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

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1 Abstract

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Recent methods for trend analysis have been developed that leverage the descriptive potential of multi-decadal monitoring data. We apply 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). 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). Trend analysis with WRTDS flow-normalized data demonstrated the potential to misinterpret changes using observed data that include 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 demonstrate use of WRTDS to provide insight into mechanisms of change with two case studies that 1) evaluate downstream changes in nitrogen following upgrades at a wastewater treatment

plant, and 2) interactions between biological invaders, chlorophyll, and flow in Suisun Bay. Overall, this analysis provides an ecological and management-based understanding of historical trends in the Delta as a means to interpret potential impacts of recent changes and expected trends.

18 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 21 time scales or the observed variation represents the combined effects of many variables. 1,2 As a practical approach for water quality evaluation, trend analysis of ecosystem response 23 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 25 also reflect long-term effects of management or policy changes. For example, chlorophyll a (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.^{3,4} Similarly, nutrient trends that vary with hydrologic loading also vary as a function of utilization rates by primary producers or decomposition processes. 5-7 Time series analysis 31 of ecosystem response indicators must simultaneously consider effects of processes at mul-32 tiple scales and interactions between variables of interest to develop a more comprehensive 33 description of system change. 34

Appropriate methods for the analysis of change depend largely on the question of interest and characteristics of the environmental dataset. Trend analyses for aquatic systems have traditionally focused on comparisons between discrete periods of time to estimate direction and magnitude of a trend using non-parametric tests. 8,9 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 development of trend analysis methods that leverage the descriptive potential of long-term time series from continuous monitoring programs. ^{10,11} These methods are often data-driven where the parameterization of a simple functional model can change smoothly over time. 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. ^{12–17} More recently, the WRTDS method was adapted for trend analysis in tidal waters, with a focus on chl-a trends in Tampa Bay ¹⁸ and the Patuxent River Estuary, ¹⁹ and tidally-influenced time series of dissolved oxygen from continuous sonde measurements. ²⁰ These studies have demonstrated the potential of WRTDS for trend analysis in tidal waters.

The Sacramento - San Joaquin River Delta (hereafter 'Delta') is a mosaic of inflows 51 upstream of the San Francisco Estuary (SFE) that receives and processes inputs from the larger watershed. 21-23 Sediment export downstream of the Delta and wastewater treatment plant (WWTP) inputs are primary sources of nutrients for the larger Bay. Background nutrient concentrations in SFE often exceed those associated with excessive primary production, although ecosystem responses symptomatic of eutrophication have historically been infrequent. Changes in response to additional stressors (e.g., variation in freshwater inputs/withdrawals, invasive species, climate change) suggests that recent conditions have not followed past trajectories and more subtle spatial and temporal variation could provide clues that describe underlying properties of this system.²⁴ A comprehensive monitoring dataset has been collected at several fixed locations in the upper estuary and Delta for the last four decades.²⁵ Moreover, nutrient dynamics in the Delta are inherently linked to flow variation 62 from inputs, withdrawal, impoundments, and downstream transport, ²⁶ suggesting that an 63 approach that explicitly considers flow effects is critical for trend analysis. To date, the regional monitoring dataset for the northern SFE, including the Delta, is under-utitilized and a comprehensive analysis with WRTDS could facilitate an understanding of historical and recent changes in water quality.

The goal of this study was to provide a comprehensive description of nutrient trends in 68 the northern SFE and Delta region to inform understanding of ecosystem response dynamics and potential causes of water quality change. We applied the newly-adapted method 70 of weighted regression for tidal waters to describe nitrogen trends in different spatial and 71 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, 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 as additional case studies to demonstrate complexities with nutrient response to flow, effects of nutrient-related source controls 77 on ambient conditions, and effects of biological invasion by benthic filter feeders on primary production.

