along a typical “evaporation line” (not shown), with higher $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values at the sites contributing less net flow, consistent with more evaporation at these sites. The much higher EC at Toe and the gradual increase in EC from DWSC to Lindsey is consistent with higher salinity produced by more evaporation, longer flowpaths, and less flushing. Our collaborative USGS-Picarro study using real-time measurements of water isotopes in the sloughs, along with real-time measurements of various constituents, shows that the simultaneous water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ measurements appear to be a useful tracer for water residence time in these marshes (Downing et al., in review).

Average nutrient concentrations at the tributary sites (Figure 5.2.61-5.2.63) are significantly different from the averages at Isleton and Rio Vista. In particular, $[\text{NH}_4]$ at all tributary sites are much lower than at Isleton or Rio Vista, and are lower than at any of the mainstem sites; hence, the environment in the CYSC is clearly a major and effective sink for NH_4 . Average $[\text{NO}_3]$ in the tributaries are significantly higher than at Isleton and slightly higher than at Rio Vista, consistent with much of the new NO_3 present at Rio Vista being derived from nitrification in the tributaries and/or in the wide parts of the CYSC.

Nutrient concentrations in the tributaries generally continue the same “downstream” trends as at upstream mainstem sites, especially for the 3 “upstream” tributary sites: DWSC, Liberty, and Lindley. As with the conservative tracers, the “downstream” trends could be viewed as gradational, or as 2 main categories with gradation sites. The $[\text{NH}_4]$ show a gradational “downstream” decrease at all 4 sites, but otherwise Toe is the outlier. For the 3 “upstream” sites, average $[\text{NO}_3]$ show a “downstream” increase and $[\text{NO}_2]$ are approximately constant. These trends are consistent with active nitrification at all these sites, with $[\text{NO}_2]$ similar to those at Rio Vista and TMS. Unlike the other sites, Toe has average $[\text{NO}_3]$ that are lower than adjacent “upstream” sites and $[\text{NO}_2]$ that are considerably lower than the other sites, perhaps indicative of less active nitrification and/or additional sinks for NO_3 at the Toe tributary.

The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3 both increase “downstream”, with slight “downstream” increases for DWSC to Lindsey and then both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ show major increases to the values at Toe. These “downstream” changes are associated with “downstream” increases in NO_3 concentrations (except for Toe) and decreases in NH_4 . These are similar to the trends in nutrient concentrations and NO_3 isotopes observed from Rio Vista to PO-2 (Figure 5.2.28), and provide good supporting evidence that nitrification is an important process affecting nutrient concentrations and isotopes in the tributaries.

The “downstream” increasing NO_3 - $\delta^{15}\text{N}$ values (Figure 5.2.65) provide a simple explanation for why the transition between “downstream” decreases and then “downstream” increases in NO_3 - $\delta^{15}\text{N}$ occurred between Isleton and Rio Vista (Figure 5.2.24): because of huge additions of new NO_3 in the CYSC. The “downstream” increases in NO_3 - $\delta^{18}\text{O}$ (Figure 5.2.66) of the tributaries parallel the “downstream” increases in water- $\delta^{18}\text{O}$ (Figure 5.2.59), showing that the nitrate at the tributary sites was primarily formed in the tributaries. If the nitrate had primarily formed in the wide and more homogeneous downstream part of the CYCS, then the nitrification of the ambient NH_4 would have resulted in NO_3 that did not show the observed strong positive correlation of NO_3 - $\delta^{18}\text{O}$ with water- $\delta^{18}\text{O}$ (Figures 5.2.69-5.2.72).

There are two big puzzles: First, why does NH_4 - $\delta^{15}\text{N}$ decrease by 4 ‰ from DWSC to Toe while $[\text{NH}_4]$ drops by about 50%? And, second, why does NH_4 - $\delta^{15}\text{N}$ decrease by 4 ‰ from DWSC to Toe while NO_3 - $\delta^{15}\text{N}$ increases by 2 ‰? Given the “downstream” decreases in $[\text{NH}_4]$, increases in $[\text{NO}_3]$, high constant $[\text{NO}_2]$, and increases in NO_3 - $\delta^{18}\text{O}$ – all consistent with nitrification – the NH_4 - $\delta^{15}\text{N}$ should have increased “downstream”, as was seen at the mainstem sites from Hood to about PO-13 in San Pablo Bay. While the NH_4 - $\delta^{15}\text{N}$ is sometimes anomalously low and the NO_3 - $\delta^{15}\text{N}$ anomalously high at Toe, the other 3 tributaries have average $\delta^{15}\text{N}$ values that explain why values of NH_4 - $\delta^{15}\text{N}$ and NO_3 - $\delta^{15}\text{N}$ are higher at Rio Vista than at Isleton: significantly nitrification within the CYSC followed by mixing.

The most plausible explanation for the low NH_4 - $\delta^{15}\text{N}$ at Toe is a source of NH_4 with a very low NH_4 - $\delta^{15}\text{N}$ value. Degradation of organic matter to produce NH_4 or influxes of NH_4 from fertilizer would result NH_4 with low $\delta^{15}\text{N}$ values. But for Toe to have such low NH_4 - $\delta^{15}\text{N}$ values and low NH_4 concentrations suggests that perhaps there needs to be an additional sink for NH_4 in the tributary. The extremely high chlorophyll concentration at Toe provides a likely explanation for part of the drop in NH_4 : algal uptake. The much higher values of NO_3 - $\delta^{15}\text{N}$ and NO_3 - $\delta^{18}\text{O}$ at the Toe site are also consistent with uptake of NO_3 ; however, they could also be explained by denitrification in the Toe tributary, which could also explain the drop in $[\text{NO}_3]$ at this site. The CYSC a very complicated part of the estuary! Further work is needed to use the isotope and chemical data to detangle the superimposed signatures of various N sources and transformational processes at these tributary sites.

Chlorophyll-a concentrations (Figure 5.2.67) for all 4 sites were higher than at most mainstem sites, with the 2 downstream sites having higher values than anywhere else. The chlorophyll ratios (Figure 5.2.68) of the tributary sites were also higher than at most mainstem sites. Hence, the data clearly show that the CYSC is a hot spot for algal growth as well as a hot spot for NH_4 loss and NO_3 production.

Temporal changes in composition.

In brief, temporal trends in the monthly averages of most constituents at the 4 tributary sites (Figures 5.2.69-5.2.72) are very similar, which is reasonable since most of the water at these sites is derived from

the Sacramento River (mainstem and distributaries). The frequency and magnitude of temporal oscillations in composition are similar to those seen at mainstem Sacramento River sites. Given the degree of oscillations, any mass balance calculations of the contributions of water and solutes from these sites to Rio Vista would need to be “date-matched.” Paired T-tests show that almost all measured constituents have statistically significant differences between the tributaries and Isleton (Kendall et al., 2015), making it possible to estimate the relative proportions of constituents from these sources to Rio Vista for all dates when we have samples; this is progress.

The similarity of the temporal trends of $[\text{NO}_3]$ and of $[\text{NH}_4]$ for the 4 sites is particularly striking (Figure 5.2.53). The seasonal trends are so nearly identical that it seems very possible that the estimated deviations from some idealized seasonal trend in the bulk water moving up and down the tributaries during the daily tidal cycles, perhaps with a different mix of processes during inward and outgoing tides, could be validly interpreted as additions and losses of constituents during the tidal flushing combined with minor net flow from the tributaries, not just as analytical or environmental noise. The main difference in temporal trends on Figure 5.2.53 is that the “persistent June NO_3 peak” observed at most mainstem sites in June, occurs in May at the tributary sites, and is very asymmetric for unknown reasons. Given the downstream persistence of NO_3 and NH_4 trends at sites upstream of SRWTP at mainstem sites miles downstream of Hood, how much of the temporal trends at the tributary sites might be due to temporal variations in the upstream water sources to the tributaries.

The nutrient isotopes for the different tributary sites also show similar temporal trends (Figures 5.2.69-5.2.72, 5.2.53), even though the averages at different sites show strong “downstream” trends (Figures 5.2.64-5.2.66). As discussed above, the NO_3 - $\delta^{18}\text{O}$ values provide convincing evidence that most of the nitrification occurs in the tributaries and not in the better-mixed, wide part of the Slough. There may be seasonality in the amount of nitrification and a seasonal component to the main location of nitrification, both of which might be determined by mass balance calculations using isotope and nutrient data, along with published or empirically derived isotope fractionation factors. Whether temporal oscillations are in phase (e.g., NO_3 - $\delta^{15}\text{N}$ and NO_3 - $\delta^{18}\text{O}$ at Toe) or not (e.g., $[\text{NO}_3]$ and NO_3 - $\delta^{18}\text{O}$ at DWSC) for different constituents provides powerful support for interpretations of mixing of sources vs nitrification, uptake, or denitrification.

There is a huge seasonal range in NH_4 - $\delta^{15}\text{N}$ at tributary sites in the Cache/Yolo Slough Complex, with ranges larger than observed at either Isleton or Rio Vista (Figure 5.2.2). The larger range of values at the tributary (slough) sites than mainstem sites reflects the different combinations of processes and sources at the different tributary sites. For example, the anomalously low NH_4 - $\delta^{15}\text{N}$ values for slough samples on Figure 5.2.2 are mostly from the Toe site where there appears to be a local source of NH_4 with a very low $\delta^{15}\text{N}$. While there is also a large range of NO_3 - $\delta^{15}\text{N}$ values at various the tributary sites (Figure 5.2.2), the NO_3 - $\delta^{15}\text{N}$ values of slough samples are generally higher than at either Isleton or Rio Vista. This is consistent with nitrification of NH_4 derived primarily from SRWTP effluent being the dominant source of new NO_3 at the tributary sites. If nitrification of the NH_4 from the local NH_4 source at or near Toe had been a significant source of new NO_3 , there would probably have been anomalously low NO_3 - $\delta^{15}\text{N}$ values.

The two major distributaries of the Sacramento River, Miner and Steamboat Sloughs have chemical and isotopic compositions with no statistically significant differences between them and the Sacramento River

at Isleton for almost all of the chemical and isotopic parameters measured (11 out of 15), and only barely statistically significant differences for the other four parameters (Kendall et al., 2015). This finding vastly simplifies the use of isotope and chemical data for mass balance calculations in this area.

The seasonal trends of all constituents at the sites near the mouths of Miner and Steamboat Sloughs (Figures 5.2.46 and 5.2.47) are very similar. Comparison of the $[\text{NO}_3]$ and $[\text{NH}_4]$ trends of these sloughs with the compositions at Isleton and Rio Vista (Figure 5.2.54) shows that magnitude and timing of oscillations at the slough sites more closely match those at Isleton than at Rio Vista. The $[\text{NO}_3]$ trends among the sites are much more similar than the $[\text{NH}_4]$ trends. Some of the lack of correspondence between these sites is probably caused by the much smaller dataset at the slough sites than at Isleton, which in turn has a smaller dataset than at Rio Vista.

The 4 tributary sites have $[\text{NO}_3]$ and $[\text{NH}_4]$ trends (Figure 5.2.53) that are more similar to those of the Miner and Steamboat Sloughs than Isleton or Rio Vista, with a better correspondence of the $[\text{NO}_3]$ trends, including the very prominent June $[\text{NO}_3]$ peaks of the slough sites. The poorer correspondence of the timing and magnitude of oscillations in $[\text{NH}_4]$ between the Cache/Yolo Slough Complex sites and those at Rio Vista, compared to the good correspondence of $[\text{NO}_3]$, might indicate additional NH_4 processing (i.e., uptake) in the wide parts of the Complex, after water parcels left the tributary and distributary sites and before the mixtures arrived at Rio Vista.

5.2.5 Conclusions and Recommendations

Appendix 5.2 provides a basic description and preliminary interpretation of the temporal and spatial variations in nutrients, nutrient isotopes, and a few other constituents in the SR etc – with the interpretations used to formulate hypothesis about causes of seasonal and spatial patterns. Formulating hypotheses based on qualitative descriptions of patterns is a necessary prerequisite for deciding how to test hypotheses with mass balance and isotope fractionation models -- to determine how much of the variation in time and space is due to mixing and how much to nitrification or other N transforming reactions.

Major findings

The description of the temporal variations at 23 sites and the spatial variations at 29 sites from Tower Bridge to Angel Island – and the simple qualitative interpretations of the data – revealed:

- hot spots of N inputs and transformations, some previously unsuspected, throughout the estuary.
- in some places, isotopes plus nutrient chemistry allowed us to determine whether nitrification is mainly occurring in adjacent marshes vs in the main river channel, or whether nutrient inputs were probably a distributed source vs a point source.
- most of the nitrification in the Cache/Yolo Slough Complex occurs in the tributaries, not in the wider parts of the Complex.
- temporal variation in effluent-derived NH_4 leaves a characteristic and persistent temporal “signature” which can be traced >40 miles down the estuary.

- the downstream persistence of the temporal oscillations in $[\text{NH}_4]$ derived from effluent provides the possibility of quantifying the downstream decreases (and sometimes increases) in magnitude of the successive oscillations in terms of temporal and spatial changes in nitrification and new sources.
- there are also persistent downstream temporal patterns of NO_3 , EC, and water isotopes – all derived from major inputs of water -- that can be used to identify new inputs and changes in downstream sites.
- several sites show seasonality in apparent nitrification rates.
- dozens of hypotheses about nutrient sources and biogeochemical processes generated in this report can be tested quantitatively with the existing data.
- the strong seasonality in most constituents provides justification for doing calculations for date-matched samples and not for monthly or yearly averages.
- the usefulness of the isotope data for detecting (and hopefully quantifying) processes using the isotopic compositions even when the changes in concentrations are ambiguous -- because the isotopic compositions are usually more robust tracers of processes and source inputs than concentrations.
- the development of what appear to be zones of steady-state mixing with marine water and removal of new nitrate, which allows additional mass balance equations to be written and thus more unknowns calculated.

Locations of hot spots.

The discussion in the above sections of Appendix 5.2 identifies and discusses the locations and characteristics of several kinds of “hot spots” in the SFE. These kinds of hot spots include entry points of new water and new nutrient sources to the estuary, and the locations of different kinds of biogeochemical processes (e.g., nitrification, denitrification, uptake). The main findings are summarized below:

Upstream watershed sources. The waters upstream of SRWTP have some distinctive chemical and isotopic attributes, making these constituents useful tracers of a specific type or source of water that enters the estuary upstream of SRWTP. Thus, the entry point of this watershed water could be viewed as a point source or “hot spot” of different water. Parker et al. (2010, 2012) and Foe et al. (2010) observed that chlorophyll-a concentrations upstream of SRWTP at Garcia Bend were usually higher than downstream of SRWTP, and the chlorophyll ratios were higher there too. Their data also showed significant concentrations of NO_2 at upstream sites. The NO_2 and chlorophyll data suggest appreciable active nitrification and uptake is occurring either in the river upstream of SRWTP or nearby.

Where is this NH_4 coming from? The temporal variations of NO_3 derived from upstream of SRWTP, perhaps augmented by new water inputs from Cache Slough and elsewhere, imparted a characteristic and persistent temporal “signature” which can be followed and traced ~ 40 miles down the estuary as the patterns are blurred or reduced/augmented or changed by additions of new NO_3 by nitrification or inputs of NO_3 from waterways. This persistent signature provides an opportunity to use the chemical and isotopic data to quantify additions of new nitrate produced by nitrification.

Hood. Temporal variation in effluent-derived NH_4 establishes a characteristic temporal “signature” which can be followed and traced > 40 miles down the estuary, including Miner and Steamboat Sloughs and the main tributaries in the Cache/Yolo Slough Complex. This persistent signature provides an opportunity to use the chemical and isotopic data to interpret and quantify the downstream decreases in magnitude of the successive oscillations in terms of temporal and spatial changes in new sources and/or biogeochemical processes.

Cache/Yolo Slough Complex. There is an approximate doubling of the flow between Isleton (RM17) and Rio Vista (RM12) because Miner and Steamboat Sloughs (actually distributaries) empty into Cache/Yolo Slough, which then merges with the mainstem at about RM14. Many important transitions in the downstream trends of chemical and isotopic compositions occur between Isleton and Rio Vista; the most prominent transitions (inversion points) reflect abrupt increases in $[\text{NO}_3]$, $[\text{NO}_2]$, $\text{NO}_3\text{-}\delta^{15}\text{N}$, and chlorophyll-a. For nutrients, the changes reflect the transition between the rapid downstream increases in $[\text{NO}_3]$ and $[\text{NO}_2]$ and the corresponding rapid decreases in $[\text{NH}_4]$ due to nitrification – to a region starting at Rio Vista where the compositions showed less downstream change. Between Isleton and Rio Vista, the average $[\text{NO}_3]$ increased by about 5 μM because of intensive nitrification.

The $\text{NO}_3\text{-}\delta^{18}\text{O}$ values indicate that the new nitrate was formed in an environment with higher water- $\delta^{18}\text{O}$ than present at either Isleton or Rio Vista. Since the average water- $\delta^{18}\text{O}$ of tributary sites in Cache Slough is 1-3 ‰ higher than the water- $\delta^{18}\text{O}$ values at Isleton and Rio Vista, this is a likely production area for most of the new nitrate. The strong correlations between water- $\delta^{18}\text{O}$ and $\text{NO}_3\text{-}\delta^{18}\text{O}$ values at the 4 sites, with the water and NO_3 at each tributary having distinctive ranges of $\delta^{18}\text{O}$ values, is fairly conclusive evidence for most of the nitrification occurring in these tributaries, not in the wide part of Cache Slough. The sloughs are not a source of NH_4 to the downstream Sacramento River. Instead, upstream and tributary sources of NH_4 to Cache Slough are nitrified and converted to algae here, and the new NO_3 and algae are transported to downstream sites. Hence, various sites in the Cache/Yolo Slough Complex are “hot spots” for of algal growth, a local NH_4 source, NH_4 sinks, NO_3 production, and perhaps denitrification.

Three Mile Slough. Comparison of the seasonal trends in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate, combined with $[\text{NO}_2]$ and $[\text{NO}_3]$ higher than at adjacent sites provide strong evidence for nitrification being the main cause of temporal variation.

SJR Confluence. There is a slight dip in $\text{NH}_4\text{-}\delta^{15}\text{N}$ at PO-649 (Point Sacramento), near where the San Joaquin River converges with the Sacramento River. At this same site, NH_4 concentrations are slightly higher than at adjacent sites. These data could mean a small local point source of NH_4 with a much lower $\delta^{15}\text{N}$ than the riverine NH_4 . Alternatively, this NH_4 might come from the San Joaquin River -- which is actually composed mostly of Sacramento River water (see Appendix 5.3) -- but may have gained some additional NH_4 from local sources prior to reaching the confluence.

Suisun Bay. The most plausible explanation for the decreasing $\text{NO}_3\text{-}\delta^{15}\text{N}$ values in this region (and the other nutrient and isotope trends described above) is that most of the new NO_3 was formed by nitrification of a local NH_4 source that took place elsewhere in Suisun Bay, perhaps in the shallow marshes, NOT in the main channel. The local NH_4 source must have originally had a much lower $\delta^{15}\text{N}$ than riverine NH_4 , resulting in new NO_3 produced by local nitrification with a significantly lower $\delta^{15}\text{N}$ than the riverine NO_3 .

Martinez channel and San Pablo Bay. Average chlorophyll-a concentrations from PO-10 downstream to PO-15 are higher than anywhere else at mainstem sites, and that the algae here is “fresher” (i.e., has a higher average ratio of chlorophyll-a to total chlorophyll) than elsewhere. Hence, the algae clearly is actively growing here. It is interesting that $[\text{NO}_2]$ and $[\text{NH}_4]$ appear to be approximately constant in this region -- whereas $[\text{NO}_3]$, like EC, shows a steady decline due to mixing with marine sources of water. One plausible explanation for these observations is that there are many small local sources of NH_4 and sites of local partial nitrification to NO_2 in this region, that continuously mix into the river water column faster than these constituents can be tidally homogenized into the normal downstream mixing gradient. EC and water isotope values at the southern end of San Pablo Bay are significantly lower than at upstream sites, suggesting a significant point source of fresh water into this narrow channel location, which is poorly mixed with water at adjacent downstream sites.

Central Bay. Average chlorophyll-a concentrations from PO-15 (Point San Pablo) downstream to PO-18 (Angel Island) are higher than any other mainstem sites except in San Pablo Bay; the algae appears to be growing *in situ*. EC and water isotopes indicate a significant local source of fresh water to the northern end of the Central Bay. The slightly elevated but steady $[\text{NH}_4]$ and the decreasing $\text{NH}_4\text{-}\delta^{15}\text{N}$ at sites downstream of PO-13 probably reflects a distributed local NH_4 source, perhaps in local marshes, as was observed in Suisun Bay – not associated with the point source of fresh water. These are the only sites in the estuary where $\text{NH}_4\text{-}\delta^{15}\text{N}$ decreases downstream, and this can only happen when there are significant inputs of local NH_4 with a significantly lower $\delta^{15}\text{N}$ than the riverine NH_4 . The associated simultaneous increases in $\text{NO}_3\text{-}\delta^{15}\text{N}$ and $\text{NO}_3\text{-}\delta^{18}\text{O}$ with decreasing $[\text{NO}_3]$ could be caused by denitrification as the waters are tidally flushed through reducing marsh environments around the margins of the Bay.

Seasonality in nitrification.

The isotope and chemical data from several locations suggested seasonality in the extent of nitrification. Although $[\text{NO}_2]$ are not available at all sites, plotting the monthly average values at sites would be a useful addition to the sets of monthly box plots. Temporal variation in effluent-derived NH_4 leaves a characteristic temporal “signature” which can be tracked >40 miles down the estuary. The persistence of the temporal trends suggest the possibility of estimating seasonality in the extent of nitrification by comparing the downstream changes in $[\text{NH}_4]$ and $\text{NH}_4\text{-}\delta^{15}\text{N}$ of traceable oscillations at successive sites.

Two small dips in the monthly $[\text{NH}_4]$ at Hood are approximately correlated with increases in $\text{NH}_4\text{-}\delta^{15}\text{N}$, consistent with nitrification; and the 2 low $\text{NO}_3\text{-}\delta^{15}\text{N}$ values at closely matching dates are also consistent with nitrification being responsible for the dips in $\text{NO}_3\text{-}\delta^{15}\text{N}$ at these dates. Hence, these data provide reliable information about seasonal changes in nitrification at Hood. For other dates, the combination of isotope and nutrient data preclude nitrification from being the main causes of variations.

Rio Vista shows the greatest temporal variability in $[\text{NO}_2]$ of any of our sites, suggesting that this site – or, more likely, the zone between Isleton and Rio Vista which includes where the Cache/Yolo Slough converges with the Sacramento River -- may have the highest seasonal range in local nitrification of any transect sites. Given the much lower $[\text{NO}_2]$ concentrations at Rio Vista in July-September 2009 and good correlations of downstream trends and relations among other constituents during the summer, it appears that there is less nitrification in the summer (July-September) than at other seasons at Rio Vista.

The presence and amount of nitrification between any two sites, at any date, leave distinctive and interpretable changes in the concentrations of NH_4 , NO_3 , and NO_2 – and in the NH_4 - $\delta^{15}\text{N}$, NO_3 - $\delta^{15}\text{N}$, and NO_3 - $\delta^{18}\text{O}$ values. The relations among these constituents are also defined by isotope fractionation equations. Isotopic data provide additional equations (and sometimes more than 1 equation per constituent) because of theoretical relations that affect how isotopes change during processes.

Other research groups have attempted to quantify nitrification rates using various different approaches including bottle incubations, mesocosm incubations, and changes in concentrations along fixed lengths of the river. These approaches often yield estimates that differ up to an order of magnitude. Rate estimates using concentrations, isotopes, and travel times derived from DSM2-QUAL provide another independent approach for calculating nitrification rates, and only require in-situ measurements without altering the system like incubation experiments. Hence, in many situations the solution of simple isotope and chemical mass balance equations will provide unique solutions, or ranges of solutions with small enough uncertainty values, for comparing estimates for different months.

Comments on IEP sites discussed in this appendix

C3. The IEP site C3 site at Hood, located at about RM38, is no longer active. It has been replaced by site C3A, located near RM44. Unfortunately, DIN is being reported at C3A instead of the separate measurements of NO_3 and NH_4 concentrations previously reported at C3. The lack of separate measurements of $[\text{NO}_3]$ and $[\text{NH}_4]$ makes the data potentially much less usable (and possibly unusable) for tracing the seasonal oscillations in effluent-derived nutrients downstream through the estuary. However, we did not actually compare the seasonal trends of data from C3 versus C3A. We only have isotope and chemical data from transect sites near both the C3 and the C3A sites for samples from the Dugdale cruises in March and April 2009 (Kendall et al., 2015).

We find that the historic monthly trends in $[\text{NO}_3]$ and $[\text{NH}_4]$ at C3 are similar enough to those seen at our transect data at Hood for us to extrapolate our interpretations of the chemical and isotope data at Hood to the longer record at the C3 site. The transect data at Hood is especially useful for establishing the upstream seasonal variations in effluent-derived $[\text{NH}_4]$ and NH_4 - $\delta^{15}\text{N}$, and the seasonal variations in upstream $[\text{NO}_3]$ and NO_3 - $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, water- $\delta^{18}\text{O}$ and $\delta^2\text{H}$, and other chemical and isotopic signatures of upstream and effluent-derived sources. The seasonal oscillations in $[\text{NH}_4]$ at Hood provide a tracer of effluent-derived NH_4 that can be traced downstream of RM0, down Miner and Steamboat Sloughs, and at most of the tributary sites in Cache Slough.

The isotopic data at Hood provides considerable information about NH_4 and NO_3 sources and N transformations that could not have been determined with chemical data alone. For example, the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of NO_3 at Hood suggest that the relatively smooth seasonal variation in $[\text{NO}_3]$ at C3 camouflage a much more complicated story of seasonality in different sources of NO_3 to the site. The large and small oscillations in EC and water- $\delta^{18}\text{O}$ are better indicators of different sources of water (and nitrate) to the site than the smooth gradational changes in $[\text{NO}_3]$. Some of these oscillations in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3 could be explained by nitrification adding new nitrate of variable $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ that mixes with old nitrate, but most of the oscillations are more likely due to differences in NO_3 sources from upstream sources. All of the $[\text{NH}_4]$ data for C3 are higher than at upstream sites. Hence, most of the NH_4 and most of the seasonal oscillations in $[\text{NH}_4]$ at C3 are probably due to seasonality in amounts of effluent NH_4 in the river.

D4. The IEP site D4 is located between PO-649 and PO-2, close to the confluence of the San Joaquin River with the Sacramento River. This site is located in an area of the Delta where all the non-conservative constituents except NO_3 - $\delta^{15}\text{N}$ show approximately constant compositions in this region, and hence the site is a useful monitoring site for the region. Historic monthly trends in $[\text{NO}_3]$ and $[\text{NH}_4]$ at D4 are probably similar enough to those seen at the transect data at PO-649 and PO-2 for us to apply our interpretations of the chemical and isotope data at these sites to explain the seasonal trends in the longer record at the D4 site.

The isotopic data at sites near D4 provide considerable information about NH_4 and NO_3 sources and N transformations that could not have been determined with chemical data alone. Samples from Rio Vista and D4 would be adequate to assess how $\delta^{15}\text{N}$ changes downstream due to nitrification. The conservative constituents (EC, water- $\delta^{18}\text{O}$, and water- $\delta^2\text{H}$) show steadily increasing values downstream in this region, but the trend lines would be easily estimated from data at D4 plus the recommended site at Rio Vista.

D8, D7, and D6. The IEP sites D8 and D6 located in the shipping channel upstream and downstream (respectively) of where the channel widens into the Suisun marshes, and D7 is located to the north of the channel where the Bay is wider. Therefore, the significant changes in many constituents near Suisun Bay were adequately monitored by the existing IEP sites in this region. The historic nutrient compositions observed at the D7 site are not significantly different from the compositions observed at D8 or D6, nor are they significantly different from the chemical compositions at nearby USGS Polaris sites. Hence, historic trends in $[\text{NO}_3]$ and $[\text{NH}_4]$ at the 3 IEP sites are sufficiently similar to the trends at nearby transect sites for us to apply our interpretations of the chemical and isotope data at these sites to explain the seasonal trends in the longer records at the IEP sites. Given the similarity in trends at the 3 IEP sites, it is not clear that all 3 of these sites are needed to assess the contributions of Suisun marshes to Delta chemistry. The isotope and chemical data at sites near the IEP sites provide considerable information about NH_4 and NO_3 sources and N transformations that could not have been determined with chemical data alone.

Recommendations for the IEP monitoring program

Are the IEP monitoring sites located appropriately to monitor the important transitions between regions discussed above? Yes, but additional sites are needed – as discussed below. Are the measurements needed to evaluate seasonal and spatial changes in N sources and transformations at these sites being performed on the discrete samples collected? Probably not since DIN is being substituted for separate measurements of NO_3 and NH_4 at the sites – as discussed below.

Based on our evaluation above of the benefits of different measurements (especially when supplemented with nutrient isotope data), critical sites should continue to have measurements of NH_4 and NO_3 concentrations, not just DIN. With just DIN data, movement between different N species cannot be determined, and the movement of N from NH_4 to NO_3 , from hot spots of N into the main channel, and from different sources of N into algae cannot be adequately assessed. Also, existing research suggests that ratios of N species may be important for favoring either desirable phytoplankton species or Harmful Algal Blooms. Therefore, the relative distributions of the N species is probably much more important than total DIN to the health of the ecosystem. In a recent paper (Lehman et al., 2015), we showed that nutrient concentrations, combined with the $\delta^{15}\text{N}$ of nutrients and *Microcystis* allowed us to prove that the N being assimilated by the HABs was NH_4 , not NO_3 , and that the NH_4 was from SRWTP, not wetlands or SJR sources.

If funding permits, it would be beneficial to include the measurement of NO_2 concentrations since it provides extremely useful information about sites of active nitrification and the seasonality of nitrification; the lack of such data at many of our sites and dates hindered our present qualitative interpretation of seasonality in nitrification rates. Alternatively, coordinate efforts with the USGS to use the nutrient data from adjacent USGS sites as part of the IEP monitoring program.

Another recommendation is for the IEP program to consider whether they would like to have the kind of interpretation that we generated in this report (and in Kendall et al., 2015) using our nutrient and water isotope data, focused on IEP sites. If so, the program might want to consider piggybacking the collection of suitable isotope samples onto their monitoring program. It takes very little effort to collect 2-3 additional liters of water, and then process the samples for archiving for possible future isotope analysis. For example, the SWC provided the funding for us to piggyback on Chris Foe's NH_4 Monitoring Program in 2009-2010, and then to process and archive the isotope samples for possible future isotope analysis. We then wrote a successful research proposal to the IEP, and a year later we had funding for the analyses and data interpretation that ultimately resulted in Kendall et al. (2015) and much of the interpretation included in this report. Isotope techniques have become an important part of many types of water quality and ecological monitoring programs worldwide (Kendall et al., 2010) because isotopes almost always provide “big bang for the bucks”.

Justification for a site at Isleton. The statistical analysis of ~ 2 years of ~ monthly chemical and isotopic data from Isleton and from near the mouths of the two main Sacramento River distributaries, Miner Slough and Steamboat Sloughs -- that combined carry flows equivalent to that at Isleton -- show no significant differences between these 3 distributaries (Kendall et al., 2015). Hence, Isleton is a suitable site for providing temporal data on the total flow of the Sacramento River. This finding provides support that chemical and isotopic data from Isleton can be used as a substitute for having additional data on the temporal and spatial variation in waters flowing down Miner and Steamboat Sloughs into the Cache/Yolo Slough Complex. Therefore, data from Isleton can be reliably used, combined with data from Rio Vista (or an adjacent site), to estimate transformations of nutrients and organics in Cache Slough.

However, Hood is **not** a suitable endmember for such nutrient transformation calculations because of the significant downstream changes in $[\text{NO}_3]$, $\text{NH}_4\text{-}\delta^{15}\text{N}$, $\text{NO}_3\text{-}\delta^{15}\text{N}$, and $\text{NO}_3\text{-}\delta^{18}\text{O}$ between Hood and Isleton discussed above, that are indicative of extensive nitrification. C3A would be an even less suitable site than Hood because of the lack of $[\text{NH}_4]$ and $[\text{NO}_3]$ data and the further distance from Isleton (meaning that the chemistry at C3A would be less evolved than at C3 and hence less similar to Isleton). Therefore, if managers are interested in quantifying N transformations, algae growth, and additional agricultural sources of nutrients in the Cache/Yolo Slough Complex, an additional IEP monitoring site at Isleton seems warranted. Walnut Grove is also not a good candidate for a monitoring site intended for sampling at or before ebb tide because samples collected there often have anomalously low $[\text{NH}_4]$, suggesting that the water parcel sampled there contains a tidally biased reduced fraction of effluent (Kendall et al., 2015).

Justification for a site at or near Rio Vista. IEP had a monitoring site at D24 near Rio Vista, but it is currently inactive. The seasonal trends in the data for this historic site were not compared with the seasonal trends at the Rio Vista transect site (PO-657). Therefore, it is not known if the two nearby sites (D24 and PO-657) had similar trends and, hence, whether the chemical and isotopic data from PO-657

could be used to interpret the trends at D24. This would be a first step if IEP wanted to consider activating D24.

The next downstream active IEP site is D22, which appears to be located near the mouth of Three Mile Slough and thus near to 3 of our transect sites (e.g., USGS 653; and Three Mile Slough (TMS) and USGS 655 – whose data were combined on plots). Based on the evaluation of seasonal and spatial data at PO-657 and the combined data for these 3 sites, USGS 655 and Rio Vista appear to have sufficiently similar seasonal trends in $[\text{NO}_3]$, $[\text{NH}_4]$, and most other constituents that the chemical and isotopic data from either of these sites could probably be used to interpret historic seasonal trends at D22. However, the TMS site (labeled PO-655) is a minor nitrification hot spot, with the highest $[\text{NO}_3]$ of any site in 2009-2010 and seasonal $\text{NO}_3\text{-}\delta^{15}\text{N}$ trends that show little resemblance to the trends seen at the adjacent sites. Therefore, the chemical and isotopic signatures at PO-655 combine local nitrification with the signature of more intense nitrification in the Cache/Yolo Slough Complex, which makes this location less than ideal as an integrator of the effects of water from the Complex. Hence, historic data from D24 and more recent data from D22 would need to be evaluated to assess whether D22 is far enough from Three Mile Slough to be an adequate substitution for the alternative of re-activating the Rio Vista site at D24.

Justification for tributary sites in the Cache/Yolo Slough Complex. The IEP sites available for the mass balance models are inadequate to characterize all the main sources of chemical and isotopic variability in the Delta. In specific: the contributions and sinks of nutrients, and the contributions of algae, from the Cache/Yolo tributaries need to be included in the model. This can be addressed by (1) using data from any IEP (or other) sites near the Cache Slough @ DWSC and Liberty Island sites (which together account for ~97% of the flow from the Cache/Yolo tributaries, according to DSM2-derived estimates by Marianne Guerin), and/or by (2) comparing the nutrient and organic loads between Isleton and Rio Vista and using this as the integrated composition of the Cache/Yolo tributaries. But probably the best and easiest solution is to add a site near Isleton and to reactivate the old site near Rio Vista (D24), measure $[\text{NH}_4]$ and $[\text{NO}_3]$ – and other constituents at both sites (possibly including isotopes) -- and calculate the impacts of the tributaries in Cache Slough by differences between date-matched samples (i.e., $\text{RV} - (\text{ISL} * 2) \approx \text{CS}$)

Justification for fewer sites at Suisun. Given the similarity in the seasonal trends at the 3 sites (as discussed above, maybe there is not a need for monthly $[\text{NH}_4]$ and $[\text{NO}_3]$ at all 3 sites in Suisun.

Justification for site or sites downstream of Martinez (PO-8). There are several IEP sites downstream of the many transitions that occur downstream of PO-10 (Crockett): sites D41 and D41A are active and D42 is currently inactive. Crockett is the downstream end of the zone in San Pablo Bay with the highest chlorophyll-a concentration in the mainstem Sacramento River, Delta, and northern Bay. If managers are interested in the local nutrient sources and their possible relationship to the higher chlorophyll levels in the section from Crockett downstream to Angel Island, addition of one or more monitoring sites at PO-10 or PO-11, at PO-14 or PO-15, and perhaps at PO-17 would provide adequate coverage for the different regions. Given the possibility of additional local sources of NH_4 and NO_3 with unusual but informative isotopic compositions in this part of the estuary, and/or the possibly a local environment providing a significant sink for N, having data at an additional site or two seems warranted.

One idea is to have one or two of the existing IEP monitoring sites in this part of the estuary measure $[\text{NH}_4]$ and $[\text{NO}_3]$ monthly -- instead of just DIN -- for a few years to determine if just DIN data provide

sufficient information compared to what can be deduced with the separate nutrient concentrations. Of course, the USGS Polaris program already has sites in these locations and has been monitoring nutrients and other constituents at these sites approximately monthly since the 1970s, although some of these sites are not as intensively monitored these days because of limited funding. Can these USGS data be integrated with data from the IEP monitoring program?

Potential future work

Compare the seasonal trends in historic data from the inactive IEP site D24 near Rio Vista with USGS data from PO-657, to see if the seasonal trends at D24 are similar to the trends at PO-657. If the trends are similar, this provides a justification for using the chemical and isotopic data from PO-657 to interpret the trends at D24, as we did at other sites. And this evaluation would provide support for D4 being reactivated for the better assessment of the impacts of transformations in the Cache/Yolo Slough Complex on nutrients and the production of algae supporting local foodwebs.

More attention needs to be focused on year-specific seasonality of constituents, not just the monthly trends averaged over several years to a decade. Do the monthly average plots and statistics bias our perspectives about suitable opportunities to test hypotheses with year-specific samples? It might be useful to take the USGS Polaris and IEP chemical data, and the isotope data available for several years at Polaris sites, for separate years and compare the downstream and monthly patterns. Perhaps this exercise would be useful for generating suitable testable hypotheses about causes of the seasonal and spatial trends for specific years that were not apparent in monthly data averaged over many years.

The USGS Polaris program already has sites in many of the locations where new sites (or reactivation of old sites or different measurements at existing sites) are recommended. The USGS has been monitoring these sites approximately monthly since the 1970s, although some of these sites are not as intensively monitored these days because of limited funding. Can these USGS data be better integrated with data from the IEP monitoring program?

The strong downstream patterns in the chemical and isotopic compositions discussed above provide many opportunities for mass balance calculations for quantifying N transformations in different sections of the Sacramento River, Delta, and northern Bay – and assessing the impacts of tidal sloshing and variations in travel times on compositions.

We have a lot of other types of isotope data from the same years discussed in this report that would benefit from being evaluated using the same kinds of monthly and transect plots, and the same kind of detailed qualitative analysis: POM-C:N, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{34}\text{S}$; DOC- $\delta^{13}\text{C}$, DIC- $\delta^{13}\text{C}$, and SO_4 - $\delta^{34}\text{S}$; a small amount of DOM-C:N, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{34}\text{S}$ data; and a lot of archived samples suitable for analysis of DOM isotopes and NH_4 - $\delta^{15}\text{N}$ (we only started routine analysis of NH_4 - $\delta^{15}\text{N}$ in 2009, and few archived samples from 2006-2008 have been subsequently analyzed for NH_4 - $\delta^{15}\text{N}$). It would be useful if we could add the evaluation of the seasonal and temporal patterns in these data to the interpretation developed in this report.

Do we have enough data to plot the spatial variations for different months or different seasons? This would provide useful information on whether some transition locations probably move up or downstream depending on temporal differences in flow and other factors. Also, the determination of transition

locations using these plots is certainly affected by the fact that the sites are plotted as though they were equi-distant.

We should replot the spatial box plots in terms of river miles since some of the transitions between regions were defined by a change in the apparent “gradient” of a downstream change in composition and the locations of these transitions may change when replotted. If they do change, we should update our plot that summarizes the transitions.

Mass balance calculations need to be “date-matched” because the seasonal variability in chemical concentrations and isotopic compositions are not always precisely in phase – probably due to tidal sloshing, non-Lagrangian sampling, and how site-specific mixing with (addition of?) a new small constituent source will affect the riverine patterns. This topic could use some further evaluation.

The recent Kendall et al. (2015) report provides “proof of concept” that the isotope data generated during our 2009-2011 studies could be validly used for quantitative studies quantifying nutrient and organic matter sources and biogeochemical processes in the estuary. This report presents a variety of testable hypotheses about N sources and transformations that could be tested with existing data to improve our understanding of the causes of seasonal and spatial changes in nutrient and water inputs and transformations – and perhaps to influence how the watershed is managed.

The strong seasonal trends seen in $[\text{NO}_3]$ and $[\text{NH}_4]$, and to a lesser extent [chlorophyll-a] on the IEP monthly box plots -- and probably EC if these data were included -- are not at all apparent in the ~20 year chemoscapes. This was a surprise. This might be because the latter plots did not divide the compositions into enough ranges. Alternatively, the statistics of averaging might simply be a better tool for reducing temporal noise so that patterns emerge. The problem with chemoscapes is the artificial bias imposed by the fact that simple kriging treats the data as isotropic when tides and flows cause profound spatial (up and downstream) biases. Since chemoscapes and isoscapes are becoming an increasingly popular tool for presenting large amounts of data in an easily digestible form, we need someone to develop suitable algorithms for removing the spatial bias imposed by kriging.

What is the cause of the small but persistent June peak in NO_3 concentration seen at many transect sites and IEP sites? The water at these sites in the summer, based on the low water- $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values at transect sites, appears to be largely derived from winter and/or high elevation precipitation and thus is probably snowmelt stored in reservoirs and released later in the year, for agricultural needs and/or to flood wetlands used by migratory birds. Talk to watershed managers?

These watershed-wide seasonal patterns are suggestive of links to management practices; does the timing of these events relate to river flow or what? Long-term data at IEP and USGS Polaris sites should be examined in terms of these apparent patterns. On a year to year basis, how variable is the timing of this summer high $[\text{NO}_3]$ event? Are the average monthly patterns giving a misleading idea of the temporal consistency of the patterns?

We have been archiving monthly or bimonthly isotope samples for our complete suite of analyses (NH_4 - $\delta^{15}\text{N}$; NO_3 - $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$; water $\delta^{18}\text{O}$ and $\delta^2\text{H}$; DOC- $\delta^{13}\text{C}$; and POM C:N, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^{34}\text{S}$ – plus archived samples for the new DOM isotope method (Silva et al., 2014; Tirumalesh et al., 2015; with a draft in co-author review) -- from all Polaris sites since 2012, despite no current funding to analyze the

samples. These samples, plus the ones that will be collected this wetter year, could provide several years of additional data on how the estuary has responded to a very uncommon period of low rainfall – and now to a wetter year. We collected a similar set of samples for 2011-2012, that are currently being evaluated.

Appendix 5.2 Figures

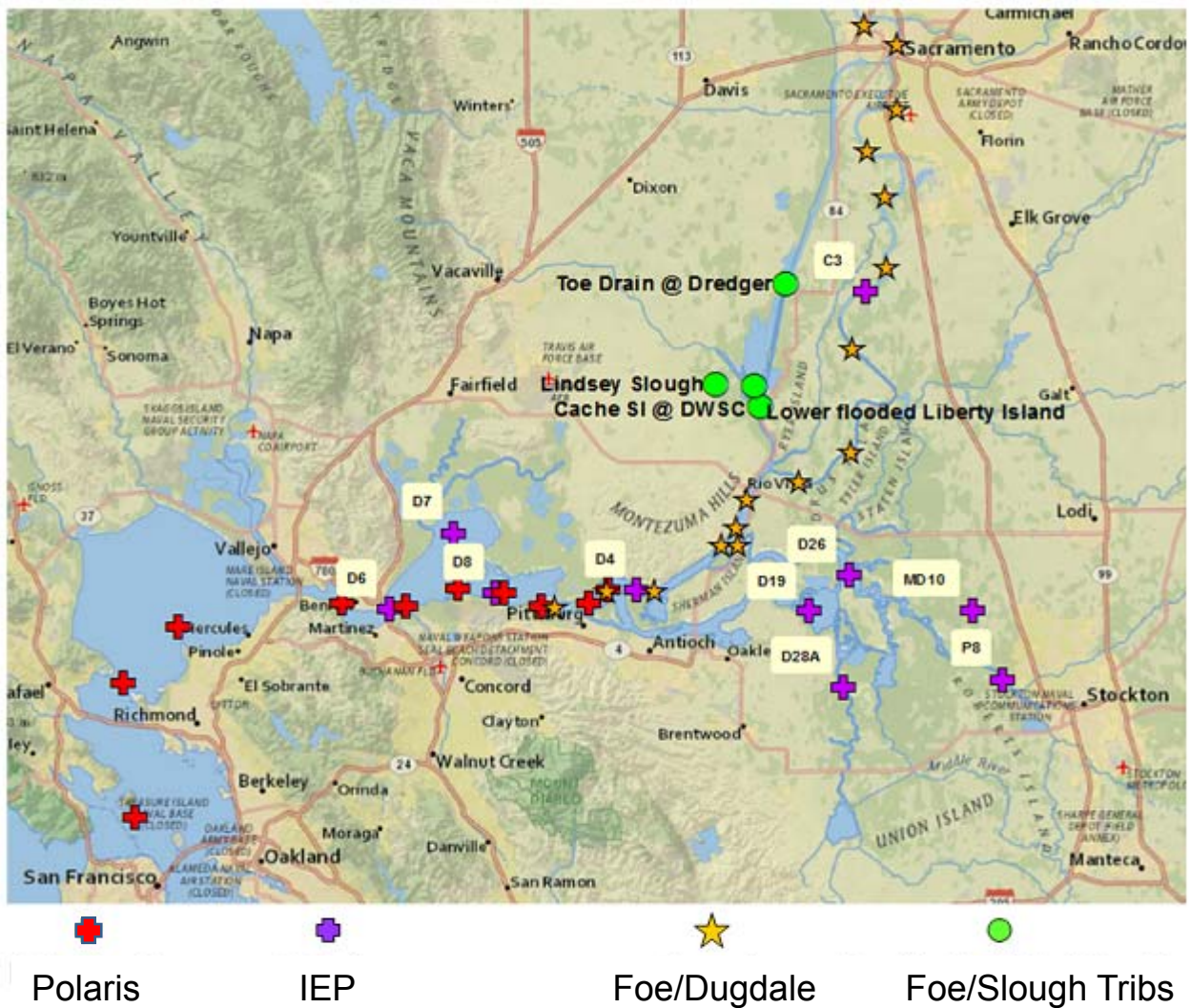


Figure 5.2.1. Map comparing locations of IEP monitoring sites with the locations of the transect sites with chemical and isotopic data that are discussed in Appendix 5.2.

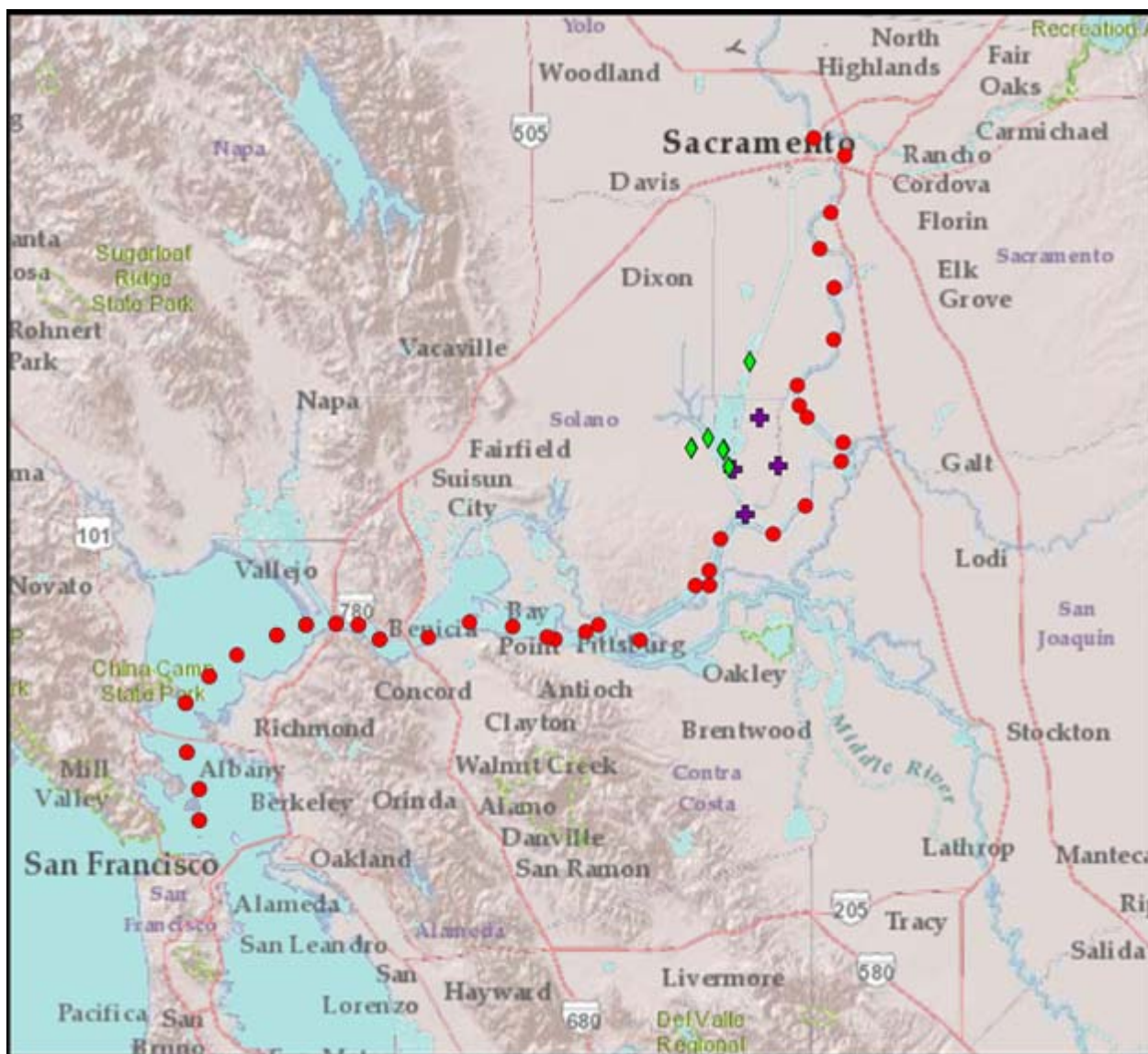


Figure 5.2.2. This map shows the location of sampling sites in the Sacramento River, Delta, northern San Francisco Bay, with different symbols for the different types of sites: mainstem, slough, and distributary. From Kendall et al. (2015).



