Title:

Riverine Nutrient Trends in the Sacramento and San Joaquin Basins, California: A Comparison to State and Regional Water Quality Policies

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Abstract:

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Non-point source (NPS) contaminant control strategies were initiated in California in the late 1980s under the authority of the State Porter–Cologne Act and eventually for the development of total maximum daily load (TMDL) plans, under the federal Clean Water Act. Most of the NPS TMDLs developed for California's Central Valley (CV) region were related to pesticides, but not nutrients. Efforts to reduce pesticide loads and concentrations began in earnest around 1990. The NPS control strategies either encouraged or mandated the use of management practices (MPs). Although TMDLs were largely developed for pesticides, the resultant MPs might have affected the runoff of other potential contaminants (such as nutrients). This study evaluates the effect of agricultural NPS control strategies implemented in California's CV before and between 1990 and 2013, on nutrients, by comparing trends in surface-water concentrations and loads. In general, use of MPs was encouraged during a "voluntary" period (1990 to 2004) and mandated during an "enforcement" period (2004 to 2013). Nutrient concentrations, loads, and trends were estimated by using a recently developed Weighted Regressions on Time, Discharge, and Season (WRTDS) model. Sufficient total phosphorus (TP), total nitrogen (TN), and nitrate (NO_3) data were available to compare the voluntary and enforcement periods for twelve sites within the lower

Sacramento and San Joaquin basins. Ammonia concentrations and fluxes were evaluated at a subset of these sites. For six of these sites, flow-normalized mean annual concentrations of TP or NO_3 decreased at a faster rate during the enforcement period than during the voluntary period. Concentration changes during similar years and ranges of flow conditions suggest that MPs designed for pesticides may also have reduced nutrient loads. Results show that enforceable NPS policies, and accelerated MP implementation, limits NPS pollution, and may control runoff of non-targeted constituents such as nutrients.

Supporting material:

Appendix A: Fluxes for Selected Constituents in Water Years (October 1 to September 30) 1975-2013

Copyright Information:

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Brandon Schlegel*[1] and Joseph L. Domagalski[2]

ABSTRACT

Non-point source (NPS) contaminant control strategies were initiated in California in the late 1980s under the authority of the State Porter–Cologne Act and eventually for the development of total maximum daily load (TMDL) plans, under the federal Clean Water Act. Most of the NPS TMDLs developed for California's Central Valley (CV) region were related to pesticides, but not nutrients. Efforts to reduce pesticide loads and concentrations began in earnest around 1990. The NPS control strategies either encouraged or mandated the use of management practices (MPs). Although TMDLs were largely developed for pesticides, the resultant MPs might have affected the runoff of other potential contaminants (such as nutrients). This study evaluates the effect of agricultural NPS control strategies implemented in California's CV before and between 1990 and 2013, on nutrients, by comparing trends in surface-water concentrations and loads. In general, use of MPs was encouraged during a "voluntary" period (1990 to 2004) and mandated during an "enforcement" period (2004 to 2013). Nutrient concentrations, loads, and trends were estimated by using a recently developed Weighted Regressions on Time, Discharge, and Season (WRTDS) model. Sufficient total phosphorus (TP), total nitrogen (TN), and nitrate (NO_3) data were available to compare the voluntary and enforcement periods for twelve sites within the lower Sacramento and San Joaquin basins. Ammonia concentrations and fluxes were evaluated at a subset of these sites. For six of these sites, flow-normalized mean annual concentrations of TP or NO_3 decreased at a faster rate during the enforcement period than during the voluntary period. Concentration changes during similar years and ranges of flow conditions suggest that MPs designed for pesticides may also have reduced nutrient loads. Results show that enforceable NPS policies, and accelerated MP implementation, limits NPS pollution, and may control runoff of non-targeted constituents such as nutrients.

KEY WORDS

Sacramento–San Joaquin River Delta, nutrients, nitrogen, phosphorus, nutrient transport, nutrient loads, agricultural drainage

INTRODUCTION

The two largest rivers of the Central Valley of California, the Sacramento and the San Joaquin, drain multiple land use types including extensive mixed agriculture and urbanization (Figure 1). These two rivers collectively drain over 100,000 km^2 of the State of California, and are the primary sources of fresh water to the Sacramento–San Joaquin Delta (Delta). Over the years, numerous regulatory actions designated load reductions of various contaminants of concern, mostly pesticides. There have also been changes in land use, cropping patterns, water management, and irrigation methodology, all of which may have had some effect on the transfer of various constituents from land to water and subsequent transport to the Bay–Delta system. Regulatory actions for pesticides resulted from 303(d) listings (*http://www.waterboards.ca.gov/water_issues/programs/tmdl/integrated2010.shtml*) of impaired water bodies as mandated by the Clean Water Act. Numerous stream segments throughout the Central Valley have listings for various impairments. Although there have been few listed impairments specifically for nutrients in the Central Valley, management practices (MPs) for other contaminants of concern and land use changes may have affected the loads of nutrients (nitrogen and phosphorus) entering the Delta from these the Sacramento and San Joaquin rivers over the last 2 or more decades.

According to the 2010 Clean Water Act 303(d) list, 51 out of 814 surface water bodies in the Central Valley Region (Region 5 in California) are impaired by nutrients (*http://www.waterboards.ca.gov/water_issues/programs/tmdl/integrated2010.shtml*). Some of those listings are for waterways of the Delta. Of those, several impairments include low dissolved oxygen; with the cause attributed to nutrients (*http://baydeltaoffice.water.ca.gov/sdb/af/index_af.cfm*) and the sources may be agriculture, point sources, urban runoff or unknown. Elevated concentrations of nutrients—primarily nitrate, ammonia, and phosphorus—contribute to the development of hypoxic waters (Wu 2002). Hypoxic waters (dissolved oxygen concentrations less than 2 mg L^{-1}) may affect fish migration and thus separate fish populations from their natural inland spawning grounds (Ekau et al. 2010).

The goal of this investigation is to relate changes in California's agricultural NPS control program to the observed changes in nutrient concentrations and loads in the Sacramento and San Joaquin river basins. To understand how nutrient concentrations and loads might have changed over time, we used historical nutrient data to produce mass flux and concentration models for long-term monitoring sites within the Sacramento and San Joaquin River basins. We used flow-normalized trends in concentrations and loads to understand what effects, if any, California's various agricultural non-point source (NPS) control programs, or other processes, might have had. These programs have mostly been implemented to control pesticide concentrations and associated toxicity. Like most other parts of the country, NPS control in California is achieved through the implementation of management (or conservation) practices. Although agricultural NPS dischargers may implement MPs for many reasons, pressures from a regulatory body likely have the greatest effect.

This study examines key "turning points" in California's plan to control NPS pollution on nutrient trends in concentration and loads in the Sacramento and San Joaquin river basins. We used these turning points to define time periods for trend analysis. The turning points refer to the incorporation of voluntary MPs and subsequent mandatory practices designed to reduce loads of specific constituents. Our goal was to understand in what direction, if any, nutrient concentrations or loads trend, and if those trends are related to time-periods of various management actions related to any type of NPS control. We do not examine any individual management practice or control program in detail, but instead focus on analyzing how nutrients have changed in these rivers and streams over a 25- to 30-year period of management. Also because detailing the many land use or water management changes was beyond our scope, to detail we used the timing of NPS control programs as a basis for comparing nutrient trends.

A variety of regulatory requirements occurred as a result of federal or state activities starting in the early 1970s (Figure 2). Most of the water pollution control activities used throughout the nation between 1972
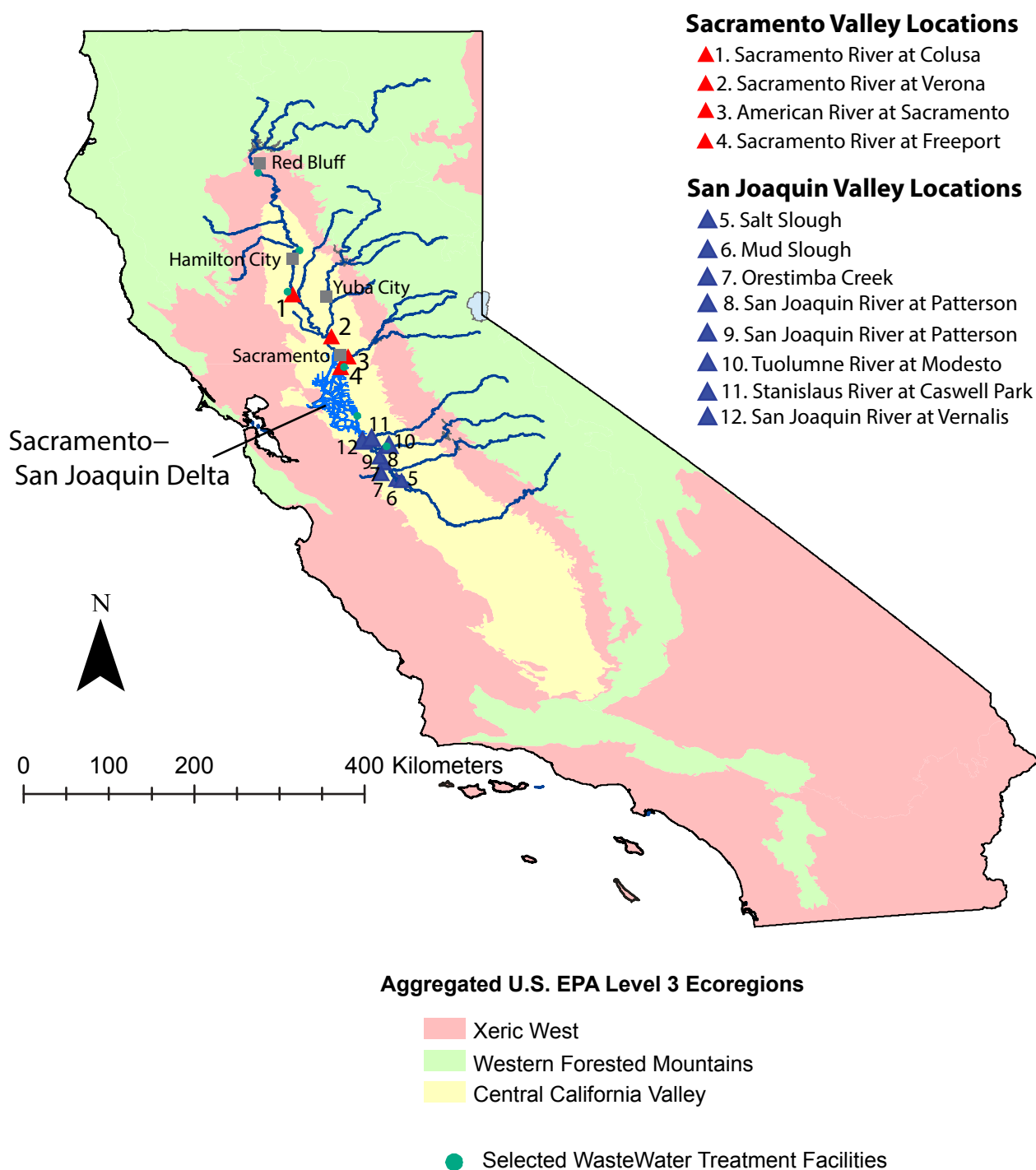
Sacramento Valley Locations
▲1. Sacramento River at Colusa
▲2. Sacramento River at Verona
▲3. American River at Sacramento
▲4. Sacramento River at Freeport

San Joaquin Valley Locations
▲5. Salt Slough
▲6. Mud Slough
▲7. Orestimba Creek
▲8. San Joaquin River at Patterson
▲9. San Joaquin River at Patterson
▲10. Tuolumne River at Modesto
▲11. Stanislaus River at Caswell Park
▲12. San Joaquin River at Vernalis

Aggregated U.S. EPA Level 3 Ecoregions

■ Xeric West
■ Western Forested Mountains
■ Central California Valley

● Selected WasteWater Treatment Facilities

Figure 1 Locations of stream sites and selected wastewater treatment facilities located within the Sacramento and San Joaquin basins. All sites are located within the Central California Valley ecoregion.

and the late 1980s focused on point sources (USEPA 1993). Because of the growing concerns of NPS pollution, the Federal Clean Water Act (CWA) was amended in 1987, and required states to adopt NPS pollution control programs (see §319 in the CWA). In response to the 1987 CWA amendment, California's State Water Resources Control Board adopted the Nonpoint Source Management Plan in 1988 (CSWRCB 1988). This plan evolved from voluntary to mandatory implementation of best management prac-tices (CSWRCB 1988, 2000). In 2004, the CSWRCB adopted the NPS Implementation and Enforcement Policy, which authorized the implementation and

enforcement of the NPS Program Plan (CVRWQCB 2011a).

