

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

*Patricia M. Glibert*

*University of Maryland Center for Environmental Science*

*Horn Point Laboratory*

*PO Box 775*

*Cambridge, MD 21613 USA*

*glibert@umces.edu*

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**Key words:** nutrient ratios, nutrient stoichiometry, eutrophication, plankton trophodynamics,  
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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.

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## INTRODUCTION

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

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

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

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

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

Yet, it has been reported, based on experimental data, that high ammonium ( $\text{NH}_4^+$ ) levels inhibit diatom growth, thus potentially restricting the availability of a preferred food source in the food chain that supports fish (Wilkerson et al., 2006; Dugdale et al., 2007). Moreover, changes in nitrogen:phosphorus (N:P) ratios of nutrients in the water have been correlated with overall declines in water column chlorophyll *a* (chl *a*) of the Bay Delta in the mid-1990s (Van Nieuwenhuyse, 2007).

The possibility of ‘bottom up’ control of fish populations in this system has been largely dismissed for several reasons: most nutrients are at levels that saturate (maximize) phytoplankton growth; phytoplankton growth is considered to be regulated primarily by light limitation (Cole and Cloern, 1984);  $\text{NH}_4^+$  is generally a preferred form of nitrogen for phytoplankton uptake; the pH of the receiving waters prevents formation of the toxic compound, ammonia gas ( $\text{NH}_3$ ); and the  $\text{NH}_4^+$  levels are typically below the criteria considered by the U.S. Environmental Protection Agency (EPA) for fish habitat (McCarthy et al., 1977; Millero, 2006; Jassby, 2008; U.S. EPA, 2010). In addition, some analyses of nutrient effects have considered only total N or P and chl *a*, rather than nutrient form and phytoplankton composition (e.g., Jassby, 2008). As a consequence, relationships between nutrients, production or food web effects have been ambiguous, leading to indecisive conclusions, as noted by Jassby (2008), “The physiological effect of ammonium ...may well play a role in the dynamics of specific phytoplankton events...But it is one factor among many, and its ecological effect relative to other sources of variability underlying long-term phytoplankton patterns is not yet clear.”

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

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

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

The quality (form) of N has long been recognized to influence the relationship between primary producers and fish. Within the field of oceanography,  $\text{NO}_3^-$ -based food webs are thought to lead to fish (export) production while those based on  $\text{NH}_4^+$  more generally support retentive or microbial food webs in nutrient- depleted marine systems, based on the classic concept of “new” and “regenerated” production (Dugdale and Goering, 1967; Eppley and Peterson, 1979; Glibert, 1998). However, the extent to which this dichotomous control of food webs applies in nutrient-enriched coastal systems is unclear. These systems receive significant inputs of “new” N in reduced form and therefore the question remains as to whether total nutrient load or form controls food webs when loadings are high (e.g., Nixon and Buckley, 2002). The fundamental ecological question is: How does the nutrient signal propagate through the food web? It has previously been suggested that variance in state variables changes with regime shifts or disturbance (e.g., Carpenter et al., 2007), but examples of trophic changes due to nutrient changes in highly impacted coastal systems are rare.

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

The goal of this analysis is to identify key relationships between nutrient concentrations, forms, ratios, and sources and the major components of the food web, from phytoplankton to zooplankton, clams and fish, based on the 30-year term time series from the San Francisco Estuary. In particular, the hypotheses that increased  $\text{NH}_4^+$  loading relative to  $\text{NO}_3^-$ , as well as changes in nitrogen (N) and phosphorus (P) stoichiometry, are related to the changes in dominant fish over time because of their effects on the dominant primary producers. As the dominant functional groups of primary producers in the system changed, so too did the food web leading to fish. Accordingly, this analysis also explores the relationships between nutrient availability and form on the invasive clam, *Corbula amurensis*, as well as its relationship to the food web.

