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Long-term Changes in Nutrient Loading and Stoichiometry and their Relationships with Changes in the Food Web and Dominant Pelagic Fish Species in the San Francisco Estuary, California

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Running head: *Relating nutrient loading and stoichiometry to fish in the CA Bay Delta*

Key words: nutrient ratios, nutrient stoichiometry, eutrophication, plankton trophodynamics, ammonium, CUSUM charts, delta smelt, pelagic organism decline

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24 ***ABSTRACT***

25 Nutrient enrichment is an important stressor in coastal ecosystems. This analysis tests the hypothesis that
26 changes in nutrient loads, imbalances in nitrogen:phosphorus, and changes in nitrogen form, especially
27 shifts to increasing loads of chemically reduced, rather than oxidized nitrogen, can have major impacts on
28 food webs, from primary producers through secondary producers to fish. The application of cumulative
29 sums of variability, the running total of deviations from normalized values over time, is a sensitive
30 method for comparing rates of change between and among all parameters, including organisms of all
31 trophic levels. This approach was applied to the San Francisco Estuary, California, demonstrating that
32 abrupt changes in nutrient loads and nutrient form over the past several decades were correlated with food
33 web changes, including pelagic fish collapse. Remediation of pelagic fish populations should be centered
34 on reduction of nitrogen loads and reestablishment of balanced nutrient ratios delivered from point source
35 discharges.

36

37

38 **INTRODUCTION**

39

40 The San Francisco Estuary, California, which encompasses the Sacramento-San Joaquin Bay
41 Delta, is one of the largest estuarine systems on the Pacific Coast as well as one of the largest managed
42 and engineered water systems in the United States. It is the largest source of municipal and agricultural
43 fresh water in California and is home to economically important fisheries. Major modifications to this
44 system have occurred over the past century, including drainage of marshes to support agriculture,
45 installation of dikes to prevent farmland flooding, expansion and deepening of shipping lanes, and
46 significant diversion of water to various users throughout the state (Atwater et al., 1979). The Bay Delta
47 system, an inverse delta, receives the majority of flows from the Sacramento and San Joaquin Rivers, of
48 which the Sacramento is the largest (Atwater et al., 1979; Nichols et al., 1986). The Bay Delta ecosystem
49 has also been significantly modified by invasive species, including clams, bay grasses, various species of
50 copepods, and fish over the past several decades (Cohen and Carlton, 1998; Kimmerer, 2002).

51 The Bay Delta is the subject of considerable national public awareness due to the sociopolitical
52 and socioeconomic tension surrounding the plight of the endemic delta smelt (*Hypomesus transpacificus*),
53 a small (length ca. 6 cm) fish whose decline has been taken as a sign of adverse environmental conditions
54 in the region. The delta smelt was put on the Threatened Species list in 1993 (Wanger, 2007a,b) and has
55 since undergone further significant population decline along with longfin smelt (*Spirinchus thaleichthys*),
56 threadfin shad (*Dorosoma petenense*) and young-of-the-year striped bass (*Morone saxatilis*; Manly and
57 Chotkowski, 2006). Accelerated losses during the last decade have been termed the “Pelagic Organism
58 Decline” (POD) period (Sommer et al., 2007). In recent years, the Federal court, under the Endangered
59 Species Act, has ordered modification of water diversion projects to protect the smelt (Wanger, 2007a,b).
60 Presently, a National Academy of Sciences panel has been convened in order to prepare a report for the
61 U.S. Congress on sustainability and the planned water management options for the Bay Delta (NRC,
62 2010).

63 To date, no single ultimate cause of the POD has been identified, and the interpretation of data has
64 favored a conclusion that multiple stressors combined to cause a population collapse (Sommer et al.,
65 2007; MacNally et al., 2010, Thompson et al., 2010). Among the major factors that are thought to stress
66 the delta smelt and other pelagic organisms are modification of the natural hydrology of the system,
67 including export pumping for domestic and agricultural water use, habitat changes that affect recruitment
68 (reproduction), invasion of exotic species including toxic algae, toxin loading, climate change, and food
69 web modification through changes in species and predation (Linville et al., 2002; Lehman et al., 2005;
70 Bennett, 2005; Sommer et al., 2007; Davis et al., 2008; Jassby, 2008). Because each of these physical,
71 chemical and biological factors potentially influences and modifies other factors, the system as a whole is
72 highly complex and prior efforts that used standard multifactor correlative analyses of 30 years of
73 ecosystem data have not been successful at identifying causality with any degree of certainty (Bennett and
74 Moyle, 1996; Sommer et al., 2007; MacNally et al., 2010; Thompson et al., 2010).

75 Of considerable interest has been the effect of export pumps on pelagic fish. The extent of
76 withdrawals of water for human and agricultural consumption is on the order of 20-25% of the inflowing
77 water (Jassby, 2008), and there is no question that these operations have had large effects on the
78 ecosystem. Flow is rigorously managed through engineering of the isohaline where salinity is equal to 2;
79 this isohaline is measured as the distance from the Golden Gate Bridge and is locally referred to as X2
80 (Jassby et al., 1995; Kimmerer, 2004). Given the current state of decline of the pelagic fish, restrictions on
81 water pumping have been imposed in recent years, resulting in public, economic, and political tensions
82 (NRC, 2010). It has been thought that regulation of flow will lead to improved conditions for endangered
83 fish.

84 It is also well recognized that the flows of energy and materials through the food web of the San
85 Francisco Estuary are complex and not well understood. The frequent changes, invasions, and effects of
86 engineering and other management actions also make these relationships complicated to interpret. Some
87 investigators have suggested that the food web of the Bay Delta is sensitive to alterations in nutrients.
88 However, no effort to date has focused on regulation of nutrients as a means to improve the declining fish.

89 Yet, it has been reported, based on experimental data, that high ammonium (NH_4^+) levels inhibit diatom
90 growth, thus potentially restricting the availability of a preferred food source in the food chain that
91 supports fish (Wilkerson et al., 2006; Dugdale et al., 2007). Moreover, changes in nitrogen:phosphorus
92 (N:P) ratios of nutrients in the water have been correlated with overall declines in water column
93 chlorophyll *a* (chl *a*) of the Bay Delta in the mid-1990s (Van Nieuwenhuysse, 2007).

94 The possibility of ‘bottom up’ control of fish populations in this system has been largely
95 dismissed for several reasons: most nutrients are at levels that saturate (maximize) phytoplankton growth;
96 phytoplankton growth is considered to be regulated primarily by light limitation (Cole and Cloern, 1984);
97 NH_4^+ is generally a preferred form of nitrogen for phytoplankton uptake; the pH of the receiving waters
98 prevents formation of the toxic compound, ammonia gas (NH_3); and the NH_4^+ levels are typically below
99 the criteria considered by the U.S. Environmental Protection Agency (EPA) for fish habitat (McCarthy et
100 al., 1977; Millero, 2006; Jassby, 2008; U.S. EPA, 2010). In addition, some analyses of nutrient effects
101 have considered only total N or P and chl *a*, rather than nutrient form and phytoplankton composition
102 (e.g., Jassby, 2008). As a consequence, relationships between nutrients, production or food web effects
103 have been ambiguous, leading to indecisive conclusions, as noted by Jassby (2008), “The physiological
104 effect of ammonium ...may well play a role in the dynamics of specific phytoplankton events...But it is
105 one factor among many, and its ecological effect relative to other sources of variability underlying long-
106 term phytoplankton patterns is not yet clear.”

107 In contrast to conditions in the 1960s and early 1970s in this system, when hypoxia was more
108 frequently noted (Nichols et al., 1986), there are presently no widespread classic symptoms of
109 eutrophication (e.g., Cole and Cloern, 1984; Kimmerer, 2004) although localized hypoxia has been
110 reported and increased frequency of cyanobacterial blooms in the past decade has been noted (Lehman et
111 al., 2005; 2008). Improvements in sewage treatment in the 1980s, in response to the U.S. Clean Water
112 Act, as well as other nutrient removal efforts, are generally credited with minimizing symptoms of
113 eutrophication. Ironically, as will be shown below, these changes in sewage treatment and other nutrient
114 removal efforts may have had unintended consequences on the food web, that, while reducing the classic

115 symptoms of eutrophication, may have resulted in significant biotic responses that propagated through the
116 food web.

117 Shifts in algal composition and food availability have been suggested as an important factor in
118 fish decline, especially in the past decade, not only because of the increasing frequency and range of
119 blooms of the cyanobacterium, *Microcystis aeruginosa* (Lehman et al., 2005, 2008), but because of
120 declines in diatoms and increases in flagellates (Lehman, 1996; Müller Solger et al., 2002, Brown, 2010).
121 Yet, how and why these phytoplankton groups have changed has not been understood. As noted by
122 Kimmerer (2004), “we do not really understand the controlling factors of some of the important fishes
123 and invertebrates of the estuary. We have almost no information on the dynamics of energy flow in higher
124 trophic levels, or how these levels are limited by productivity at the base of the food web.” The current
125 analysis attempts to begin to understand these relationships from a broad, long-term perspective. Key
126 pathways of nutrient effects were discerned from the analysis herein. Nevertheless, Kimmerer’s (2004)
127 analysis continues to stand correct in that much remains to be understood with regard to understanding the
128 dynamics and mechanisms of nutrient flow and its effect on trophodynamics.

129 The quality (form) of N has long been recognized to influence the relationship between primary
130 producers and fish. Within the field of oceanography, NO_3^- -based food webs are thought to lead to fish
131 (export) production while those based on NH_4^+ more generally support retentive or microbial food webs
132 in nutrient- depleted marine systems, based on the classic concept of “new” and “regenerated” production
133 (Dugdale and Goering, 1967; Eppley and Peterson, 1979; Glibert, 1998). However, the extent to which
134 this dichotomous control of food webs applies in nutrient-enriched coastal systems is unclear. These
135 systems receive significant inputs of “new” N in reduced form and therefore the question remains as to
136 whether total nutrient load or form controls food webs when loadings are high (e.g., Nixon and Buckley,
137 2002). The fundamental ecological question is: How does the nutrient signal propagate through the food
138 web? It has previously been suggested that variance in state variables changes with regime shifts or
139 disturbance (e.g., Carpenter et al., 2007), but examples of trophic changes due to nutrient changes in
140 highly impacted coastal systems are rare.

141 This analysis focuses on those pelagic species whose populations have changed significantly in
142 the San Francisco Estuary over the past decade or more: delta smelt, longfin smelt, striped bass,
143 largemouth bass (*Micropterus salmoides*), inland silversides (*Menidia beryllina*), threadfin shad
144 (*Dorosoma petenense*) and sunfish (*Lepomis* spp.). The delta smelt has undergone significant population
145 declines in the past few years, along with longfin smelt, threadfin shad, and striped bass, while
146 largemouth bass, inland silversides, and sunfish, among other species have recently increased in
147 abundance (Kimmerer et al., 2000; Bennett, 2005; Rosenfield and Baxter, 2007). The latter trends have
148 led to suggestions that increased predation is another factor contributing to declines in smelt and other
149 POD species.

150 The goal of this analysis is to identify key relationships between nutrient concentrations, forms,
151 ratios, and sources and the major components of the food web, from phytoplankton to zooplankton, clams
152 and fish, based on the 30-year term time series from the San Francisco Estuary. In particular, the
153 hypotheses that increased NH_4^+ loading relative to NO_3^- , as well as changes in nitrogen (N) and
154 phosphorus (P) stoichiometry, are related to the changes in dominant fish over time because of their
155 effects on the dominant primary producers. As the dominant functional groups of primary producers in
156 the system changed, so too did the food web leading to fish. Accordingly, this analysis also explores the
157 relationships between nutrient availability and form on the invasive clam, *Corbula amurensis*, as well as
158 its relationship to the food web.

159 This analysis applies the cumulative sums of variability (CUSUM) approach (Page, 1954) to
160 identify trends in nutrients, plankton communities, and fish over time. Comparisons of CUSUM charts of
161 time series data can detect changes not readily apparent in mean values (e.g., Manly and Mackenzie,
162 2003; Mesnil and Petitgas, 2009), and they are sensitive to the timing and directional change in trends.
163 This approach, displaying a running total of deviations from normalized values, was used to compare
164 changes between and among all parameters, i.e., from nutrients to the trophic links to fish. The CUSUM
165 approach, commonly used in some other disciplines, has not been previously applied in an end-to-end
166 (*sensu* Steele et al. 2007) ecological assessment. It provides a powerful tool to test whether a particular

167 variable drives ecosystem change. It is an alternative to complex, multi-parameter, nonlinear models of
168 food web interactions that are often limited by available data or knowledge of key interactions.

169 These nutrient and trophodynamic relationships developed here are also contrasted with those of
170 system water flow. In total, nutrient availability and stoichiometry were found to be more strongly
171 correlated with long-term changes in dominants in each trophic level than was water flow over a multi
172 decadal period. Lastly, given the scientific, management and legal issues related to water management in
173 the Bay Delta, specific management recommendations are suggested for nutrient control that have high
174 probability for success in restoring endangered pelagic fish.

175

176 ***MATERIALS AND METHODS***

177

178 ***Site Description***

179

180 The estuary consists of South San Francisco Bay, Central Bay, San Pablo Bay, Suisun Bay and
181 the Sacramento-San Joaquin Bay Delta, a complex of rivers, channels, wetlands, and floodplains (Fig. 1;
182 Atwater et al., 1979; Nichols et al., 1986; Müller Solger et al., 2002). With exception of the deeper
183 Central Bay, the mean depths of the various sub-embayments in the estuary range from 3.3 to 5.7 m
184 (Kimmerer, 2004). In the context of estuarine typology (e.g., Madden et al., 2010), Suisun Bay is river-
185 dominated, while the South Bay is lagoonal (Kimmerer, 2004). The focus of this analysis is on Suisun
186 Bay, and its main river source, the Sacramento River. Nutrient data are provided from the lower San
187 Joaquin River for comparison.

188 The upper reaches of the Sacramento River drain 61,721 km², while the upper San Joaquin River
189 drains 19,030 km² (Sobota et al., 2009). On a long-term basis, the Sacramento River contributes >80% of
190 river inflow to the Bay Delta, while the San Joaquin delivers ~12%, the remainder coming from minor
191 sources flowing into the Delta from the east (IEP, 2006; Jassby, 2008). River flow has varied by about

192 ten-fold over the past several decades due to effects of El Niño, prolonged droughts, and ENSO wet years
193 (Jassby, 2008).

194

195 ***Overall Approach***

196

197 A retrospective analysis was conducted of 26 to 30 years (depending on variable), spanning 1975
198 (or 1979) to 2005, of monitoring data from the San Francisco Estuary and Bay Delta. Data were obtained
199 from publically available portals that provide long-term monitoring programs of numerous agencies, or,
200 for some recent years, by direct request from state or federal agencies.

201 Although the sources and brief methodological descriptions are given here of the source data, the
202 reader is referred to the actual sources for more thorough metadata descriptions. The analysis here
203 highlights those species which are either dominant, or which have received considerable attention because
204 they represent invasive species that have had effects on the food web. Note that there are no long-term
205 data available on bacteria, ciliates or most other microzooplankton. Kimmerer (2004) provides a more
206 thorough review of the complexities of the food web for San Francisco Estuary.

207

208 ***Data Sources***

209

210 Flow data were obtained from the California Department of Water Resources Dayflow record,
211 <http://www.water.ca.gov/dayflow/>. Dayflow is a computational program that accounts for natural, tidally
212 averaged flows, as well as inflows, exports, and transfers of managed, tidally averaged flow into, within,
213 and out of the Sacramento-San Joaquin Delta (IEP 2006). The Sacramento outflow data were used here.