Materials and Methods

81 Study system

The Delta region drains a 200 thousand km² 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 km² of agricultural land. Water enters the SFE through the Sacramento and San Joaquin rivers that have a combined inflow of approximately 28 km³ 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 (Figure 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. 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. ²⁴ Notable drought periods have occurred
 from 1976-1977, 1987-1992, and recently from 2013-2015. ²⁷

Orthophosphate (PO_4^{3-}) and dissolved inorganic nitrogen (DIN) enter the Delta primarily 94 through the Sacramento and San Joaquin rivers and from municipal WWTP inputs. Annual 95 nutrient export from the Delta region has been estimated as approximately 30 thousand kg 96 d⁻¹ of total nitrogen (varying with flow²⁶), with 90% of ammonium (NH₄⁺) originating solely from the Sacramento Regional WWTP.²³ Although nitrogen and phosphorus inputs are considerable, primary production is relatively low and not nutrient-limited.^{22,28} The resistance of SFE to the negative effects of eutrophication has historically been attributed to its unique 100 physical and biological characteristics, including strong tidal mixing that limits stratifica-101 tion in the larger estuary 3,29 and limits on phytoplankton growth from high turbidity and 102 filter-feeding by bivalve mollusks in the northern portion. ^{29,30} However, recent water quality 103 trends have suggested that resilience to nutrient inputs is decreasing, 31-33 which have have 104 been attributed to biological invasions 34 and departures from the historical flow record, 24,35 105 among other factors acting at global scales (e.g., variation in sea surface temperatures). 32 106 The role of nutrients in stimulating primary production in SFE has been the focus of several 107 recent investigations. 36-38

109 Data sources

Nutrient time series from 1976 to 2013 were obtained for ten discrete sampling stations (Figure 1, http://water.ca.gov/bdma/meta/Discrete/data.cfm). 39 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 were chosen based on continuity of the water quality time series and significance of their geographic location for understanding regional trends. Time series were complete for all stations except for an approximate ten year gap from 1996-2014 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 pro-123 gram. 40 The WRTDS models described below require a matched flow record with the appro-124 priate station to evaluate nutrient trends. Given the complexity of inflows and connectivity 125 of the system, only the inflow estimates from the Sacramento and San Joaquin rivers were 126 used as measures of freshwater influence at each station. Initial analyses indicated that 127 model fit was not significantly improved with flow estimates from locations closer to each 128 station, nor was model fit improved using lagged times series. As such, the Sacramento daily 129 flow time series was used to account for flow effects at C3, D19, D26, D28, and MD10, and 130 the San Joaquin time series was used for C10 and P8 based on station proximity to each 131 inflow. Salinity observations at D4, D6, and D7 in Suisun Bay were used as more appropriate 132 measures of freshwater variation, given the stronger tidal influence at these stations. Salinity 133 has been used as a tracer of freshwater influence for the application of WRTDS models in tidal waters. 18

136 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 12 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 depending on station). The seasonal trend is modeled as a sinusoidal component to capture 142 periodicity between years. The WRTDS model is a moving window regression that fits 143 unique parameters at each observation point in the time series. A unique set of weights 144 is used for each regression to control the importance of observations used to fit the model 145 relative to the observation at the center of the window. The complete model for the time 146 series contains a parameter set for every time step that considers the unique context of the 147 data. The WRTDS models applied herein were based on a tidal adaptation of the original 148 method¹⁸ and were fit to describe the conditional mean response using a weighted Tobit 149 model for left-censored data. 41 All analyses used the WRTDStidal package written by the 150 authors for the R statistical programming language. 42? 151

A hallmark of the WRTDS approach is the description of flow-normalized trends that 152 are independent of variation from freshwater inflows. Although variation in nutrients can be 153 caused by the combined effects of several variables acting at different temporal and spatial 154 scales, flow-normalization provides a basis for further exploration by removing a critical 155 confounding variable that could affect the interpretation of trends. A flow-normalized value 156 is the average of predictions at a given observation using all flow values that are expected to occur for the relevant month across years in the record. Flow-normalized trends for each analyte at each station were used to describe long-term changes in different annual and 159 seasonal periods. Specifically, flow-normalized trends in each analyte were summarized as 160 both medians and percent changes from the beginning to end of annual groupings from 1976-161 1995 and 1996-2013, and seasonal groupings of March-April-May (spring), June-July-August 162 (summer), September-October-November (fall), and December-January-February (winter) 163 within each annual grouping. These annual and seasonal groupings were chosen for continuity 164 with similar comparisons in Ref. 25 and as approximate twenty year midpoints in the time 165 series. 166

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

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flow-normalized predictions. This test is a modification of the non-parametric Kendall test that accounts for variation across seasons in the response variable. 43 Results from the test 169 can be used to evaluate the direction, magnitude, and significance of a monotonic change 170 within the period of observation. The estimated rate of change per year is also returned 171 as the Theil-Sen slope and was interpreted as the percent change per year when divided by 172 the median value of the response variable in the period of observation.²³ Trends in annual 173 groupings were based on all monthly observations within relevant years, whereas seasonal 174 groupings were based only on the relevant months across years. Seasonal Kendall tests were 175 also used to describe trends in the observed data. These trends were compared with those 176 based on the flow-normalized trends to evaluate the improved ability of WRTDS to describe 177 trends that are independent of flow. Functions in the EnvStats package in R were used for 178 the seasonal Kendall tests. 44 179

