Four decades of water quality change in the upper San Francisco Estuary[†]

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Abstract

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Recent methods for trend analysis have been developed that leverage the descriptive potential of long-term time series. Combined with these methods, multi-decadal datasets of water quality in coastal systems can provide valuable opportunities to gain insights into ecosystem properties and drivers of change. This study describes use of an estuarine adaptation of the Weighted Regressions on Time, Discharge, and Season (WRTDS) model to describe water quality trends over four decades in the Delta region of the San Francisco Estuary (SFE). This region is a complex mosaic of inflows that are primary sources of nutrients into the larger Bay. To date, a comprehensive evaluation of flow-normalized trends using the long-term monitoring dataset at multiple stations in the Delta has not been conducted despite the importance of nutrient transport from the region for water quality in the entire bay. The WRTDS technique is data-driven

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where the parameterization of the functional model changes smoothly over time following dynamic patterns of season and flow. Water quality trends that have not been previously quantified can be described, including variation in flow-normalized concentrations, frequency occurrence of extreme events, and response to historical changes in the watershed, all of which are important needs for understanding changes in the SFE. Model results from multiple stations in the Delta provided novel descriptions of historical trends and relationships between key species of dissolved inorganic nitrogen (ammonium, nitrate/nitrite, total). This variation was described in the context of varying contributions of input flows from the Sacramento and San Joaquin rivers, as well as tidal exchange with the central SFE. Conceptual relationships between water quality and drivers of change were used to generate and test hypotheses of mechanistic relationships using selected examples from the trend descriptions. Overall, this analysis provides an ecological and management-based understanding of historical trends in the SFE as a means to interpret potential impacts of recent changes and expected trends in this dynamic system. An argument is also made for more comprehensive evaluations of long-term monitoring datasets to understand relationships between response endpoints and causal mechanisms in coastal waters.

30 1 Introduction

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Trend analysis is a broad discipline that has been applied to time series for the interpretation of environmentally-relevant changes. Direct evaluation of an observed time series is often insufficient given that a long-term change can be masked by variation at shorter time scales or the observed variation represents the combined effects of many variables. ^{1,2} Climate, local, regional, and historical effects may act individually or together to impose a change on time series, such that methods that account for variation at different scales have been used for trend analysis. ³⁻⁶ As a practical approach for water quality evaluation, trend analysis of eutrophication endpoints often focuses on tracking the change in concentrations or loads of

nutrients over many years. Indicators of eutrophication can vary naturally with variation in flow conditions and may also reflect long-term effects of management or policy changes. 40 For example, chlorophyll a (chl-a) concentration as a measure of phytoplankton response 41 to nutrient inputs can follow seasonal patterns with cyclical variation in temperature and 42 light changes throughout each year, whereas annual trends can follow long-term variation 43 in nutrient inputs to the system.^{7,8} Similarly, nutrient trends that vary with hydrologic loading also vary as a function of utilization rates by primary producers or decomposition 45 processes. 9-11 Time series analysis of water quality indicators must simultaneously consider effects of processes at multiple scales and interactions between variables of interest to develop 47 a more comprehensive description of system change.

Appropriate methods for the analysis of change depend largely on the question of inter-49 est and on characteristics of the environmental dataset. Trend analyses for aquatic systems have traditionally focused on comparisons between discrete periods of time to estimate a direction and magnitude of a trend using non-parametric tests. 12,13 Development of these conventional approaches addressed limitations in historical monitoring datasets related to infrequent sampling and relatively few years of continuous data. Increased availability of multi-decadal datasets, particularly for high profile environments, has accelerated recent development of trend analysis methods that leverage the descriptive potential of long-term time series from continuous monitoring programs. 6,14 These methods are often data-driven where the parameterization of a simple functional model can change smoothly over time given that relationships between water quality variables and potential drivers are dynamic. 59 The Weighted Regressions on Time, Discharge, and Season (WRTDS) approach was developed under this context and has been used to characterize decadal trends in running-water 61 systems. 15-19 This method has the potential to provide a spatially and temporally robust 62 description of trends by fitting a dynamic model with parameters that change relative to the domain of interest. More recently, the WRTDS method was adapted for trend analysis in tidal waters, with a focus on chl-a trends in Tampa Bay²⁰ and the Patuxent River Estuary, ²¹

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and tidally-infleunced time series of dissolved oxygen from continuous sonde measurements.²²
These studies have demonstrated potential for the use WRTDS for trend analysis in tidal
waters and further application to alternative datasets could provide additional insight into
drivers of change in aquatic systems.

{acro:sfe}

The San Francisco Estuary (SFE) on the Pacific Coast of the United States is one of the 70 most prominent and culturally significant estuaries in the western hemisphere. 23 Background 71 nutrient concentrations in the Bay often exceed those associated with excessive primary 72 production, although eutrophication events have historically been infrequent. Recent changes 73 in response to additional stressors (e.g., variation in freshwater inputs/withdrawals, invasive species, climate change) suggests that Bay condition has not followed past trajectories and more subtle spatial and temporal variation could provide clues that describe underlying 76 properties of this system.²⁴ The unique ecological and social context of the Bay provides a 77 valuable opportunity to gain insight into ecosystem properties of estuaries that define water quality dynamics at different scales. The Delta region of SFE in particular is a mosaic of inflows that receives and processes inputs from the larger watershed to the lower Bay. $^{25-27}$ A 80 comprehensive monitoring dataset has been collected at several fixed locations in the Delta 81 for the last four decades.²⁸ Morever, nutrient dynamics in the Delta are inherently linked to flow variation from inputs, withdrawal, impoundments, and downstream transport, ²⁹ suggesting an approach that explicitly considers flow effects is critical for trend analysis. To date, the Delta monitoring dataset is an under-utitilized data source and a comprehensive analysis with WRTDS could facilitate an understanding of historical and recent changes in SFE water quality. 87

