# Four decades of water quality change in the upper San Francisco Estuary

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## *Abstract*

Quantitative descriptions of water quality, physical, and biological characteristics in estuaries is critical for developing an ecological understanding of drivers of change. Historical trends and relationships between key species of dissolved inorganic nitrogen (ammonium, nitrate/nitrite, total) from the Delta region of the San Francisco Estuary (SFE) were modeled with an estuarine adaptation of the Weighted Regressions on Time, Discharge, and Season (WRTDS). Trend analysis with flow-normalized results demonstrated the potential to interpret different changes relative to observed data that included flow effects, such that several trends with flow-normalized data had changes in magnitude and even reversal of trends relative to the observed. We further described mechanisms of change with two case studies that evaluated 1) downstream changes in nitrogen following upgrades at a wastewater treatment plant, and 2) interactions between biological invaders, chlorophyll, and flow in Suisun Bay. WRTDS results for ammonium trends showed a distinct signal as a result of upstream wastewater treatment plant (WWTP) upgrades, with specific reductions observed in the winter months during low-flow conditions. Results for Suisun Bay showed that chlorophyll $a$ (chl-$a$) production in early years was directly stimulated by flow, whereas the relationship with flow in later years was indirect and influenced by grazing pressure. Although these trends and potential causes of change have been described in the literature, results from WRTDS provided an approach to test alternative hypotheses of spatiotemporal drivers of nutrient dynamics in the Delta.

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# 1 Introduction

Understanding drivers of water quality changes in large estuaries depends on accurate descriptions of source inputs from the watershed. The Sacramento - San Joaquin River Delta (hereafter 'Delta') is a mosaic of inflows in the upper San Francisco Estuary (SFE) that receives and processes inputs from the highly agricultural watershed of the Central Valley (Jassby and Cloern 2000, Jassby et al. 2002, Jassby 2008). Sediment transport and wastewater treatment plant (WWTP) inputs from the Delta are primary sources of nutrients for the estuary (Dugdale et al. 2007, Cornwell et al. 2014). Although water quality conditions in SFE symptomatic of eutrophication have historically been infrequent, changes in response to stressors suggests that recent conditions have not followed past trajectories. Increases in phytoplankton biomass, reductions in dissolved oxygen, and increasing abundance of species associated with harmful algal blooms (e.g., *Pseudo-nitzschia*, *Alexandrium*, *Dinophysis spp.*) have been a recent concern for the management of this prominent system (Lehman et al. 2005, Cloern et al. 2005, 2007, Shellenbarger et al. 2008). As a result, chlorophyll *a* (chl-*a*) thresholds to assess and manage levels of concern for phytoplankton biomass in the lower estuary have been proposed (Sutula et al. 2017). Although these changes are linked to drivers at different spatial and temporal scales, describing inputs from the Delta is critical to understand downstream effects.

Rates of primary production in coastal habitats are often defined by nutrient concentrations, although a simple relationship between enrichment and water quality changes can be difficult to determine (Cloern 2001). Nutrient concentrations are generally non-limiting for phytoplankton growth in the upper SFE. In contrast, light conditions have long been considered the primary limiting factor preventing accumulation of phytoplankton biomass (Cole and Cloern

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1984, Alpine and Cloern 1988), whereas grazing pressure from pelagic fishes and benthic

invertebrates can reduce phytoplankton during periods of growth (Nichols 1985, Jassby 2008,

Kimmerer and Thompson 2014). Moreover, changes in flow management practices compounded

with climate variation have altered flushing rates and turbidity as key factors that moderate

phytoplankton growth in the system (Alpine and Cloern 1992, Lehman 2000, Wright and

Schoellhamer 2004, Canuel et al. 2009). Glibert et al. (2014) attributed recent phytoplankton

blooms in Suisun Bay to a drought, during which residence times and nitrification rates increased.

Speciation changes in the dominant forms of nitrogen are considered key factors that contribute to

phytoplankton blooms, particularly seasonal reductions in ammonium that allow uptake of nitrate

that stimulates growth (Dortch 1990, Dugdale et al. 2007). Changes in phytoplankton biomass

and the effects on pelagic organisms have also been of concern. Jassby (2008) described decadal

trends in phytoplankton biomass to understand mechanisms of decline for pelagic fish populations

in the Delta. Although phytoplankon concentrations have been relatively consistent in Suisan

Bay, biomass in the upper Delta has been increasing. Much of these trends were explained by

invasion of benthic grazers in polyhaline areas and changes in the mean flow conditions observed

in the Delta.

     Long-term monitoring data are powerful sources of information that can facilitate

descriptions of water quality change in coastal regions. A comprehensive water quality

monitoring program has been in place in the Delta for several decades (Fig. 1, IEP 2013).

Although these data have been used extensively, water quality trends covering the full spatial and

temporal coverage of the monitoring dataset have not been systematically evaluated. Quantitative

descriptions of nutrient dynamics in the Delta are challenging given multiple sources and the

volume of water that is exchanged with natural and anthropogenic processes. An evaluation using

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mass-balance models to describe nutrient dynamics in the Delta demonstrated that the majority of ammonium entering the system during the summer is nitrified or assimilated, whereas a considerable percentage of total nitrogen load to the Delta is exported (Novick et al. 2015). Seasonal and annual changes in the delivery of water inflows and water exports directly from the system can also obscure trends (Jassby and Cloern 2000, Jassby 2008).

Formal methods for trend analysis are required to describe water quality changes that vary by space and time. As a practical approach for water quality evaluation, trend analysis of ecosystem response indicators often focuses on tracking the change in concentrations or loads of nutrients over many years. Response indicators can vary naturally with changing flow conditions and may also reflect long-term effects of management or policy changes. For example, chl-*a* concentration as a measure of phytoplankton response to nutrient inputs can follow seasonal patterns with cyclical variation in temperature and light changes throughout each year, whereas annual trends can follow long-term variation in nutrient inputs to the system (Cloern 1996, Cloern and Jassby 2010). Similarly, nutrient trends that vary with hydrologic loading also vary as a function of utilization rates by primary producers or decomposition processes (Sakamoto and Tanaka 1989, Schultz and Urban 2008, Harding et al. 2016).

The Weighted Regressions on Time, Discharge, and Season (WRTDS) approach was developed in this context and has been used to characterize decadal trends in running-water systems (Hirsch et al. 2010, Sprague et al. 2011, Medalie et al. 2012, Hirsch and De Cicco 2014, Pellerin et al. 2014, Zhang et al. 2016). The WRTDS method has been adapted for trend analysis in tidal waters, with a focus on chl-*a* trends in Tampa Bay (Beck and Hagy III 2015) and the Patuxent River Estuary (Beck and Murphy 2017). Although the WRTDS method has been effectively applied to describe changes in freshwater systems, use in coastal ecosystems has not

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been as extensive. Application of WRTDS to describe trends in estuaries could reveal new

insights given the disproportionate effects of physical drivers, such as flow inputs and tidal

exchange, on water quality. The effects of biological drivers may also be more apparent because

hydrological effects can be removed by WRTDS. As such, application of WRTDS models for

trend analysis could facilitate a broader discusion on the need to focus beyond nutrients to

develop integrated plans for water quality management.

The goal of this study was to provide a comprehensive description of nutrient trends in the

Delta region to inform understanding of ecosystem response dynamics and potential causes of

water quality change. This study also supports a general need to more effectively use long-term

monitoring data to inform management priorities for water quality in coastal regions. The specific

objectives were to 1) quantify and interpret trends over four decades at ten stations in the Delta,

including annual, seasonal, and spatial changes in nitrogen analytes and response to flow

variation, and 2) provide detailed descriptions of two case studies in the context of conceptual

relationships modeled with WRTDS. The second objective evaluated two specific water quality

stations to demonstrate complexities with nutrient response to flow, effects of nutrient-related

source controls on ambient conditions, and effects of biological invasion by benthic filter feeders

on primary production. Our general hypothesis was that the results were expected to support

previous descriptions of trends in this well-studied system, but that new insight into spatial and

temporal variation in response endpoints was expected, particuarly in flow-normalized model

predictions.

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# 2   *Materials and Methods*

## 2.1   Study system

The Delta region drains a 200 thousand km$^2$ watershed into the SFE, which is the largest

estuary on the Pacific coast of North America. The watershed provides water to over 25 million

people and irrigation for 18 thousand km$^2$ of agricultural land. Water enters the SFE through the

Sacramento and San Joaquin rivers that have a combined inflow of approximately 28 km$^3$ per

year, with the Sacramento accounting for 84% of inflow to the Delta. The SFE system includes

the Delta and subembayments of San Francisco Bay (Fig. 1). Water dynamics in the SFE and

Delta are governed by inflows from the watershed, tidal exchange with the Pacific Ocean, and

water withdrawals for municipal and agricultural use (Jassby and Cloern 2000). Seasonally,

inflows from the watershed peak in the spring and early summer from snowmelt, whereas

consumption, withdrawals, and export have steadily increased from 1960 to present, but vary

depending on inter-annual climate effects (Cloern and Jassby 2012). Notable drought periods

have occurred from 1976-1977, 1987-1992, and recently from 2013-2015 (Cloern 2015).

Orthophosphate ($PO_4^{3-}$) and dissolved inorganic nitrogen (DIN) enter the Delta primarily

through the Sacramento and San Joaquin rivers and from municipal WWTP inputs. Annual

nutrient export from the Delta region has been estimated as approximately 30 thousand kg d$^{-1}$ of

total nitrogen (varying with flow, Novick et al. 2015), with 90% of ammonium ($NH_4^+$) originating

solely from the Sacramento Regional WWTP (Jassby 2008). Although nitrogen and phosphorus

inputs are considerable, primary production is relatively low and not nutrient-limited (Jassby et al.

2002, Kimmerer et al. 2012). The resistance of SFE to the negative effects of eutrophication has

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historically been attributed to its unique physical and biological characteristics, including strong tidal mixing that limits stratification in the larger estuary (Cloern 1996, Thompson et al. 2008), limits on phytoplankton growth from high turbidity, and filter-feeding by bivalve mollusks in the northern portion (Thompson et al. 2008, Crauder et al. 2016). However, recent water quality trends have suggested that resilience to nutrient inputs is decreasing(Lehman et al. 2005, Cloern et al. 2007, Lehman et al. 2010), which has been attributed to biological invasions (Cohen and Carlton 1998) and departures from the historical flow record (Enright and Culberson 2009, Cloern and Jassby 2012), among other factors acting at global scales (e.g., variation in sea surface temperatures, Cloern et al. 2007).