Of the major agricultural NPS pollutants, pesticides have received the greatest attention in California's Central Valley region and thus have paved the way in the development of NPS control strategies. A review of the 2010 303(d) list for California's Central Valley region shows the relative focus on pesticides compared to nutrients; 31%)of the 814 TMDL listings identified pesticides as the contaminant of concern; whereas, only about 6% of listings were identified as nutrients.
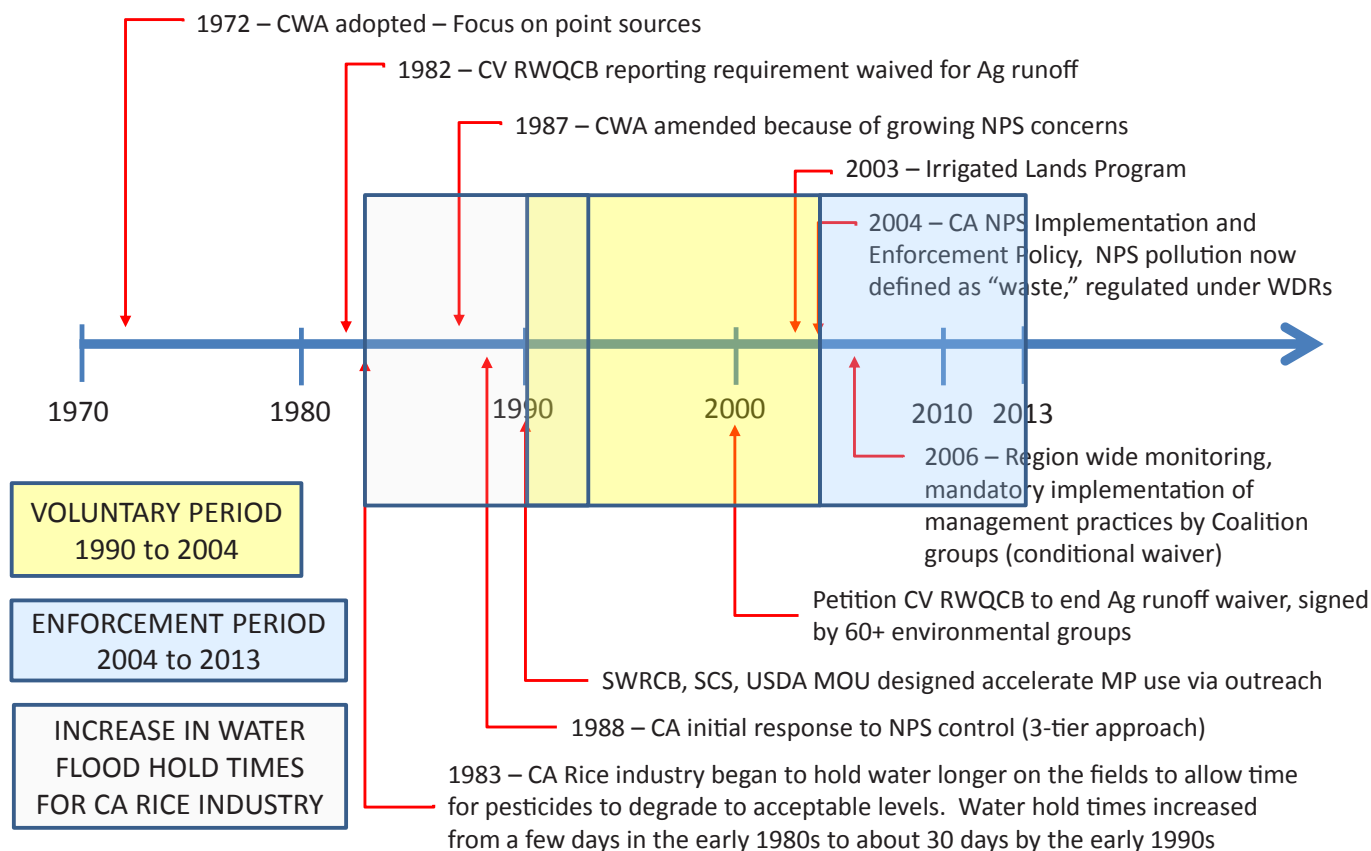

Figure 2 Timeline of selected regulatory requirements or management decisions related to agricultural non-point source pollution control

The primary sources of total nitrogen to the Sacramento and San Joaquin rivers are from agricultural activities, atmospheric deposition, urban runoff, runoff from forested land, and wastewater discharges as determined by a recently published SPARROW model (Saleh and Domagalski 2015). The two major sources of total nitrogen to the Delta from the Sacramento River were fertilizer and manure (47%) and point sources (32%) (Saleh and Domagalski 2015). Atmospheric deposition accounted for about 12%; developed land only accounted for about 3%. The remainder was from forested land (Saleh and Domagalski 2015). For the San Joaquin River system, fertilizer and manure accounted for 62% of the total nitrogen load and point sources about 19%. In the absence of anthropogenic activities, geological sources of phosphorus are the most important. Results from the SPARROW model for total phosphorus indicate that 65% of the phosphorus load in the lower Sacramento River originates from cultivated land and 21% from point sources with the remainder from geological sources (Domagalski and Saleh 2015). For the San Joaquin River system, about 58% of the phosphorus load to the Delta originates from cultivated land, while 15% is from point sources, and the remainder is from geological sources (Domagalski and Saleh 2015).

Surface runoff is the primary pathway of land-to-water transport of pesticides (CVRWQCB 2008) and the major pathway for most nutrients. Groundwater can contribute nitrogen in the form of nitrate to rivers, but under longer transport times. Agricultural runoff from fields or feedlots occurs in response to storm water or as irrigation return flow. Some reductions in pollutant loads in irrigation return flows can be attributed to the vegetative MPs (discussed later) and the water-use efficiency practices implemented in the early 1990s. Micro-irrigation use increased 138% in California, from about 324,000 ha in 1990 to about 770,000 ha in 2000 (CADWR 2009a).

A variety of MPs is available to reduce runoff, including the use of cover crops, vegetative buffers, and riparian buffers. As an MP, cover crops planted throughout a field anchor the soil, thereby limiting the transport of sediments, which may contain pesticides and nutrients. Vegetative buffers located at the edge of fields serve not only to trap sediment, but also to slow runoff waters, allowing dissolved pollutants time to infiltrate the surface. Riparian buffers, consisting of deep-rooted trees, can also use nitrate in groundwater before it enters the stream (CVRWQCB 2008). (These might be more important near larger streams than agricultural drains.) Riparian buffers are most effective where there is a connection of groundwater to the stream (Hill 1995; Bredehoeft 2015).

Options for controlling discharges from irrigated lands were reported on in 2001 (CVRWQCB 2011a, 2011b, 2011c). In 2003, the Central Valley RWQCB initiated the Irrigated Lands Regulatory Program (ILRP). In 2006, in order to comply with new waste discharge requirements for irrigated lands, Central Valley farmers were allowed to join coalition groups and receive coverage under a conditional wavier (*http://www.waterboards.ca.gov/centralvalley/water_issues/irrigated_lands/app_approval/index.shtml*). As a condition to this wavier, coalition group members were required to implement MPs (CVRWQCB 2011c).

Our trend analysis focuses, therefore, on the period of record of available water chemistry data (1970s to 2013) with an emphasis on a voluntary period of MP implementation, (1990 to 2004) and an enforcement period (2004 to 2013).

METHODS, STUDY AREA, DATA SOURCES, AND EXPLANATION OF MODEL INPUTS

Study Area

The study area was the Central Valley of California with selected river sites in both the Sacramento and San Joaquin valleys. We used data from twelve monitoring sites (four in the Sacramento Basin and eight in the San Joaquin Basin) to evaluate nutrient fluxes and trends (Figure 1). Given the focus on irrigated agriculture and urbanization, all twelve of the sites are located on the valley floor. The model required that data on water chemistry and discharge should be on the order of at least 20 years. Most sites had sufficient data for all nutrient species under considerations (TN, TP, NH_3, NO_3). Also shown on Figure 1 are the areal extents of aggregated U.S.

Environmental Protection Agency (USEPA) Level 3 ecoregions and locations of selected wastewater treatment plants. The USEPA defined Level 3 ecoregions to facilitate specifying numerical nutrient criteria for specific regions in the U.S. (*http://www2.epa.gov/ nutrient-policy-data/ecoregional-criteria-documents*).

Sacramento Basin

The Sacramento River receives drainage from three ecoregions (Figure 1). Nutrients in either the Sacramento or San Joaquin rivers are derived mostly from natural sources as these rivers enter the valley from the upland regions. Organic nitrogen is the dominant form from natural sources. Most of the nitrogen in the upper part of the watersheds derives from forest soils: most of the phosphorus is from geological sources. Various geologic formations yield different amounts of total phosphorus from weathering. Volcanic rocks, such as andesites, tend to release more phosphorus than granitic rocks do (Norris and Webb 1990).

The Sacramento River drains about 70,000 km^2 and averages approximately 80% of the inflow into the Delta under un-impaired conditions (CDWR 2009a). The four major rivers (Sacramento, Feather, American, and Yuba) are all impounded with a total capacity of approximately 10 million acre-feet or about 12 cubic kilometers (km^3). Water in the Sacramento River is diverted for agricultural and flood control purposes. Major agricultural diversions include the Tehama–Colusa and Corning canals near Red Bluff, and the Glenn–Colusa Canal at Hamilton City among others.

Agriculture is the main land use on the valley floor, with 749,000 ha (7,490 km^2) irrigated (CDWR 2009a). Rice is the major crop in the Sacramento Basin portion of the Central Valley. Since their peak in the 1980s, some agricultural lands have been replaced by managed wetlands and urban development (CDWR 2009a).

San Joaquin Basin

The San Joaquin River also drains three ecoregions (Figure 1). The San Joaquin River drains 35,080 km^2 of the basin; however, a section of the upper San Joaquin River goes dry because of agricultural diversions. The perennial lower section of the river drains 19,150 km^2 (Zamora et al. 2013). All three major tributaries to the lower San Joaquin River (Merced, Tuolumne, and Stanislaus) have impoundments, with a total capacity of approximately 5.5 million acre-feet or 6.8 km^3 (CDWR 2009b). Agricultural diversions are more numerous in the San Joaquin Basin than in the Sacramento Basin. Kratzer and Shelton (1998) reported more than 100 diversion and return flow points in the San Joaquin Basin. Much of the San Joaquin River flow, as it leaves the Central Valley, is captured by the export pumps and some is recycled back to agricultural use. Agriculture is the main land use on the valley floor [approximately 810,000 ha (8,100 km^2) irrigated; (CDWR 2009b)].

Calculation of Nutrient Concentrations and Fluxes

Previous calculations of nutrient fluxes in the Central Valley used the LOADEST model, which utilizes a relation between concentration and discharge to predict a daily load. Kratzer et al. (2010) evaluated nutrient trends and loads in the Sacramento, San Joaquin, and Santa Ana basins, from 1975 to 2004, using this model. All models may result in bias when an inadequate relation is developed between concentration and river discharge (Stenback et al. 2011). To gain a better understanding from long-term water quality data, Hirsch et al. (2010) developed the Weighted Regressions on Time, Discharge, and Season (WRTDS) model. The theory, function, and capabilities of WRTDS approach are described in detail in Hirsch et al. (2010) and Hirsch and De Cicco (2014). This model has been successfully used to evaluate nutrient loads and trends in rivers within the state of Iowa (Green et al. 2014), the Chesapeake Bay Watershed (Moyer et al. 2012), and the Mississippi River Basin (Sprague et al. 2011). Although the WRTDS model uses a regression equation similar to LOADEST, WRTDS does not rely on constancy of seasonal trends in concentration or constancy of the concentration–flow relationship (Hirsch et al. 2010; Moyer et al. 2012; Hirsch 2014). Instead, WRTDS calculates the dependencies of concentrations on time, discharge, and season by re-evaluating coefficients for each day of estima-

tion. WRTDS, therefore, differs from LOADEST in being more nonparametric and data driven. Because of the need for extensive data, WRTDS is only applicable to data sets of at least 20 years. Furthermore, a flow-normalization estimation procedure in WRTDS provides a method to assess changes in concentration and load independent of varying discharge from year to year.

To more clearly identify nutrient trends that are potentially related to management control practices, it is important to eliminate from the analysis the random variation in discharge. For example, loads may appear to be decreasing because of an extended drought, but the load reductions may have nothing to do with the MPs. Flow normalization is used to accomplish this. The model output also estimates actual loads; however, flow-normalized trends more clearly represent a watershed's response to "land-use change, point-source controls, or the implementation of best management practices" (Hirsch et al. 2010), and can be used to determine if progress toward attaining water quality objectives is being made in a watershed. Flow-normalized concentrations or loads aggregated over longer time-frames (monthly or annually) results in a time series of less variability. Flow-normalized concentrations and loads are essentially averages of WRTDS daily estimates. The equation for flow normalization is:

$$E\left[C_{fn}(T)\right] = \int_{0}^{\infty} w(Q,T) \bullet f_{Ts}(Q) \, dQ$$

(1)

where $E[C_{fn}(T)]$ is the flow-normalized concentration for time T (a specific day of a specific year); $w(Q,T)$ is the WRTDS estimate of concentration as a function of Q (discharge) and T (time in years); and $f_{Ts}(Q)$ is the probability density function of discharge (Q), specific to a particular time of year designated as T_s. T_s is restricted to values between 0 and 1, and it is defined as the fractional part of the time variable T (and thus T_s is the decimal portion of a year, or decimal time [Hirsch and De Cicco 2014]).

Input parameters for WRTDS include continuous mean daily discharge, with sufficient chemical concentration data. Water quality sampling should span the range of seasons and flow conditions. A record

of near 20 years is considered a minimum to produce a good model (Hirsch and De Cicco 2014). The first step in obtaining annual flow-normalized estimates involves calculating daily estimates of concentration. WRTDS uses the following regression equation to estimate the daily natural logarithm (ln) of concentration values:

$$\ln(c) = \beta_0 + \beta_1 t + \beta_2 \ln(Q) + \beta_3 \sin(2\pi t) + \beta_4 \cos(2\pi t) + \varepsilon$$

(2)

In the above equation, c is concentration, Q is discharge, t is time in decimal years, β are fitted coefficients, and ε is the unexplained variation. β and ε are estimated for every combination of Q and t. The regression model estimates concentrations based on the product of three weighted functions, which consider time, discharge, and season. Weights are assigned according to "distance" measures, which are the "distances" between an estimation point and an observation point. Therefore, the values of β are not static for the period of record but vary according to the weighted regression (Hirsch et al. 2010). The weighted functions of time, discharge, and season look similar to a normal distribution curve. The distance between the estimation and observation point establishes a "window" in which the time, discharge, and season variables are given weight.

The average concentration estimated from all discharges on a given day is equal to the daily flow-normalized concentration. Conceptually, the model assembles all the discharges of a given day and then estimates daily concentrations based on each discharge. The daily flow-normalized load is equal to the product of the daily flow normalized concentration and the average discharge for the given day. These daily flow-normalized values can be aggregated into monthly and/or yearly averages. Operationally, the WRTDS model is run in *R*, a statistical computing and graphics program, (*http://www.r-project.org*), and requires the Exploration and Graphics for RivEr Trends (EGRET) package (*https://github.com/USGS-R/EGRET/wiki*). See Hirsch et al. (2010) and Hirsch and De Cicco (2014) for additional background on the WRTDS approach, model development, and the boundary conditions used to define model functionality.

The assessment of bias from the models produced is accomplished using the flux bias statistic (B, in Equation 3). The statistic is calculated with the following equation (Hirsch and De Cicco 2014):

$$B = (P - O)/P \qquad (3)$$

where:

$$O = \sum_{i=1}^{n} L_i = \sum_{i=1}^{n} k \times c_i \times Q_i$$

$$P = \sum_{i=1}^{n} \hat{L}_i = \sum_{i=1}^{n} k \times \hat{c}_i \times Q_i \qquad (4)$$

Where

L_i is the observed load on the ith-sampled day in kg d^{-1}

$\hat{L}_i$ is the estimated load on the ith-sampled day in kg d^{-1}

k is a unit conversion factor with a value of 86.4

c_i is the measured concentration on the ith-sampled day (in mg L^{-1})

$\hat{c}_i$ is the estimated concentration on the ith-sampled day

Q_i is the discharge on the ith-sampled day (in m^3 s^{-1}), and

n is the number of sampled days

As described in Hirsch and De Cicco (2014), when the value of B is near zero, the model is nearly unbiased. When the value of B is between -0.1 and $+0.1$, "the bias in estimates of the long-term mean flux is likely to be less than 10 percent" (Hirsch and De Cicco 2014).