214 All nutrient, chlorophyll *a* (chl *a*) and phytoplankton data were obtained from the Interagency
215 Ecology Program Bay Delta and Tributary project data portal, <http://www.bdat.ca.gov/>. Nutrient samples
216 were collected from the subsurface on a bimonthly to monthly basis, filtered through Whatman GF/F
217 filters, and frozen until analysis by autoanalyzer techniques. Concentrations of chl *a* were also determined

218 on subsurface samples on a bimonthly to monthly basis. Samples for phytoplankton composition were
219 collected by submersible pump, preserved in Lugol's solution, and subsequently enumerated
220 microscopically to species level. Nutrient data, as NH_4^+ concentration, ratio of dissolved inorganic
221 nitrogen:phosphorus (DIN:DIP), and the ratio of oxidized to reduced inorganic forms of N ($\text{NO}_3^- + \text{NO}_2^-$:
222 NH_4^+) were examined herein. Values for $\text{NO}_3^- + \text{NO}_2^-$ are referred to as NO_3^- . Phytoplankton data, while
223 available as individual species counts, were grouped into dominant functional groups: diatoms, green
224 algae, cryptophytes, other flagellates, and cyanobacteria. For each function group, values were calculated
225 as average species cell number mL^{-1} . The cyanobacterium *Microcystis aeruginosa* has increased in this
226 system since ~1999 (Lehman et al., 2005), but these data are not included in this analysis because they are
227 not in the long-term data base. Picocyanobacteria are also not included herein because they are not
228 routinely enumerated. Where frequency of data was greater than monthly for nutrients or phytoplankton,
229 monthly averages were calculated.

230 Zooplankton data were retrieved from the monthly zooplankton surveys conducted by the
231 California Department of Fish and Game (<http://www.dfg.ca.gov/delta/>). These samples were collected
232 from spring to fall using a Clarke-Bumpus net (154 μm mesh) for meso-zooplankton and, for the micro-
233 zooplankton, a pumped sample was passed through a 43 μm mesh net. All samples were preserved with
234 5% formalin and subsequently enumerated microscopically. This analysis focuses on 3 dominant
235 copepods species, *Eurytemora affinis*, *Pseudodiaptomis forbesi*, and *Limnoithona tetraspina*. The analysis
236 does not include ciliates, other microzooplankton or mysids, nor does it include bacteria.

237 Data on the abundance of the exotic clam *Corbula amurensis* were also obtained from the
238 Interagency Ecological program database (<http://bdat.ca.gov/>). Those samples were collected using a
239 hydraulic winch and Ponar dredge, which samples a bottom area of ~ 0.05 m^2 and which penetrates to
240 variable depths depending on local conditions. Repeated samples are collected and slurried before
241 enumeration according to Standard Methods for the Examination of Water and Wastewater (1998). In the

242 laboratory, identifications were made using a stereoscopic dissecting microscope (70-120x) or a
243 compound light microscope if needed.

244 Fish data were obtained from the California Department of Fish and Game
245 (<http://www.dfg.ca.gov/delta/>). The summer townet surveys (delta smelt only) were conducted by
246 undertaking up to 3, 10-min, stepped, oblique tows using gear with 1.5 m mouth opening attached to a
247 hoop frame and mounted on skis. Surveys were conducted from late June to early August. Fall midwater
248 trawl (FMWT) data were obtained from samples that were collected from 10- min diagonal tows using
249 variable meshes starting with 20 cm at the mouth of the net and tapering to 1.25 cm. One survey was
250 conducted each month from September-December from San Pablo Bay into Sacramento-San Joaquin
251 Delta. Volume- weighted catch-per-unit-effort data for each survey were summed to produce the annual
252 FMWT indices of abundance.

253 Effluent discharges to the upper Sacramento River were compiled by the State Water
254 Contractors (<http://www.swc.org/>) based on monthly discharger self-monitoring reports to the Regional
255 Water Quality Control Board. Although the Sacramento wastewater treatment plant came on line in 1982,
256 NH_4^+ discharge data are only available beginning in 1984. Annual averages of discharge of N and P prior
257 to 1992 have previously been published (Van Nieuwenhuysse, 2007).

258 This analysis emphasizes results from the upper Sacramento River station C3, and Suisun Bay
259 stations D8 and D7, although additional NH_4^+ data from the delta region (station D28) are presented for
260 comparison (Fig. 1). The intervening region between the upper Sacramento River and Suisun Bay
261 encompasses much of the natural habitat for the delta smelt and the other pelagic fish discussed above.

262

263 *Statistical Analysis*

264

265 CUSUM trends were calculated for the 3-decade data record for flow, nutrient concentrations,
266 nutrient ratios, effluent loadings, phytoplankton abundance as chl *a* and as dominant functional groups,
267 and abundance of the major zooplankton, as well as clams and pelagic fish species. There are numerous

268 approaches for CUSUM calculations; the approach herein applies the z-score CUSUM method (Page,
269 1954). All data for which CUSUM scores were calculated were first transformed to z-scores. This
270 involves calculation of a ‘population’ mean and standard deviation, where population refers to all data of
271 that parameter in the time series. Each data point (either monthly or annual, depending on the parameter)
272 was normalized by first subtracting the population mean and then dividing the result by the population
273 standard deviation. The second step in the CUSUM approach is to sum all of the z-scores over time to
274 obtain a long-term trend. The effect of such manipulation is to filter the short term or seasonal variance,
275 thereby revealing the long-term patterns in the data.

276 Although not equivalent, the trends in CUSUM over time for time series data are similar to long-
277 term running averages (Glibert et al., in review). It is the change in CUSUM over time, or the
278 comparison of CUSUM changes in one parameter relative to another, that is of interest. Absolute
279 CUSUM values are not important to the understanding of relationships. Absolute CUSUM values will
280 change depending on the length of the time series, as inclusion of additional data will change the
281 ‘population’ mean and standard deviation. CUSUM curves are particularly useful in identifying change
282 points, or periods when the long-term mean changes from being, for example, above the long-term mean
283 to below the mean. These points in time are identified from inflection points on the curves. Downward
284 trends in CUSUM charts indicate values below the long-term mean and upward trends indicate values
285 above the long-term mean.

286 If CUSUM charts of two different variables exhibit similar ascendancy, descendancy and
287 inflection points, the changes in these variables are correlated. In relating CUSUM charts of one variable
288 to another, it is recognized that such correlations do not equate to correlations of the raw data. The former
289 is a comparison of how the long-term trends in the variables compare, whereas the latter is a comparison
290 of how the concentration of individual parameters compare at any one point in time. Relationships
291 between CUSUM trends for different nutrients or between different components of the food web, as
292 shown herein, allow investigators to infer mechanistic relationships supported by known physiological or
293 trophic relationships, or can lead to further testable hypotheses of the relationships between trophic

294 components. It is in this context that they are used here. As with all correlations, the variables may have a
295 cause-and-effect relationship or both may be related to another variable.

296 All correlations between CUSUM plots were fit to linear models. No attempt was made to
297 examine the fit of the relationships with a temporal offset of one variable relative to another. Refining the
298 fit to these relationships is an ongoing effort; here the goal was to identify broad patterns. All reported
299 CUSUM relationships herein are significant at $p < 0.0001$ unless otherwise indicated; they were not
300 corrected for autocorrelation; all short term variance in these data were removed through the
301 standardization calculation (transformation and summing of z-scores).

302

303 ***RESULTS***

304

305 ***Overview***

306

307 The data presentation in the following sections follows a ‘bottom-up’ approach. Beginning with
308 flow, then nutrients, phytoplankton, zooplankton, clams and fish, each major section starts with the
309 changes over time, followed by their relationships with lower trophic levels and/or nutrients and flow.

310

311 ***Flow***

312

313 The time series encompassed varying Sacramento River flows (Fig. 2A). The early to mid 1980s
314 was a period of relatively high flow and the late 1980s a period of lower flow. The early 1990s was a
315 period of very low flow, but flow increased in the late 1990s and decreased in the early 2000s, but this
316 latter period of low flow was not as low as in the early 1990s. The X2 metric, the isohaline where salinity
317 is 2, is related to flow, as X2 moves inland when flow is low and seaward when flow is high (Fig. 2B).
318 Thus, the CUSUM calculations of flow and X2 are inversely related (Fig. 2A,B).

319

320 *Nutrients*

321

322 Concentrations of NH_4^+ , the dominant inorganic N form in the upper Sacramento River (station
323 C3) and in Suisun Bay (stations D8, D7), approximately 75-80 km downstream, were lower before the
324 mid-1980s than in later years, as evidenced in both the raw data and in the declining CUSUM trends
325 (Figs. 3A-C). NH_4^+ concentrations in the Sacramento and Suisun Bay were high in the late 1980s to early
326 1990s, coincident with the dry period, declined in the late 1990s, and then increased significantly after the
327 year 2000; the upward trend in the CUSUM charts of these sites after 2000 indicates that the NH_4^+
328 concentrations were well above the long-term mean. In contrast to these sites, the concentrations of NH_4^+
329 in the lower San Joaquin River have not fluctuated over the time series to the same degree, and thus the
330 CUSUM trends for this site are different than those of stations C3, D7 or D8 (Fig. 3D). The CUSUM
331 trends for this site show no indication of increasing NH_4^+ since 2000; instead, there has been a decline in
332 these values.

333 The fluctuating concentrations of NH_4^+ are also reflected in the changing $\text{NO}_3^-:\text{NH}_4^+$ ratio in
334 the upper Sacramento and Suisun Bay (Fig. 4). For the upper Sacramento River, the CUSUM trend
335 increased until the mid-1980s, declined, and then increased again in the late 1990s (Fig. 4A). In contrast,
336 the CUSUM chart for this ratio for the Suisun Bay stations declined until about 1990, increased for the
337 next several years, and then declined from 1993 onward (Fig. 4B,C). The CUSUM charts of flow and the
338 ratio of $\text{NO}_3^-:\text{NH}_4^+$ in the receiving waters of the upper Sacramento River revealed similar patterns
339 (compare Figs. 2A and 4A). This is interpreted to mean that under periods of low flow, the point source
340 discharges of NH_4^+ (see below) represented a greater fraction of the total N load in the upper Sacramento
341 River, while under high flow there was greater dilution of the effluent NH_4^+ by other riverine nutrients
342 (Fig. 2). Under very low flow conditions (1987-1993), the ratio of $\text{NO}_3^-:\text{NH}_4^+$ changed to a greater degree
343 from upstream (station C3) to Suisun Bay (stations D7 and D8; Fig. 4), suggesting a greater degree of
344 nitrification was occurring when flow was low. Although quite variable within years, the DIN:DIP ratio
345 was below the long-term mean until the mid-1990s, when there was an increase (Fig. 5).

346 Long-term trends in nutrient concentrations and ratios were related to changes in nutrient loading,
347 with a major source being the Sacramento Regional wastewater treatment plant (Van Nieuwenhuysse,
348 2007; Jassby, 2008). The concentration of NH_4^+ discharged increased from $\sim 10 \mu\text{g L}^{-1}$ when the plant
349 came on line in the early 1980s to $>20 \mu\text{g L}^{-1}$ in the 2000s (Fig. 6A). Concentration of NO_3^- discharged
350 has remained $<1.5 \mu\text{g L}^{-1}$, except for a few periods in the late 1990s (Fig. 6B). Concentration of PO_4^{3-} in
351 the wastewater discharge declined precipitously in the early to mid-1990s (Fig. 6C), coincident with
352 removal of P from domestic detergents by most U.S. manufacturers (Litke 1999). Total nutrient load, a
353 function of changing concentration and volumetric rate of discharge, also increased over time, now
354 averaging $>500 \text{ ML day}^{-1}$ (Fig. 6D). The molar ratio of DIN:DIP of the discharge increased from <10
355 prior to 1994 to >20 in recent years, with few exceptions (Figs. 6E). Thus, the change in DIN:DIP in the
356 upper Sacramento River and in Suisun Bay (Fig. 5) in the 1990s occurred around the same time as the
357 DIN:DIP changed in the effluent discharge.

358 CUSUM trends in NH_4^+ concentration in wastewater effluent over time are highly correlated with
359 CUSUM trends in NH_4^+ concentration in the upper Sacramento River (at C3). For the time period over
360 which NH_4^+ discharge data are available (1992-2005), the R^2 correlation between these trends was 0.70
361 ($n=167$; Fig. 7A), and for the POD period (2000-2005), the R^2 was 0.92 ($n=71$; data not shown).
362 Moreover, CUSUMs for NH_4^+ concentration in the upper Sacramento River (at C3) were highly
363 correlated with those in Suisun Bay (at D8; $R^2=0.92$, $n=246$; Fig. 7B) and at D7 ($R^2=0.95$, $n=246$, data
364 not shown) for the period of 1984-2005.

365 The correlations between flow (dayflow values) and nutrients, as total NH_4^+ , $\text{NO}_3^-:\text{NH}_4^+$ or
366 DIN:DIP were variable for both the upper Sacramento River and Suisun Bay (stations C3 and D8) for the
367 years since the wastewater facility began operation (Fig. 8). In all cases the slope of these correlations
368 were lower in the pre-POD years (1984-1999) than during the POD years (2000-2005). The increase in
369 slope in the POD was related to the increase in NH_4^+ concentrations (Fig. 6).

370

371 ***Phytoplankton***

372

373 Overall phytoplankton biomass as chl *a* was high before 1987, often reaching values $>30 \mu\text{g L}^{-1}$
374 (Fig. 9A). In 1986, these values declined abruptly, and the associated CUSUM chart has an inflection
375 point at this time (Fig. 9A). The CUSUM trend in diatoms indicates that their abundances were above the
376 long-term population mean prior to 1982, but subsequent abundances declined to well below the long-
377 term mean (Fig. 9B). Trends in cryptophytes and green algae were opposite those of chl *a*: these algal
378 groups were not abundant prior to 1986, increased and remained abundant until the late 1990s, and then
379 declined (Fig. 9C). Abundance of other flagellate abundance was high in the mid to late 1980s, and again
380 around 1996 (Fig. 9D). The trend in cyanobacteria was similar to that of cryptophytes through most of the
381 time course, first increasing in the mid 1980s when chl *a* levels were declining, but unlike cryptophytes,
382 cyanobacteria continued to increase since 2000, a trend apparent even when the most recent increase in
383 *M. aeruginosa* was not included (Fig. 9E; Lehman et al., 2005, 2008).

384 When CUSUM charts of NH_4^+ concentration in Suisun Bay and those of major phytoplankton
385 groups were compared, the correlations were all strong, but the relationship was negative for diatoms and
386 positive for the other algal groups (Fig. 10). When these correlations were calculated only for the years
387 since the wastewater treatment plant has been in operation (1984-2005), they were much higher than
388 when the entire period of record was considered. For example, for diatoms, the R^2 with CUSUM NH_4^+
389 increased to 0.83 (n=147), that for cryptophytes increased to 0.76 (n=133) and that for cyanobacteria
390 increased to 0.97 (n=8; not shown).

391

392 ***Copepods***

393

394 The dominant copepod species also changed over time: *E. affinis* declined in 1986, and *P. forbesi*
395 began increasing soon thereafter, and by the late 1990s, both *P. forbesi* and *L. tetraspina* were well
396 established (Fig. 11). For the entire record (1975-2005), the relationship (R^2) between the CUSUM of chl

397 *a* and *E. affinis* is 0.93 (n=360; Fig. 12A). Relationships between different algal groups and copepods
398 varied. The most pronounced were those of other flagellates and *P. forbesi* when it was dominant (1986-
399 2000), a period for which the R^2 of their CUSUMs is 0.53 (n=36; Fig. 12B) and cyanobacteria and *L.*
400 *tetraspina* (1988-2005), a period for which the R^2 of their CUSUMs is 0.96 (n=5, p=0.003; not shown).

401

402 ***Clams***

403

404 The clam *Corbula amurensis* first appeared in significant numbers in Suisun Bay in 1987 (Fig.
405 13). It thus appeared around the same time that the copepod *P. forbesi* began to appear (Fig. 11B), and
406 around the time that the phytoplankton assemblage had increasingly become dominated by cryptophytes
407 and green algae (Fig. 9C). Moreover, the CUSUM of NH_4^+ for Suisun Bay was highly and positively
408 related to that of clam abundance (Fig 14A), as was the CUSUM trend in DIN:DIP (Fig. 14B).