The goal of this study was to provide a comprehensive description of nutrient trends in
the Delta to inform understanding of eutrophication dynamics and potential causes of water
quality change in the larger Bay. We applied the newly-adapted method of weighted regression for tidal waters to describe nitrogen trends in different spatial and temporal contexts.
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, 2) provide detailed descriptions of two case studies in the 94 context of conceptual relationships modelled with WRTDS. The second objective evaluated two specific water quality stations in the Delta to demonstrate complexities with nutrient 96 response to flow, effects of wastewater treatment plant (WWTP) upgrades on water quality, 97 and effects of biological invasion by benthic filter feeders on primary production. Although 98 quantitative descriptions of change can be ends in themselves, the results were expected 99 to have greater impact as a means to more detailed understanding of ecosystem proper-100 ties. Products derived from WRTDS can be used to inform additional analyses, such as 101 water quality response after removing annual, seasonal, or flow effects. Overall, this analysis 102 is expected to further an ecological and management-based understanding of dynamics in 103 San Francisco Bay, with implications for water quality restoration and protection of this 104 prominent system. 105

{acro:wwtp}

¹⁰⁶ 2 Materials and Methods

¹⁰⁷ 2.1 Study system

The SFE drains a 200 thousand km² watershed and is the largest bay on the Pacific coast of 108 North America. The watershed provides drinking water to over 25 million people, including irrigation for 18 thousand km² of agricultural land in the Central Valley. Water enters the Bay through the Sacramento and San Joaquin rivers that have a combined inflow of 111 approximately 28 km³ per year, with the Sacramento accounting for 84% of inflow to the 112 Delta. The SFE system is divided into several sub-bays, including Suisun Bay immediately 113 downstream of the Delta, San Pablo Bay to the north, South Bay, and the Central Bay 114 that drains to the Pacific Ocean through the Golden Gate. Water dynamics in SFE are 115 governed by inflows from the watershed, tidal exchange with the Pacific Ocean, and water 116 withdrawals for municipal and agricultural use.²⁵ Seasonally, inflows into SFE peak in the 117

spring and early summer from snowmelt in the upper watershed, whereas consumption, withdrawals, and export have steadily increased from 1960 to present but vary considerably 119 depending on inter-annual climate effects.²⁴ The system is mixed mesotidal and significant 120 exchange with the ocean occurs daily, although the extent of landward saltwater intrusion 121 varies with inflow and annual water use patterns. Notable drought periods have occurred 122 from 1976-1977, 1987-1992, and recently from 2013-2015. 23 Oceanic upwelling and climatic 123 variation are also significant external factors that have influenced water quality dynamics in 124 the Bay. 30 125

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Nutrient loading in SFE is comparable to other large estuaries that exhibit symptomatic effects of cultural eutrophication (e.g., Chesapeake Bay). 31 Orthophosphate (PO $_4^{3-}$) and 127 dissolved inorganic nitrogen (DIN) enter the Bay primarily through riverine sources in the 128 north and municipal WWTP inputs in the densely-populated area immediately surrounding 129 SFE. Annual nutrient export from the Delta region has been estimated as approximatelly 30 130 thousand kg d⁻¹ of total nitrogen (varying with flow²⁹), with 90% of ammonium (NH₄⁺) orig-131 inating solely from the Sacramento Regional WWTP.²⁷ Although nitrogen and phosphorus 132 inputs are considerable, primary production is relatively low and not nutrient-limited. 26,32 133 The resistance of SFE to the negative effects of eutrophication has historically been attributed to the unique physical and biological characteristics of the Bay, including strong tidal mixing that limits stratification 7,33 and limits on phytoplankton growth from high turbidity and filter-feeding by bivalve mollusks. 33,34 However, recent water quality trends have 137 suggested that resistence of the system to nutrient inputs is decreasing given documented 138 changes in chlorophyll biomass, ³⁰ increased occurrence of hypoxic conditions, ³⁵ and increased 139 abundance of phytoplankton species associated with harmful algal blooms. 36,37 These recent 140 changes have been attributed to variation in global sea surface temperatures associated with 141 climate change, 30 biological invasions, 38 and departures from the historical flow record. 24,39 142 The role of nutrients in stimulating primary production in SFE has been the focus of several 143 recent investigations. 40-42

{acro:din}

The Delta region is of particular interest for understanding historical patterns and po-145 tential trajectories of water quality response to nutrient inputs into the Bay (Figure 1). The 146 Delta is a mosaic of linked channels or tracts that receive, process, and transport inflows 147 from the Sacramento and San Joaquin rivers. 25,27,29 Quantitative descriptions of nutrient 148 dynamics in the Delta are challenging given many nutrients sources and the volume of water 149 that is exchanged through the system with natural and anthropogenic processes. A com-150 prehensive evaluation using mass-balance models to describe nutrient dynamics in the Delta 151 demonstrated that nitrogen enters the system in different forms and is processed at differ-152 ent rates before export or removal.²⁹ For example, a majority of ammonium entering the 153 system during the summer is nitrified or assimilated, whereas a considerable percentage of 154 total nitrogen load to the Delta is lost. Although, the focus of our analysis is not to quan-155 tify sources or sinks of nitrogen species, a quantitative evaluation of long-term trends will 156 provide a more comprehensive historical interpretation to hypothesize the effects of future 157 changes in the context of known dynamics. Nutrients in the Delta also vary with seasonal 158 and annual changes in the delivery of water inflows, including water exports directly from the 159 system. 25,27 Our analysis also explicitly accounts for the effects of flow changes on nutrient 160 response to better understand variation both within the Delta and potential mechanisms of downstream transport.

163 2.2 Data sources

Multi-decadal time series of nutrients and flow records were used to develop a quantitative description of nitrogen trends in the Delta. The Interagency Ecological Program (IEP) is a consortium of state and federal agencies that have maintained the Environmental Monitoring Program (EMP) in the Delta region since 1975. ⁴³ The EMP collects monthly water quality samples at 19 stations in the Delta, Suisun Bay, and northeastern San Pablo Bay. Water samples were collected using a Van Dorn sample, a submersible pump, or a flow through system depending on site. All samples were processed with standard QA/QC at the California