Uncertainty in flow-normalized trends is accomplished in WRTDS using a bootstrap test. The test returns a two-sided p-value associated with the likelihood of a trend, the direction of the trend, and the magnitude of the trend. Full details of this part of the model are described Hirsch et al. (2015). For this analysis, we chose a p-value of <0.05 to be significant. All calculations of load are included in the supplemental appendix (Appendix A).

Trend Analysis Periods

We evaluated trends initially on the full data sets, most of which extend to 1975, and then on the MP period as described below. We based the year start and end points used in the nutrient trend analysis on key turning points in state and Central Valley agricultural NPS control policy decisions.

Based on a review of the laws and regulations governing agricultural NPS pollution control, 2 years (1990 and 2004) stand out as key turning points in the Central Valley RWQCB's response to control agricultural NPS pollution (Figure 1). The 1990 to 2004 and 2004 to 2013 periods are hereafter referred to as the "voluntary" and "enforcement" periods. These time-periods were used as year points for nutrient trend analysis.

Nutrient Water Quality Data

The types of nutrients and related compounds discussed in this report include total nitrogen (TN), nitrate (NO$_3$), ammonia (NH$_3$), and total phosphorus (TP). TN includes all forms of nitrogen, including particulate organic N. Similarly, TP includes both dissolved and particulate forms. Ammonia and nitrate are assumed to be totally dissolved in water. We based the nutrient fluxes and trends evaluated in this study on water quality sampling data collected from 1975 to 2013. We obtained most of the data from the U.S. Geological Survey National Water Inventory System (NWIS) and from sources Kratzer et al. (2010) previously reported. The data Kratzer et al. (2010) used were mostly from NWIS, but also included data from universities and other government agencies. We assumed that most, but not all, samples collected represented the entire cross section of the channel.

Fertilizer Sales and Manure Data

One of the major sources of nutrients in the Sacramento and San Joaquin basins is agricultural fertilizer and animal manure. To better understand nutrient trends during the trend evaluation period, we had to understand fertilizer application and manure production. Fertilizer sales are used as a surrogate for fertilizer application. We obtained county fertil-

izer sales data for the years 1987 to 2010 from the *Association of American Plant Food Control Officials, 2010, Commercial Fertilizer*, which are available online at *http://www.aapfco.org/publications.html*. We estimated manure data for the years 2002 and 2007 from the Census of Agriculture records using previously described methods (*http://water.usgs.gov/ GIS/metadata/usgswrd/XML/manure.xml*).

We used only fertilizer sales and manure data from counties likely to contribute to the study area. We compiled fertilizer sales and manure data for the following Central Valley counties: Butte, Colusa, Fresno, Glenn, Madera, Merced, Sacramento, San Joaquin, Stanislaus, Solano, Sutter, Tehama, Yolo, and Yuba. to estimate fertilizer application and manure production, we summed annual fertilizer sales data for each of the selected counties within the basins. Because non-farm sales data were less than 1% of farm sales, we used only sales data for farms in this trend evaluation.

RESULTS

Flux Bias Statistics

Flux bias statistics were calculated for each site and nutrient type (TP, TN, NO_3, and NH_3) at the 12 study sites (Table 1).

No model results were generated for TN and NH_3 at the Colusa site (Sacramento River) because of limited data (for TN) or excessive censored values (less than reporting limit; for NH_3). Therefore, 46 total flux bias estimates were recorded. Flux bias ranged from negative 62.4% to positive 13.6% (Table 1) with a median value of negative 1.6%. We found a bias higher than 10% (absolute values; Table 1) for four models: (Mud Slough NH_3; Tuolumne River NH_3; Orestimba Creek TN; San Joaquin River near Crows Landing TN. Three models (highlighted in amber color on Table 1) had unacceptably high bias, and were not further considered in the analysis: Sacramento River at Colusa TP; San Joaquin River at Crows Landing TP; and Orestimba Creek TP.

Table 1 Flux bias calculated in the WRTDS model. The flux bias statistic in WRTDS is equal to the difference between the sum of estimated fluxes of sampled days and the sum of true fluxes on sampled days. As shown, most constituent/site combinations had estimated bias less than 10% (absolute value). Sites listed with an NA indicate that data were not available to develop a model for that constituent.

Station	Flux bias (%)			
	TP	TN	NO_3	NH_3
Sacramento River at Freeport	−1.5	−2.1	−1.3	7.8
American River at Sacramento	−5.5	−0.35	0.32	8.3
Sacramento River at Verona	−3.5	1.8	1.5	1.2
Sacramento River at Colusa	−22.9	NA	−5.6	NA
San Joaquin River at Vernalis	−1.5	−2.14	−3.9	−2.1
San Joaquin River at Patterson	2.3	−0.3	0.921	2.4
San Joaquin River at Crows Landing	−2.0	13.6	−1.7	−62.4
Salt Slough near Sevinso	0.6	−5.07	−2.1	0.13
Mud Slough near Gustine	3.1	−1.4	1.4	10.7
Stanislaus River at Ripon	−3.5	−5.8	−4.9	−7.4
Tuolumne River at Shiloh	0.5	−4.7	−4.8	−10.7
Orestimba Creek at Crows Landing Road	−38.3	−10.6	1.0	−2.7

Discharge, Fluxes, and Trends

Consistent with the precipitation record (Western Regional Climate Center (*http://www.wrcc. dri.edu/ cgi-bin/cliMONtpre.pl?ca7630*) and the Modesto Irrigation District (*http://www.mid.org/weather/ wthr-hist2.jsp*), discharge varies significantly on a year-to-year basis. High discharge at the downstream Sacramento and San Joaquin river sites (Figures 3 and 11) matches the peak storm years of 1983 and 1998. Minimum, maximum, and median flows in the Sacramento River at Freeport site between the years of 1974 and 2014 were 112 m^3 s^{-1}, 3,256 m^3 s^{-1}, and 450 m^3 s^{-1}, respectively. Maximum flow represents that of the main channel and does take into account that which was diverted to the flood control channel (Yolo Bypass). Over the same period, the minimum, maximum, and median flows at the San Joaquin River at Vernalis site were 1.6 m^3 s^{-1}, 1537 m^3 s^{-1}, and 61 m^3 s^{-1}, respectively.

Sacramento Basin

For the Sacramento River at Freeport, results from the WRTDS model show that the slope of the flow-normalized TP concentrations and loads follow a similar pattern in time (Figure 3). Concentrations and fluxes of TP declined sharply between the mid-1970s to the early 1990s, rose gradually until the mid-2000s, then gradually declined through the 2013 water year. The overall declining trend for TP concentration for the full time-period is significant ($p < 0.04$) and the declining trend for flux is also significant ($p < 0.05$). Loads vary significantly over the modeled period, which, as expected, directly relates to the variation in discharge. Flow-normalized TP concentrations decreased at a rate of 1.0% per year during the enforcement period, and increased by a rate of 0.7% per year during the voluntary period (Table 2). We estimated the total load of TP that entered the Delta through the Sacramento River to be approximately 1.1 million kg for the 2013 water year.

Similar to TP trends, flow-normalized concentrations and flux of TN follow a similar pattern with time (Figure 4). Unlike TP trends, however, flow-normalized TN concentration and flux trends (Figure 4) increased during the initial modeled period (from the mid 1970s to the mid 1980s), then declined sharply to the late 1990s. Concentration and flux continued to decline, but only gradually, to 2013. The overall trends in both concentration and load were declining, and trend is significant ($p < 0.04$). Flow-normalized TN concentrations decreased 2.0% per year and 2.4% per year during the enforcement and voluntary periods, respectively (Table 2). The total load of TN entering the Delta through the Sacramento River was estimated to be approximately 4.9 million kg during the 2013 water year.

For the Sacramento Basin sites upstream of Freeport, results of concentration and load changes (Table 2, Figures 5-8) vary between the voluntary and enforcement period (Table 2). There is an increasing trend in TN at the Sacramento River at Verona site, followed by a decreasing trend after 1990 (Table 2). At the Sacramento River at Freeport site, there was a significant ($p < 0.025$) decline in nitrate concentration (Figure 7), for the entire period of record, although the range in modeled concentrations was small (0.1 to 0.15 mg L^{-1}). There was a slight declining trend in nitrate load, but the p value was not as favorable ($p < 0.07$). Downward trends for ammonia concentration and flux at the Sacramento River at Freeport site (Figure 8) for the entire period of record were also significant ($p < 0.04$). The ammonia concentrations at the Sacramento River at Freeport site were measured above the outflow for the Sacramento Regional Wastewater Treatment facility, and therefore, only indicate the upstream watershed and not the wastewater discharge.

In the Sacramento Basin, trend reversals between the voluntary and enforcement periods occurred at Colusa (for TP and NO_3, Figures 5 and 7), at the American (for TP, Figure 5), at Freeport (for TP, Figure 4), and at Verona (for TN, Figure 6). To identify flow and seasonal effects on concentration changes we generated contour difference plots via the WRTDS model (Figure 9 and 10). Concentration contour plots show the change in concentration between two trend periods for every day of the year. Changes in TP and NO_3 concentrations at the Sacramento River at Colusa site appeared during the wet season beginning in October and ending in April (Figure 9). For the wet season, concentrations of TP and NO_3
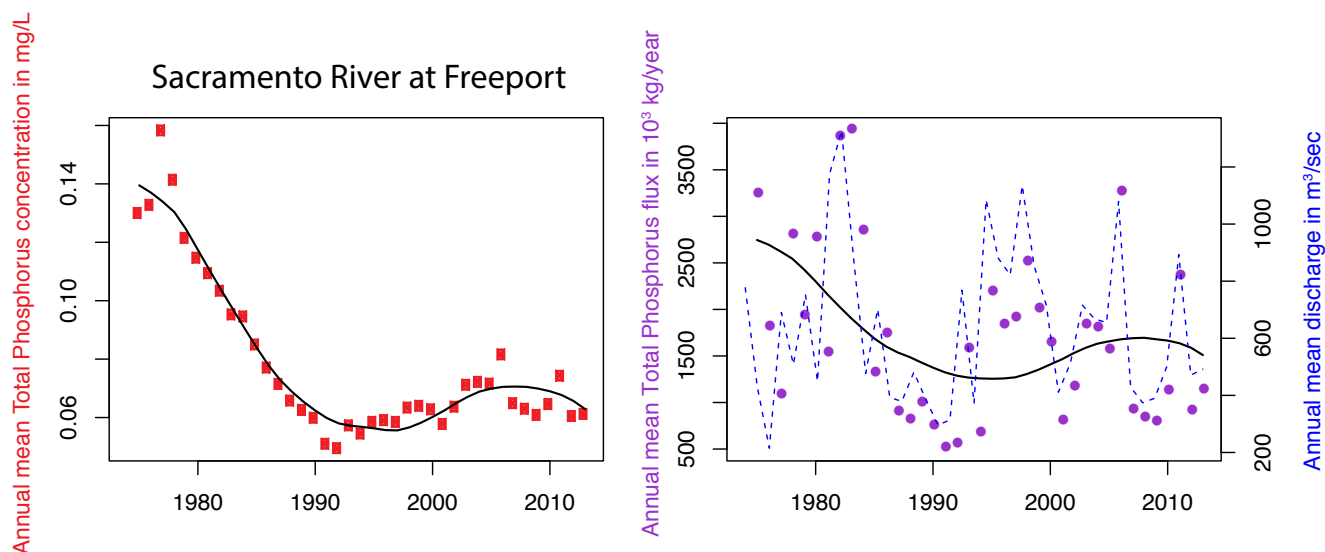
Figure 3 TP concentration and flux at the Sacramento River at Freeport site. Annual mean concentrations of TP (solid red dots), annualized total load of TP (purple dots), annual mean discharge (dashed blue line), and flow normalized trends (solid black lines) are shown.
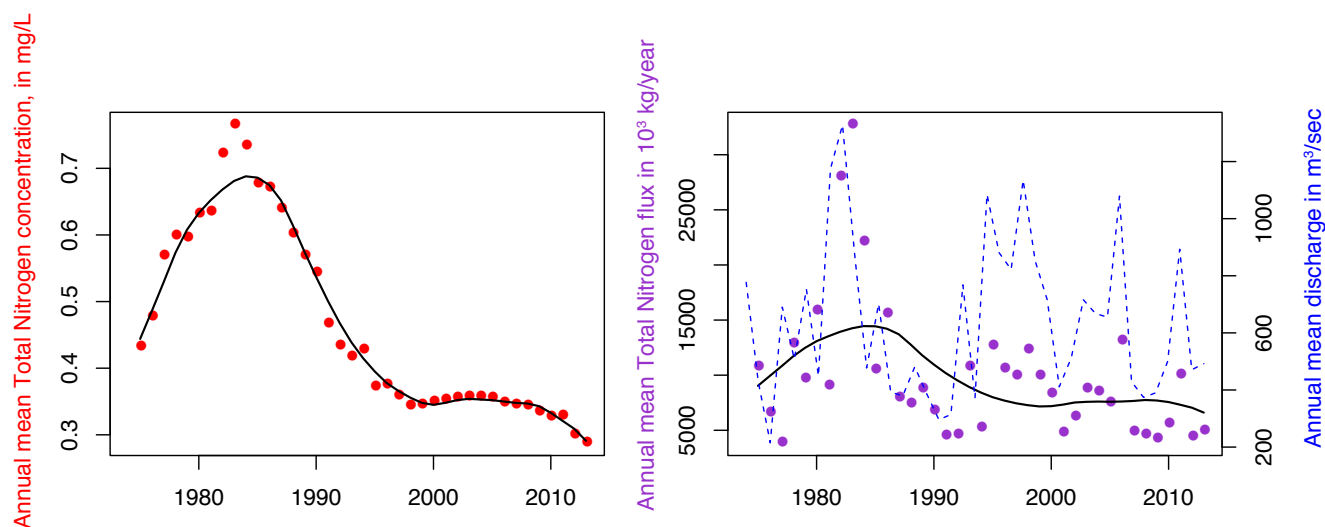

Figure 4 TN concentration and flux at the outlet of the Sacramento River at Freeport site. Annual mean concentrations of TN (solid red dots), annualized total load of TN (purple dots), annual mean discharge (dashed blue line), and flow normalized trends (solid black lines) are shown.