409

410 ***Pelagic Fish***

411

412 Pelagic fish populations changed over time, coincident with changes in lower trophic levels.
413 Delta smelt (estimated from both summer townet or fall midwater trawl indices), as well as longfin smelt,
414 began to decline in ~1982 (Figs. 15A,B). Within roughly a year of the start of the decline in the smelt
415 populations, young-of-the-year striped bass also began to decline (Fig. 15C).

416 The size of delta smelt changed over time as well, becoming smaller around 1990 (Fig. 16). The
417 timing of the change in smelt length corresponded to the time period when *P. forbesi* became established,
418 replacing *E. affinis* as the dominant copepod (Fig. 11).

419 In contrast, other fish species increased in numbers over the time series (Fig. 17), including
420 largemouth bass (Fig. 17A), inland silversides (Fig. 17B), threadfin shad (Fig. 17C) and sunfish (Fig.
421 17D). Largemouth bass and sunfish, in particular, began to increase in the POD years since 2000. Inland
422 silversides and threadfin shad increased in the late 1990s, but subsequently decreased in the POD years.

423 The overall trends in these groups of fish were related to changes in their food. The CUSUM
424 trends in delta smelt (summer townet index), longfin smelt and young-of-the-year striped bass were
425 positively and highly correlated with CUSUM trends in *E. affinis* (Fig. 18), but were negatively correlated
426 with *P. forbesi* and *L. tetraspina* (Fig. 18). The CUSUM trends in delta smelt FMWT index and
427 zooplankton were more complex than those of the summer townet, and these relationships are being
428 developed further elsewhere and thus are not presented here. In brief, they showed a positive correlation
429 with *P. forbesi* for the years after it became dominant, but before the POD collapse. In contrast to smelt
430 and young-of-the-year striped bass, the CUSUM trends in largemouth bass, silversides, threadfin shad
431 and sunfish were all negatively correlated with CUSUM trends in *E. affinis*, but were all (with the
432 exception of largemouth bass and *P. forbesi*) positively correlated with CUSUM trends in the other
433 copepods. Silversides, threadfin shad, and sunfish especially had very strong correlations with *L.*
434 *tetraspina* (Fig. 19F,I,L).

435 Considering that the various planktonic members of the food web were related to nutrient
436 availability and composition, and given that the fish were related to trends in zooplankton, fish
437 abundances were also strongly related to nutrients. CUSUM trends in delta smelt, longfin smelt and
438 young-of-the-year striped bass were negatively correlated with CUSUM trends in NH_4^+ and in DIN:DIP
439 (Fig. 20), while CUSUM trends in largemouth bass, silversides, threadfin shad and sunfish were
440 positively correlated with CUSUM trends in NH_4^+ and in DIN:DIP (Fig. 21)

441 The delta smelt ultimately were related to changes in NH_4^+ of the wastewater discharge in the
442 upper Sacramento River: The relationship between the CUSUM delta smelt summer townet index and
443 CUSUM NH_4^+ discharge was highly significant for the period over which discharge data are available
444 ($R^2=0.97$; $n=13$; Fig. 22).

445 There were no significant relationships between CUSUM trends in fish or clam abundance and
446 the CUSUM of X2 (Table 1).

447

448

449 **DISCUSSION**

450

451 ***Value of the CUSUM Approach***

452

453 The CUSUM approach, originally developed in 1954 (Page, 1954) is only beginning to be used in
454 ecological time series analysis (e.g., MacNally and Hart, 1997; Breton et al., 2006; Mesnil and Petigas,
455 2009). It is more widely used in the manufacturing industry, as well as in public health monitoring of
456 clinical outcomes (e.g., Sibanda and Sibanda, 2007), among other applications. It is similar to other
457 statistical time series approaches involving examination of standard deviations of key variables
458 (Carpenter et al., 2007). The advantages of the CUSUM approach are that it provides visually accentuated
459 patterns making it easy to discriminate timing of shifts in variables, it is insensitive to irregularly spaced
460 data that often occur in long-term time series where collection frequency changes over time, and *a priori*
461 knowledge of relationships is not required, as is the case where parameterization of relationships affects
462 complex multivariate food web models. As there is a great need for ecological models that reliably predict
463 the composition of algal species and assemblages occurring under conditions of changing nutrient loads,
464 the CUSUM approach may allow scientists and managers to investigate relationships and trends that
465 previously were considered too complex to tease apart.

466 The CUSUM approach has recently been applied in several relevant ecological studies of long-
467 term changes in nutrient loading and/or phytoplankton blooms in coastal lagoons or estuaries. For
468 example, it has been applied to the long-term nutrient and plankton relationships in Florida Bay and
469 ecosystem recovery from the effects of hurricanes (Briceño and Boyer, 2010). It has also been applied to
470 an analysis of a 14 year (1988–2001) data set on phytoplankton in the central Belgian Coastal Zone in
471 order to understand the relationships between nutrient loading and the North Atlantic Oscillation (NAO)
472 and a shift in species dominance of the phytoplankton between diatoms and *Phaeocystis* (Breton et al.,
473 2006). In the Coastal Bays of Maryland, CUSUM has been applied to understand the relationships
474 between freshwater flow and increased nutrient loading over a period of 15 years (Glibert et al., in

475 review). Where abiotic and biotic factors are changing, often on different scales, CUSUM is a powerful
476 approach to understand their relationships.

477

478 *Nutrients as a Strong Driver of Trophic Changes Leading to Fish*

479

480 Enrichment of coastal estuaries by nutrients is a function of population growth and intensified
481 production of food and energy (Howarth et al., 2000, 2002; Smil, 2001; Cloern, 2001; Seitzinger et al.,
482 2002; Glibert et al., 2006). Total quantity and composition of nutrients in coastal waters have changed
483 over time (Seitzinger et al., 2002; Burkholder et al., 2006; Glibert et al., 2006), and this can lead to system
484 changes associated with eutrophication, including hypoxia, harmful algal bloom development and loss of
485 submerged aquatic vegetation (Nixon, 1995; Anderson et al., 2002; Glibert and Burkholder, 2006). While
486 N and P loading have increased globally over time, N loading has increased at a rate faster than P loading
487 in many regions (Seitzinger et al., 2002; Glibert et al., 2006), in some cases leading to expressions of
488 eutrophication that differ from those classically considered, including inhibition of primary production by
489 high N (Yoshiyama and Sharp, 2006). There are several reasons for the disparity in N and P loading: first,
490 use of N fertilizers has increased faster than P fertilizers over the past several decades (Glibert et al.,
491 2006, 2010), and, use of P in detergents has declined in the U.S. and many parts of the world (Litke,
492 1999). The shift in the form of N loading noted herein has also occurred in many regions throughout the
493 world because of changes in fertilizer composition (Glibert et al., 2006). Both these changes in total N
494 and P loading and in N form can affect food webs by altering phytoplankton species composition.

495 This analysis has provided an evaluation of the end-to-end, inorganic nutrient-to-fish,
496 relationships in a highly impacted, and historically nutrient-rich estuary. Numerous studies, ranging from
497 whole lake manipulations (e.g., Mills and Chalanchuk, 1987) to oceanic food web analyses (e.g., Steele et
498 al., 2007), have shown that alterations in nutrient loading affect trophic linkages to fish. Here, evidence
499 has been provided that such regime shifts in the San Francisco estuary correspond to periods of abrupt
500 changes in nutrient loading. Regime shifts, fish declines and alterations in zooplankton and

501 phytoplankton in the San Francisco Estuary have been previously described, but have heretofore been
502 attributed to climate change (e.g., Lehman, 2004; Cloern et al., 2007), introductions of invasive species
503 (Cohen and Carlton, 1998; Kimmerer, 2002, 2004) or other abiotic variables, such as water clarity and
504 temperature (Feyrer et al., 2007; Nobriga and Feyrer, 2008). Understanding the factors changing this
505 ecosystem is crucial to water management, but understanding how aquatic trophic cascades are modified
506 by nutrients and other factors is a key scientific question and a major challenge more broadly (e.g.,
507 Carpenter and Kitchell, 1993; Polis and Strong, 1996).

508 The relationships shown here between nutrient composition, concentration, and dominant
509 plankton and fish for the San Francisco Estuary can be conceptualized as 3 different major food webs
510 over time (Fig. 23): a diatom-*Eurytemora*- delta smelt period prior to 1982, a mixed phytoplankton
511 (cryptophytes-green algae-flagellates)-*Pseudodiaptomus*- bass-shad period from 1982--~2000, and a
512 cyanobacteria-*Limnoithona*-silverside-largemouth bass-sunfish period post 2000. The availability and
513 accessibility of long-term monitoring data at both the species-level and nutrient form-level was
514 fundamental in this analysis.

515 Before 1982, chl *a* concentrations in Suisun Bay were relatively high, averaging $\sim 9 \mu\text{g L}^{-1}$, with
516 numerous values exceeding $30 \mu\text{g L}^{-1}$, and diatoms, *E. affinis*, and delta smelt were all abundant. The
517 decline in diatoms, which began in 1982, was highly correlated with the increase in NH_4^+ loading. This
518 relationship illustrates two well known physiological processes. First, although NH_4^+ may be a preferred
519 N form under N limitation, it can be inhibitory at high concentrations (e.g., Syrett, 1981). Second,
520 diatoms prefer and, under some conditions, physiologically require, NO_3^- over NH_4^+ , unlike many other
521 algae which preferentially use NH_4^+ over other N forms (McCarthy et al., 1977; Syrett 1981; Berg et al.,
522 2001; Glibert et al., 2004, 2006). NO_3^- is used in the energy balance of these cells as a photoprotective
523 mechanism (Lomas and Glibert, 1999a,b). As NO_3^- became less available relative to NH_4^+ in Suisun Bay
524 (Fig. 4B,C), the competitive advantage shifted to phytoplankton taxa that can more efficiently use
525 reduced forms of N. Among the phytoplankton groups that replaced diatoms in this system, cyanobacteria

526 and many flagellates have a preference for chemically reduced forms of N (Berg et al., 2001; Glibert et
527 al., 2004, 2006; Brown, 2010). As diatoms declined, so did *E. affinis*. Prey selectivity in zooplankton is
528 well known; diatoms have been shown to support *E. affinis* growth and the proportion of diatoms in their
529 diet, as well as their physiological state, affect copepod egg production and metabolism (Jones and Flynn,
530 2005; Ask et al., 2006).

531 From 1982-1986 chl *a* continued to decline, as did *E. affinis*. The virtual disappearance of chl *a*
532 from Suisun Bay in 1987 has been attributed to the proliferation of the invasive clam, *C. amurensis*,
533 thought to have filtration rates sufficient to remove most of the chl *a* (Kimmerer, 2002; Jassby et al.,
534 2002). As mentioned, this exotic clam became established in Suisun Bay in ~1986-1987, coincident with
535 the collapse in chl *a* (Fig. 13). Its increase was positively correlated with both NH_4^+ and DIN:DIP changes
536 over time (Fig. 14), suggesting that it thrived when the food web changed due to nutrient loading. While
537 clams may have continued to keep phytoplankton chl *a* low due to their filtering, the earlier decline in
538 diatoms (in 1982) is better explained by the inhibitory effect of the elevated NH_4^+ loading than due to the
539 clam invasion. Clams also have been shown to consume *E. affinis* nauplii (Kimmerer et al., 1994), but *E.*
540 *affinis* was already in decline (Fig. 11A) before clams became well established (Fig. 13).

541 One of the largest changes in nutrient loading occurred in the mid 1990s when the N:P ratio
542 roughly doubled (Fig. 5). The change in N:P ratios is evident in wastewater discharge (Fig. 6E), in the
543 upper Sacramento River (Fig. 5A), and in Suisun Bay (Figs. 5B,C). One of the reasons for the alteration
544 in the nutrient ratios is the reduction in P, most likely a result of the removal of P in domestic detergents
545 (Litke, 1999). However, this was not the only change that occurred in ~ 1990. Concentrations of NH_4^+ in
546 the upper Sacramento River and throughout the estuary declined slightly (Fig. 3), likely due to higher
547 flows, leading to greater dilution of the incoming effluent. Thus, the ratio of $\text{NO}_3^-:\text{NH}_4^+$ increased in the
548 upper Sacramento (Fig. 4A) in the mid to late 1990s. This increase led to a very modest increase in
549 diatoms in the upper Sacramento River (not shown), but diatoms were apparently not able to recover in
550 Suisun Bay (Fig. 9B). Their recovery likely was hampered because the DIN:DIP was higher than in the
551 early 1980s. Instead, other flagellates proliferated (Fig. 9D; Brown, 2010), and different copepod species

552 became dominant (Fig. 11). Cryptophytes and green algae were still abundant, but declined in ensuing
553 years (Fig. 9C). The copepods *P. forbesi* and *L. tetraspina* responded to an altered phytoplankton
554 assemblage. *Pseudodiaptomus forbesi* has experimentally been shown to feed on diatoms and
555 dinoflagellates in the laboratory (Bouley and Kimmerer, 2006). In contrast, *L. tetraspina* does poorly
556 when feeding on diatoms (e.g., Kimmerer, 2004; Bouley and Kimmerer, 2006), and it developed after the
557 decline in diatoms. This copepod also consumes ciliates among other food sources, but the available time
558 series data did not allow exploration of this relationship.

559 Cyanobacteria began to increase in the late 1980s (Fig. 9E) although, as noted above, the
560 cyanobacterial abundances reported here are underestimated for the most recent decade (Lehman et al.,
561 2005, 2008, 2010a). Cyanobacteria thus proliferated as the DIN:DIP ratio increased (Fig. 5). It has been
562 suggested that some cyanobacteria can proliferate in low P environments when other algal classes are P-
563 limited, due to their lower P cell quota or their ability to substitute P-containing lipids in membranes with
564 non-P containing lipids under P limitation (Bertilsson et al., 2003; Van Mooy et al., 2009). The
565 proliferation of cyanobacteria during the most recent decade illustrates that nutrient stoichiometry may
566 indirectly, as well as directly, affect phytoplankton assemblages: while cyanobacteria can tolerate
567 elevated N:P levels, its dominance may also reflect the decline in other species without such tolerances.
568 Cyanobacteria do not have to grow faster at elevated N:P than at lower N:P values to become abundant,
569 they merely have to grow faster than competing species groups.

570 Beginning in the early to mid 1980s, the ecosystem was characterized by sharp declines in delta
571 smelt, longfin smelt, and young-of-the-year striped bass (Fig. 15). And, when *P. forbesi* became
572 established and the dominant food for delta smelt, the fish declined in size (Fig. 16). As zooplankton
573 changed, the community of fish did also, with species such as largemouth bass and silversides becoming
574 more prevalent when *E. affinis* began its decline. While smelt is a planktivore, not all the fish studied here
575 are, but all require zooplankton as food at least in their larval or juvenile stages or rely on prey that rely
576 on zooplankton (Kimmerer, 2004). As predators increased, those fish that were in decline due to changes
577 in food supply were subjected to additional stresses of predation. In the most recent decade, there were

578 further declines in smelt, along with silversides and threadfin shad (Fig. 17; e.g., Bennett, 2005; Sommer
579 et al., 2007; Thompson et al., 2010). During this time, NH_4^+ loading from wastewater discharge increased
580 25%, from ~ 9 metric tons day^{-1} to 12 metric tons day^{-1} (the product of Figs. 6A and 6D; Van
581 Nieuwenhuyse, 2007), leading to a strong correlation over the time series of CUSUM trends in
582 wastewater effluent NH_4^+ and the delta smelt (Fig. 22).