Figure 5.2.3. Locations and names of mainstem Sacramento River sampling sites. From Kendall et al. (2015).

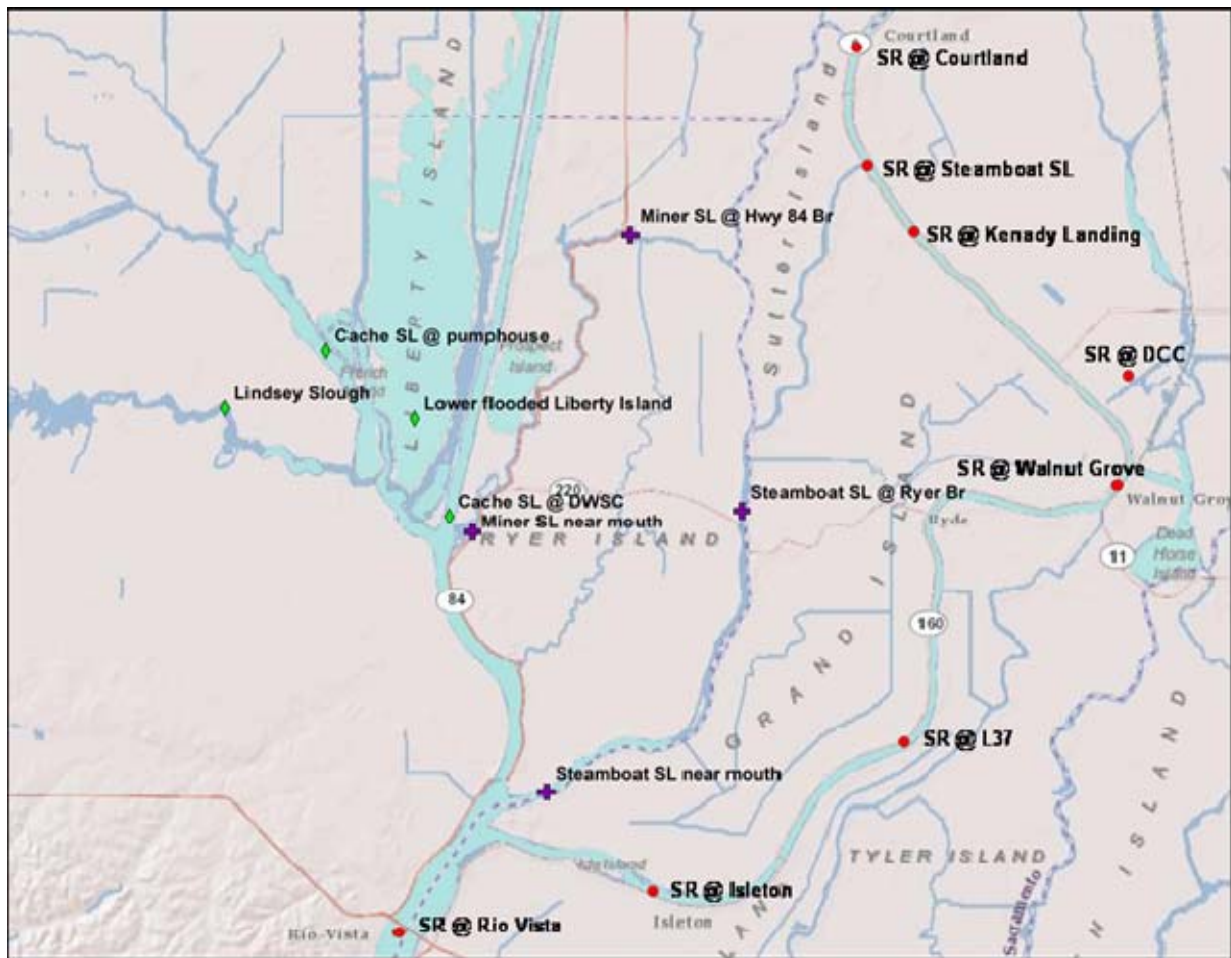


Figure 5.2.4. Locations and names of slough and distributary sampling sites. This map is an expanded version of the previous figure that includes the site names for sampling sites on **sloughs** in the Cache/Yolo Complex and **distributaries** on Miner and Steamboat Sloughs – and at some upper Sacramento River **mainstem** locations. From Kendall et al. (2015).

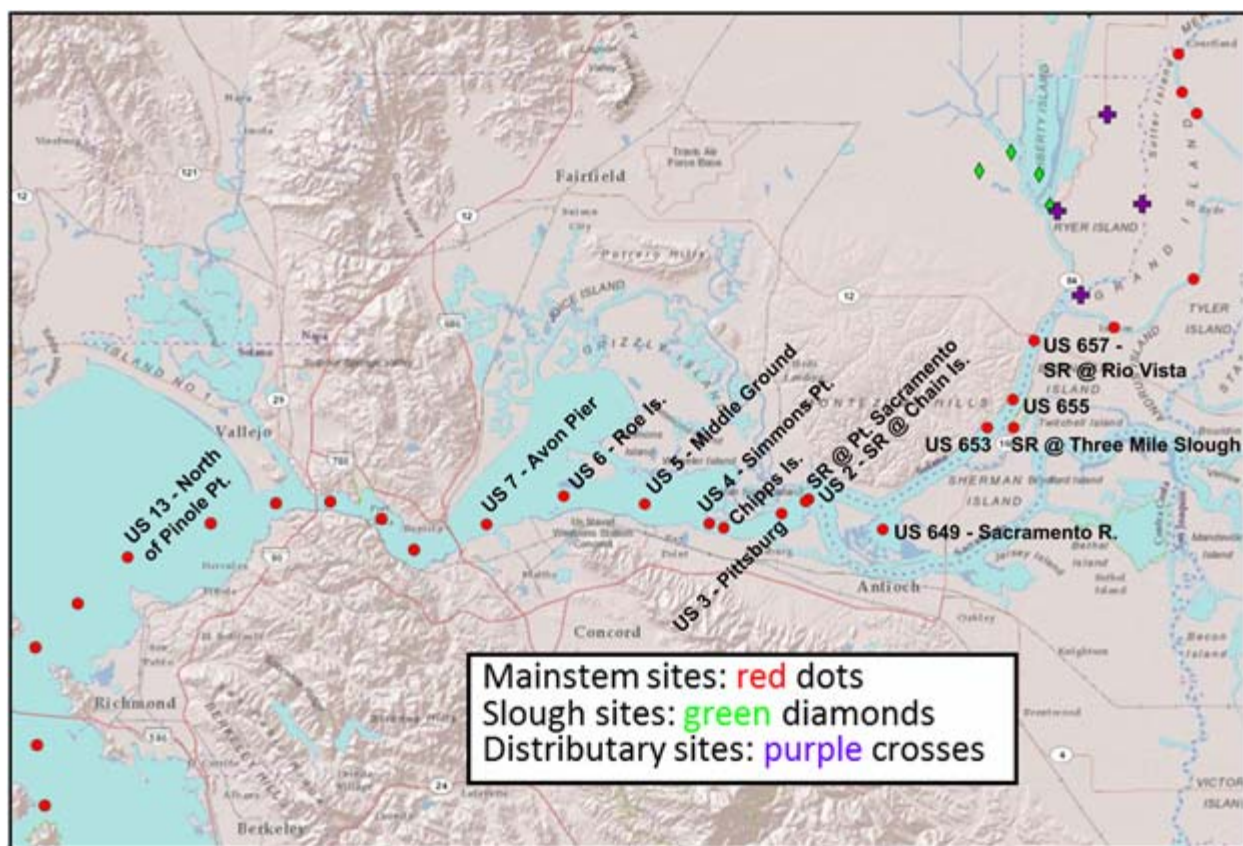


Figure 5.2.5. Locations and names of Delta and Bay sampling sites. This map includes the site names for **mainstem** Sacramento River sampling sites in the Delta and Northern San Francisco Bay. From Kendall et al. (2015).

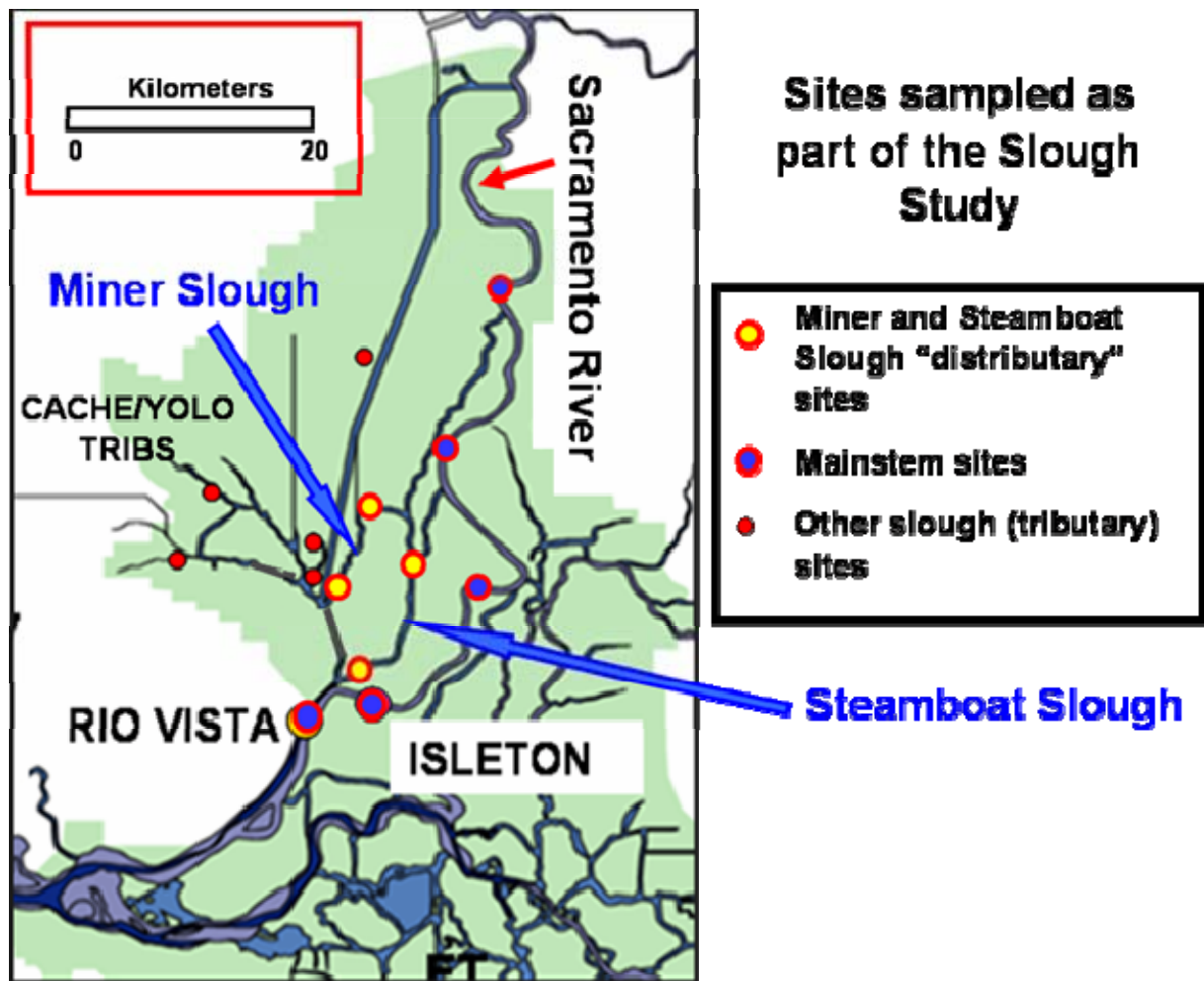


Figure 5.2.6. Locations of the sites used for the evaluation of whether mainstem Sacramento River water (as collected at Isleton, RM17) is chemically and isotopically distinctive from waters from Miner Slough and Steamboat Slough, both distributaries of the Sacramento River. The water in these distributaries is mainly derived from the Sacramento River at Courtland, but some other agricultural drainages may be seasonally important. The combined flow from Miner and Steamboat Sloughs is about the same flow as at Isleton, and they contribute roughly half the flow to Rio Vista. From Kendall et al. (2015).

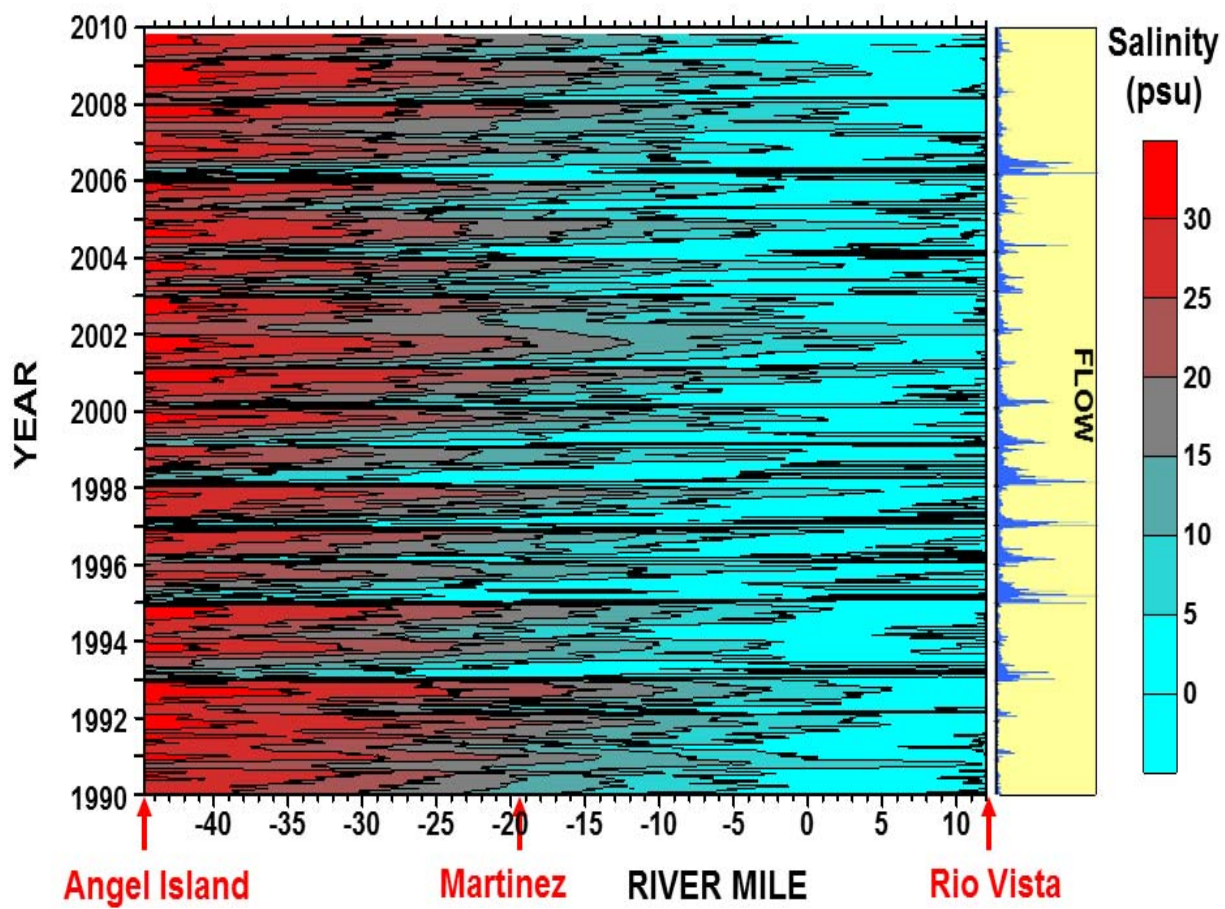


Figure 5.2.7. Temporal and spatial changes in salinity, 1990-2010, at USGS Polaris sites.

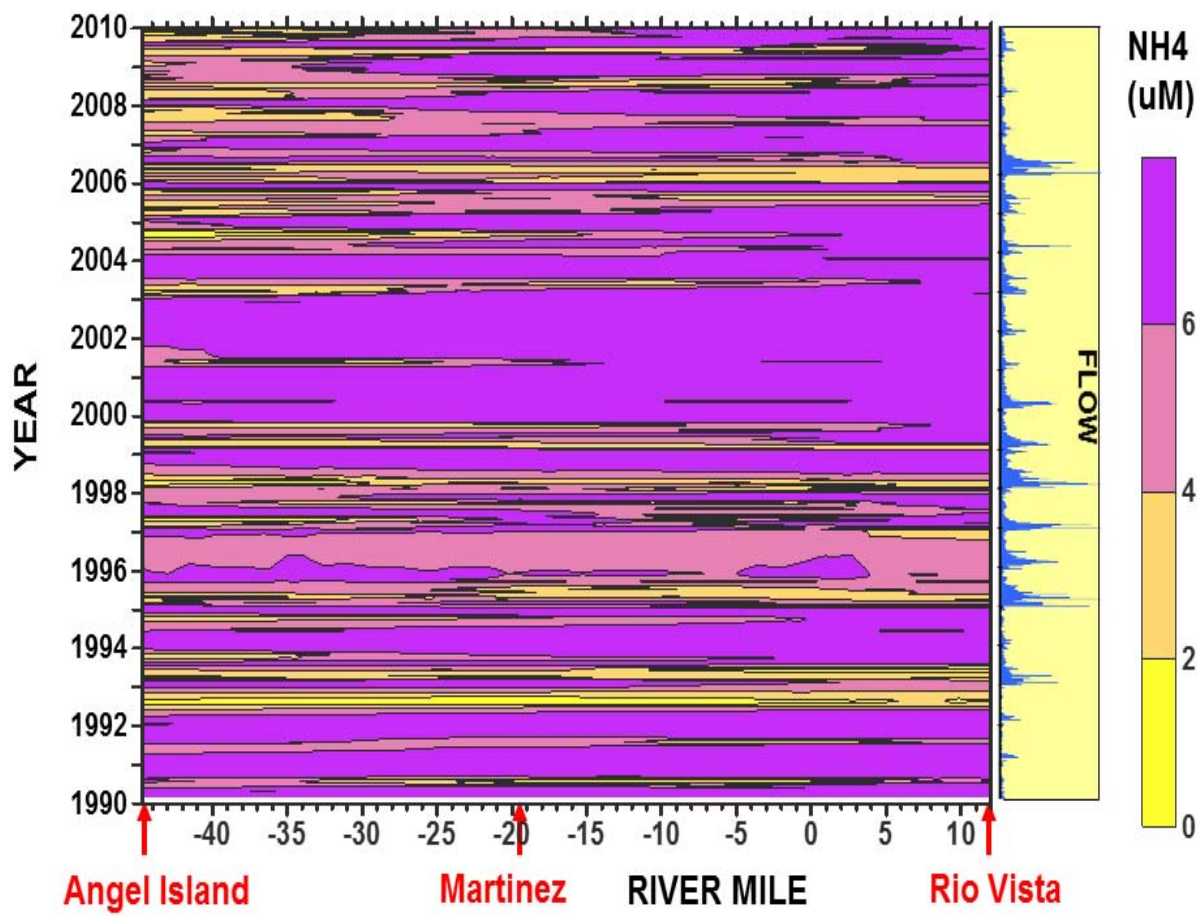


Figure 5.2.8. Temporal and spatial changes in $[NH_4]$, 1990-2010, at USGS Polaris sites.

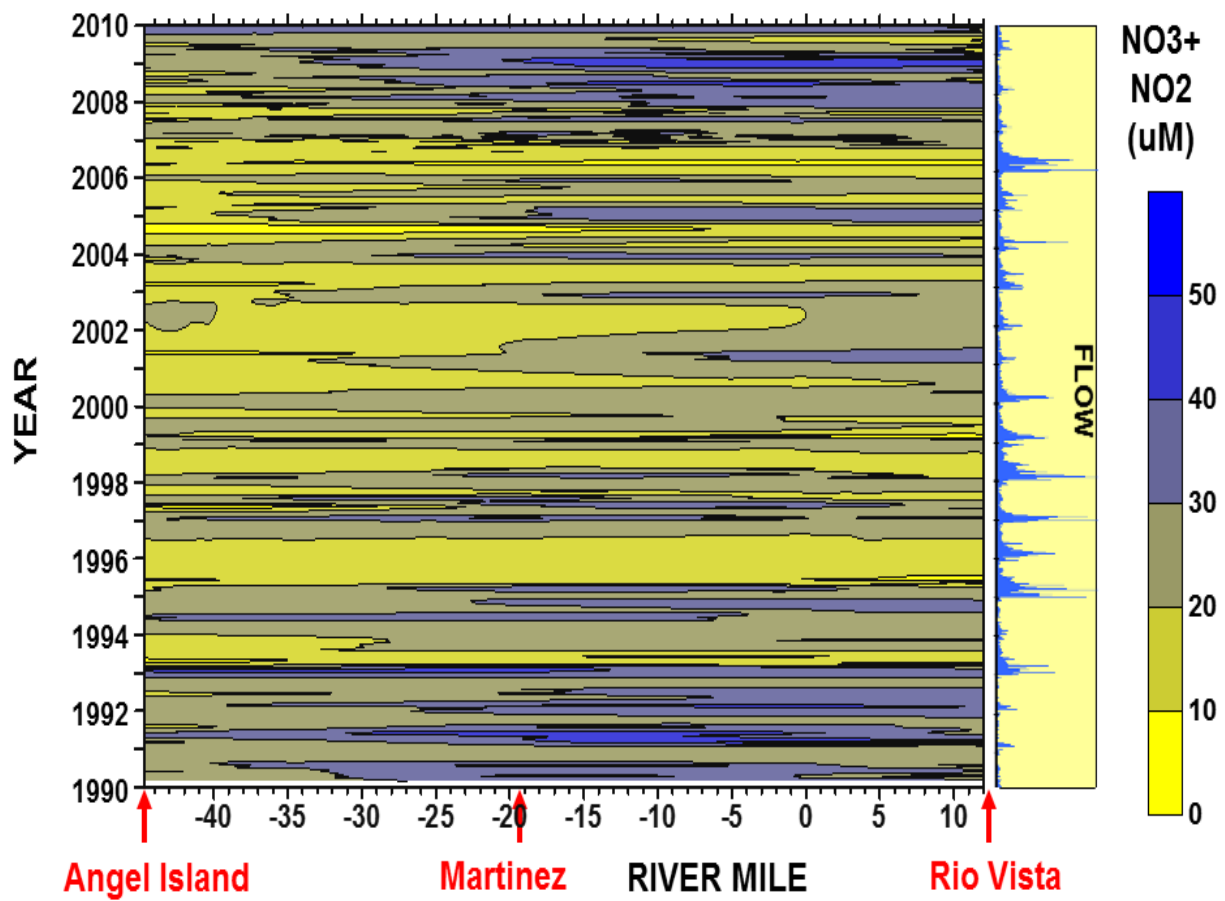


Figure 5.2.9. Temporal and spatial changes in $\text{NO}_3 + \text{NO}_2$, 1990-2010, at USGS Polaris sites.

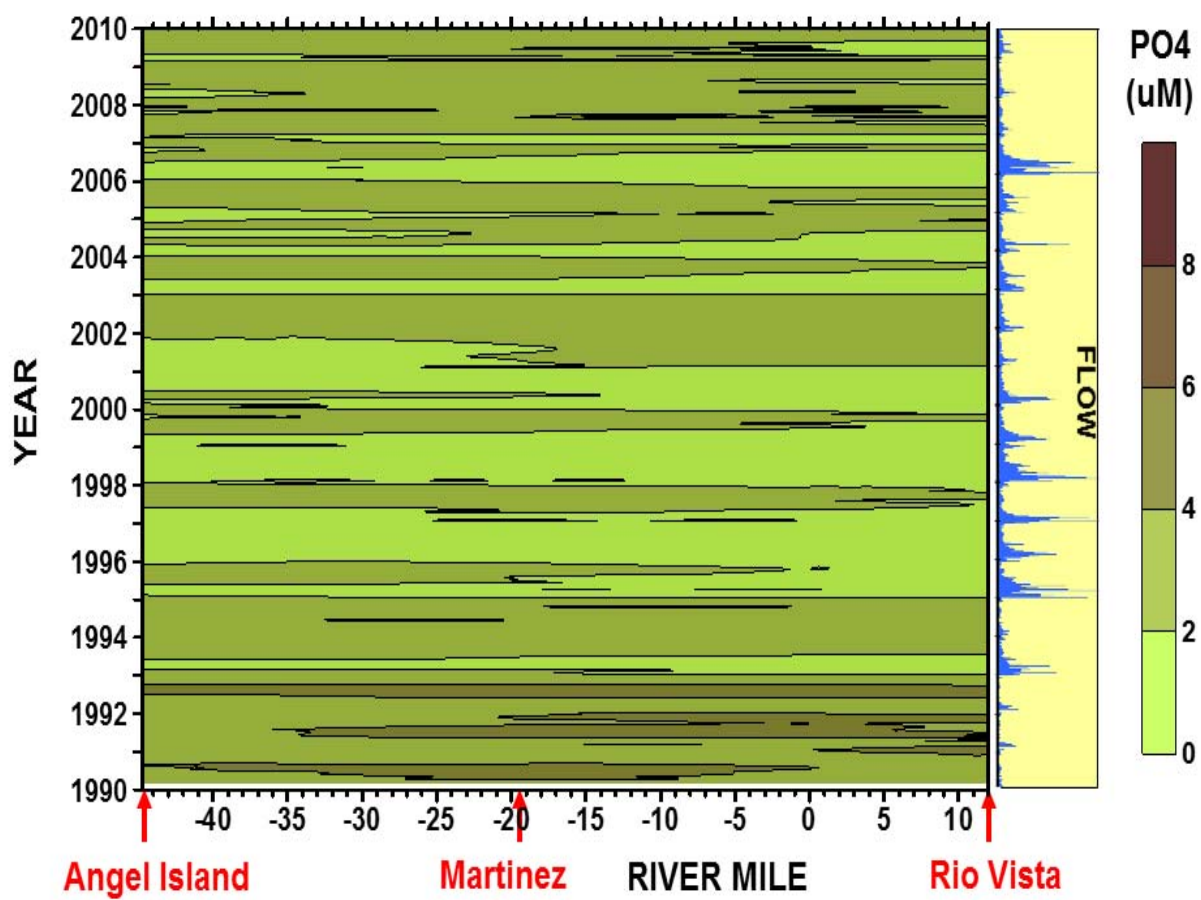


Figure 5.2.10. Temporal and spatial changes in PO₄, 1990-2010, at USGS Polaris sites.

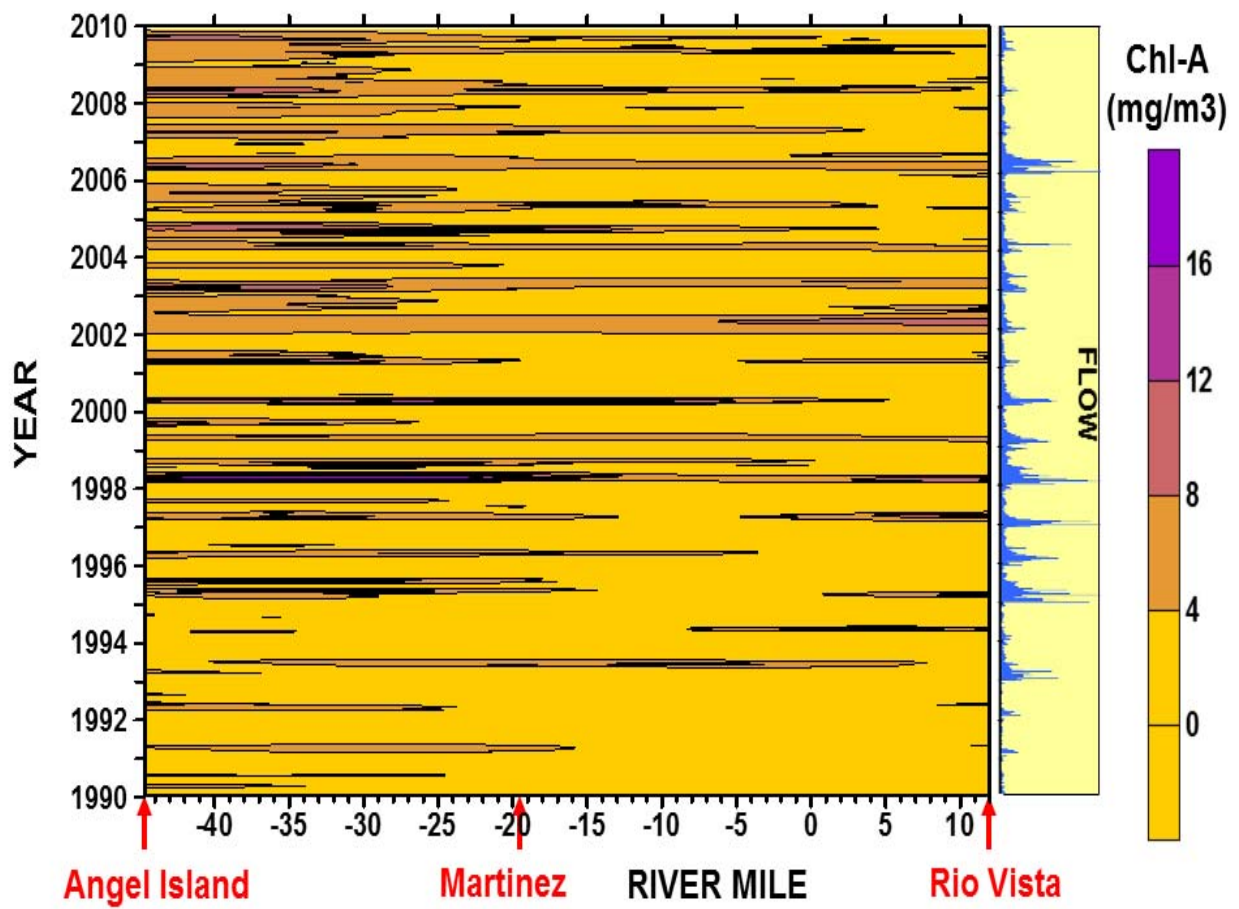


Figure 5.2.11. Temporal and spatial changes in Chlorophyll-a, 1990-2010, at USGS Polaris sites.

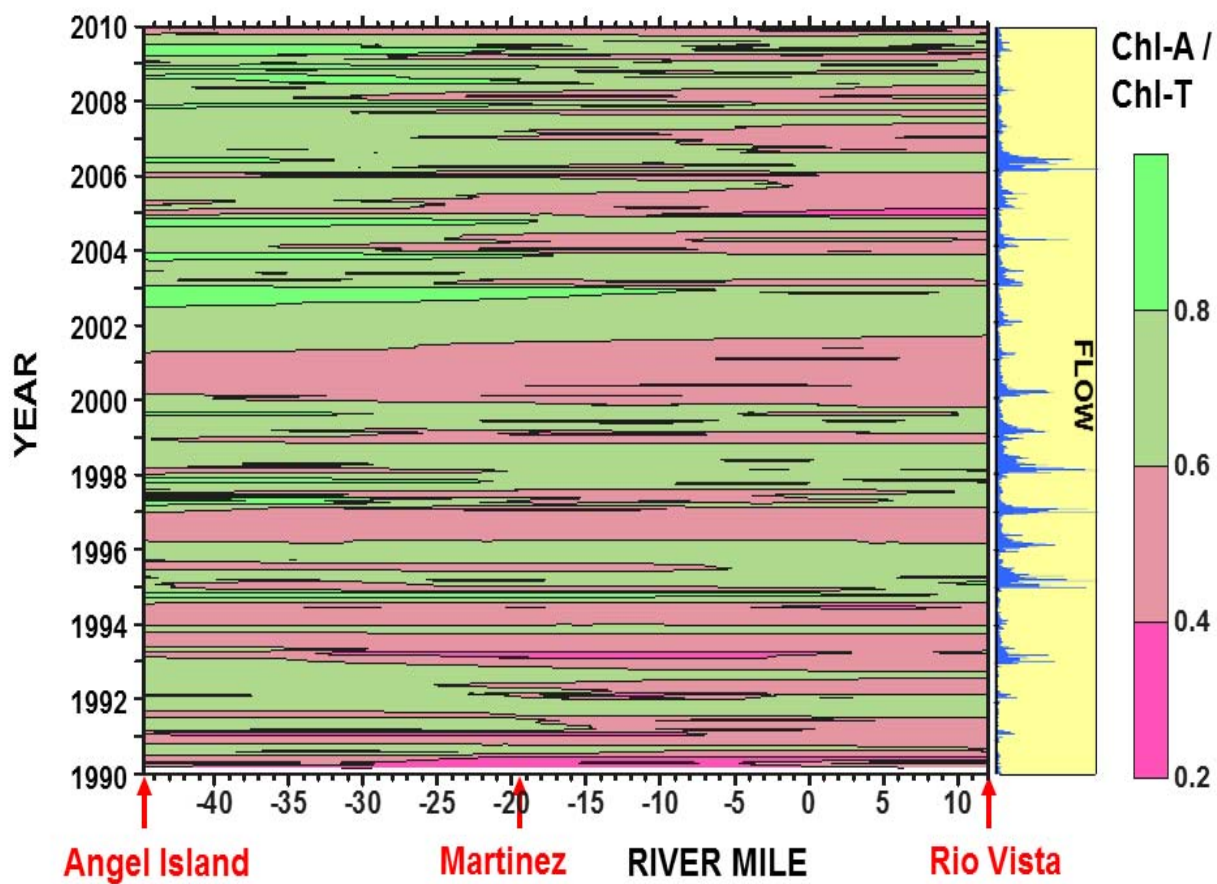


Figure 5.2.12. Temporal and spatial changes in Chlorophyll-a / Chlorophyll-T, 1990-2010, at USGS Polaris sites.

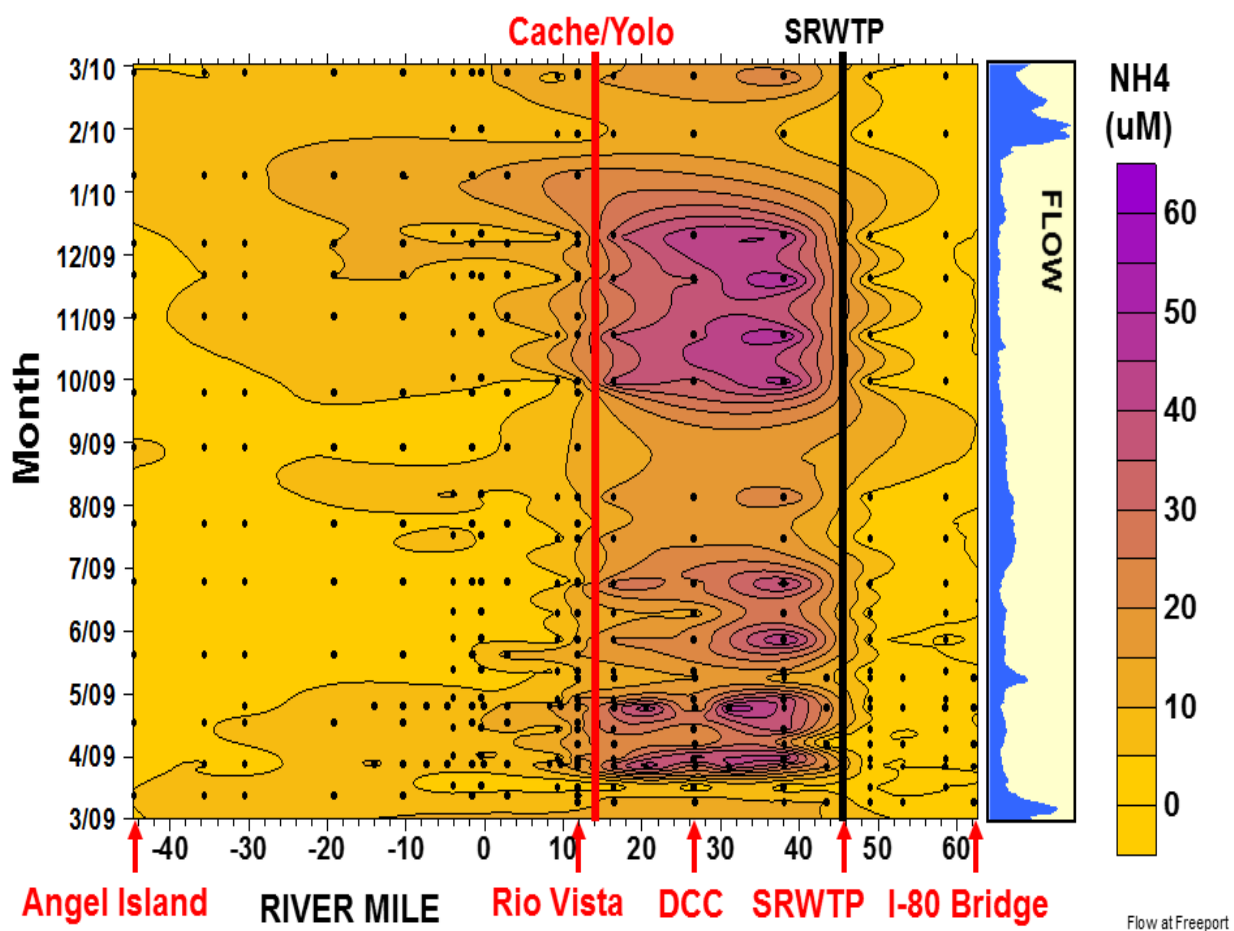


Figure 5.2.13. Temporal and spatial variability in the $[\text{NH}_4]$; from Kendall et al. (2015)

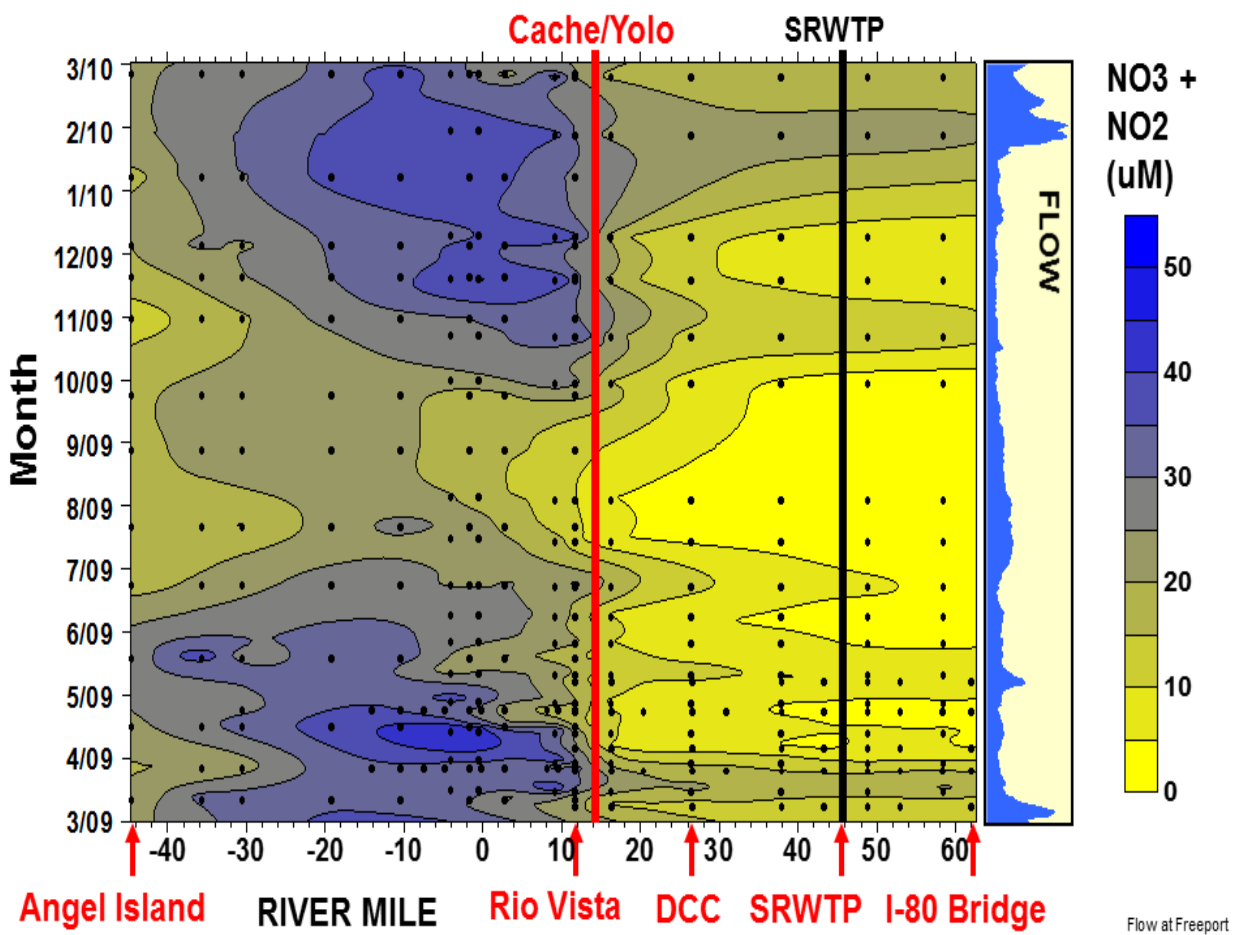


Figure 5.2.14. Temporal and spatial variability in the $[NO_3+NO_2]$; from Kendall et al. (2015).

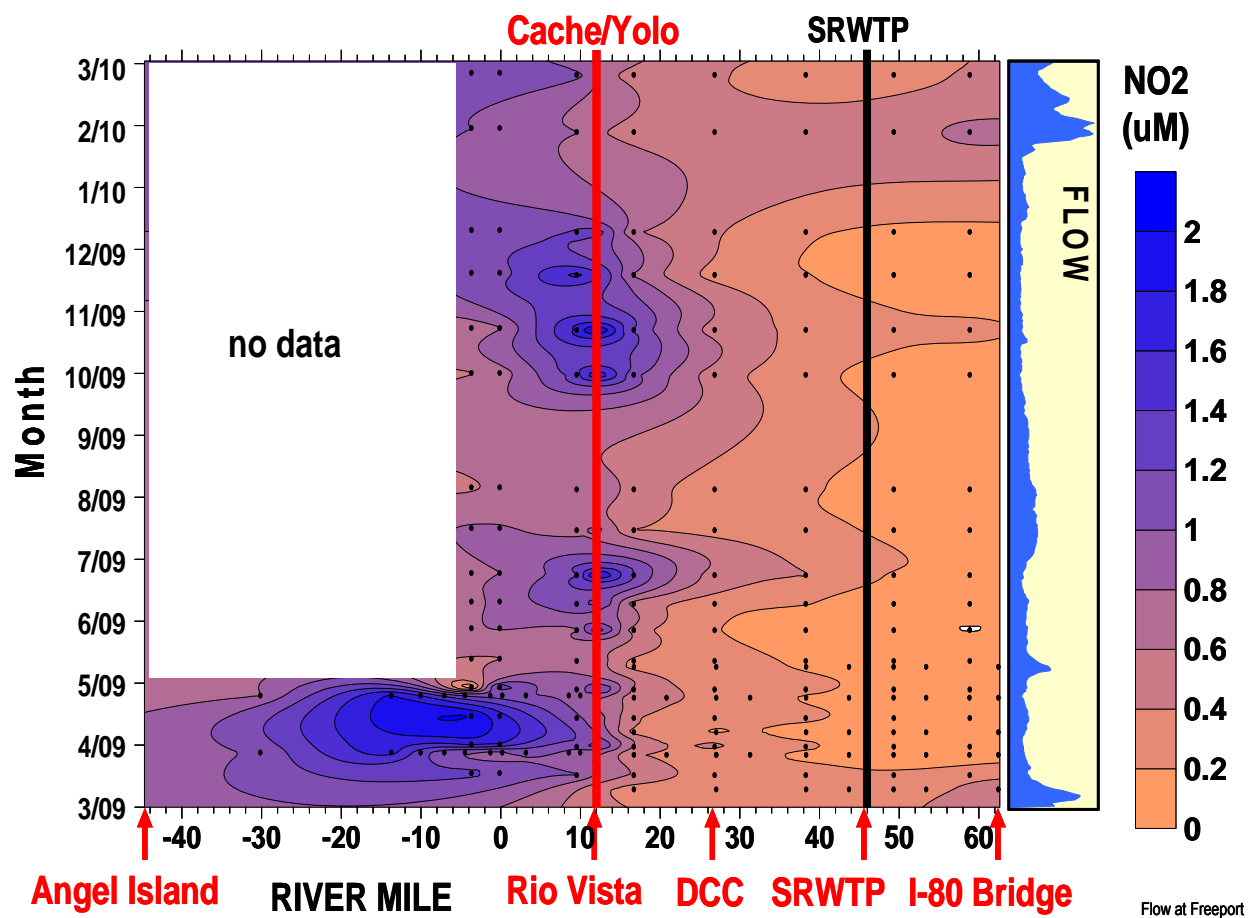


Figure 5.2.15. Temporal and spatial variability in the $[\text{NO}_2]$; from Kendall et al. (2015).

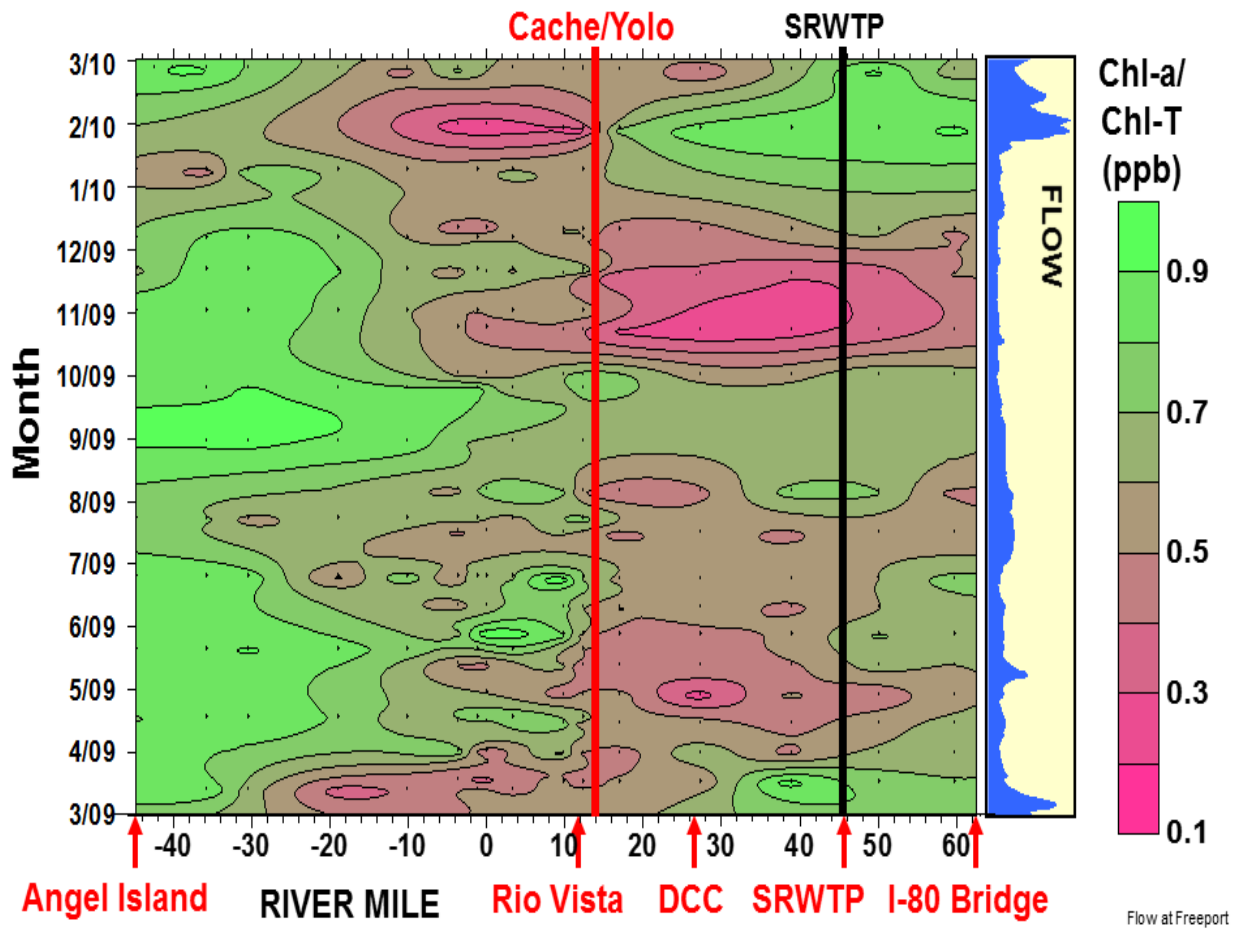


Figure 5.2.16. Temporal and spatial variability in the ratio of chlorophyll-a to total chlorophyll concentration; from Kendall et al. (2015).