180 Results and Discussion

181 Observed Data

The observed time series for the ten Delta - Suisun Bay stations had substantial variation 182 in scale among the nitrogen analytes and differences in apparent seasonal trends (Figure 2). 183 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 185 other stations (e.g., P8, D26) had higher concentrations of ammonium during winter months 186 when phytoplankton assimilation is lower.²⁶ By location, observed concentrations of DIN for 187 the entire time series were higher on average for the peripheral stations (C3, C10, MD10, 188 P8; mean \pm s.e.: 1.04 \pm 0.03 mg L⁻¹) and similar for the interior (D19, D26, D28, 0.43 \pm 0.01) 189 and Suisun Bay stations (D4, D6, D7, 0.44±0.01). Average concentrations were highest at 190 P8 $(1.63\pm0.05 \text{ mg L}^{-1})$ and lowest at C3 (0.4 ± 0.01) for DIN, highest at P8 (0.28 ± 0.02) and 191 lowest at D28 (0.05 ± 0.003) for ammonium, and highest at C10 (1.4 ± 0.04) and lowest at C3 192

(0.15±0.004) 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±0.01 mg L⁻¹for 1976-1995, compared to 0.7±0.01 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, D7, Figure 2).

200 Trends

Application of seasonal Kendall tests to evaluate trends in observed data provided infor-201 mation on the direction, magnitude, and statistical significance of changes between years. Trends estimated for 1976-1995 and 1996-2013 varied considerably between sites and ana-203 lytes (Figure 3). Significant trends were observed from 1976-1995 for eight of ten sites for 204 DIN (seven increasing, one decreasing), eight sites for ammonium (six increasing, two de-205 creasing), and six sites for nitrite/nitrate (five increasing, one decreasing). Decreasing trends 206 were more common for the observed data from 1996-2013. Eight sites had significant trends 207 for DIN (four increasing, four decreasing), seven sites for ammonium (five increasing, two 208 decreasing), and eight sites for nitrite/nitrate (four increasing, four decreasing). P8 had a 209 relatively large decrease in ammonium (-8.3% change per year) for the second annual pe-210 riod compared to all other sites (see next section). Trends by season were similar such that 211 increases were generally observed in all seasons from 1976-1995 (Figure S1) and decreases 212 were observed for 1996-2013 (Figure S2). Trends for the seasonal comparisons were noisier 213 and significant changes were less common compared to the annual comparisons. 214

Relationships between flow and observed water quality are complex and can change significantly through space and time. ^{12,17} These principles have been demonstrated for monitoring
data in the Delta region, ^{23,25,26} suggesting that trend analyses using the observed time series are confounded by flow effects. As such, 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 Figure 3 (flow-normalized values in Table S1) regardless of site, nitrogen analyte, and time period, thirteen comparisons had trends that were insignificant with the observed data but significant with flow-normalized results, 222 whereas only one trend changed to insignificant. This suggests that time series that include 223 flow effects had sufficient noise to obscure or prevent identification of an actual trend of a 224 water quality parameter. Further, changes in the magnitude of the estimated percent change 225 per year were also apparent for the flow-normalized trends, such that fourteen comparisons 226 showed an increase in magnitude (more negative or more positive) and twenty five had a 227 decrease (less positive or less negative) compared to observed trends. Eleven comparisons 228 showed a trend reversal from positive to negative estimated change, nine sites went from no 229 change to negative estimated change, and one site went from no change to a positive trend for 230 the flow-normalized results. Differences by season in the observed relative to flow-normalized 231 trends from WRTDS were also apparent (Figures S1 and S2 and Tables S2 and S3). The 232 most notable changes were an overall decrease in the estimated trend for most sites in the 233 summer and fall seasons for 1996-2013, including an increase in the number of statistically 234 significant trends. 235