583 The elemental composition of fish has been the subject of a considerable number of studies, from
584 fish bioenergetics to whole system nutrient models (e.g., Kraft, 1992; Vanni, 1996; Sterner and George,
585 2000). Fish composition and fish size previously have been related to nutrient availability. Sterner and
586 George (2000) speculated that the P content of fish “relates to their ‘boniness’”. Clearly there is much to
587 be examined with regard to the ecological stoichiometry of all the components of the food web and how
588 changes in the nutrient availability may be related not only to the food web of the San Francisco Estuary,
589 but to the metabolism of dominant fishes as well.

590

591 *Relationships of Fish Abundance with Food vs. Flow*

592

593 This analysis was not intended to be a review of X2, its relationships, or the management thereof;
594 there have been numerous other such efforts and others are ongoing. Instead, this analysis reviewed
595 nutrients and their food web effects. The overwhelming conclusion here is the fact that relationships
596 between nutrients and fish are stronger than those of flow and fish (comparison of Figs. 20, 21 and Table
597 1). Furthermore, changes in flow are not correlated with all nutrients and nutrient ratios over the entire
598 time series (Fig. 8), although there were significant, but different, relationships for the pre-POD and the
599 POD years. The slope of the relationship between CUSUM flow and nutrients changed in the POD years,
600 coincident with the increase in effluent NH_4^+ discharge, a major driver of NH_4^+ concentrations and the
601 nutrient ratios shown.

602

603

604 *Nutrient Management Implications*

605

606 Water management in California is challenging and contentious, and a significant fraction of the
607 water supply for state needs is extracted from the Delta. This is done through extensive waterways and
608 engineering projects exporting water from the Delta, via pumps and aqueducts, to the southern, drier, part
609 of the state (Brown et al., 2009). In recent years, restrictions in water use have been mandated through
610 federal court decisions because of declines in delta smelt abundance and its listing as a threatened and/or
611 endangered species (Wanger, 2007a,b). Water restrictions are thought to be required to reduce further loss
612 of these fish by entrainment in export pumps. However, management strategies to date have not reversed
613 fish declines because they have not addressed the ultimate cause of the change at the base of the food web
614 and the complex role of nutrient form and quantity. When food web analyses are not linked to ultimate
615 causes of change, management guidance is inconclusive, as in the MacNally et al. (2010) multivariate
616 analysis of fish decline in the Delta. MacNally et al. (2010) state, “The relatively large proportions of
617 variance explained by interactions among the declining fishes and their prey suggest that trophic
618 interactions also are important, but it is less clear how management actions could modify such
619 relationships.”

620 The present study supports the premise that reduction of the NH_4^+ effluent into the Bay Delta is
621 essential to restoring historic pelagic fish populations and that until such reductions occur, other
622 measures, including regulation of water pumping or manipulations of salinity, as has been the current
623 strategy, will likely show little beneficial effect. By altering nutrient composition and nutrient load, it is
624 likely that a healthy phytoplankton assemblage including diatoms could be restored. A clear management
625 path is the application of nitrification and denitrification processing of the dominant nutrient source, the
626 wastewater effluent, prior to discharge into the estuary to 1) decrease NH_4^+ concentration in the river; 2)
627 reduce N:P ratio of the effluent; and 3) increase $\text{NO}_3^-:\text{NH}_4^+$ ratio to a level required to increase diatom
628 abundance to support a more favorable food web for fish production (Fig. 22). Pre-1982 nutrient
629 concentrations and ratios could serve as a management target. Historic data can serve as the “reference

630 condition” to establish numeric nutrient criteria when, as is the case here, there is knowledge of how the
631 system functioned prior to the nutrient loading impacts (U.S. EPA 2001, 2010).

632 The findings herein point to an important consideration in the development of numeric criteria for
633 nutrients in estuaries, a challenge that many states are now facing (U.S. EPA 2010; Glibert, 2010). Many
634 such criteria, or integrated indices of water quality status and trends, are based on total N or P, rather than
635 specific forms of N or P (U.S. EPA 2010). These findings show that nutrient form is related to the
636 “quality” of phytoplankton. Thus, nutrient forms or ratios should be considered in criteria development if
637 effects on food webs are to be related to such criteria.

638 Prior studies in the Bay Delta suggested that phytoplankton assemblage composition and total
639 phytoplankton biomass were related to NH_4^+ availability or dissolved inorganic N:P ratios (Wilkerson et
640 al., 1996; Dugdale et al., 1997; Van Nieuwenhuysse 2007). However, there have been no prior efforts
641 linking these changes through the food web. In fact, the suggestion that nutrient loading (particularly
642 NH_4^+) affects the food web was discounted because it was assumed that NH_4^+ is a preferred form of N for
643 phytoplankton uptake (of all species), and in order to have effects on higher trophic levels, the levels must
644 be in the range causing direct toxicity. The pH of the receiving waters prevents formation of the toxic
645 NH_3 , and NH_4^+ levels are generally below levels considered by the U.S. Environmental Protection
646 Agency criteria for fish habitat (McCarthy et al., 1977; Millero, 2006; U.S. EPA 2009). The latter treats
647 NH_4^+ as a toxicant. The more subtle ecological impacts of NH_4^+ loading and the importance of changes in
648 $\text{NO}_3^-:\text{NH}_4^+$ in phytoplankton succession have not been appreciated. Moreover, the potential for P
649 limitation (Van Nieuwenhuysse, 2007) has not been given full consideration because the concentrations are
650 not at levels normally taken to be indicative of limitation, i.e., less than the half saturation constant for
651 uptake (e.g. Reynolds, 2006; Jassby, 2008). The analysis herein reconciles the seeming inconsistencies of
652 the nutrient regulation hypotheses advanced by Wilkerson et al. (2006) and Dugdale et al. (2007) and by
653 Van Nieuwenhuysse (2007). While Wilkerson et al. (2006) and Dugdale et al. (2007) have suggested that
654 the controlling nutrient is N, especially NH_4^+ inhibition, Van Nieuwenhuysse (2007) suggested that P
655 limitation was limiting to phytoplankton. From the analysis here, it appears that both have had significant

656 effects on phytoplankton communities, but their major effects have occurred at different points along the
657 time course.

658 The changes in food web structure with changes in nutrient form and/or nutrient ratio suggest that
659 the Eppley and Peterson (1979) paradigm applies in this nutrient rich estuary. That paradigm, which
660 suggests that NO_3^- -based food webs are fundamentally different from those of NH_4^+ -based food webs,
661 was originally developed for oligotrophic, oceanic waters. Here, as in the oceanic condition, NO_3^- -based
662 food webs were supported by higher proportions of diatoms and the NH_4^+ -based food webs were
663 supported by higher proportions of flagellates, cryptophytes and cyanobacteria. Both food webs supported
664 fish, although different species.

665 The analysis described here should be highly relevant to other systems that have been subject to
666 alterations in N and P loading and N form. The fact that chl *a* declined over time as N loading increased
667 has deflected management attention away from nutrients. It is counterintuitive to the normal progression
668 of eutrophication, typically resulting in higher algal biomass and a shift from benthic to pelagic
669 production (Cloern, 2001). The inhibitory effect of NH_4^+ on diatoms seen here has, however, been
670 observed in other estuaries, such as the Delaware Estuary and the inner bay of Hong Kong Harbor
671 (Yoshiyama and Sharp, 2006; Xu et al., 2010). In the Delaware Estuary, inhibition by NH_4^+ was greatest
672 in the colder months, when diatoms dominated (Yoshiyama and Sharp, 2006). From a management
673 perspective, not only is near-field alteration of phytoplankton growth important, but so too is the potential
674 for large down-stream impacts - impacts not often associated with discharges far removed in space. In this
675 study, CUSUM trends in discharge of NH_4^+ from the treatment plant were highly related to those of NH_4^+
676 concentrations far downstream, ~80 km from the treatment plant (Fig. 7). The Sacramento River acted as
677 a conduit for transport of N downstream.

678 Supporting the idea that correct balance of nutrients is important for restoration of delta smelt and
679 other pelagic fish, there is a small but apparently successful subpopulation of delta smelt in a restored
680 habitat, Liberty Island. Liberty Island is outside the immediate influence of Sacramento River nutrients. It
681 has abundant diatoms among a mixed phytoplankton assemblage, as well as lower NH_4^+ levels and higher

682 ratios of $\text{NO}_3^-:\text{NH}_4^+$ than the main Sacramento River (Lehman et al., 2010b). Thus, if efforts are made to
683 restore additional habitat, consideration should be given to location of the habitat to be restored relative to
684 the main sources of nutrients. This system demonstrates that alterations in nutrient forms do indeed alter
685 food webs, even when all major nutrients are abundant, as was the case prior to 1994, or when one
686 nutrient (in this case P) is controlled, as is the current condition in the upper Sacramento River.
687 Additionally, nutrients that are abundant when one nutrient is controlled can be displaced in space, having
688 significant effects on the ecology and food chain downstream. The CUSUM approach was an effective,
689 sensitive, simple means to detect these relationships. These relationships also lead to directly testable
690 hypotheses and experiments that can further understanding about the role of changing nutrient loads and
691 composition on the dynamics of the food web in this system

692

693 **SUMMARY**

694

695 Nutrient changes in concentration and form in the San Francisco Estuary and Bay Delta are
696 significantly correlated with changes in components of the food web over time. These changes are highly
697 related to loadings from a single major point source. The long-term changes in NH_4^+ , the dominant N
698 form that is discharged from the Sacramento River effluent plant are similar in the upper Sacramento
699 River (C3) and 80 km in Suisun Bay (D8 and D7). However, they are not similar in lower San Joaquin
700 River (D28), consistent with previous findings that inflow from the Sacramento River and its chemical
701 constituents dominate over those of the San Joaquin. Changes in nutrient loadings and forms were related
702 to changes in the phytoplankton assemblage, which in turn were related to changes in zooplankton, and in
703 turn, related to clam abundance, and to the abundance of various fish species. The invasive copepods *P.*
704 *forbesi* and *L. tetraspina* became dominant when the phytoplankton community shifted from diatom to
705 flagellate and cyanobacterial dominance. Fish species fell into two groups: those whose long-term,
706 CUSUM trends were positively correlated with trends in abundance of *E. affinis* and negatively correlated
707 with *P. forbesi* and *L. tetraspina*, and those whose long-term, CUSUM trends were negatively correlated

708 with *E. affinis* and positively correlated with *P. forbesi* and *L. tetraspina*. Trends in the former group of
709 fish also were related negatively to trends in NH_4^+ and DIN:DIP, while the opposite pattern emerged for
710 the latter group of fish species. Long-term trends in abundance of the clam, *C. amurensis*, were also
711 highly related to trends in NH_4^+ and DIN:DIP, suggesting that this invasive species was opportunistically
712 responding to a change in ambient conditions when it proliferated. All of these relationships were
713 significantly more robust than relationships with flow or X2; there were no significant relationships
714 between the CUSUMs of X2 and nutrients, phytoplankton species, zooplankton or fish over the entire
715 time series. Thus, a clear management strategy is the regulation of effluent N discharge through
716 nitrification and denitrification. Until such reductions occur, other measures, including regulation of water
717 pumping or manipulations of salinity, as has been the current strategy, will likely show little beneficial
718 effect. Without such action, the recovery of the endangered pelagic fish species is unlikely at best.

719

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721

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971 **Figure Legends**

972 Figure 1. Map of the Sacramento-San Joaquin Estuary, with sites of the major wastewater discharge site
973 in the upper Sacramento River, and the sites of data analyzed herein indicated.

974

975 Figure 2. CUSUM values (primary axis, filled diamonds) as a function of time for A) flow, estimated
976 from Dayflow (see text) and B) X2, the distance in km from the Golden Gate Bridge where the isohaline
977 is 2. The secondary axis (open squares) for both panels gives the actual data in the units indicated. The
978 vertical dashed lines are guides to delineate the major periods discussed in text.

979

980 Figure 3. CUSUM values (primary axis, filled diamonds) as a function of time for ammonium (NH_4^+)
981 concentrations for A) the upper Sacramento at station C3, B and C) Suisun Bay at stations D8 and D7,
982 and D) the lower San Joaquin at station D28. The secondary axis (open squares) for all panels gives the
983 actual data in $\mu\text{g L}^{-1}$. The vertical dashed lines are guides to delineate the major periods discussed in text.

984

985 Figure 4. CUSUM values (primary axis, filled diamonds) as a function of time for the ratio of nitrate:
986 ammonium ($\text{NO}_3^-:\text{NH}_4^+$) concentrations for A) the upper Sacramento at station C3, B and C) Suisun Bay
987 at stations D8 and D7. The secondary axis (open squares) for all panels gives the actual data in $\mu\text{g L}^{-1}:\mu\text{g}$
988 L^{-1} . The vertical dashed lines are guides to delineate the major periods discussed in text.

989

990 Figure 5. CUSUM values (primary axis, filled diamonds) as a function of time for the ratio of dissolved
991 inorganic nitrogen:phosphorus (DIN:DIP) concentrations for A) the upper Sacramento at station C3, B
992 and C) Suisun Bay at stations D8 and D7. The secondary axis (open squares) for all panels gives the

993 actual data in $\mu\text{g L}^{-1}$: $\mu\text{g L}^{-1}$. The vertical dashed lines are guides to delineate the major periods discussed
994 in text.

995

996 Figure 6. Nutrient concentrations (mg L^{-1}) of the wastewater effluent as a function of time for A) NH_4^+ ,
997 B) $\text{NO}_3^- + \text{NO}_2^-$, C) PO_4^{3-} , D) the volumetric daily rate of effluent discharge (ML day^{-1}) from the
998 wastewater facility, and E) the molar ratio of dissolved inorganic nitrogen:phosphorus (DIN:DIP) for the
999 major wastewater treatment facility in the upper Sacramento River. Although the plant came on line in
1000 1982, monitoring data are only available from 1992.

1001

1002 Figure 7. (A) Correlation between the CUSUM trend in NH_4^+ concentration in wastewater discharge and
1003 that in the upper Sacramento River for the period of discharge data availability (1992-2005); and (B)
1004 Correlation between the CUSUM trend in NH_4^+ concentration in the upper Sacramento River at station
1005 C3 and that in Suisun Bay at station D8 (1984-2005).

1006

1007 Figure 8. Correlation between the CUSUM trend in dayflow and the CUSUMS of (A) NH_4^+ at C3; (B)
1008 ratio of $\text{NO}_3^-:\text{NH}_4^+$ at C3; (C) ratio of DIN:DIP at C3; (D) NH_4^+ at D8; (E) ratio of $\text{NO}_3^-:\text{NH}_4^+$ at D8; (F)
1009 ratio of DIN:DIP at D8. All trends are for the period since the establishment of the wastewater treatment
1010 facility in the upper Sacramento (1984-2005). For each panel, the open triangles are for 1984-1999 and
1011 the closed circles are for the POD years, 2000-2005.

1012

1013 Figure 9. CUSUM values (primary axis) as a function of time for A) total chlorophyll *a* (filled diamonds)
1014 in Suisun Bay at station D8, B) diatom abundance (filled diamonds) at station D8, C) cryptophytes (filled

1015 diamonds) and green algae (gray circles) at station D8, D) total flagellates (filled diamonds) and
1016 dinoflagellates (gray circles) at station D8, and E) cyanobacteria at station D8 (filled diamonds) and at
1017 station C3 (gray circles). The secondary axis (open squares) for all panels gives the actual data in $\mu\text{g L}^{-1}$
1018 (panel A) or in average per species cells mL^{-1} (panels B-E). Actual data for green algae (panel C),
1019 dinoflagellates (panel D) and cyanobacteria at station C3 (panel E) are not shown. The vertical dashed
1020 lines are guides to delineate the major periods discussed in text.