## 2.2   Data sources

Nutrient time series of monthly observations from 1976 to 2013 were obtained for ten active sampling stations in the Delta (Fig. 1 and Table 1, IEP 2013). Stations were grouped by location in the study area for comparison: peripheral Delta stations C3 (Sacramento inflow), C10 (San Joaquin inflow), MD10, P8; interior Delta stations D19, D26, D28; and Suisun stations D4, D6, and D7. These stations cover all of the major inflows and outflows to the Delta and were selected for analysis based on the continuity of the period of observation (Jabusch and Gilbreath 2009). Although many other stations are available for the region, the stations were chosen because they are actively maintained by the regional monitoring program and they capture dominant seasonal and annual modes of nitrogen variability characteristic of the region (Jabusch et al. 2016). Time series were complete for all stations except for an approximate ten year gap from 1996-2004 for D19. Data were minimally processed, with the exception of averaging replicates that occurred on the same day. The three nitrogen analytes that were evaluated were

ammonium, nitrite/nitrate, and DIN (as the sum of the former two). Less than 3% of all observations were left-censored, although variation was observed between analytes and location. The ammonium time series had the most censored observations at sites C10 (25.4% of all observations), MD10 (18.1%), D28 (17.8%), D19 (12%), and D7 (7.9%).

Daily flow estimates for the Delta region were obtained from the Dayflow software program (IEP 2016). The WRTDS models described below require a matched flow record with the appropriate station to evaluate nutrient trends. Given the complexity of inflows and connectivity of the system, only the inflow estimates from the Sacramento and San Joaquin rivers were used as measures of freshwater influence at each station. Initial analyses indicated that model fit was not significantly improved with flow estimates from locations closer to each station, nor was model fit improved using lagged times series. As such, the Sacramento daily flow time series was used to account for flow effects at C3, D19, D26, D28, and MD10, and the San Joaquin time series was used for C10 and P8 based on station proximity to each inflow. Daily flow estimates were matched with the corresponding sample dates for the nutrient data. Salinity observations at D4, D6, and D7 in Suisun Bay were used as more appropriate measures of freshwater variation, given the stronger tidal influence at these stations. Salinity has been used as a tracer of freshwater influence for the application of WRTDS models in tidal waters (Beck and Hagy III 2015). Salinity was not used as a covariate at the interior and peripheral stations becuase initial analyses showed improved performance using flow estimates from the Sacramento and San Joaquin rivers.

## 2.3 Analysis method and application

A total of thirty WRTDS models were created, one for each nitrogen analyte at each station. The functional form of WRTDS is a simple regression (Hirsch et al. 2010) that models the log-transformed response variable as a function of time, flow, and season:

$$\ln\left(N\right) = \beta_0 + \beta_1 t + \beta_2 \ln\left(Q\right) + \beta_3 \sin\left(2\pi t\right) + \beta_4 \cos\left(2\pi t\right) \tag{1}$$

where $N$ is one of three nitrogen analytes, time $t$ is a continuous variable as decimal time to capture the annual ($\beta_1$) or seasonal trend ($\beta_3$, $\beta_4$), and $Q$ is the flow variable (either flow or salinity depending on station). Generally, the WRTDS model is a moving window regression that fits unique parameters (i.e., $\beta_0, \ldots, \beta_4$) at each observation point in the time series ($n$ ranging from 433 at D19 to 571 at C3). Rather than fitting a global model to the entire time series, one regression is fit to every observation. Observations within a window for each regression are weighted relative to annual, seasonal, and flow distances from the observation at the center of the window. Observations with distances farther from the center (i.e., greater time and different flow values from the center) have less weight during parameter estimation for each regression. This approach allows for a type of smoothing where the observed fit is specific to the data characteristics within windows. Models applied herein were based on a tidal adaptation of the original method that can use either flow or salinity estimates as nutrient predictors (Beck and Hagy III 2015). All models were fit to describe the conditional mean response using a weighted Tobit model for left-censored data (Tobin 1958). Model predictions were evaluated as monthly values or as annual values that averaged monthly results within each water year (October to September). All analyses used the WRTDStidal package for the R statistical programming

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language (Beck 2017, RDCT (R Development Core Team) 2017). The default model fitting

procedures were used that set half-window widths as six months for seasonal weights, ten years

for annual weights, and half the range of salinity or flow in the input data for $Q$ weights.

A hallmark of the WRTDS approach is the description of flow-normalized trends that are

independent of variation from freshwater inflows (Hirsch et al. 2010). Flow-normalized trends for

each analyte at each station were used to describe long-term changes in different annual and

seasonal periods. Flow-normalization predictions for each month of each year were based on the

average of predictions for flow values that occur in the same month across all years, weighted

within each specific month and year for every observation. Flow-normalized trends in each

analyte were summarized as both medians and percent changes from the beginning to end of

annual groupings from 1976-1995 and 1996-2013, and seasonal groupings of March-April-May

(spring), June-July-August (summer), September-October-November (fall), and

December-January-February (winter) within each annual grouping. Annual groupings were

chosen as approximate twenty year midpoints in the time series and seasonal groupings were

chosen to evaluate inter-annual changes while keeping season constant.

Trends in each annual and seasonal grouping were based on seasonal Kendall tests of the

flow-normalized predictions. This test is a modification of the non-parametric Kendall test that

accounts for variation across seasons in the response variable (Hirsch et al. 1982, Millard 2013).

Results from the test can be used to evaluate the direction, magnitude, and significance of a

monotonic change within the period of observation. The estimated rate of change per year is also

returned as the Theil-Sen slope and was interpreted as the percent change per year when divided

by the median value of the response variable in the period of observation (Jassby 2008). Trends in

annual groupings were based on all monthly observations within relevant years, whereas seasonal

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groupings were based only on the relevant months across years. Seasonal Kendall tests were also used to describe trends in the observed data. These trends were compared with those based on the flow-normalized trends to evaluate potential differences in conclusions caused by flow effects.

## 3 Results

### 3.1 Observed and modelled Data

The observed time series for the ten Delta - Suisun Bay stations had substantial variation in scale among the nitrogen analytes and differences in apparent seasonal trends (Fig. 2). DIN for most stations was dominated by nitrite/nitrate, whereas ammonium was a smaller percentage of the total. However, C3 had a majority of DIN composed of ammonium and other stations (e.g., P8, D26) had higher concentrations of ammonium during winter months when assimilation rates are lower (Novick et al. 2015). By location, observed concentrations of DIN for the entire time series were higher on average for the peripheral stations (C3, C10, MD10, P8; mean $\pm$ s.e.: $1.04\pm0.03$ mg L$^{-1}$) and similar for the interior (D19, D26, D28, $0.43\pm0.01$) and Suisun Bay stations (D4, D6, D7, $0.44\pm0.01$). Average concentrations were highest at P8 ($1.63\pm0.05$ mg L$^{-1}$) and lowest at C3 ($0.4\pm0.01$) for DIN, highest at P8 ($0.28\pm0.02$) and lowest at D28 ($0.05\pm0.003$) for ammonium, and highest at C10 ($1.4\pm0.04$) and lowest at C3 ($0.15\pm0.004$) for nitrite/nitrate. Mean observed concentrations were also higher later in the time series for all analytes. For example, average DIN across all stations was $0.61\pm0.01$ mg L$^{-1}$for 1976-1995, compared to $0.7\pm0.01$ for 1996-2013. Seasonal changes across all years showed that nitrogen concentrations were generally lower in the summer and higher in the winter, although observed patterns were inconsistent between sites. For example, site MD10 had distinct seasonal spikes for elevated DIN in the winter, whereas other stations had less prominent seasonal maxima (e.g., C3,

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240    Long-term trends between stations for the different nitrogen analytes were apparent from

241 the modelled results (Fig. 3). Although each station varied in the overall concentrations, patterns

242 within the three Deltra regions (peripheral, interior, and Suisun) were observed. Concentrations

243 for all nitrogen analytes were highest in the peripheral stations. Ammonium concentrations at P8

244 and C3 were highest and showed a consistent increase over time, followed by a reduction

245 beginning in the early 2000s, whereas ammonium concentrations at C10 and MD10 were low and

246 gradually decreasing throughout the period of record. By contrast, DIN and nitrite/nitrate

247 concentrations at the peripheral stations showed increases at P8 and C10 followed by a decline in

248 the early 2000s, whereas concentrations at C3 and MD10 were lower and did not show any

249 noticeable trends. Trends in the interior stations showed a gradual increase in ammonium

250 followed by a gradual decrease beginning in the early 1990s, particularly for D26. Trends in DIN

251 and nitrite/nitrate for the interior stations showed a reduction early in the time series, followed by

252 a slight increase beginning in the mid-1980s, and finally a reduction beginning in the late 1990s.

253 These trends were similar for the Suisun stations, although the reduction in the late 1990s did not

254 occur. By contrast, ammonium concentrations were low in Suisun but a gradual increase over the

255 period of record was observed.

## 3.2   Trend tests

257    Estimated trends from Seasonal Kendall tests on the raw time series varied considerably

258 between sites and analytes (Fig. 4). Significant trends were observed from 1976-1995 for eight of

259 ten sites for DIN (seven increasing, one decreasing), eight sites for ammonium (six increasing,

260 two decreasing), and six sites for nitrite/nitrate (five increasing, one decreasing). Decreasing

trends were more common for the observed data from 1996-2013. Eight sites had significant

trends for DIN (four increasing, four decreasing), seven sites for ammonium (five increasing, two

decreasing), and eight sites for nitrite/nitrate (four increasing, four decreasing). P8 had a

relatively large decrease in ammonium ($-8.3\%$ change per year) for the second annual period

compared to all other sites. Trends by season were similar such that increases were generally

observed in all seasons from 1976-1995 (Fig. 5) and decreases were observed for 1996-2013

(Fig. 6). Trends for the seasonal comparisons were noisier and significant changes were less

common compared to the annual comparisons.

A comparison of flow-normalized results from WRTDS relative to observed data

identified changes in the magnitude, significance, and direction of trends. For all sixty trend

comparisons in Fig. 4 (flow-normalized values in Table 2) regardless of site, nitrogen analyte, and

time period (annual or seasonal aggregations), thirteen comparisons had trends that were

insignificant with the observed data but significant with flow-normalized results, whereas only

one trend changed to insignificant. This suggests that time series that include flow effects had

sufficient noise to obscure or prevent identification of an actual trend of a water quality parameter.

Further, changes in the magnitude of the estimated percent change per year were also apparent for

the flow-normalized trends, such that fourteen comparisons showed an increase in magnitude

(more negative or more positive) and twenty five had a decrease (less positive or less negative)

compared to observed trends. Eleven comparisons showed a trend reversal from positive to

negative estimated change, nine sites went from no change to negative estimated change, and one

site went from no change to a positive trend for the flow-normalized results. Differences by

season in the observed relative to flow-normalized trends from WRTDS were also apparent

(Figs. 5 and 6 and Tables 3 and 4). The most notable changes were an overall decrease in the

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estimated trend for most sites in the summer and fall seasons for 1996-2013, including an

increase in the number of statistically significant trends.

## 3.3 Selected examples

Two stations were chosen to demonstrate use of WRTDS to develop a more

comprehensive description of decadal trends in the Delta. The selected case studies focused on

1) effects of wastewater treatment upgrades upstream of P8, and 2) effects of biological invasion

on nutrient dynamics in Suisun Bay using observations from D7. Each case study is built around

hypotheses that results from WRTDS models were expected to support, both as a general

description and for additional testing with alternative methods.