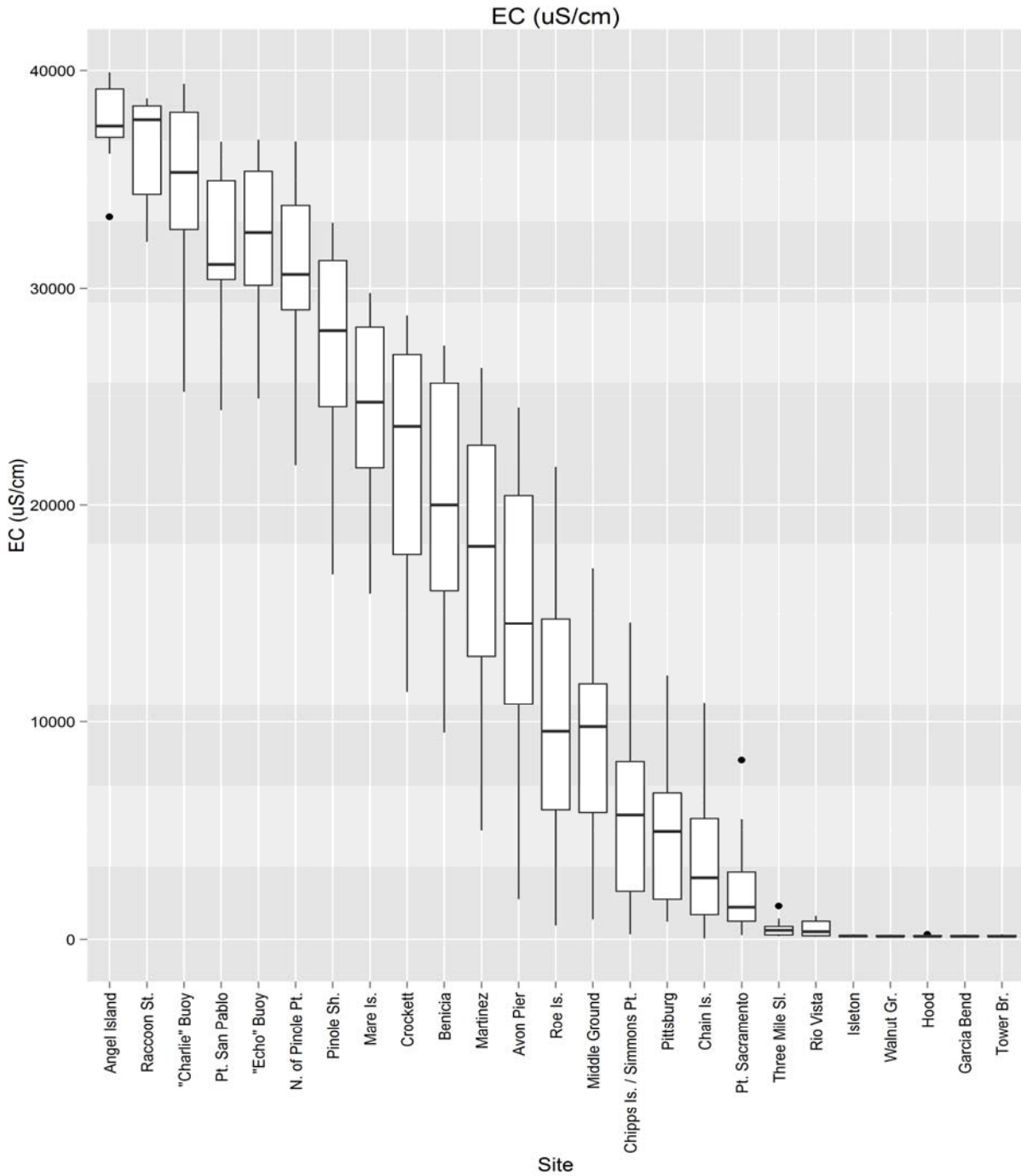


Figure 5.2.17. Electrical conductivity data for samples collected 2006-2010 from sites in the SFE from Tower Bridge (RM59) in the Sacramento River downstream to Angel Island in the San Francisco Bay (RM-45).

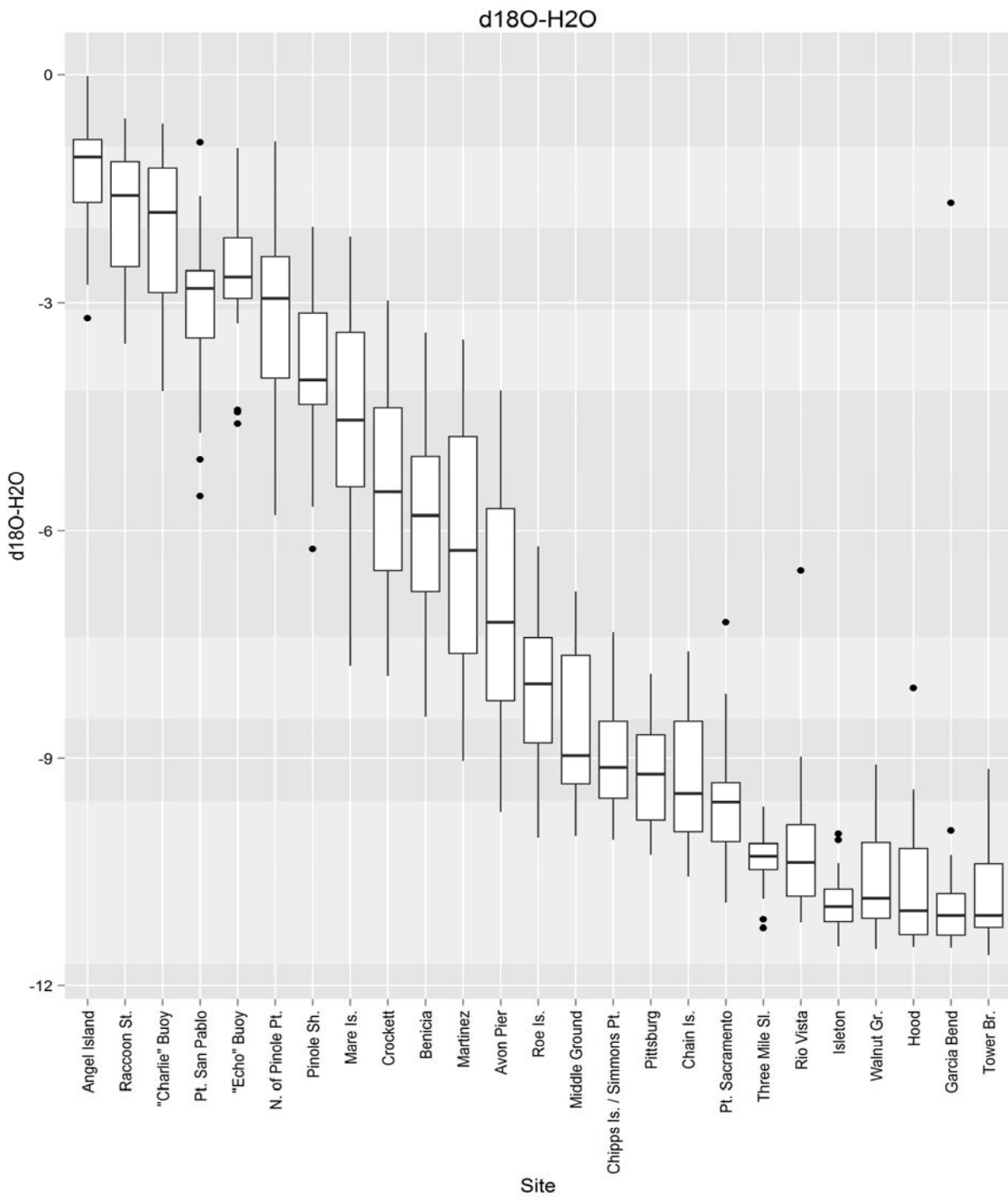


Figure 5.2.18. Water- $\delta^{18}\text{O}$ data for samples collected 2006-2010 from sites in the SFE from Tower Bridge (RM59) in the Sacramento River downstream to Angel Island in the San Francisco Bay (RM-45).

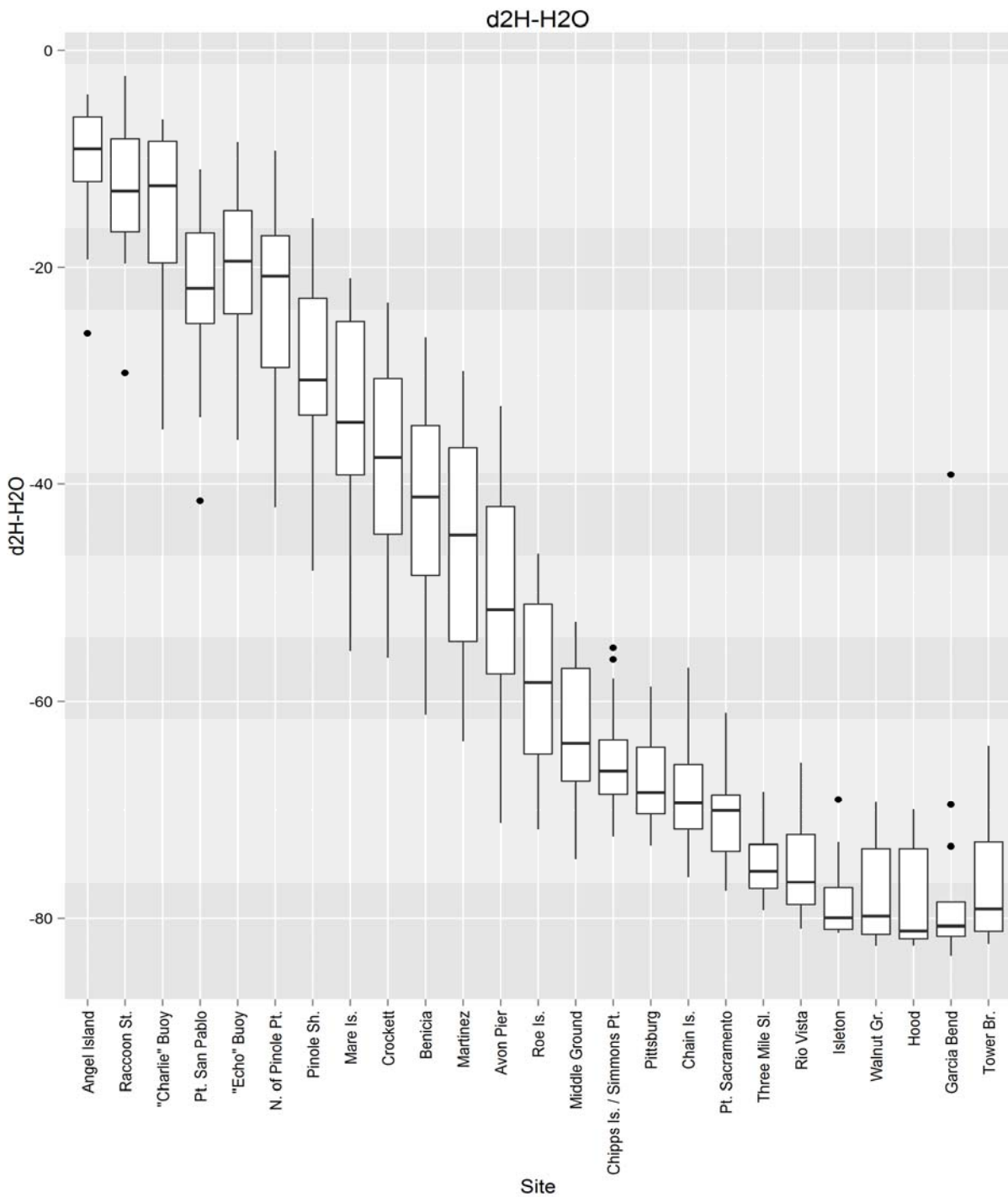


Figure 5.2.19. Water- $\delta^2\text{H}$ data for samples collected 2006-2010 from sites in the SFE from Tower Bridge (RM59) in the Sacramento River downstream to Angel Island in the San Francisco Bay (RM-45).

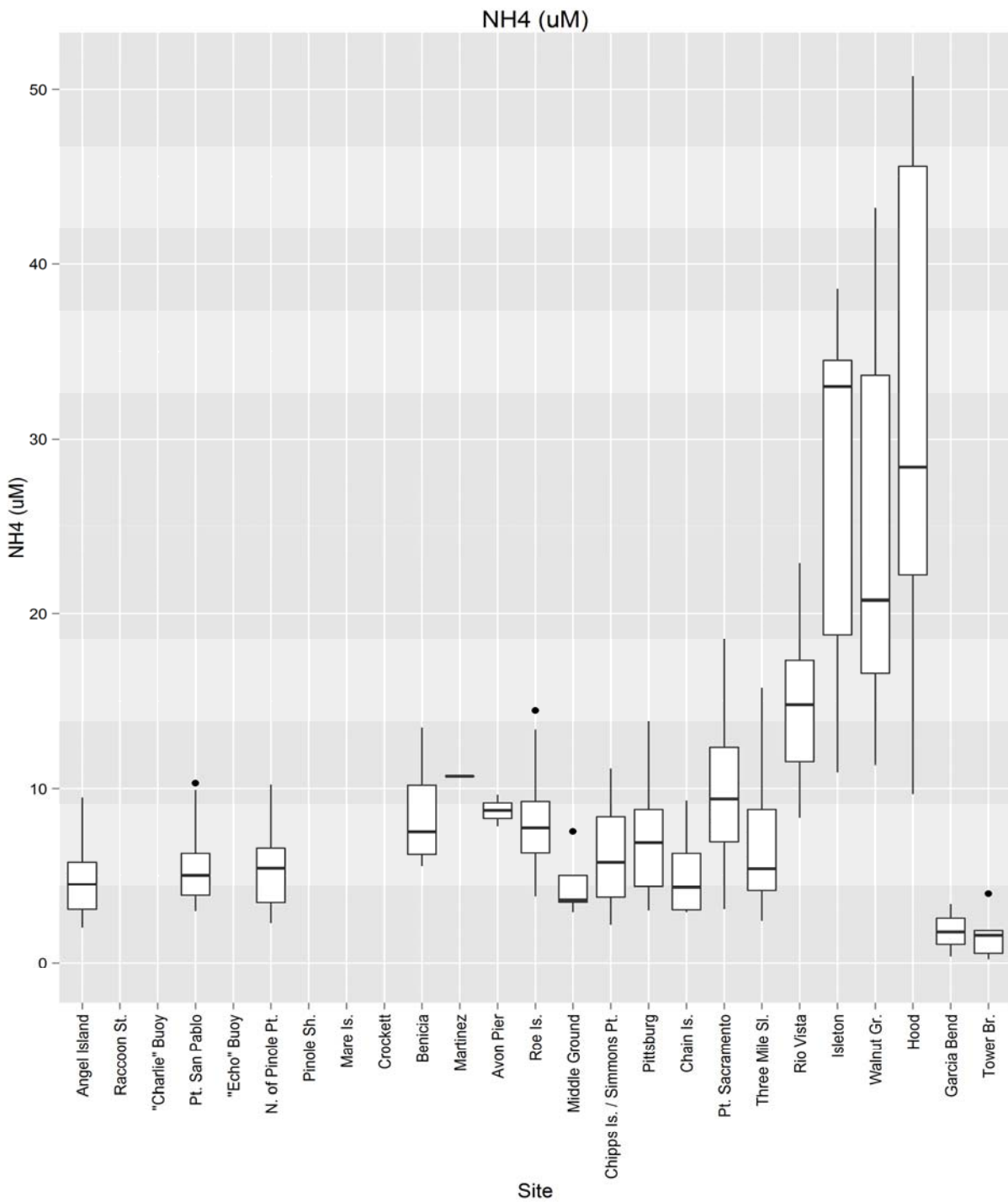


Figure 5.2.20. Ammonium concentration data for samples collected 2006-2010 from sites in the SFE from Tower Bridge (RM59) in the Sacramento River downstream to Angel Island in the San Francisco Bay (RM-45).

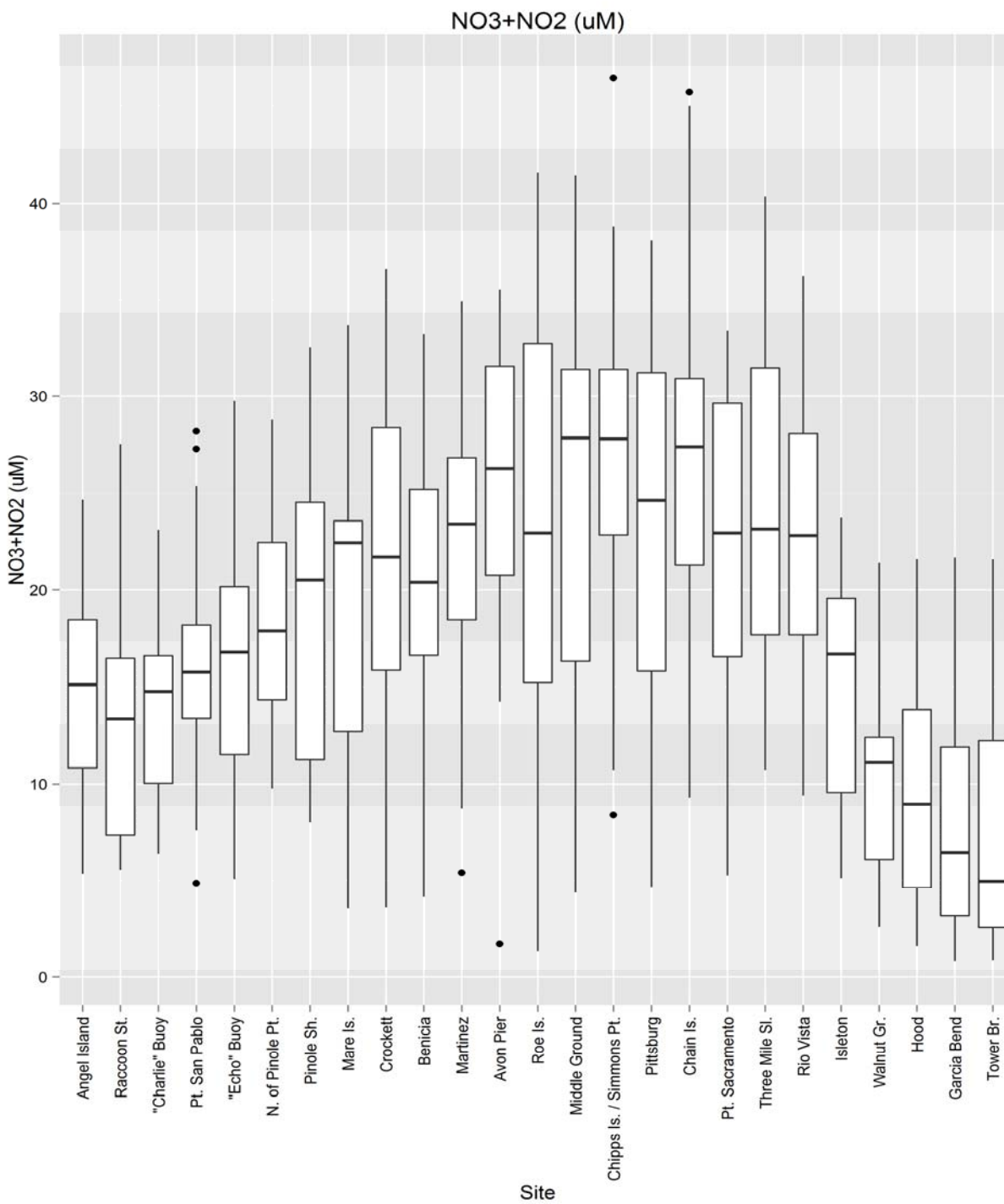


Figure 5.2.21. Nitrate + nitrite concentration data for samples collected 2006-2010 from sites in the SFE from Tower Bridge (RM59) in the Sacramento River downstream to Angel Island in the San Francisco Bay (RM-45).

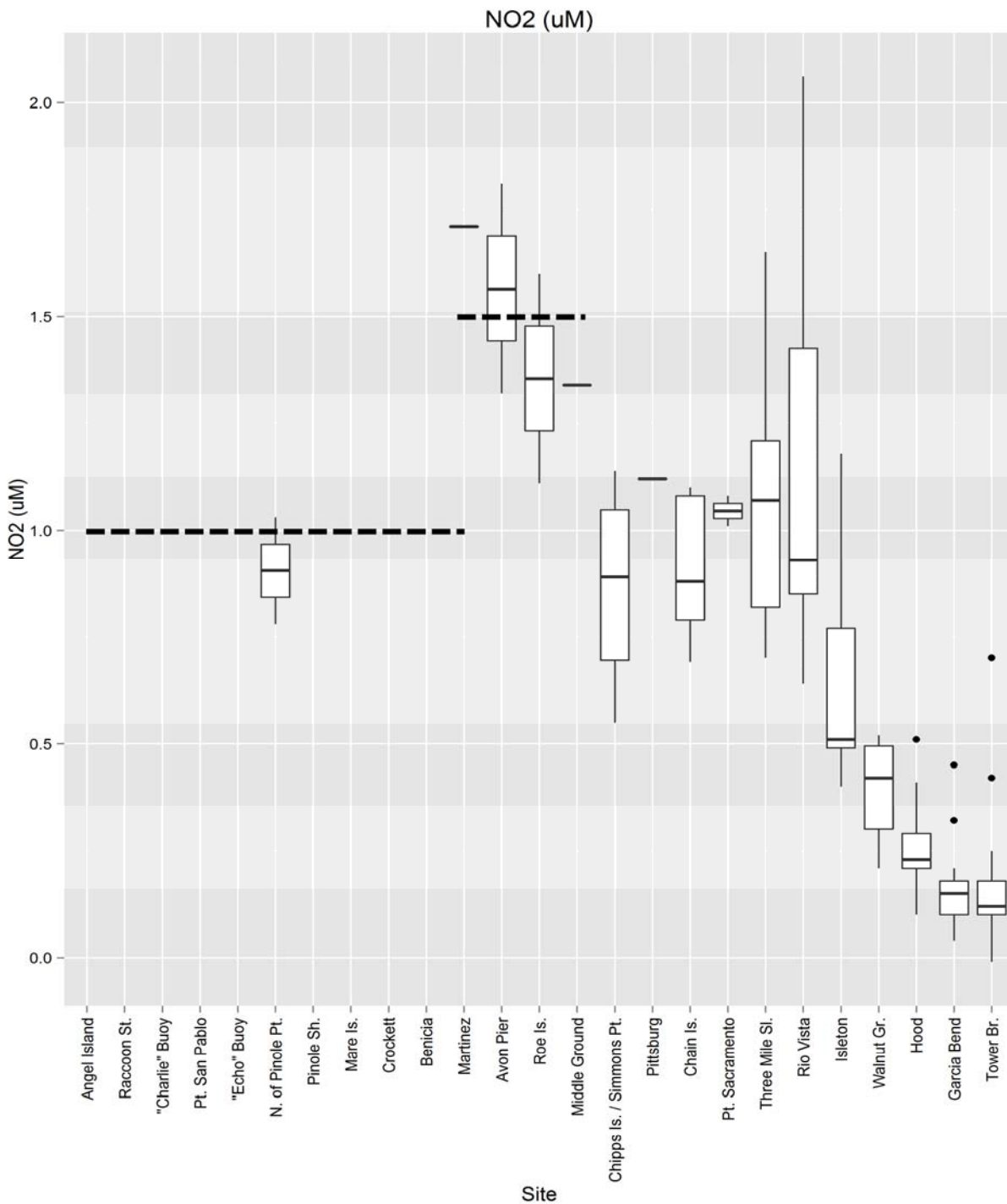


Figure 5.2.22. Nitrite concentration data for samples collected 2006-2010 from sites in the SFE from Tower Bridge (RM59) in the Sacramento River downstream to Angel Island in the San Francisco Bay (RM-45). The dashed lines show the approximate trend of data from a longer time span.

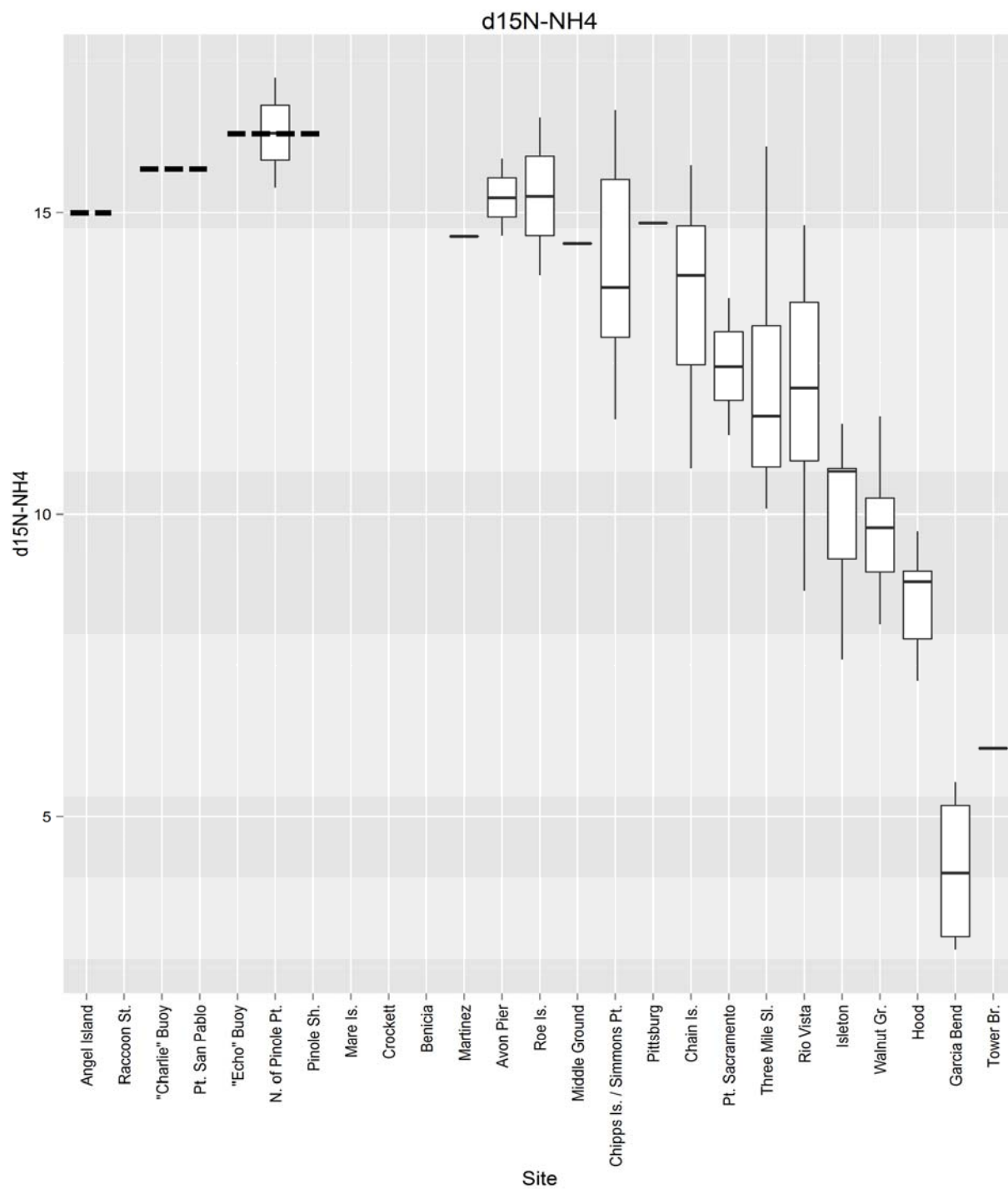


Figure 5.2.23. $\text{NH}_4\text{-}\delta^{15}\text{N}$ data for samples collected 2006-2010 from sites in the SFE from Tower Bridge (RM59) in the Sacramento River downstream to Angel Island in the San Francisco Bay (RM-45). The dashed lines show the approximate trend of data from a longer time span.

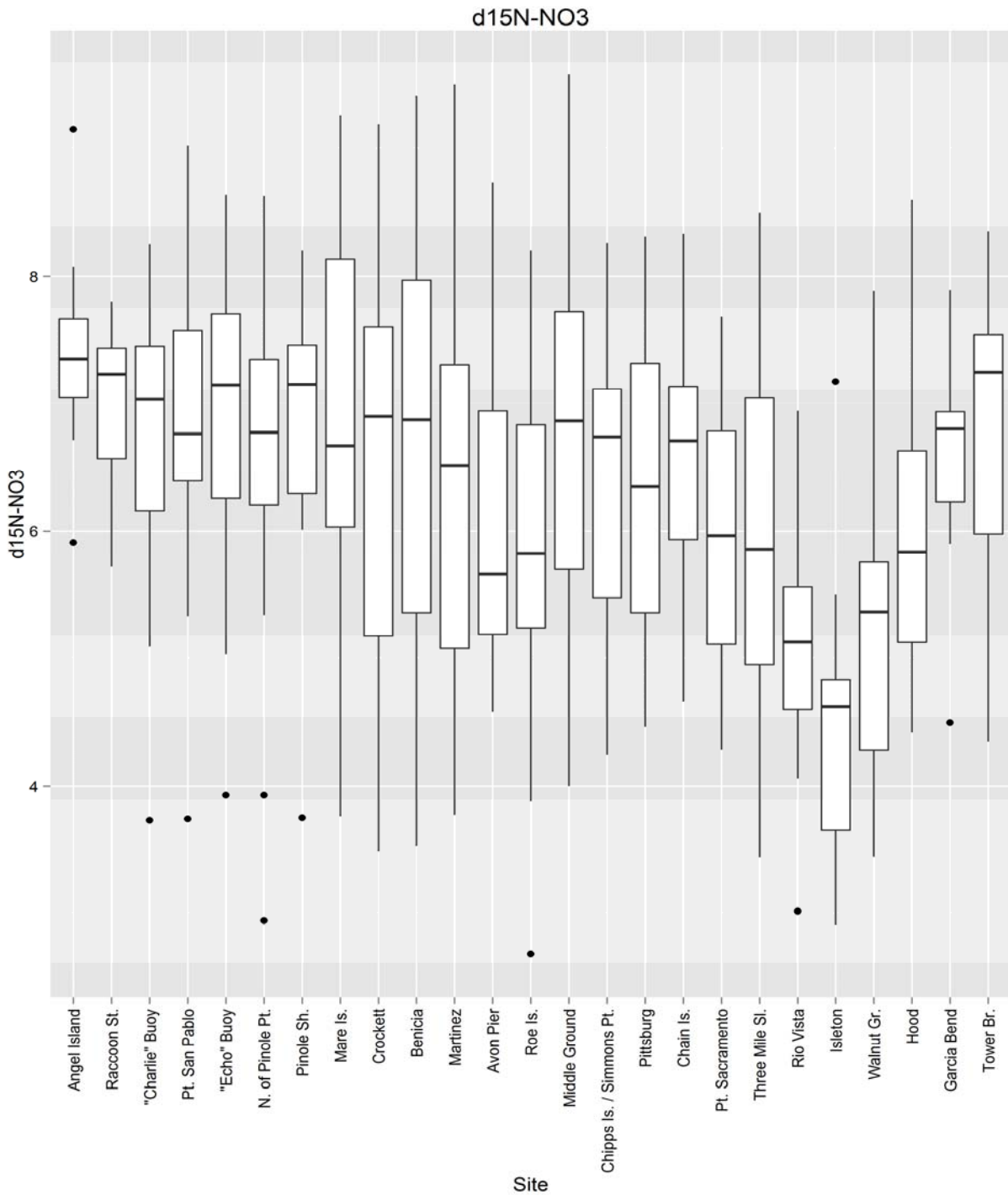


Figure 5.2.24. Nitrate- $\delta^{15}\text{N}$ data for samples collected 2006-2010 from sites in the SFE from Tower Bridge (RM59) in the Sacramento River downstream to Angel Island in the San Francisco Bay (RM-45)

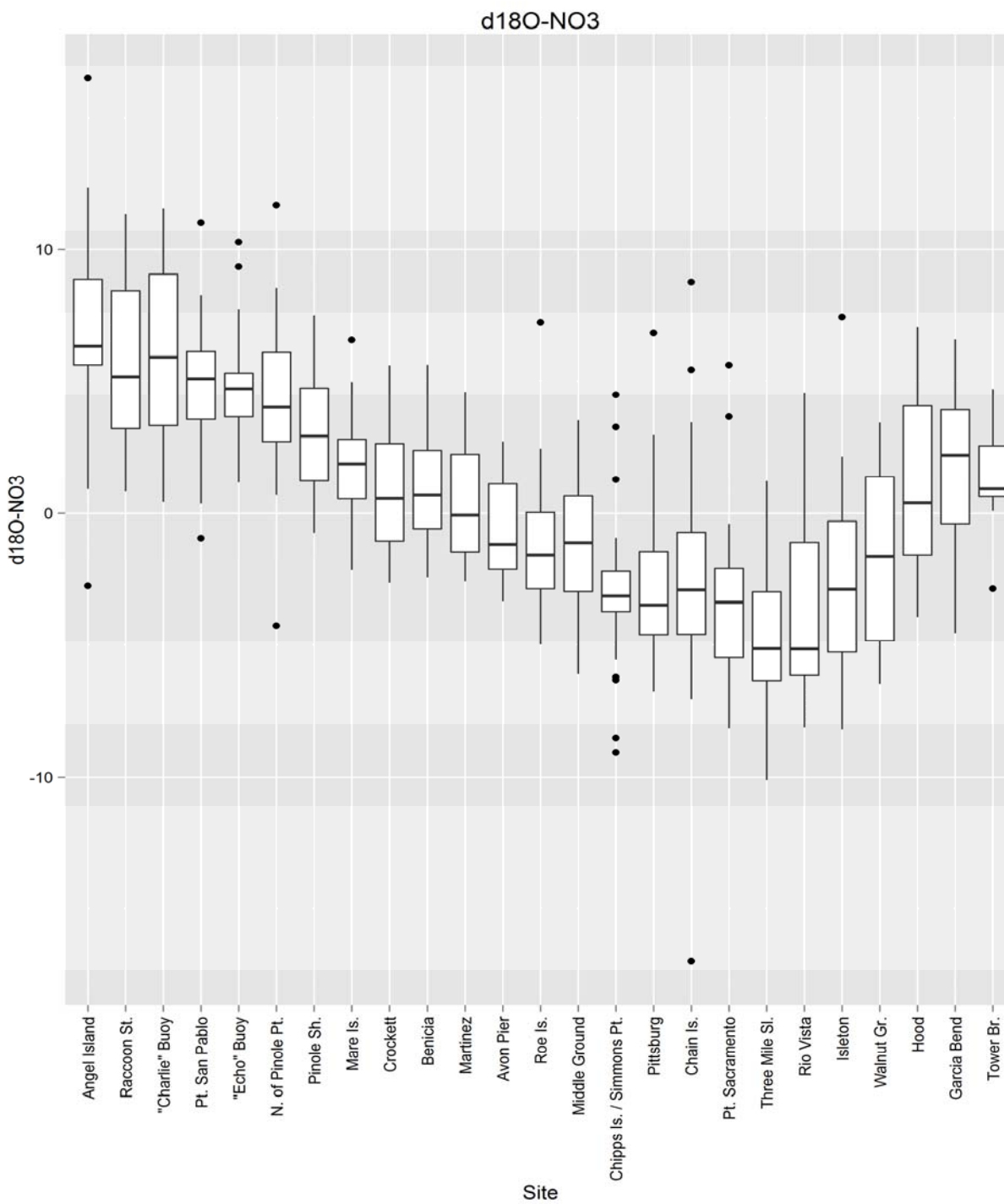


Figure 5.2.25. Nitrate- $\delta^{18}\text{O}$ data for samples collected 2006-2010 from sites in the SFE from Tower Bridge (RM59) in the Sacramento River downstream to Angel Island in the San Francisco Bay (RM-45).

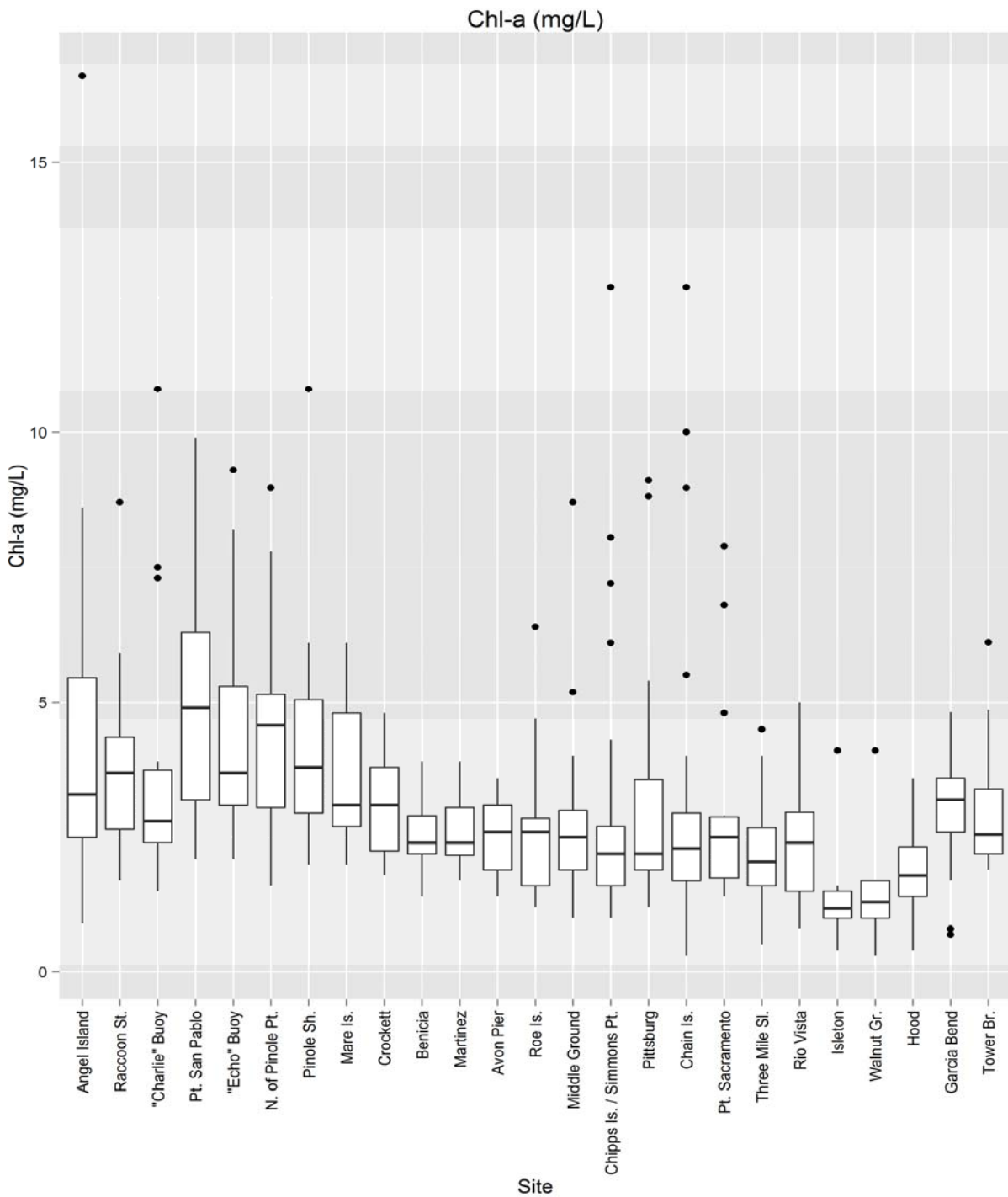


Figure 5.2.26. Chlorophyll-a concentration data for samples collected 2006-2010 from sites in the SFE from Tower Bridge (RM59) in the Sacramento River downstream to Angel Island in the San Francisco Bay (RM-45).

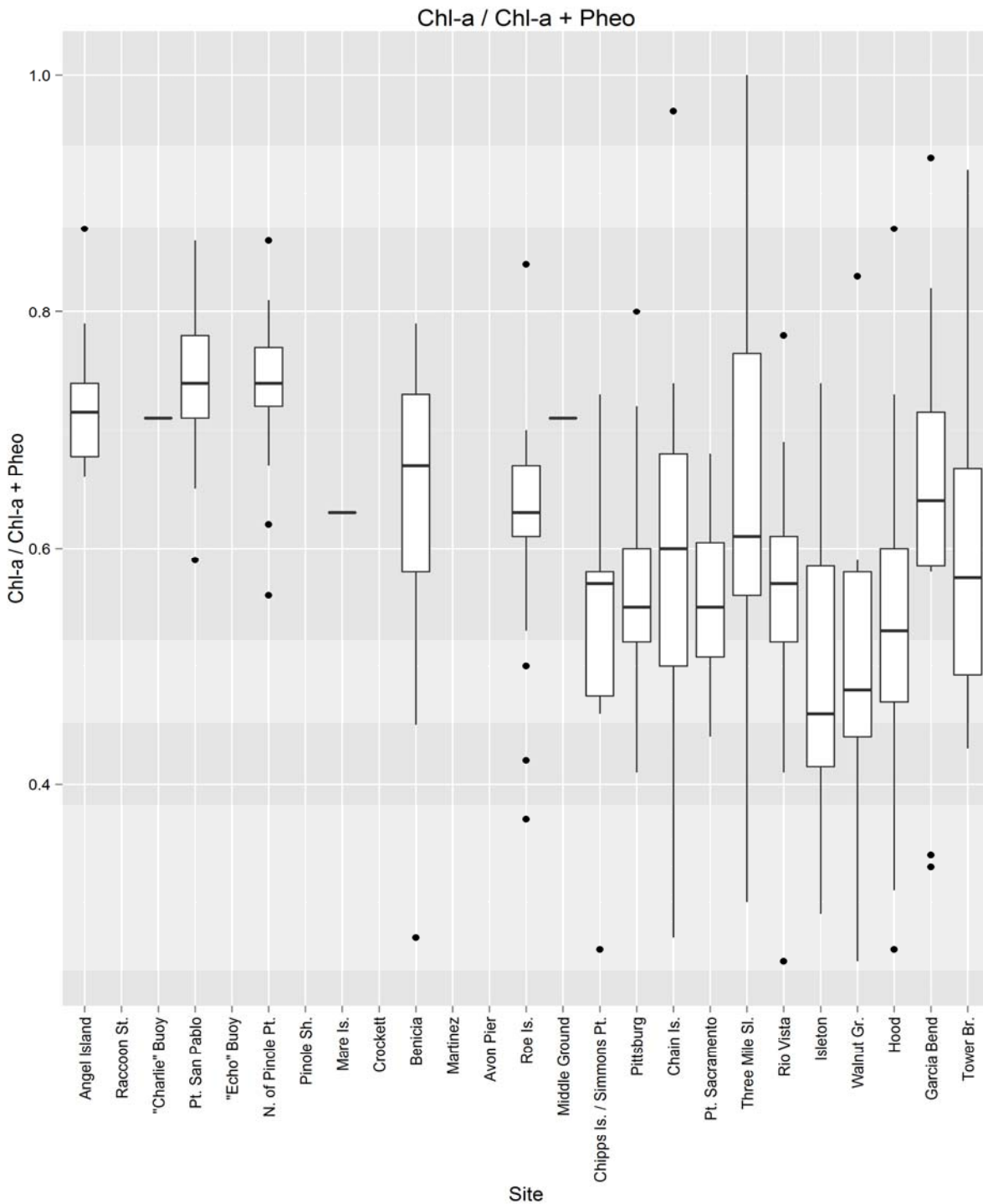


Figure 5.2.27. Chlorophyll-a ratio data for samples collected 2006-2010 from sites in the SFE from Tower Bridge (RM59) in the Sacramento River downstream to Angel Island in the San Francisco Bay (RM-45).

Downstream trends in regions

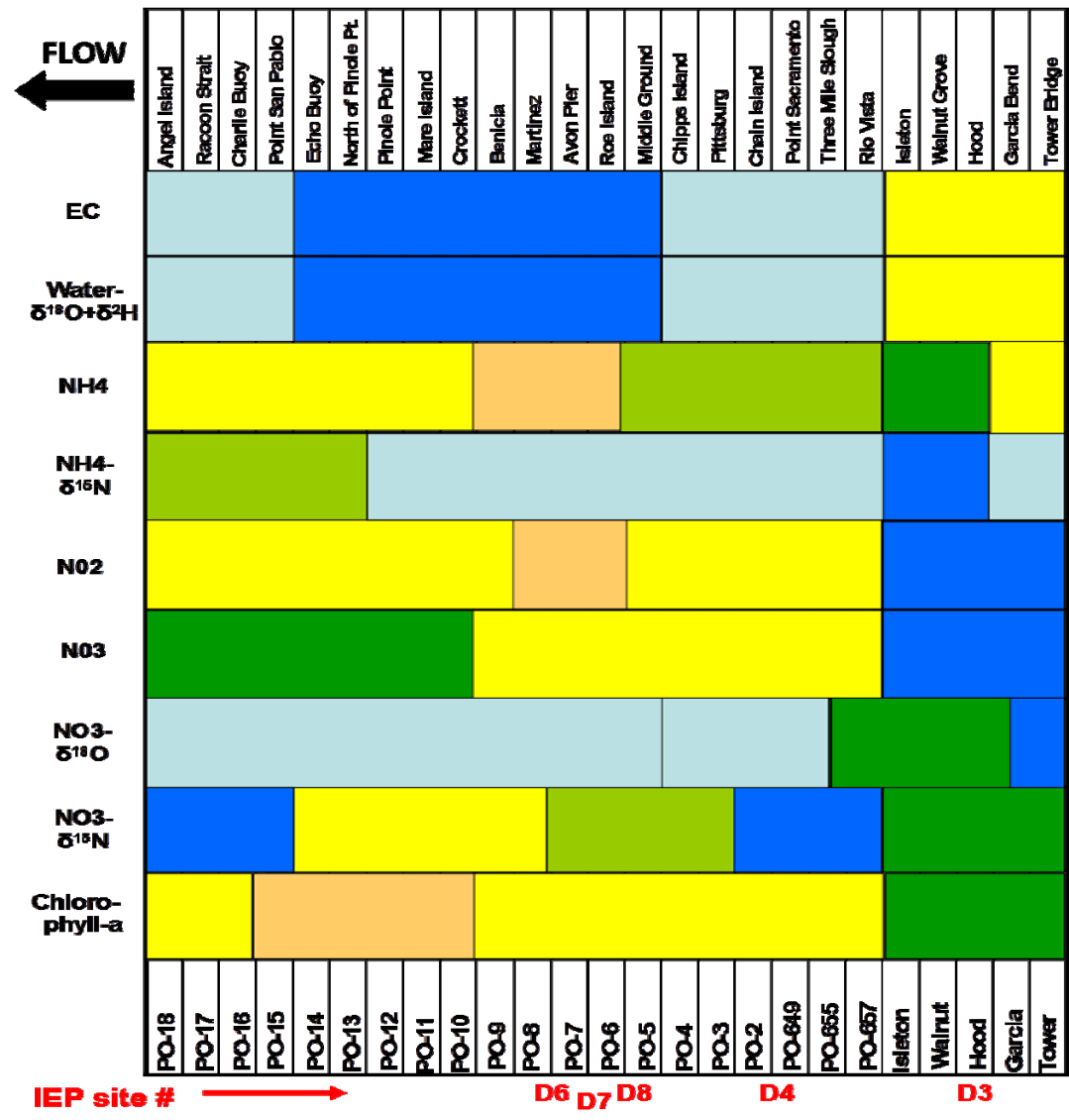
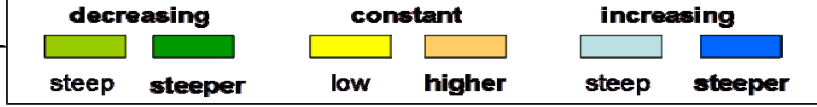


Figure 5.2.28. Summary of the locations of the regions and the transitions between regions for data from 10 constituents (listed to the left, water- $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are combined), for 25 transect sites from Tower Bridge to Angel Island. The transect site numbers are listed at the bottom and site names at the top (in black). The approximate locations of the 5 IEP sites relative to the transect sites are denoted by the red site numbers at the bottom.

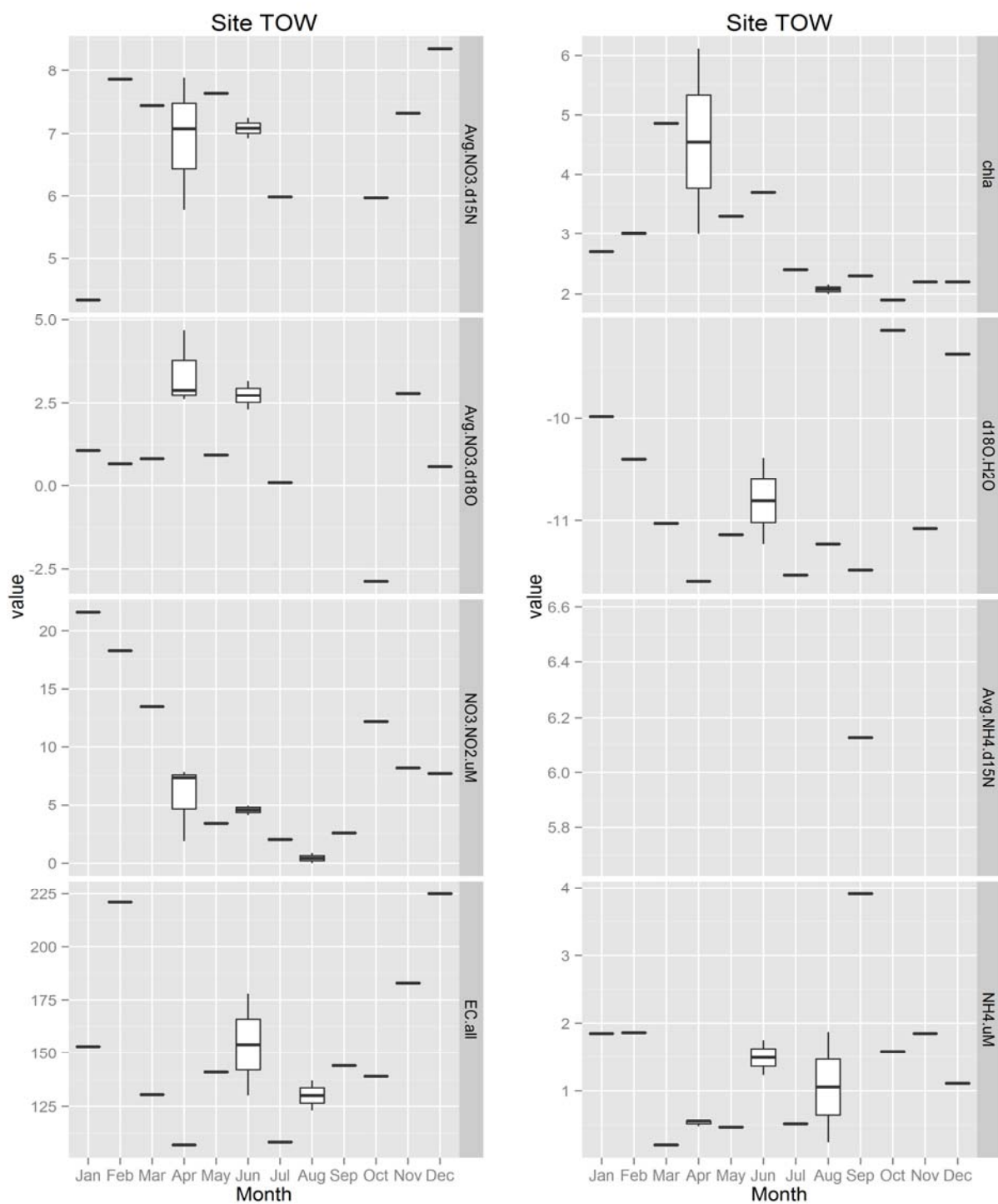


Figure 5.2.29. Chemical and isotopic data plotted by month for Tower Bridge in the Sacramento River. Samples collected from 2009-2010.