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

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

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

## ***MATERIALS AND METHODS***

### ***Site Description***

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

The upper reaches of the Sacramento River drain 61,721 km<sup>2</sup>, while the upper San Joaquin River drains 19,030 km<sup>2</sup> (Sobota et al., 2009). On a long-term basis, the Sacramento River contributes >80% of river inflow to the Bay Delta, while the San Joaquin delivers ~12%, the remainder coming from minor sources flowing into the Delta from the east (IEP, 2006; Jassby, 2008). River flow has varied by about



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

### ***Overall Approach***

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

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

### ***Data Sources***

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

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

on subsurface samples on a bimonthly to monthly basis. Samples for phytoplankton composition were collected by submersible pump, preserved in Lugol's solution, and subsequently enumerated microscopically to species level. Nutrient data, as  $\text{NH}_4^+$  concentration, ratio of dissolved inorganic nitrogen:phosphorus (DIN:DIP), and the ratio of oxidized to reduced inorganic forms of N ( $\text{NO}_3^- + \text{NO}_2^-$ :  $\text{NH}_4^+$ ) were examined herein. Values for  $\text{NO}_3^- + \text{NO}_2^-$  are referred to as  $\text{NO}_3^-$ . Phytoplankton data, while available as individual species counts, were grouped into dominant functional groups: diatoms, green algae, cryptophytes, other flagellates, and cyanobacteria. For each function group, values were calculated as average species cell number  $\text{mL}^{-1}$ . The cyanobacterium *Microcystis aeruginosa* has increased in this system since ~1999 (Lehman et al., 2005), but these data are not included in this analysis because they are not in the long-term data base. Picocyanobacteria are also not included herein because they are not routinely enumerated. Where frequency of data was greater than monthly for nutrients or phytoplankton, monthly averages were calculated.

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

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

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

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

Effluent discharges to the upper Sacramento River were compiled by the State Water Contractors (<http://www.swc.org/>) based on monthly discharger self-monitoring reports to the Regional Water Quality Control Board. Although the Sacramento wastewater treatment plant came on line in 1982,  $\text{NH}_4^+$  discharge data are only available beginning in 1984. Annual averages of discharge of N and P prior to 1992 have previously been published (Van Nieuwenhuysen, 2007).

This analysis emphasizes results from the upper Sacramento River station C3, and Suisun Bay stations D8 and D7, although additional  $\text{NH}_4^+$  data from the delta region (station D28) are presented for comparison (Fig. 1). The intervening region between the upper Sacramento River and Suisun Bay encompasses much of the natural habitat for the delta smelt and the other pelagic fish discussed above.

### *Statistical Analysis*

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

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

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

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

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

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

## **RESULTS**

### ***Overview***

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

### ***Flow***

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

## *Nutrients*

Concentrations of  $\text{NH}_4^+$ , the dominant inorganic N form in the upper Sacramento River (station C3) and in Suisun Bay (stations D8, D7), approximately 75-80 km downstream, were lower before the mid-1980s than in later years, as evidenced in both the raw data and in the declining CUSUM trends (Figs. 3A-C).  $\text{NH}_4^+$  concentrations in the Sacramento and Suisun Bay were high in the late 1980s to early 1990s, coincident with the dry period, declined in the late 1990s, and then increased significantly after the year 2000; the upward trend in the CUSUM charts of these sites after 2000 indicates that the  $\text{NH}_4^+$  concentrations were well above the long-term mean. In contrast to these sites, the concentrations of  $\text{NH}_4^+$  in the lower San Joaquin River have not fluctuated over the time series to the same degree, and thus the CUSUM trends for this site are different than those of stations C3, D7 or D8 (Fig. 3D). The CUSUM trends for this site show no indication of increasing  $\text{NH}_4^+$  since 2000; instead, there has been a decline in these values.