### 3.3.1 Effects of wastewater treatment

Significant efforts have been made in recent years to reduce nitrogen loading from regional

WWTPs given the disproportionate contribution of nutrients relative to other sources (Cornwell

et al. 2014, Novick et al. 2015). Several WWTPs in the Delta have recently been or are planned to

be upgraded to include tertiary filtration and nitrification to convert biologically available

ammonium to nitrate. The City of Stockton WWTP was upgraded in 2006 and is immediately

upstream of station P8 (Jabusch et al. 2016), which provides a valuable opportunity to assess how

nutrient or nutrient-related source controls and water management actions have changed ambient

concentrations downstream. A modal response of nutrient concentrations at P8 centered around

2006 is expected as a result of upstream WWTP upgrades, and water quality should exhibit 1) a

shift in the ratio of the components of DIN from the WWTP before/after upgrade, and 2) a

flow-normalized annual trend at P8 to show a change concurrent with WWTP upgrades.

Effluent measured from 2003 to 2009 from the Stockton WWTP had a gradual reduction

in ammonium concentration relative to total DIN (Fig. 7). Ammonium and nitrate concentrations

were comparable prior to 2006, whereas nitrate was a majority of total nitrogen after the upgrade,

with much smaller percentages from ammonium and nitrite. As expected, flow-normalized

nitrogen trends at P8 shifted in response to upstream WWTP upgrades (Fig. 8a), with ammonium

showing an increase from 1976 followed by a large reduction in the 2000s. Interestingly,

nitrite/nitrate concentrations at P8 also showed a similar but less dramatic decrease despite an

increase in the WWTP effluent concentrations following the upgrade (Fig. 7). Percent changes

from seasonal Kendall tests on flow-normalized results (Table 5) showed that both nitrogen

species increased prior to WWTP upgrades (2% per year for nitrite/nitrate, 2.8% for ammonium),

followed by decreases after upgrades ($-1.9\%$ for nitrite/nitrate, $-16.6\%$ for ammonium).

Seasonally, increases prior to upgrades were highest in the summer for nitrite/nitrate (2.4%) and

in the fall for ammonium (4.9%). Similarly, seasonal reductions post-upgrade were largest in the

summer for nitrite/nitrate ($-4.3\%$) and largest for ammonium in the winter ($-26.7\%$).

Relationships of nitrite/nitrate with flow described by WRTDS showed an inverse flow

and concentration dynamic with flushing or dilution at higher flow (Fig. 8b). Seasonal variation

was even more apparent for ammonium, although both nitrite/nitrate and ammonium typically

had the highest concentrations at low flow in the winter (January). Additionally, strength of the

flow/nutrient relationship changed between years. Nitrite/nitrate typically had the strongest

relationship with flow later in the time series (i.e., larger negative slope), whereas ammonium had

the strongest relationship with flow around 2000 in January.

### 3.3.2 *Effects of biological invasions*

Invasion of the upper SFE by the Asian clam *Potamocorbula amurensis* in 1986 caused

severe changes in phytoplankton abundance and species composition. Reduction in phytoplankton

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biomass has altered trophic networks in the upper SFE and is considered an important mechanism in the decline of the protected delta smelt (*Hypomesus transpacificus*) and other important fisheries (Feyrer et al. 2003, Mac Nally et al. 2010). Changes in the physical environment have also occurred, particularly increased water clarity from a reduction of particle transport and erodible sediment supply (Jassby 2008, Schoellhamer 2011, Cloern and Jassby 2012), although decreases in phytoplankton by clam biofiltration may have also increased clarity (Mac Nally et al. 2010). The clams are halophilic such that drought years are correlated with an increase in biomass and further upstream invasion of the species (Parchaso and Thompson 2002, Cloern and Jassby 2012). We hypothesized that results from WRTDS models would show 1) a decline in annual, flow-normalized chlorophyll concentrations over time coincident with an increase in abundance of invaders, and 2) variation in the chlorophyll/clam relationship through indirect or direct controls of flow. Although the relationship between phytoplankton and clams have been well described in SFE (Kimmerer and Thompson 2014), we use WRTDS to develop additional evidence that an increase in DIN was facilitated in part by clam invasion and the relationship of phytoplankton with clam abundance was mediated by flow and climatic variation in recent years.

Invasion in the 1980s showed a clear reduction of *Corbicula fluminea* and increase of *P. amurensis* (Fig. 9a), where biomass of the latter was negatively associated with flow from the Sacramento river (Fig. 9b). The increase in clam abundance was associated with a notable decrease in annually-averaged chl-*a* from WRTDS results (Fig. 9c), as expected if WRTDS is adequately capturing flow variation and identifying the well-established phytoplankton decrease beginning in the 1980s. A seasonal shift in the flow-normalized results was also observed such that chl-*a* concentrations were generally highest in July/August prior to invasion, whereas a spring maximum in April was more common in recent years (Fig. 9f). An increase in

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annually-averaged silicon dioxide (Fig. 9d) was coincident with the chl-*a* decrease, with the

largest increases occuring in August (Fig. 9g). Further, DIN trends were similar to silicon-dioxide

in both annual and seasonal changes (i.e., Figures 9e and 9h compared to 9d and 9g), such that an

increase in both nutrients earlier in the time series corresponded with the decrease in chl-*a*.

The relationship of chl-*a* with clam biomass was significant (Fig. 9i), with lower chl-*a*

associated with higher biomass, confirming results from earlier studies (Alpine and Cloern 1992,

Thompson et al. 2008). However, the effect of flow on both clams and phytoplankton as a

top-down or bottom-up control changed throughout the time series. The chl-*a*/flow relationship

showed that increasing flow (decreasing salinity) was associated with a slight increase in chl-*a*

followed by a decrease early in the time series (Fig. 9j), whereas overall chl-*a* was lower but a

positive association with flow (negative with salinity) was observed later in the time series.

Following clam invasion, chl-*a* concentrations were reduced by grazing but showed a positive and

monotonic relationship with increasing flow. The increase in clam abundance was concurrent with

decline in chl-*a* concentration, although variation in abundance between years was also observed.

Clam abundance was reduced during high flow years in the late 1990s, 2006, and 2011 (9a). In

the same years, WRTDS predictions for chl-*a* were higher than the flow-normalized component

(Fig. 9c), which further suggests a link between increased flow and phytoplankton production.

# 4 Discussion

Water quality conditions in the Delta are dynamic and not easily characterized from

observed time series. Annual aggregations of WRTDS modelled results and application of formal

trend analyses provided insight into the spatial and temporal variation of nitrogen analytes in

three distinct regions of the Delta that is not possible with raw observations. A general conclusion

is that nitrogen concentrations have decreased overall throughout the approximate forty years of observation. These results are confirmed visually from WRTDS (Fig. 3) and through significant results from trend tests (Fig. 4, Table 2). Although the overall trends suggest a system-wide reduction, considerable differences by location and analyte were characterized by the analysis and are important independent of overall trends. Nutrient concentrations were highest at the peripheral stations (C3, MD10, P8, and C10) that monitor inflows from the Sacramento, San Joaquin, Cosumnes, and Mokelumne rivers. The highest concentrations among all nitrogen analytes, ammonium in particular, were observed at P8 as a direct consquence of WWTP inputs upstream. Elevated ammonium concentrations were also observed at C3 as a measure of upstream contributions from the Sacramento Regional County Sanitation District. By contrast, nitrite/nitrate concentrations were highest at C10 as a measure of contributions from the San Joaquin River to the south that drains a predominantly agricultural watershed. Although the Sacramento River drains a much larger area, the dominant ammonium signal as compared to nitrite/nitrate at C3 underscores the importance of WWTP control for water quality issues downstream.

Differing magnitudes of nitrogen analytes between stations as a function of source type can have an effect on the relationship between flow and nutrients. Both Hirsch et al. (2010) and Beck et al. (2015) used WRTDS results to demonstrate variation between flow and nutrient dynamics depending on pollutant sources. In particular, a chemodynamic response of nutrients with flow variation is common if nutrients originate primarily from the watershed through diffuse sources (Thompson et al. 2011, Wan et al. 2017). Increased flow may induce a change in nutrient concentrations, such that reduction may occur with flushing or an increase may occur through mobilization. By contrast, nutrient loads are relatively chemostatic or invariant with changes in

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flow if point-sources are the dominant contributor. These relationships are modelled particularly

well with WRTDS, which can provide a means of hypothesizing unknown sources or verifying

trends in response to management actions. As noted above, C10 at the inflow of the San Joaquin

River is dominated by nitrite/nitrate consistent with diffuse, agricultural inputs from the

watershed. A logical expectation is that trends from observed data may vary considerably from

trends with modelled results that are flow-normalized. Accordingly, trend analysis of

nitrate/nitrate by year and season showed that percent changes at C10 were typically

underestimated with the observed data during the recent period from 1996-2013 (Tables 2 and 4).

This is consistant with an expected effect of flow on raw time series, particularly for

chemodynamic behavior at locations that drain highly developed watersheds (Wan et al. 2017).

Differences in apparent trends underscore the importance of considering flow effects in

the interpretation of environmental changes, particularly if trend evaluation is used to assess the

effects of nutrients on ecosystem health or the effectiveness of past nutrient management actions.

Our results demonstrated the potential to interpret different trends if flow effects are not

considered, where the difference could vary from a simple change in the magnitude and

significance of a trend, to more problematic changes where the flow-normalized trend could

demonstrate a complete reversal relative to the observed (e.g., DIN trends for all Suisun stations

from 1996-2013, Fig. 4). A more comprehensive evaluation of flow in the Delta demonstrated

that flow contributions of different end members vary considerably over time at each station

(Novick et al. 2015). For example, flow at MD10 represents a changing percentage by season of

inputs from the Sacramento, San Joaquin, Cosumnes, Mokelumne rivers, and agricultural returns.

For simplicity, water quality observations in our analyses were matched with large-scale drivers

of flow into the Delta where most sites were matched to Sacramento or San Joaquin daily flow

estimates. Given that substantial differences with flow-normalized results were apparent from relatively coarse estimates of flow contributions, more precise differences could be obtained by considering the influence of multiple flow components at each location. Output from the Dayflow software program (IEP 2016) provides a complete mass balance of flow in the Delta that could be used to develop a more comprehensive description.

Long-term trends in nutrient and phytoplankton concentations in Suisun Bay have also been the focus of intense study for many years (Cloern et al. 1983, Lehman 1992, Dugdale et al. 2007, Jassby 2008, Glibert et al. 2014). Although nitrite/nitrate concentrations generally exceed ammonium about five-fold at the Suisun Bay stations, changes in ammonium concentration below 0.072 mg $L^{-1}$ (4 $\mu$mol $L^{-1}$) is a concern given the affect on the uptake of nitrate by phytoplankton (Dugdale et al. 2007). Energetic costs of ammonium for phytoplankton growth are lower than nitrate such that the former tends to stimulate growth in most cases. Although phytoplankton communities in SFE generally utilize ammonium when growth conditions are favorable, seasonal variation in the dominant forms has contributed to occurrence of bloom events in recent years. In particular, reduction of ammonium in the spring in Suisun Bay below thresholds of 4 $\mu$mol $L^{-1}$ has contributed to uptake of nitrate that stimulates bloom development. Our results demonstrated an overall increase in ammonium from the late 1970s to 2000, with initial flow-normalized values of annual averages estimated as approximately 0.05 mg $L^{-1}$ for the Suisun stations in 1976 to a maximum ranging from 0.08 mg $L^{-1}$ (station D4) to above 0.1 mg $L^{-1}$ (D6) in 2000 (Fig. 3). Trends from 1996-2005 evaluated in (Jassby 2008) showed a similar increase in ammonium. However, a reversal of trends in in recent years may also be occuring in Suisun Bay, as model estimates suggest either relatively constant concetratrations or even a decrease at some stations beginnign around 2000 (e.g., D6, D7, Fig. 4). Combined with the shift

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towards a dominant spring peak in chloropyll growth (Fig. 9f), changing nitrogen ratios continue

to be a concern for the management of production in the upper SFE.