Differences in apparent trends underscore the importance of considering flow effects in 236 the interpretation of environmental changes, particularly if trend evaluation is used to assess 237 the effects of nutrients on ecosystem health or the effectiveness of past nutrient management 238 actions. Our results demonstrated the potential to misinterpret trends if flow effects are not 239 considered, where the misinterpretation could vary from a simple change in the magnitude 240 and significance of a trend, to more problematic changes where the flow-normalized trend 241 could demonstrate a complete reversal relative to the observed (e.g., DIN trends for all Suisun 242 stations from 1996-2013, Figure 3). A more comprehensive evaluation of flow in the Delta 243 demonstrated that flow contributions of different end members vary considerably over time 244 at each station.²⁶ 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-247 scale drivers of flow into the Delta where most sites were matched to Sacramento or San 248 Joaquin daily flow estimates. Given that substantial differences with flow-normalized results 249 were apparent from relatively coarse estimates of flow contributions, more precise differences 250 could be obtained by considering the influence of multiple flow components at each location. 251 Output from the Dayflow software program 40 provides a complete mass balance of flow in 252 the Delta that could be used to develop a more comprehensive description of flow-normalized 253 trends that considers changing contributions over time. 254

Selected examples 255

256 Effects of wastewater treatment

Significant efforts have been made in recent years to reduce nitrogen loading from regional 257 WWTPs given the disproportionate contribution of nutrients relative to other sources. 26,45 258 Several WWTPs in the Delta have recently been or are planned to be upgraded to include 259 tertiary filtration and nitrification to convert biologically available ammonium to nitrate. 260 The City of Stockton WWTP was upgraded in 2006 and is immediately upstream of station 26 P8, 25 which provides a valuable opportunity to assess how nutrient or nutrient-related source 262 controls and water management actions have changed ambient concentrations downstream. 263 A modal response of nutrient concentrations at P8 centered around 2006 is expected as a 264 result of upstream WWTP upgrades, and water quality should exhibit 1) a shift in the ratio 265 of the components of DIN from the WWTP before after upgrade, and 2) a flow-normalized 266 annual trend at P8 to show a change concurrent with WWTP upgrades. 267

Effluent measured from 2003 to 2009 from the Stockton WWTP had a gradual reduction in ammonium concentration relative to total DIN (Figure S3). 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 (Figure 4a), with ammonium showing an increase from 1976 followed by a large reduction in the 273 2000s. Interestingly, nitrite/nitrate concentrations also showed a similar but less dramatic decrease despite an increase in the WWTP effluent concentrations following the upgrade. 275 Percent changes from seasonal Kendall tests on flow-normalized results showed that both 276 nitrogen species increased prior to WWTP upgrades (2% per year for nitrite/nitrate, 2.8%) 277 for ammonium), followed by decreases after upgrades (-1.9%) for nitrite/nitrate, -16.6% for 278 ammonium, Table 1). Seasonally, increases prior to upgrades were highest in the summer 279 for nitrite/nitrate (2.4%) and in the fall for ammonium (4.9%). Similarly, seasonal reduc-280 tions post-upgrade were largest in the summer for nitrite/nitrate (-4.3%) and largest for 281 ammonium in the winter (-26.7%). 282

Relationships of nitrite/nitrate with flow described by WRTDS showed an inverse flow 283 and concentration dynamic with flushing or dilution at higher flow (Figure 4b). Seasonal vari-284 ation was even more apparent for ammonium, although both nitrite/nitrate and ammonium 285 typically had the highest concentrations at low flow in the winter (January). Additionally, 286 strength of the flow/nutrient relationship changed between years. Nitrite/nitrate typically 287 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. A general conclusion is that ammonium reductions were concurrent with WWTP upgrades, 290 but the reduction was most apparent at low-flow in January. These dynamics are difficult 291 to characterize from the observed time series, and further, results from WRTDS can be 292 used to develop additional hypotheses of factors that influence nutrient concentrations at 293 P8. For example, estimated ammonium concentrations in July were low for all flow lev-294 els which suggests either nitrogen inputs were low in the summer or nitrogen was available 295 and uptake by primary consumers was high. Seasonal patterns in the relationship between 296 flow and nitrite/nitrate were not as dramatic as compared to ammonium, and in particular, 297 low-flow events in July were associated with higher concentrations. This could suggest that 298

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.