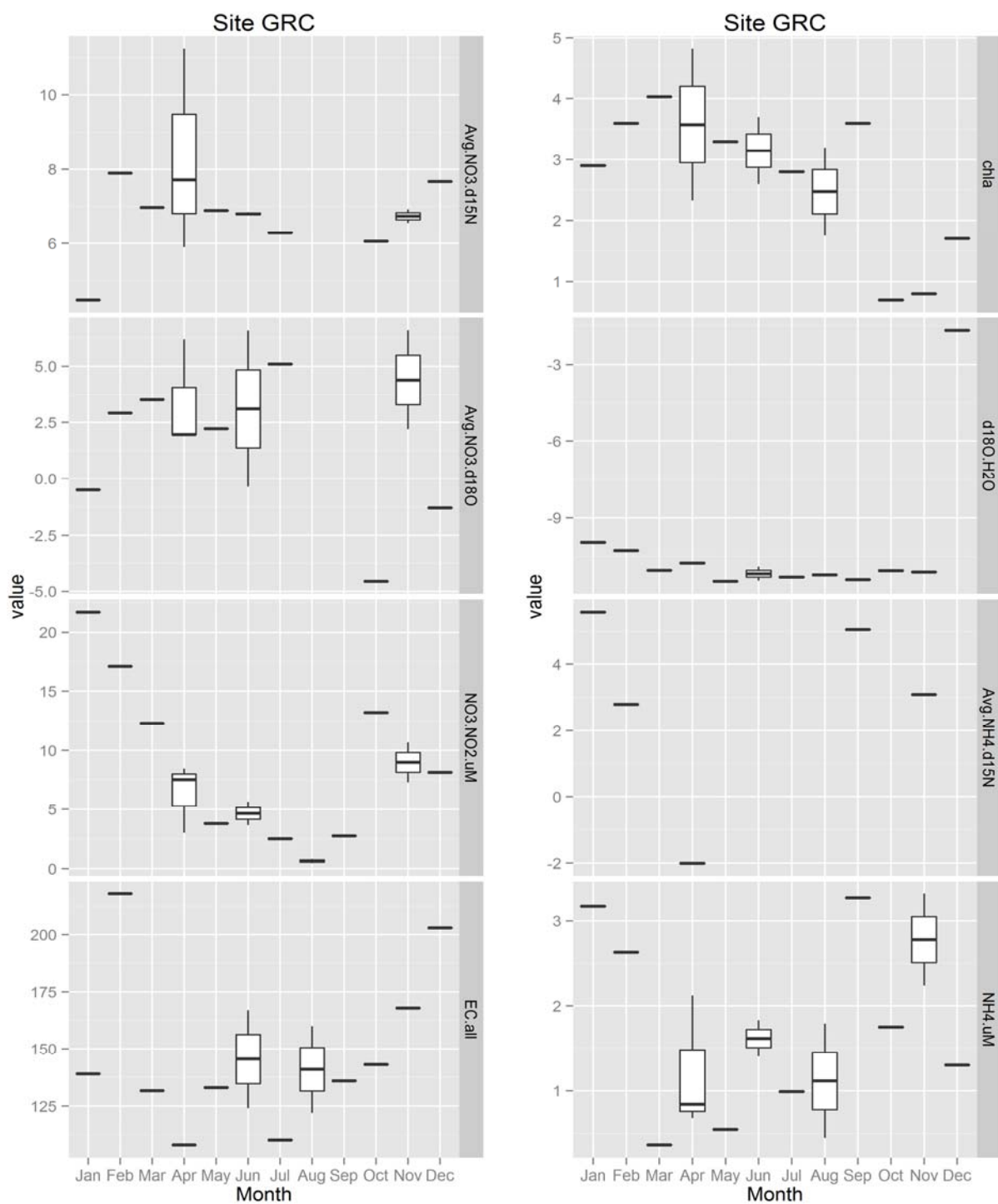


Figure 5.2.30. Chemical and isotopic data plotted by month for Garcia Bend in the Sacramento River. Samples collected from 2009-2010.

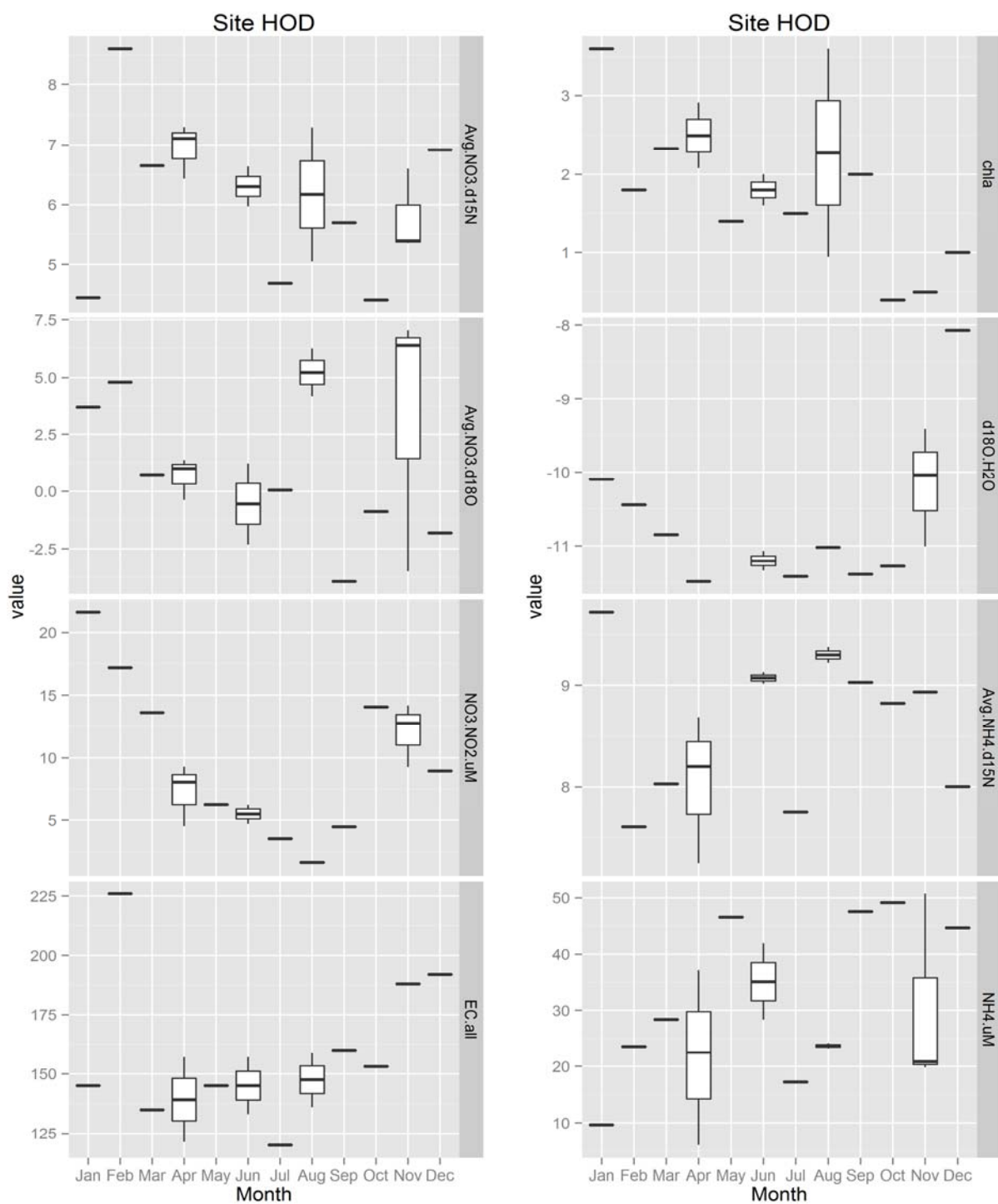


Figure 5.2.31. Chemical and isotopic data plotted by month for Hood in the Sacramento River. Samples collected from 2009-2010.

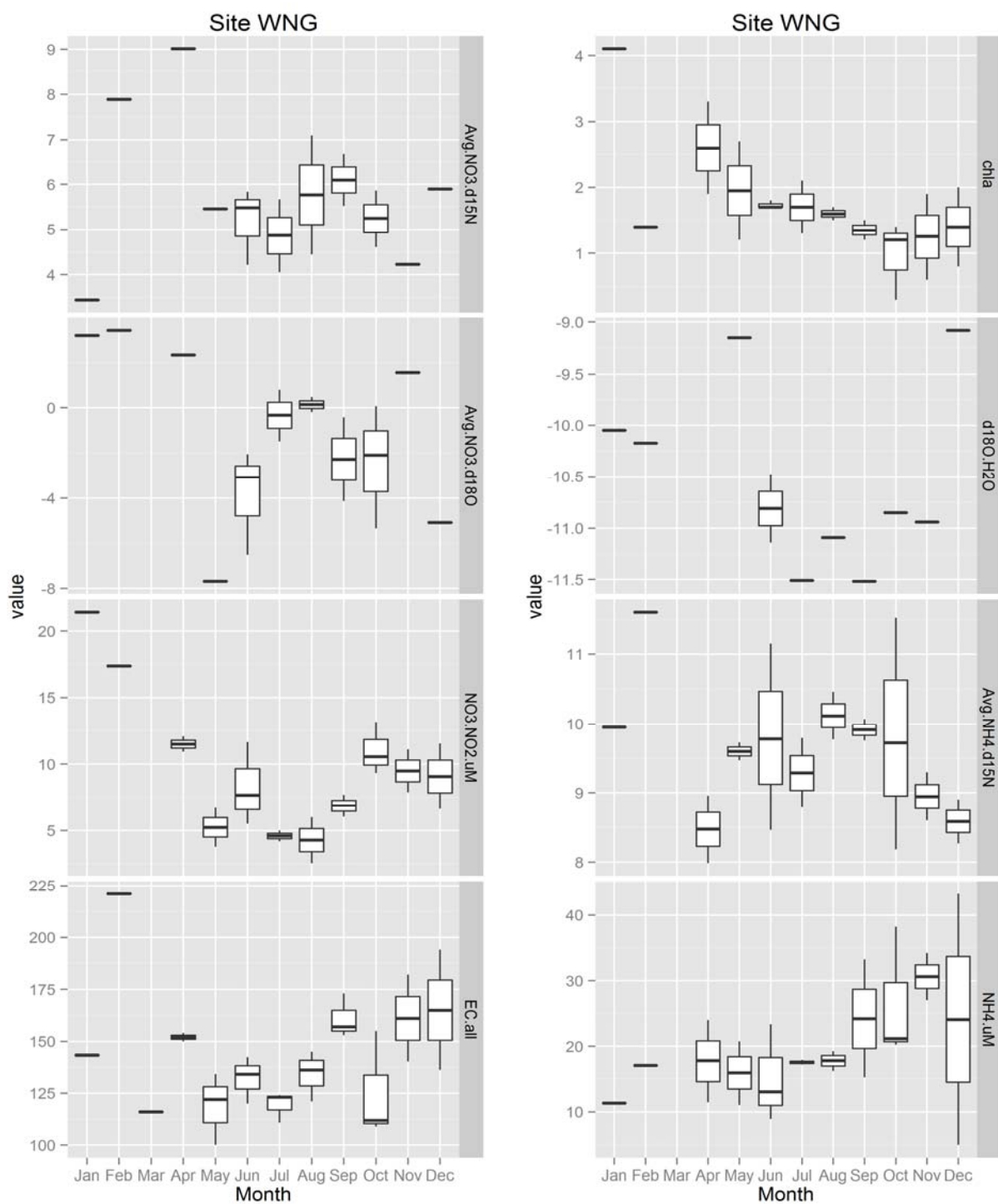


Figure 5.2.32. Chemical and isotopic data plotted by month for Walnut Grove in the Sacramento River. Samples collected from 2009-2010.

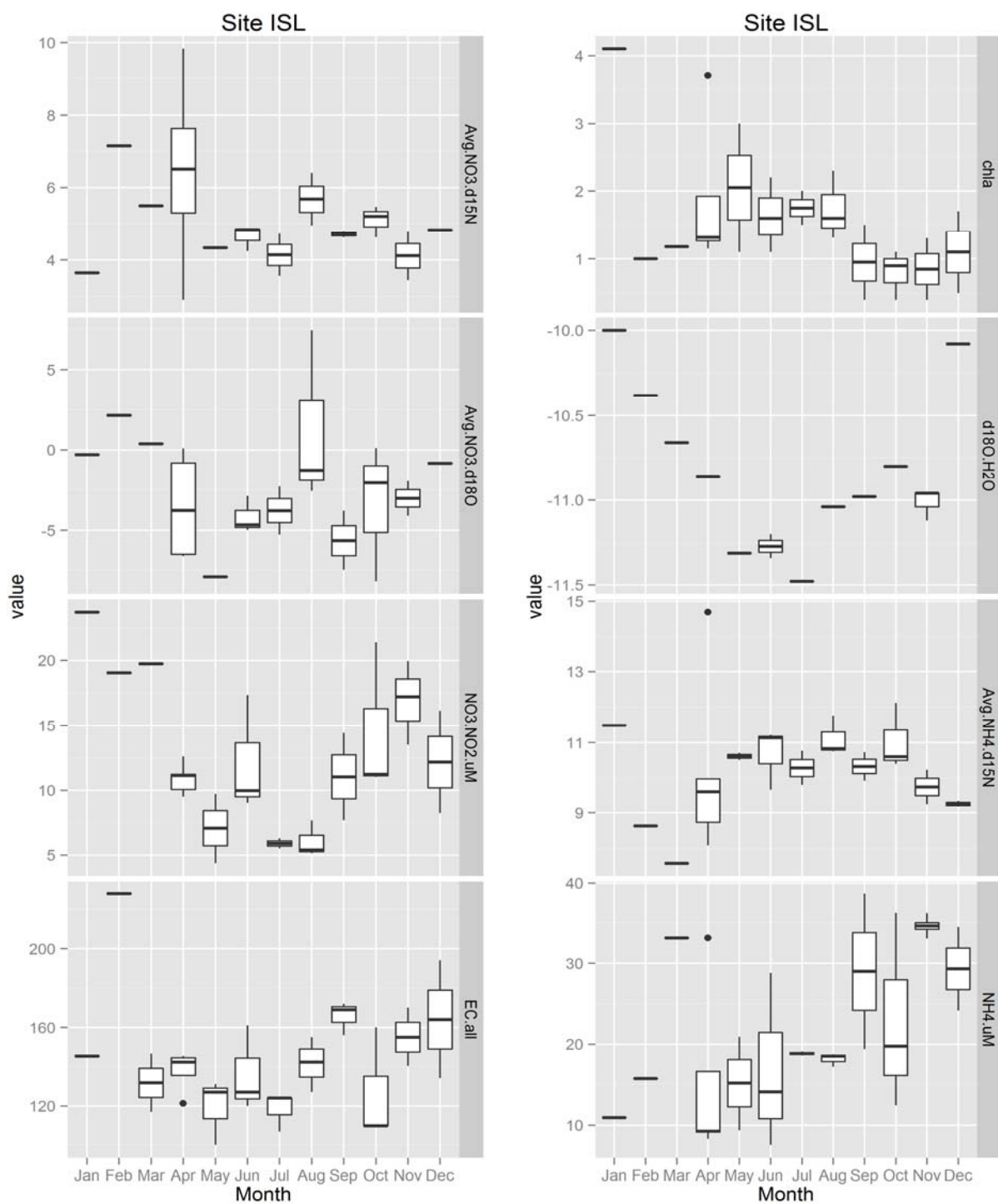


Figure 5.2.33. Chemical and isotopic data plotted by month for Isleton in the Sacramento River. Samples collected from 2009-2011.

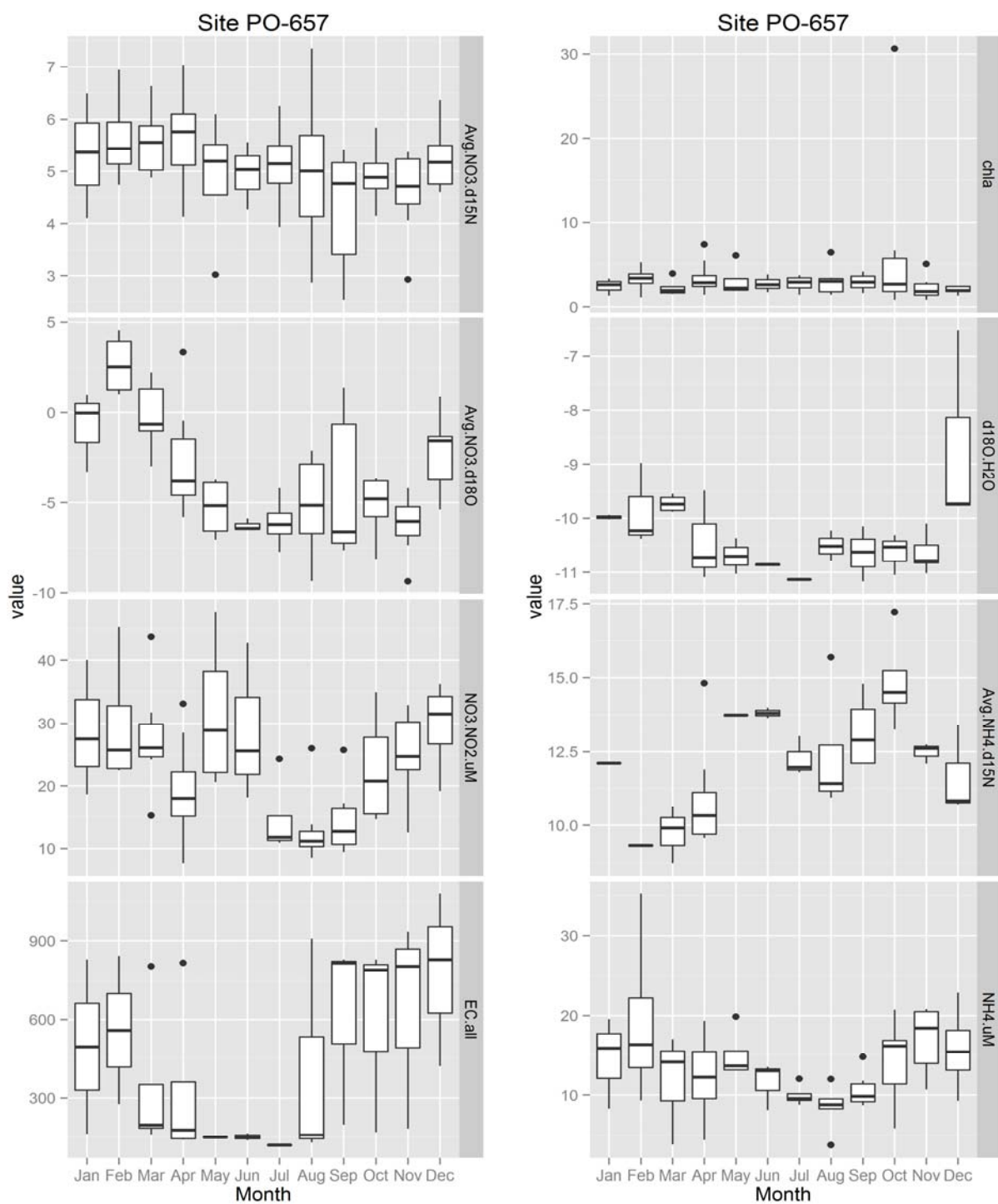


Figure 5.2.34. Chemical and isotopic data plotted by month for Rio Vista (PO-657) in the Sacramento River. Samples collected from 2006-2010.

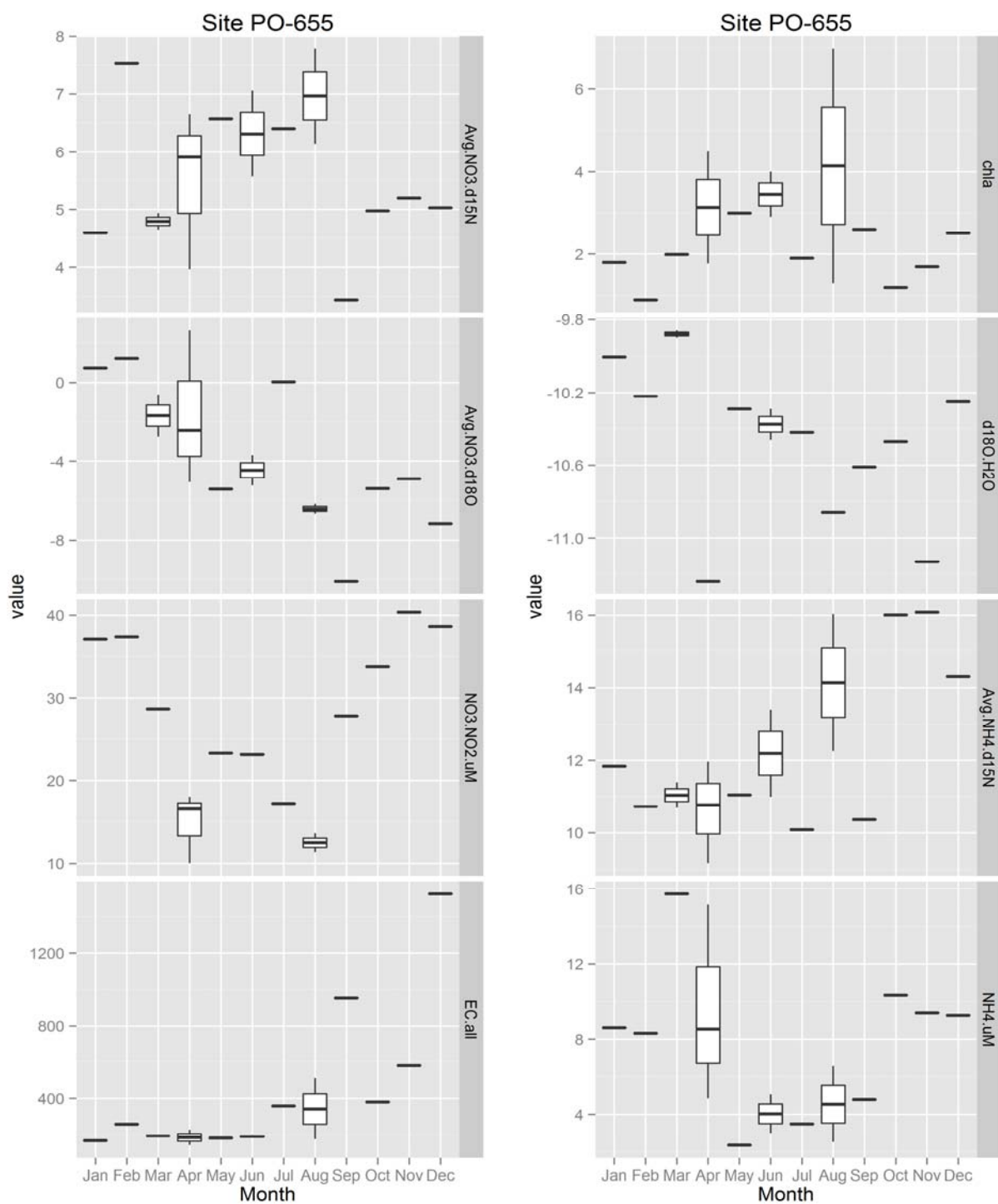


Figure 5.2.35. Chemical and isotopic data plotted by month for Three Mile Slough (PO-655) in the Sacramento River. Samples collected from 2006-2010.

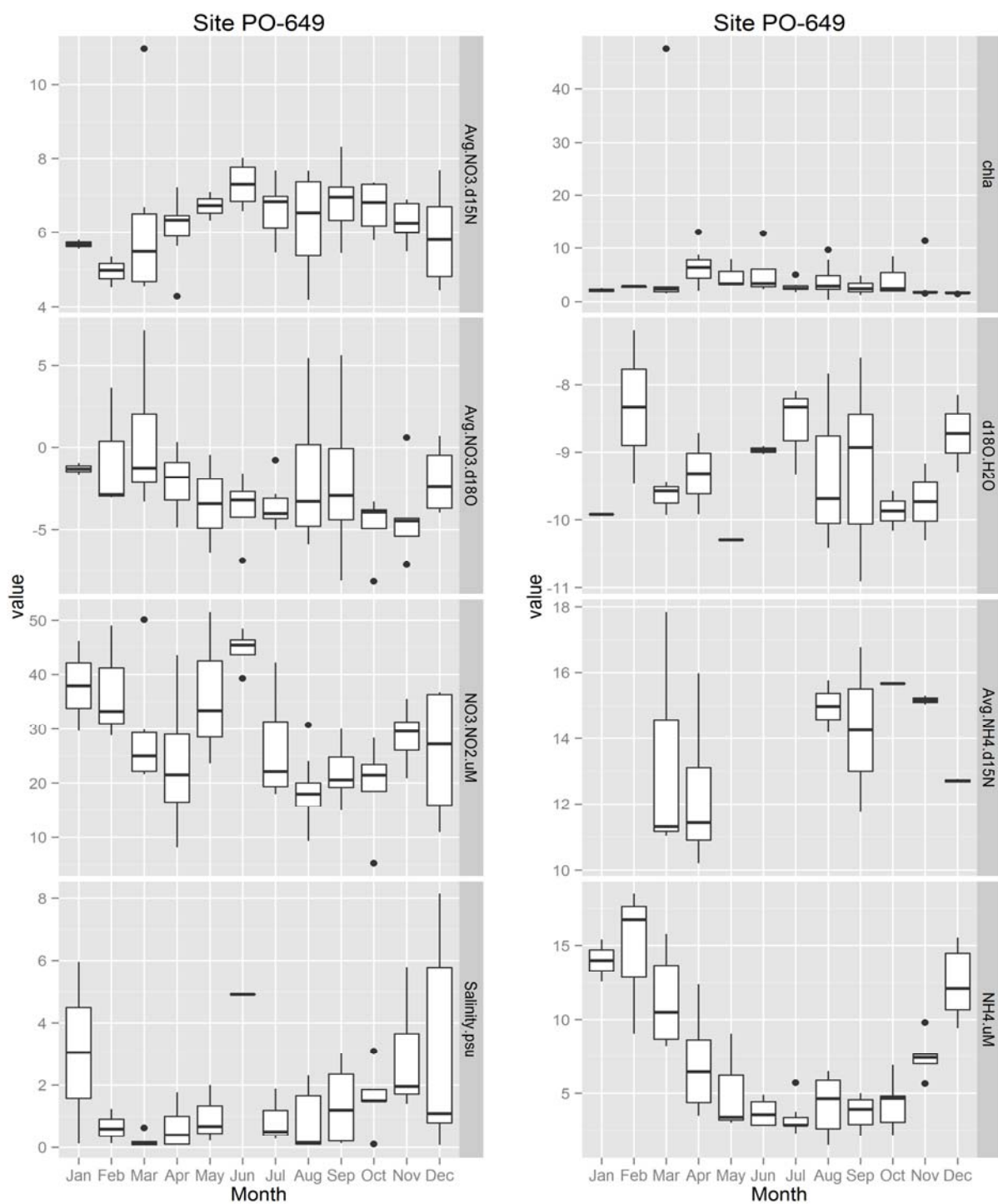


Figure 5.2.36. Chemical and isotopic data plotted by month for Pt. Sacramento (PO-649) in the Sacramento River. Samples collected from 2006-2010. Note substitution of salinity for EC.

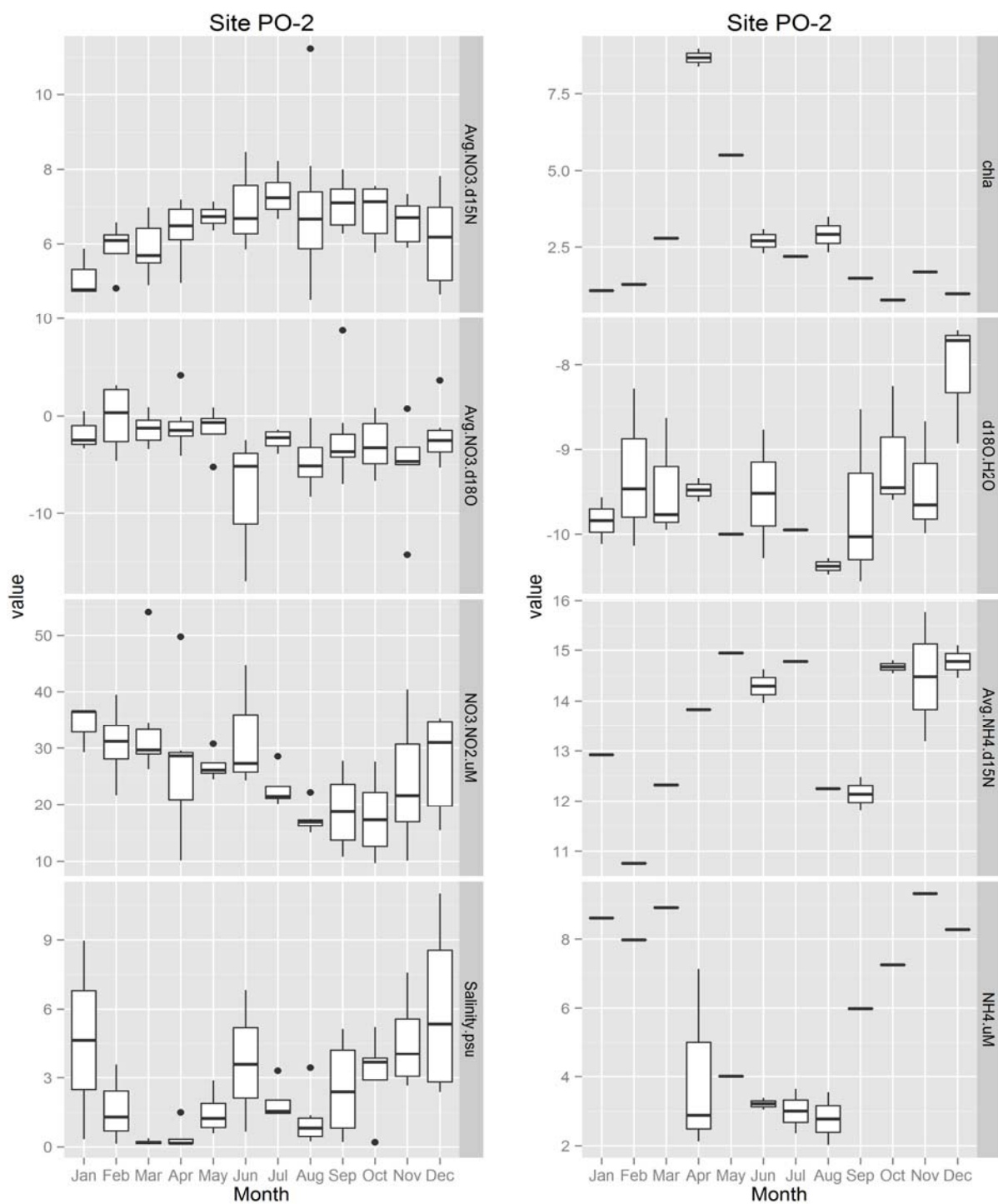


Figure 5.2.37. Chemical and isotopic data plotted by month for Chain Is. (PO-2) at the confluence of the Sacramento and San Joaquin Rivers. Samples collected from 2006-2010. Note substitution of salinity for EC.

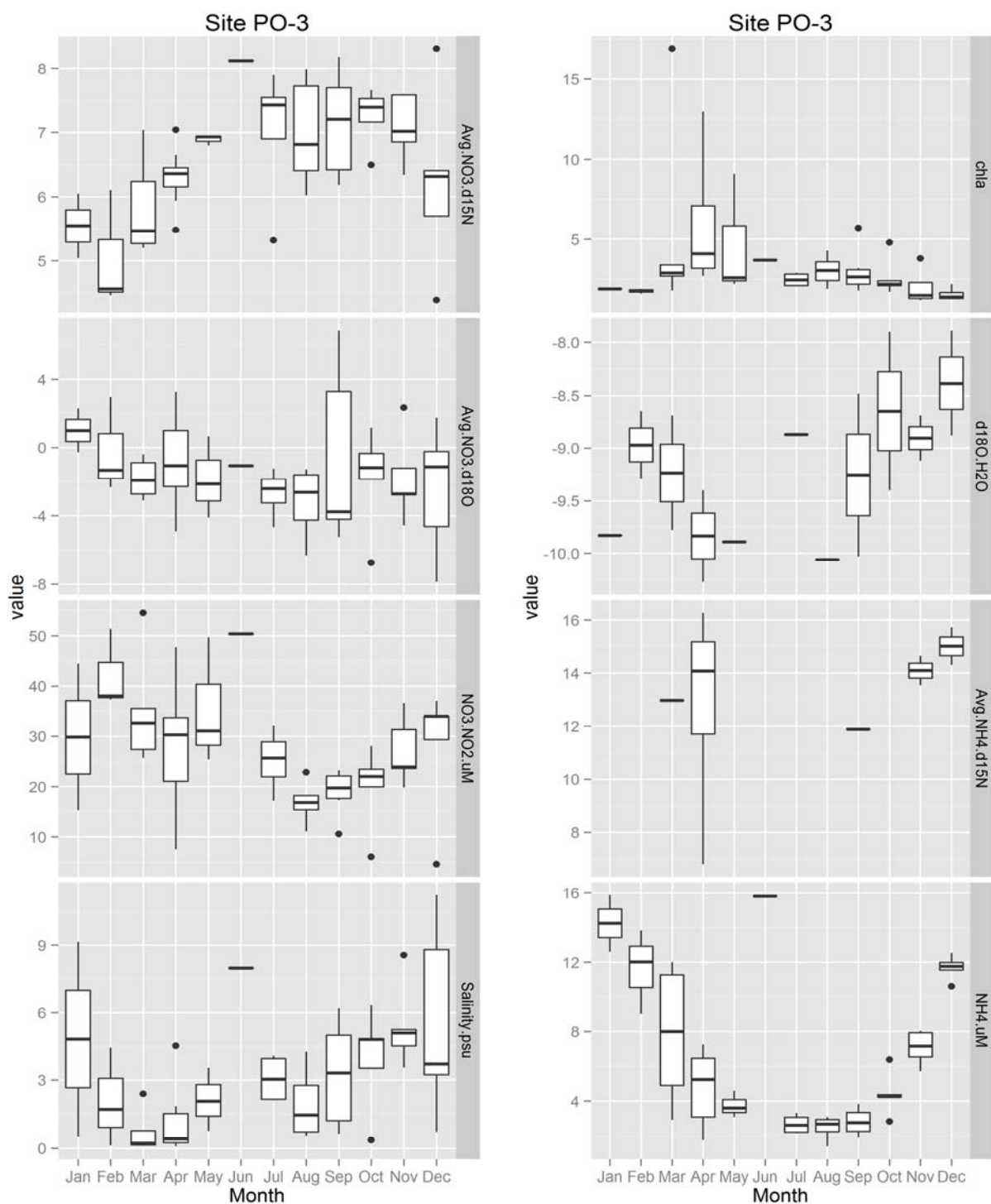


Figure 5.2.38. Chemical and isotopic data plotted by month for Pittsburgh (PO-3) in the San Francisco Bay. Samples collected from 2006-2010. Note substitution of salinity for EC.

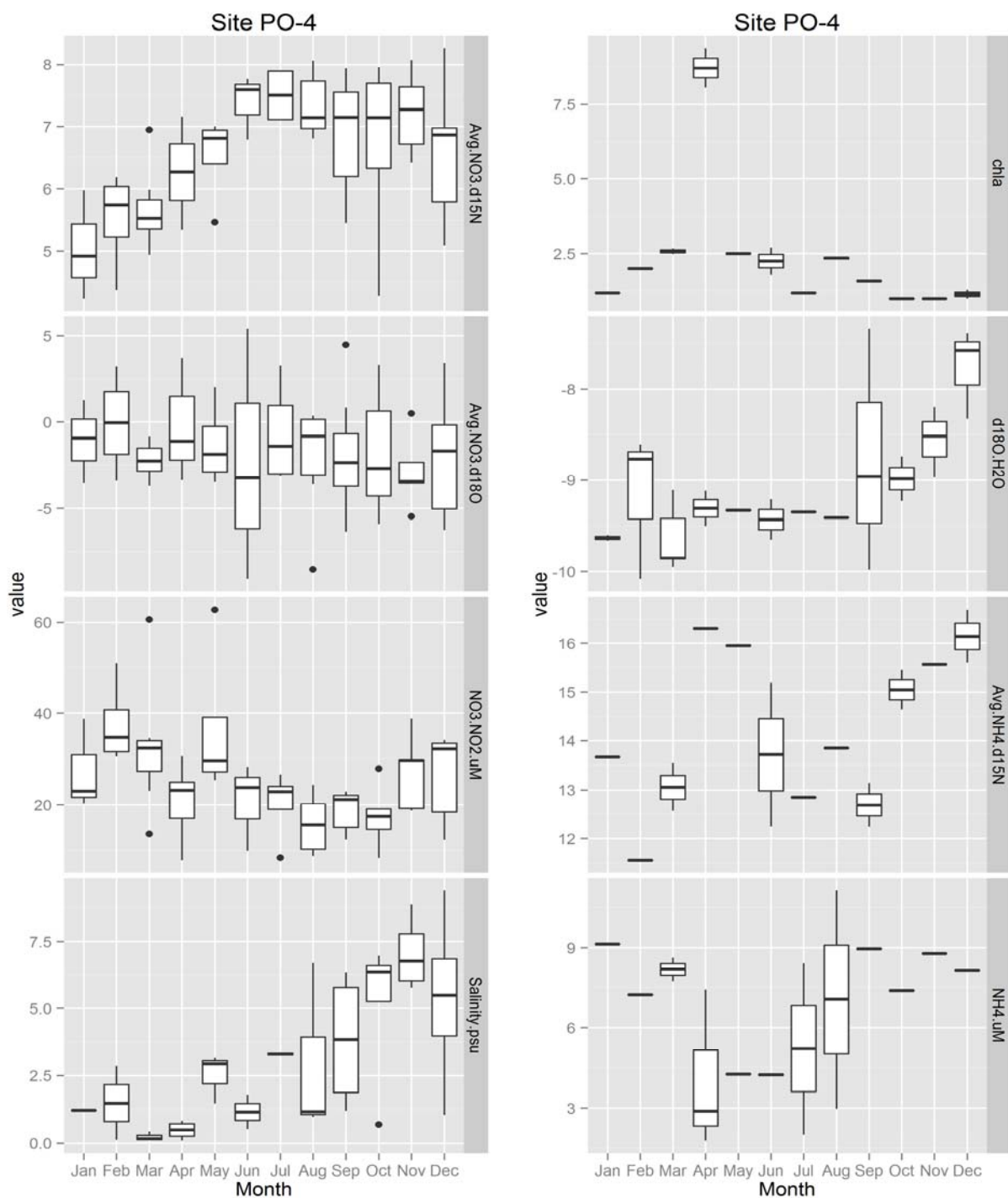


Figure 5.2.39. Chemical and isotopic data plotted by month for Chipps Island (PO-4) in the San Francisco Bay. Samples collected from 2006-2010. Note substitution of salinity for EC.

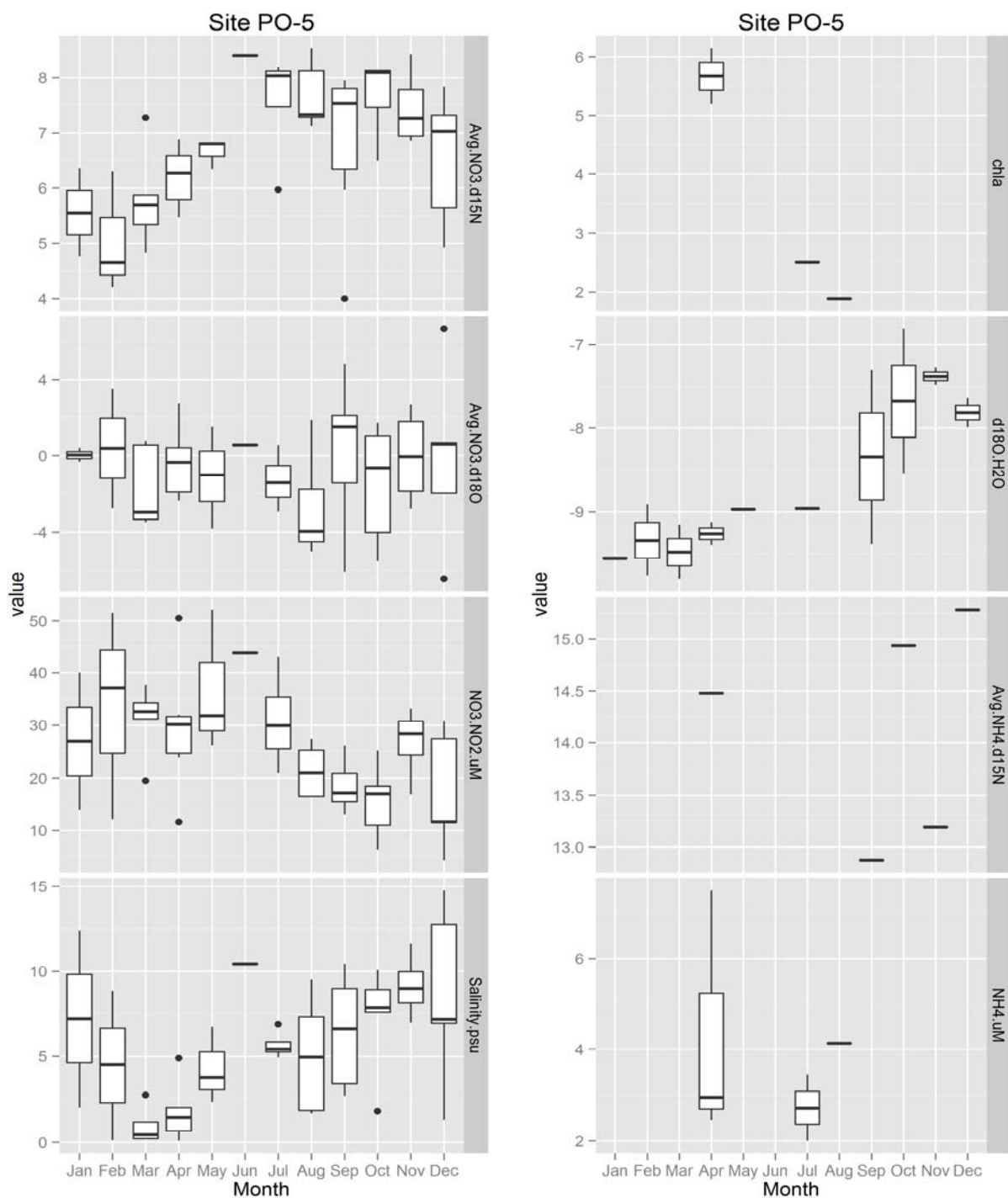


Figure 5.2.40. Chemical and isotopic data plotted by month for Middle Ground (PO-5) in the San Francisco Bay. Samples collected from 2006-2010. Note substitution of salinity for EC.

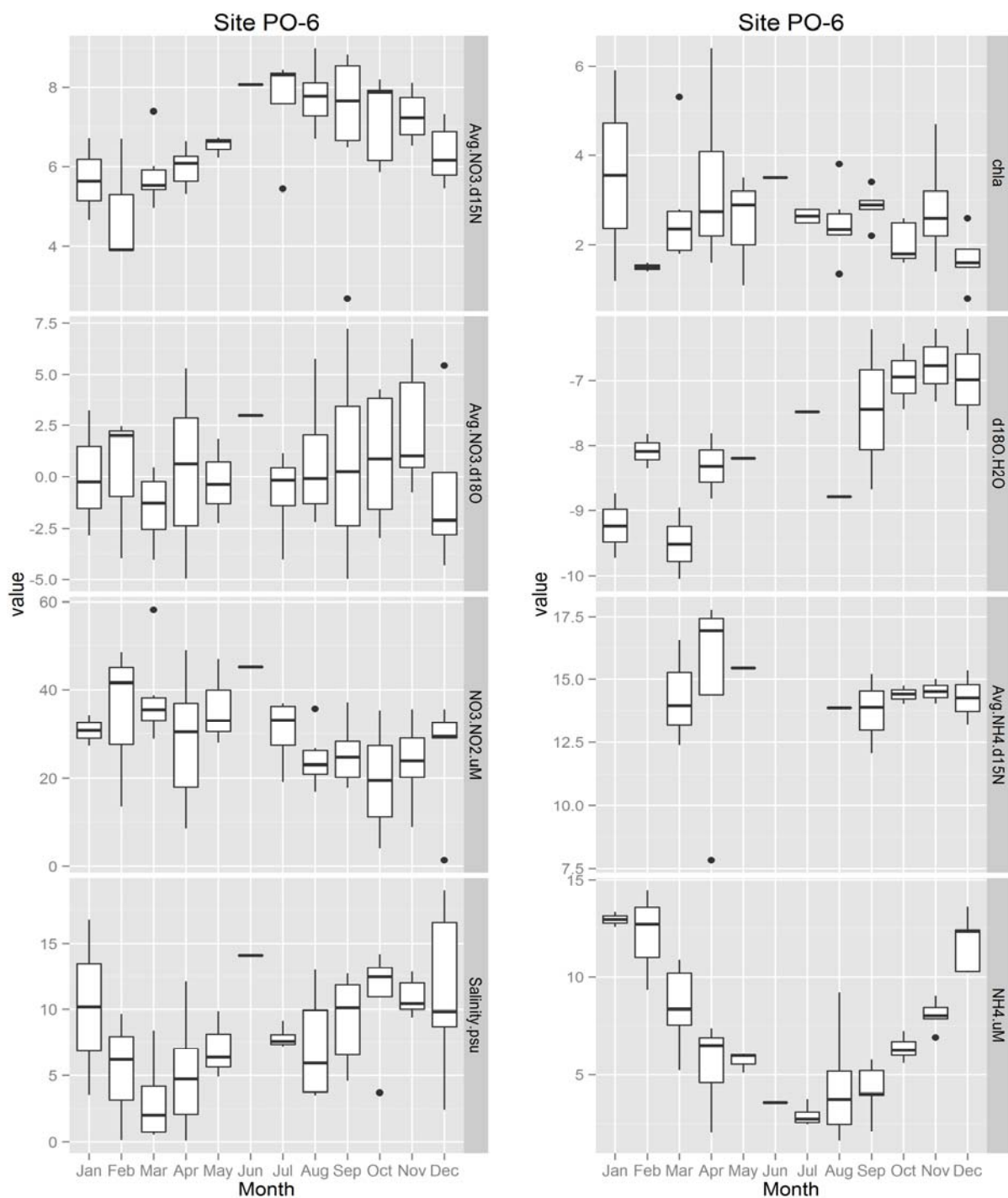


Figure 5.2.41. Chemical and isotopic data plotted by month for Roe Is. (PO-6) in the San Francisco Bay. Samples collected from 2006-2010. Note substitution of salinity for EC.

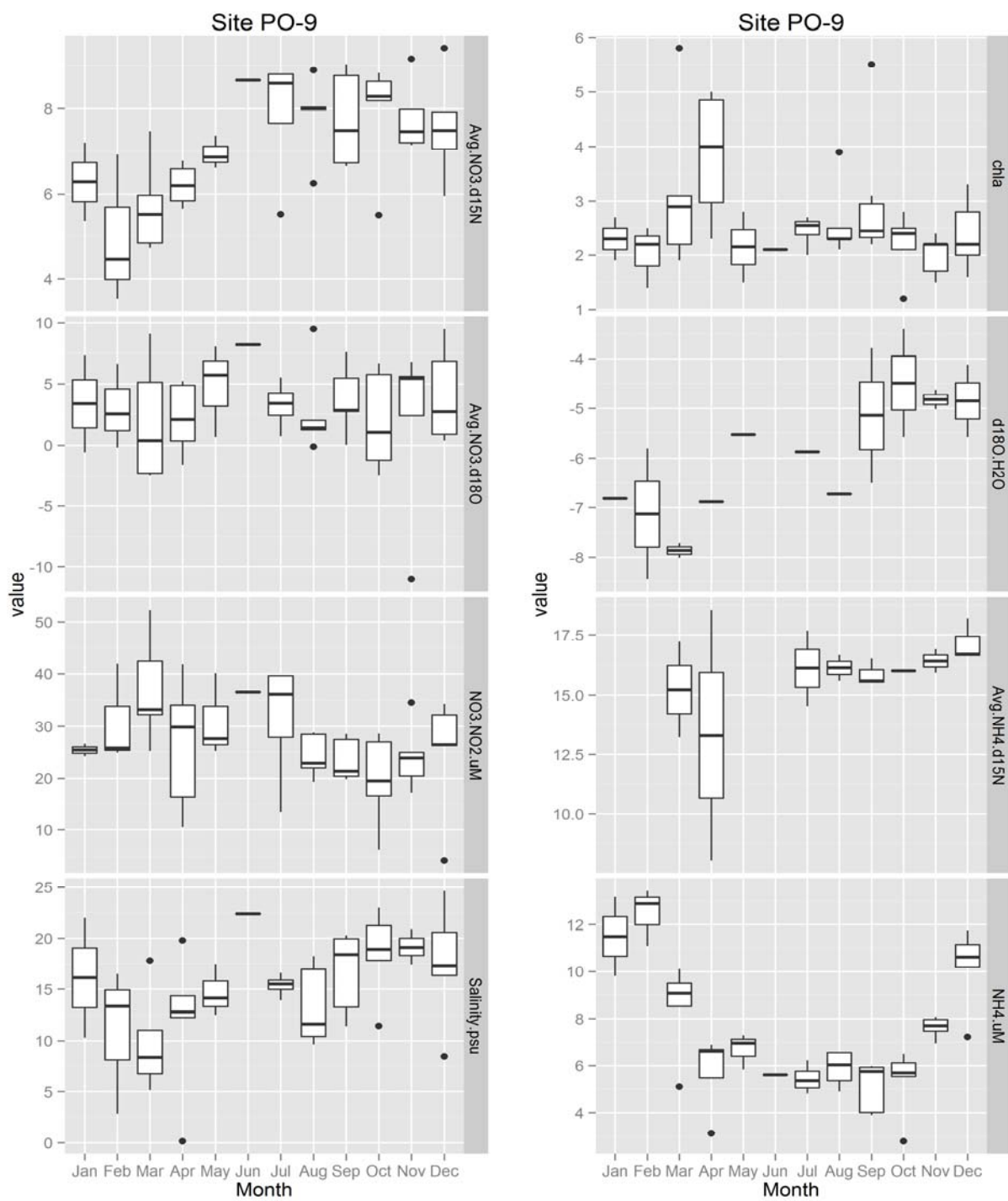


Figure 5.2.42. Chemical and isotopic data plotted by month for Avon Pier (PO-9) in the San Francisco Bay. Samples collected from 2006-2010. Note substitution of salinity for EC.