## 4.1 Interpretation of case studies

A general conclusion from the analysis of nitrogen trends at P8 is that ammonium

reductions were concurrent with WWTP upgrades, but the reduction was most apparent at

low-flow in January. These dynamics are difficult to characterize from the observed time series,

and further, results from WRTDS can be used to develop additional hypotheses of factors that

influence nutrient concentrations at P8. For example, estimated ammonium concentrations in July

were low for all flow levels, which suggests either nitrogen inputs were low in the summer or

nitrogen was available but uptake by primary consumers and bacterial processing were high.

Seasonal patterns in the relationship between flow and nitrite/nitrate were not as dramatic as

compared to ammonium, and in particular, low-flow events in July were associated with higher

concentrations. This could suggest that ammonium concentrations at P8 are driving

phytoplankton production at low flow during warmer months, and not nitrite/nitrate given the

higher estimated concentrations in July at low flow. As such, these simple observations provide

quantitative support of cause and effect mechanisms of nutrient impacts on potentially adverse

environmental conditions as they relate to nutrient-related source controls upstream. Additional

research could investigathese hypotheses to better describe mechanisms of change as a basis for

more informed management.

In addition to the above comments, our results for Suisun Bay provide additional

descriptions of change in production as it relates to flow, grazing, and nitrogen ratios. In general,

our results suggested that diatoms were the dominant genera early in the time series, particularly

in late summer, whereas the spring peak observed in later years represents a shift to an earlier

seasonal maxima. This supports past research that showed a decrease in silica uptake by diatoms

following invasion (Cloern 1996, Kimmerer 2005). Anontrivial portion of the DIN increase could

be related to the decrease in a major 'sink', i.e., decreased DIN uptake by phytoplankton due to

top down grazing pressure from *P. amurensis*. Flow effects on phytoplankton production have

also changed over time. In the absence of benthic grazing prior to invasion, chl-*a* production was

limited at low flow as less nutrients were exported from the Delta, stimulated as flow increases,

and reduced at high flow as either nutrients or phytoplankton biomass are exported to the larger

bay (Fig. 9j). Recent years have shown a decrease in overall chlorophyll, with particularly low

concentrations at low flow (high salinity). As such, chl-*a* production in early years is directly

related to flow, whereas the relationship with flow in later years is indirect as increased flow

reduces clam abundance and releases phytoplankton from benthic grazing pressure. These

relationships have been suggested by others (Cloern et al. 1983, Alpine and Cloern 1992,

Parchaso and Thompson 2002, Jassby 2008), although the precise mechanism demonstrated by

WRTDS provides a quantitative description of factors that drive water quality in the Delta.

## 4.2  Conclusions

As demonstrated by both case studies and the overall trends across all stations, water

quality dynamics in the Delta are complex and driven by multiple factors that change through

space and time. At a minimum, WRTDS provides a description of change by focusing on

high-level forcing factors that explicitly account for annual, seasonal, and flow effects on trend

interpretations. We have demonstrated the potential for imprecise or inaccurate conclusions of

trend tests that focus solely on observed data and emphasize that flow-normalized trends have

more power to quantify change. Moreover, trends in nutrient loads from point sources in the Delta have previously been described, e.g., Sacramento WWTP increases (Jassby 2008) and exports to Suisun Bay (Novick and Senn 2014). The results from WRTDS demonstrating these changes are not unexpected, and consequently, we are not detracting from the potential implications of such increases. The important conclusion is that the physical/hydrological and biogeochemical factors that influence nutrient cycling and ambient concentrations in the Bay-Delta, and changes to those factors, are substantial enough that they can be comparable in magnitude to anthropogenic load increases or comparable to the effects of management actions to decrease nutrient levels. Therefore, methods that adjust for the effects of these factors are critical when studying long-term records to assess the impacts or effectiveness of load increases or management actions, respectively.

Combined with additional data, WRTDS results can support hypotheses that lead to a more comprehensive understanding of ecosystem dynamics. Additional factors to consider include the effects of large-scale climatic patterns, more detailed hydrologic descriptions, and additional ecological components that affect trophic interactions. For example, a more rigorous matching of flow time series with water quality observations at each station that considers varying source contributions over time could provide a more robust description of flow-normalized results. Alternative methods for time series analysis could also be used to address a wider range of questions, particularly those with more generic structural forms that can explicitly include additional variables (e.g., generalized additive models, Beck and Murphy (2017)). Overall, statistical interpretations of multiple factors can provide a basis for quantitative links between nutrient loads and adverse effects on ecosystem conditions, including the identification of thresholds for the protection and restoration of water quality.

# *Acknowledgments*

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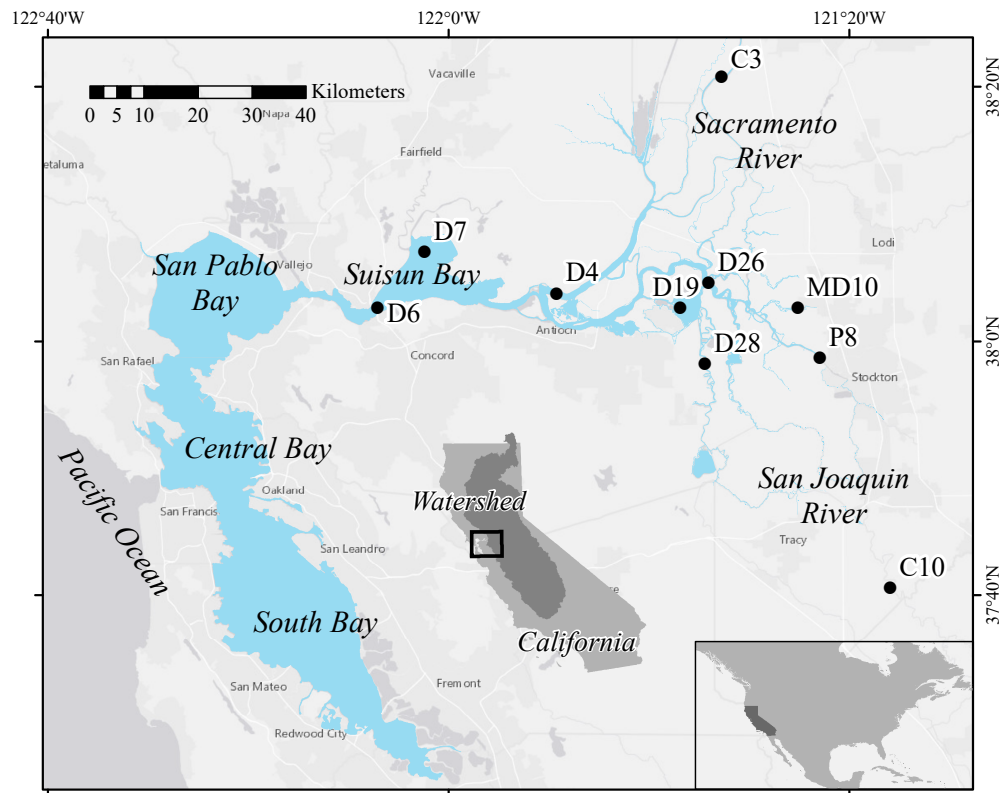
Fig. 1: The San Francisco Estuary and Delta region with monitoring stations used for analysis. The Delta drains the combined watersheds of the Sacramento and San Joaquin rivers (inset). All data were obtained from the Interagency Ecological Program website (http://water.ca.gov/bdma/meta/Discrete/data.cfm, IEP (2013)). See Table 1 for station descriptions.

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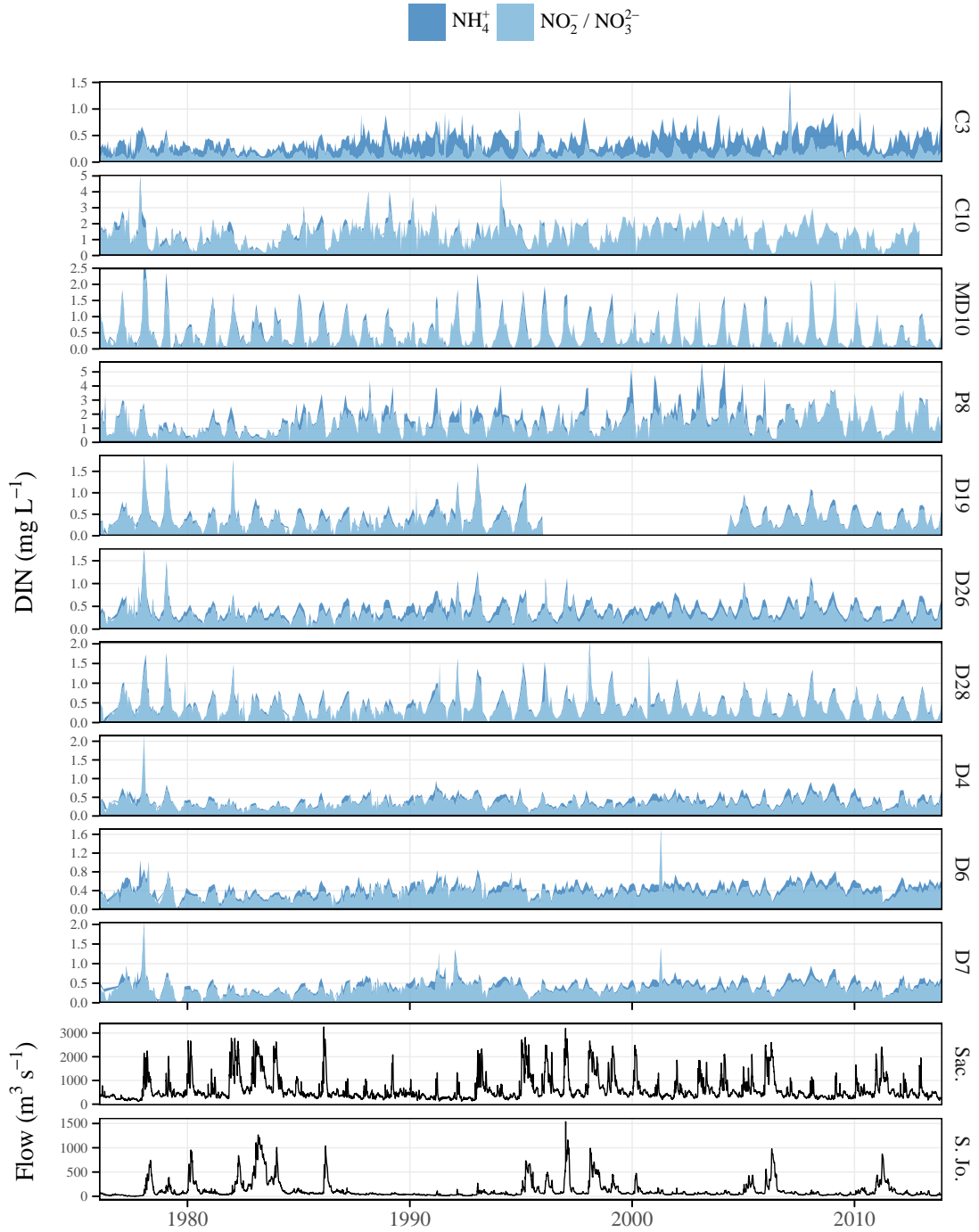
Fig. 2: Observed DIN ($NH_4^+ + NO_2^-/NO_3^{2-}$) from ten stations in the upper SFE Delta and flow from the Sacramento and San Joaquin rivers. Data were collected monthly and evaluated with WRTDS models using daily flow estimates from 1976 to 2013. Note different y-axis scales. See Fig. 1 for station locations.