Table 2 Concentration and load changes of total nitrogen (TN) and total phosphorus (TP) during trend analysis periods. The values shown here were calculated from the difference between the later year and earlier year average flow-normalized values. These values were calculated from the years shown in the period column. Since the total number of years is different between the periods, percent change per year is also shown. Positive or negative changes are shown in reddish or bluish colors, respectively.

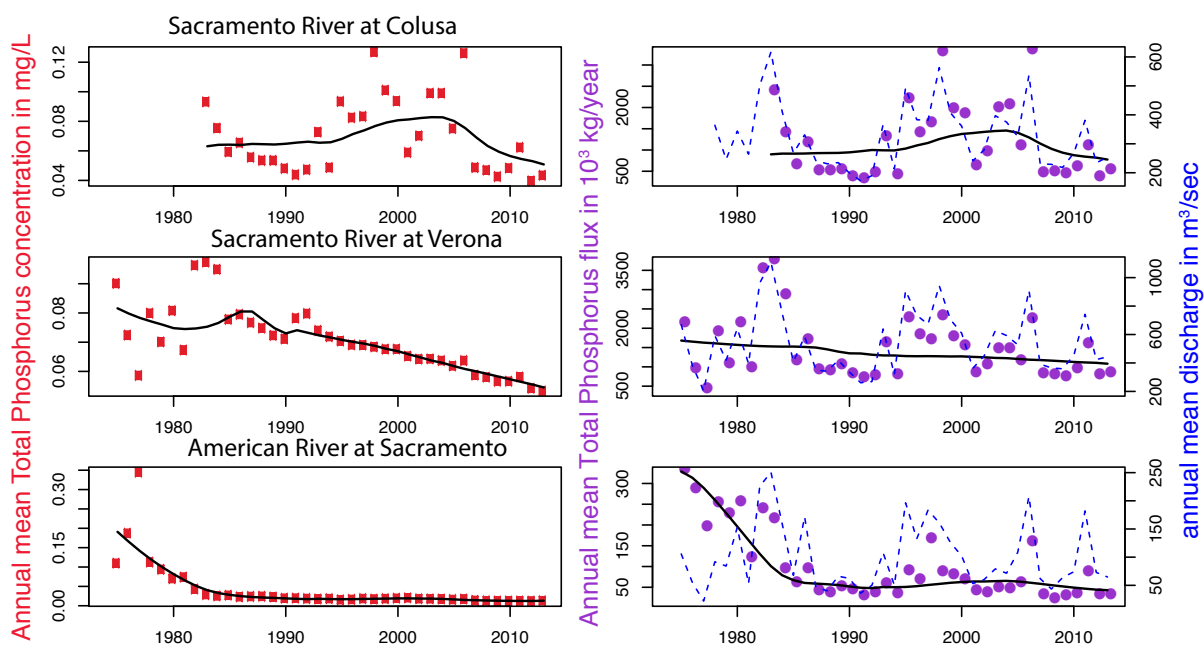| Site	Voluntary period	TN Concentration		TN Flux		Enforcement period	TN Concentration		TN Flux	
		Change (%)	Slope (% yr⁻¹)	Change (%)	Slope (% yr⁻¹)		Change (%)	Slope (% yr⁻¹)	Change (%)	Slope (% yr⁻¹)
Salt Slough	1990 to 2004	−64	−4.6	−59	−4.2	NA	NA	NA	NA	NA
Mud Slough	1990 to 2004	89	6.4	72	5.1	2004 to 2012	−62	−7.8	−61	−7.6
Orestimba Creek	1993 to 2004	−21	−1.9	−27	−2.5	2004 to 2013	−29	−3.2	−26	−2.9
San Joaquin River at Crows Landing	NA	NA	NA	NA	NA	2004 to 2012	−34	−4.3	−55	−6.9
San Joaquin River at Patterson	1990 to 2004	9.9	0.7	75	5.4	NA	NA	NA	NA	NA
Tuolumne River	1990 to 2004	69	4.9	13	0.9	NA	NA	NA	NA	NA
Stanislaus River	1990 to 2004	−21	−1.5	−40	−2.9	NA	NA	NA	NA	NA
San Joaquin River at Vernalis	1990 to 2004	−2.6	−0.2	−14	−1.0	2004 to 2013	−31	−3.4	−30	−3.3
Sacramento River at Colusa	1990 to 2004	NA	NA	NA	NA	2004 to 2013	NA	NA	NA	NA
Sacramento River at Verona	1990 to 2004	−7.6	−0.5	−6	−0.4	2004 to 2013	3.8	0.4	4.4	0.5
American River	1990 to 2004	8.6	0.6	19	1.4	2004 to 2013	31	3.4	52	5.8
Sacramento River at Freeport	1990 to 2004	−34	−2.4	−31	−2.2	2004 to 2013	−18	−2.0	−13	−1.4
Sacramento River at Colusa	1990 to 2004	28	2.0	54	3.9	2004 to 2013	−39	−4.3	−47	−5.2
Sacramento River at Verona	1990 to 2004	−14	−1.0	−9.2	−0.7	2004 to 2013	−13	−1.4	−12	−1.3
American River	1990 to 2004	−7.3	−0.5	26	1.9	2004 to 2013	−27	−3.0	−34	−3.8
Sacramento River at Freeport	1990 to 2004	10	0.7	19	1.4	2004 to 2013	−8.7	−1.0	−7.5	−0.8
Salt Slough	1990 to 2004	9	0.6	7.3	0.5	NA	NA	NA	NA	NA
Mud Slough	1990 to 2004	−28	−2.0	−19	−1.4	2004 to 2012	15	1.9	−1.7	−0.2
Orestimba Creek	1993 to 2004	4	0.4	−14	−1.3	2004 to 2013	−35	−3.9	−20	−2.2
San Joaquin River at Crows Landing	NA	NA	NA	NA	NA	2004 to 2012	−20	−2.5	−21	−2.6
San Joaquin River at Patterson	1990 to 2004	2.7	0.2	22	1.6	NA	NA	NA	NA	NA
Tuolumne River	1990 to 2004	−2	−0.1	−8	−0.6	NA	NA	NA	NA	NA
Stanislaus River	1990 to 2004	−18	−1.3	−43	−3.1	NA	NA	NA	NA	NA
San Joaquin River at Vernalis	1990 to 2004	−17	−1.2	−14	−1.0	2004 to 2013	−22	−2.4	−14	−1.6

Figure 5 TP concentration and flux for three Sacramento River Basin sites. Annual mean concentrations of TP (solid red dots), annualized total load of TP (purple dots), annual mean discharge (dashed blue line), and flow normalized trends (solid black lines) are shown.
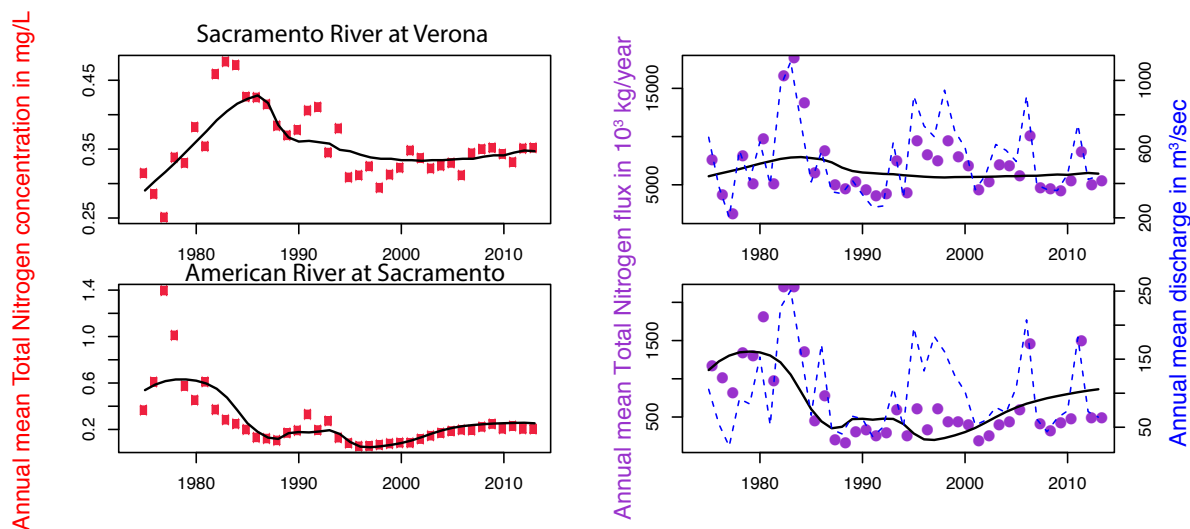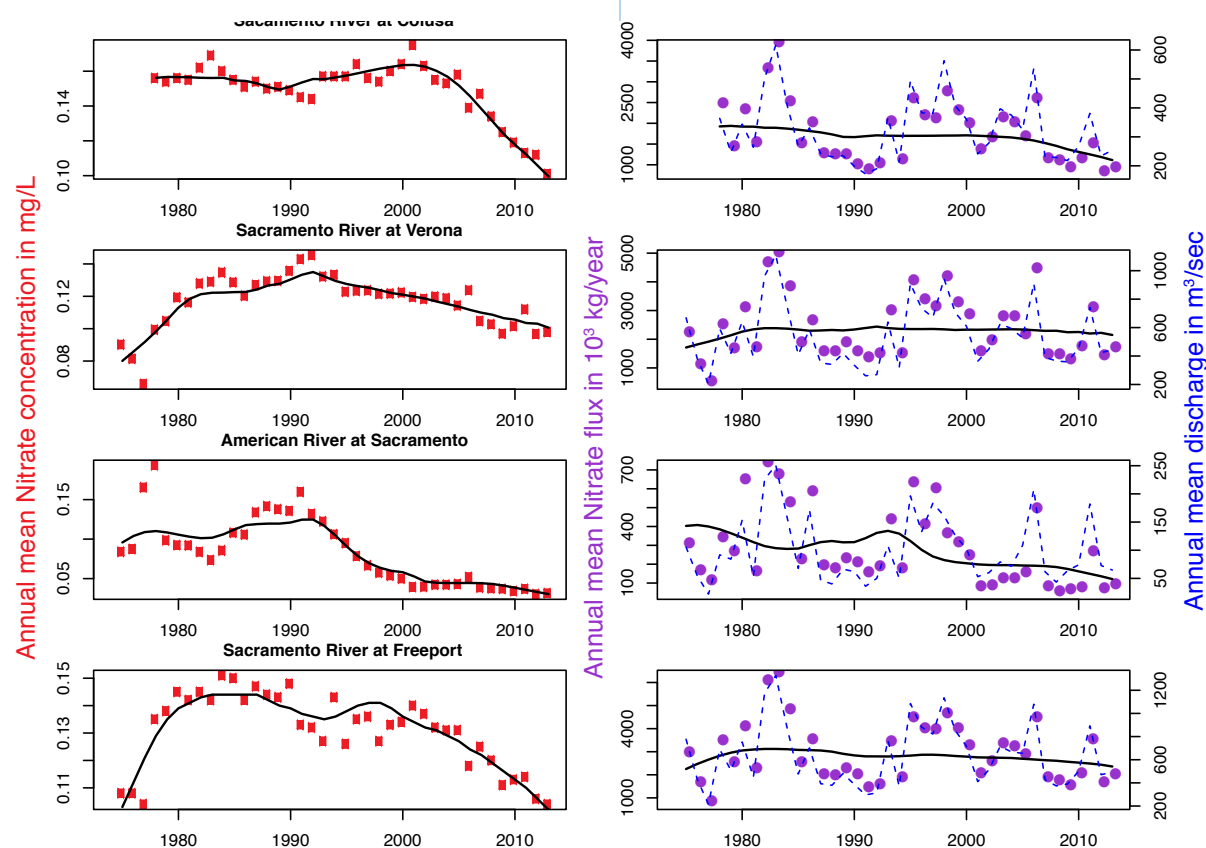

Figure 6 TN concentration and flux for the Sacramento River at Verona and the American River at Sacramento. Annual mean concentrations of TN (solid red dots), annualized total load of TN (purple dots), annual mean discharge (dashed blue line) and flow normalized trends (solid black lines) are shown.

Figure 7 Nitrate concentration and flux for the four Sacramento River basin sites modeled. Annual mean concentrations of nitrate (solid red dots), annual total load of nitrate (purple dots), annual mean discharge (dashed blue line), and flow normalized trends (solid black lines) are shown.

were approximately 0.15 mg L^{-1} greater in 2004 than in 1990. For the enforcement period, concentrations of TP and NO$_3$ were approximately 0.2 mg L^{-1} less than 2004 concentrations. It appears that changes in TP and NO$_3$ concentrations at the Colusa site occur on a seasonal basis. Significant changes in concentration for TP and NO$_3$ appear to occur during the wet season under high and normal flow conditions, respectively.

The upward trend in NH$_3$ at the Verona site (Figure 8) is very different from those of the American River at Sacramento and the San Joaquin River at Vernalis sites. Both flow-normalized concentration and flux increased throughout the entire period of record. As shown in Figure 10, concentration increases have occurred throughout most of the year, but primarily during the wet season at low discharge. In contrast,

flow-normalized flux of nitrate (Figure 7) at the Sacramento River at Verona site does not show much of a trend.