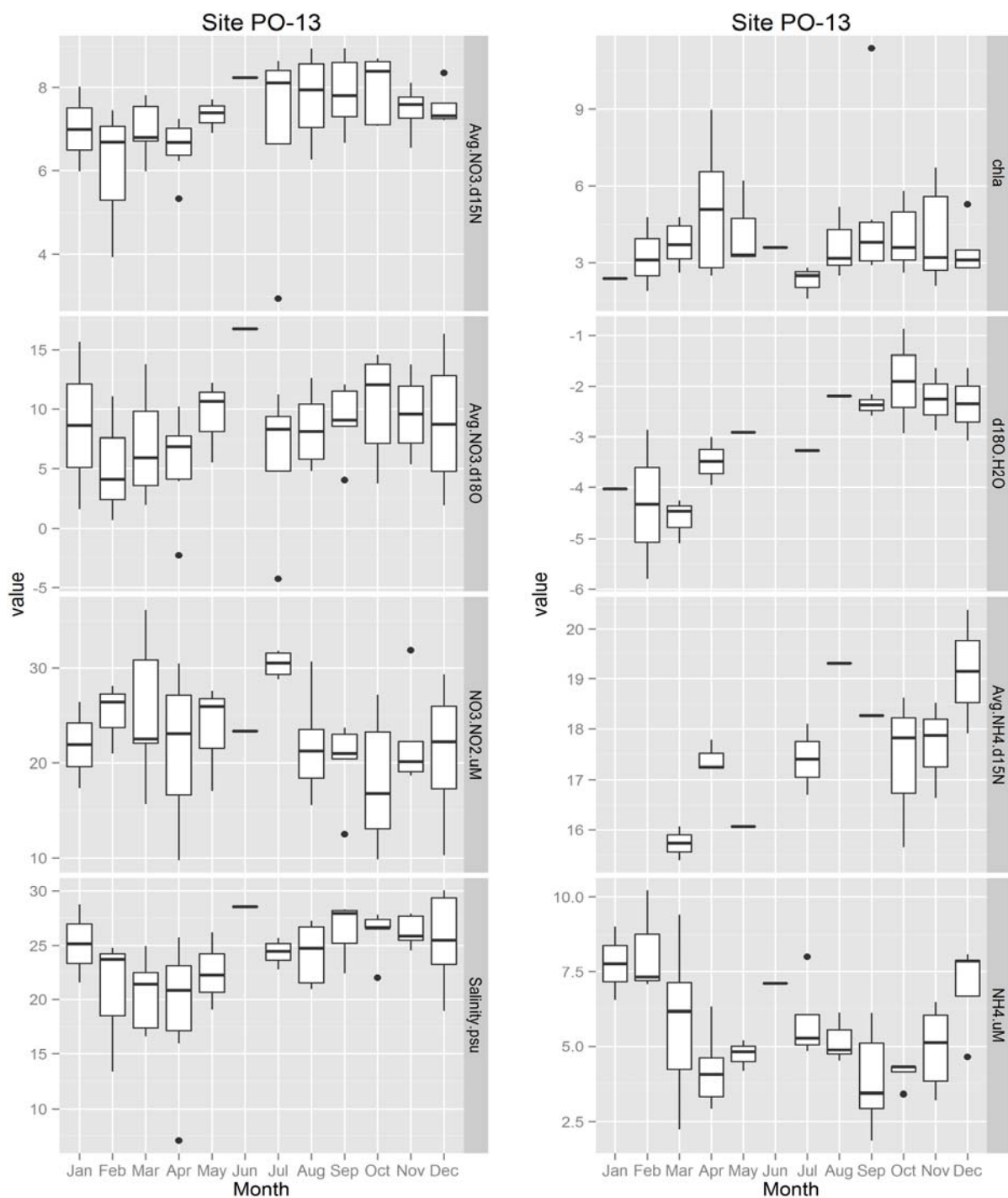


Figure 5.2.43. Chemical and isotopic data plotted by month for north of Pinole Point (PO-13) in the San Francisco Bay. Samples collected from 2006-2010. Note substitution of salinity for EC.

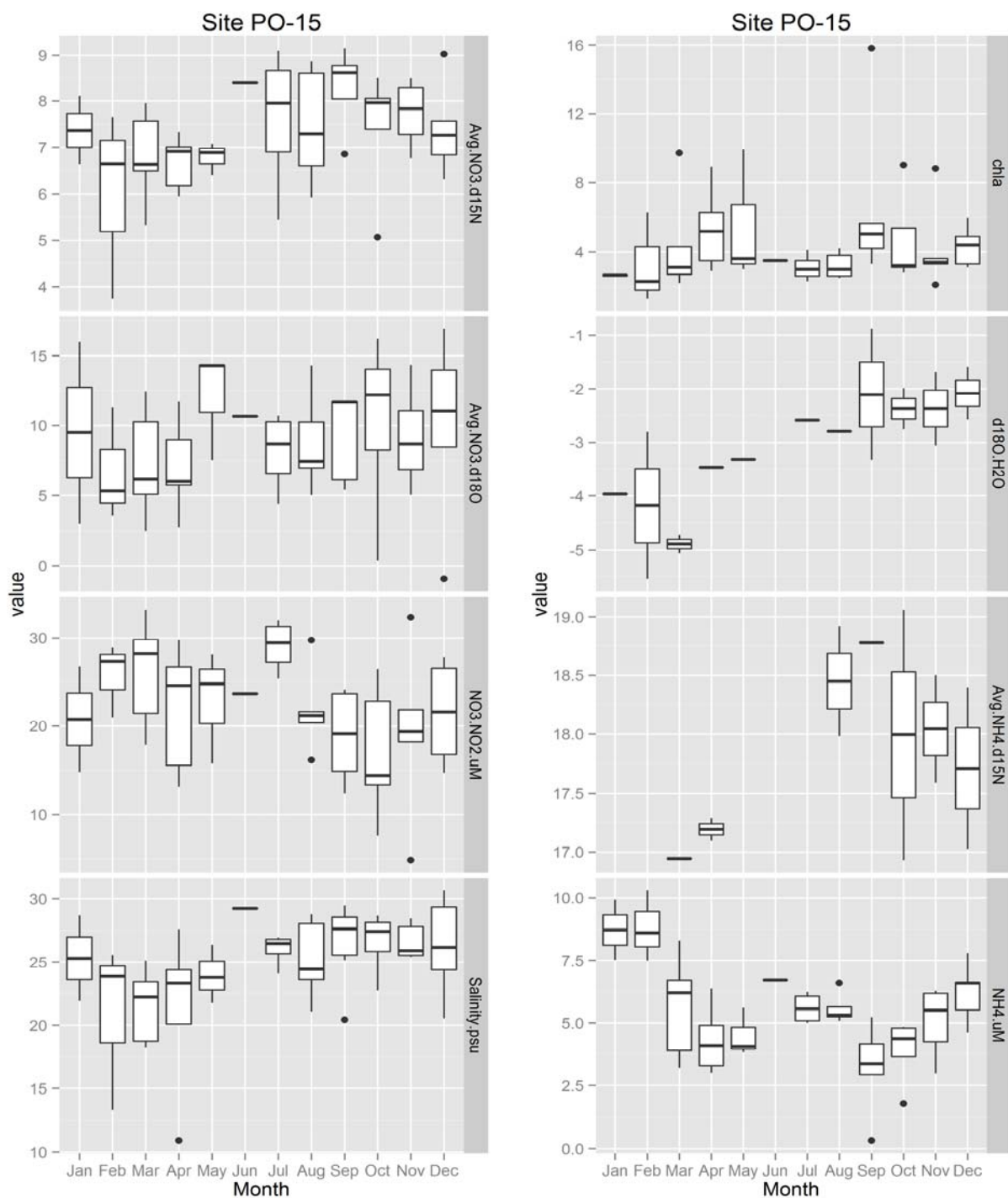


Figure 5.2.44. Chemical and isotopic data plotted by month for Pt. San Pablo (PO-15) in the San Francisco Bay. Samples collected from 2006-2010. Note substitution of salinity for EC.

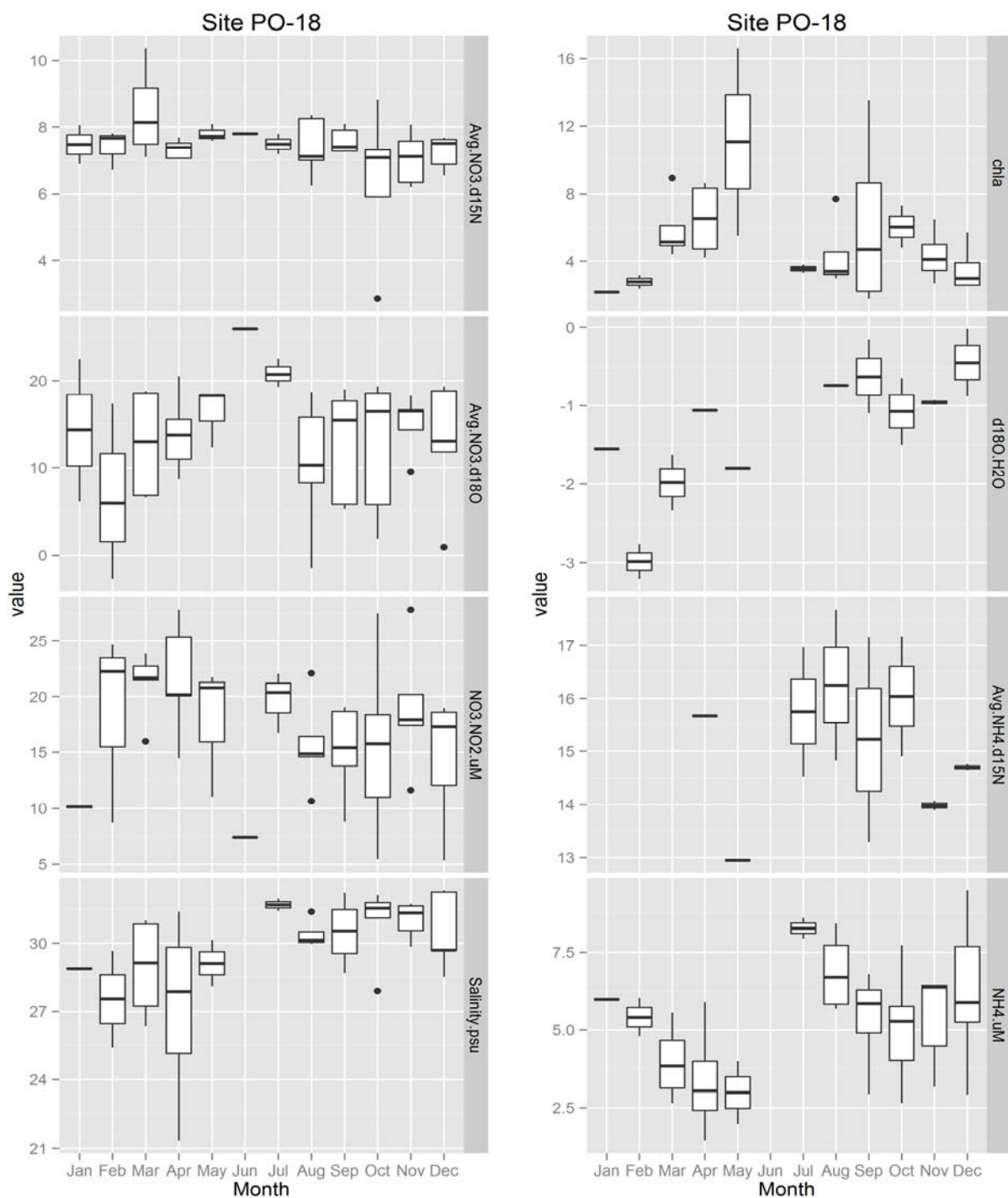


Figure 5.2.45. Chemical and isotopic data plotted by month for Angel Island (PO-18) in the San Francisco Bay. Samples collected from 2006-2010. Note substitution of salinity for EC.

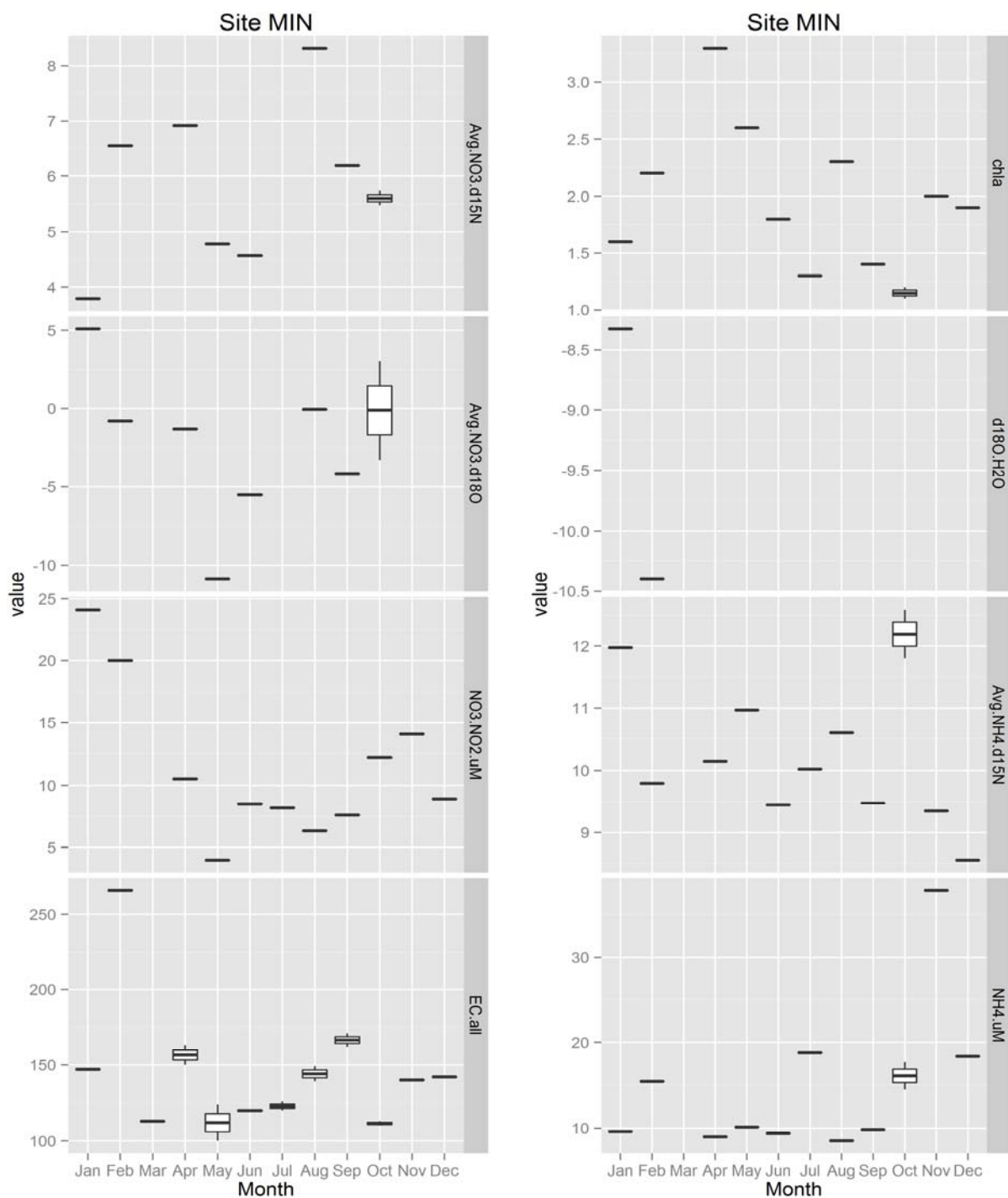


Figure 5.2.46. Chemical and isotopic data plotted by month for Miner Slough near the Sacramento River. Samples collected from 2010-2011.

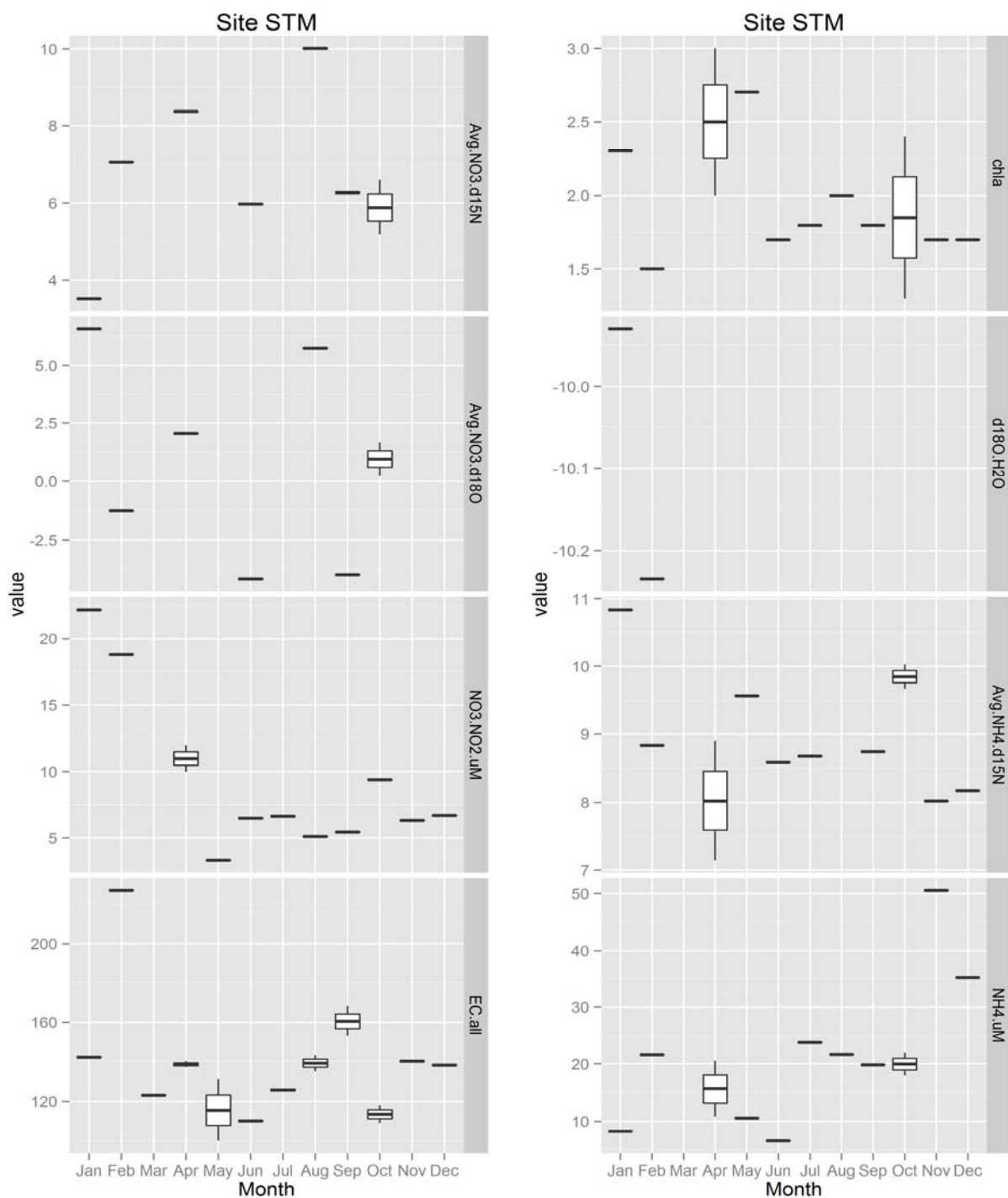


Figure 5.2.47. Chemical and isotopic data plotted by month for Steamboat Slough near the Sacramento River. Samples collected from 2010-2011.

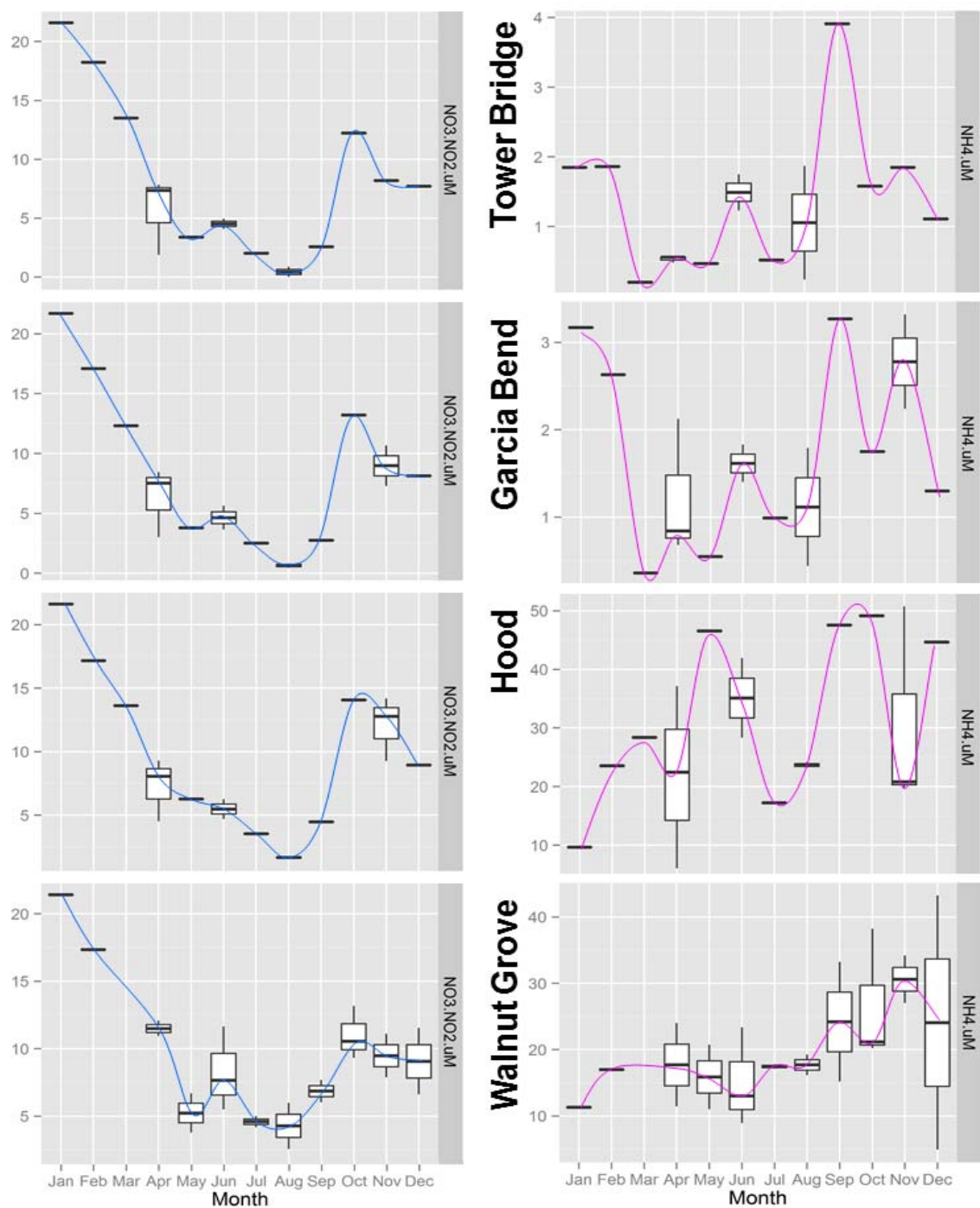


Figure 5.2.48. Seasonal variation in the concentrations of NH_4 and NO_3 at adjacent sites in the Sacramento River (Tower Bridge downstream to Walnut Grove).

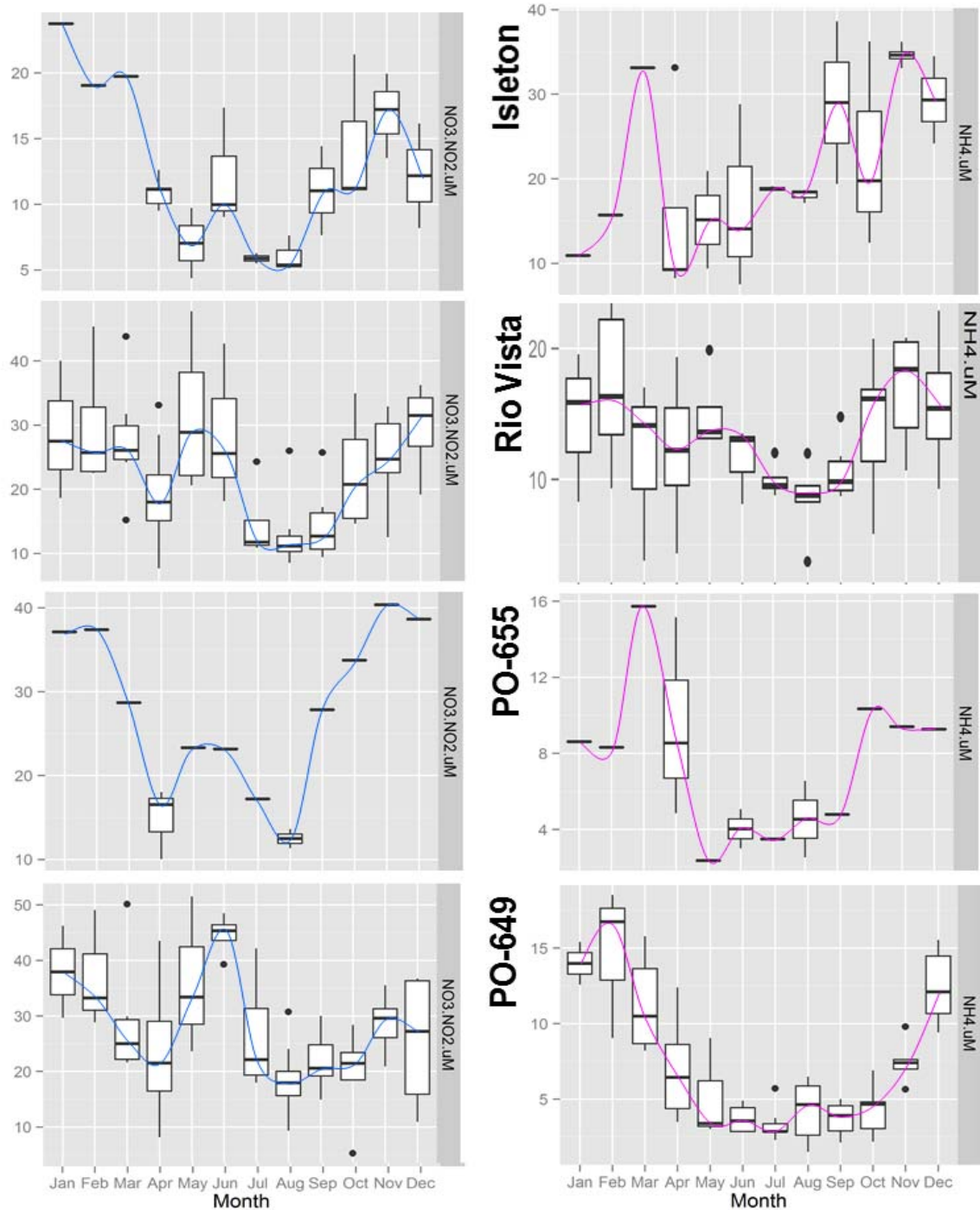


Figure 5.2.49. Seasonal variation in the concentrations of NH_4 and NO_3 at adjacent sites in the Sacramento River (Isleton downstream to PO-649)..

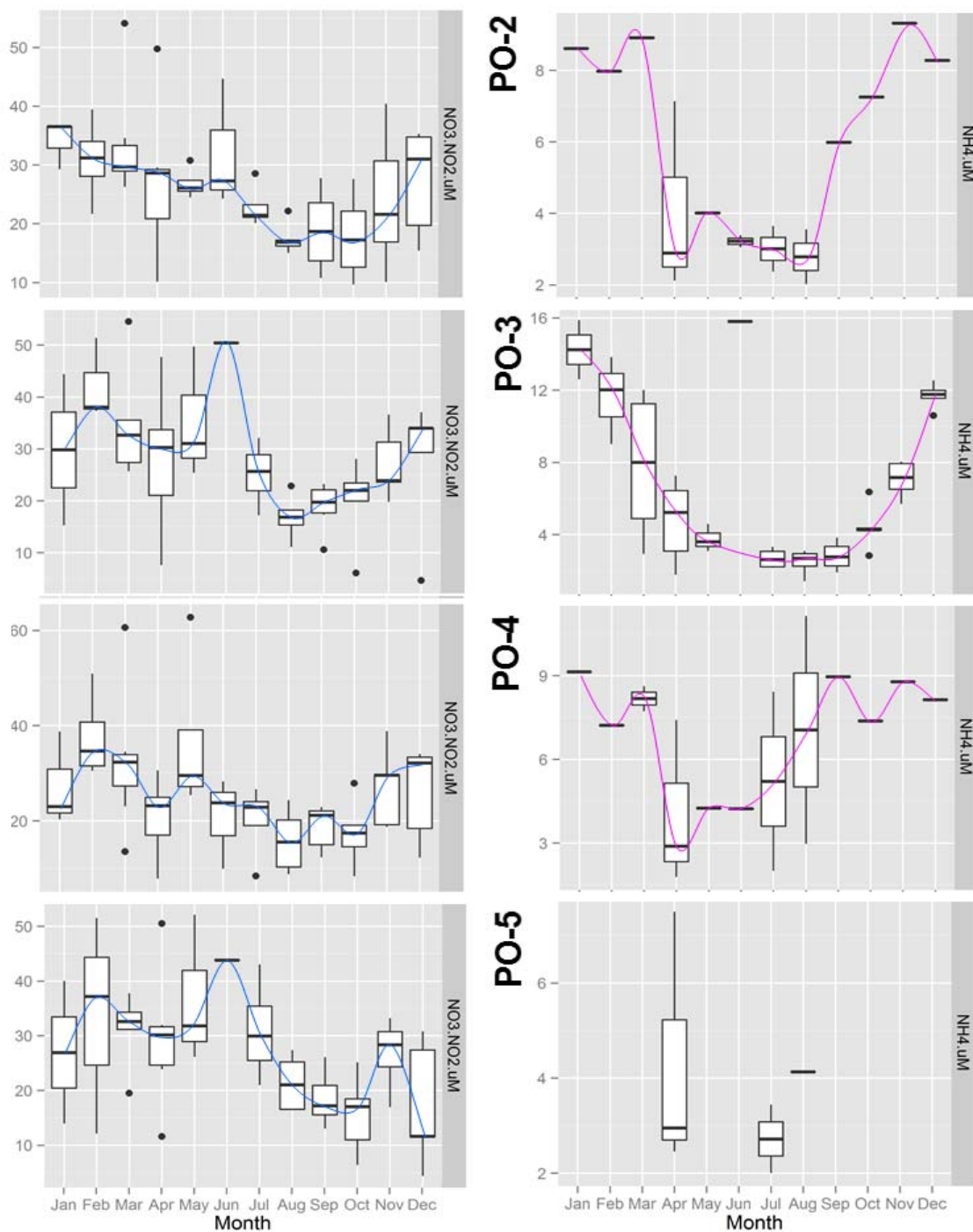


Figure 5.2.50. Seasonal variation in the concentrations of NH₄ and NO₃ at adjacent sites in the Sacramento River Delta (PO-2 downstream to PO-5).

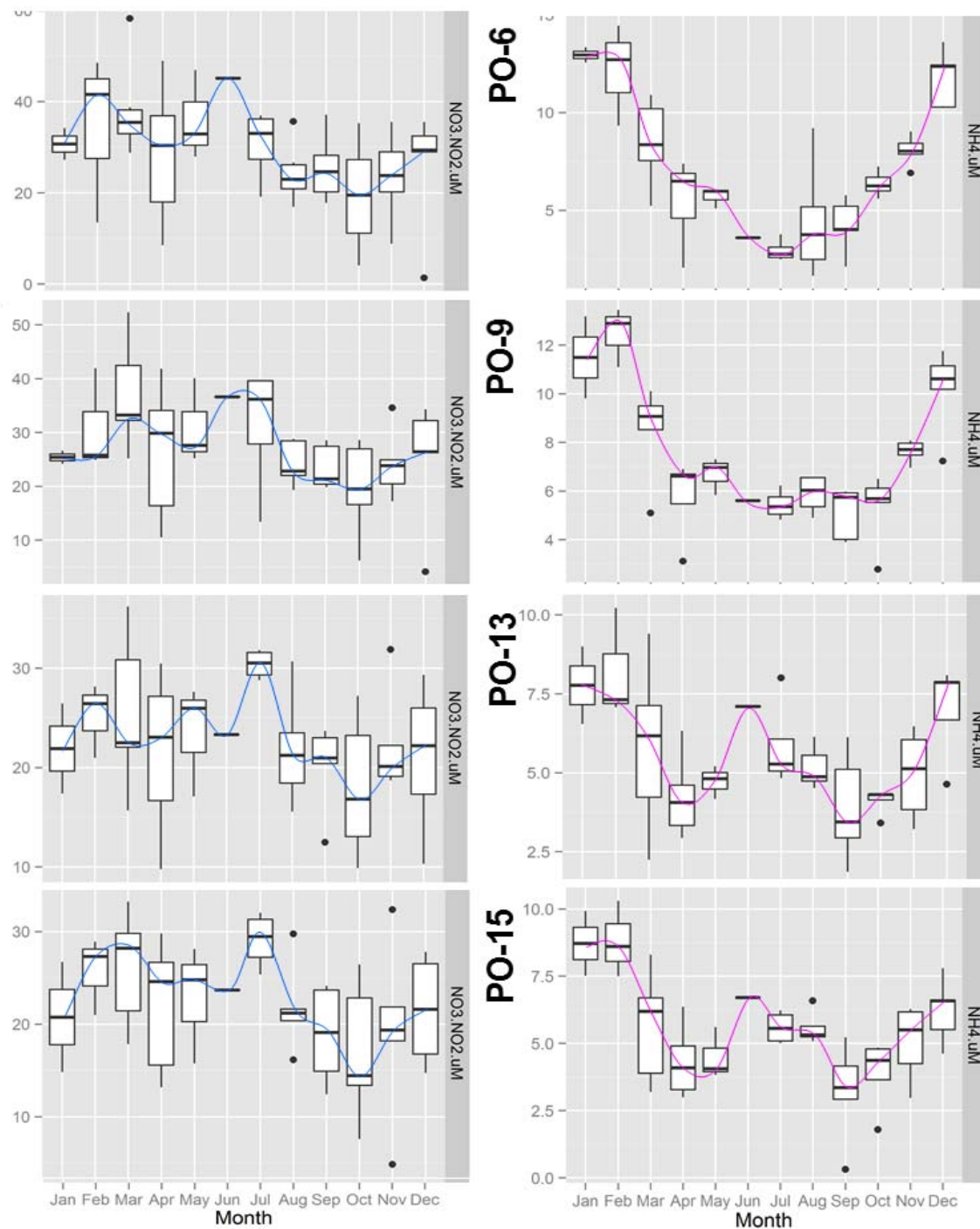


Figure 5.2.51. Seasonal variation in the concentrations of NH₄ and NO₃ at adjacent sites in the Delta and Bay (PO-6 downstream to PO-15).

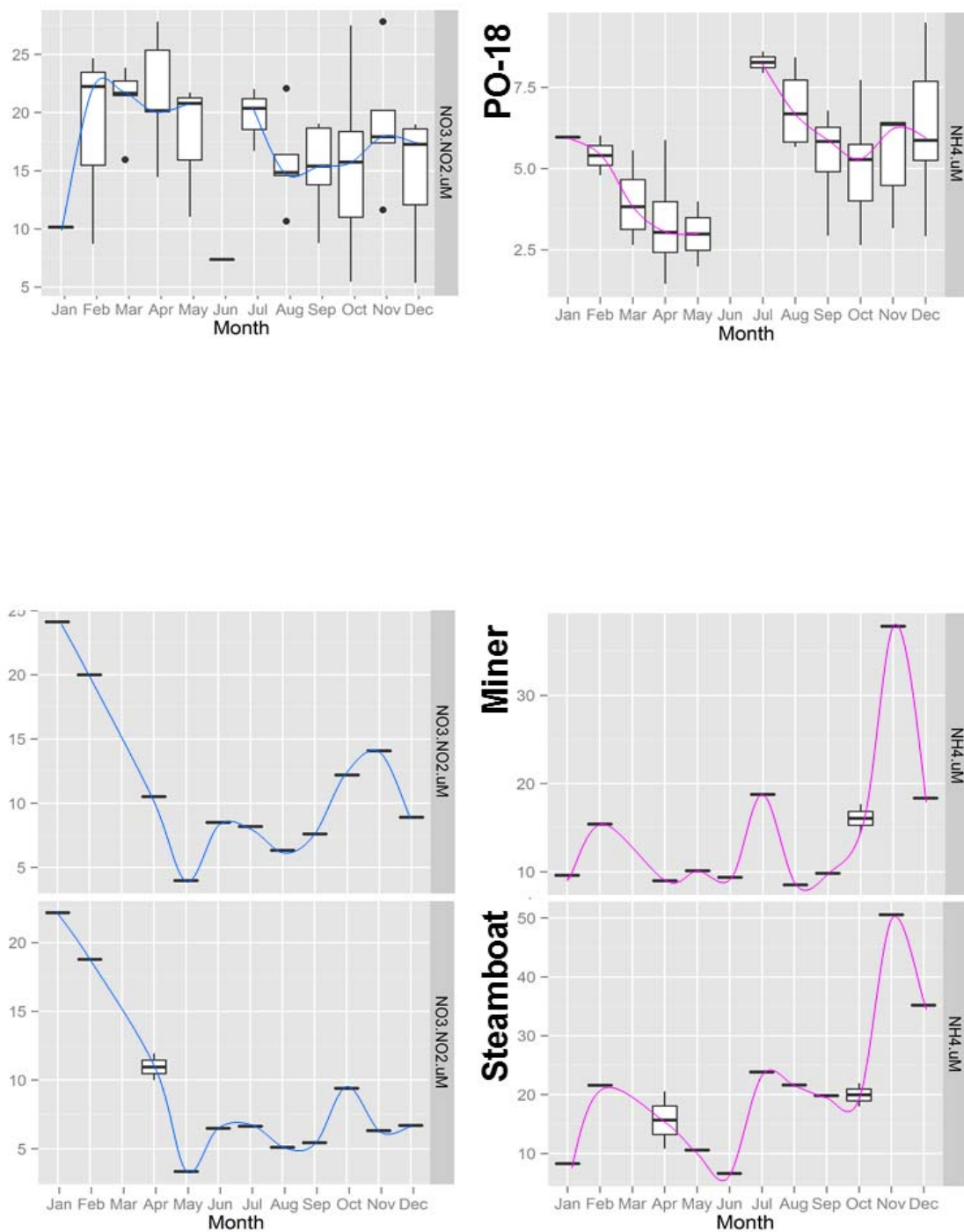


Figure 5.2.52. Seasonal variation in the concentrations of NH_4 and NO_3 at PO-18 and at Miner and Steamboat Sloughs.

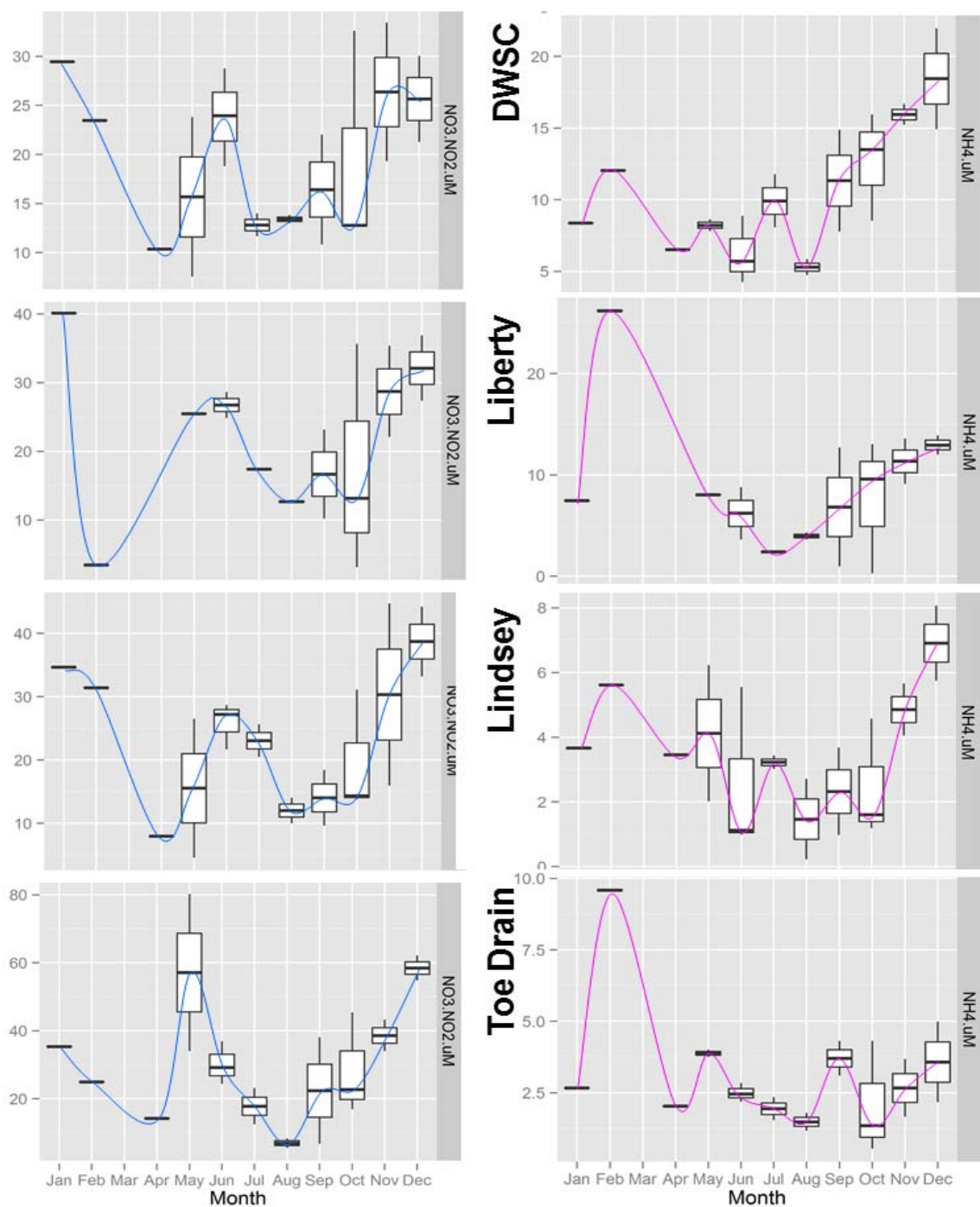


Figure 5.2.53. Seasonal variation in the concentrations of NH_4 and NO_3 at 4 tributary sites in the Cache/Yolo Slough Complex in the Sacramento River.

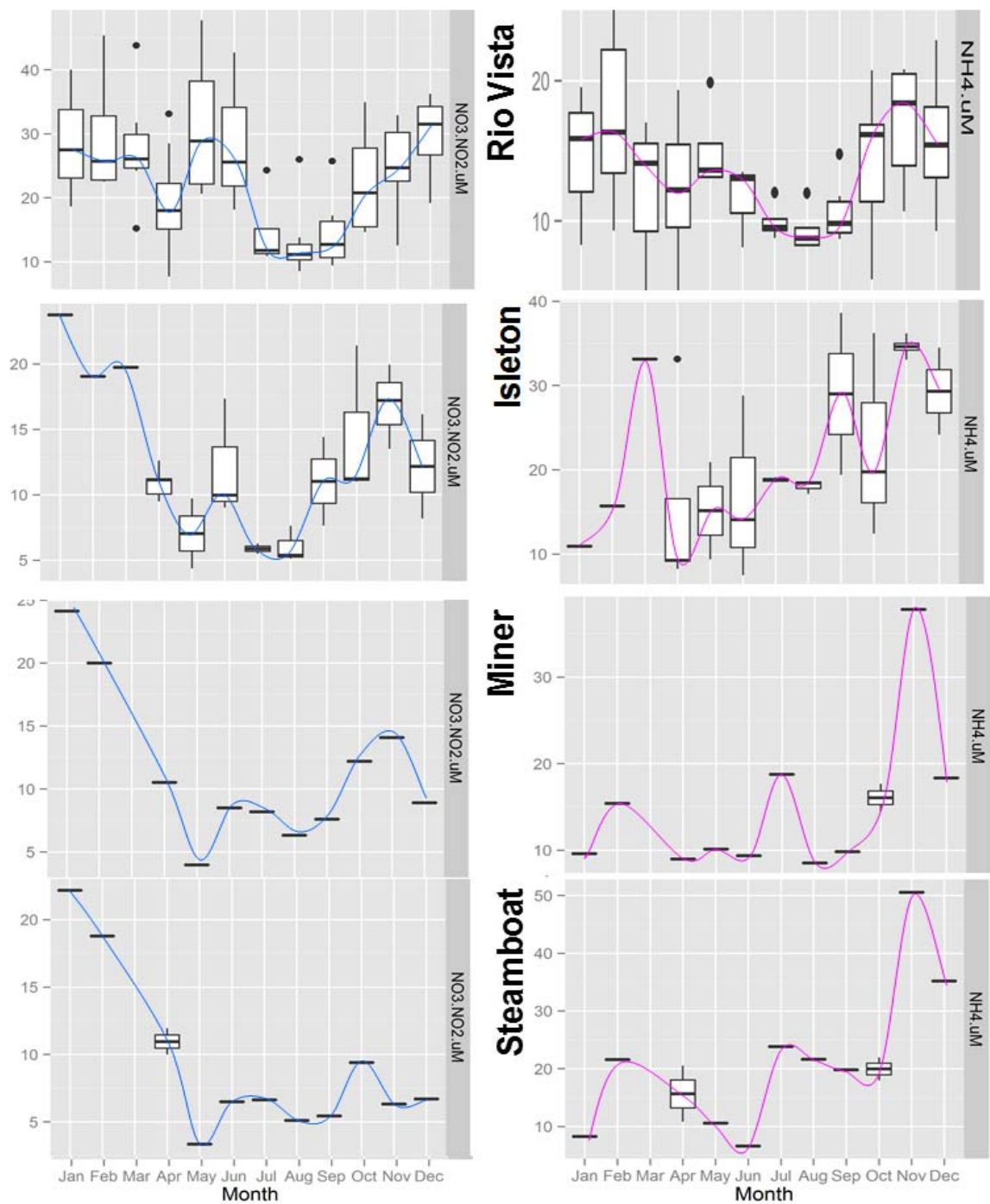


Figure 5.2.54. Seasonal variation in the concentrations of NH₄ and NO₃ at nearby sites in the Sacramento River (Rio Vista, Isleton, Miner Slough, and Steamboat Slough).