1021

1022 Figure 10. Correlations between the CUSUM trends in NH_4^+ and A) diatoms; B) Cryptophytes; C) Green
1023 algae; D) Cyanobacteria; and E) Flagellates

1024

1025 Figure 11. CUSUM values (primary axis, filled diamonds) as a function of time for the major copepods
1026 A) *Eurytemora affinis*, B) *Pseudodiaptomus forbesi*, and C) *Limnoithona tetraspina* in Suisun Bay. The
1027 secondary axis (open squares) gives the actual abundance data in number of individuals m^{-3} . The vertical
1028 dashed lines are guides to delineate the major periods discussed in text.

1029

1030 Figure 12. Correlations between the CUSUM trends in A) chlorophyll *a* at station D8 and the copepod
1031 *Eurytemora affinis* in Suisun Bay, and B) flagellate abundance at station D8 and the copepod
1032 *Pseudodiaptomus forbesi*.

1033

1034 Figure 13. CUSUM values (primary axis, filled diamonds) as a function of time for the clam *Corbula*
1035 *amurensis*. The secondary axis (open squares) gives the actual abundance data in individuals m^{-2} . The
1036 vertical dashed lines are guides to delineate the major periods discussed in text.

1037

1038 Figure 14. Correlations between the CUSUM trends in A) NH_4^+ and B) DIN:DIP and the abundance of
1039 the clam *Corbula amurensis*.

1040

1041 Figure 15. CUSUM values (primary axis, diamonds, triangles) as a function of time for the fish A) delta
1042 smelt, *Hypomesus transpacificus* (fall midwater trawl- filled diamonds, summer townet-open diamonds),
1043 B) longfin smelt, *Spirinchus thaleichthys*, and C) young-of-the-year striped bass, *Morone saxatilis*. The
1044 secondary axis (open squares) gives the actual data based on fall midwater trawl index. The vertical
1045 dashed lines are guides to delineate the major periods discussed in text.

1046

1047 Figure 16. CUSUM values (primary axis, diamonds, triangles) as a function of time for the delta smelt,
1048 *Hypomesus transpacificus* length. The secondary axis (open squares) gives the actual data. The vertical
1049 dashed lines are guides to delineate the major periods discussed in text.

1050

1051 Figure 17. As for Figure 15, except for largemouth bass (*Micropterus salmoides*), inland silversides
1052 (*Menidia beryllina*), threadfin shad (*Dorosoma petenense*) and sunfish (*Lepomis* spp.). Actual data for
1053 threadfin shad are based on the fall midwater trawl survey, and for largemouth bass, inland silversides,
1054 and sunfish are based on estimates of the annual average catch per tow across stations regularly occupied
1055 by delta smelt.

1056

1057 Figure 18. Correlations between the CUSUM trends in the copepods *Eurytemora affinis*,
1058 *Pseudodiaptomus forbesi* and *Limnoithona tetraspina* in Suisun Bay and CUSUM trends in delta smelt

1059 (panels A-C; summer townet index), longfin smelt (panels D-F) and young-of-the-year striped bass
1060 (panels G-I). All correlations cover the period 1975-2005 for *E. affinis*, and 1987-2005 for the other
1061 copepods.

1062

1063 Figure 19. As for Figure 18, except for largemouth bass (panels A-C), inland silversides (panels D-F),
1064 threadfin shad (panels G-I) and sunfish (panels J-L).

1065

1066 Figure 20. Correlations between the CUSUM trends in NH_4^+ and DIN:DIP at station D8 in Suisun Bay
1067 and CUSUM trends in delta smelt (panels A-B; summer townet index), longfin smelt (panels C-D) and
1068 young-of-the-year striped bass (panels E-F). All correlations cover the period 1975-2005.

1069

1070 Figure 21. As for Figure 20, except for largemouth bass (panels A-B), inland silversides (panels C-D),
1071 threadfin shad (panels E-F) and sunfish (panels G-H).

1072

1073 Figure 22. Correlation between the trend in CUSUM in NH_4^+ concentration in wastewater discharge in
1074 the upper Sacramento River and the trend in CUSUM delta smelt, estimated from the summer townet
1075 index.

1076

1077 Figure 23. Conceptual diagram of some of the hypothesized changes in the food chain from
1078 phytoplankton to fish that have occurred in the Sacramento-San Joaquin Estuary over the past 30 years.
1079 Each of these hypothesized food chains has different dominant nitrogen forms or amounts relative to
1080 phosphorus. This conceptual model is intended simply to highlight some of the major flows of energy and

1081 materials and does not include all organisms, pathways or flows. The size of the symbols is meant to
1082 infer relative importance.

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1084



Fig. 1

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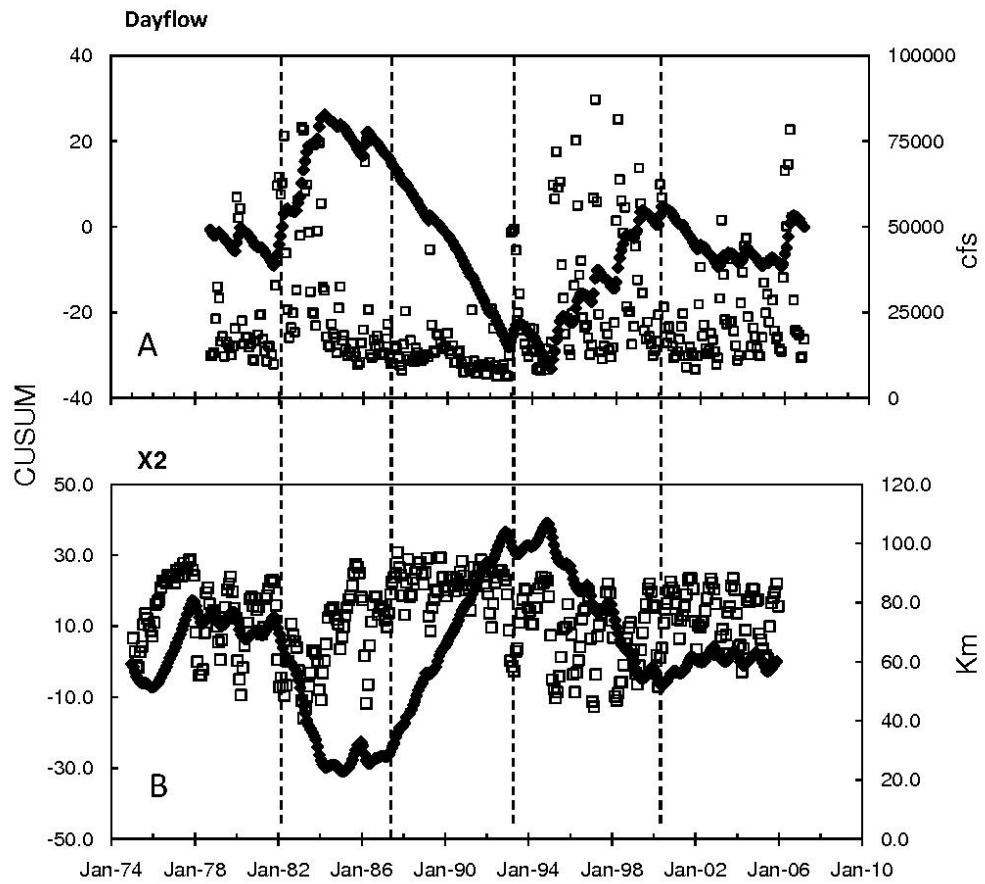


Fig. 2

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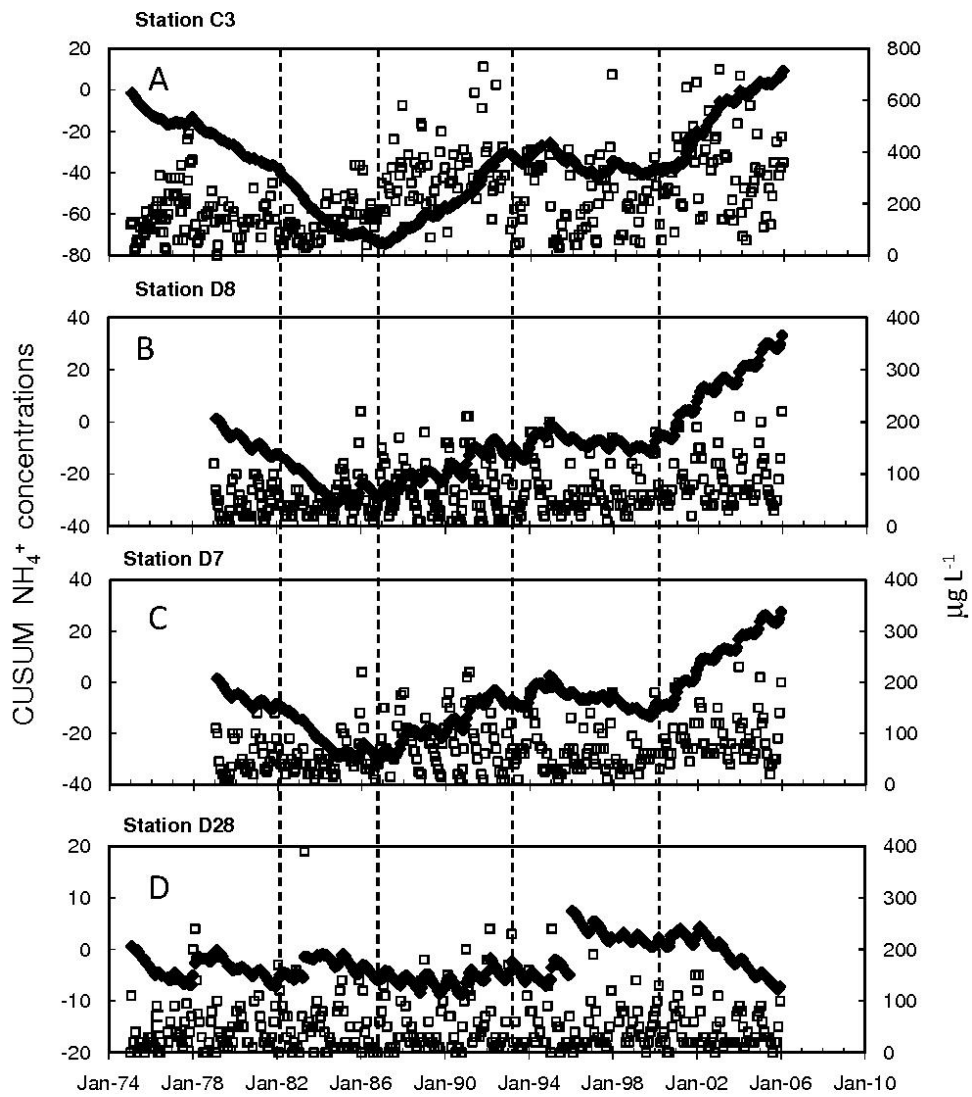


Fig. 3

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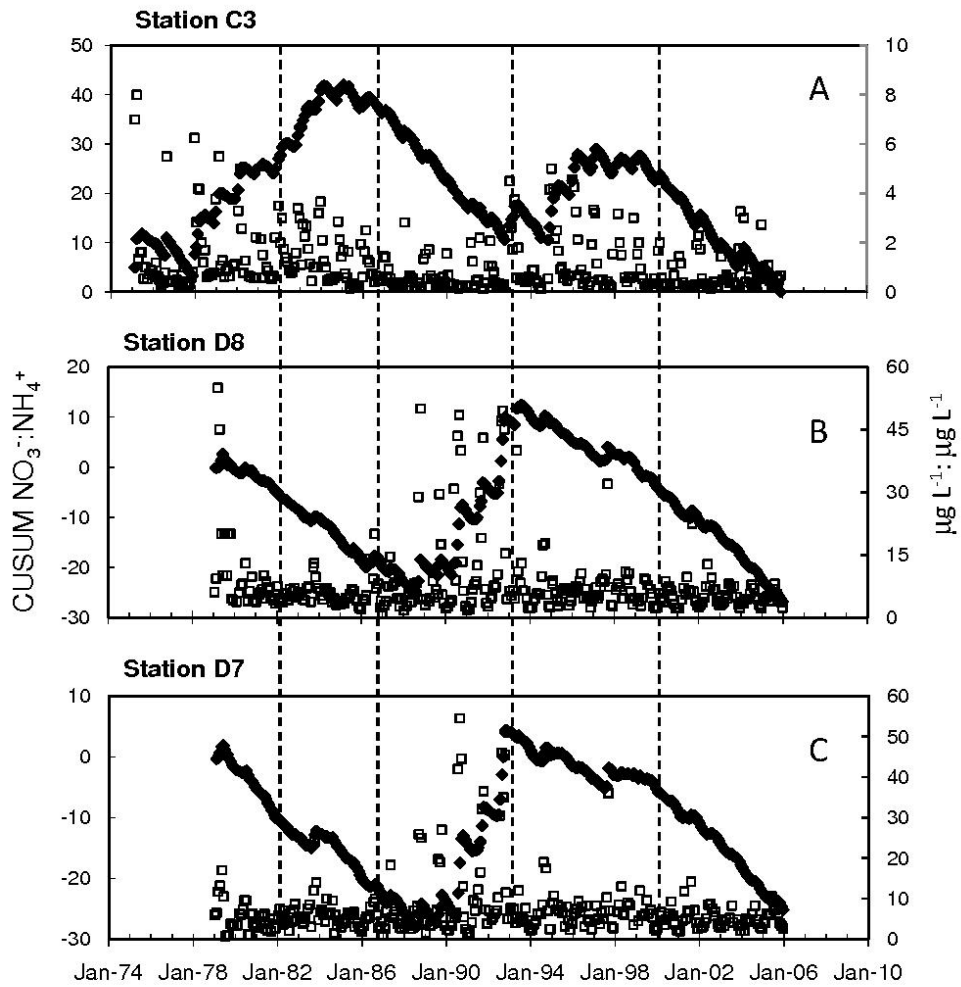


Fig. 4

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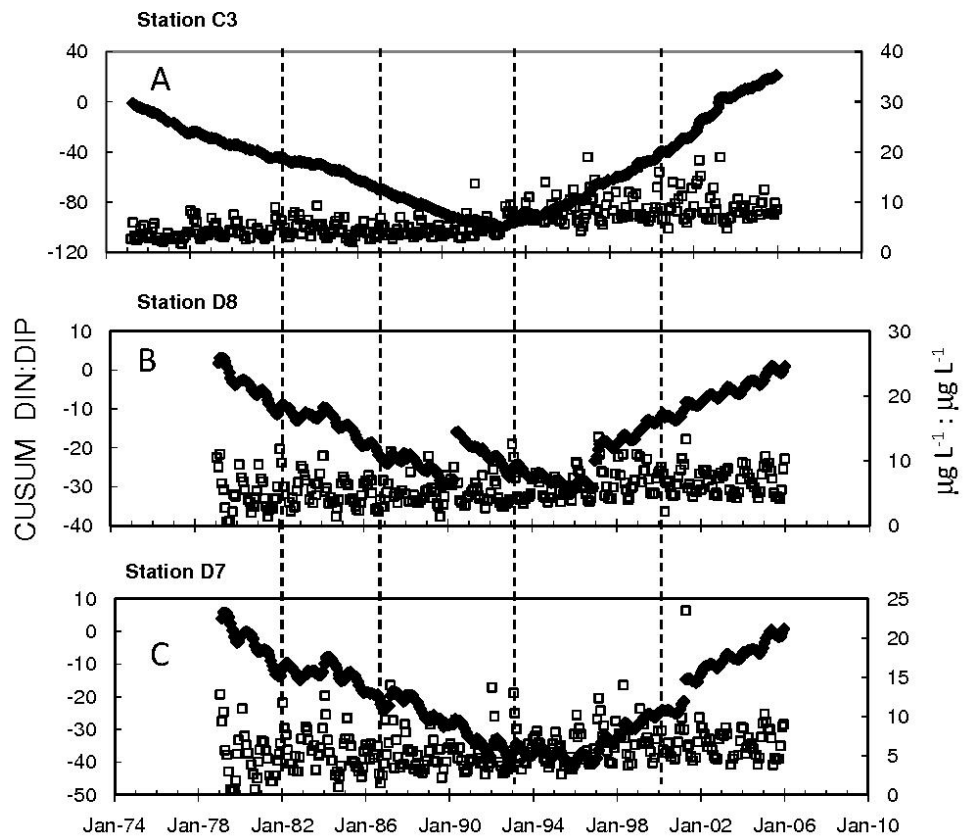