fig:obsdat

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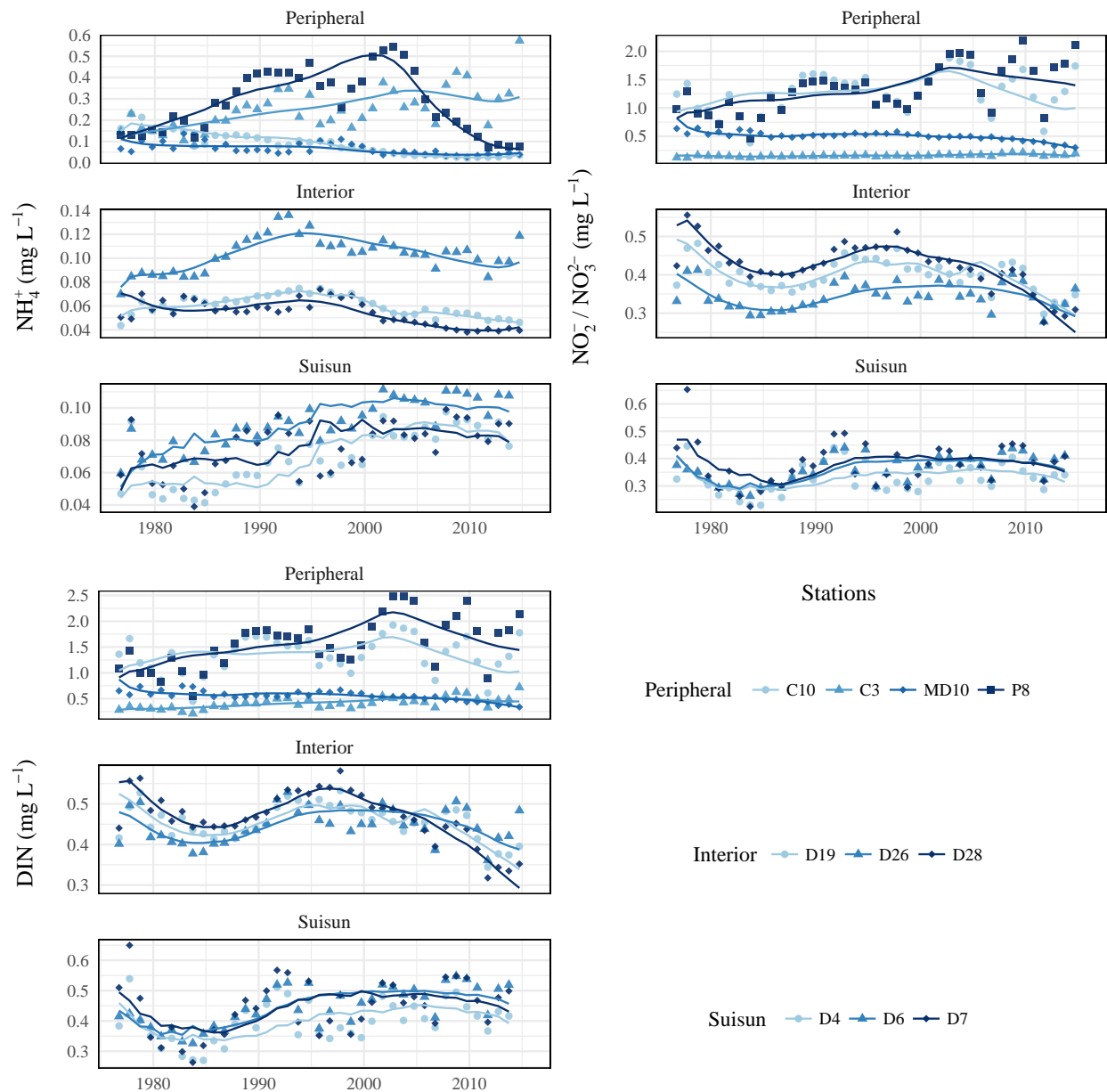
Fig. 3: Model predictions for ten stations grouped by nitrogen analyte and geographic location in the Delta region (locations in Fig. 1). Results are annually-averaged for each water year from October to September. Points are model predictions and lines are flow-normalized predictions.

fig:prddat

Fig. 4: Results from seasonal Kendall tests on observed data (triangles) and flow-normalized predictions (circles) from WRTDS for nitrogen analytes. Results are shown as the percent change per year as the estimated Theil-Sen slope divided by the median for a given aggregation period (significance evaluated at $\alpha = 0.05$, based on $\tau$). Trends are shown separately for different annual groupings. See Figs. 5 and 6 for seasonal groupings.