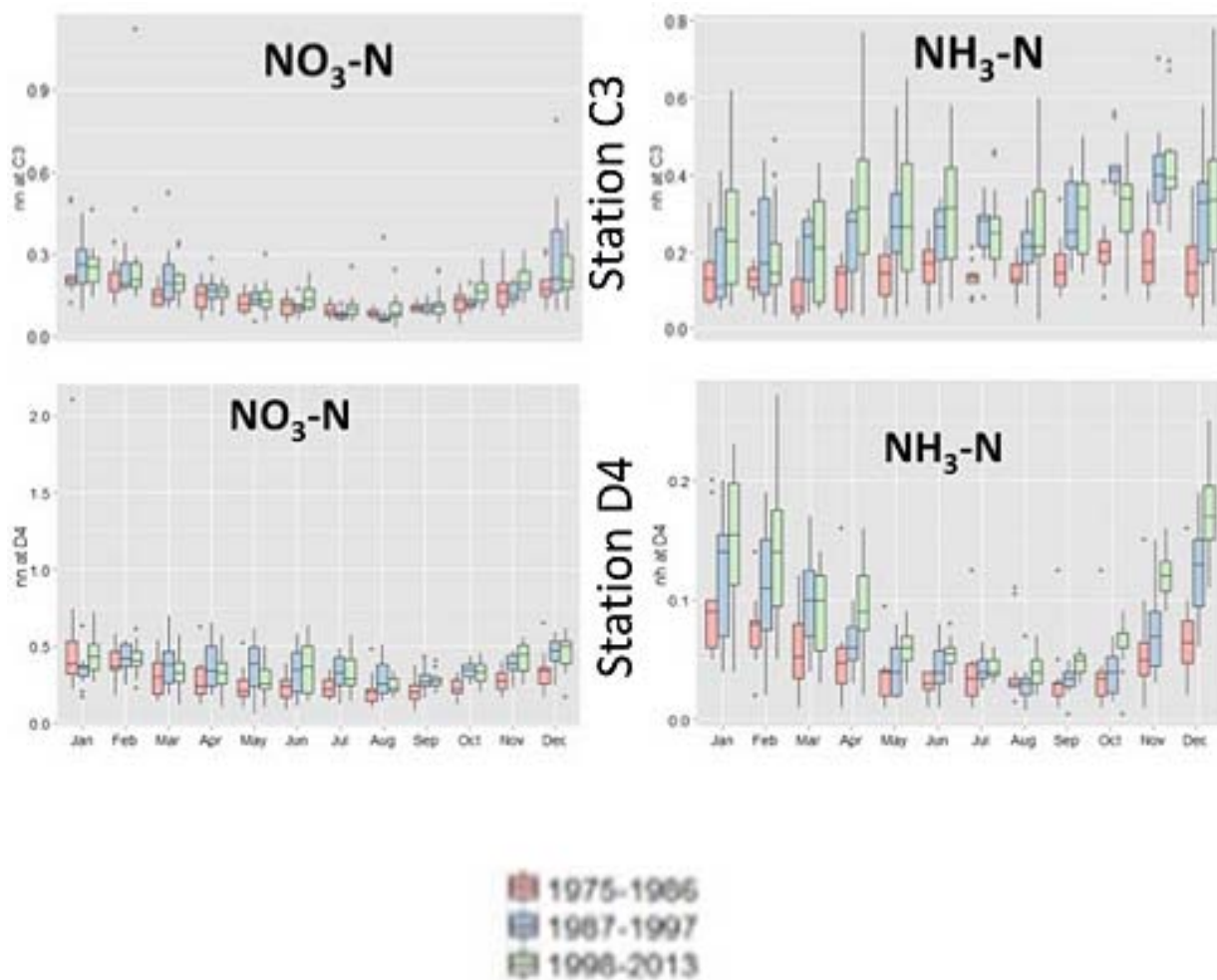


Figure 5.2.55. Monthly IEP plots for NO_3 and NH_4 (copied from Appendix 4, Figures 15-20).

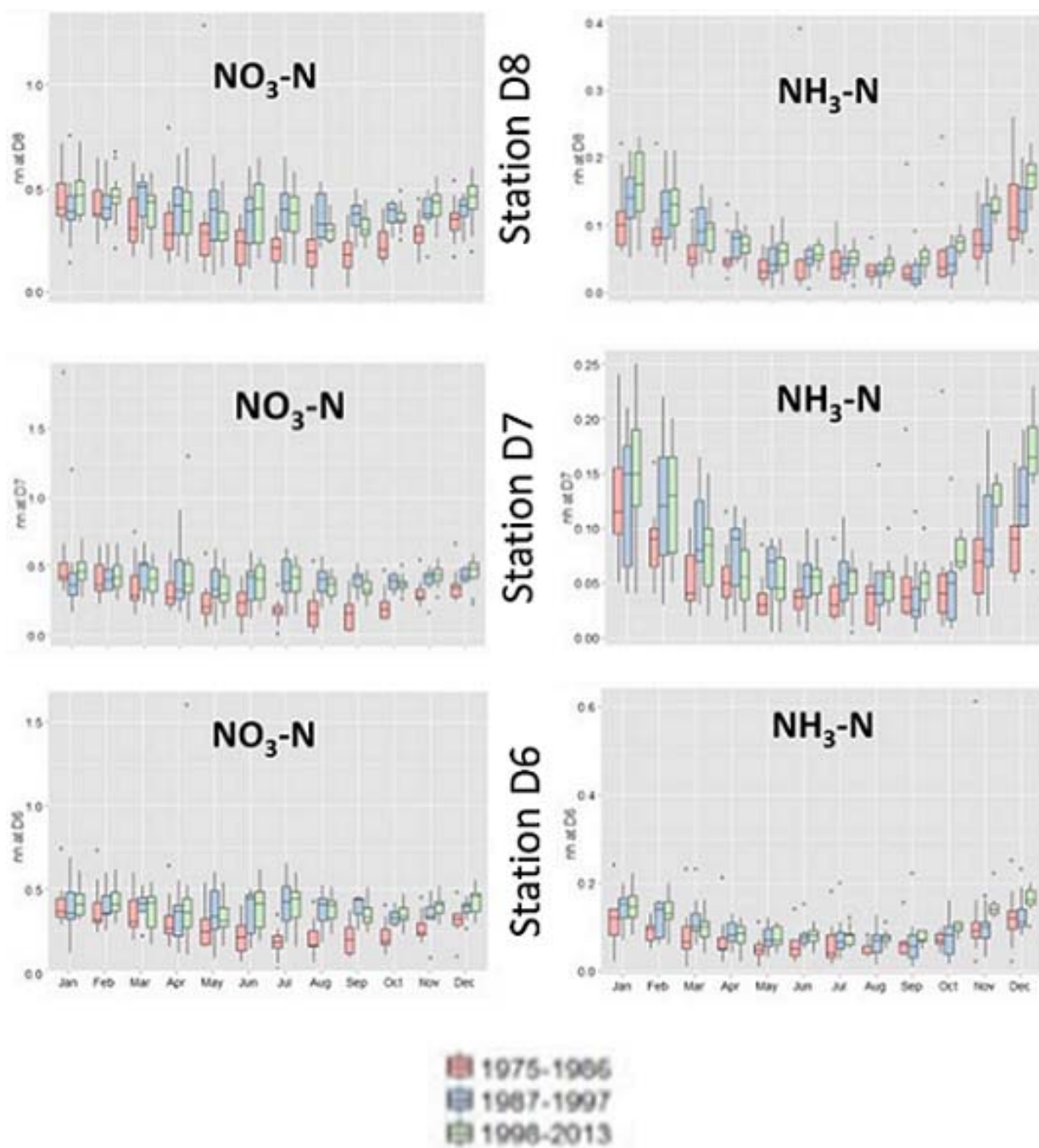


Figure 5.2.56. Monthly IEP plots for NO_3 and NH_4 (copied from Appendix 4, Figures 15-20).

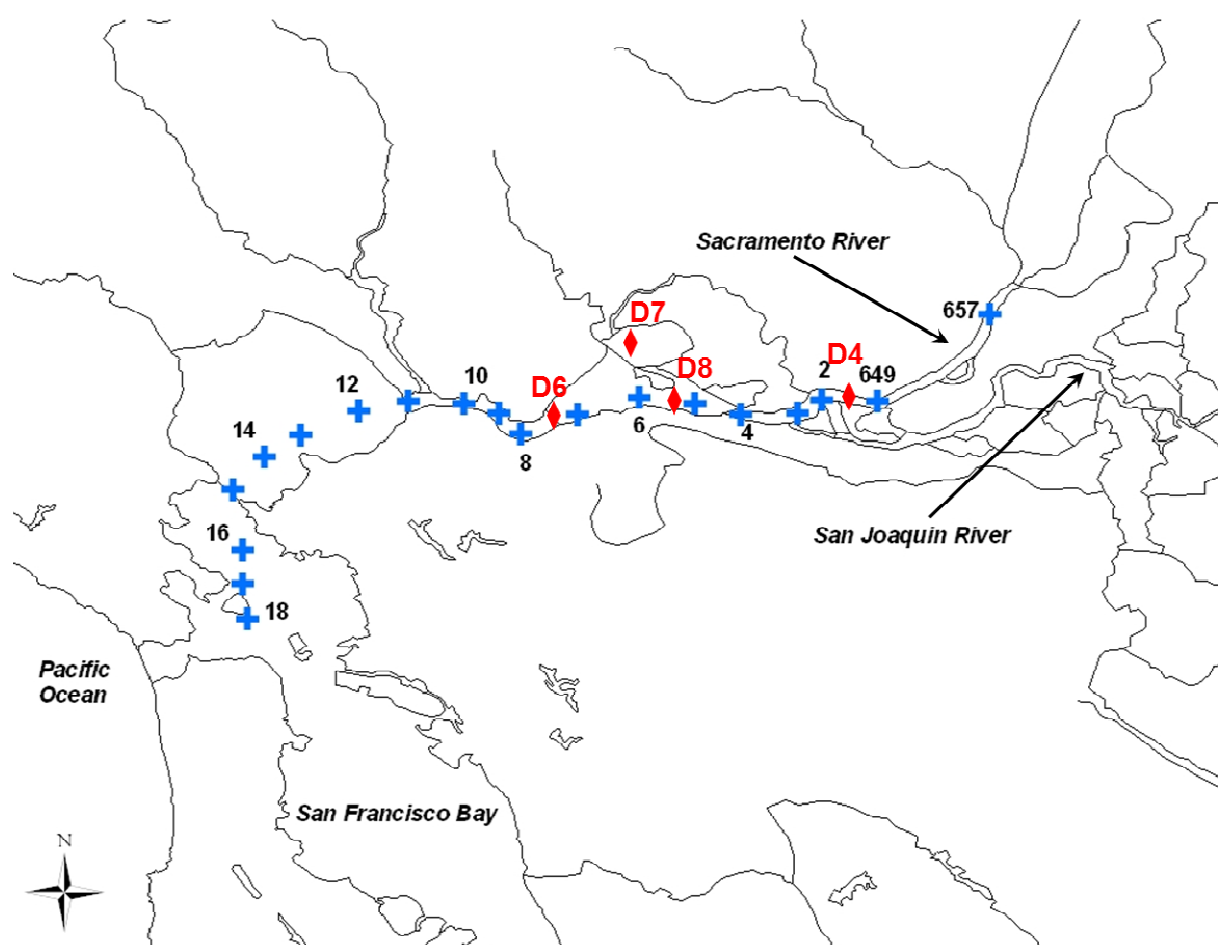


Figure 5.2.57. Map of sites sampled by the USGS R/V *Polaris* Water Quality Monitoring cruises (blue), and the Sacramento River and Delta IEP-EMP sites (red) discussed in Appendix 5.2.

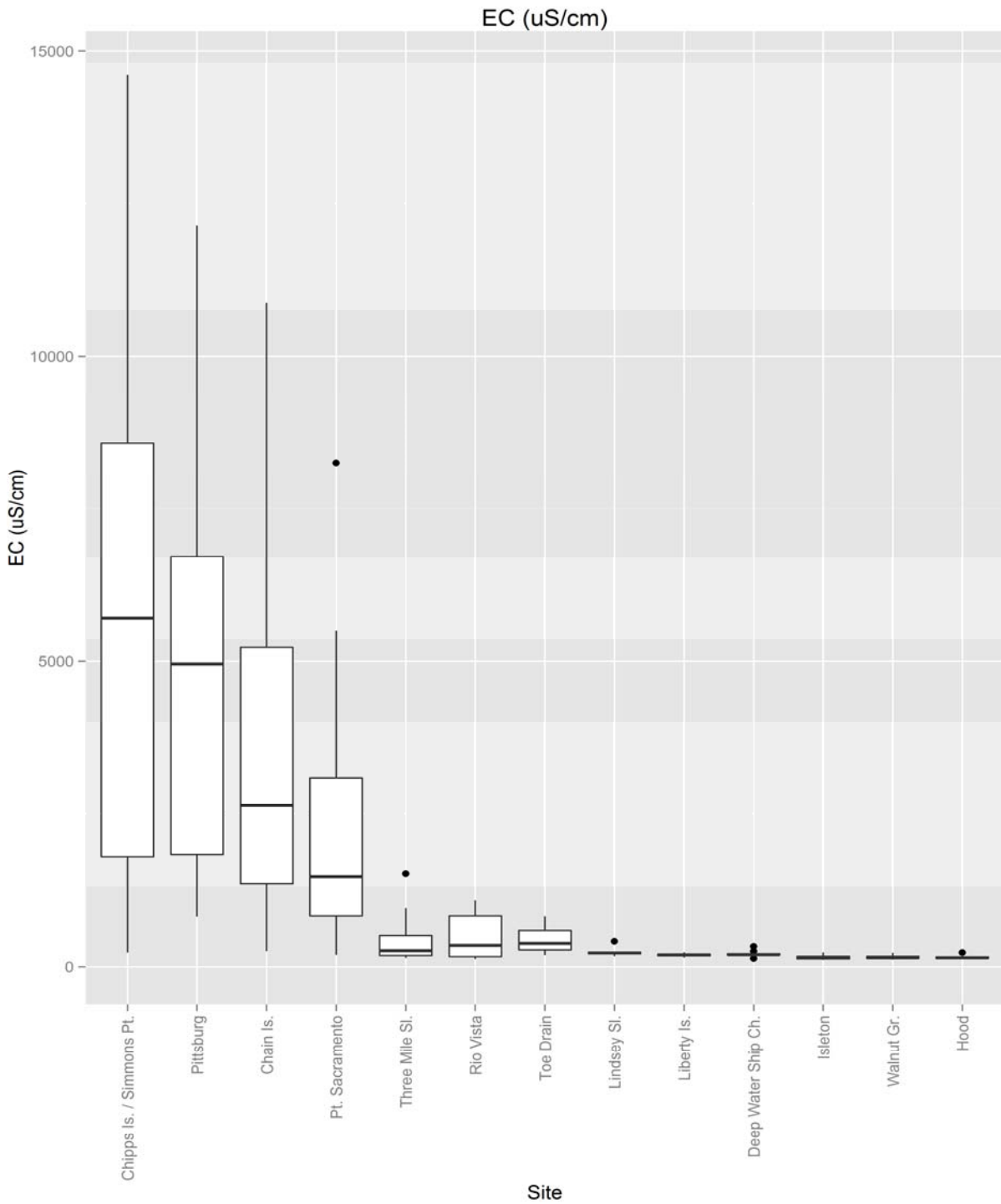


Figure 5.2.58. Downriver variation in electrical conductivity at Sacramento River and Cache/Yolo Slough Complex sites.

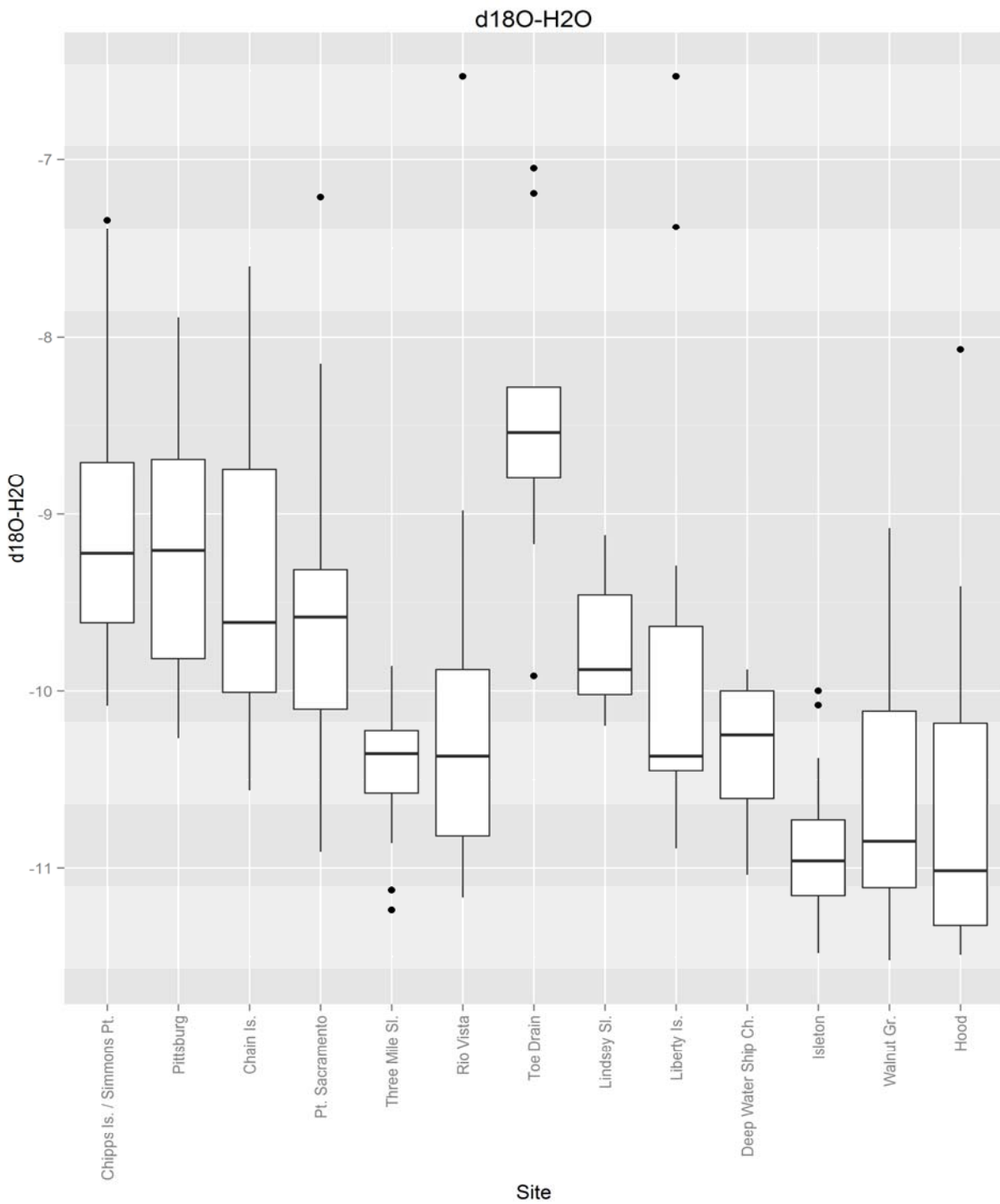


Figure 5.2.59. Downriver variation in $\delta^{18}\text{O}\text{-H}_2\text{O}$ at Sacramento River and Cache/Yolo Slough Complex sites.

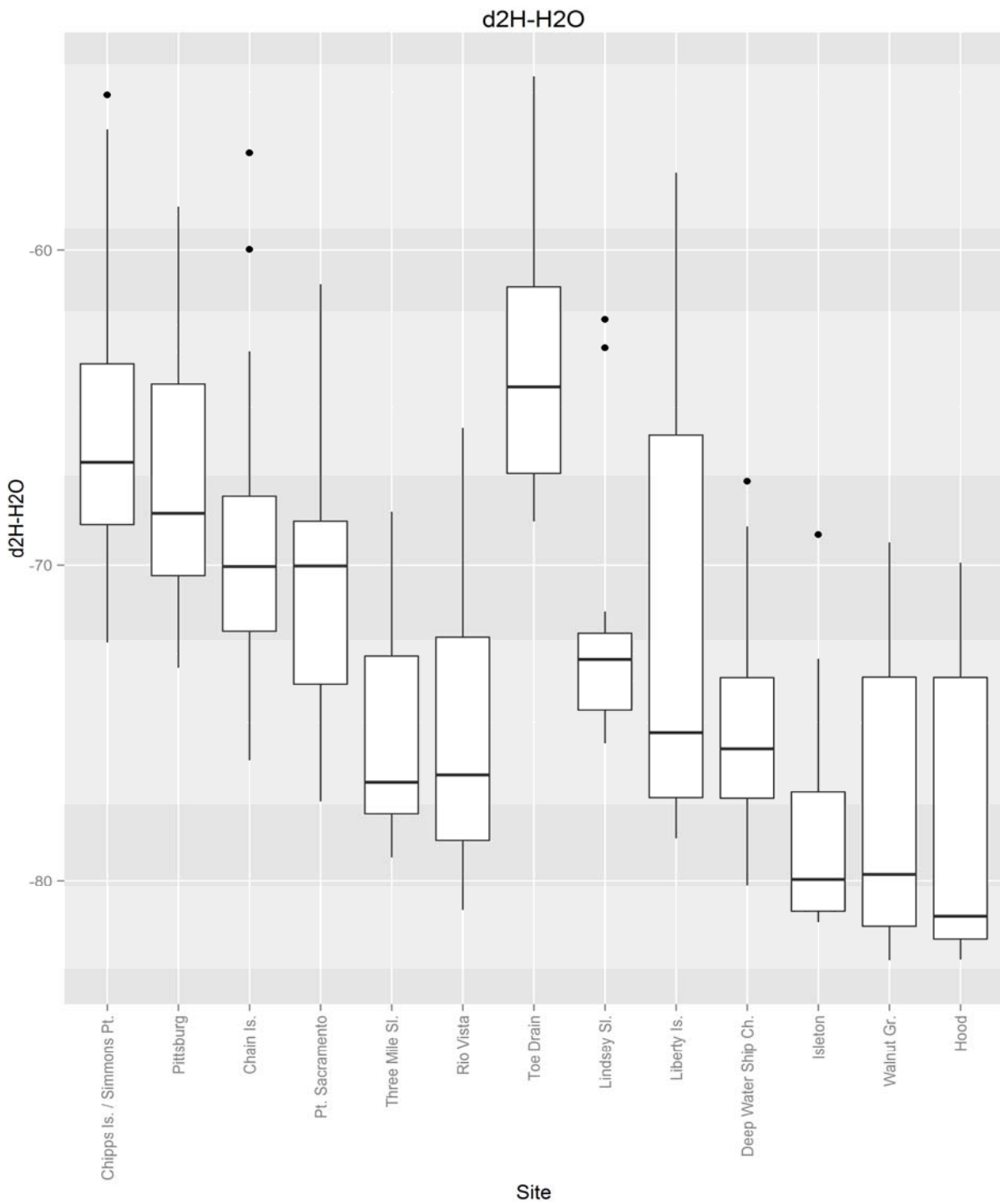


Figure 5.2.60. Downriver variation in $\delta^2\text{H-H}_2\text{O}$ at Sacramento River and Cache/Yolo Slough Complex sites.

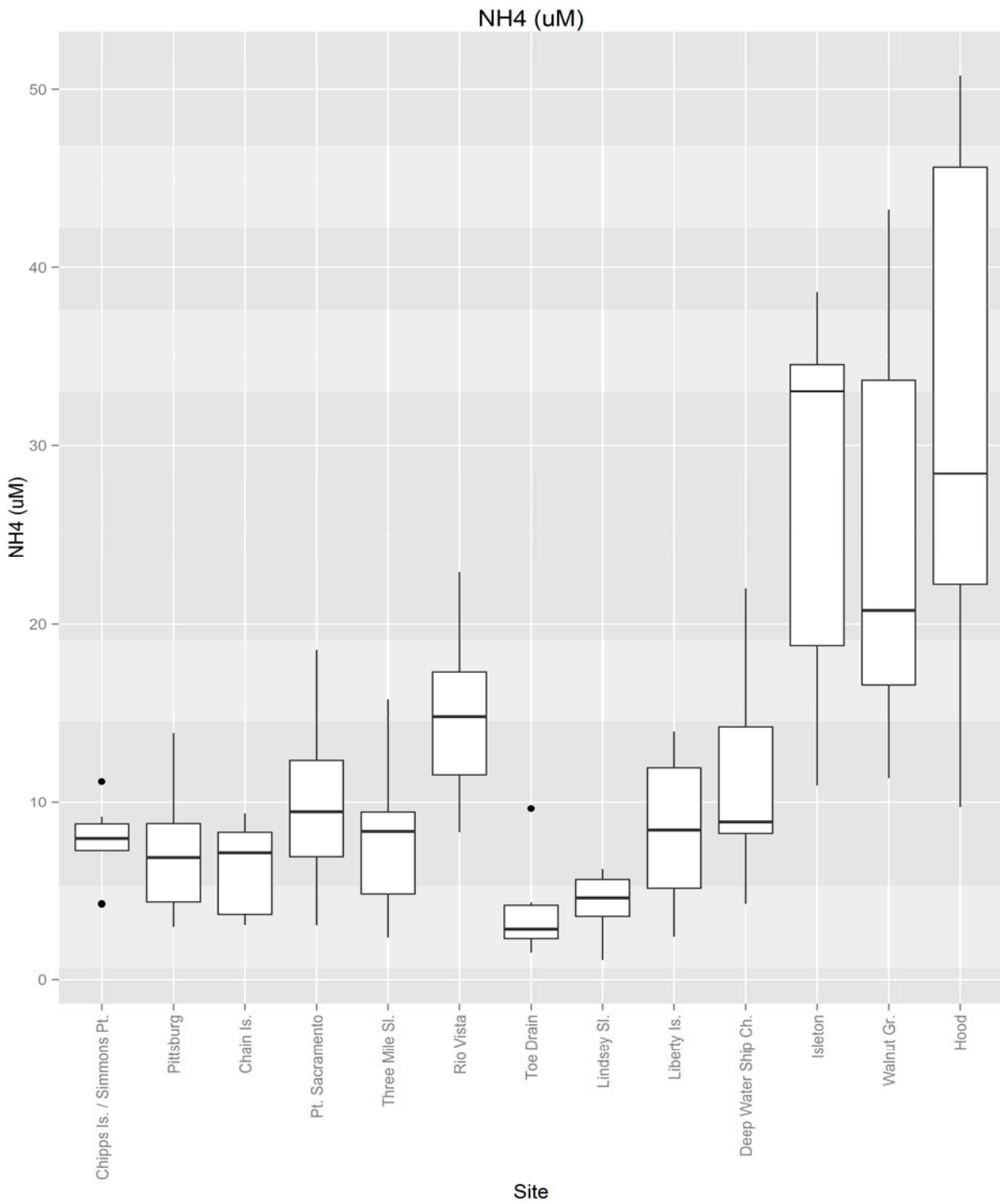


Figure 5.2.61. Downriver variation in the concentration of NH_4 at Sacramento River and Cache/Yolo Slough Complex sites.

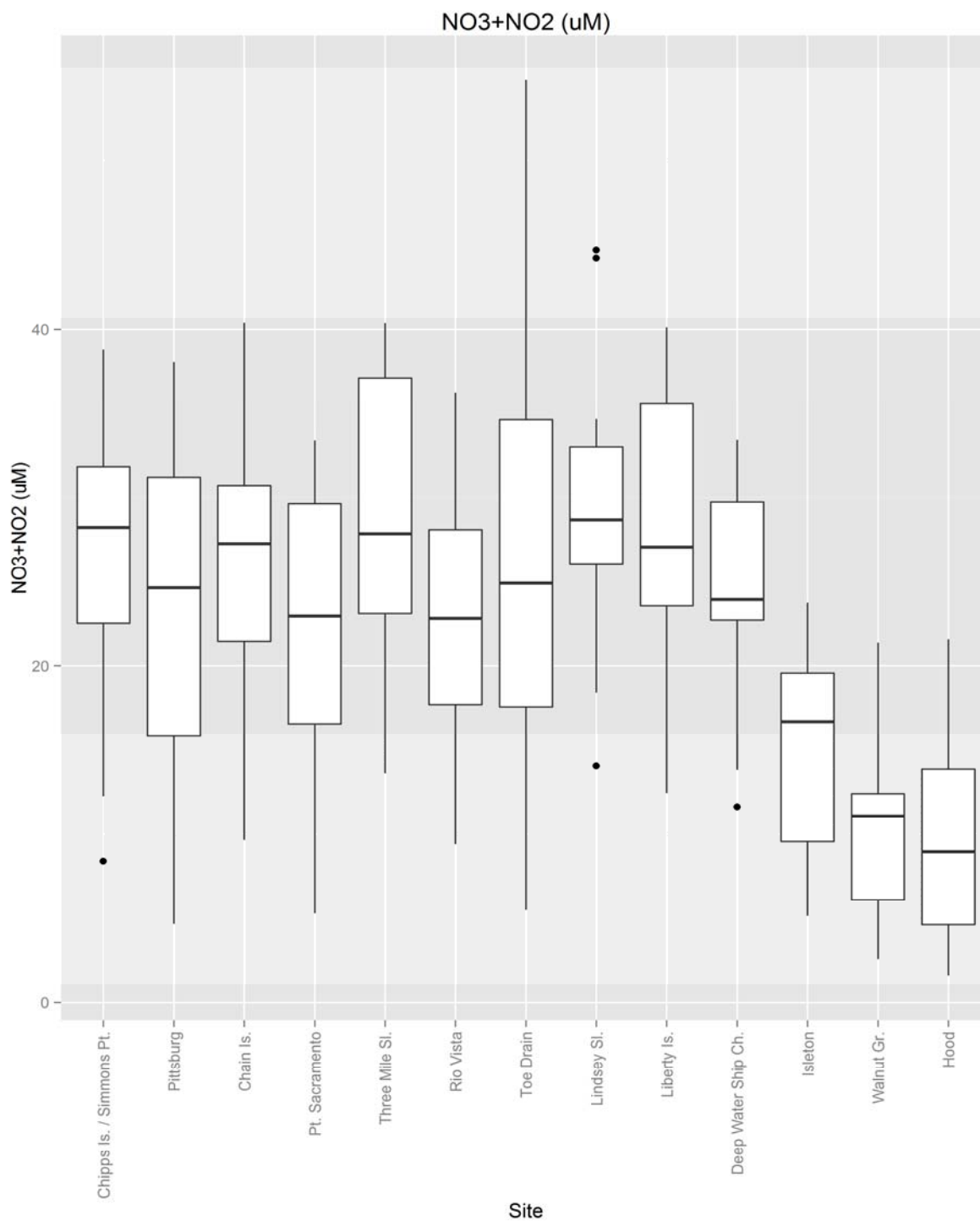


Figure 5.2.62. Downriver variation in the concentration of $\text{NO}_3 + \text{NO}_2$ at Sacramento River and Cache/Yolo Slough Complex sites.

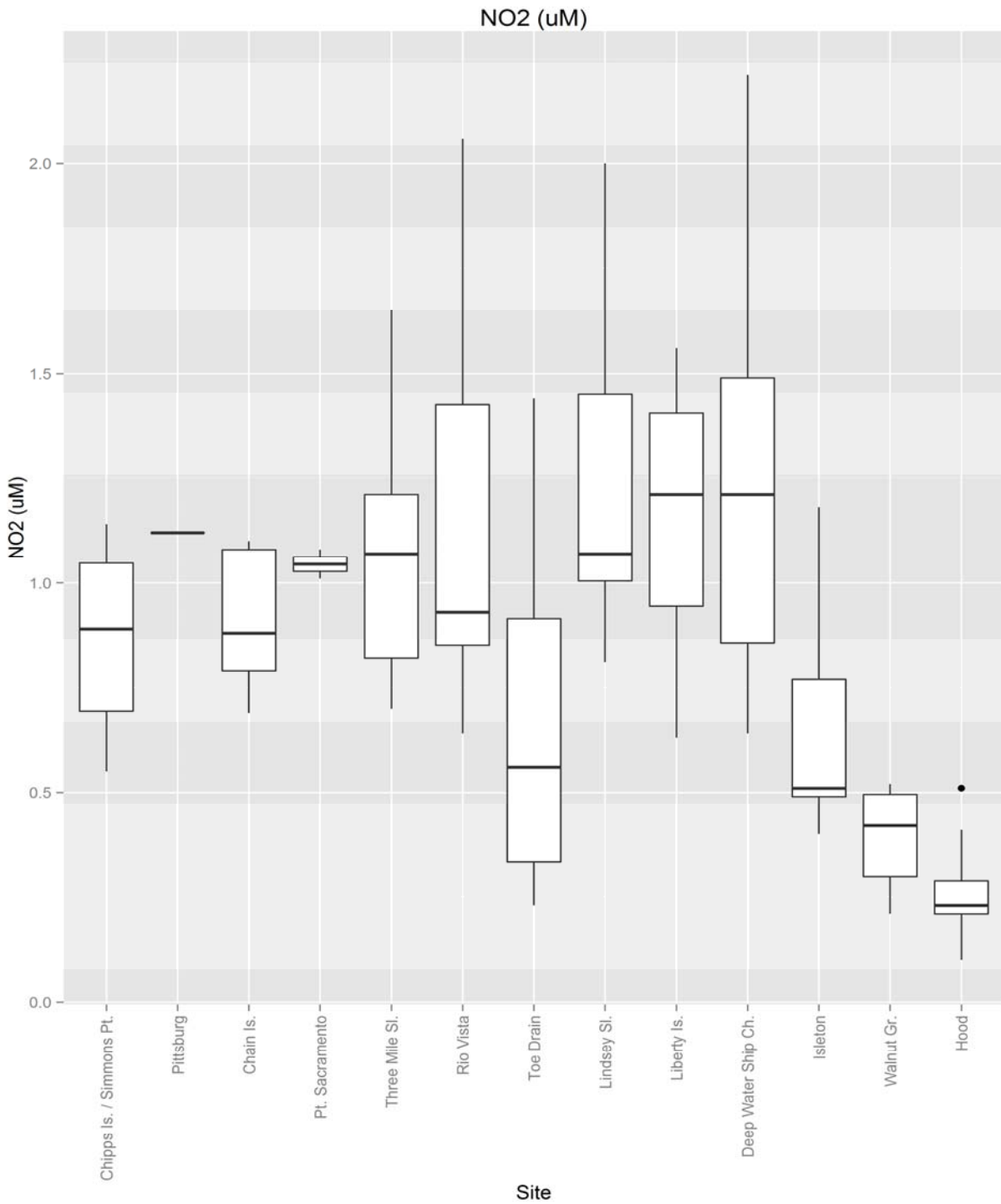


Figure 5.2.63. Downriver variation in the concentration of NO₂ at Sacramento River and Cache/Yolo Slough Complex sites.

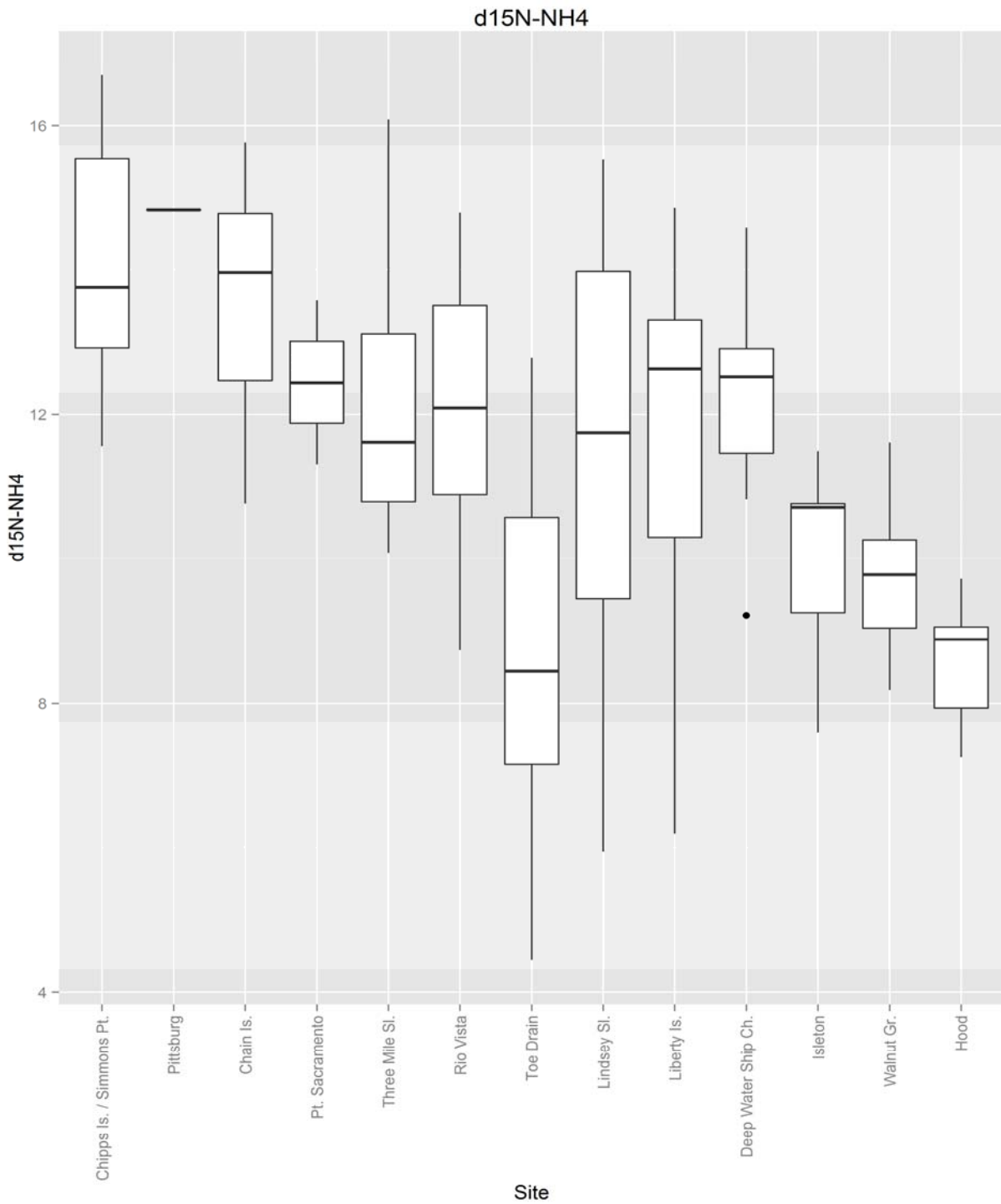


Figure 5.2.64. Downriver variation in $\delta^{15}\text{N-NH}_4$ at Sacramento River and Cache/Yolo Slough Complex sites.

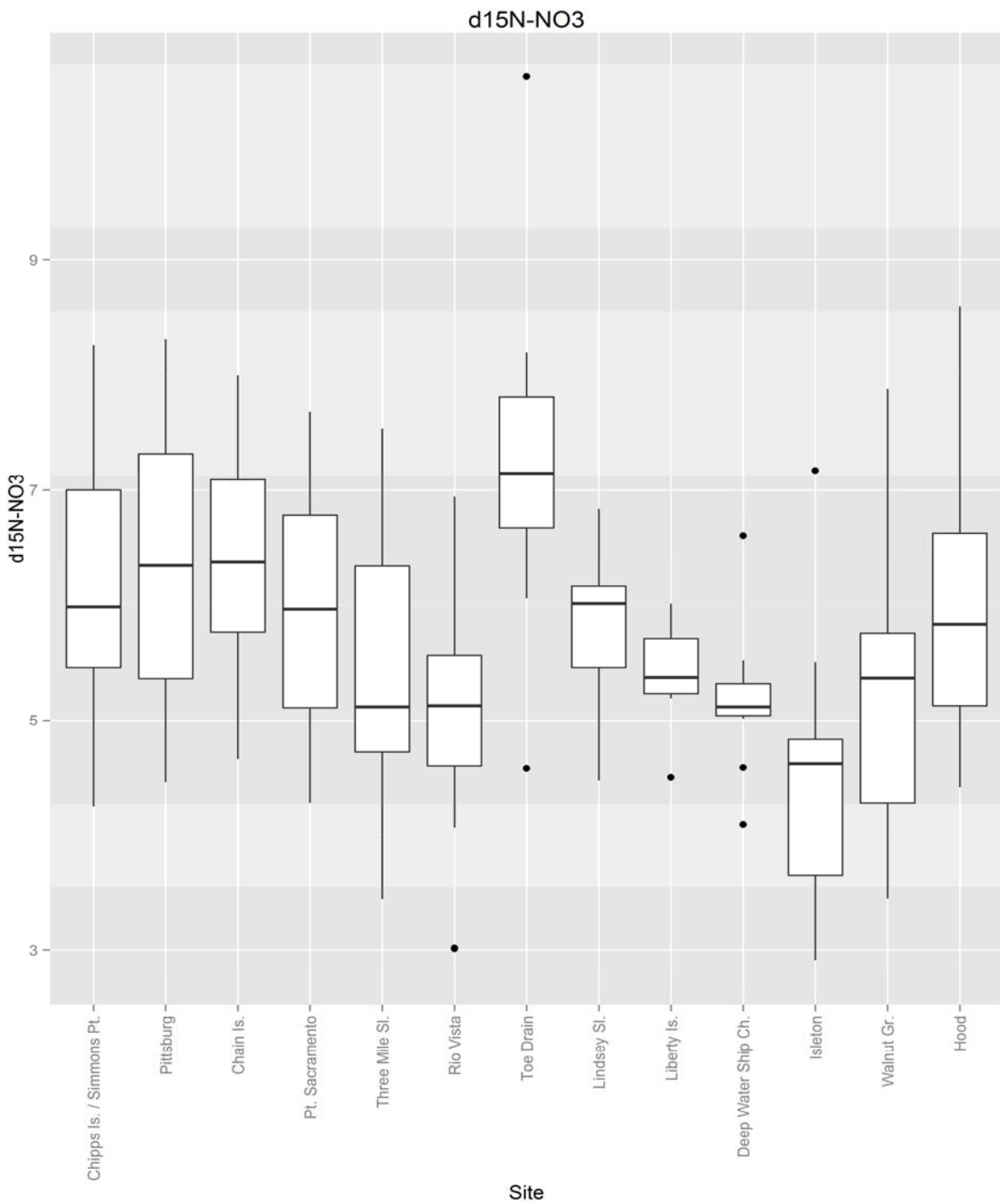


Figure 5.2.65. Downriver variation in $\delta^{15}\text{N-NO}_3$ at Sacramento River and Cache/Yolo Slough Complex sites.

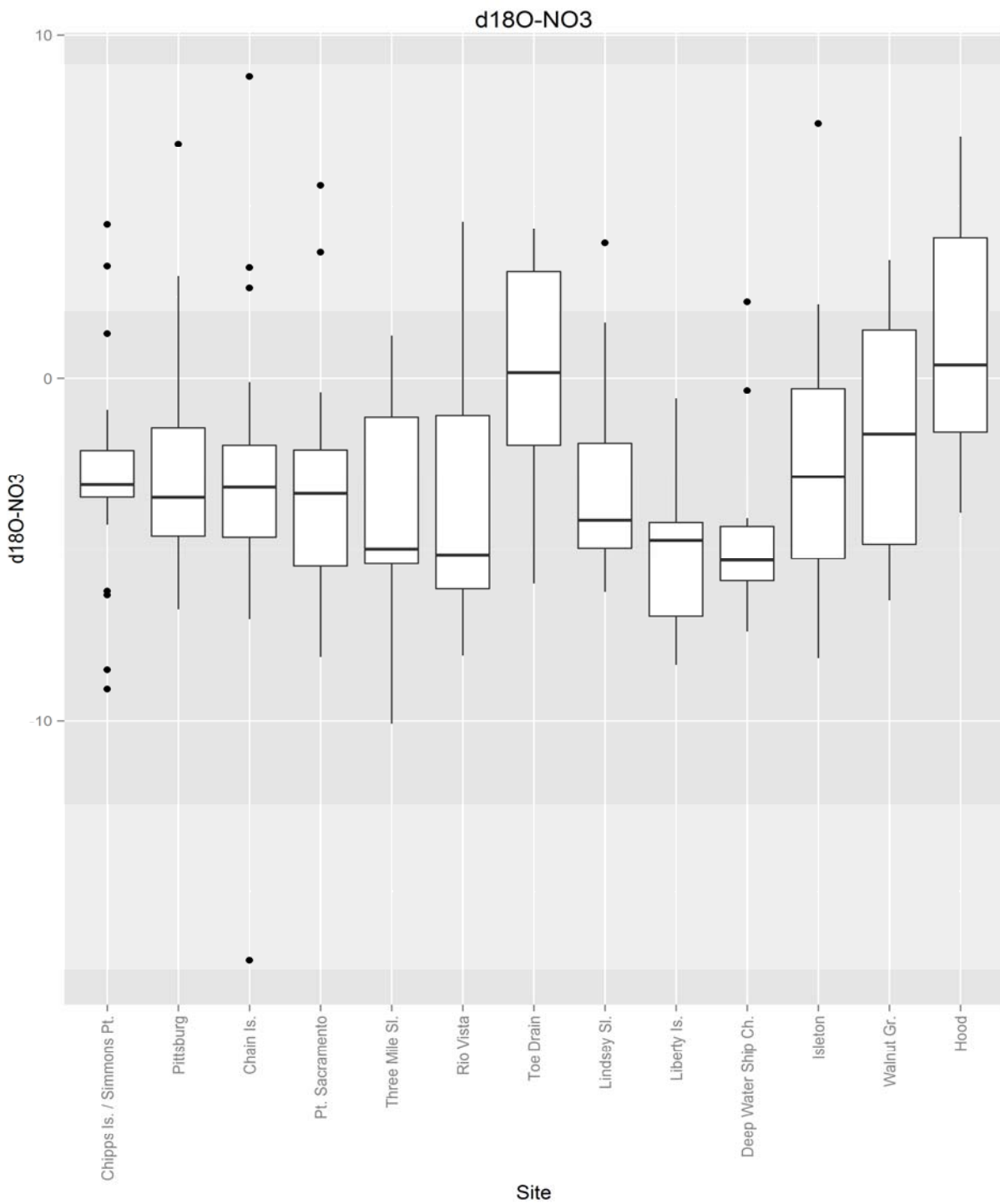


Figure 5.2.66. Downriver variation in $\delta^{18}\text{O-NO}_3$ at Sacramento River and Cache/Yolo Slough Complex sites.

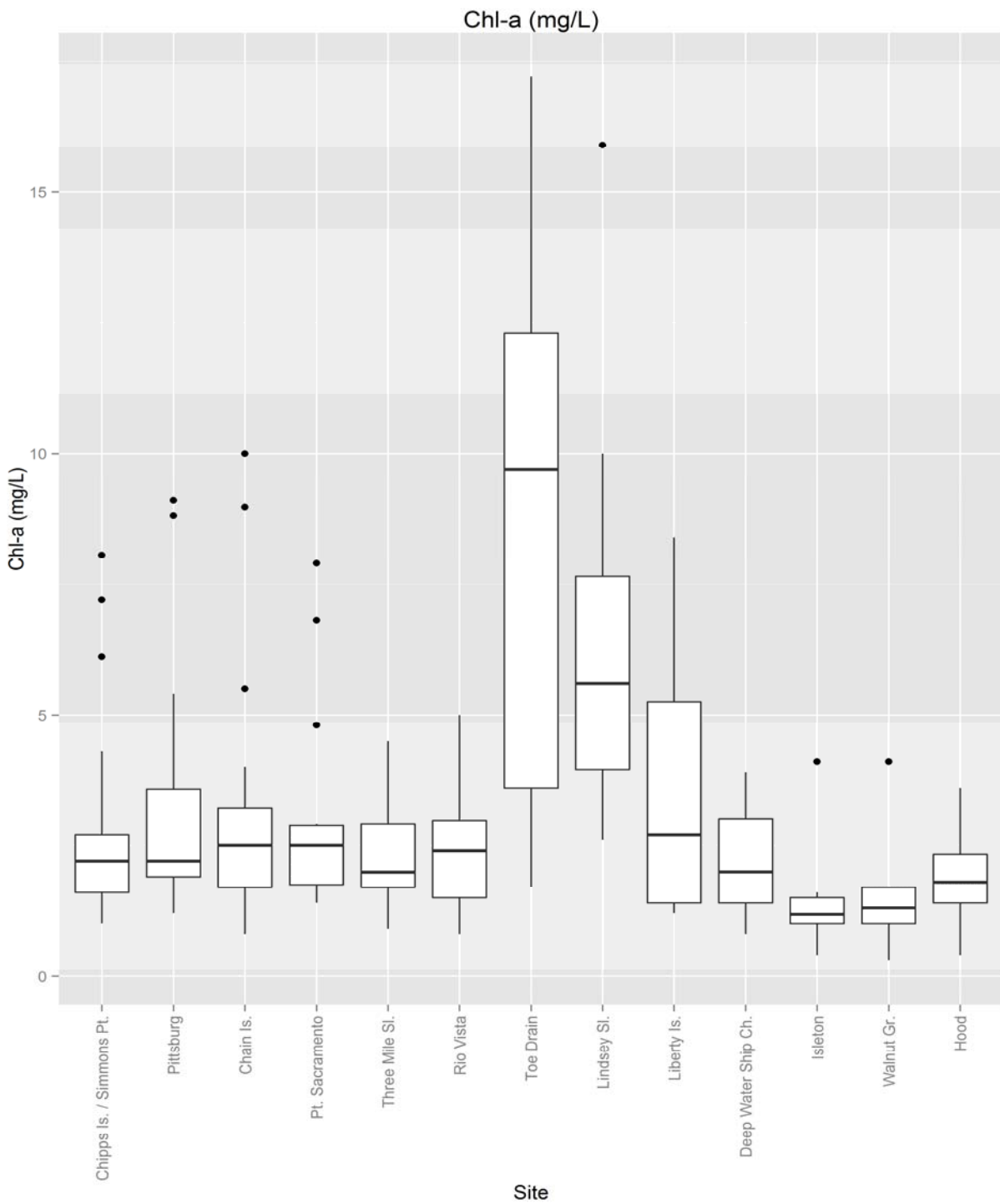


Figure 5.2.67. Downriver variation in chlorophyll-a at Sacramento River and Cache/Yolo Slough Complex sites.