San Joaquin Basin

The flow normalized trend in TP flux at the San Joaquin at Vernalis site does not match flow normalized concentration changes (Figure 11). There is a significant downward trend in TP concentration ($p < 0.04$), after 1990, preceded by an upward trend but there is no significantly significant trend in either direction for flux ($p < 0.78$). Even though concentrations of TP continued to decline steadily throughout the 2000s, flow-normalized TP fluxes appear to be relatively constant throughout the 2000s. TP concentrations decreased 2.4% per year and 1.2% per year during the enforcement and voluntary periods,
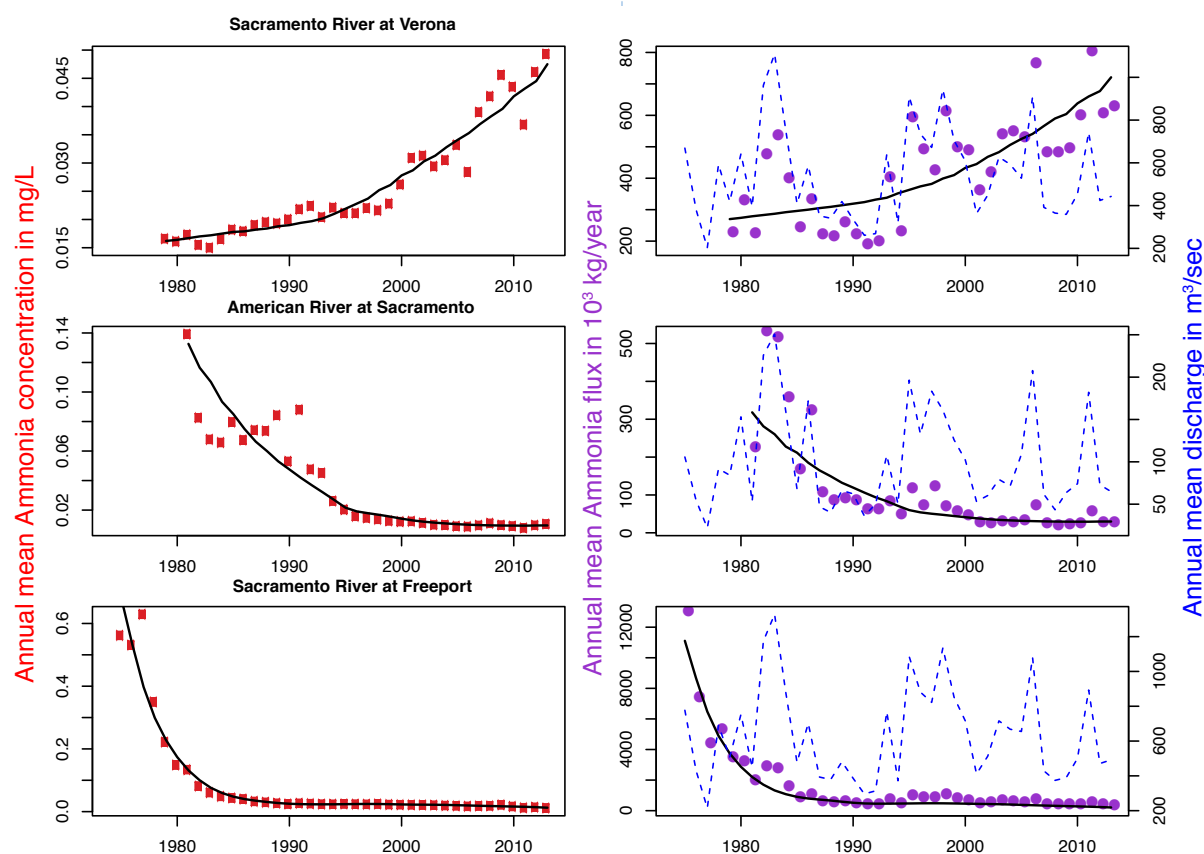
Figure 8 Ammonia concentration and flux for three Sacramento River basin sites modeled. Annual mean concentrations of ammonia (solid red dots), annual total load of ammonia (purple dots), annual mean discharge (dashed blue line), and flow normalized trends (solid black lines) are shown.

respectively (Table 2). We estimated the total load of TP that entered the Delta through the San Joaquin River to be approximately 226,000 kg for the 2013 water year, which is approximately 20% of the total load at Freeport.

Flow-normalized trends of concentrations and fluxes of TN at the San Joaquin River at Vernalis site (Figure 12) are similar in form. Trends in both concentration and flux were upward until about 1990 after which both trended downward. For the entire period of record, trends in both concentration and flux of TN are downward ($p < 0.04$). In other words, changes in load appear to respond to changes in concentration. TN concentrations decreased at a rate of 3.4% per year during the enforcement period and at only a 0.2%-per-year decrease during the voluntary period (Table 2). We estimated the total load of TN

entering the Delta through the San Joaquin River to be approximately 2.3 million kg during the 2013 water year, which is approximately 47% of the load from the Sacramento River. Only three of the eight sites modeled in the San Joaquin Basin had nutrient data that spanned both periods.

Flow-normalized concentrations and loads of TP and TN decreased during the latter 2004 to 2013 period relative to the earlier 1990 to 2004 period for some but not all San Joaquin Basin sites (Figures 13 and 14). The Mud Slough site had an increasing trend for both TN and TP concentration and flux up to about 2002 and then a decrease. TN concentration at the Tuolumne River shows a weak upward trend in the latter part of the period, but there is no trend in flux. TP concentration showed a weak downward trend at the upstream site on the San Joaquin River
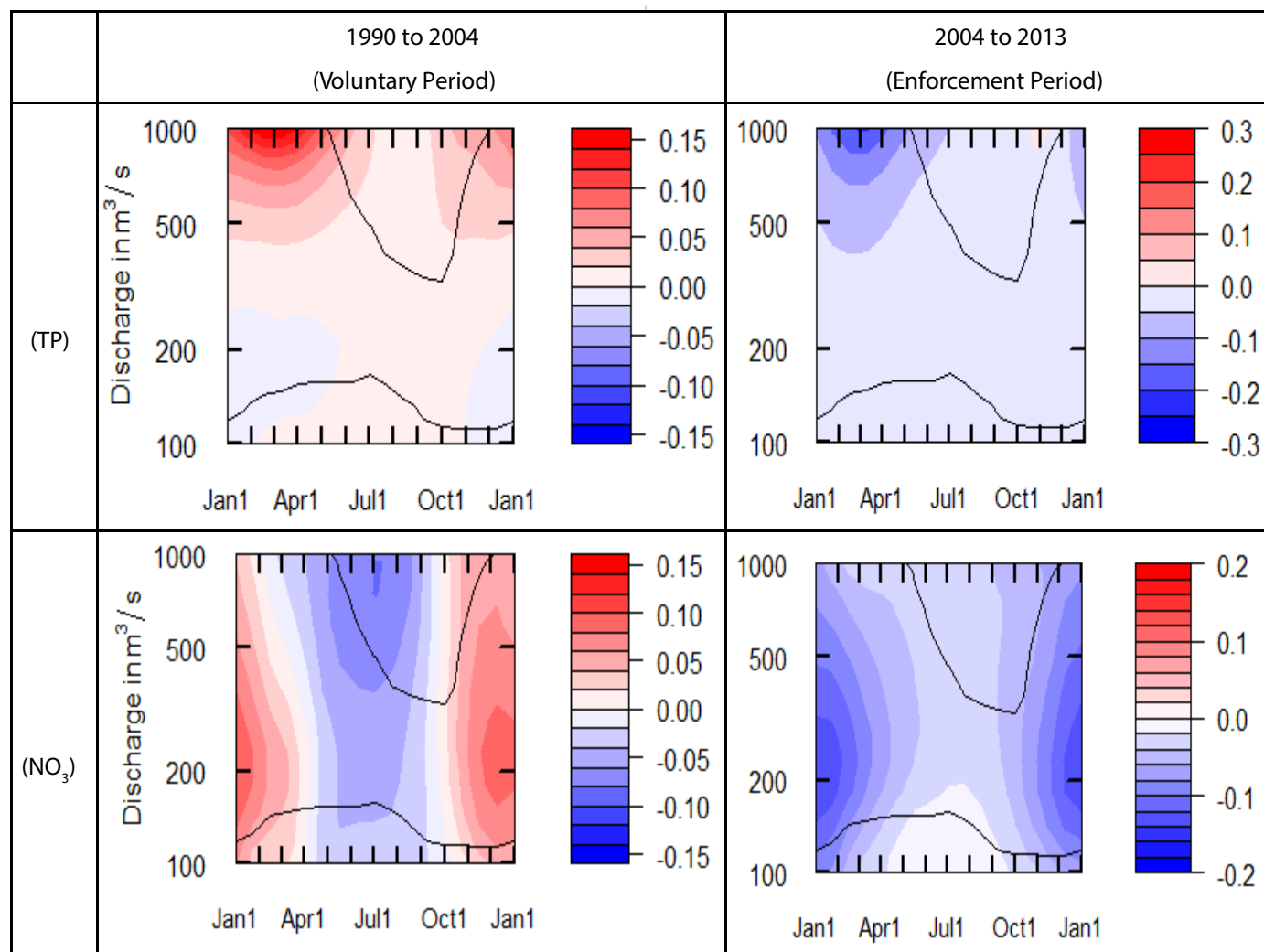
Figure 9 Estimated changes in concentrations of TP (A) and NO_3 (B) from 1990 to 2004 (left column plots) and 2004 to 2013 (right column plots) for the Sacramento River at Colusa site. The upper and lower solid black lines represent the 95% and 5% percentiles of flows. Months are shown on the X-axis and integrate all data for the time period shown. Red indicates increasing concentrations and blue indicates decreasing concentrations.

at Patterson ($p < 0.04$). However, the trend in flux was not significant ($p < 0.07$). There is no trend in either TN or TP in flux or concentration at the San Joaquin River at Patterson site ($p < 0.6$).

Nitrate concentrations and loads at the San Joaquin River at Vernalis site did not change for the entire period of record (Figure 15). The trends are not significant in either concentration or load, with p-values above 0.39. However, after 2000, nitrate declines significantly for both concentration and flux ($p < 0.04$).

A shorter record of nitrate concentrations and fluxes (1985–2004) is available for the upstream San Joaquin River at Patterson site (Figure 15). Although the trend appears upward for both concentration and flux, neither is significant ($p < 0.3$).

After an initial slight increase in ammonia concentration at the San Joaquin River at Vernalis site up to 1980, both concentration and load appear to decline (Figure 16). The decline is significant, but just barely ($p < 0.04$ for concentration; $p < 0.05$ for flux). For
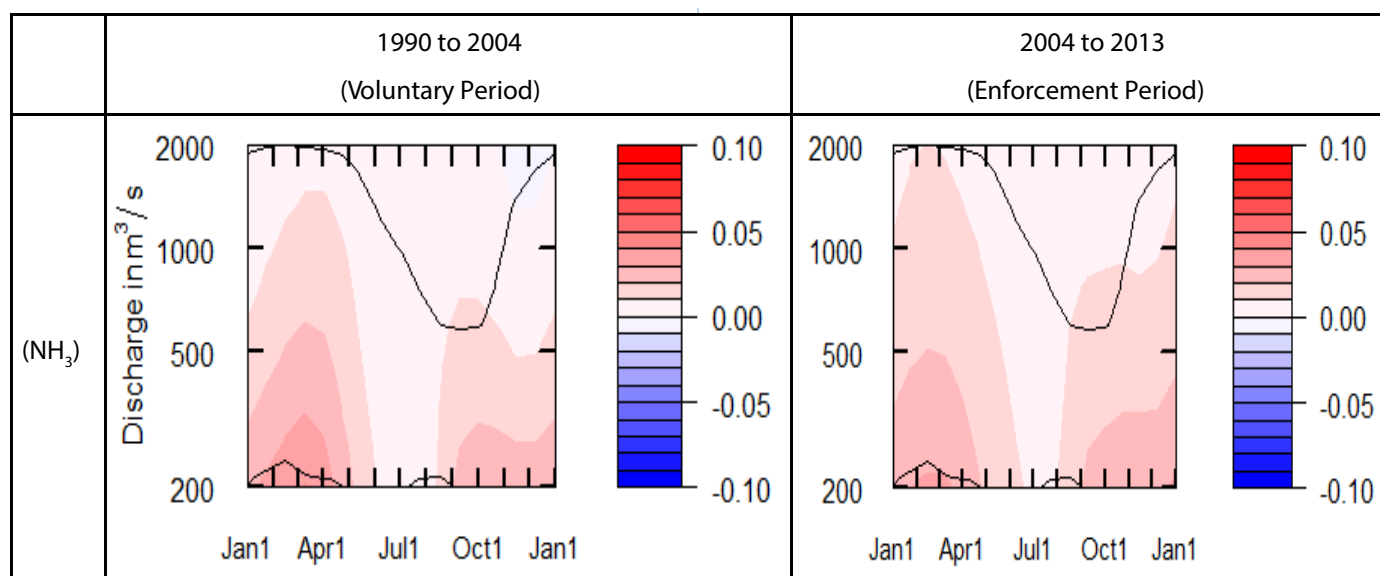
Figure 10 Estimated change in NH₃ concentration from 1990 to 2004 (left column plot) and 2004 to 2013 (right column plot) for the Verona station. The upper and lower solid black lines represent the 95% and 5% percentiles of flows. Months are shown on the x axis and integrate all data for the time period shown. Months are shown on the X-axis and integrate all data for the time period shown. Red indicates increasing concentrations and blue indicates decreasing concentrations.

other locations (Figure 16), concentration trends are sometimes up and sometimes down, but ammonia fluxes tends to be either slightly trending downward or flat.

During the voluntary period, increases in TP concentration occurred at high flow (greater than 95 percentile flow) during the beginning of the irrigation season (approximately mid-March) or during low flow (less than 5 percentile flow) earlier in the year for the Mud Slough site (Figure 17). Other than that, concentrations of TP decreased throughout the year under flow conditions between the 5th and 95th percentile. TP concentrations were approximately 0.1 to 0.3 mg L^{-1} greater in 2012 than 2004 between February and August with the greatest concentration change occurring during February to March at below normal flows. TP concentrations at Mud Slough decreased primarily during the wet season under high-flow conditions. However, during the enforcement period, TP concentrations showed an increase across all flow conditions from the beginning of the year (January) until the end of October (Figure 17). Concentrations show a noticeable decrease at high flow from about December to January.

Concentration changes (whether positive or negative) of TN and NO₃ appear to occur during the middle of the wet season to beginning of the irrigation season under moderate to low flow conditions at Mud Slough (Figure 18). Clearly, seasonal effects control changes in TN and NO₃ concentrations at the Mud Slough site. Significant changes in concentration for TN and NO₃ appear to occur during the beginning of the irrigation season under low to normal flow conditions, respectively.