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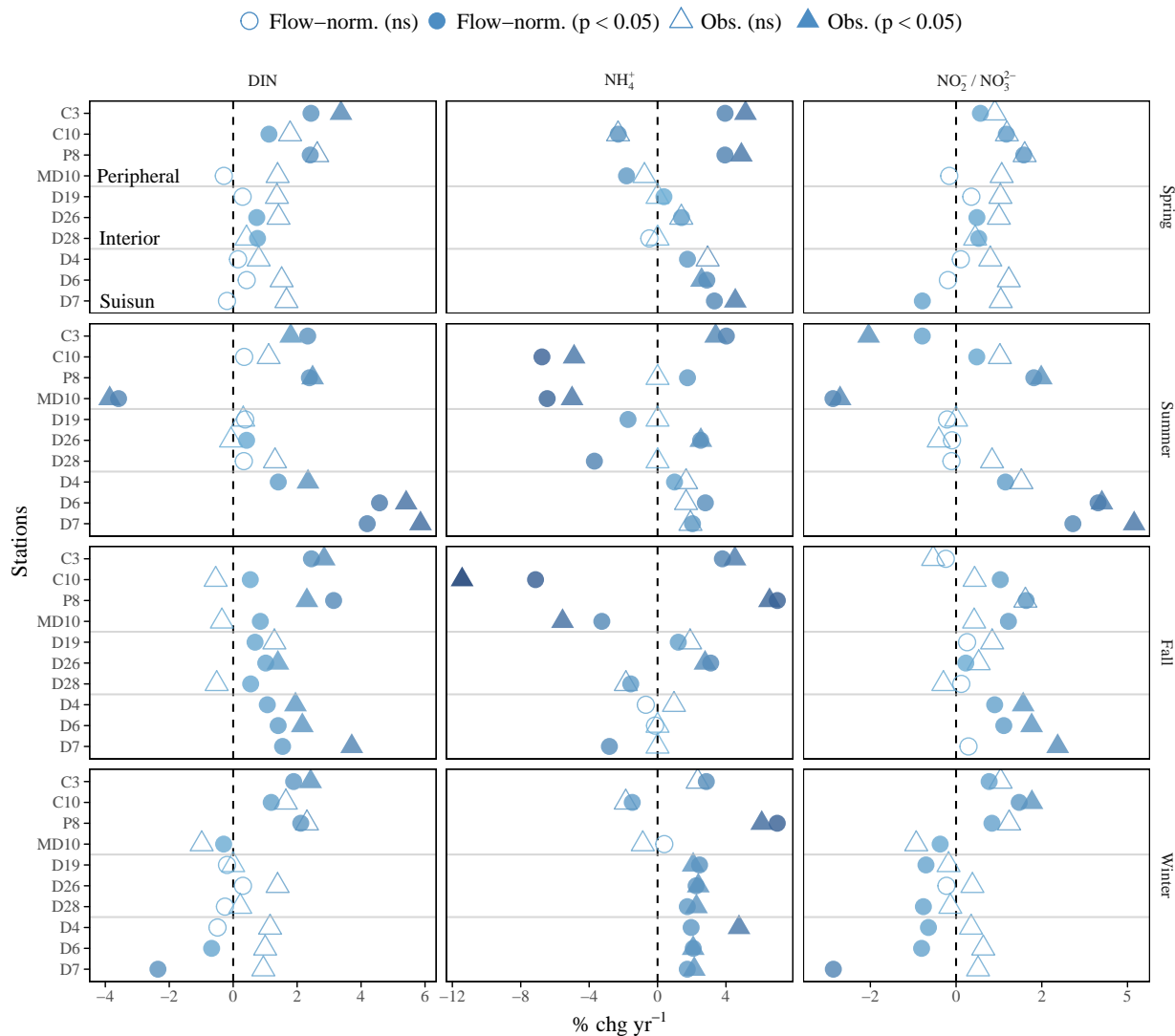
Fig. 5: Results from seasonal Kendall tests on observed data (triangles) and flow-normalized predictions (circles) from WRTDS for nitrogen analytes. Results are shown as the percent change per year as the estimated Theil-Sen slope divided by the median for a given aggregation period (significance evaluated at $\alpha = 0.05$, based on $\tau$). Trends are shown separately for different seasonal groupings from 1976-1995. Months for each season are Spring: MAM, Summer: JJA, Fall: SON, Winter: DJF. See Fig. 4 for annual comparisons.
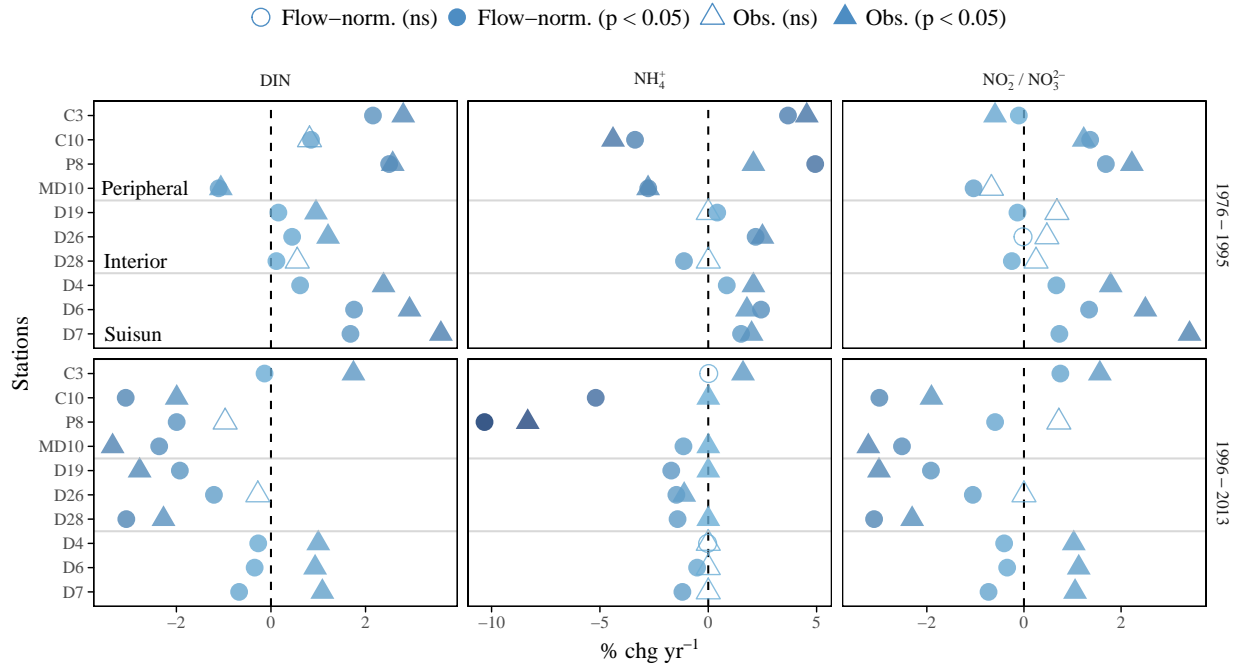
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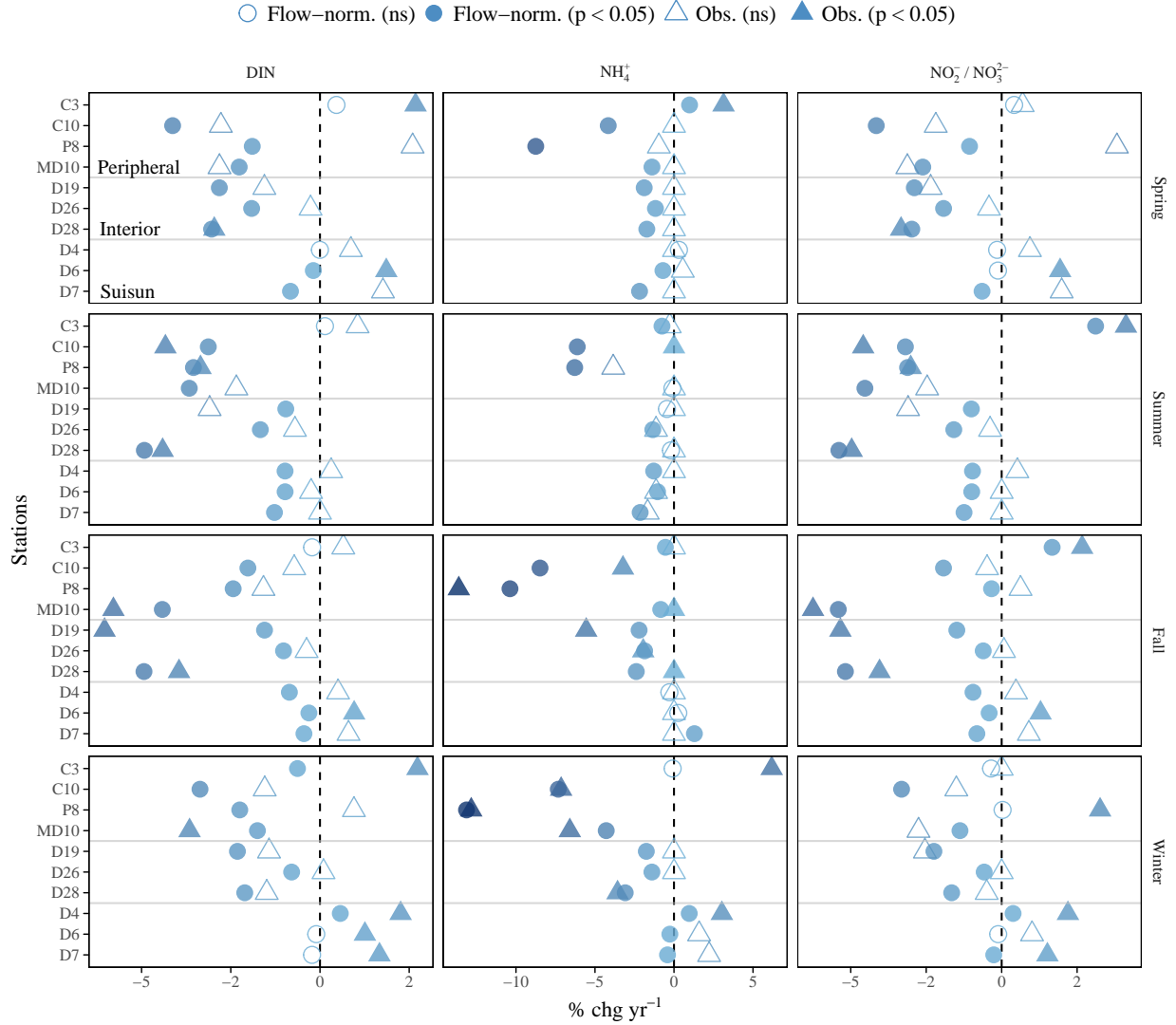
Fig. 6: Results from seasonal Kendall tests on observed data (triangles) and flow-normalized predictions (circles) from WRTDS for nitrogen analytes. Results are shown as the percent change per year as the estimated Theil-Sen slope divided by the median for a given aggregation period (significance evaluated at $\alpha = 0.05$, based on $\tau$). Trends are shown separately for different seasonal groupings from 1996-2013. Months for each season are Spring: MAM, Summer: JJA, Fall: SON, Winter: DJF. See Fig. 4 for annual comparisons.