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Department of Water Resources Bryte Laboratory in Sacramento. 43 Nutrient time series were obtained from the IEP website (http://water.ca.gov/bdma/meta/Discrete/data.cfm) at ten discrete sampling stations from 1976 through 2013 (Figure 1). Stations were grouped 173 by location in the study area for comparison: Delta stations C3 (Sacramento inflow), C10 174 (San Joaquin inflow), MD10, P8; middle stations D19, D26, D28; and Suisun stations D4, 175 D6, and D7. These stations were chosen based on continuity of the water quality time series 176 and geographic location for understanding trends. Time series were complete for all stations 177 except for an approximate ten year gap from 1996-2014 for D19. Data were minimally pro-178 cessed with the exception of averaging replicates that occurred on the same day. The three 179 nitrogen analytes that were evaluated were ammonium, nitrite/nitrate, and DIN (as the sum 180 of the former two). Less than 3% of all observations were left-censored, although variation 181 was observed between analytes and location. The most censored observations were observed 182 for ammonium time series at sites C10 (25.4%), MD10 (18.1%), D28 (17.8%), D19 (12%), 183 and D7 (7.9%). 184

Daily flow estimates for the Delta region were obtained from the Dayflow software pro-185 gram that provides estimates of average Delta outflow. 44 Because of the complexity of water 186 inflow, exports, and outflows from the Delta, the Dayflow program combines observations 187 with estimates based on mass balance to reconstruct historical and daily flow estimates. The WRTDS models described below require a matched flow record with the appropriate 189 station to evaluate nutrient trends. Given the complexity of inflows and connectivity of the 190 system, only the inflow estimates from the Sacramento and San Joaquin rivers were used as 191 measures of freshwater influence at each station. Initial analyses indicated that model fit 192 was not significantly improved with flow estimates from locations closer to each station, nor 193 was model fit improved using lagged times series. As such, the Sacramento daily flow time 194 series was used to account for flow effects at C3, D19, D26, D28, and MD10, and the San 195 Joaquin time series was used for C10 and P8. The salinity observations at D4, D6, and D7 196 in Suisun Bay were used as a more appropriate measure of variation in freshwater balance 197

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.²⁰

200 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 15 that models the log-transformed response variable as a function of time, flow, and season:

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

where N is one of three nitrogen analytes, time t is a continuous variable as decimal time to capture the annual or seasonal trend, and Q is the flow variable (either flow or salinity 205 depending on station). The seasonal trend is modelled as a sinusoidal component to capture 206 periodicity between years. The WRTDS model is a moving window regression that fits 207 a unique set of parameters at each observation point in the time series. A unique set of 208 weights is used for each regression to control the relevance of observations used to fit the 209 model to the observation at the center of the window. The weights are based on a scaled 210 Euclidean distance to estimate the differences of all points from the center in relation to 211 annual time, season, and flow. The final vector used to fit the model at each point weights 212 observations more similar to the center of the window with more importance. The complete 213 model for the time series contains a parameter set for every time step that considers the 214 unique context of the data. As such, predictions from WRTDS are more precise than those 215 from more conventional models that fit a single parameter set to the entire time series. 20,45 216 The WRTDS model applied to the Delta time series was based on a tidal adaptation of the 217 original method.²⁰ The WRTDS models were fit to describe the conditional mean response 218 using a weighted Tobit model for left-censored data. 46 Previous adaptations of WRTDS to 219 tidal waters have used quantile regression to describe trends in the conditional quantiles, 220

such as changes in the frequency of occurrence of extreme events. The application to the
Delta data focused only on the conditional mean models to establish a baseline response
which has not been previously quantified. All analyses used the WRTDStidal package for
R. 47,48

A hallmark of the WRTDS approach is the description of flow-normalized trends that 225 are independent of variation from freshwater inflows. Flow-normalized trends have value for 226 the interpretation of changes that are potentially caused by drivers other than flow, such as 227 WWTP upgrades or phytoplankton grazing by benthic filter-feeders.²⁰ Although variation 228 in nutrients is caused by the combined effects of several variables acting at different temporal 229 and spatial scales, flow-normalization provides a basis for further exploration by removing a 230 critical confounding variable that could affect the interpretation of trends. A flow-normalized 231 value is the average of predictions at a given observation using all flow values that are ex-232 pected to occur for the relevant month across years in the record. Flow-normalized trends for 233 each analyte at each station were used to describe long-term changes in different annual and 234 seasonal periods. Specifically, flow-normalized trends in each analyte were summarized as 235 both medians and percent changes from the beginning to end of annual groupings from 1976-236 1995 and 1996-2013, and seasonal groupings of March-April-May (spring), June-July-August 237 (summer), September-October-November (fall), and December-January-February (winter) 238 within each annual grouping. These annual and seasonal groupings were chosen for conti-239 nuity with similar comparisons reported in Ref. 28 and as approximate twenty year midway 240 points in the time series. 241

Trends within 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. 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. ²⁷ Trends within annual groupings were based on all monthly observations within relevant years, whereas seasonal groupings were based only on the relevant months across years. Seasonal Kendall tests were also used to describe trends in the model predictions for the observed data. These trends were compared with those based on the flow-normalized trends to evaluate the improved ability of WRTDS to describe trends that are independent of flow. Functions in the EnvStats package in R were used for the seasonal Kendall tests. ⁵⁰

255 3 Results and Discussion

256 3.1 Observed Data

The observed time series for the ten Delta stations had substantial variation in scale among 257 the nitrogen analytes and differences in apparent seasonal trends (Figure 2). In general, long-258 term (inter-annual) trends were not easily observed from the raw data. DIN for most stations 259 was dominated by nitrite/nitrate, whereas ammonium was a smaller percentage of the total. 260 However, C3 had a majority of DIN composed of ammonium and other stations (e.g., P8, 26: D16) had higher concentrations of ammonium during winter months when phytoplankton 262 assimilation is lower.²⁹ By location, observed concentrations of DIN for the entire time 263 series were higher on average for the upper Delta stations (C3, C10, MD10, P8; maximum likelihood estimation of mean \pm standard error: 1.04 ± 0.03 mg L⁻¹) and similar for the 265 middle (D19, D26, D28, 0.43 ± 0.01) and Suisuan Bay stations (D4, D6, D7, 0.44 ± 0.01). 266 Average concentrations were highest at P8 $(1.63\pm0.05 \text{ mg L}^{-1})$ and lowest at C3 (0.4 ± 0.01) 267 for DIN, highest at P8 (0.28 ± 0.02) and lowest at D28 (0.05 ± 0.003) for ammonium, and 268 highest at C10 (1.4 \pm 0.04) and lowest at C3 (0.15 \pm 0.004) for nitrite/nitrate. Mean observed 269 concentrations were also higher later in the time series for all analytes. For example, average 270 DIN across all stations was $0.61\pm0.01~\mathrm{mg}~\mathrm{L}^{-1}$ for 1976-1995, compared to 0.7 ± 0.01 for 1996-271 2013. Seasonal changes across all years also suggested that nitrogen concentrations were 272

lower in the summer and higher in the winter. However, observed seasonality 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 variation between years (D6, D7, Figure 2).