Fig. 5

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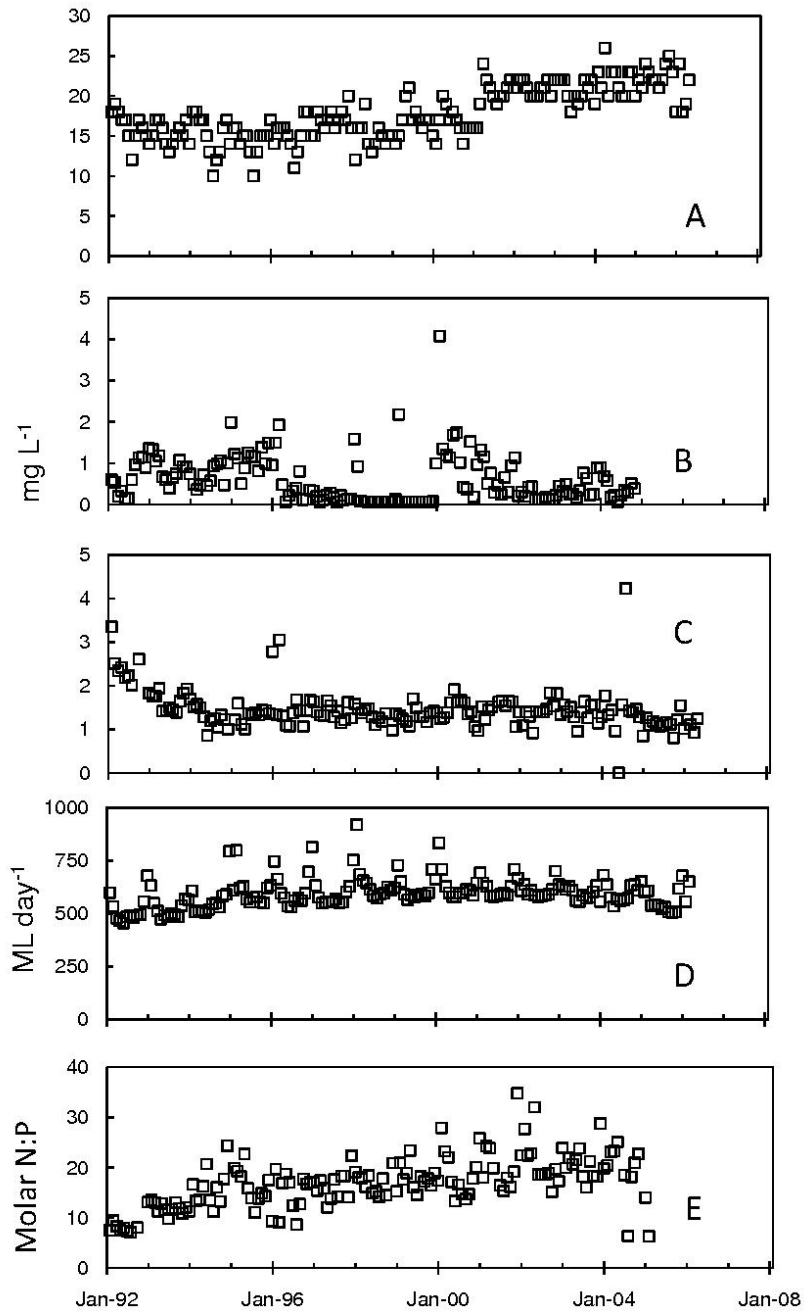


Fig. 6

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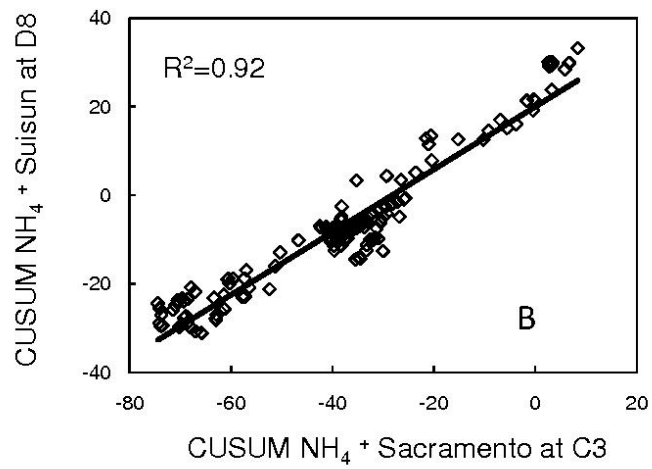
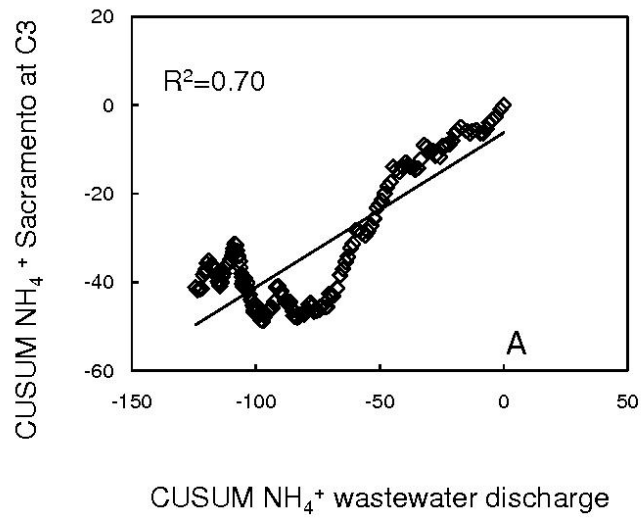


Fig. 7

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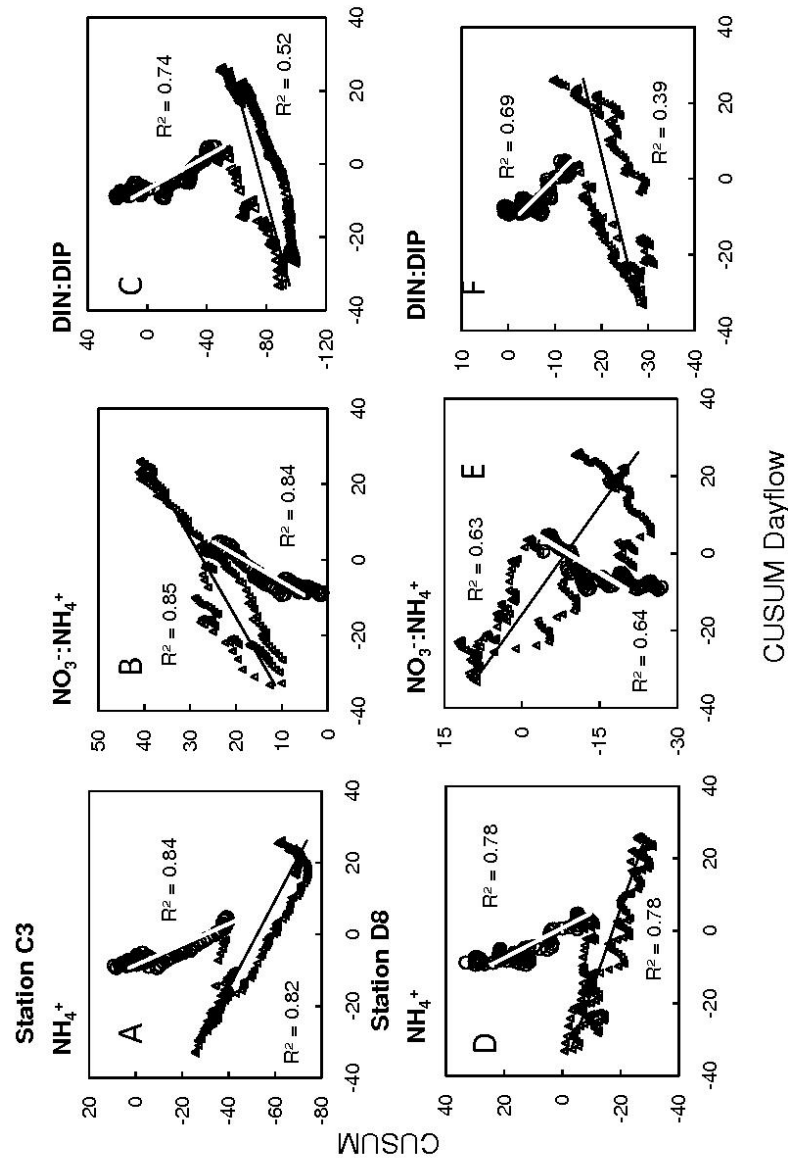


Fig. 8

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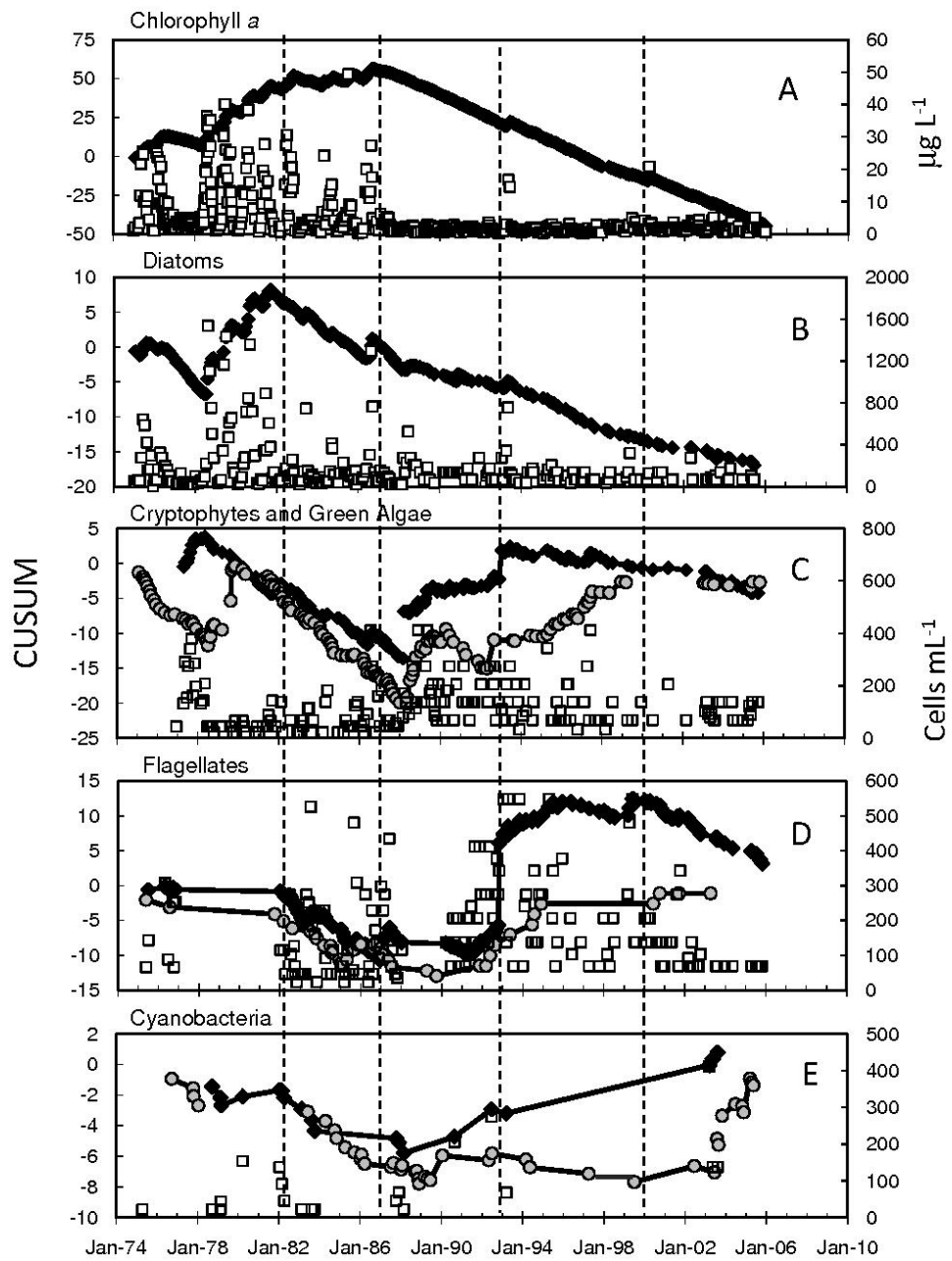


Fig. 9

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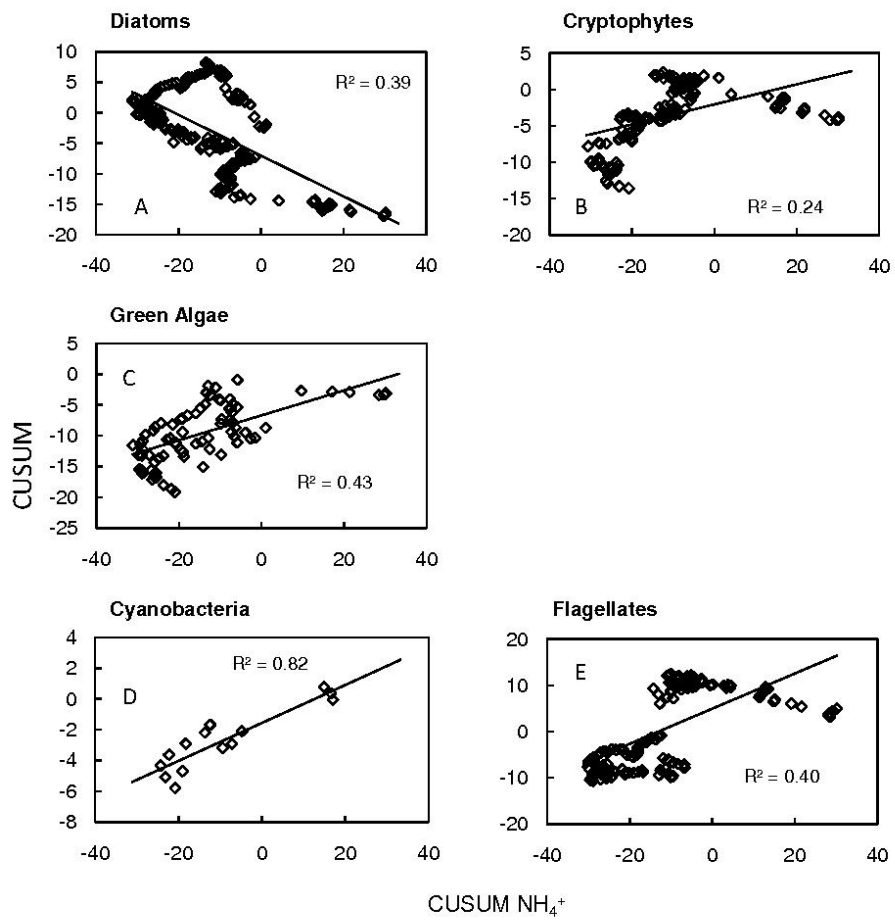