fig:trndcomp3
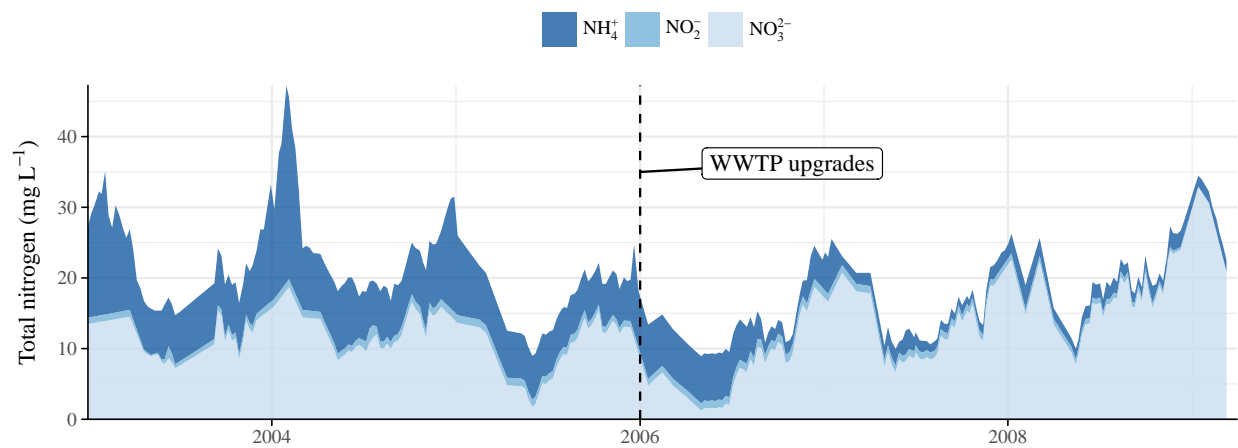
Fig. 7: Nitrogen concentration measurements (mg L$^{-1}$) from the City of Stockton Wastewater Treatment Plant, San Joaquin County. Wastewater discharge requirements were implemented in 2006 for nitrification/denitrification and tertiary filtration to convert ammonium to nitrate. fig:stock
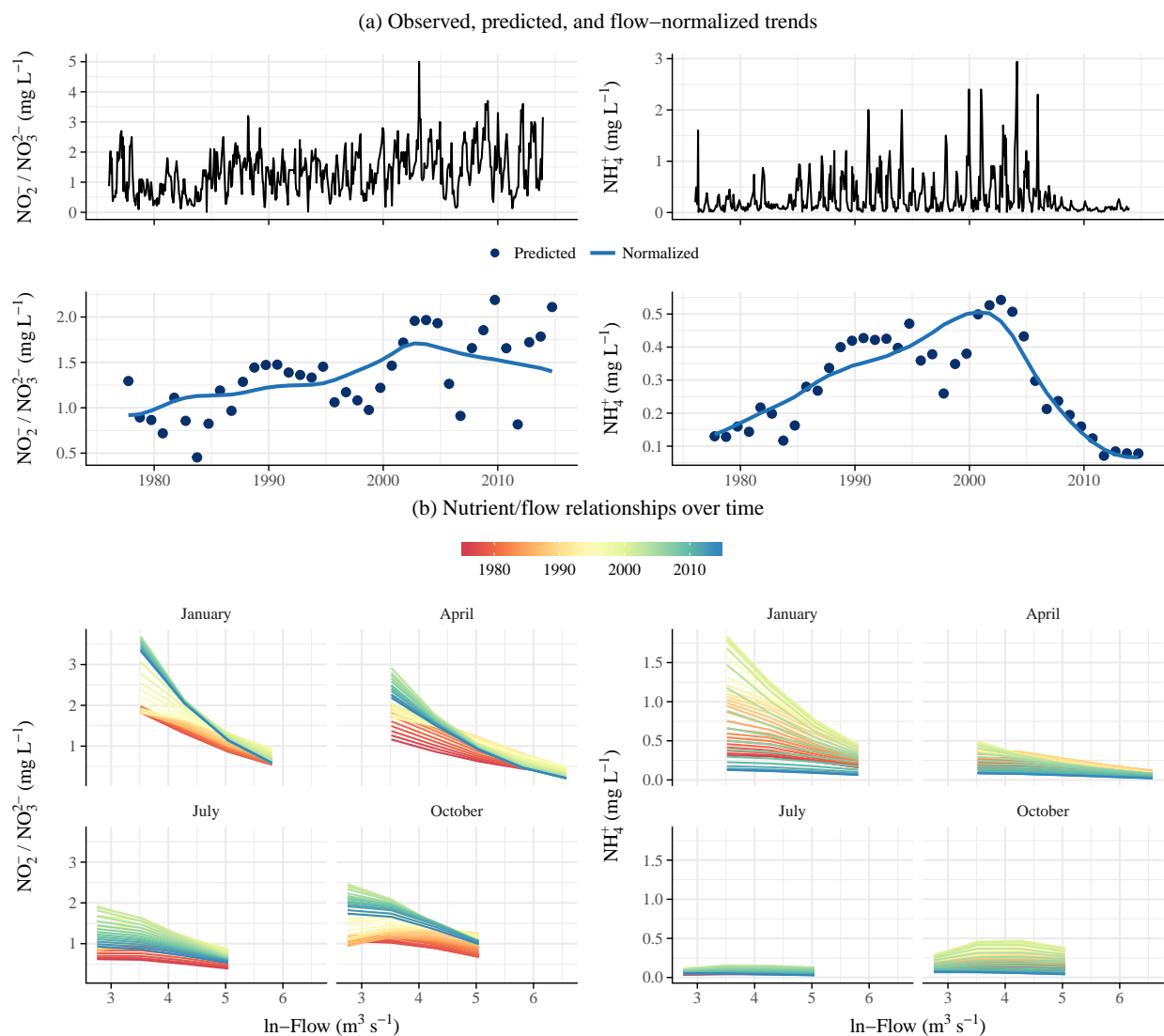
Fig. 8: Nitrogen trends at P8 as (a, top) observed, (a, bottom) predicted and flow-normalized estimates from WRTDS, and (b) relationships with flow over time from WRTDS. Nitrite/nitrate trends are on the left and ammonium trends are on the right. Wastewater treatment plant upgrades at the City of Stockton (San Joaquin County) were completed in 2006 (Fig. 7). `fig:p8trnds`
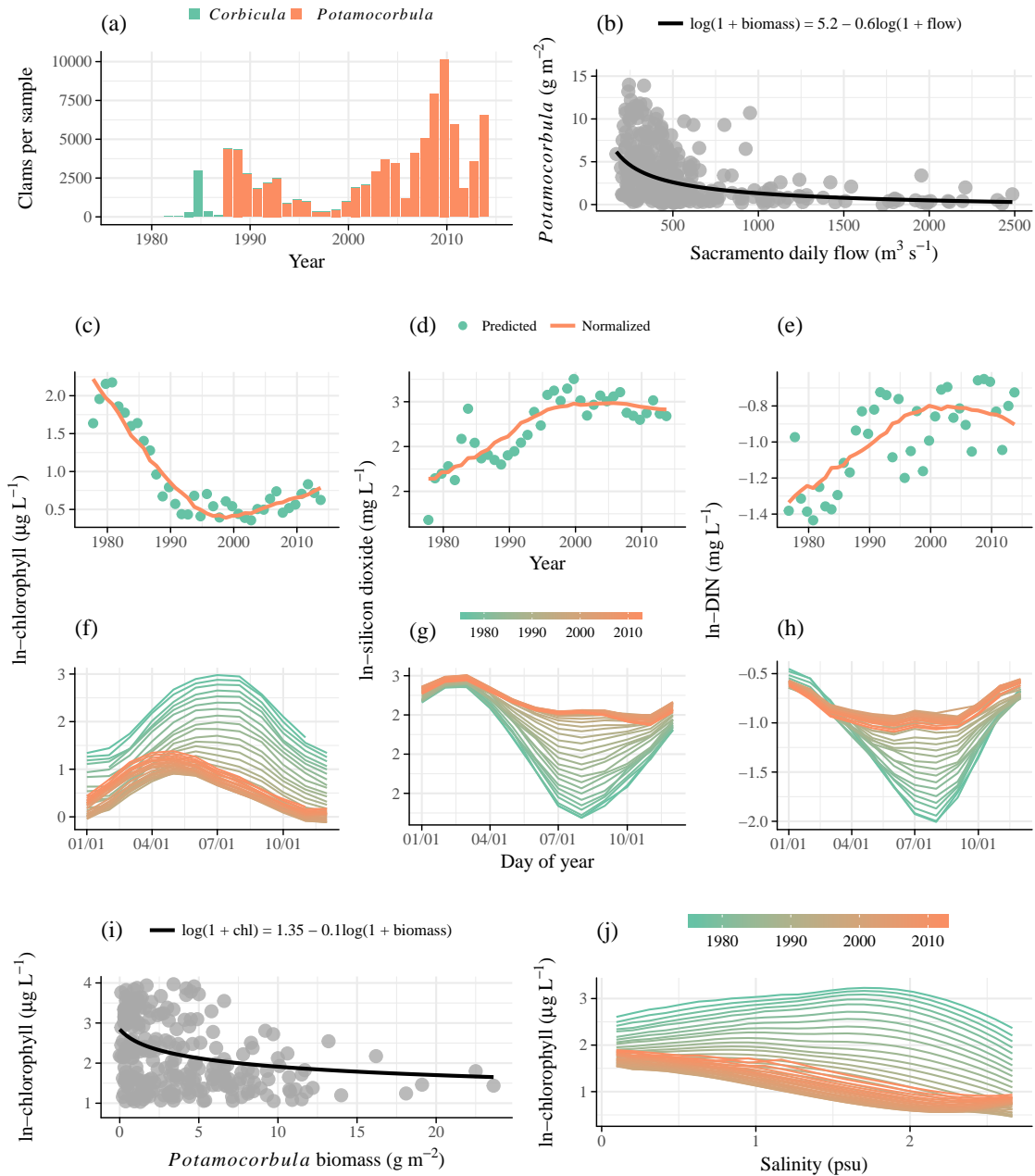
Fig. 9: Trends in clam abundance and chl-*a* concentration from 1976 to 2013 at station D7 in Suisun Bay. Invasion by *Potamocorbula amurensis* clams in the late 1980s and reduction of *Corbicula fluminea* was shown by changes in clam density (a, annual means), with biomass linked to salinity (b). A decrease in chl-*a* concentration was also observed by changes in annual (c) and seasonal trends (f) based on WRTDS results. Reductions in chl-*a* concentration were coincident with an increase in $SiO_2$ and DIN concentrations (d, e), with the greatest increases in August (g, h). A significant ($p < 0.001$) relationship between clam biomass and chl-*a* concentration is shown in subfigure (i). Flow relationships with chl-*a* concentration shown by WRTDS have also changed over time (j, observations from June).

fig:clmchl

Table 1: Monitoring stations in the upper San Francico Estuary used to evaluate nitrogen trends. Records from 1976 to 2013 were evaluated using the total observations ($n$) at each station. Median values are reported in mg L$^{-1}$. tab:stdescrp

| Station | | | DIN | | NH$_4^+$ | | NO$_2^-$/NO$_3^{2-}$ | |
|---|---|---|---|---|---|---|---|---|
| | Lat | Lon | $n$ | Med. | $n$ | Med. | $n$ | Med. |
| **Peripheral** | | | | | | | | |
| C3 | 38.35 | $-121.55$ | 569 | 0.36 | 569 | 0.22 | 571 | 0.13 |
| C10 | 37.68 | $-121.27$ | 539 | 1.44 | 539 | 0.04 | 558 | 1.40 |
| MD10 | 38.04 | $-121.42$ | 548 | 0.31 | 548 | 0.03 | 570 | 0.28 |
| P8 | 37.98 | $-121.38$ | 556 | 1.46 | 556 | 0.12 | 563 | 1.20 |
| **Interior** | | | | | | | | |
| D19 | 38.04 | $-121.61$ | 433 | 0.35 | 435 | 0.04 | 462 | 0.31 |
| D26 | 38.08 | $-121.57$ | 556 | 0.38 | 556 | 0.09 | 565 | 0.29 |
| D28 | 37.97 | $-121.57$ | 529 | 0.38 | 535 | 0.03 | 555 | 0.33 |
| **Suisun** | | | | | | | | |
| D4 | 38.06 | $-121.82$ | 546 | 0.38 | 546 | 0.05 | 565 | 0.32 |
| D6 | 38.04 | $-122.12$ | 534 | 0.45 | 534 | 0.08 | 562 | 0.35 |
| D7 | 38.12 | $-122.04$ | 535 | 0.44 | 535 | 0.06 | 561 | 0.36 |

Table 2: Summaries of flow-normalized trends in nitrogen analytes for all stations and annual aggregations tab:trndsann

| Analyte/Station | Annual | |
|---|---|---|
| | 1976-1995 | 1996-2013 |
| **DIN** | | |
| C10 | 1.3 (**0.8**)* | 1.4 (-3.1)* |
| C3 | 0.3 (**2.2**)* | 0.5 (-0.1)* |
| D19 | 0.4 (**0.2**)* | 0.4 (-1.9)* |
| D26 | 0.4 (**0.4**)* | 0.5 (-1.2)* |
| D28 | 0.4 (**0.1**)* | 0.4 (-3.1)* |
| D4 | 0.3 (**0.6**)* | 0.4 (-0.3)* |
| D6 | 0.4 (**1.8**)* | 0.5 (-0.3)* |
| D7 | 0.4 (**1.7**)* | 0.5 (-0.7)* |
| MD10 | 0.4 (-1.1)* | 0.3 (-2.4)* |
| P8 | 1.3 (**2.5**)* | 1.7 (-2)* |
| **$NH_4^+$** | | |
| C10 | 0.1 (-3.4)* | 0 (-5.2)* |
| C3 | 0.2 (**3.7**)* | 0.3 (**0**) |
| D19 | 0 (**0.4**)* | 0 (-1.7)* |
| D26 | 0.1 (**2.2**)* | 0.1 (-1.5)* |
| D28 | 0 (-1.1)* | 0 (-1.4)* |
| D4 | 0 (**0.9**)* | 0.1 (**0**) |
| D6 | 0.1 (**2.4**)* | 0.1 (-0.5)* |
| D7 | 0.1 (**1.5**)* | 0.1 (-1.2)* |
| MD10 | 0.1 (-2.8)* | 0 (-1.1)* |
| P8 | 0.2 (**4.9**)* | 0.1 (-10.3)* |
| **$NO_2^-/NO_3^{2-}$** | | |
| C10 | 1.2 (**1.4**)* | 1.4 (-3)* |
| C3 | 0.1 (-0.1)* | 0.2 (**0.7**)* |
| D19 | 0.4 (-0.1)* | 0.4 (-1.9)* |
| D26 | 0.3 (**0**) | 0.4 (-1.1)* |
| D28 | 0.4 (-0.2)* | 0.4 (-3.1)* |
| D4 | 0.3 (**0.7**)* | 0.3 (-0.4)* |
| D6 | 0.3 (**1.3**)* | 0.4 (-0.3)* |
| D7 | 0.4 (**0.7**)* | 0.4 (-0.7)* |
| MD10 | 0.4 (-1)* | 0.3 (-2.5)* |
| P8 | 1.2 (**1.7**)* | 1.5 (-0.6)* |

Summaries are medians (mg L$^{-1}$) and percent change per year in parentheses (increasing in bold). Changes and significance estimates are based on seasonal Kendall tests of flow-normalized results within each time period. *$p < 0.05$