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

Long-term trends in nutrient concentrations and ratios were related to changes in nutrient loading, with a major source being the Sacramento Regional wastewater treatment plant (Van Nieuwenhuysse, 2007; Jassby, 2008). The concentration of  $\text{NH}_4^+$  discharged increased from  $\sim 10 \mu\text{g L}^{-1}$  when the plant came on line in the early 1980s to  $>20 \mu\text{g L}^{-1}$  in the 2000s (Fig. 6A). Concentration of  $\text{NO}_3^-$  discharged has remained  $<1.5 \mu\text{g L}^{-1}$ , except for a few periods in the late 1990s (Fig. 6B). Concentration of  $\text{PO}_4^{3-}$  in the wastewater discharge declined precipitously in the early to mid-1990s (Fig. 6C), coincident with removal of P from domestic detergents by most U.S. manufacturers (Litke 1999). Total nutrient load, a function of changing concentration and volumetric rate of discharge, also increased over time, now averaging  $>500 \text{ ML day}^{-1}$  (Fig. 6D). The molar ratio of DIN:DIP of the discharge increased from  $<10$  prior to 1994 to  $>20$  in recent years, with few exceptions (Figs. 6E). Thus, the change in DIN:DIP in the upper Sacramento River and in Suisun Bay (Fig. 5) in the 1990s occurred around the same time as the DIN:DIP changed in the effluent discharge.

CUSUM trends in  $\text{NH}_4^+$  concentration in wastewater effluent over time are highly correlated with CUSUM trends in  $\text{NH}_4^+$  concentration in the upper Sacramento River (at C3). For the time period over which  $\text{NH}_4^+$  discharge data are available (1992-2005), the  $R^2$  correlation between these trends was 0.70 ( $n=167$ ; Fig. 7A), and for the POD period (2000-2005), the  $R^2$  was 0.92 ( $n=71$ ; data not shown). Moreover, CUSUMs for  $\text{NH}_4^+$  concentration in the upper Sacramento River (at C3) were highly 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 not shown) for the period of 1984-2005.

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

## Phytoplankton

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

When CUSUM charts of  $\text{NH}_4^+$  concentration in Suisun Bay and those of major phytoplankton groups were compared, the correlations were all strong, but the relationship was negative for diatoms and positive for the other algal groups (Fig. 10). When these correlations were calculated only for the years since the wastewater treatment plant has been in operation (1984-2005), they were much higher than when the entire period of record was considered. For example, for diatoms, the  $R^2$  with CUSUM  $\text{NH}_4^+$  increased to 0.83 ( $n=147$ ), that for cryptophytes increased to 0.76 ( $n=133$ ) and that for cyanobacteria increased to 0.97 ( $n=8$ ; not shown).

## Copepods

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



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

## ***Clams***

The clam *Corbula amurensis* first appeared in significant numbers in Suisun Bay in 1987 (Fig. 13). It thus appeared around the same time that the copepod *P. forbesi* began to appear (Fig. 11B), and around the time that the phytoplankton assemblage had increasingly become dominated by cryptophytes and green algae (Fig. 9C). Moreover, the CUSUM of  $\text{NH}_4^+$  for Suisun Bay was highly and positively related to that of clam abundance (Fig 14A), as was the CUSUM trend in DIN:DIP (Fig. 14B).

## ***Pelagic Fish***

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

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

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

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

Considering that the various planktonic members of the food web were related to nutrient availability and composition, and given that the fish were related to trends in zooplankton, fish abundances were also strongly related to nutrients. CUSUM trends in delta smelt, longfin smelt and young-of-the-year striped bass were negatively correlated with CUSUM trends in  $\text{NH}_4^+$  and in DIN:DIP (Fig. 20), while CUSUM trends in largemouth bass, silversides, threadfin shad and sunfish were positively correlated with CUSUM trends in  $\text{NH}_4^+$  and in DIN:DIP (Fig. 21)

The delta smelt ultimately were related to changes in  $\text{NH}_4^+$  of the wastewater discharge in the upper Sacramento River: The relationship between the CUSUM delta smelt summer townet index and CUSUM  $\text{NH}_4^+$  discharge was highly significant for the period over which discharge data are available ( $R^2=0.97$ ;  $n=13$ ; Fig. 22).