Fig. 10

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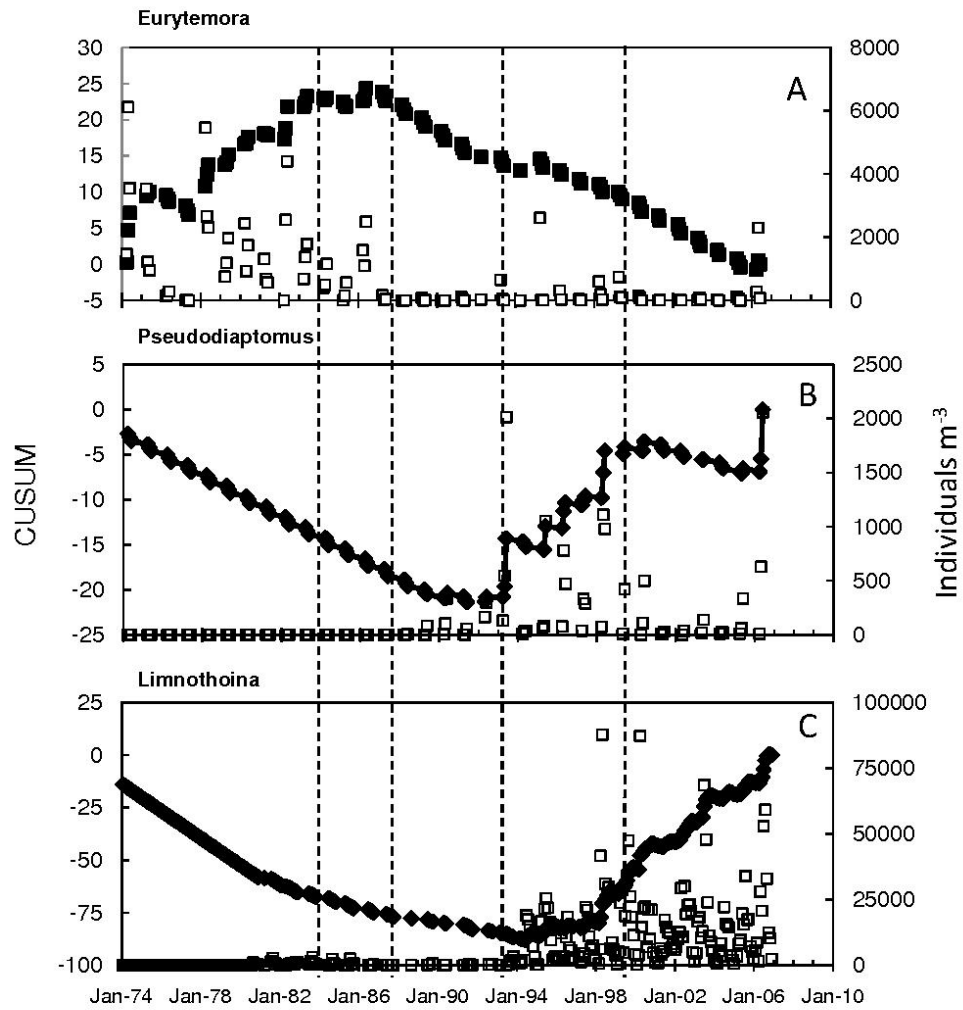


Fig. 11

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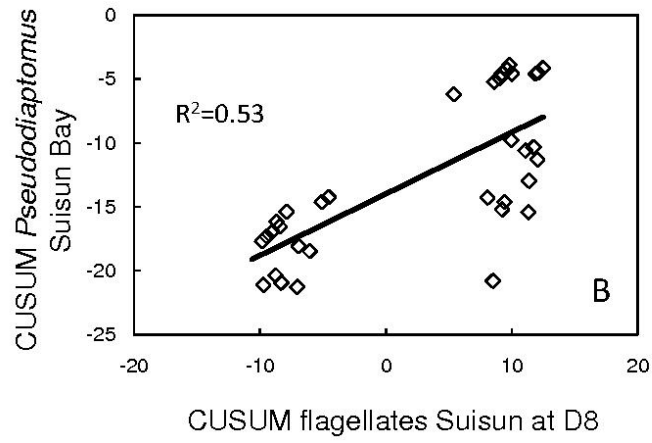
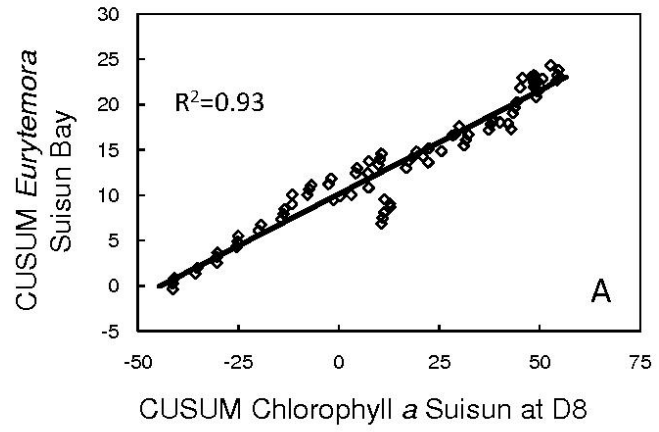


Fig. 12

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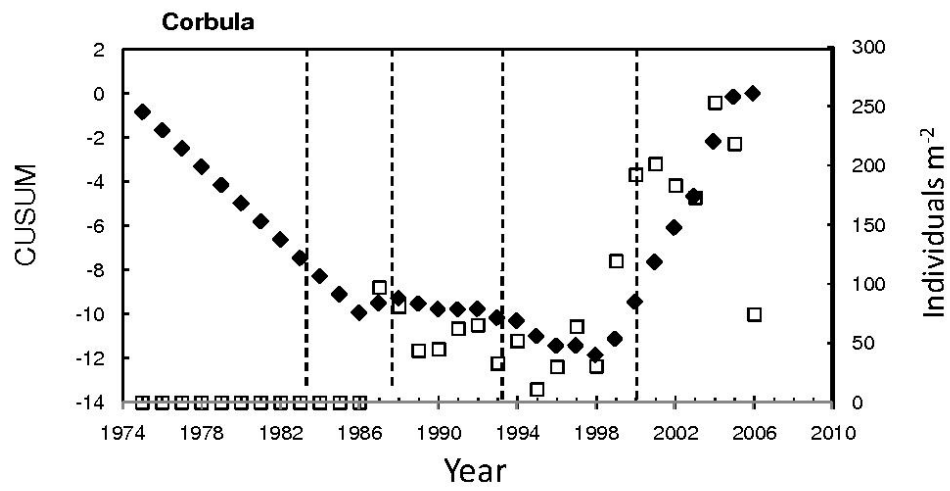


Fig. 13

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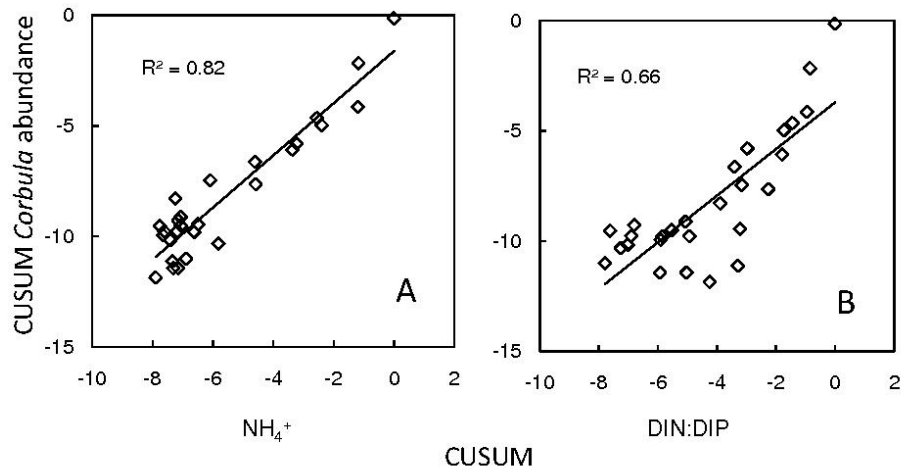


Fig. 14

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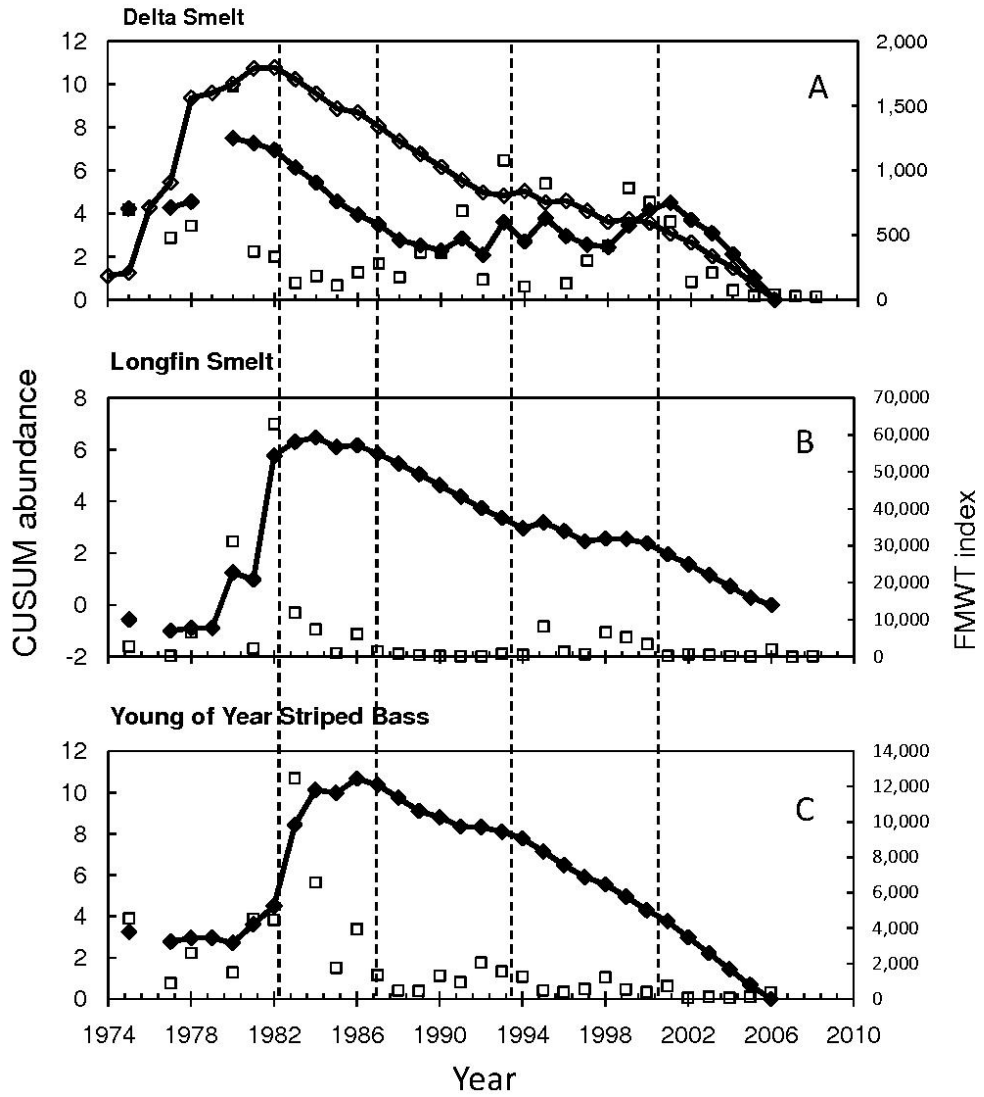


Fig. 15

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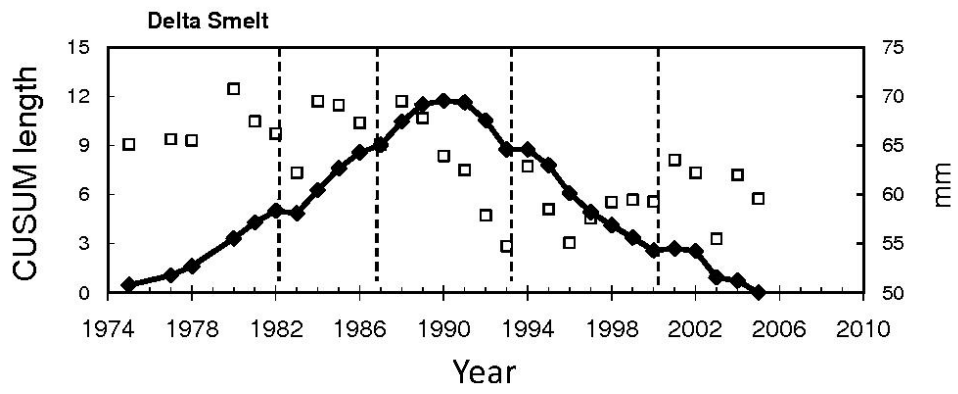


Fig. 16

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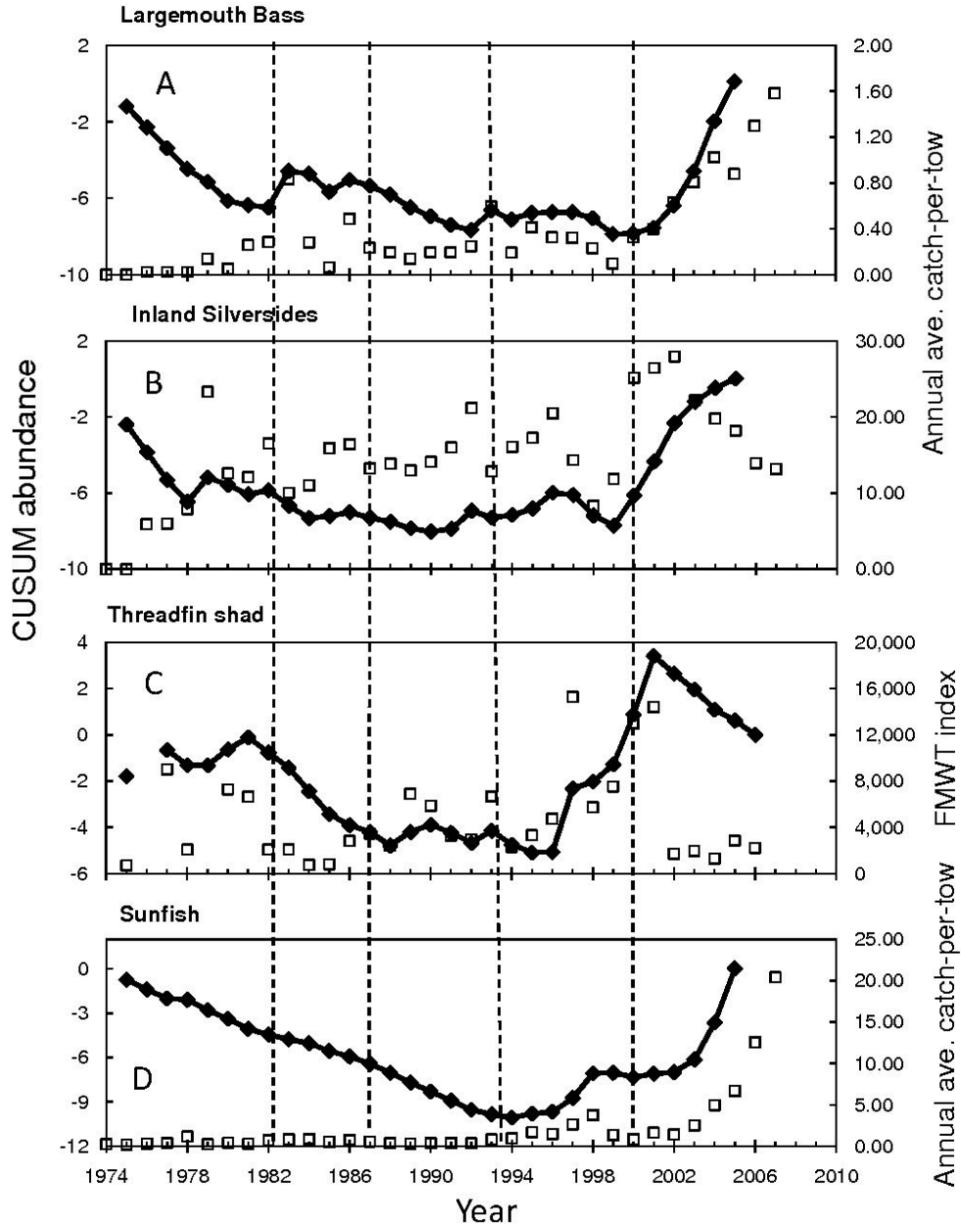