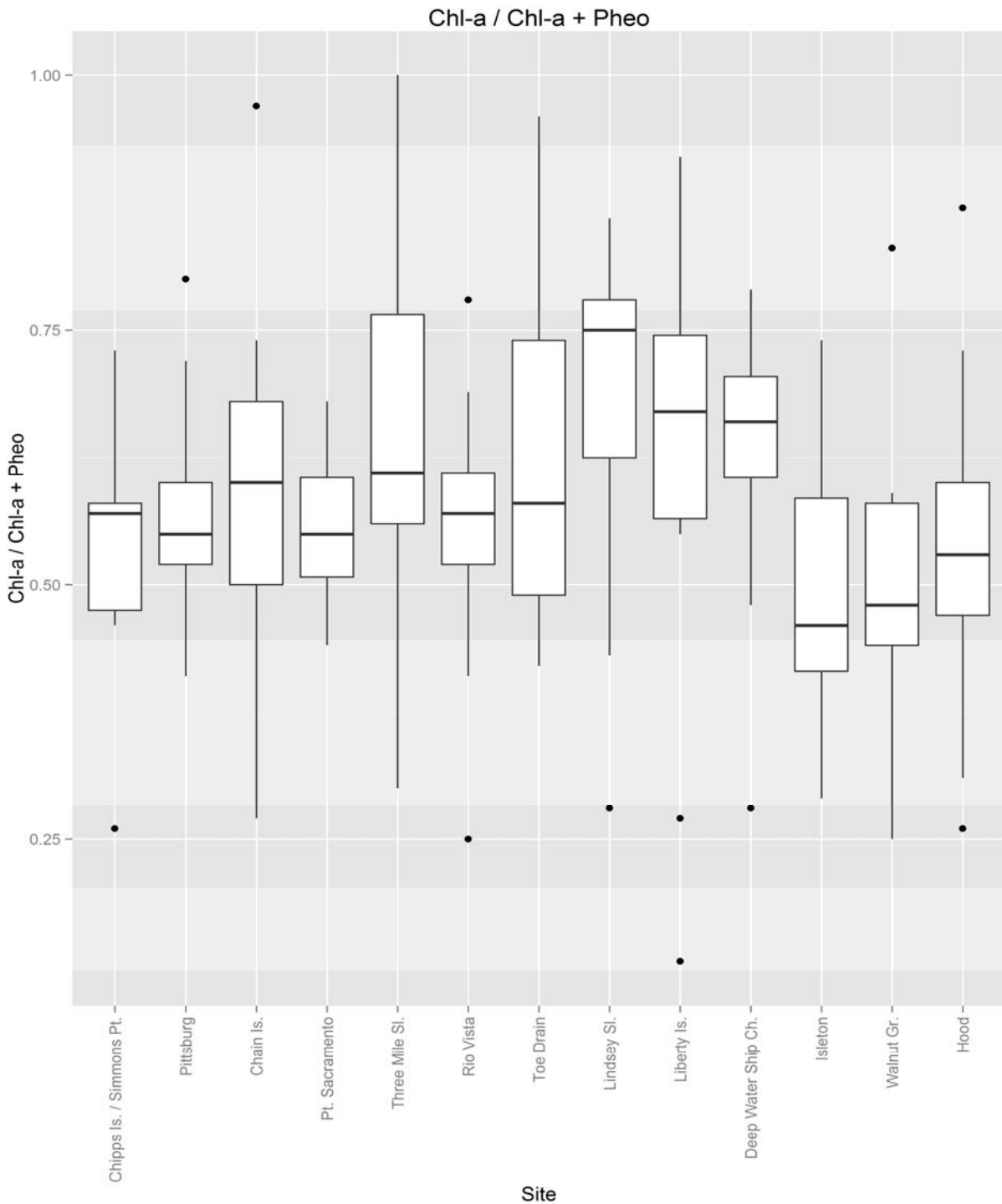


Figure 5.2.68. Downriver variation in the Chlorophyll ratio (the ratio of Chlorophyll-a to Chlorophyll-a + Pheophytin) at Sacramento River and Cache/Yolo Slough Complex sites.

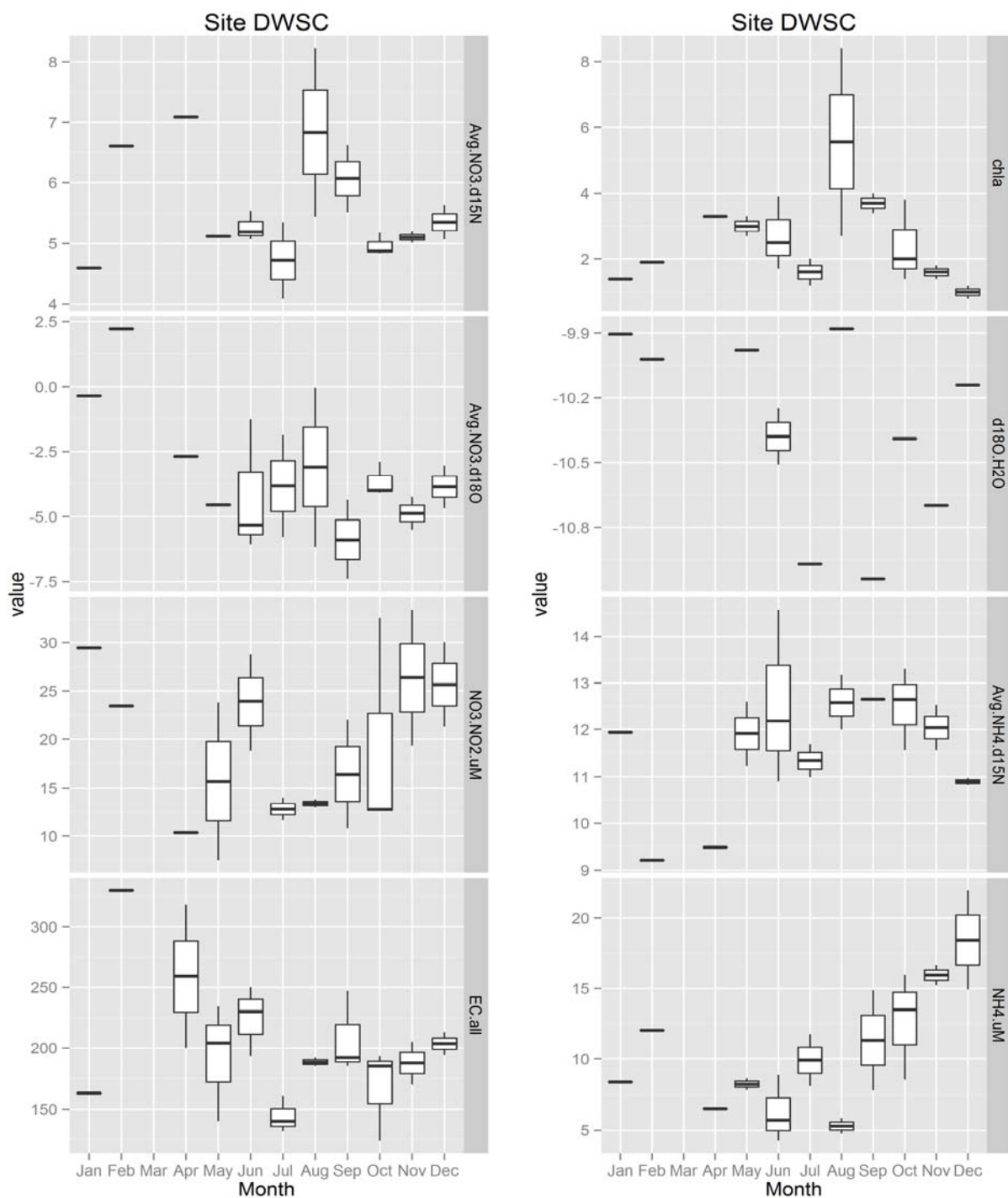


Figure 5.2.69. Chemical and isotopic data plotted by month for Cache Slough @ Deep Water Shipping Channel in the Cache/Yolo Slough Complex. Samples collected from 2009-2011.

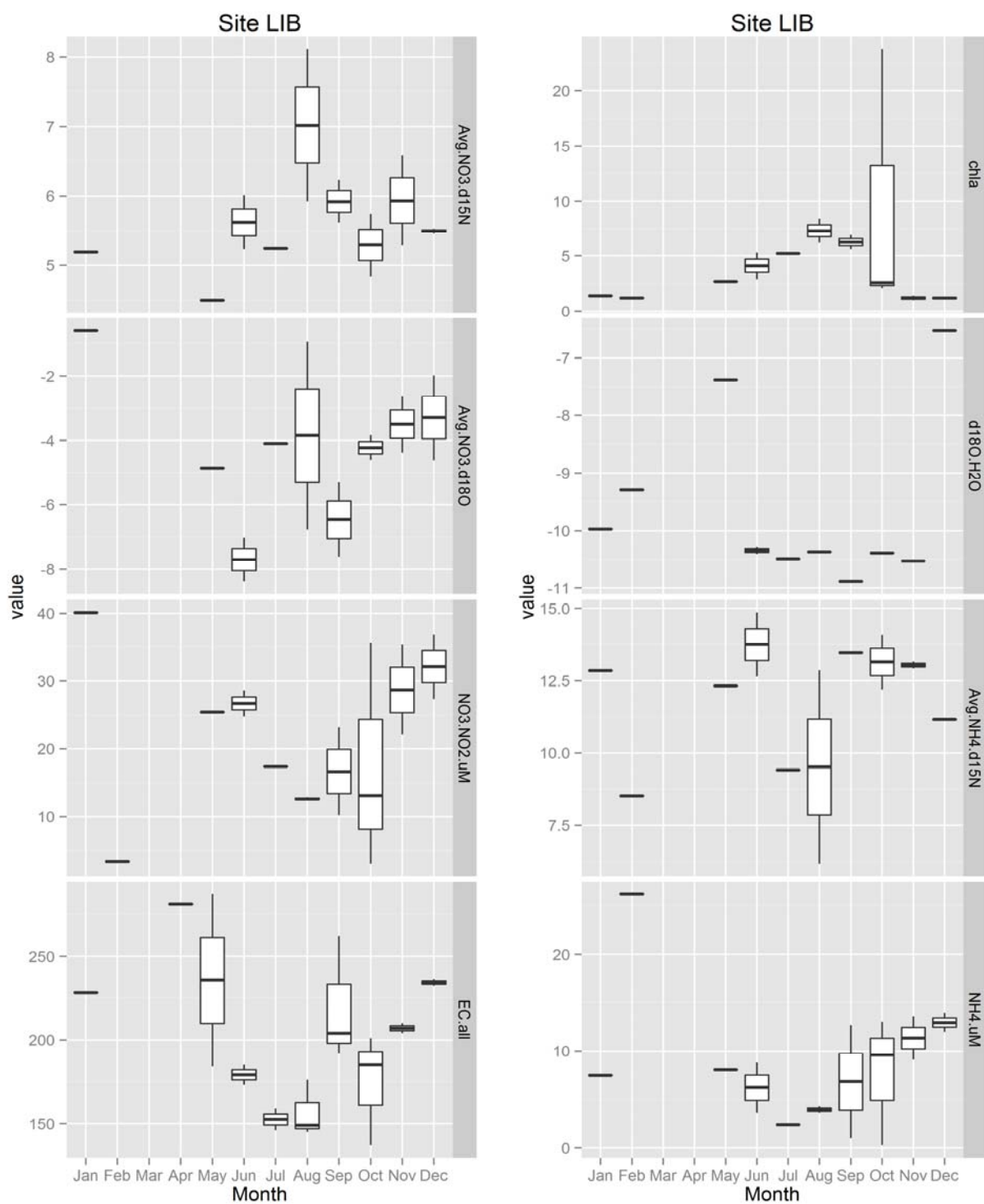


Figure 5.2.70. Chemical and isotopic data plotted by month for Liberty Island in the Cache/Yolo Slough Complex. Samples collected from 2009-2011.

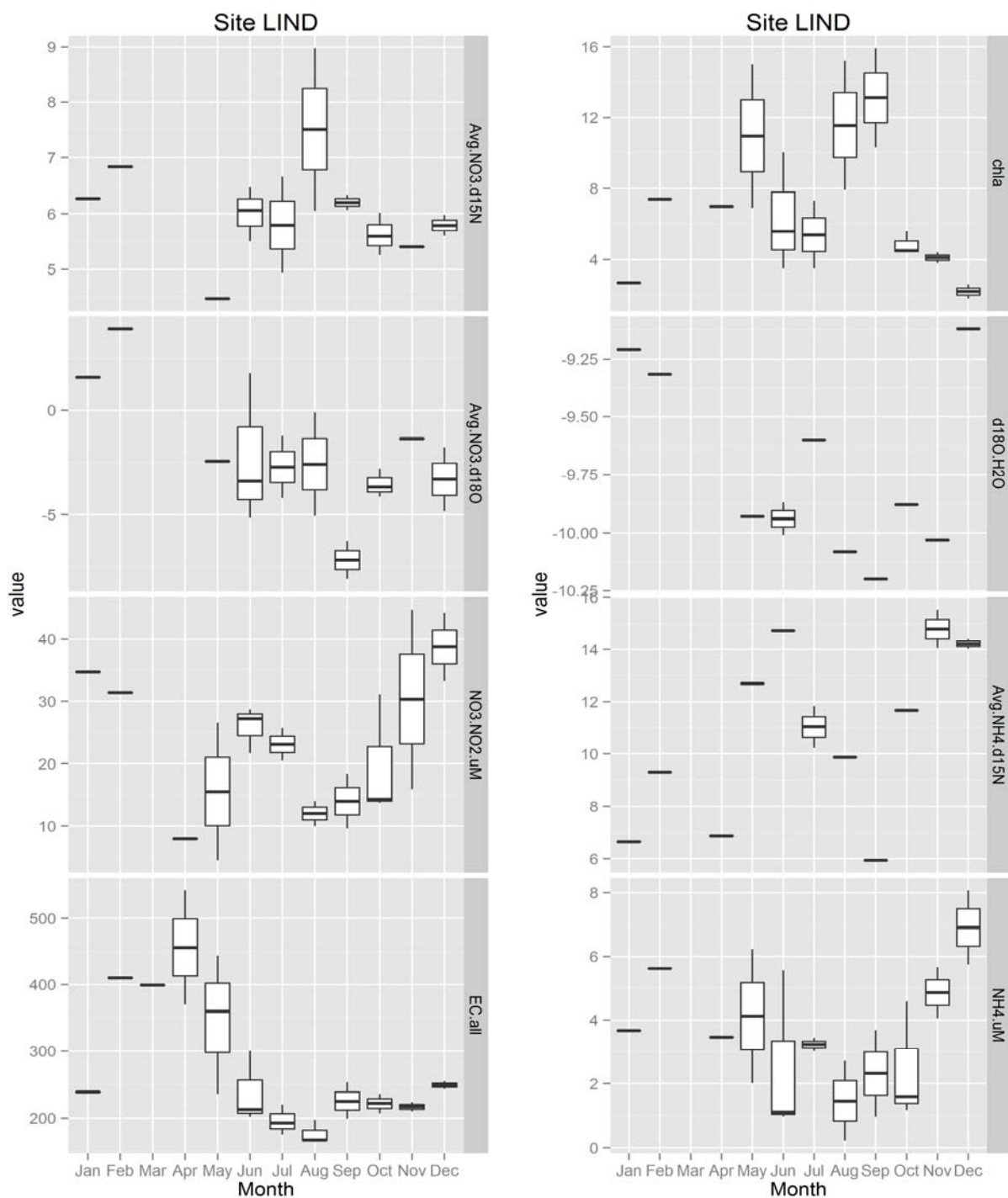


Figure 5.2.71. Chemical and isotopic data plotted by month for Lindsey Slough in the Cache/Yolo Slough Complex. Samples collected from 2009-2011.

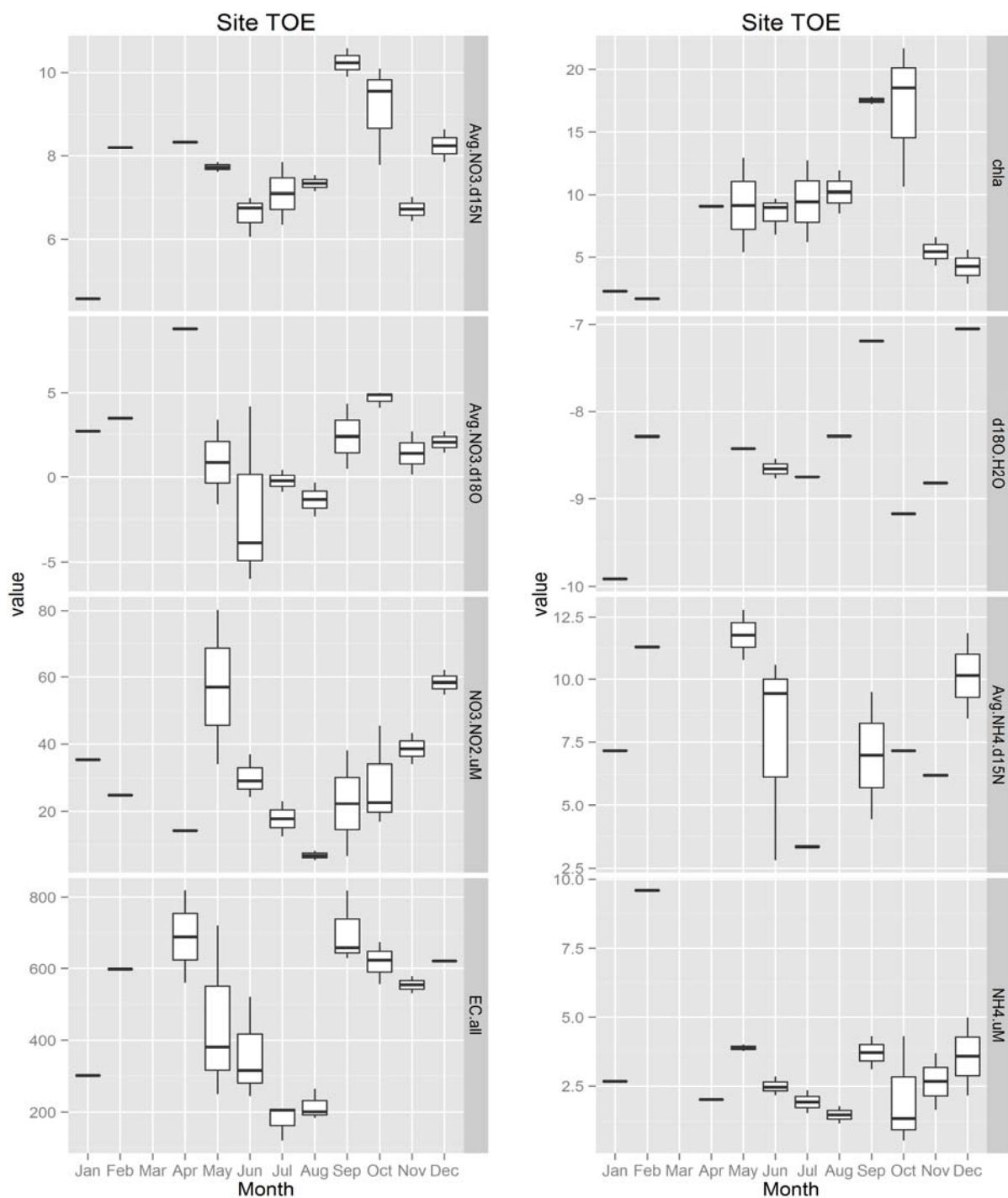


Figure 5.2.72. Chemical and isotopic data plotted by month for Toe Drain @ Dredger in the Cache/Yolo Slough Complex. Samples collected from 2009-2011.

Appendix 5.3 Combined use of stable isotopes and hydrologic modeling to better understand nutrient dynamics in the Stockton Deep Water Ship Channel, San Joaquin River and Delta

Summary

In order to better understand the factors controlling nitrogen sources and cycling within the Stockton Deep Water Ship Channel portion of the Delta, concentration and stable isotope measurements of nitrate (NO_3) were combined with estimates of volumetric water source contributions calculated using the DSM2-QUAL hydrodynamic model. The San Joaquin River (SJR) typically carries high concentrations of NO_3 partway into the Central Delta, while the Sacramento River downstream of the Sacramento Regional Waste Water Treatment Plant (SRWWTP) carries higher concentrations of ammonium (NH_4) and lower NO_3 concentrations.

Samples used in this portion of the investigation were collected by the USGS Isotope Tracers Project through participation in several different monitoring programs, and additional data was provided by the Stockton Wastewater Treatment Plant monitoring program. The monitoring programs used to collect isotope samples were the Upstream DO TMDL Monitoring Program in the San Joaquin River (2005-2007), the Department of Water Resources Dissolved Oxygen Runs in the Stockton Deep Water Ship Channel portion of the San Joaquin River (2006-2007), and the San Francisco Bay USGS R/V Polaris Water Quality Monitoring Program (2006-2008).

The combination of concentration and isotopic measurements with results from the DSM2-QUAL model provided insights into nutrient dynamics in the Stockton Deep Water Ship Channel and Sacramento-San Joaquin confluence region which could not be obtained with only concentration measurements. The primary findings from this part of the investigation are summarized below:

- The average $\delta^{15}\text{N}$ of NO_3 entering the tidal reach from the upstream San Joaquin River (SJR) was consistently higher (11.3 ± 2.4 ‰, upstream of pumping diversion) in comparison to the Sacramento River (5.3 ± 0.9 ‰, sampled at Rio Vista), indicating that $\delta^{15}\text{N}$ - NO_3 can be useful for tracking NO_3 from the two watersheds as it mixes in the Delta.
- Nitrate isotope measurements downstream of the Sacramento-San Joaquin Rivers confluence and into Suisun Bay indicate that nitrate in this downstream section of the Bay-Delta is primarily derived from the Sacramento River region, not from the San Joaquin River.
- There are large temporal variations in the amount of mixing between SJR and Sacramento R. water, and this mixing exerts significant control on the downstream distribution of nutrients, particularly nitrate, derived from the SJR.
- Nitrate isotope measurements and volumetric water source estimates from the DSM2-QUAL model show that the mixing of water sources (and not biological processes) is the dominant control on nitrate distribution in the Stockton Deep Water Ship Channel portion of the SJR.
- In general, nitrate concentrations in the upper part of the Stockton DWSC closely matched nitrate concentrations in samples collected at the site of the long term monitoring station at Vernalis on the SJR. However, there is some indication that during the winter months when nitrate concentrations in the effluent from the Stockton WWTP are at their highest, nitrate concentrations

at Vernalis do not match nitrate concentrations in the upper Stockton DWSC. Therefore, nitrate patterns in the effluent discharge from the Stockton WWTP must be taken into account when using water quality data from Vernalis as an end-member contribution to the Delta.

5.3.1 Introduction

A large section of the San Joaquin River lies within the boundaries of the Delta. Although the physical confluence of the San Joaquin River and Sacramento River is located more than 40 miles downstream of the Stockton Turning Basin and 72 miles downstream of the long-term monitoring station at Vernalis, results from isotopic analysis of surface waters and hydrodynamic modeling show that Sacramento River water is present and may even be the dominant water source up to 32 miles above the confluence in the San Joaquin River channel.

Nutrient distributions within the Delta and San Francisco Bay can significantly influence primary productivity, and may also influence species composition of both desirable primary producers and toxic cyanobacteria. Therefore, identifying nutrient sources and distributions, and tracking changes in spatial and temporal nutrient distributions is critical for monitoring and understanding the health of the Bay-Delta ecosystem.

The Stockton WWTP discharges effluent to the San Joaquin River near River Mile 42, just north of the Stockton Turning Basin, and 30 miles downstream of the long-term SJR monitoring station at Vernalis. In 2006, the Stockton WWTP transitioned to tertiary treatment, resulting in significant changes to the forms and concentrations of nitrogen discharged to the tidal portion of the San Joaquin River. Historic surface water transects demonstrate changes in dominant biological processes due to changes in effluent composition.

The main objectives for Appendix 5.3 are:

1. Describe the patterns in nitrate isotope composition found in sections of the San Joaquin River, Stockton Deep Water Ship Channel, Sacramento River, and downstream toward Suisun Bay. Demonstrate how these differences can be used to identify and trace nitrate sources through the Bay-Delta.
2. Characterize the spatial, seasonal and temporal variability of nitrogen forms and isotopic composition in the Stockton Deep Water Ship Channel portion of the San Joaquin River, as related to both water quality at the Vernalis long-term monitoring station and effluent composition from the Stockton WWTP
3. Combine nutrient concentration and isotopic composition data with the results of hydrodynamic modeling to differentiate the effects of water mixing from the effects of biogeochemical processes.
4. Use isotope measurements and hydrodynamic modeling to better understand the primary factors controlling the distribution of SJR-derived nitrogen within the Delta, and the influence of Sacramento River water (and associated nutrients) within the San Joaquin River channel.

5.3.2 Material and methods

Samples used for this part of the report were collected by the USGS Isotope Tracers Group working in conjunction with existing water quality monitoring programs conducted by the Department of Water

Resources, the U.S. Geological Survey, and the DO TMDL Monitoring Program led by William Stringfellow of the University of the Pacific (Figure 5.3.1). Detailed descriptions of each of these sampling programs, sample collection methods, and analytical methods are described in detail in Appendix section 5.1. Land-based sampling of the San Joaquin River and tributaries was conducted between March 2005 and December 2007 as part of the CALFED-funded Upstream DO TMDL Monitoring Project. Samples were collected in the north Bay, Delta, and lower Sacramento River at the USGS R/V *Polaris* Water Quality stations. Samples were collected monthly at 19 stations on the R/V *Polaris* from August 2006 through May 2008, except for some months during which the *Polaris* was in dry dock, and when storms prevented sampling. Samples were collected at 14 stations in the Stockton DWSC between Prisoner's Point and the Stockton Turning Basin (STB) during the Department of Water Resources Dissolved Oxygen Runs (DWR DO Runs) between August 2006 and December 2007 (Figure 5.3.2). The DWR DO Runs were conducted biweekly starting around June of each year (depending upon the commencement of low DO conditions), and continued through November or December. Water quality and nutrient concentration data was obtained from the Stockton Wastewater Treatment Plant for both the final effluent and upstream and downstream monitoring stations (Figure 5.3.3). Isotope samples were not collected as part of this monitoring program, however, several of the downstream sites were located at or near sites sampled for isotopes during the DWR DO Runs. The locations of these sites are shown on Figures 5.3.1 through 5.3.3.

5.3.3 Results and Discussion

5.3.3.1 Nitrate concentrations and isotopic compositions

Samples collected during the SJR DO TMDL Monitoring program show that nitrate concentrations and isotopic compositions were very similar at both the Vernalis sampling site (RM 72.2), which is also a long-term monitoring station, and the Mossdale sampling site (RM 56.2), which was the most downstream site sampled as part of the DO TMDL study (Figure 5.3.4). The Mossdale site is located within the area of tidal influence, while the Vernalis site is upstream of all tidal influence, and therefore only experiences downstream flow.

Average nitrate concentrations in mg/L N were 1.28 ± 0.64 at Vernalis and 1.25 ± 0.61 at Mossdale. Average $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ values were 10.6 ± 1.8 ‰ and 4.3 ± 1.8 ‰ at Vernalis and 11.3 ± 2.4 ‰ and 4.2 ± 2.6 ‰ at Mossdale (Stringfellow et al., 2008; Kendall et al., 2008a).

Average nitrate concentration at the Rio Vista station (representing Sacramento River water upstream of the confluence) was 0.29 ± 0.11 mg/L N, and the average $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ values at Rio Vista during the study period were 5.3 ± 0.9 ‰ and -3.7 ± 3.8 ‰ respectively (Kendall et al., 2008b). Average nitrate concentrations and isotope values were significantly different between the upstream SJR stations (Mossdale and Vernalis) and the Rio Vista Sacramento River station, indicating that the isotopic composition of nitrate throughout the Delta could be a useful tracer of nitrate source as long as the isotope values are not completely altered by biological cycling.

The USGS *Polaris* stations PO-04 through PO-07 span a sampling transect through Suisun Bay. During the study period, average nitrate concentrations across these four stations were 0.31 ± 0.14 mg/L N, and the average $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ values were 6.3 ± 1.4 ‰ and -1.3 ± 2.7 ‰ respectively (Kendall et al., 2008b). Both the nitrate concentrations and isotopic compositions in Suisun Bay were much more similar

to those measured in the Sacramento River in comparison to those measured upstream in the San Joaquin River (Figure 5.3.5 and 5.3.6).

Although the stations sampled as part of the DWR DO Runs were located within the San Joaquin River channel, between 24.4 and 40.7 miles upstream of the Sacramento and San Joaquin River confluence nitrate concentrations and isotopic compositions demonstrated patterns that did not match what was observed upstream at the Mossdale and Vernalis stations, suggesting significant influence from either biological processes or additional nitrate sources. Nitrate concentrations in the upper part of the Stockton DWSC showed similar patterns and values compared to the Mossdale and Vernalis stations, while downstream sites had both lower concentrations and isotopic compositions which more closely matched values measured in the Sacramento River at Rio Vista and downstream in Suisun Bay (Figure 5.3.7 and Figure 5.3.8).

5.3.3.2 Nitrogen mixing dynamics in the Stockton Deep Water Ship Channel

The wide range of both nitrate concentrations and isotopic compositions within the Stockton DWSC suggest that nitrogen in this area behaves very differently in comparison to other areas of the Delta, where much less variability is observed. When the measured nitrate concentrations and isotopic compositions are plotted by transect, a large step-like decrease in both nitrate concentration and $\delta^{15}\text{N-NO}_3$ is apparent in many of the transects (Figure 5.3.9 and 5.3.10). Transects from 2007 often showed large, step-like decreases in $\delta^{15}\text{N-NO}_3$ over relatively short spatial scales. All the transects in 2006 showed both smoother transitions downstream, and smaller differences between the $\delta^{15}\text{N-NO}_3$ of the major end members, the Sacramento R. and the San Joaquin River (Table 5.3.2).

Both the abrupt, step-like pattern and the smoother transition observed across these transects can best be explained by physical mixing processes, where Sacramento River water carrying lower nitrate concentrations and distinctly lower $\delta^{15}\text{N-NO}_3$ meets the high nitrate, high $\delta^{15}\text{N-NO}_3$ San Joaquin River water far upstream within the San Joaquin River DWSC.

The patterns in nitrate concentrations and isotopic compositions observed in these transects are consistent with physical mixing processes between two end members, rather than biological cycling such as denitrification or algal uptake. There is evidence that biological processes may be dominant at specific times and locations, for example there are several transects in which only the Turning Basin site exhibits higher $\delta^{15}\text{N-NO}_3$ and lower $\text{NO}_3\text{-N}$ in comparison to the rest of the transect samples, suggesting strong biological nitrogen uptake and the associated isotopic fractionation. Other than the Turning Basin site, biological processes do not seem to have a significant impact on nitrate concentrations or distributions in the Stockton DWSC.

Even with these observations, it is still possible that significant algal uptake of nitrogen is still occurring, particularly in the upper portion of the Stockton DWSC, where San Joaquin River water and nitrate is still present. The high concentrations of nitrate from the San Joaquin River may mask the effects of biological processes- even with very high productivity, algal uptake will not significantly reduce the nitrate concentrations, and therefore also will not cause a measureable shift in the isotopic compositions.

5.3.3.3 Hydrodynamic and Volumetric Modelling for the Stockton DWSC

In order to strengthen understanding of the observed nitrate patterns in the Stockton DWSC, water source mixing for each location and time was calculated using the DSM2-QUAL model (see Appendix 6). For the sites and locations used in this study, the model showed that Sacramento River water and San Joaquin River water were the two dominant water sources, with varying but always extremely small contributions from other potential water sources.

The model output clearly shows that a transition occurs between primarily San Joaquin River water into primarily Sacramento River water centered around SJR River Mile 32 in the Stockton Deep Water Ship Channel (Figure 5.3.11). Both the shape of the transition and the location of the transition vary somewhat between transects, although the overall pattern is quite consistent. The patterns seen in the calculated water source contributions match the patterns observed in the nitrate isotopic compositions, strongly supporting the conclusion that nitrate dynamics in the Stockton DWSC are controlled primarily by physical mixing process and not by biological processes (Figure 5.3.12).

Combining the model output with the observed nitrate concentrations and isotopic compositions shows that Water source mixing as calculated by the DSM2-QUAL model partially controls the distribution of nitrate and nitrate isotopes in the DWSC, however, changes in the nitrate concentrations and isotopic compositions of the end members also play a critical role. The times when an abrupt step decrease in $\delta^{15}\text{N-NO}_3$ occurs along the transect coincide with times when the end members (SJR and Sac R) have the largest differences in nitrate isotopic composition. Using data from two of the Stockton DWSC transect sites, Light 19 and Light 34, it can be seen how strongly the percent of San Joaquin River water at each site is controlled by flow from the San Joaquin River (Figure 5.3.13).

5.3.3.4 Stockton Water Treatment Plant Effluent and Nitrate Dynamics

The Stockton WTP discharges treated effluent into the San Joaquin River at a site located between the Mossdale sampling site and the DWR DO Run transect sites discussed in this study. In 2006, the Stockton WTP completed treatment upgrades, and the form of nitrogen discharged in the effluent changed from ammonium to nitrate (Figure 5.3.14). Although nitrate concentrations in the effluent are very high (compared to nitrate concentrations in the Stockton DWSC (Figure 5.3.15), it appears that nitrate originating upstream in the San Joaquin River usually exerts a stronger influence on downstream nitrate concentrations in comparison to the effluent (Figure 5.3.16).

However, there are times when nitrate concentrations in the upper Stockton DWSC are significantly elevated in comparison to nitrate concentrations at both the Mossdale and Vernalis stations (Figure 5.3.17). This pattern reversal appears to occur during times of higher nitrate concentrations in the effluent, however, downstream nitrate concentrations are not well matched to the pattern of nitrate concentrations seen in the effluent (Figure 5.3.18). This suggests that there are more complicated interactions controlling the times when downstream nitrate is elevated above nitrate concentrations from the upstream San Joaquin River, possibly related to San Joaquin River flow, changes in nitrate sources within the upstream San Joaquin River, and additional nitrate sources in the local area.

The complex relationship between upstream San Joaquin River nitrate, Stockton WTP effluent, and nitrate dynamics in the Stockton DWSC suggest that although measurements collected at the Vernalis

long term monitoring station are usually a good indicator of the most significant nitrate inputs entering the Stockton DWSC from upstream, there are times when the Vernalis station data would not accurately reflect nitrate concentrations in the upper Stockton DWSC moving into the Central Delta. The Stockton WTP provides nitrate concentration information at their monitoring sites, however, future nutrient monitoring studies should make sure to include at least one additional station between Vernalis and the effluent discharge site in order to better understand the different nitrate dynamics observed at certain times.

5.3.4 Conclusions and Recommendations

Nutrient and water mixing dynamics are quite complicated within the Delta region, and different parts of the Delta show different primary controls on nutrient forms and distributions. The Stockton Deep Water Ship Channel (part of the San Joaquin River) is characterized by large spatial and temporal changes in nitrate concentrations.

By combining data from several different monitoring studies, we have shown that nitrate isotope data combined with hydrodynamic modeling outputs can be a powerful tool for tracking different nitrate sources entering the Delta and San Francisco Bay, and can provide information about which processes (physical or biological) are dominant at specific times and locations.

As stated in the Appendix Summary:

- The average $\delta^{15}\text{N}$ of NO_3 entering the tidal reach from the upstream San Joaquin River (SJR) was consistently higher (11.3 ± 2.4 ‰, upstream of pumping diversion) in comparison to the Sacramento River (5.3 ± 0.9 ‰, sampled at Rio Vista), indicating that $\delta^{15}\text{N}$ - NO_3 can be useful for tracking NO_3 from the two watersheds as it mixes in the Delta.
- Nitrate isotope measurements downstream of the Sacramento-San Joaquin Rivers confluence and into Suisun Bay indicate that nitrate in this downstream section of the Bay-Delta is primarily derived from the Sacramento River region, not from the San Joaquin River.
- There are large temporal variations in the amount of mixing between SJR and Sacramento R. water, and this mixing exerts significant control on the downstream distribution of nutrients, particularly nitrate, derived from the SJR.
- Nitrate isotope measurements and volumetric water source estimates from the DSM2-QUAL model show that the mixing of water sources (and not biological processes) is the dominant control on nitrate distribution in the Stockton Deep Water Ship Channel portion of the SJR.
- In general, nitrate concentrations in the upper part of the Stockton DWSC closely matched nitrate concentrations in samples collected at the site of the long term monitoring station at Vernalis on the SJR. However, there is some indication that during the winter months when nitrate concentrations in the effluent from the Stockton WWTP are at their highest, nitrate concentrations at Vernalis do not match nitrate concentrations in the upper Stockton DWSC. Therefore, nitrate patterns in the effluent discharge from the Stockton WWTP must be taken into account when using water quality data from Vernalis as an end-member contribution to the Delta.

Recommendations:

Although nitrate concentrations in the upper Stockton DWSC can usually be well-predicted based on nitrate data from the Vernalis long-term monitoring stations, there are certain times when nitrate dynamics in the upper Stockton DWSC appear to be de-coupled from nitrate dynamics at Vernalis. During these periods, there appears to be a loose relationship with nitrate concentrations in the Stockton effluent, however, changes in the effluent alone do not explain the observed variability in nitrate in the upper Stockton DWSC. Nutrient monitoring and sampling programs aiming to understand nitrogen dynamics in this part of the Delta should include at least an additional monitoring station both between Mossdale and the effluent discharge, and in the upper DWSC below the discharge point.

Nitrate derived from the San Joaquin River has a very distinct isotopic composition compared to nitrate derived from the Sacramento River. Studies designed to examine nutrient sources and movement through the Delta would greatly benefit from making isotopic measurements in addition to concentration measurements.

Appendix 5.3 Tables and Figures

Combined use of stable isotopes and hydrologic modeling to better understand nutrient dynamics in the Stockton Deep Water Ship Channel, San Joaquin River and Delta

Table 5.3.1 (Excel File)

Water quality data from the Stockton Wastewater Treatment Plant for effluent and receiving water monitoring station R2A.

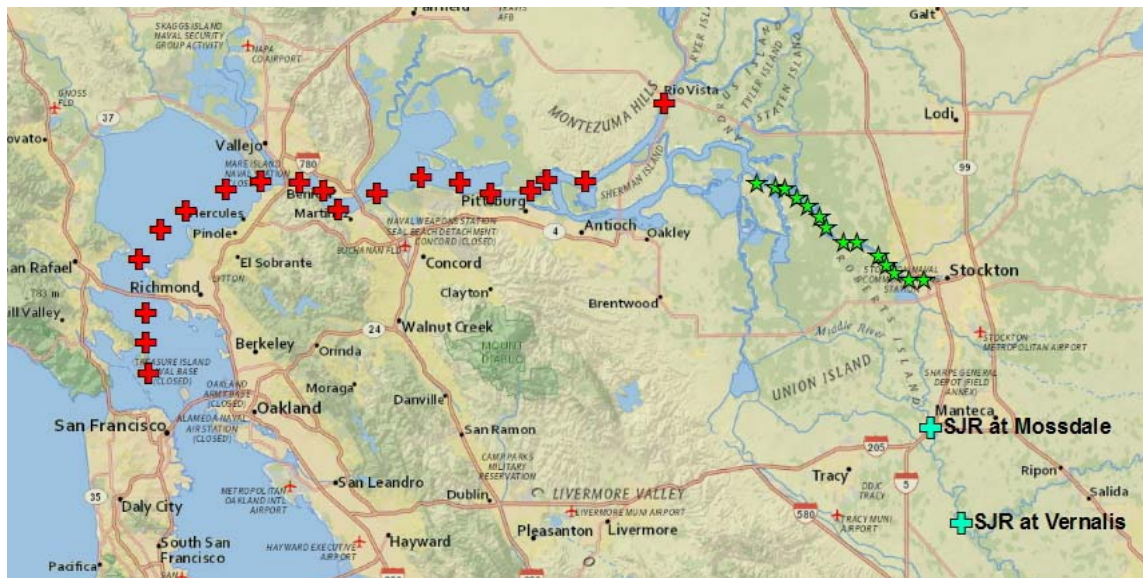
Table 5.3.2 Minimum and maximum $\delta^{15}\text{N-NO}_3$ values measured at DWR Dissolved Oxygen Run stations in the Stockton Deep Water Ship Channel 2006-2007.

Date	Minimum $\delta^{15}\text{N-NO}_3$	Maximum $\delta^{15}\text{N-NO}_3$	Difference	Pattern
9-Aug-06	6.28	11.03	4.75	Smooth transition
7-Sep-06	7.65	11.51	3.87	Smooth transition
19-Sep-06	5.73	11.58	5.86	Smooth transition
5-Oct-06	6.37	11.74	5.38	Smooth transition
6-Nov-06	6.47	12.27	5.80	Smooth transition
20-Nov-06	5.71	11.74	6.04	Smooth transition
28-Jun-07	8.17	14.38	6.20	Moderate step decrease
12-Jul-07	6.20	15.20	9.00	Moderate step decrease
26-Jul-07	6.11	13.18	7.07	Moderate step decrease
10-Aug-07	4.13	13.81	9.69	Strong step decrease
23-Aug-07	3.22	16.21	13.00	Very strong step decrease
10-Sep-07	2.88	17.31	14.44	Very strong step decrease
25-Sep-07	2.68	17.16	14.48	Very strong step decrease
11-Oct-07	3.29	16.86	13.57	Very strong step decrease*
25-Oct-07	6.60	13.63	7.03	Moderate step decrease*
9-Nov-07	7.80	12.85	5.05	Moderate step decrease*
26-Nov-07	6.03	13.03	7.00	Moderate step decrease*
12-Dec-07	5.28	12.21	6.94	Moderate step decrease*

*step decrease in $\delta^{15}\text{N-NO}_3$ occurred further downstream in comparison to previous transects.

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Figure 5.3.1. Map of the Delta region with DWR Dissolved Oxygen Run stations, Polaris Water Quality Monitoring Stations, and DO TMDL/ PIN700 monitoring stations at Mossdale and Vernalis in the SJR.

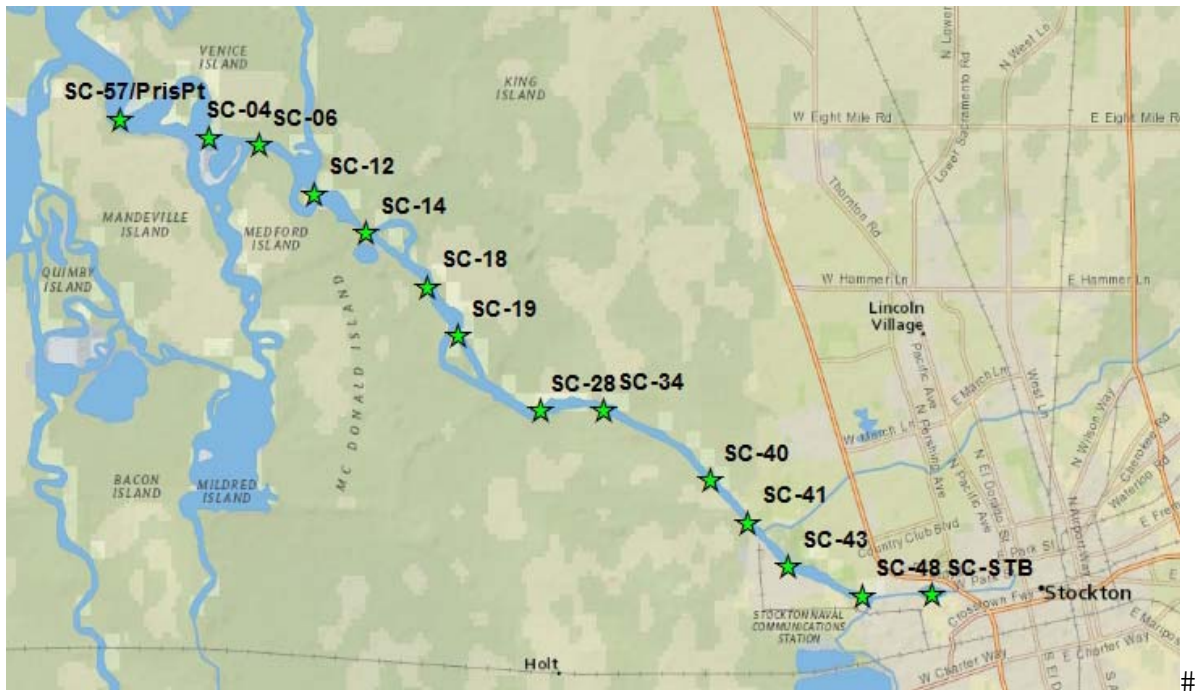


Figure 5.3.2. Detailed map of DWR DO Run stations.

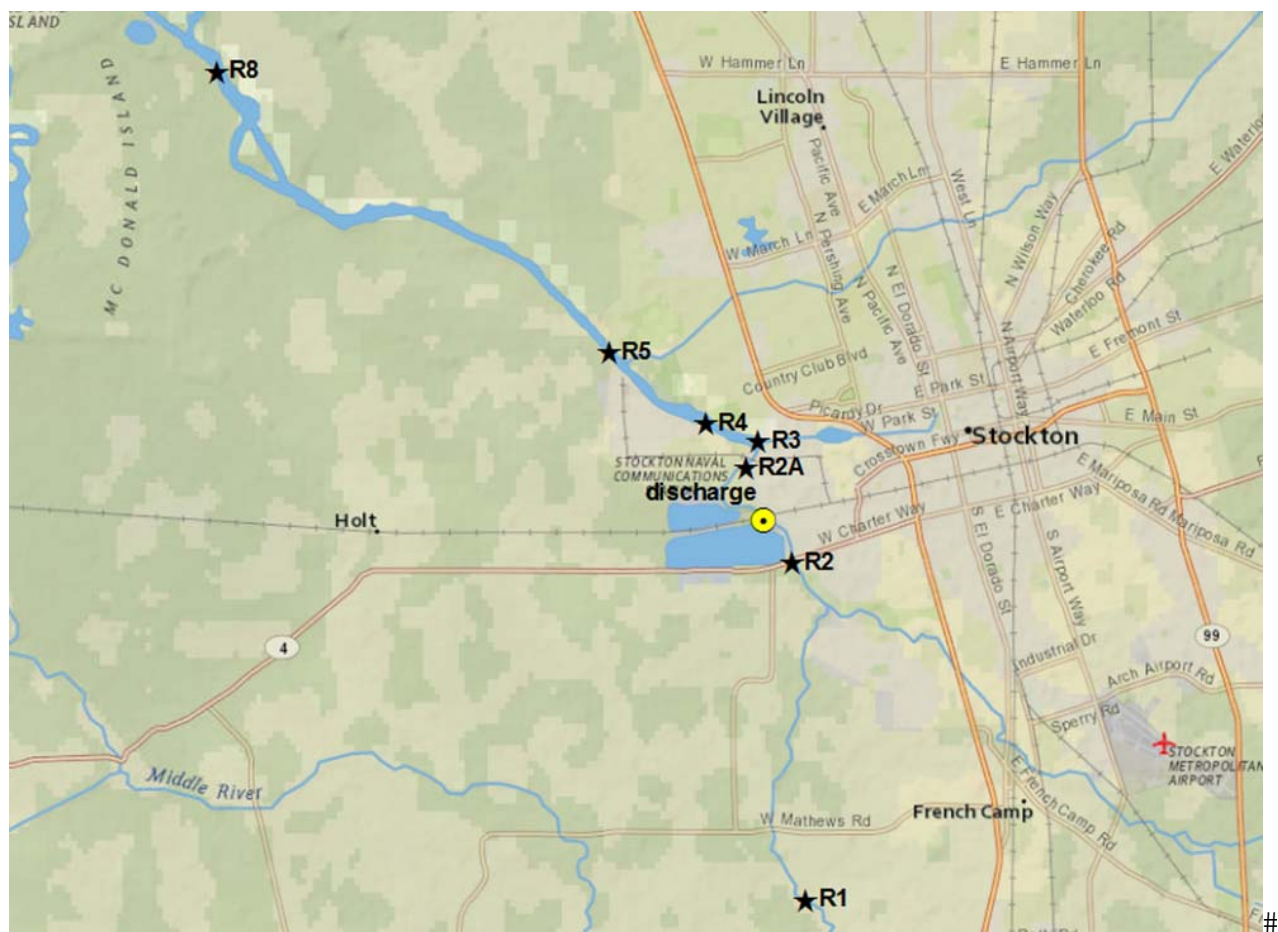
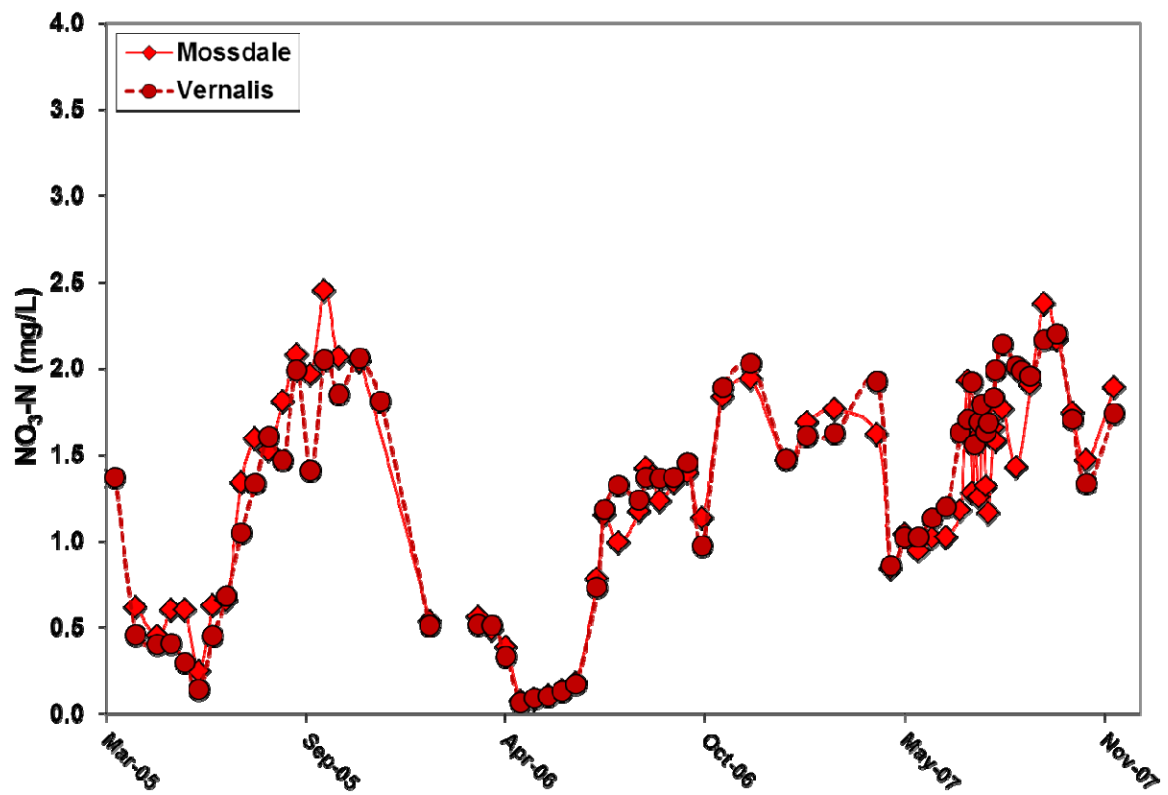


Figure 5.3.3. Map showing effluent discharge location and selected receiving water sampling stations for the Stockton WWTP.



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Figure 5.3.4. Variations in nitrate concentration at Mossdale and Vernalis stations throughout the DO TMDL Monitoring study.