$_{277}$ 3.2 Trends

Application of seasonal Kendall tests to evaluate trends in observed data provided explicit information on the direction, magnitude, and statistical significance of changes between years. 279 Trends estimated from the observed data for 1976-1995 and 1996-2013 varied considerably 280 between sites and analytes (Figure 3). Significant trends were observed from 1976-1995 for 281 eight of ten sites for DIN (seven increasing, one decreasing), eight sites for ammonium (six increasing, two decreasing), and six sites for nitrite/nitrate (five increasing, one decreasing). More sites had decreasing trends for the observed data from 1996-2013. Eight sites had 284 significant trends for DIN (four increasing, four decreasing), seven sites for ammonium (five 285 increasing, two decreasing), and eight sites for nitrite/nitrate (four increasing, four decreas-286 ing). Trends by location (upper Delta, middle, and Suisun stations) were not apparent, 287 suggesting individual sites had trends that differed independent of relative location. For 288 example, P8 had a relatively large decrease in ammonium (-8.3%) change per year) for the 289 second annual period compared to all other sites. Trends by season were similar such that 290 increases were generally observed in all seasons from 1976-1995 (Figure S1) and decreases 291 were observed for 1996-2013 (Figure S2). Trends for the seasonal comparisons were noisier 292 and significant changes were less common compared to the annual comparisons. 293

Relationships between flow and observed water quality are complex and can change significantly through space and time. ^{15,19} These principles have been demonstrated for monitoring
data in the Delta region, ^{27–29} suggesting that trend analyses using the observed time series
are confounded by flow effects. Change over for time in observed data could reflect mobilization or dilution effects of flow on concentration rather than an interpretable system

response to changes in nutrient sources. As a proof of concept, Figure 4 demonstrates use of WRTDS to isolate a flow-normalized time series from the observed DIN data at C10. 300 Raw data are presented in Figure 4a and the annual results by water year (October through 301 September) from WRTDS are shown in Figure 4b. In addition to removing the seasonal 302 component, Figure 4b shows the flow-normalized component (solid line) independent of the 303 model predictions. The difference between the two is shown in Figure 4c such that years with 304 predictions greater or less than the flow-normalized values correspond with long-term trends 305 in flow shown in Figure 4d. For example, 1984 is a period of high flow and a large, negative 306 difference between prediction and flow-normalized concentration, suggesting a dilution effect 307 of increased flow on nutrient concentration. Further, Figure 4e shows seasonal variation in 308 the relationships of DIN with flow throughout the period of record. Increases in flow (y-axis) 309 were associated with an increase in DIN (colors) for flow values within the observed range. 310 Seasonal patterns also differed througout the time period with a wider range of DIN within 311 a growing season in the early 2000s relative to the 1980s. 312

A comparison of trends with flow-normalized results from WRTDS relative to observed 313 data is justified because flow and nutrient concentrations were linked at many of the stations 314 in the study area, similar to Figure 4. These comparisons are made relative to changes in the 315 magnitude, significance, and direction of trends, all of which have important implications for decision-making. For all sixty trend comparisons in Figure 3 (flow-normalized values in 317 Table S1) regardless of site, nitrogen analyte, and time period, thirteen comparisons had 318 trends that were insignificant with the observed data but significant with flow-normalized 319 results, whereas only one trend changed to insignificant. Changes in the magnitude of the 320 estimated percent change per year were also apparent for the flow-normalized trends, such 321 that fourteen comparisons showed an inrease in magnitude (more negative or more positive) 322 and twenty five had a decrease (less positive or less negative) compared to observed trends. 323 More importantly, eleven comparisons showed a trend reversal from positive to negative 324 estimated change and ten sites went from no change to negative estimated trends for the 325

flow-normalized results. Differences by season in the observed relative to flow-normalized results from WRTDS were also apparent (Figures S1 and S2 and Tables S2 and S3). The most notable changes were an overall decrease in the estimated trend for most sites in the summer and fall seasons for 1996-2013.

Differences in apparent trends underscore the importance of considering flow effects in 330 the interpretation of environmental changes. Our results demonstrated the potential to 331 misinterpret trends if flow effects are not considered, where the misinterpretation could vary 332 from a simple change in the magnitude and significance of a trends, to more problematic 333 changes where the flow-normalized trend could demonstrate a complete reversal relative to 334 the observed. A more comprehensive evaluation of flow in the Delta demonstrated that 335 flow contributions of different end members vary considerably over time at each station.²⁹ 336 For example, flow at MD10 represents a changing percentage by season of inputs from 337 the Sacramento, San Joaquin, Cosumnes, Mokelumne rivers, and agricultural returns. For 338 simplicity, water quality observations in our analyses were matched with large-scale drivers of 339 flow into the Delta where most sites were matched to Sacramentao or San Joaquin daily flow 340 estimates. Given that substantial differences with flow-normalized results were apparent from 341 relatively coarse estimates of flow contributions, more precise differences could be obtained by considering the influence of multiple flow components at each locaiton. Output from the Dayflow software program 44 provides a complete mass balance of flow in the Delta that could be used to develop a more comprehensive description of flow-normalized trends that considers changing contributions over time. 346

347 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 as an example. 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 355 WWTPs given the disproportionate contribution of nutrients relative to other sources (e.g., 356 watershed agricultural load, sediment flux, etc.,). 29,51 Several WWTPs in the Delta have 357 recently been or are planned to be upgraded to include tertiary filtration and nitrification 358 to convert biologically available ammonium to nitrate. The City of Stockton WWTP was 359 upgraded in 2006 and is immediately upstream of station P8.²⁸ Therefore, a modal response 360 of nutrient concentrations at P8 centered around 2006 is expected as a result of upstream 361 WWTP upgrades, and water quality should exhibit 1) a shift in nutrient contributions from 362 the WWTP before/after upgrade, and 2) a flow-normalized annual trend at P8 to show a 363 change concurrent with WWTP upgrades.