304 Effects of biological invasions

Invasion of the upper SFE by the Asian clam Potamocorbula amurensis in 1986 caused severe 305 changes in phytoplankton abundance and species composition. Reduction in phytoplankton 306 biomass has altered trophic networks in the upper SFE and is considered an important 307 mechanism in the decline of the protected delta smelt (Hypomesus transpacificus) and other 308 important fisheries. 46,47 Changes in the physical environment have also occurred, particu-309 larly increased water clarity from a reduction of particle transport and erodible sediment 310 supply, ^{23,24,48} although decreases in phytoplankton by clam biofiltration may have also in-311 creased clarity. 47 The clams are halophilic such that drought years are correlated with an 312 increase in biomass and further upstream invasion of the species. 24,49 We hypothesized that 313 results from WRTDS models would show 1) a decline in annual, flow-normalized chlorophyll 314 concentrations over time coincident with an increase in abundance of invaders, and 2) varia-315 tion in the chlorophyll/clam relationship through indirect or direct controls of flow. Although 316 the relationship between phytoplankton and clams have been well described in SFE.⁵⁰ we 317 use WRTDS to develop additional evidence that an increase in DIN was facilitated in part 318 by clam invasion. 319

Invasion in the 1980s showed a clear reduction of *Corbicula fluminea* and increase of *P. amurensis* (Figure 5a), where biomass of the latter was negatively associated with flow from the Sacramento river (Figure 5b). The increase in clam abundance was associated with a notable decrease in annually-averaged chl-*a* from WRTDS results (Figure 5c), as expected if WRTDS is adequately capturing flow variation and identifying the well-established phyto-

plankton 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 326 invasion, whereas a spring maximum in April was more common in recent years (Figure 5f). 327 An increase in annually-averaged silicon dioxide (Figure 5e) was coincident with the chl-a 328 decrease, with the largest increases occurring in August (Figure 5g). These relationships 329 suggest that diatoms were the dominant genera early in the time series, particularly in late 330 summer, whereas the spring peak observed in later years represents a shift to an earlier 331 seasonal maxima. This supports past research that showed a decrease in silica uptake by 332 diatoms following invasion.^{3,51} Further, DIN trends were similar to silicon-dioxide in both 333 annual and seasonal changes (compare Figures 5e and 5e with 5d and 5g) such that an in-334 crease in both nutrients earlier in the time series corresponded with the decrease in chl-a. 335 Overall, these results suggest that a nontrivial portion of the DIN increase could be related 336 to the decrease in a major 'sink', i.e., decreased DIN uptake by phytoplankton due to top 337 down grazing pressure from *P. amurensis*. 338

The relationship of chl-a with clam biomass was significant (Figure 5g), with lower chl-a339 associated with higher biomass, confirming results from earlier studies.^{29,52} However, the 340 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 (Figure 5j), whereas overall chl-a was lower but a positive association with 344 flow (negative with salinity) was observed later in the time series. In the absence of benthic 345 grazing prior to invasion, this dynamic suggests that chl-a production may be limited at low 346 flow as less nutrients are exported from the Delta, stimulated as flow increases, and reduced 347 at high flow as either nutrients or phytoplankton biomass are exported to the larger bay. 348 Following clam invasion, chl-a concentrations were reduced by grazing but showed a positive 349 and monotonic relationship with increasing flow. The increase in clam abundance was con-350 current with decline in chl-a concentration, although variation in abundance between years 351

was also observed. Clam abundance was reduced during high flow years in the late 1990s, 352 2006, and 2011 (5a). In the same years, WRTDS predictions for chl-a were higher than the 353 flow-normalized component (Figure 5c), which further suggests a link between increased flow and phytoplankton production. As such, chl-a production in early years is directly related 355 to flow, whereas the relationship with flow in later years is indirect as increased flow reduces 356 clam abundance and releases phytoplankton from benthic grazing pressure. These relation-357 ships have been suggested by others, ^{23,49,52} although the precise mechanism demonstrated by 358 WRTDS provides a quantitative description of factors that drive water quality in the Delta. 359 As demonstrated by both case studies and the overall trends across all stations, water 360 quality dynamics in the Delta are complex and driven by multiple factors that change through 361 space and time. At a minimum, WRTDS provides a description of change by focusing on 362 high-level forcing factors that explicitly account for annual, seasonal, and flow effects on trend 363 interpretations. We have demonstrated the potential for imprecise or inaccurate conclusions 364 of trend tests that focus solely on observed data and emphasize that flow-normalized trends 365 have more power to quantify change. Moreover, trends in nutrient loads from point sources in 366 the Delta have previously been described, e.g., Sacramento WWTP increases²³ and exports 367 to Suisun Bay. 53 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 370 influence nutrient cycling and ambient concentrations in the Bay-Delta, and changes to those 371 factors, are substantial enough that they can be comparable in magnitude to anthropogenic 372 load increases or comparable to the effects of management actions to decrease nutrient levels. 373 Therefore, methods that adjust for the effects of these factors are critical when studying longterm records to assess the impacts or effectiveness of load increases or management actions, 375 respectively. 376