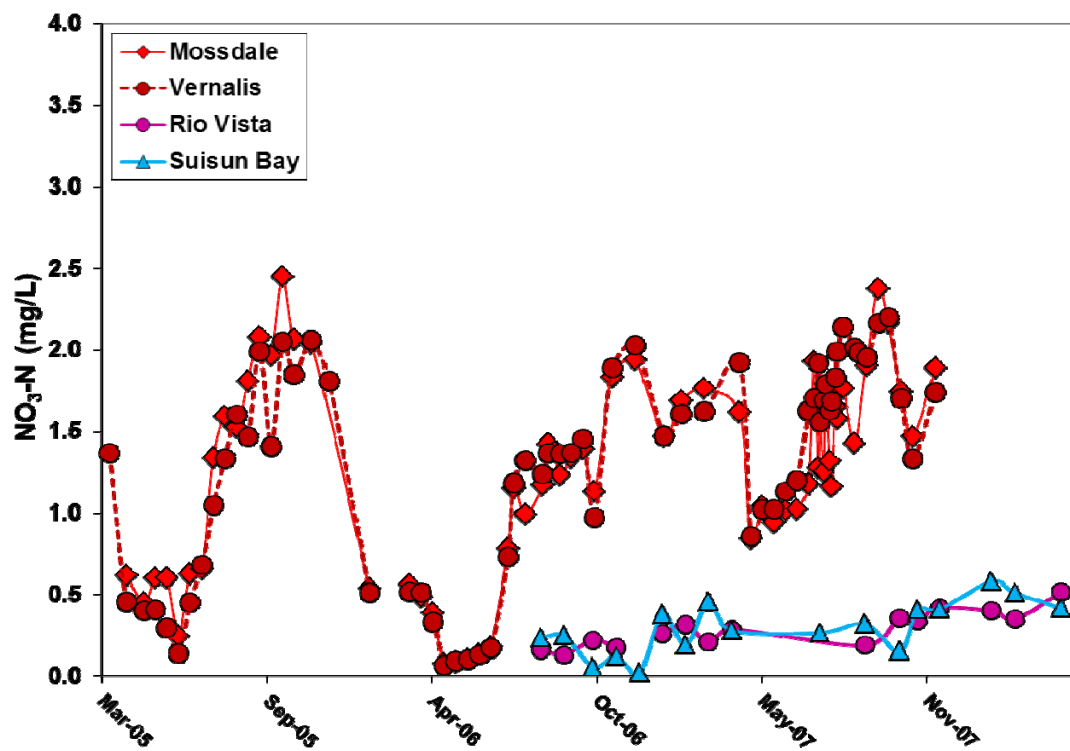


Figure 5.3.5. Temporal patterns of nitrate concentrations at the San Joaquin River monitoring stations in comparison to nitrate concentrations measured at Rio Vista and at one the Suisun Bay stations (PO-06).

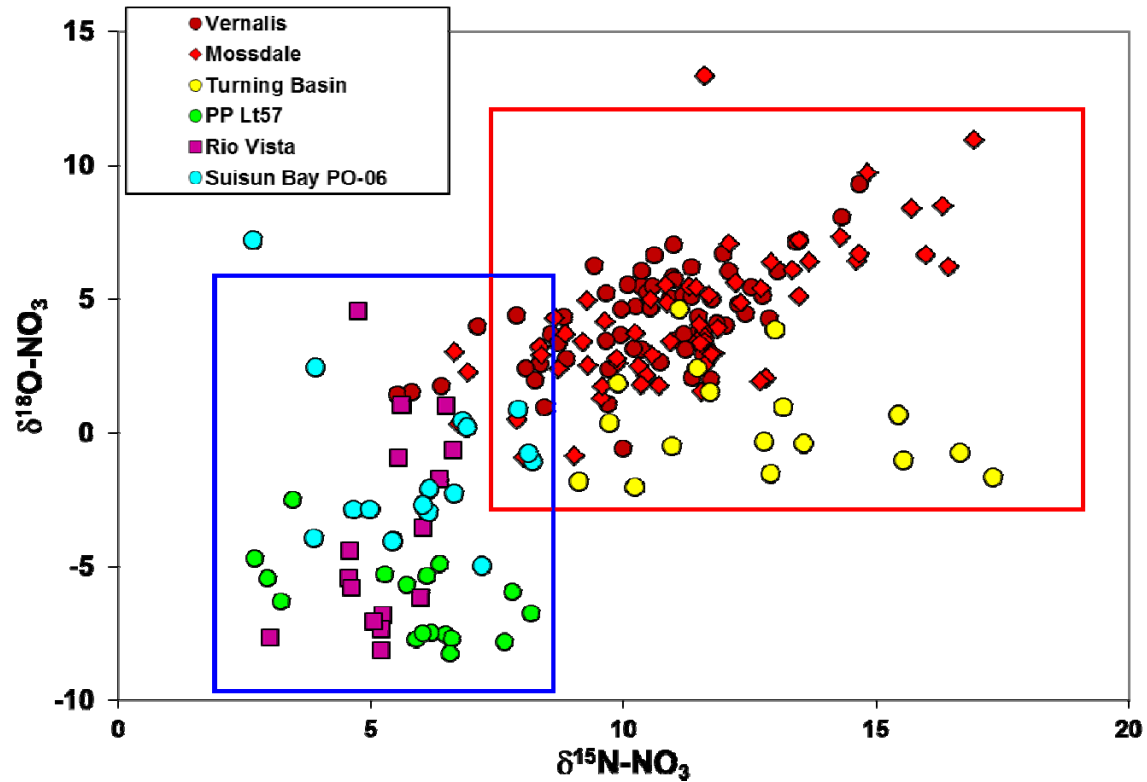


Figure 5.3.6. Dual nitrate isotope compositions of samples collected at upstream San Joaquin River monitoring stations, Rio Vista (Sacramento River), Suisun Bay, and the first and last stations of the DWR DO Run in the SJR Stockton Deep Water Ship Channel. Upstream San Joaquin River samples are characterized by higher $\delta^{15}\text{N}$ and $\delta^{18}\text{O-NO}_3$ in comparison to Sacramento River samples and samples from Suisun Bay.

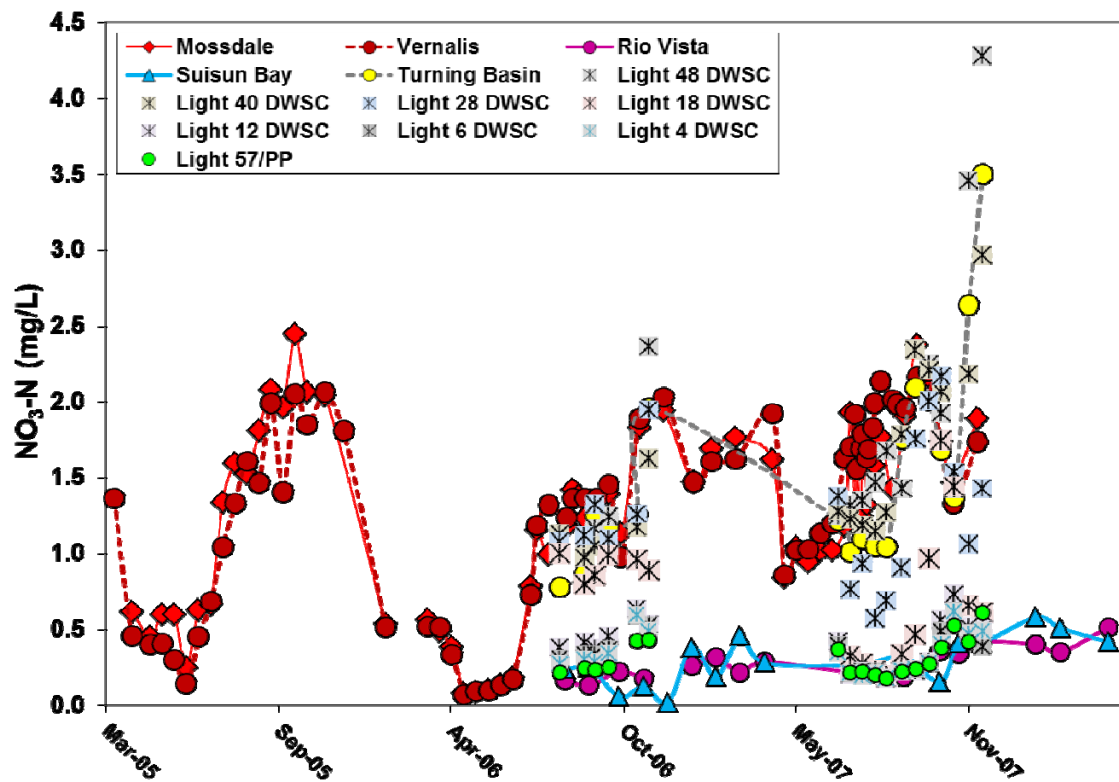


Figure 5.3.7. Temporal variations in nitrate concentrations measured in the DWR DO Run samples from the Stockton DWSC in comparison to concentrations measured upstream in the San Joaquin River, in the Sacramento River at Rio Vista, and in Suisun Bay.

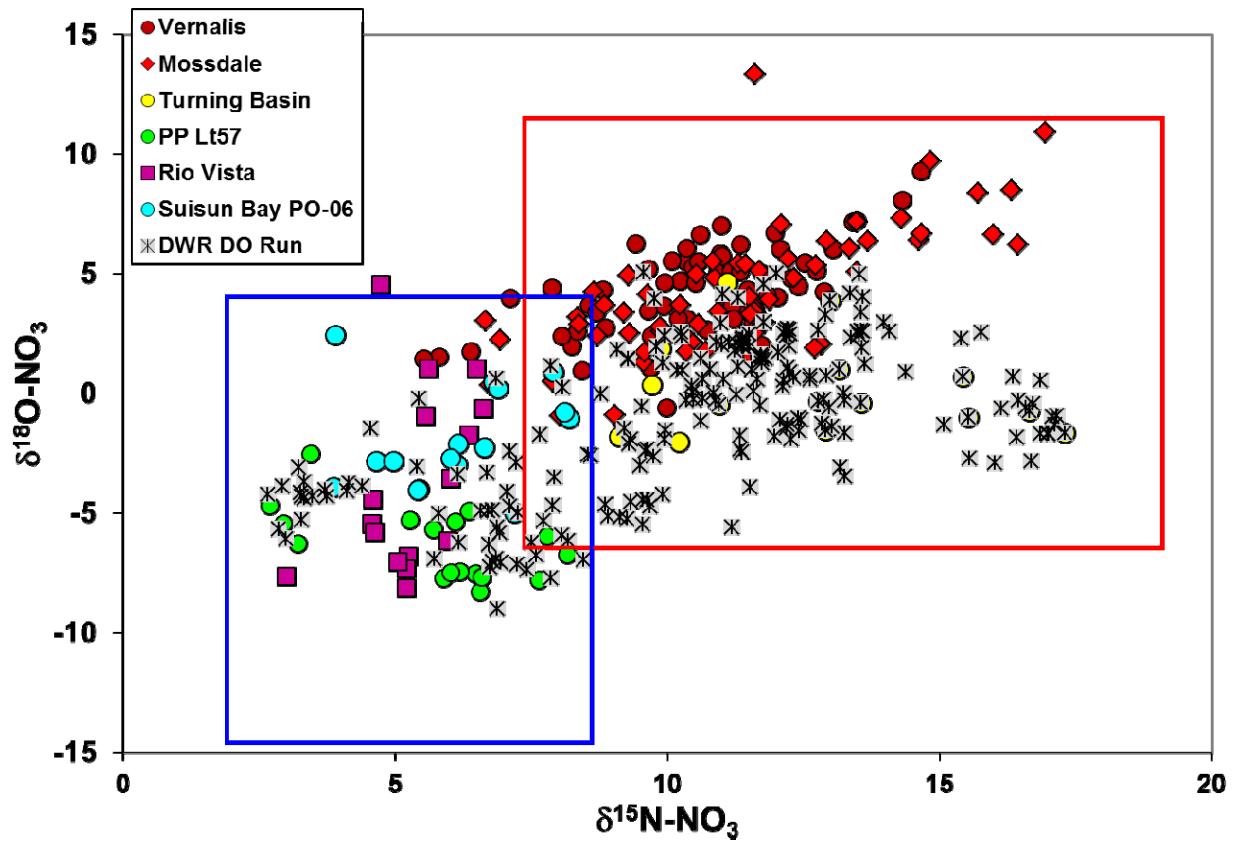
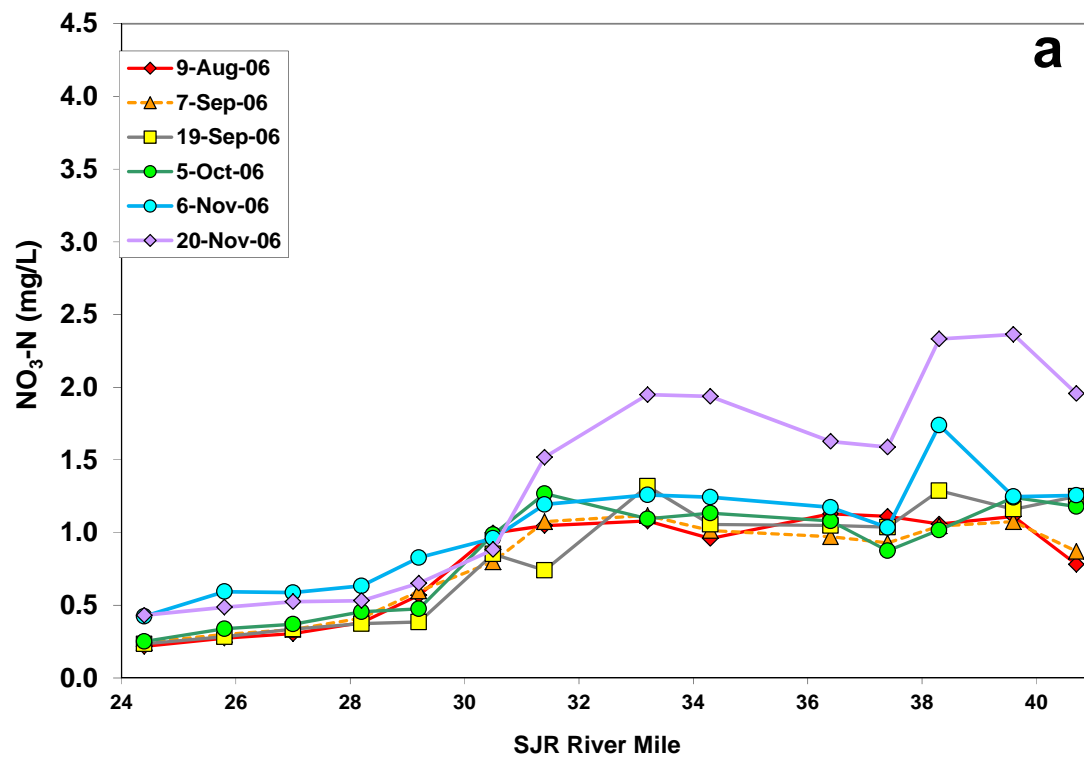
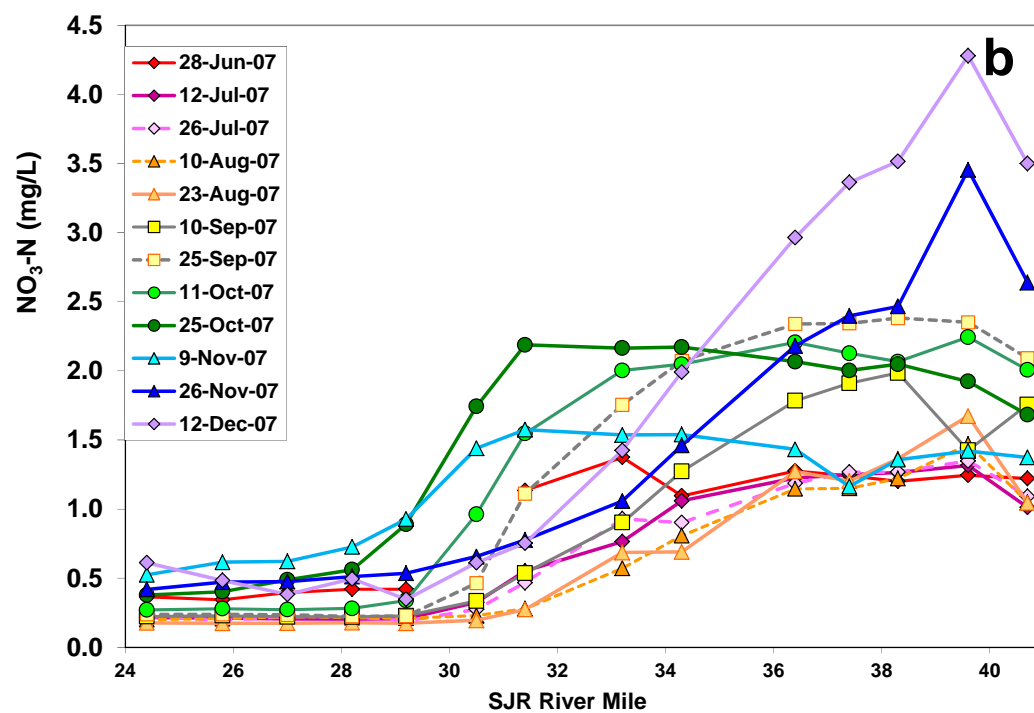


Figure 5.3.8. Dual nitrate isotope compositions of samples collected at upstream San Joaquin River monitoring stations, Rio Vista (Sacramento River), and Suisun Bay. Samples collected from the DWR DO Run transect are shown in gray for comparison, and have isotopic compositions within the ranges of both the San Joaquin River and the Sacramento River/ Suisun Bay samples.



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Figure 5.3.9. NO₃-N (mg/L) in the Stockton DWSC measured during DWR Dissolved Oxygen Runs in a) 2006 and b) 2007.

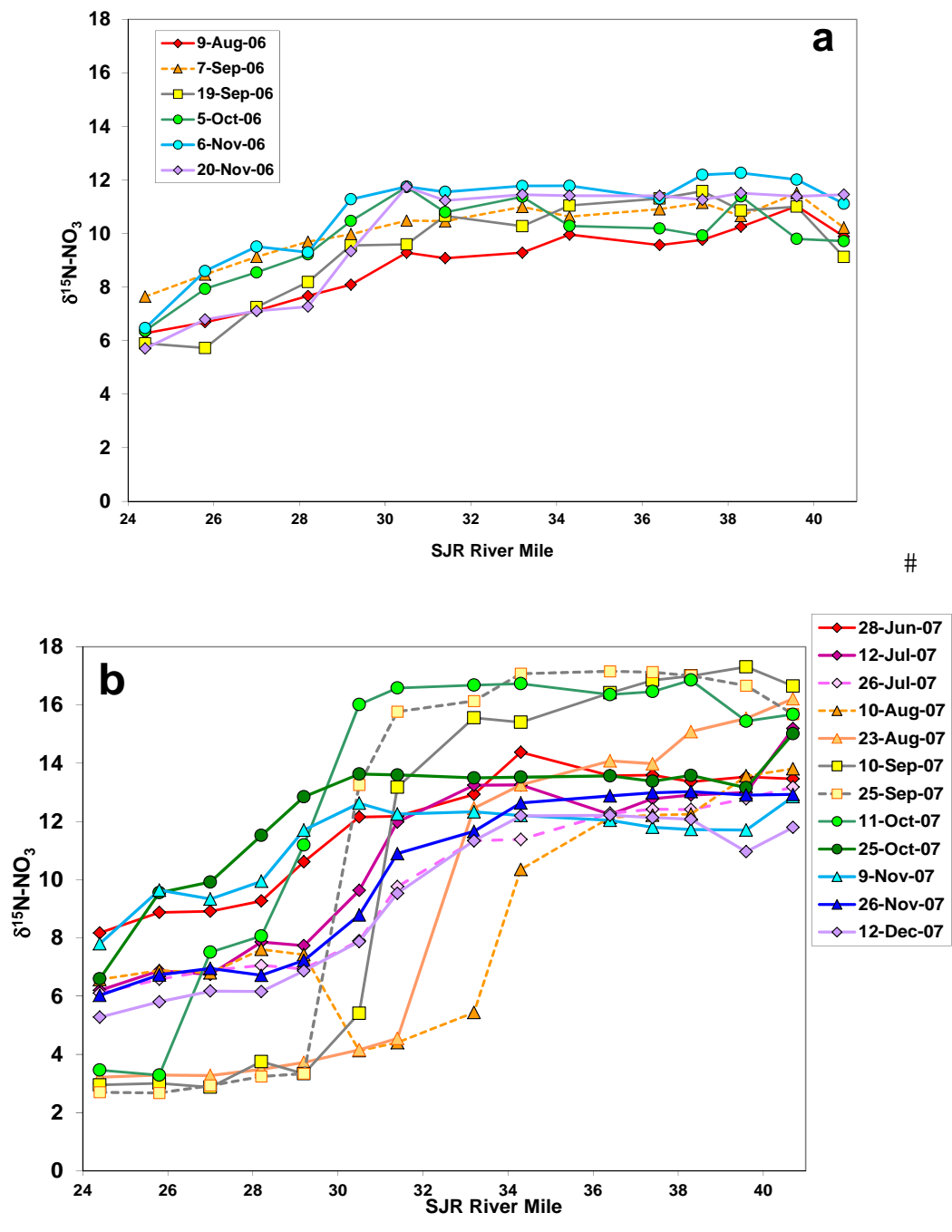
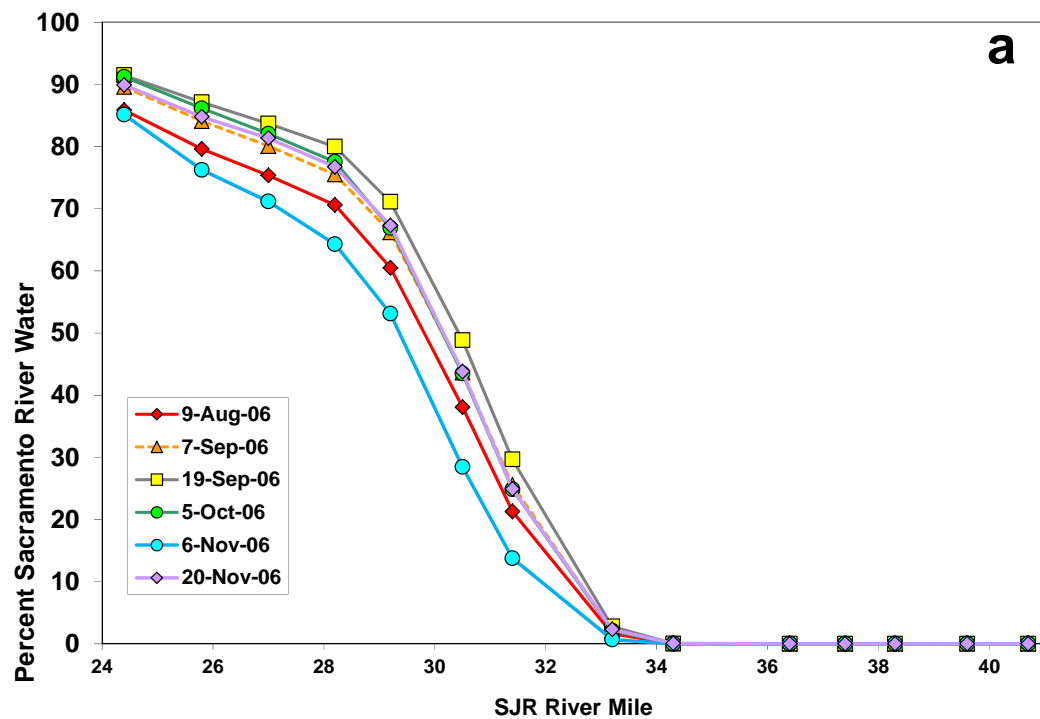
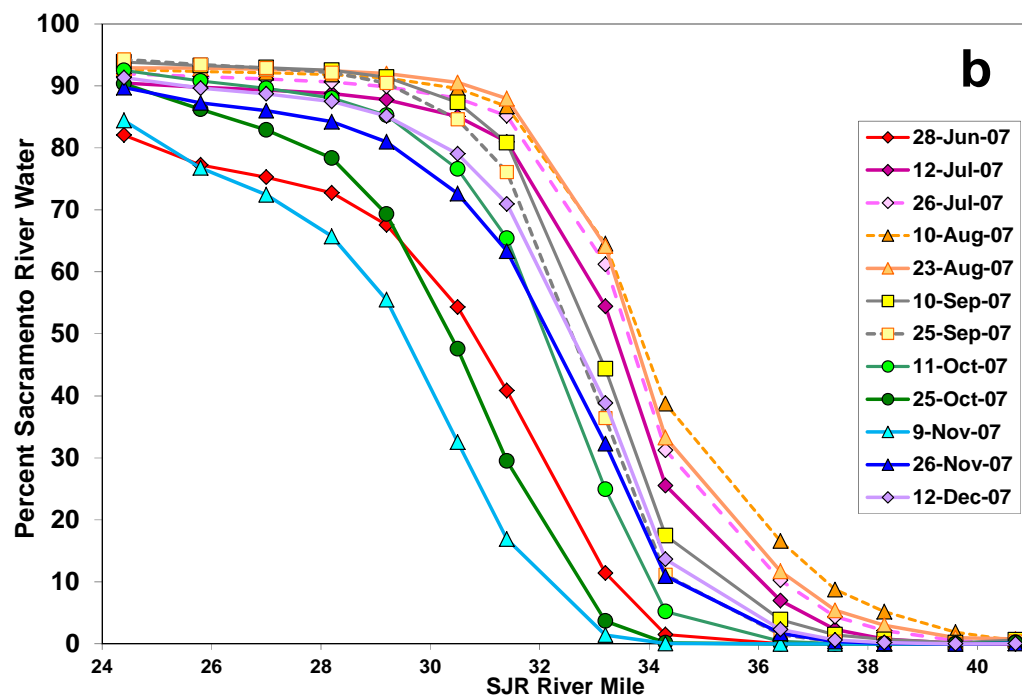


Figure 5.3.10. $\delta^{15}\text{N-NO}_3$ in the Stockton DWSC measured during DWR Dissolved Oxygen Runs in a) 2006 and b) 2007.

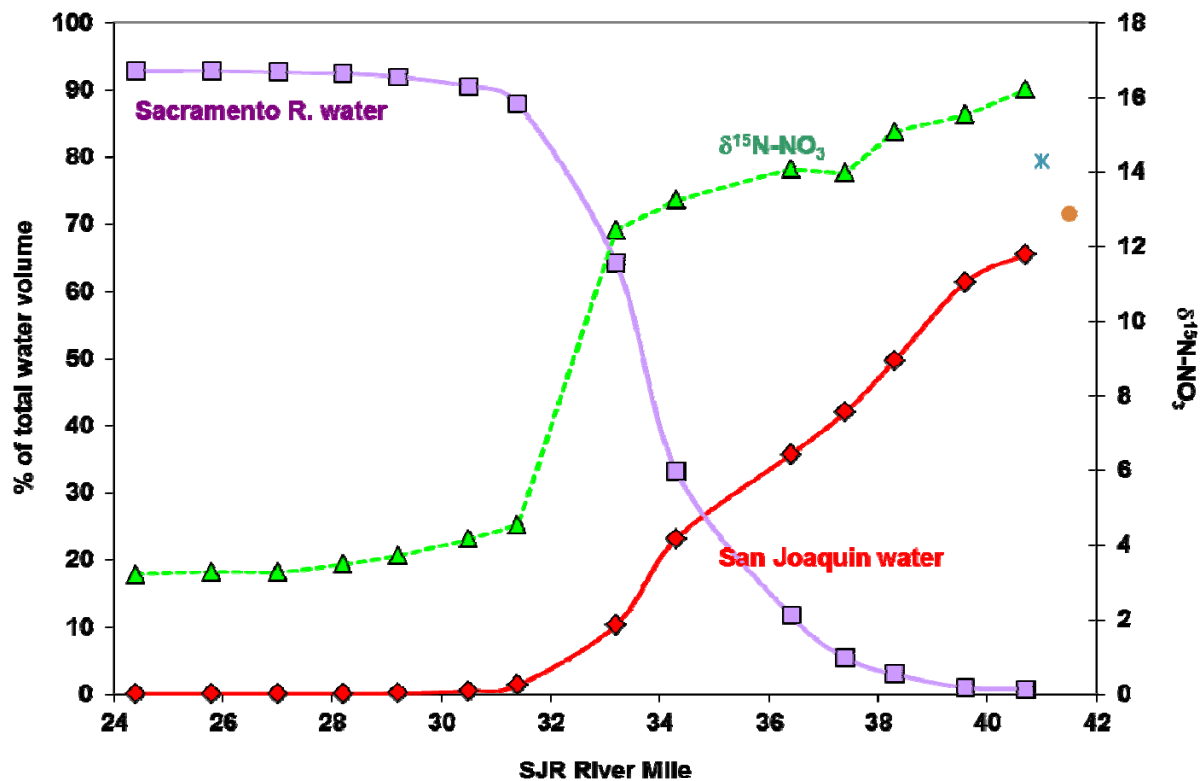


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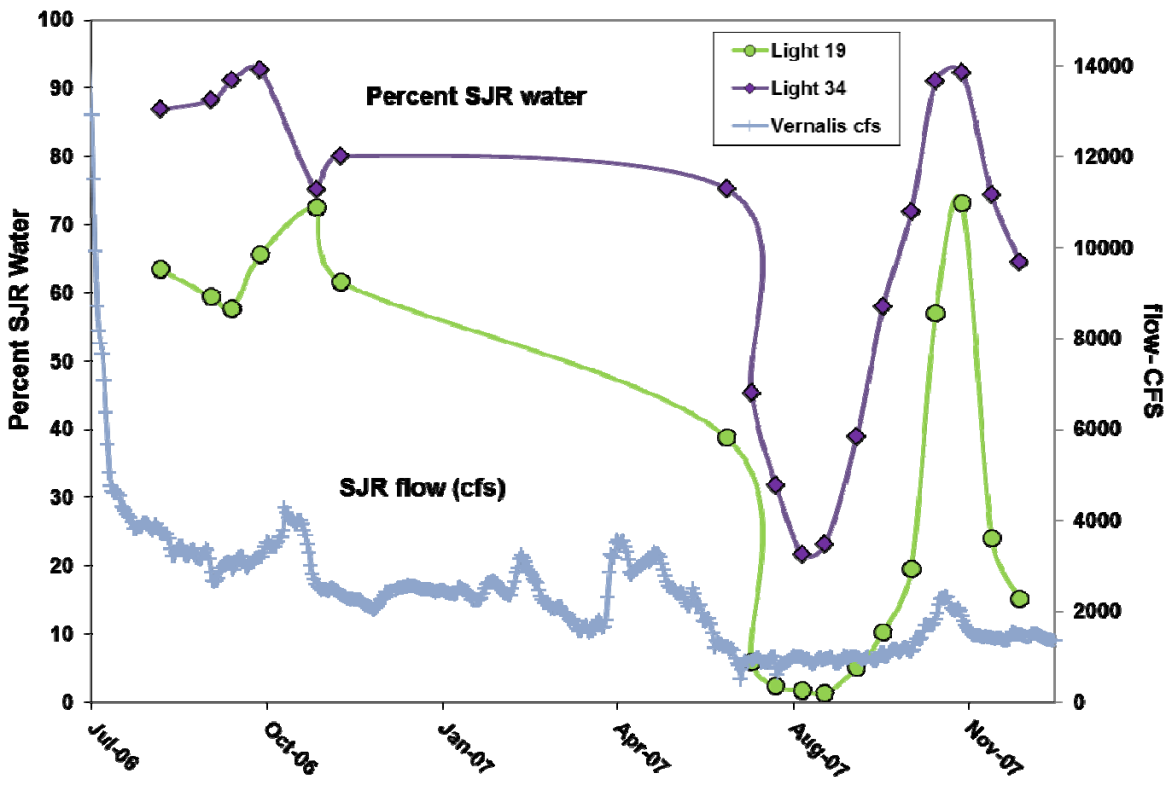
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Figure 5.3.11. Percent Sacramento River Water calculated with the DSM2-QUAL model for DWR Dissolved Oxygen Runs sites in the Stockton DWSC in a) 2006 and b) 2007.



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Figure 5.3.12. Graph showing measured $\delta^{15}\text{N-NO}_3$ values during a single transect in the Stockton Deep Water Ship Channel (green triangles), along with estimated percent volumetric inputs (DSM2-QUAL) from Sacramento River water (purple squares) and San Joaquin River water (red diamonds). This graph show the strong agreement between the modeled estimates of Sacramento River water and San Joaquin River water, and the presence of nitrate derived from each river.



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Figure 5.3.13. Changes in percent San Joaquin River water calculated by the DSM2-QUAL model (the remainder is always Sacramento River water) at two stations in the Stockton DWSC sampled as part of the DWR DO Runs. Note how the percent of SJR water decreases during times of lower flows at Vernalis, which allow Sacramento River water to move further up the SJR channel.

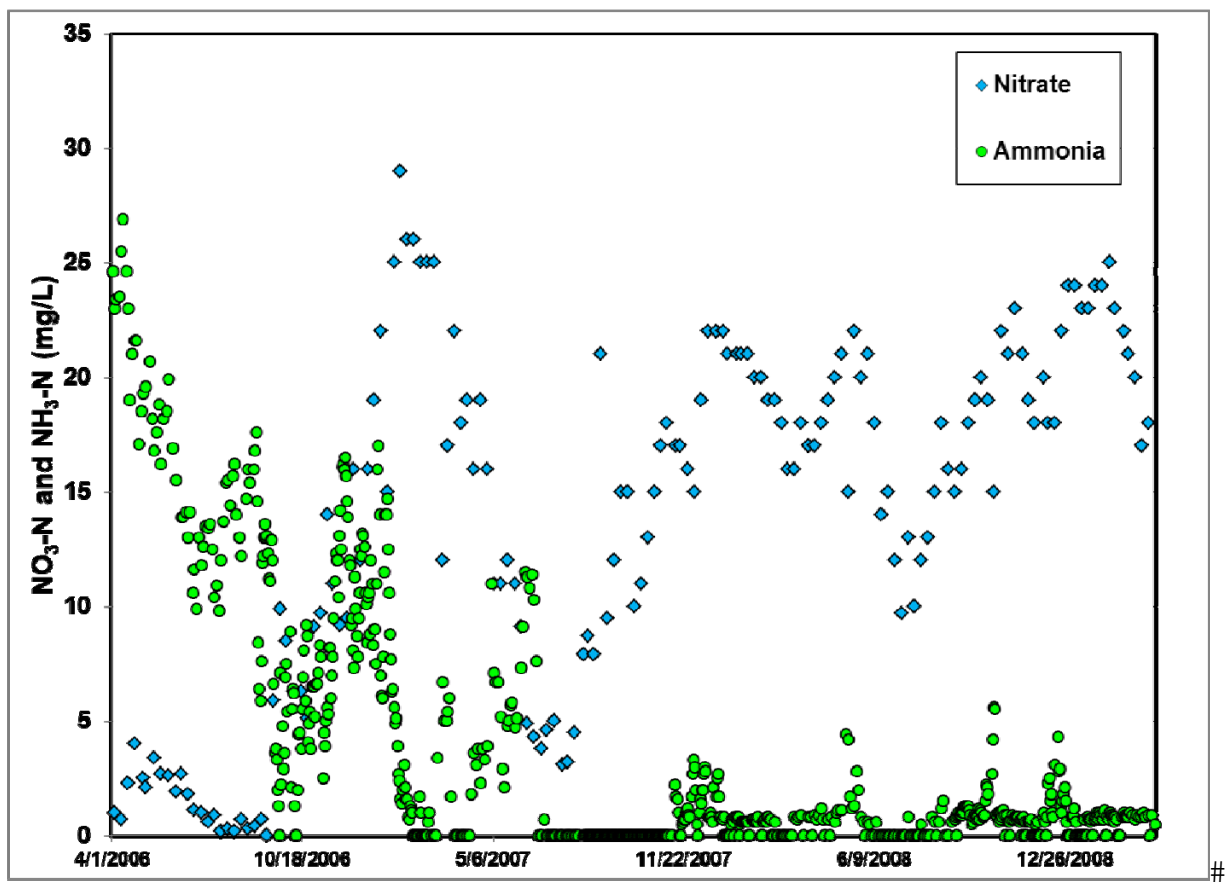


Figure 5.3.14. Ammonia and nitrate concentrations (in mg/L N) in the Stockton WTP effluent over time. Data provided by the Stockton WTP's monitoring program.

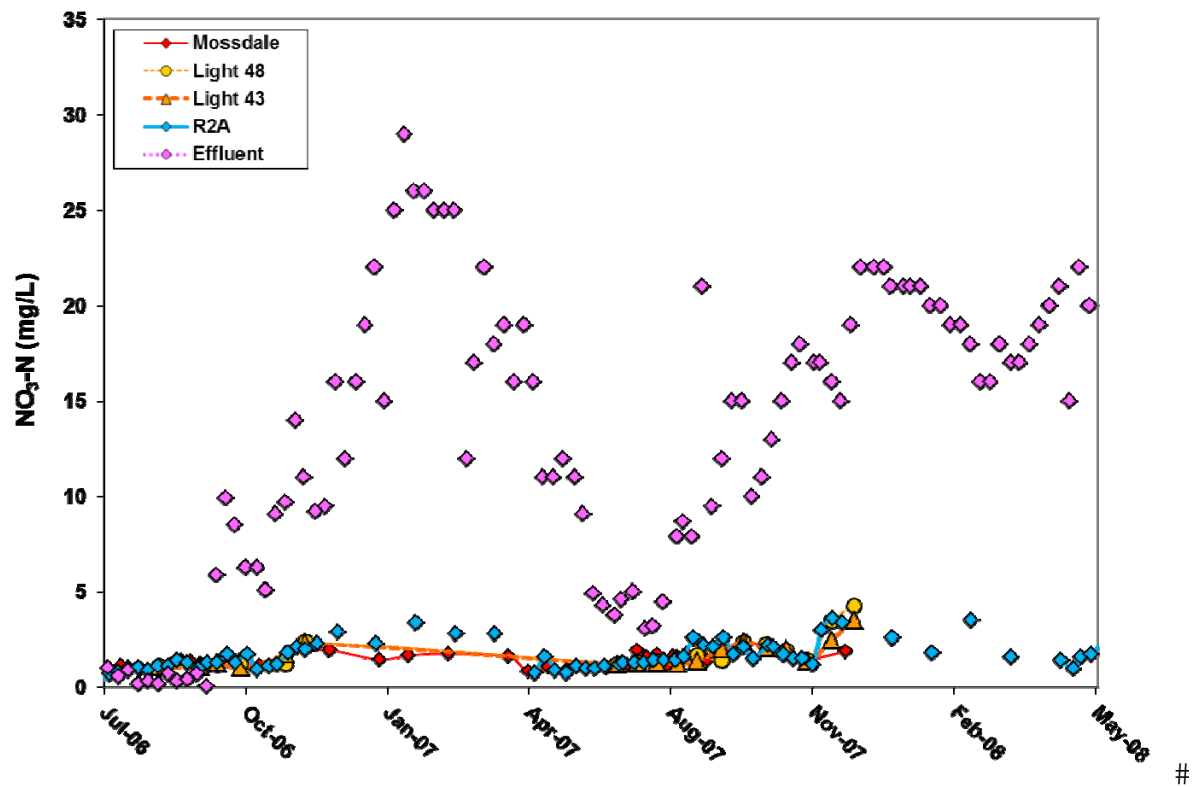


Figure 5.3.15. Nitrate concentrations from the DWR DO Run sites Light 48 and Light 43, downstream in the Stockton DWSC, in comparison to nitrate concentrations in the effluent and in the Stockton WTP monitoring site R2A immediately downstream of the effluent discharge location.

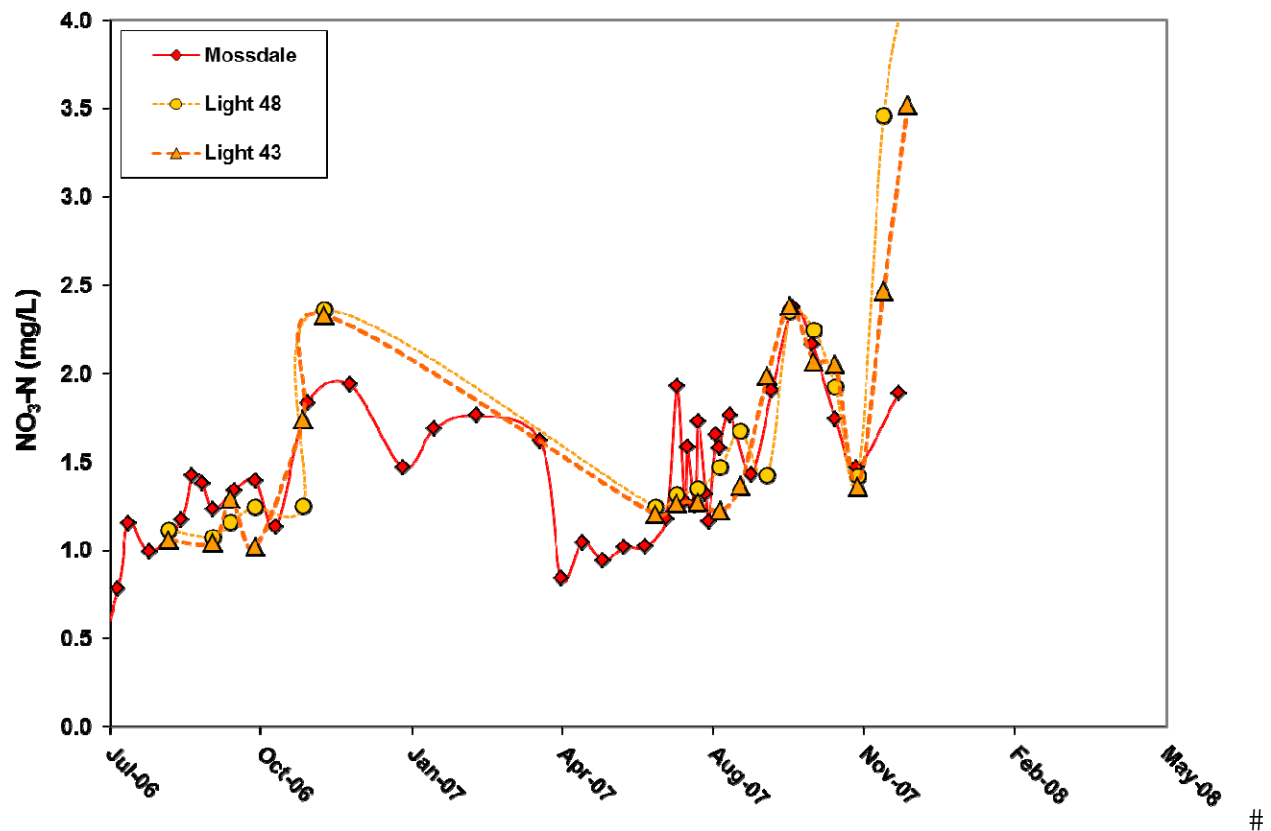


Figure 5.3.16. Nitrate concentrations at Mossdale, in the San Joaquin River above the Stockton WTP and the Stockton DWSC, in comparison to nitrate concentrations at sites just downstream in the Stockton DWSC (but still within the influence of SJR, not Sacramento River, water). Nitrate concentrations at Mossdale are often higher than those downstream, and the downstream nitrate often follows the same pattern as those seen at Mossdale.

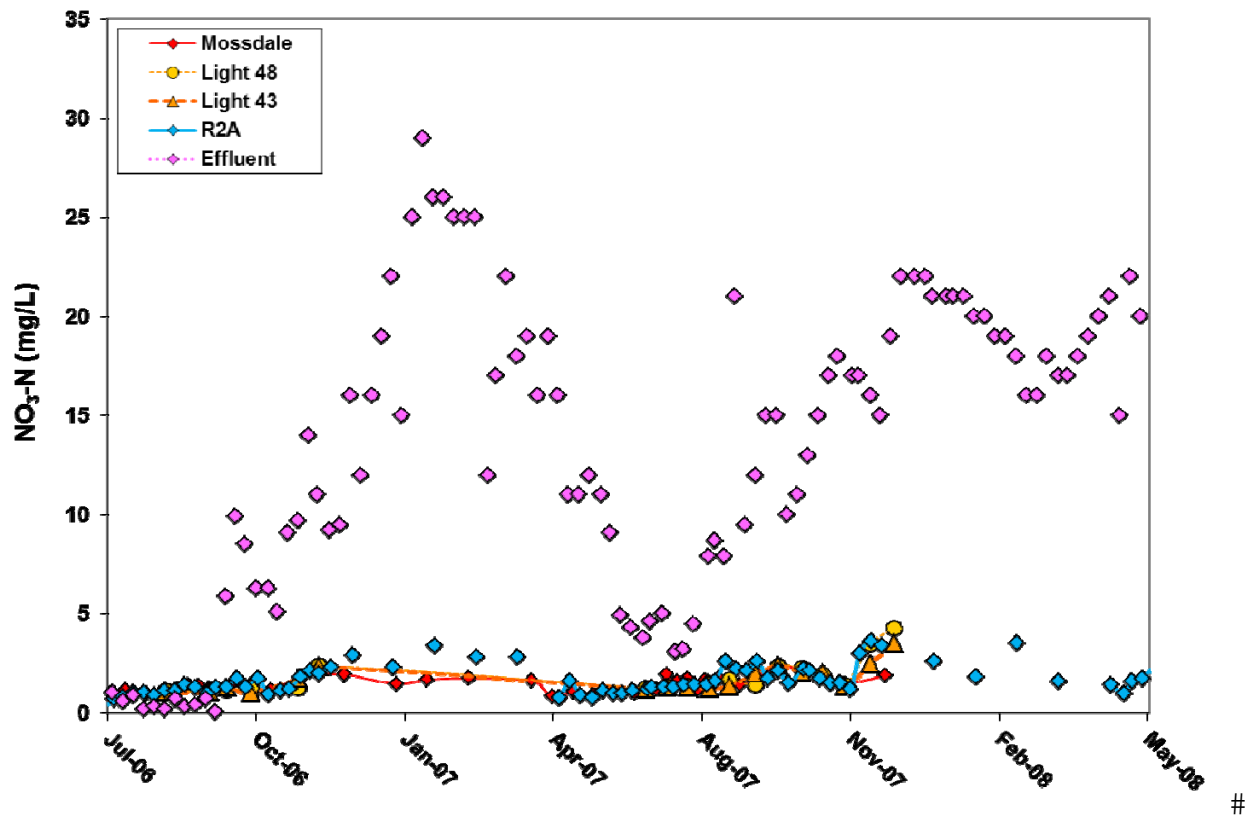


Figure 5.3.17. Nitrate concentrations in the Stockton WTP effluent in comparison to the Mossdale San Joaquin River site and selected downstream sites.

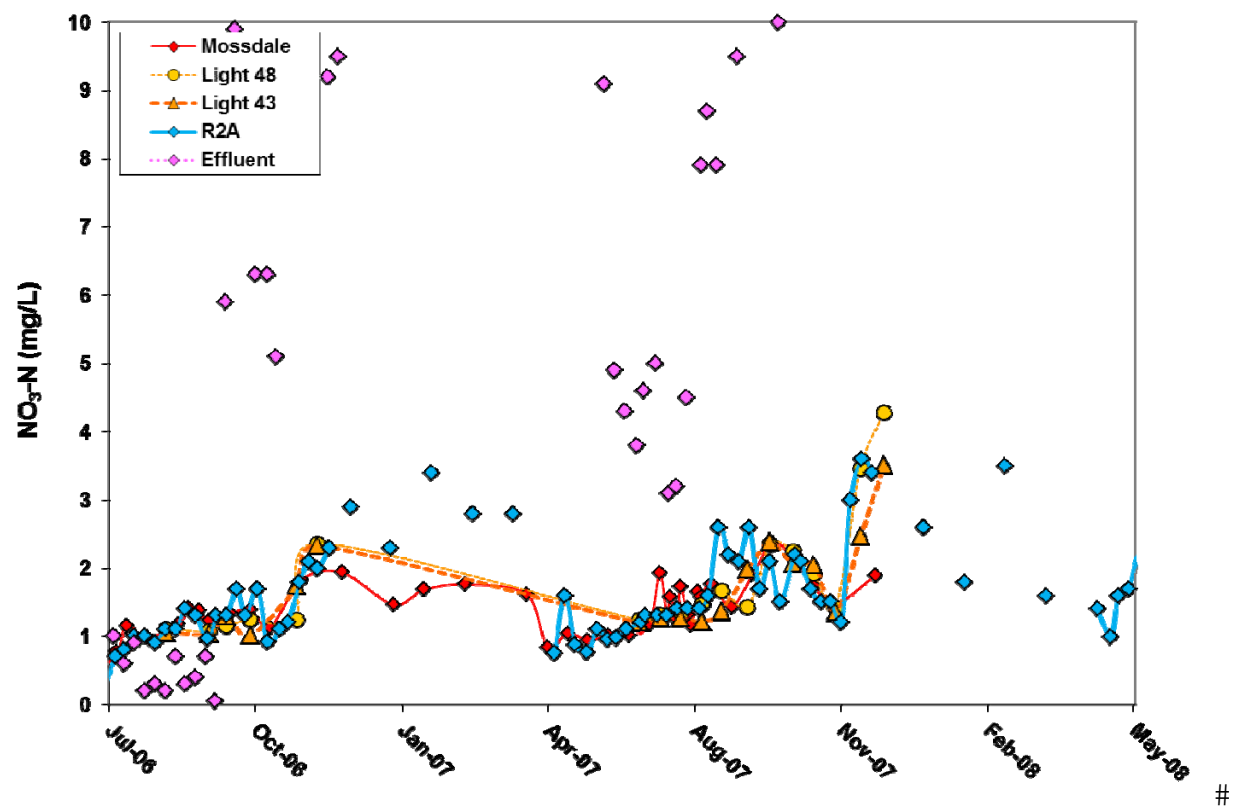


Figure 5.3.18. Detail of Figure 5.3.17.