Effluent concentations measured from 2003 to 2009 from the Stockton WWTP showed 365 a gradual shift in ammonium relative to the total (Figure S3). Ammonium and nitrate 366 concentrations were generally balanced prior to 2006, whereas nitrate was a majority of 367 total nitrogen after the upgrade with much smaller percentages from ammonium and ni-368 trite. As expected, flow-normalized nitrogen trends at P8 shifted in response to upstream 369 WWTP upgrades (Figure 5a), with ammonium showing an increase form 1976 followed by 370 a large reduction in the 2000s. Interestingly, nitrite/nitrate concentrations also showed a 371 similar but less dramatic decrease despite an increase in the WWTP effluent concentrations 372 following the upgrade. Percent changes from seasonal Kendall tests on flow-normalized re-373 sults showed that both nitrogen species increased prior to WWTP upgrades (2\% per year 374 for nitrite/nitrate, 2.8% for ammonium), followed by decreases after upgrades (-1.9% for 375 nitrite/nitrate, -16.6\% for ammonium, Table 1). Seasonally, increases prior to upgrades 376 were highest in the summer for nitrite/nitrate (2.4%) and in the fall for ammonium (4.9%). 377

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 nitrogen with flow described by WRTDS showed an inverse flow and 380 concentration dynamic with flushing or dilution at higher flow (Figure 5b). Seasonal variation 381 was more apparent for ammonium, although both typically had the highest concentrations 382 at low flow in the winter (January). Additionally, strength of the flow/nutrient relationship 383 changed between years. Nitrite/nitrate typically had the strongest relationship with flow 384 later in the time series, whereas ammonium had the strongest relationship with flow in the 385 early 2000s. Using WRTDS, an empirical link is created between upstream changes and 386 observed effects downstream that is characterized by differences in analytes between years 387 and season. A general conclusion is that ammonium reductions were concurrent with WWTP 388 upgrades, but the reduction was most apparent at low-flow in January. These dynamics are 389 difficult to characterize from the observed time series, and further, results from WRTDS can 390 be used to develop additional hypotheses of factors that influence nutrient concentrations at 391 P8. For example, estimated ammonium concentrations in July were low for all flow levels 392 which suggests either nitrogen inputs were low in the summer, or nitrogen was available and 393 uptake by primary consumers was high. Seasonal patterns in the relationship between flow and nitrite/nitrate were not as dramatic as compared to ammonium, and in particular, lowflow events in July were generally 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 observed concentrations in July 398 at low flow. As such, these simple observations from WRTDS can facilitate further testing 399 of cause and effect mechanisms of nutrient impacts on potentially adverse environmental 400 conditions as they relate to upstream management actions. 401

$_{\scriptscriptstyle{02}}$ 3.3.2 Effects of biological invasions

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The San Francisco Estuary is considered one of the most invaded ecosystems in the world 403 with an estimated 234 exotic species by the turn of the century, half of which have been 404 reported after 1965.³⁸ The invasion of benthic grazers as ecosystem engineers is one of the 405 more notable events that has been characterized by dramatic shifts in primary production 406 of the Bay's trophic network. 34,52-54 In particular, invasion of the upper estuary by the 407 Asian clam Potamocorbula amurensis in 1986 caused dramatic changes in phytoplankton 408 abundance and species composition with increased grazing. Reduction in phytoplankton 409 biomass has altered trophic networks in the Bay and is considered a primary mechanism in 410 the decline of the protected delta smelt and other important fisheries. 55,56 Changes in the 411 physical environment have also occurred with the most notable effect being increased water 412 clarity following a reduction of phytoplankton. ⁵⁶ The clams are halophilic such that drought 413 years are generally correlated with an increase in biomass and further upstream invasion of 414 the species. 24,57 415

We hypothesized that WRTDS models applied to water quality observations in the upper estuary would show 1) a decline in annual, flow-normalized chlorophyll concentrations
over time coincident with an increase in abundance of invaders, 2) changes in ratios of limiting nutrients (nitrogen, SiO₂) suggesting different uptake rates by grazers with a shift in
community composition, and 3) seasonal shifts in limiting nutrients based on changes in
community composition and relative abundances with seasonal succession. The application
of WRTDS to water quality observations at station D7 in Suisun Bay and comparison with
clam abundance and biomass data (see Ref 34) was expected to reveal the competing effects
of inflow on phytoplankton and benthic grazers.

Data from ^{27,34} describes phytoplankton community changes in the upper estuary, including chlorophyll response to flow. Figure 10 in Ref. 27 showed that chlorophyll generally decreased with flow in 1980 but inreased with flow in 2000.

Note the decrease in Potamocorbula abundance in 2011, 2012. These are wet years where

abundance/biomass of the clams is driven down by lower salinity. Contrased with the annual chlorophyll trends in the same years, the predicted values are above the flow-normalized trend suggesting an increase in chlorophyll with higher flow. The potential mechanism is therefore a decrease in clam abundance with high flow that releases phytoplankon from filtration pressure. This also explains the positive association of chlorophyll with flow in recent years (bottom right dynaplot). See suggestions in Ref. 57,58 regarding flow/grazer relationships in the Bay.

Further, chlorophyll trends early in the time series generally show a decrease with high flow with a distinct maximum at moderate flow. This may suggest stratification events at moderate flow contributed to phytoplankton blooms early in the time series. Water withdrawals later in the time series could have also altered environmental conditions to reduce the frequency occurrence of stratification events. Look into this more...

What about biomass/density relationships for Potamocorbula? Although clam density increases throughout the period, What about initial decrease in chlorophyll prior to clam invasion? Is this related to water withdrawals (i.e., decrease in stratification events at moderate flow)?

Figure 6, Table 2

What do nitrogen trends mean? Have to interpret relative to trends in other variables. A decrease in nitrogen or constant nitrogen does not mean nitrogen inputs have stayed the same, they might actually be increasing if nitrogen. A change in chlorophyll relative to 448 change in nitrogen could be informative, and even moreso, a change in silica relative to 449 change in chlorophyll suggests diatom biomass has changed. However, there are mismatches 450 in these trends that suggest other processes are at play, e.g., residence times and flow in-451 puts, etc. Trends in Suisun relative to trends in Delta provide an example, e.g., Suisun is 452 decrease in chlorophyll, increase in silica, increase in nitrogen, delta is decrease in silica, in-453 crease/decrease in DIN (depending on time period/season), decrease in chlorophyll, what's 454 going on? See Senn slide 14 (from burial?). The WRTDS model lets us at least address 455

- trends in the context of season, time, and flow. This allows for more improved interpretion
- relative to observing raw data. Also explain more information by looking at ammonium,
- nitrative/nitrite, relative to DIN. What about other variables (light level as suspended par-
- ticulate matter, temperature)?