Nitrogen and Phosphorus Fertilizer and Manure Use Trends

Sales of nitrogen and phosphorus fertilizers gradually increased throughout the 1990s and then peaked in the early to middle 2000s (Figure 19). Nitrogen fertilizer sales for selected San Joaquin counties rose from 140.8 million kg in 1990 to 234.6 million kg in 2004 (Figure 19). This represents a 67% increase from 1990 to 2004 or approximately 4.8% per year. Nitrogen fertilizer farm sales were approximately 9% less in 2010 than in 2004, which equates to a decline of approximately a 1.5% per year. Similar trends were shown for phosphorus fertilizer farm sales, which
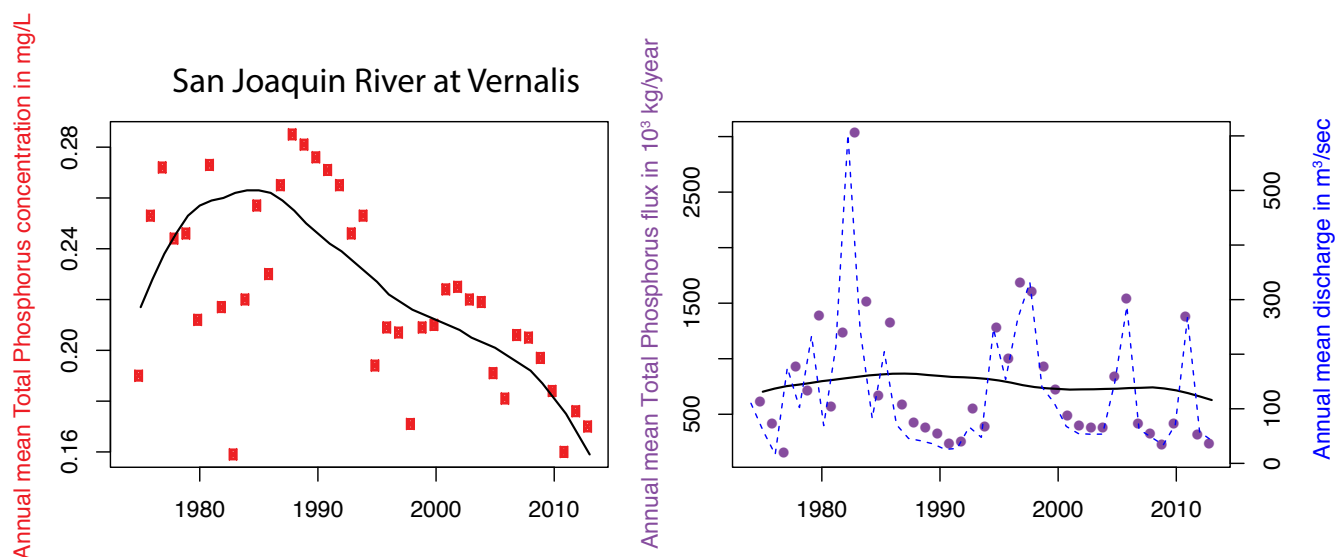
Figure 11 TP concentration and flux at the outlet of the San Joaquin River at Vernalis site. Annual mean concentrations of TP (solid red dots), annual total load of TP (purple dots), annual mean discharge (dashed blue line), and flow normalized trends (solid black lines) are shown.
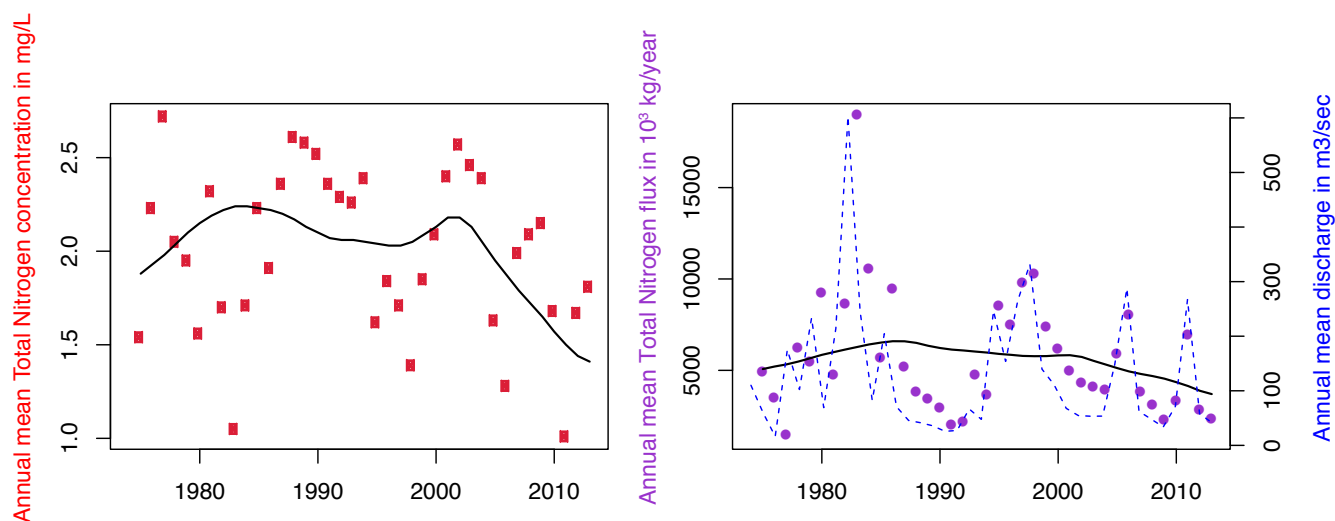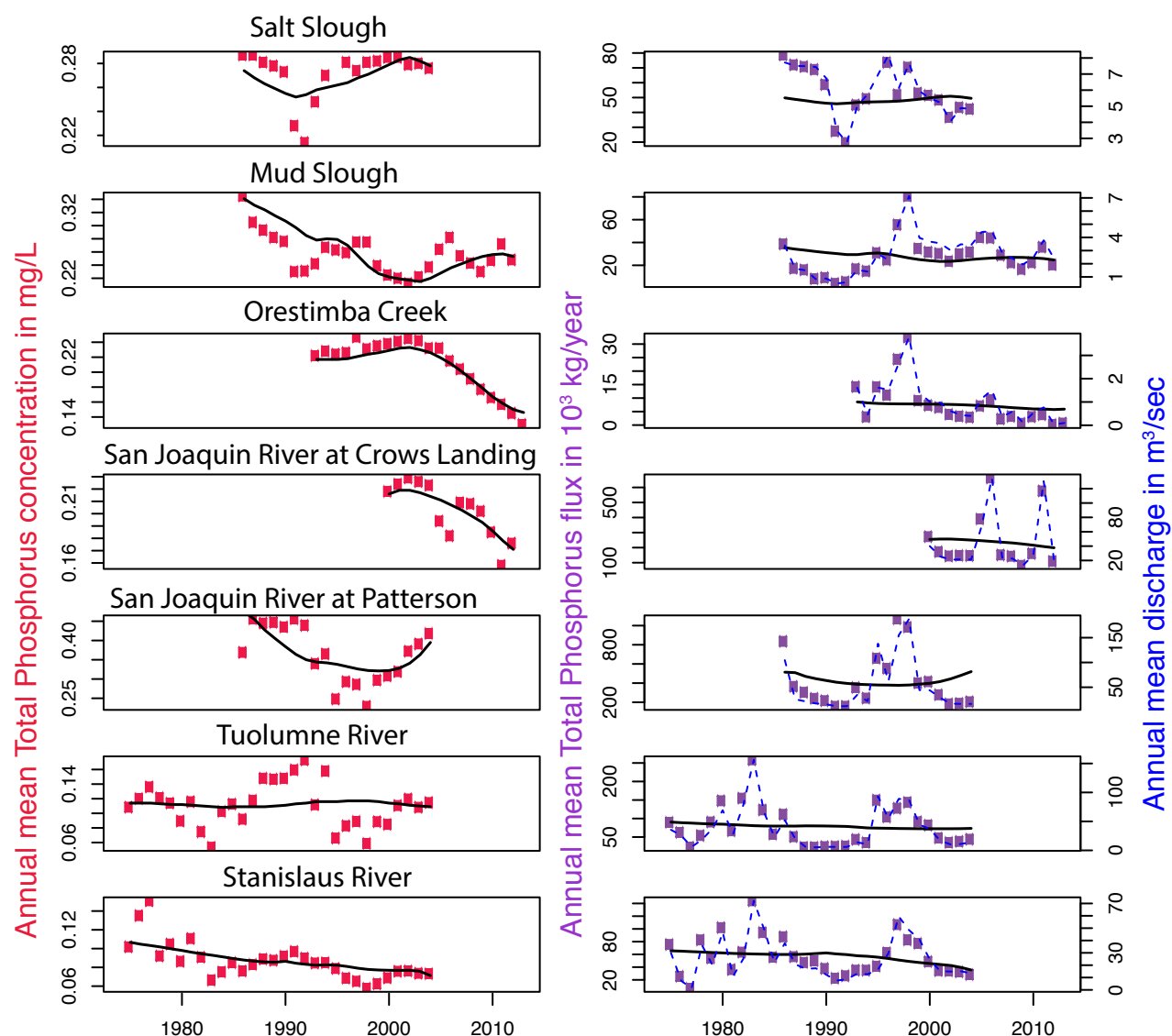

Figure 12 TN concentration and flux at the outlet of the San Joaquin River at Vernalis site. Annual mean concentrations of TN (solid red dots), annual total load of TN (purple dots), annual mean discharge (dashed blue line), and flow normalized trends (solid black lines) are shown.