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

## DISCUSSION

### *Value of the CUSUM Approach*

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

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

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

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

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

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

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

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

Before 1982, chl *a* concentrations in Suisun Bay were relatively high, averaging  $\sim 9 \mu\text{g L}^{-1}$ , with numerous values exceeding  $30 \mu\text{g L}^{-1}$ , and diatoms, *E. affinis*, and delta smelt were all abundant. The decline in diatoms, which began in 1982, was highly correlated with the increase in  $\text{NH}_4^+$  loading. This relationship illustrates two well known physiological processes. First, although  $\text{NH}_4^+$  may be a preferred N form under N limitation, it can be inhibitory at high concentrations (e.g., Syrett, 1981). Second, diatoms prefer and, under some conditions, physiologically require,  $\text{NO}_3^-$  over  $\text{NH}_4^+$ , unlike many other algae which preferentially use  $\text{NH}_4^+$  over other N forms (McCarthy et al., 1977; Syrett 1981; Berg et al., 2001; Glibert et al., 2004, 2006).  $\text{NO}_3^-$  is used in the energy balance of these cells as a photoprotective mechanism (Lomas and Glibert, 1999a,b). As  $\text{NO}_3^-$  became less available relative to  $\text{NH}_4^+$  in Suisun Bay (Fig. 4B,C), the competitive advantage shifted to phytoplankton taxa that can more efficiently use reduced forms of N. Among the phytoplankton groups that replaced diatoms in this system, cyanobacteria

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

From 1982-1986 chl *a* continued to decline, as did *E. affinis*. The virtual disappearance of chl *a* from Suisun Bay in 1987 has been attributed to the proliferation of the invasive clam, *C. amurensis*, thought to have filtration rates sufficient to remove most of the chl *a* (Kimmerer, 2002; Jassby et al., 2002). As mentioned, this exotic clam became established in Suisun Bay in ~1986-1987, coincident with the collapse in chl *a* (Fig. 13). Its increase was positively correlated with both  $\text{NH}_4^+$  and DIN:DIP changes over time (Fig. 14), suggesting that it thrived when the food web changed due to nutrient loading. While clams may have continued to keep phytoplankton chl *a* low due to their filtering, the earlier decline in diatoms (in 1982) is better explained by the inhibitory effect of the elevated  $\text{NH}_4^+$  loading than due to the clam invasion. Clams also have been shown to consume *E. affinis* nauplii (Kimmerer et al., 1994), but *E. affinis* was already in decline (Fig. 11A) before clams became well established (Fig. 13).

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

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

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

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

further declines in smelt, along with silversides and threadfin shad (Fig. 17; e.g., Bennett, 2005; Sommer et al., 2007; Thompson et al., 2010). During this time,  $\text{NH}_4^+$  loading from wastewater discharge increased 25%, from ~ 9 metric tons day<sup>-1</sup> to 12 metric tons day<sup>-1</sup> (the product of Figs. 6A and 6D; Van Nieuwenhuyse, 2007), leading to a strong correlation over the time series of CUSUM trends in wastewater effluent  $\text{NH}_4^+$  and the delta smelt (Fig. 22).

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

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

This analysis was not intended to be a review of X2, its relationships, or the management thereof; there have been numerous other such efforts and others are ongoing. Instead, this analysis reviewed nutrients and their food web effects. The overwhelming conclusion here is the fact that relationships between nutrients and fish are stronger than those of flow and fish (comparison of Figs. 20, 21 and Table 1). Furthermore, changes in flow are not correlated with all nutrients and nutrient ratios over the entire time series (Fig. 8), although there were significant, but different, relationships for the pre-POD and the POD years. The slope of the relationship between CUSUM flow and nutrients changed in the POD years, coincident with the increase in effluent  $\text{NH}_4^+$  discharge, a major driver of  $\text{NH}_4^+$  concentrations and the nutrient ratios shown.