Fig. 17

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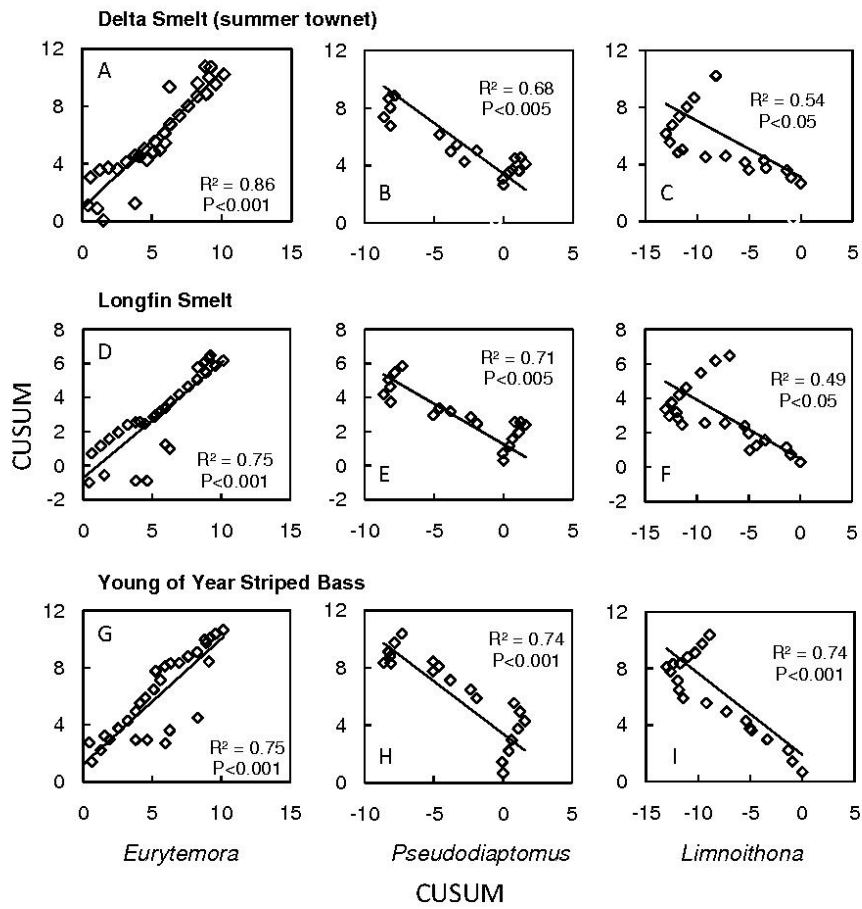


Fig. 18

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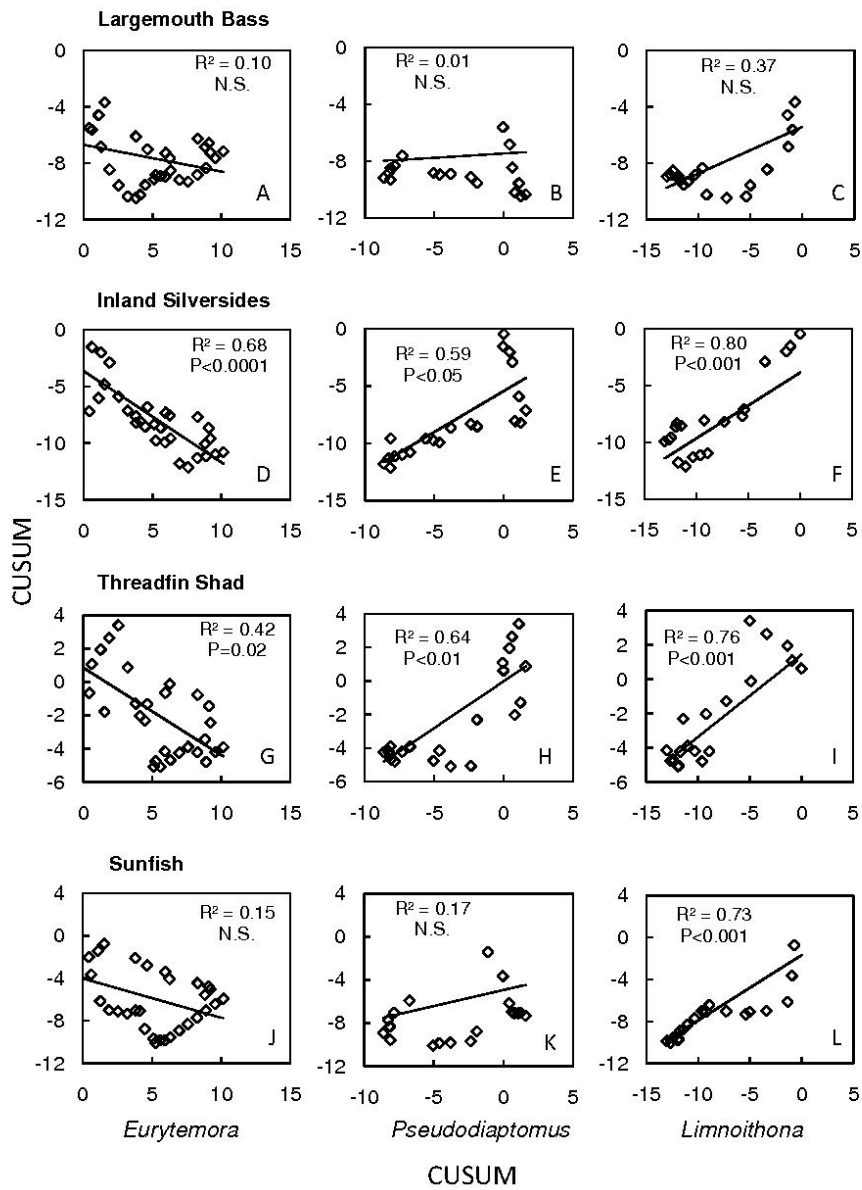


Fig. 19

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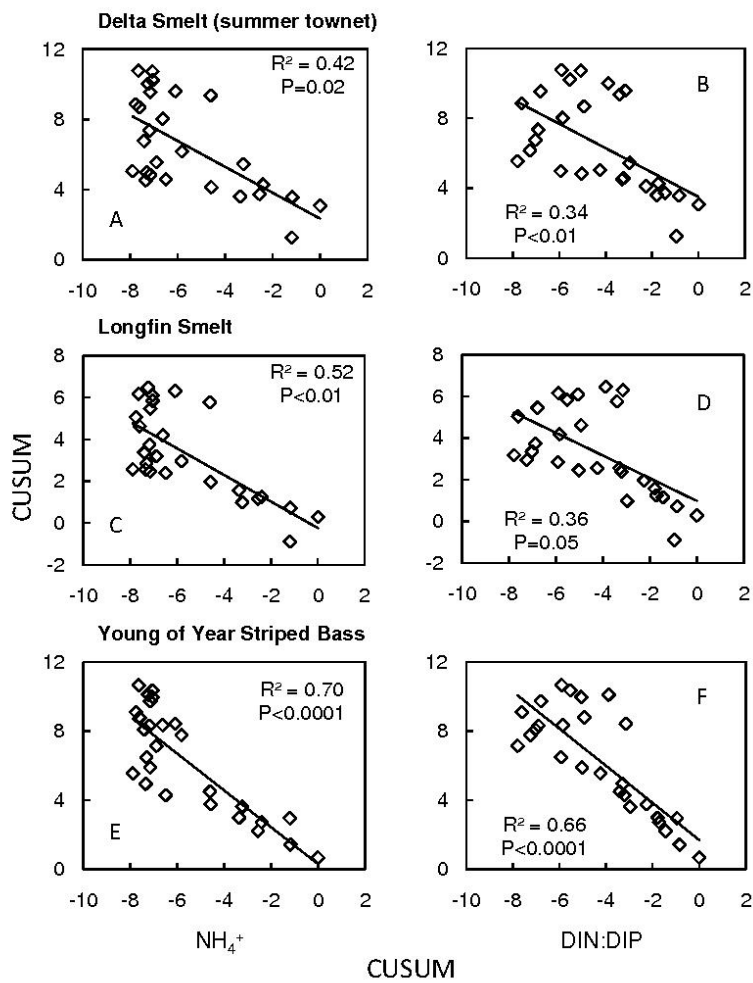
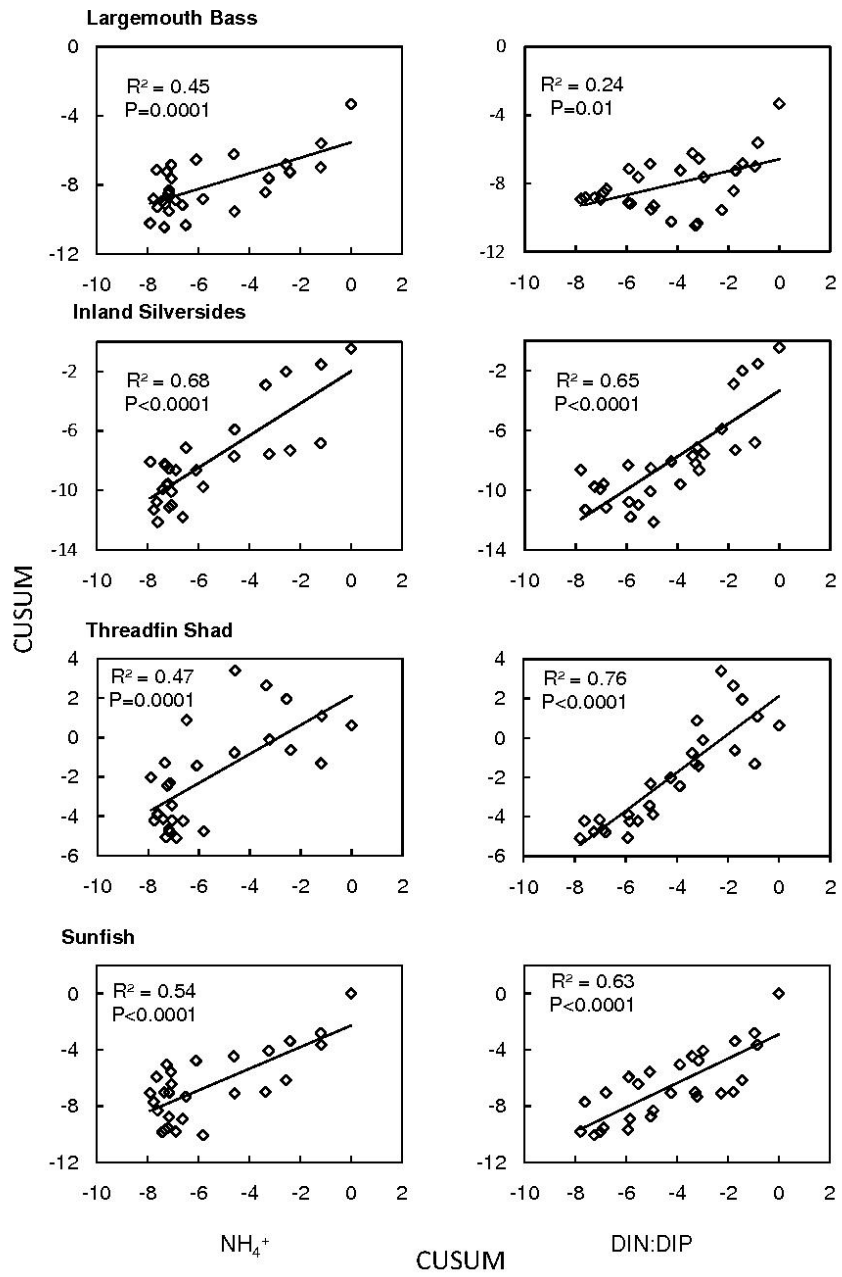


Fig. 20

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1125

1126 Fig. 21.

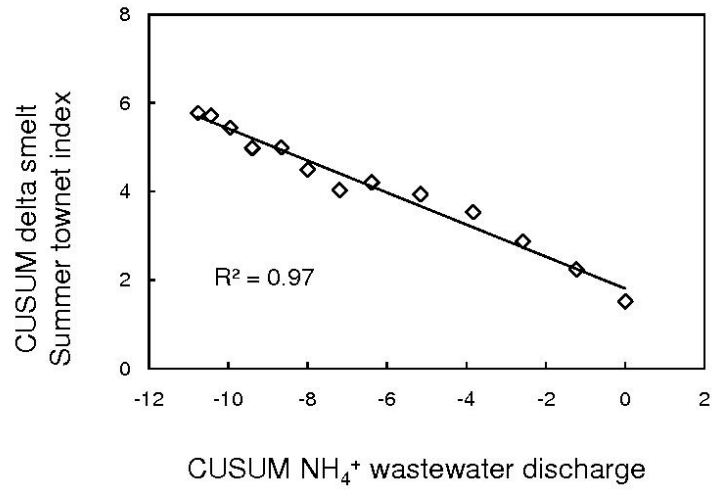
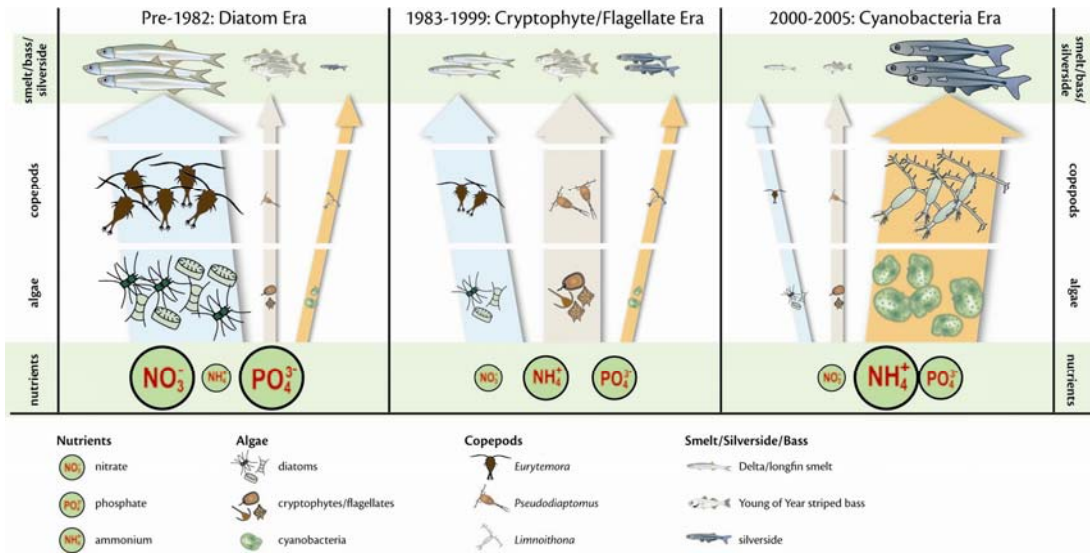


Fig. 22

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Table 1. Correlations between CUSUM X2, the measured distance from the Golden Gate Bridge and the isohaline where salinity is 2, and CUSUM of the fish or clam species indicated. All fish data encompass the period from 1975-2005; the clam correlations encompass the period from 1987-2005. None of these relationships were significant.

Species	R ²
Delta smelt, <i>Hypomesus transpacificus</i> (summer townet index)	0.073
Delta smelt, <i>Hypomesus transpacificus</i> (fall midwater trawl index)	0.097
Longfin smelt, <i>Spirinchus thaleichthys</i>	0.167
Young-of-the-year striped bass, <i>Morone saxatilis</i>	0.037
Largemouth bass, <i>Micropterus salmoides</i>	0.089
Inland silversides, <i>Menidia beryllina</i>	0.004
Threadfin shad, <i>Dorosoma petenense</i>	0.051
Sunfish, <i>Lepomis</i> spp.	0.176