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 380 rigorous matching of flow time series with water quality observations at each station that 381 considers varying source contributions over time could provide a more robust description of 382 flow-normalized results. Alternative methods for time series analysis could also be used to 383 address a wider range of questions, particularly those with more generic structural forms 384 that can explicitly include additional variables (e.g., generalized additive models). 19 Overall. 385 statistical interpretations of multiple factors can provide a basis for quantitative links be-386 tween nutrient loads and adverse effects on ecosystem conditions, including the identification 387 of thresholds for the protection and restoration of water quality. 388

389 Acknowledgments

We thank the staff of the San Francisco Estuary Institute and the Delta Regional Monitoring
Program. We thank Larry Harding for providing comments on an earlier draft. This study
was reviewed and approved for publication by the US EPA, National Health and Environmental Efects Research Laboratory. The authors declare no competing financial interest.
The views expressed in this paper are those of the authors and do not necessarily reflect the
views or policies of the US EPA.

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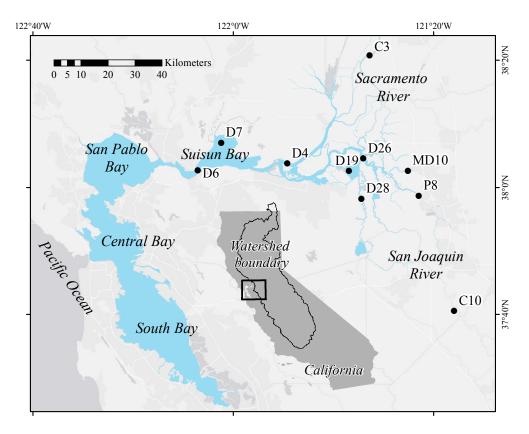


Figure 1: The San Francisco Estuary and Delta region with monitoring stations used for analysis. The Delta drains the combined watersheds of the Sacramento and San Joaquin rivers (inset). All data were obtained from the Interagency Ecological Program website (http://water.ca.gov/bdma/meta/Discrete/data.cfm). 39

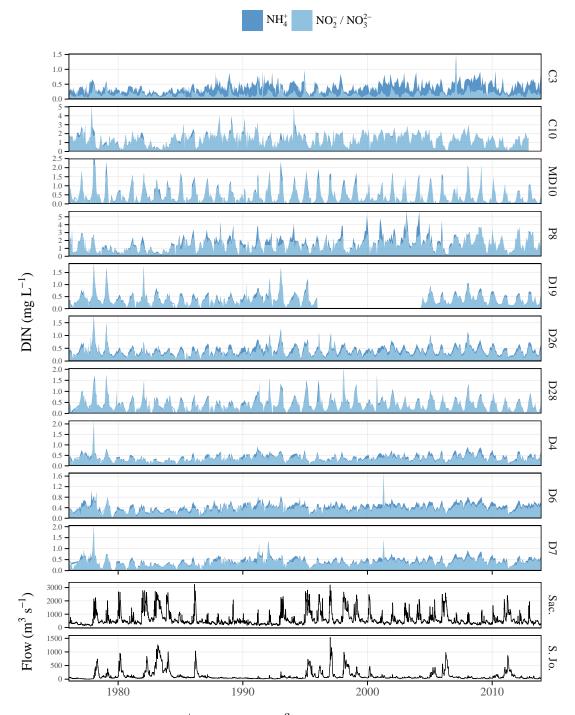


Figure 2: Observed DIN ($\mathrm{NH_4^+} + \mathrm{NO_2^-/NO_3^{2-}}$) from ten stations in the upper SFE Delta and flow from the Sacramento and San Joaquin rivers. Data were collected monthly and evaluated with WRTDS models using daily flow estimates from 1976 to 2013. Note different y-axis scales.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