Table 3: Summaries of flow-normalized trends in nitrogen analytes for all stations and seasonal aggregations from 1976-1995 tab:trndsbef

| Analyte/Station | Seasonal, 1976-1995 | | | |
|---|---|---|---|---|
| | Spring | Summer | Fall | Winter |
| **DIN** | | | | |
| C10 | 1.2 (**1.1**)* | 1.2 (**0.3**) | 1.3 (**0.5**)* | 1.7 (**1.2**)* |
| C3 | 0.3 (**2.4**)* | 0.3 (**2.3**)* | 0.4 (**2.4**)* | 0.4 (**1.9**)* |
| D19 | 0.5 (**0.3**) | 0.2 (**0.4**) | 0.3 (**0.7**)* | 0.7 (-0.2) |
| D26 | 0.4 (**0.7**)* | 0.3 (**0.4**)* | 0.4 (**1**)* | 0.6 (**0.3**) |
| D28 | 0.5 (**0.8**)* | 0.2 (**0.3**) | 0.3 (**0.5**)* | 0.8 (-0.3) |
| D4 | 0.4 (**0.2**) | 0.3 (**1.4**)* | 0.3 (**1.1**)* | 0.5 (-0.5) |
| D6 | 0.4 (**0.4**) | 0.3 (**4.6**)* | 0.4 (**1.4**)* | 0.5 (-0.7)* |
| D7 | 0.4 (-0.2) | 0.3 (**4.2**)* | 0.4 (**1.5**)* | 0.6 (-2.4)* |
| MD10 | 0.6 (-0.3) | 0.2 (-3.6)* | 0.3 (**0.8**)* | 1.3 (-0.3)* |
| P8 | 1.3 (**2.4**)* | 0.9 (**2.4**)* | 1.3 (**3.1**)* | 1.9 (**2.1**)* |
| **$NH_4^+$** | | | | |
| C10 | 0.1 (-2.3)* | 0 (-6.8)* | 0.1 (-7.1)* | 0.3 (-1.5)* |
| C3 | 0.2 (**3.9**)* | 0.2 (**4**)* | 0.3 (**3.8**)* | 0.2 (**2.9**)* |
| D19 | 0.1 (**0.4**)* | 0 (-1.7)* | 0 (**1.2**)* | 0.1 (**2.5**)* |
| D26 | 0.1 (**1.4**)* | 0.1 (**2.5**)* | 0.1 (**3.1**)* | 0.1 (**2.3**)* |
| D28 | 0.1 (-0.5) | 0 (-3.7)* | 0 (-1.6)* | 0.1 (**1.7**)* |
| D4 | 0.1 (**1.7**)* | 0 (**1**)* | 0 (-0.7) | 0.1 (**2**)* |
| D6 | 0.1 (**2.9**)* | 0.1 (**2.8**)* | 0.1 (-0.1) | 0.1 (**2.1**)* |
| D7 | 0.1 (**3.3**)* | 0 (**2**)* | 0.1 (-2.8)* | 0.1 (**1.7**)* |
| MD10 | 0.1 (-1.8)* | 0 (-6.5)* | 0 (-3.3)* | 0.2 (**0.4**) |
| P8 | 0.2 (**3.9**)* | 0.1 (**1.8**)* | 0.2 (**7**)* | 0.6 (**7**)* |
| **$NO_2^-/NO_3^{2-}$** | | | | |
| C10 | 1.1 (**1.5**)* | 1.2 (**0.6**)* | 1.2 (**1.3**)* | 1.5 (**1.8**)* |
| C3 | 0.2 (**0.7**)* | 0.1 (-1)* | 0.1 (-0.3) | 0.2 (**1**)* |
| D19 | 0.4 (**0.4**) | 0.2 (-0.3) | 0.3 (**0.3**) | 0.6 (-0.9)* |
| D26 | 0.4 (**0.6**)* | 0.2 (-0.1) | 0.3 (**0.3**)* | 0.5 (-0.3) |
| D28 | 0.5 (**0.7**)* | 0.2 (-0.1) | 0.3 (**0.2**) | 0.7 (-1)* |
| D4 | 0.3 (**0.1**) | 0.3 (**1.4**)* | 0.3 (**1.1**)* | 0.4 (-0.8)* |
| D6 | 0.4 (-0.2) | 0.3 (**4.1**)* | 0.3 (**1.4**)* | 0.4 (-1)* |
| D7 | 0.4 (-1)* | 0.3 (**3.4**)* | 0.4 (**0.4**) | 0.4 (-3.6)* |
| MD10 | 0.5 (-0.2) | 0.2 (-3.6)* | 0.2 (**1.5**)* | 1.2 (-0.5)* |
| P8 | 1.2 (**2**)* | 0.9 (**2.3**)* | 1.1 (**2**)* | 1.4 (**1**)* |

Summaries are medians (mg L$^{-1}$) and percent change per year in parentheses (increasing in bold). Changes and significance estimates are based on seasonal Kendall tests of flow-normalized results within each time period. Months for each season are Spring: MAM, Summer: JJA, Fall: SON, Winter: DJF. *$p < 0.05$

Table 4: Summaries of flow-normalized trends in nitrogen analytes for all stations and seasonal aggregations from 1996-2013 tab:trndsaft

| Analyte/Station | Seasonal, 1996-2013 | | | |
|---|---|---|---|---|
| | Spring | Summer | Fall | Winter |
| **DIN** | | | | |
| C10 | 1.1 (-4.1)* | 1.3 (-3.1)* | 1.6 (-2)* | 1.7 (-3.4)* |
| C3 | 0.5 (**0.5**) | 0.4 (**0.1**) | 0.6 (-0.2) | 0.5 (-0.6)* |
| D19 | 0.5 (-2.8)* | 0.2 (-1)* | 0.3 (-1.6)* | 0.7 (-2.3)* |
| D26 | 0.5 (-1.9)* | 0.3 (-1.7)* | 0.4 (-1)* | 0.6 (-0.8)* |
| D28 | 0.5 (-3)* | 0.2 (-4.9)* | 0.2 (-4.9)* | 0.7 (-2.1)* |
| D4 | 0.4 (**0**) | 0.4 (-1)* | 0.4 (-0.9)* | 0.5 (**0.6**)* |
| D6 | 0.5 (-0.2)* | 0.5 (-1)* | 0.5 (-0.3)* | 0.5 (-0.1) |
| D7 | 0.5 (-0.8)* | 0.4 (-1.3)* | 0.4 (-0.4)* | 0.6 (-0.2) |
| MD10 | 0.4 (-2.3)* | 0.2 (-3.7)* | 0.2 (-4.4)* | 1 (-1.8)* |
| P8 | 1.5 (-1.9)* | 1.2 (-3.5)* | 1.8 (-2.4)* | 2.7 (-2.2)* |
| **$NH_4^+$** | | | | |
| C10 | 0 (-4.2)* | 0 (-6.1)* | 0 (-8.5)* | 0.1 (-7.3)* |
| C3 | 0.3 (**1**)* | 0.3 (-0.8)* | 0.4 (-0.5)* | 0.2 (-0.1) |
| D19 | 0 (-1.9)* | 0 (-0.4) | 0 (-2.2)* | 0.1 (-1.8)* |
| D26 | 0.1 (-1.2)* | 0.1 (-1.3)* | 0.1 (-1.9)* | 0.1 (-1.4)* |
| D28 | 0 (-1.7)* | 0 (-0.2) | 0 (-2.4)* | 0.1 (-3.1)* |
| D4 | 0.1 (**0.3**) | 0 (-1.3)* | 0.1 (-0.3) | 0.1 (**1**)* |
| D6 | 0.1 (-0.7)* | 0.1 (-1)* | 0.1 (**0.3**) | 0.1 (-0.3)* |
| D7 | 0.1 (-2.2)* | 0 (-2.1)* | 0.1 (**1.3**)* | 0.1 (-0.4)* |
| MD10 | 0 (-1.4)* | 0 (-0.1) | 0 (-0.8)* | 0.1 (-4.3)* |
| P8 | 0.2 (-8.7)* | 0.1 (-6.3)* | 0.2 (-10.4)* | 0.5 (-13.1)* |
| **$NO_2^-/NO_3^{2-}$** | | | | |
| C10 | 1.1 (-4.2)* | 1.2 (-3.2)* | 1.6 (-1.9)* | 1.6 (-3.3)* |
| C3 | 0.2 (**0.4**) | 0.1 (**3.1**)* | 0.2 (**1.7**)* | 0.2 (-0.4) |
| D19 | 0.4 (-2.9)* | 0.2 (-1)* | 0.3 (-1.5)* | 0.6 (-2.2)* |
| D26 | 0.4 (-1.9)* | 0.2 (-1.6)* | 0.3 (-0.6)* | 0.5 (-0.6)* |
| D28 | 0.5 (-3)* | 0.2 (-5.4)* | 0.2 (-5.2)* | 0.7 (-1.7)* |
| D4 | 0.3 (-0.1) | 0.3 (-1)* | 0.3 (-1)* | 0.4 (**0.4**)* |
| D6 | 0.4 (-0.1) | 0.4 (-1)* | 0.4 (-0.4)* | 0.4 (-0.1) |
| D7 | 0.4 (-0.6)* | 0.4 (-1.2)* | 0.4 (-0.8)* | 0.4 (-0.3)* |
| MD10 | 0.4 (-2.6)* | 0.1 (-4.5)* | 0.2 (-5.4)* | 1 (-1.4)* |
| P8 | 1.3 (-1.1)* | 1.1 (-3.1)* | 1.6 (-0.3)* | 2.2 (**0**) |

Summaries are medians (mg L$^{-1}$) and percent change per year in parentheses (increasing in bold). Changes and significance estimates are based on seasonal Kendall tests of flow-normalized results within each time period. Months for each season are Spring: MAM, Summer: JJA, Fall: SON, Winter: DJF. *$p < 0.05$

Table 5: Summaries of flow-normalized trends in nitrite/nitrate and ammonium (mg $L^{-1}$) concentrations before and after WWTP upgrades upstream of station P8 tab:p8chg

| Period | $NO_2^-/NO_3^{2-}$ | | $NH_4^+$ | |
|---|---|---|---|---|
| | Median | % change | Median | % change |
| **Annual** | | | | |
| 1976-2006 | 1.3 | **2**\* | 0.2 | **2.8**\* |
| 2007-2013 | 1.4 | -1.9\* | 0.1 | -16.6\* |
| **Seasonal, pre** | | | | |
| Spring | 1.2 | **1.6**\* | 0.2 | **1.4**\* |
| Summer | 1 | **2.4**\* | 0.1 | **3.3**\* |
| Fall | 1.3 | **2.2**\* | 0.2 | **4.9**\* |
| Winter | 1.5 | **2.1**\* | 0.7 | **4.8**\* |
| **Seasonal, post** | | | | |
| Spring | 1.3 | -1.6\* | 0.1 | -16.2\* |
| Summer | 0.9 | -4.3\* | 0.1 | -15.7\* |
| Fall | 1.5 | -1.7\* | 0.1 | -19.3\* |
| Winter | 2.2 | -0.8\* | 0.2 | -26.7\* |

Upgrades were completed in 2006 at the City of Stockton WWTP (San Joaquin County, Fig. 7). Summaries are medians and percent change per year in parentheses (increasing in bold). Changes and significance estimates are based on seasonal Kendall tests of flow-normalized results within each time period. Increasing values are in bold-italics. Months for each season are Spring: MAM, Summer: JJA, Fall: SON, Winter: DJF. \*$p < 0.05$