$_{460}$ 4 References

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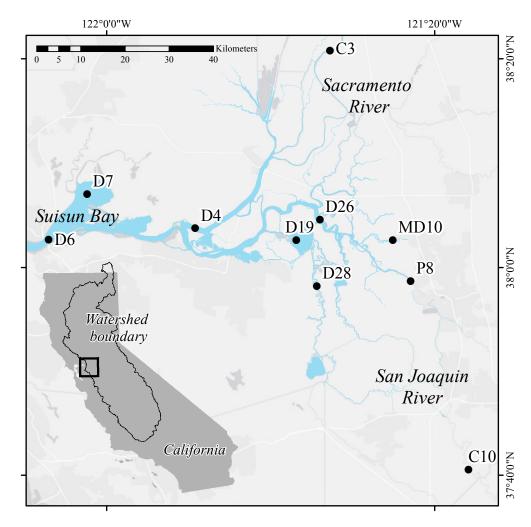


Figure 1: The San Francisco Estuary Delta and monitoring stations used for analysis. The Delta drains the combined watershed from the Sacramento and San Joaquin rivers (bottom left). All data were obtained from the Interagency Ecological Program website (http://water.ca.gov/bdma/meta/Discrete/data.cfm). 43

{fig:delt_m

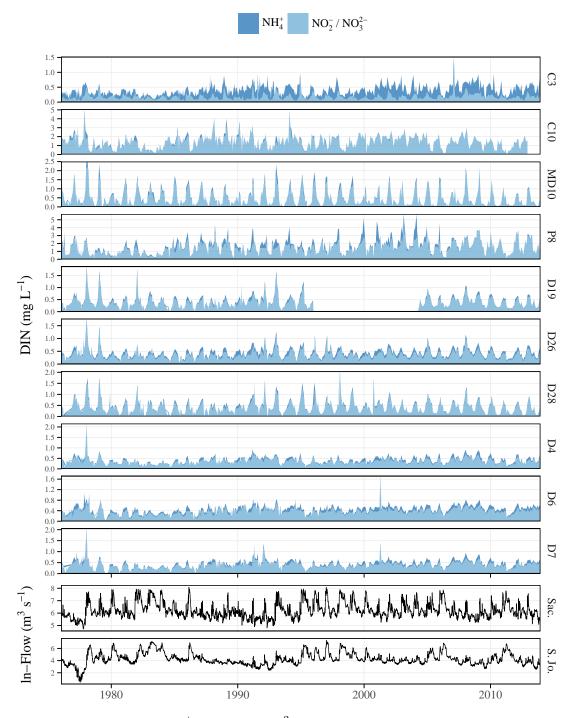


Figure 2: Observed DIN (NH $_4^+$ + NO $_2^-$ /NO $_3^{2-}$) from ten stations in the upper SFE Delta and flow from the Sacramento and San Joaquin rivers. Data were collected monthly and evaluated with WRTDS models using daily flow estimates from 1976 to 2013. Note different y-axis scales. See Figure 1 for station locations.

{fig:obsdat

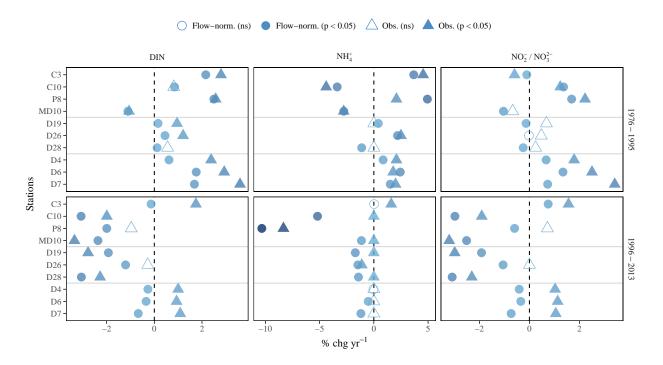


Figure 3: Results from seasonal Kendall tests on observed data (triangles) and flow-normalized predictions (circles) from WRTDS for nitrogen analytes. Results are shown as the percent change per year as the estimated Theil-Sen slope divided by the median for a given aggregation period (significance evaluated at $\alpha=0.05$, based on τ). Trends are shown separately for different annual groupings. See Figures S1 and S2 for seasonal groupings.

{fig:trndcd

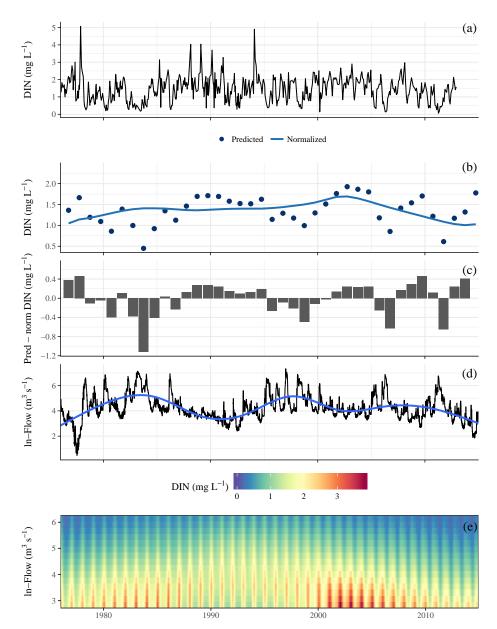


Figure 4: Time series of DIN and flow at station C10. Subfigure (a) shows the observed DIN time series and subfigure (b) shows the annual (water year starting in October) predictions from WRTDS for the conditional mean response. The points in subfigure (b) are predictions of observed DIN and the lines are flow-normalized predictions. Subfigure (c) shows the difference between the model predictions and flow-normalized predictions. Subfigure (d) shows the flow time series of the San Joaquin River with a locally-estimated (loess) smooth to emphasize the long-term trend. Subfigure (e) shows the modelled relationships between DIN, flow, and time. Flow values in (e) are truncated by 5th and 95th percentiles of observed.