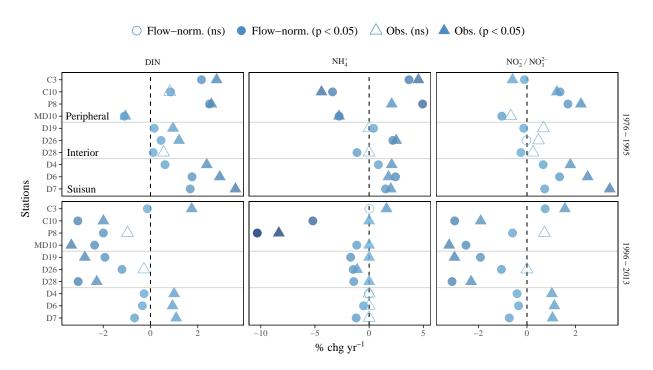


Figure 3: Results from seasonal Kendall tests on observed data (triangles) and flow-normalized predictions (circles) from WRTDS for nitrogen analytes. Results are shown as the percent change per year as the estimated Theil-Sen slope divided by the median for a given aggregation period (significance evaluated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

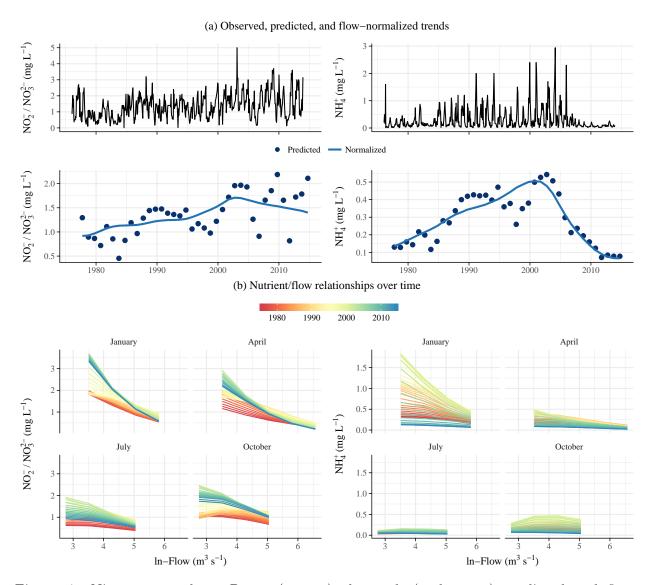


Figure 4: Nitrogen trends at P8 as (a, top) observed, (a, bottom) predicted and flow-normalized estimates from WRTDS, and (b) relationships with flow over time from WRTDS. Nitrite/nitrate trends are on the left and ammonium trends are on the right. Wastewater treatment plant upgrades at the City of Stockton (San Joaquin County) were completed in 2006 (Figure S3).

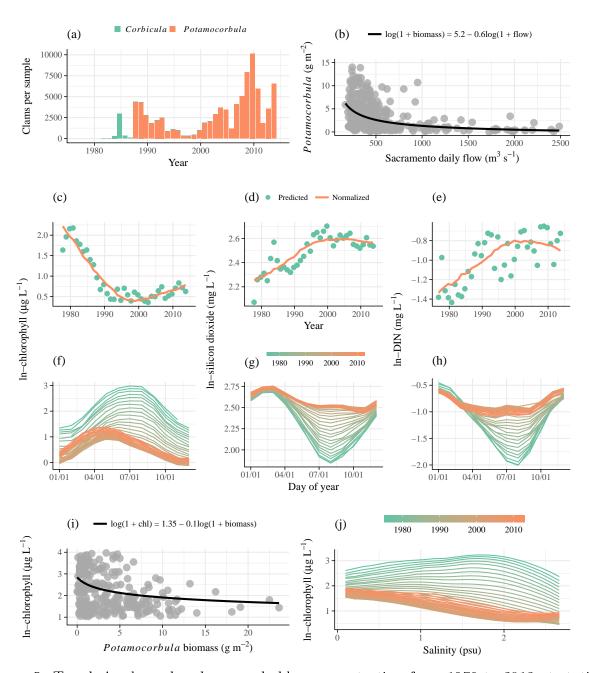


Figure 5: Trends in clam abundance and chl-a concentration from 1976 to 2013 at station D7 in Suisun Bay. Invasion by Potamocorbula amurensis clams in the late 1980s and reduction of Corbicula fluminea was shown by changes in clam density (a, annual means), with biomass linked to salinity (b). A decrease 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).

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

Period	$\mathbf{NO}_2^-/\mathbf{NO}_3^{2-}$		\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**

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. *p < 0.05; *p < 0.005