Figure 13 TP concentration and flux for seven San Joaquin River basin sites modeled. Annual mean concentrations of TP (solid red dots), annual total load of TP (purple dots), annual mean discharge (dashed blue line), and flow normalized trends (solid black lines) are shown.
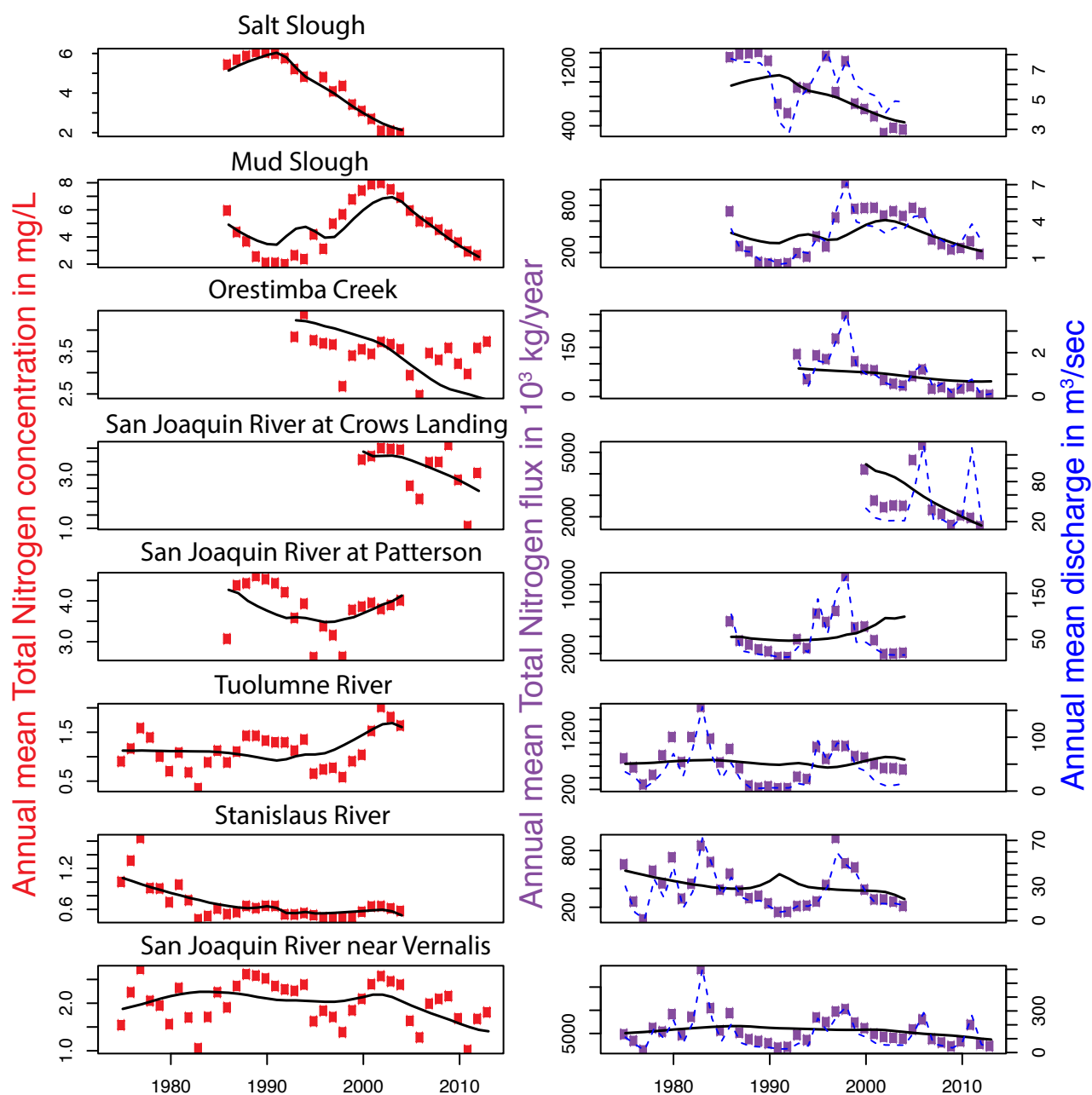
Figure 14 TN concentration and flux for seven San Joaquin River basin sites modeled. Annual mean concentrations of TN (solid red dots), annual total load of TN (purple dots), annual mean discharge (dashed blue line), and flow normalized trends (solid black lines) are shown.
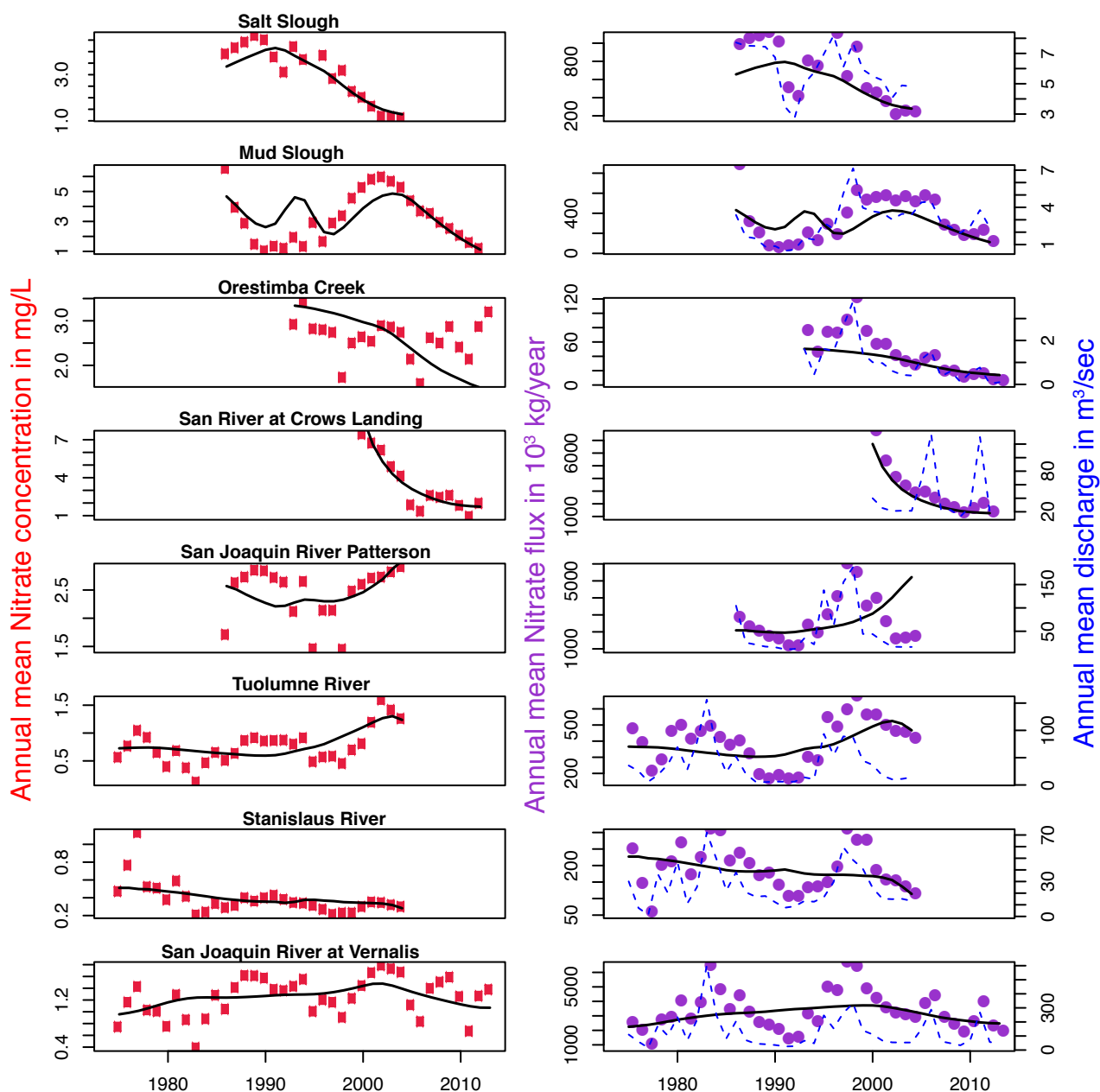
Figure 15 Nitrate concentration and flux for the eight San Joaquin River basin sites modeled. Annual mean concentrations of nitrate (solid red dots), annual total load of nitrate (purple dots), annual mean discharge (dashed blue line), and flow normalized trends (solid black lines) are shown.
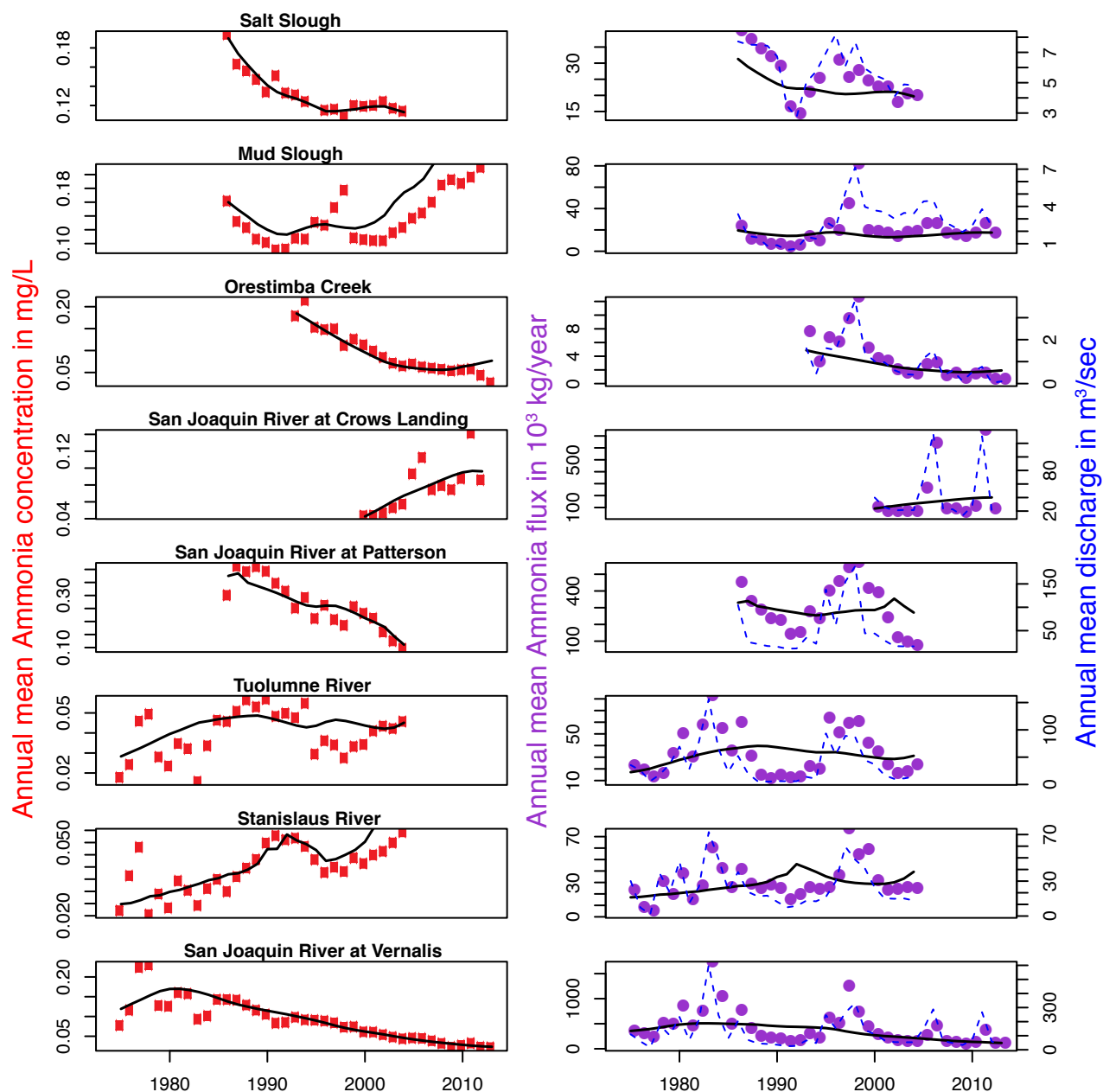
Figure 16 Ammonia concentration and flux for the eight San Joaquin River basin sites modeled. Annual mean concentrations of ammonia (solid red dots), annual total load of ammonia (purple dots), annual mean discharge (dashed blue line), and flow normalized trends (solid black lines) are shown.
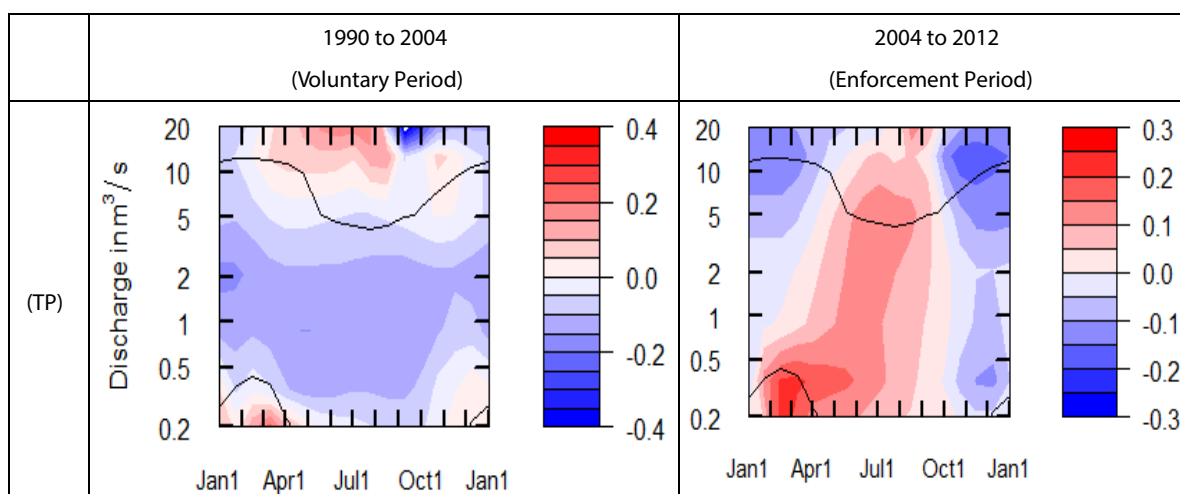
Figure 17 Estimated change in TP concentration from 1990 to 2004 (left column plot) and 2004 to 2013 (right column plot) at the Mud Slough site. The upper and lower solid black lines represent the 95% and 5% percentiles of flows. Months are shown on the x axis and integrate all data for the time period shown.

Figure 18 Estimated changes in concentrations of TN (A) and NO_3 (B) from 1990 to 2004 (left column plots) and 2004 to 2012 (right column plots) for the Mud Slough site. The upper and lower solid black lines represent the 95% and 5% percentiles of flows. Months are shown on the X-axis and integr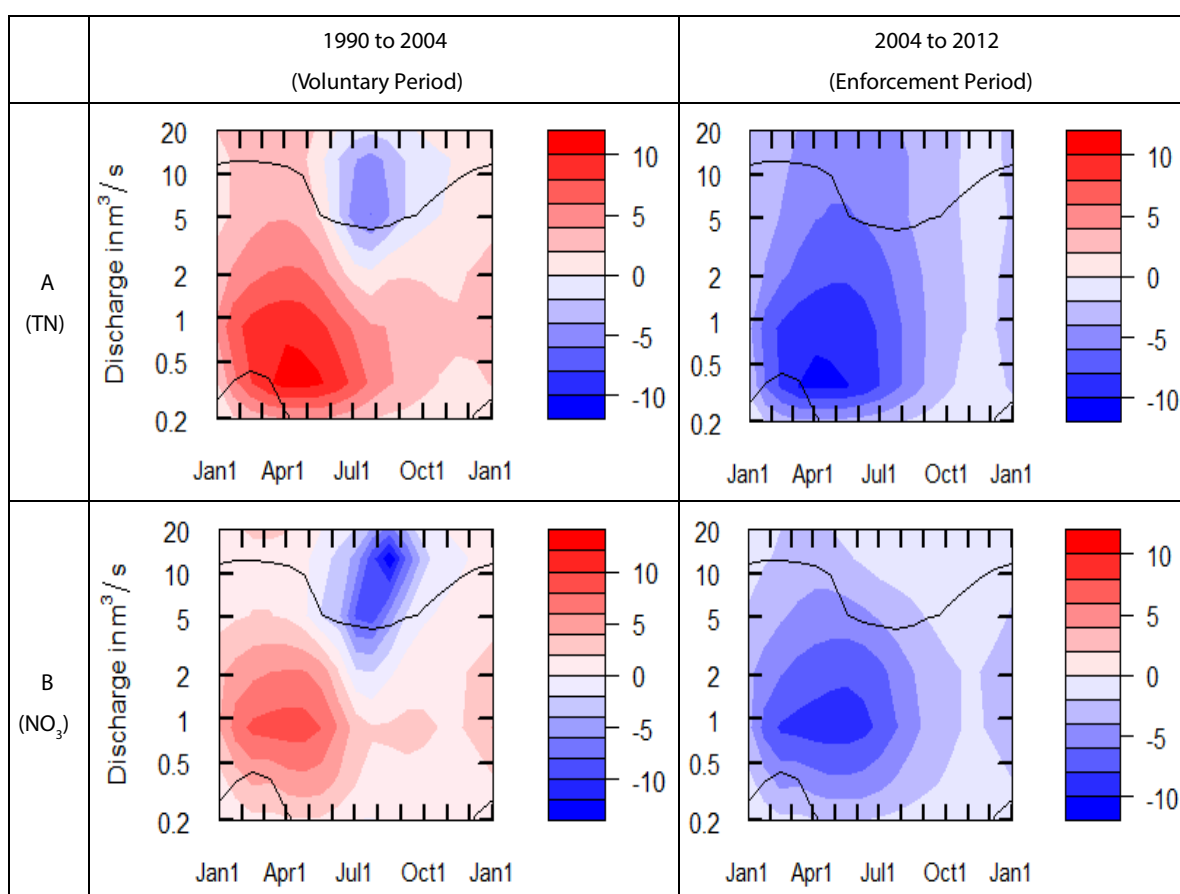ate all data for the time period shown. Months are shown on the X-axis and integrate all data for the time period shown. Red indicates increasing concentrations and blue indicates decreasing concentrations.
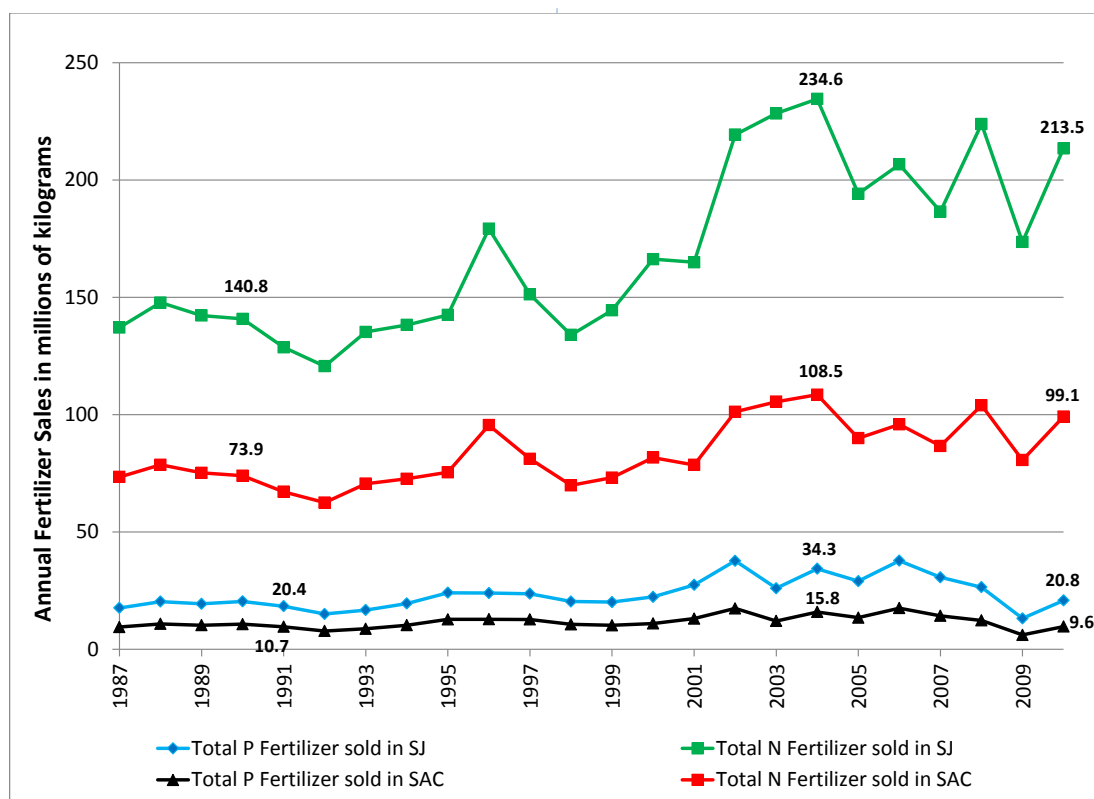
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Figure 19 Total nitrogen and phosphorus fertilizer sales data for selected Sacramento and San Joaquin basin counties. Values are shown for the 1990, 2004, and 2010 years for trend evaluations.

resulted in a 4.9% average per year increase over the 1990–2004 period, and a 6.6% decrease during the 2004 to 2010 period.