{fig:dinc10

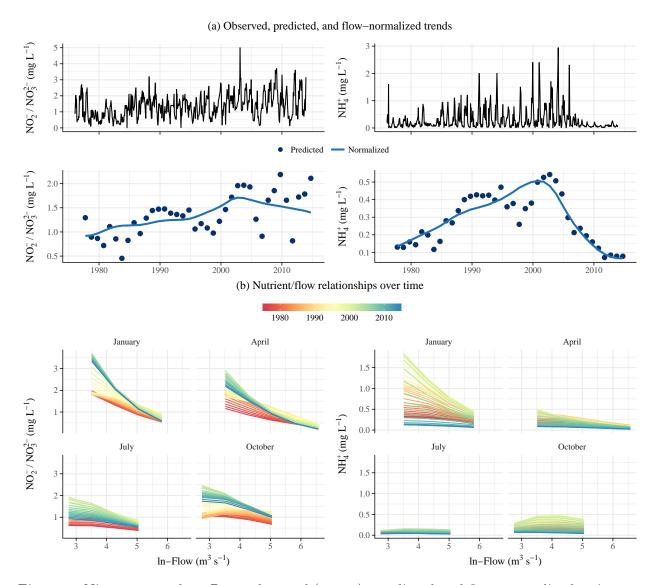


Figure 5: Nitrogen trends at P8 as observed (a, top), predicted and flow-normalized estimates from WRTDS (a, bottom), and relationships with flow over time (b). Nitrite/nitrate trends are on the left and ammonium trends are on the right. Wastewater treatment plant upgrades at the City of Stockton (San Joaquin County) were completed in 2006 (Figure S3), coincident with a dramatic decrease in ammonium at P8.

{fig:p8trnd

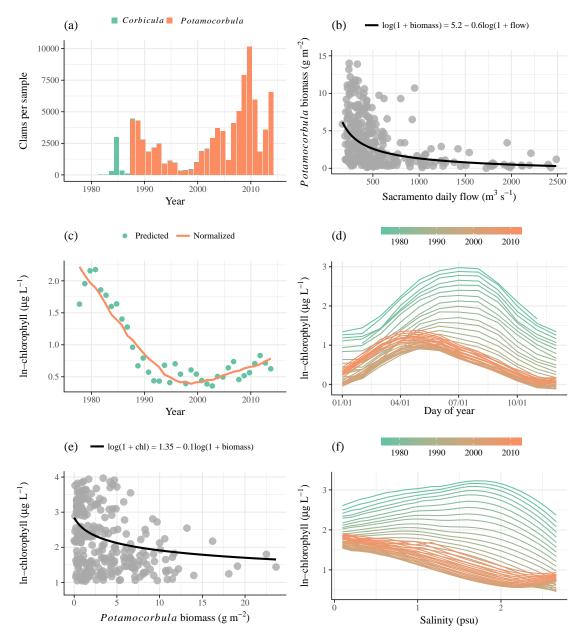


Figure 6: Trends in clam abundance and chl-a concentration from 1976 to 2013 at station D7 in Suisun Bay. Invasion by $Potamocorbula\ amurensis$ clams in the late 1980s and displacement of $Corbicula\ fluminea$ was shown by changes in clam density (a, annual means), with biomass linked to salinity (b). A coincident decrease in chl-a concentration was also observed by changes in annual (c) and seasonal trends(d). A significant (p < 0.001) relationship between clam biomass and chl-a concentration is shown in subfigure (e). Flow relationships with chl-a concentration have also changed over time (f, observations from June).

{fig:clmchl

Table 1: Summaries of flow-normalized trends in nitrite/nitrate and ammonium (mg L⁻¹) concentrations before and after WWTP upgrades upstream of station P8. Upgrades were completed in 2006 at the City of Stockton WWTP (San Joaquin County, Figure S3). Summaries are medians and percent change per year in parentheses (increasing in bold-italic). 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.

{tab:p8chg}

Period	$\mathrm{NO_2^-/NO_3^{2-}}$		\mathbf{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	<i>1.6</i> **	0.2	<i>1.4</i> **
Summer	1	2.4**	0.1	3.3^{**}
Fall	1.3	2.2**	0.2	<i>4.9</i> **
Winter	1.5	<i>2.1</i> **	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**

p < 0.05; p < 0.005

Table 2: Summaries of flow-normalized trends in dissolved inorganic nitrogen (mg L^{-1}), chlorophyll (μ g L^{-1}), and silicon dioxide (mg L^{-1}) concentrations for different time periods at station D7. Summaries are medians and percent change per year in parentheses (increasing in bold-italic). 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.

{tab:d7chg}

Period	DIN		\mathbf{C}	Chl-a		${f SiO}_2$	
	Median	% change	Median	% change	Median	% change	
All							
1976-2013	0.4	<i>0.6</i> **	3	-6.7**	12.7	0.7^{**}	
Annual							
1976 - 1985	0.4	-2.1**	8.8	-10.7**	10.2	-0.2	
1986-1994	0.4	<i>3.6</i> **	2.6	-13.5**	11.9	2.3^{**}	
1995-2003	0.5	-0.1	1.8	<i>1.9</i> **	13.3	0.7^{**}	
2004-2013	0.5	-1.3**	2.1	2.9**	13.1	-0.3**	
Seasonal							
Spring	0.5	-0.1	3.4	-1	14.7	0.1^{**}	
Summer	0.4	1.5**	3.4	-8.8**	12.2	1.2**	
Fall	0.4	$ extbf{0.6}$	1.7	-8.8**	12.1	1**	
Winter	0.6	-0.2	1.4	-3.1**	14.5	0.3^{**}	

p < 0.05; *p < 0.005

Supporting Information Available

The following files are available free of charge.

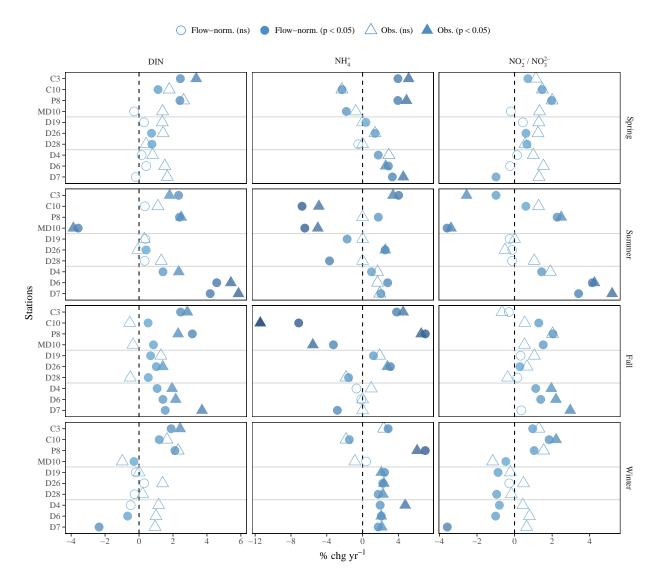


Figure S1: Results from seasonal Kendall tests on observed data (triangles) and flow-normalized predictions (circles) from WRTDS for nitrogen analytes. Results are shown as the percent change per year as the estimated Theil-Sen slope divided by the median for a given aggregation period (significance evaluated at $\alpha=0.05$, based on τ). 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 Figure 3 for annual comparisons.

{fig:trndco

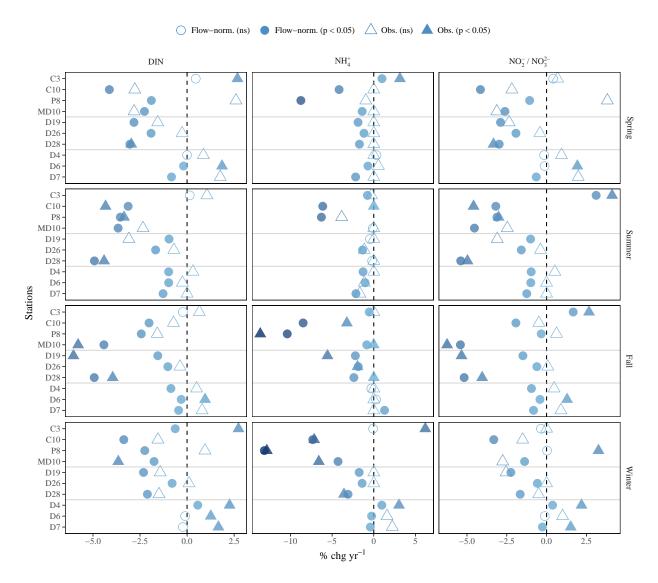


Figure S2: Results from seasonal Kendall tests on observed data (triangles) and flow-normalized predictions (circles) from WRTDS for nitrogen analytes. Results are shown as the percent change per year as the estimated Theil-Sen slope divided by the median for a given aggregation period (significance evaluated at $\alpha=0.05$, based on τ). 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 Figure 3 for annual comparisons.

{fig:trndco

Table S1: Summaries of flow-normalized trends in nitrogen analytes for all stations and annual aggregations. Summaries are medians (mg L^{-1}) and percent change per year in parentheses (increasing in bold-italic). Changes and significance estimates are based on seasonal Kendall tests of flow-normalized results within each time period. See ?? for a summary of spatial trends.

{tab:trndsa

Analyte/Station	Annual		
<i>y</i> /	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)**	
$\overline{\mathrm{NH}_{4}^{+}}$			
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)**	
$\mathrm{NO_2^-/NO_3^{2-}}$			
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)**	

p < 0.05; p < 0.005

Table S2: Summaries of flow-normalized trends in nitrogen analytes for all stations and seasonal aggregations from 1976-1995. Summaries are medians (mg L⁻¹) and percent change per year in parentheses (increasing in bold-italic). Changes and significance estimates are based on seasonal Kendall tests of flow-normalized results within each time period. See ?? for a summary of spatial trends. Months for each season are Spring: MAM, Summer: JJA, Fall: SON, Winter: DJF.

{tab:trndsh

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)**	$0.4 \ (\textbf{1.9})**$
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)**
$\overline{\mathrm{NH_4^+}}$				
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)**	$0.2 \; (\textbf{0.4})$
P8	0.2 (3.9)**	0.1 (1.8)**	0.2 (7)**	0.6 (7)**
$\overline{\mathrm{NO_2^-/NO_3^{2-}}}$				
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	$0.4 \; (\textbf{0.6})^*$	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)**	$0.2 \ (\textbf{1.5})^{**}$	1.2 (-0.5)*
P8	1.2 (2)**	0.9 (2.3)**	1.1 (2)**	1.4 (1)**

p < 0.05; *p < 0.005

Table S3: Summaries of flow-normalized trends in nitrogen analytes for all stations and seasonal aggregations from 1996-2013. Summaries are medians (mg L⁻¹) and percent change per year in parentheses (increasing in bold-italic). Changes and significance estimates are based on seasonal Kendall tests of flow-normalized results within each time period. See ?? for a summary of spatial trends. Months for each season are Spring: MAM, Summer: JJA, Fall: SON, Winter: DJF.

{tab:trndsa

$\overline{ m Analyte/Station}$	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	$0.5 \; (0.5)$	$0.4 \; (\textbf{0.1})$	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)**	$0.5 \ (\textbf{0.6})^{**}$
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)**	$0.1 \; (\textbf{0.3})$	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)**
$\overline{\mathrm{NO_2^-/NO_3^{2-}}}$				
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)

p < 0.05; *p < 0.005

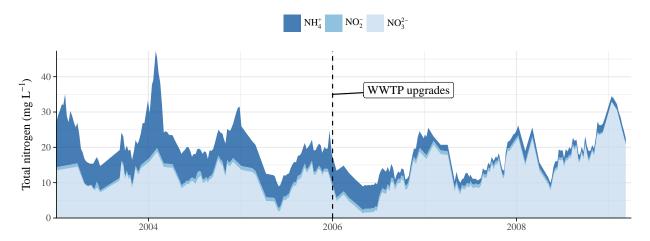


Figure S3: Nitrogen concentration measurements (mg $\rm L^{-1}$) from the City of Stockton Wastewater Treatment Plant, San Joaquin County. Wastewater discharge requirements were implemented in 2006 for nitrification/denitrification and tertiary filtration to convert ammonium to nitrate.

{fig:stock}