For selected Sacramento Basin counties, we calculated manure use to be approximately 18.5 million kg in 2002 and 15.1 million kg in 2007; total manure as *P* used was calculated to be approximately 4.7 million kg in 2002 and 3.7 million kg in 2007. Less manure was produced in the Sacramento Basin in 2007 than in 2002. The ratio of manure production to fertilizer sales for 2007 for selected Sacramento Basin counties equates to approximately 17% for nitrogen (15/87) and 26% for phosphorus (3.7/14).

In contrast to the Sacramento River Basin portion of the study area, more manure was produced in the San Joaquin Basin in 2007 than in 2002, which can probably be attributed to a larger amount of animal feeding operations, such as dairies. For selected San Joaquin counties, we calculated total manure as

nitrogen produced to be approximately 99.0 million kg in 2002 and 116.2 million kg in 2007; we calculated total manure as phosphorus produced to be approximately 22.3 million kg in 2002 and 25.9 million kg in 2007.

DISCUSSION

Results show that nutrient loading was more likely to trend downward or at greater reductions per year after 2004 (Table 2). These declines may be linked to the expanded implementation of certain types of MPs. There were some exceptions to this. For example, there was a steep decline in both TN concentration and flux at the Sacramento River at Freeport site before to 1990 (Figure 4). This may be attributable to increased holding times of water on rice fields in the Sacramento Valley beginning in the mid-1980s (Figure 2). The main MPs used to control some pesticides in agricultural runoff include pesti-

cide application practices, and vegetation and water MPs (McClure et al. 2006). Of these MPs, expanded use of vegetation and water MPs might explain reductions in nutrient loads. Beginning shortly after 2004, an accelerated use of vegetation and water management MPs, particularly within the lower San Joaquin basin, have occurred. Specific cases or broad implementation of vegetative or water MPs in the Sacramento Basin after 2004 are limited. Based on our review of the 2005, 2006, and 2007 Sacramento River Watershed Order Coalition (SRWOC) reports, the focus of SRWOC was on public outreach and education during this time to encourage farmers to adopt MPs that limited runoff.

A previous study on trends in pesticide concentrations in the Central Valley showed that management actions to reduce concentrations and associated toxicity have had some success (Johnson et al. 2011). That study examined pesticide concentration trends from 1993 to 2005. Two sites examined in the San Joaquin Valley were the San Joaquin River at Vernalis and Orestimba Creek at River Road. Before implementation of the TMDL (early to mid-1990s), Orestimba Creek concentrations exceeded a numerical target for up to half the year (Johnson et al. 2011). By 2005, the numerical targets were being met most of the time. Improvements in water quality for the San Joaquin River at Vernalis also occurred with respected to diazinon.

For areas within the lower San Joaquin basin, there appears to be a continued expansion of vegetative and water MPs after 2004. Based on a 2006 survey, over one quarter of respondents (growers) "indicated that they had employed a new MP" on lands adjacent to waterways in the eastern San Joaquin Basin (Johnson 2007). Moreover, several survey respondents reported use of various MPs, including those related to erosion and sediment control, and water and nutrient management (Johnson 2007). To the west of the San Joaquin River (SJR) within the Orestimba Creek sub-watershed, over 186 ha of farmland have converted to high-efficiency irrigation systems since 2006 (Summers Engineering, Inc. 2008).

The results of this study suggest the positive effects of agricultural NPS control strategies (or MPs designed

for pesticides) on reducing nutrient concentrations and loads. Decreases in mean annual TP and NO_3 concentrations occurred at six of the seven sites during the enforcement period. Although the number of monitoring sites is small for this comparison (only seven), concentration or load decreases occurred frequently.

As shown on Figure 19, nitrogen fertilizer sales increased in both the Sacramento and San Joaquin valleys after 1990, although sales started to flatten out or slightly decrease after about 2004. Phosphorus fertilizer sales in both valleys are much less compared to nitrogen fertilizer sales. Although nutrient concentrations and loads have also declined in the Central Valley region since 2004, that decline is not expected to be attributable to fertilizers since there was only a slight decrease in recorded sales. Several factors may explain the recent decline in fertilizer sales, including changing land use and economics.

Positive results (declining concentrations) for TP and NO_3 at the Sacramento River at Colusa site appear to be related to MPs as changes during both periods occurred during similar discharges and season. Total phosphorus tends to adsorb onto fine-grained sediments, and transport to surfaces waters occurs primarily through erosion; therefore, elevated concentrations should be related to higher discharges. Results show this to be the case (Figure 9A) for the voluntary period. Erosion control practices may explain the decline in TP concentrations at higher discharges, for the enforcement period (Figure 9A) relative to the voluntary period, although we found no direct evidence of recent (post-2004) erosion-control MPs to have been used in the Sacramento Basin (see above).

A similar effect (water quality improvement as a result of MPs) is evident for NO_3 at Colusa (Figure 9B), and for TN and NO_3 at Mud Slough (Figures 18A and 18B); whereby, changes in the concentrations of nutrients occurred during similar flows and seasons.

The clay soils and shallow groundwater common throughout much of the western San Joaquin Valley prevent deep infiltration of irrigation and rainwater and results in the build-up of salts in the root zone (Quinn et al. 1998). Beginning in the late 1940s, agricultural subsurface drains (tile drains) were

installed to flush salts away from the root zone. Approximately 85% of the tile drains (Kratzer et al. 2010) in the San Joaquin Basin are located in the Grassland Drainage Area (west side of the San Joaquin Valley and south of Mud Slough). In 1996, Grassland Drainage Area tile drains were connected to a section of the San Luis drain, which bypassed the wildlife refuge, where drainage then flowed north into Mud Slough. Virtually all flow passing through Mud Slough comes from the Grassland Drainage Area. Consistent with that flow from the Grassland Drainage Area is an increase in both flow-normalized flux and annual fluxes of nitrate at Mud Slough around and after 1996 (Figure 15). Through improved irrigation systems and the recycling of drainage waters with irrigation waters, Grassland Drainage Area farmers have reduced the volume of drainage that enters Mud Slough (GBPOC 2013). As a result, a decrease in nitrate flux was observed in Mud Slough around 2005. The concentration and flux increases of NO_3 at Mud Slough and decreases in Salt Slough (Figure 15) from 1996 to 2004 are the result of drainage flow diverted to Mud Slough (originally proposed by Kratzer et al. [2010], and observed by this analysis). From 2004 to 2011, mean annual concentrations of NO_3 (WRTDS calculated) have declined steadily from $5.28\,\text{mg L}^{-1}$ in 2004 to $1.59\,\text{mg L}^{-1}$ in 2011, which represents a decrease of approximately 70%. The total drainage volume entering Mud Slough from the Grassland Drainage Area decreased approximately 33% between 2004 and 2011 (GBPOC 2013). Since the Grassland Drainage Area controls flow at Mud Slough, we would expect similar rates of decrease between NO_3 concentrations (70%) and the volume of drainage (33%).

Other Management Implications

The EGRET software produces concentration difference plots that can be used to demonstrate what months or discharges could be targeted for further load reductions. An example (Figure 20) is shown for nitrate and total phosphorus at the Sacramento River at Freeport and San Joaquin River at Vernalis sites. As shown in Figure 7, changes in concentrations and fluxes of nitrate at the Sacramento River at Freeport site have been negligible for the period

of this study. Accordingly, concentration changes by month for the period of record at the Freeport site are also very slight, with very little change in the spring to summer months, and only small increases in concentration ($<0.1\,\text{mg L}^{-1}$ in the winter months. In contrast, nitrate concentrations have increased more than $0.5\,\text{mg L}^{-1}$ in the late fall and winter months at the San Joaquin River at Vernalis, across the entire range of discharges. Nitrate concentrations in the lower San Joaquin River show reducing concentrations in the spring through summer at low discharge. Therefore, fluxes of nitrate in the late fall or winter may be a cause of concern. TP concentrations at the Sacramento River at Freeport actually show mostly decreases for the period of this study, except for some slight increases in concentration in the fall. In contrast, TP concentrations show more increases in the San Joaquin River at Vernalis for mid to high levels of discharge throughout most of the year. Concentrations have decreased through most of the year, especially for lower discharges.

CONCLUSION

Long-term monitoring of nutrients (TN, TP, NO_3, NH_3) indicates variable directions of trends since the mid-1970s, as shown by our examination of flow-normalized concentrations and fluxes. Some locations showed decreasing trends in both the voluntary and enforcement periods, while a number of sites clearly showed a statistically significant change in the trend in load reduction (negative) during the enforcement period where fluxes increased (positive) during the voluntary period. Most, but not all sites showed decreasing trends in ammonia concentration and load before 1990, however there are locations where ammonia has increased. The two largest rivers, the Sacramento and San Joaquin, both have a decreasing trend in ammonia. For the Sacramento River site, the monitoring location is upstream of a large wastewater treatment facility and does include those discharges. Continued monitoring at these locations will be necessary to determine how trends will change in future years. The EGRET software provides a straightforward way to calculate loads and flow-normalized loads for locations with long-term data sets.
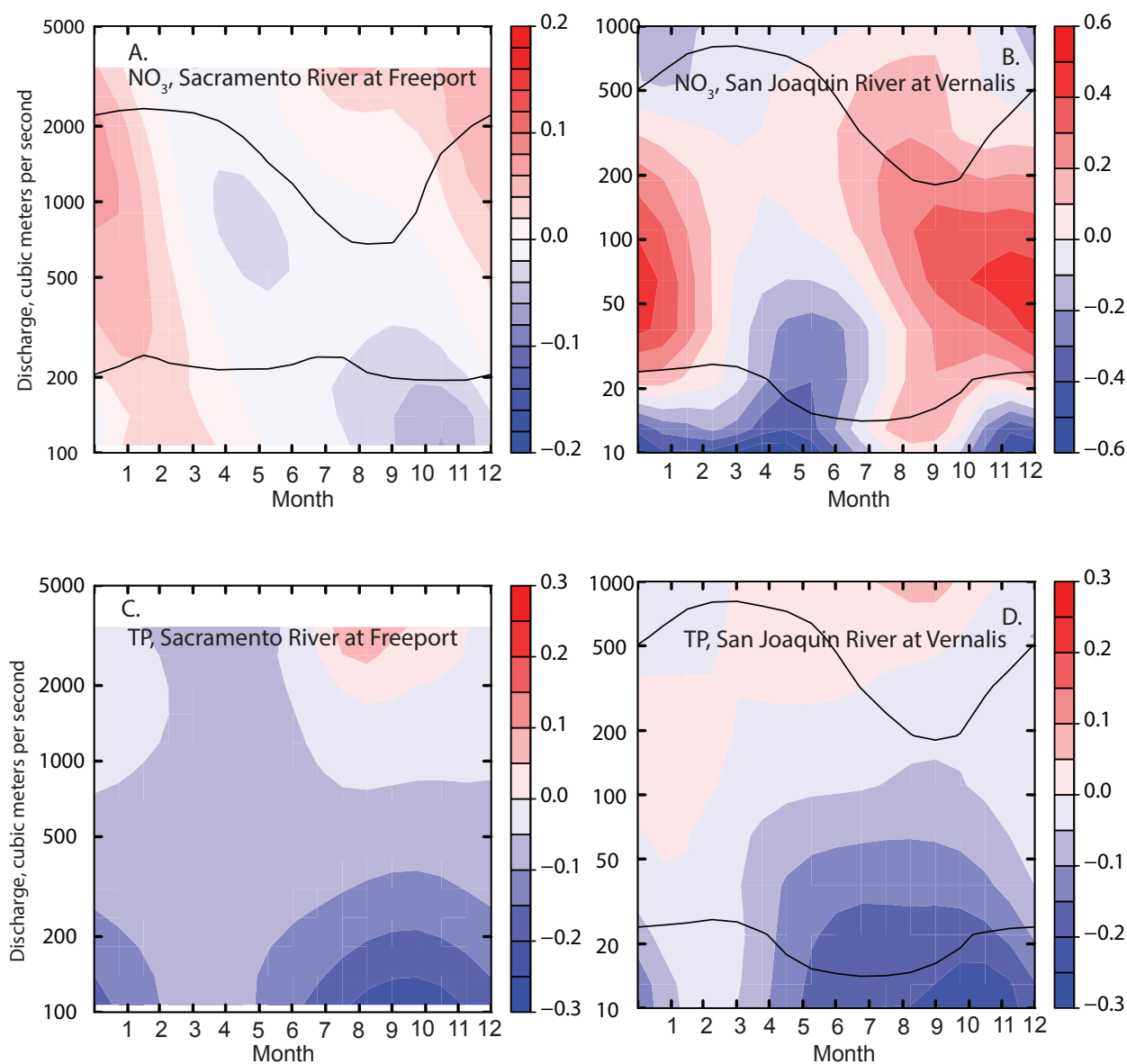
Figure 20 Estimated changes in concentrations of nitrate in the Sacramento River at Freeport site **(A)** and nitrate in the San Joaquin River at Vernalis site **(B)** from 1975 to 2012; and estimated changes in TP in the Sacramento River at Freeport site **(C)** and the San Joaquin River at Vernalis site **(D)**. The upper and lower solid black lines represent the 95% and 5% percentiles of flows. Months are shown on the X-axis and integrate all data for the time period shown. Red indicates increasing concentrations and blue indicates decreasing concentrations.

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