## *Nutrient Management Implications*

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

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

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

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

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

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

The changes in food web structure with changes in nutrient form and/or nutrient ratio suggest that the Eppley and Peterson (1979) paradigm applies in this nutrient rich estuary. That paradigm, which suggests that  $\text{NO}_3^-$ -based food webs are fundamentally different from those of  $\text{NH}_4^+$ -based food webs, was originally developed for oligotrophic, oceanic waters. Here, as in the oceanic condition,  $\text{NO}_3^-$ -based food webs were supported by higher proportions of diatoms and the  $\text{NH}_4^+$ -based food webs were supported by higher proportions of flagellates, cryptophytes and cyanobacteria. Both food webs supported fish, although different species.

The analysis described here should be highly relevant to other systems that have been subject to alterations in N and P loading and N form. The fact that chl *a* declined over time as N loading increased has deflected management attention away from nutrients. It is counterintuitive to the normal progression of eutrophication, typically resulting in higher algal biomass and a shift from benthic to pelagic production (Cloern, 2001). The inhibitory effect of  $\text{NH}_4^+$  on diatoms seen here has, however, been observed in other estuaries, such as the Delaware Estuary and the inner bay of Hong Kong Harbor (Yoshiyama and Sharp, 2006; Xu et al., 2010). In the Delaware Estuary, inhibition by  $\text{NH}_4^+$  was greatest in the colder months, when diatoms dominated (Yoshiyama and Sharp, 2006). From a management perspective, not only is near-field alteration of phytoplankton growth important, but so too is the potential for large down-stream impacts - impacts not often associated with discharges far removed in space. In this study, CUSUM trends in discharge of  $\text{NH}_4^+$  from the treatment plant were highly related to those of  $\text{NH}_4^+$  concentrations far downstream, ~80 km from the treatment plant (Fig. 7). The Sacramento River acted as a conduit for transport of N downstream.

Supporting the idea that correct balance of nutrients is important for restoration of delta smelt and other pelagic fish, there is a small but apparently successful subpopulation of delta smelt in a restored habitat, Liberty Island. Liberty Island is outside the immediate influence of Sacramento River nutrients. It has abundant diatoms among a mixed phytoplankton assemblage, as well as lower  $\text{NH}_4^+$  levels and higher

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

## ***SUMMARY***

Nutrient changes in concentration and form in the San Francisco Estuary and Bay Delta are significantly correlated with changes in components of the food web over time. These changes are highly related to loadings from a single major point source. The long-term changes in  $\text{NH}_4^+$ , the dominant N form that is discharged from the Sacramento River effluent plant are similar in the upper Sacramento River (C3) and 80 km in Suisun Bay (D8 and D7). However, they are not similar in lower San Joaquin River (D28), consistent with previous findings that inflow from the Sacramento River and its chemical constituents dominate over those of the San Joaquin. Changes in nutrient loadings and forms were related to changes in the phytoplankton assemblage, which in turn were related to changes in zooplankton, and in turn, related to clam abundance, and to the abundance of various fish species. The invasive copepods *P. forbesi* and *L. tetraspina* became dominant when the phytoplankton community shifted from diatom to flagellate and cyanobacterial dominance. Fish species fell into two groups: those whose long-term, CUSUM trends were positively correlated with trends in abundance of *E. affinis* and negatively correlated with *P. forbesi* and *L. tetraspina*, and those whose long-term, CUSUM trends were negatively correlated

with *E. affinis* and positively correlated with *P. forbesi* and *L. tetraspina*. Trends in the former group of fish also were related negatively to trends in  $\text{NH}_4^+$  and DIN:DIP, while the opposite pattern emerged for the latter group of fish species. Long-term trends in abundance of the clam, *C. amurensis*, were also highly related to trends in  $\text{NH}_4^+$  and DIN:DIP, suggesting that this invasive species was opportunistically responding to a change in ambient conditions when it proliferated. All of these relationships were significantly more robust than relationships with flow or X2; there were no significant relationships between the CUSUMs of X2 and nutrients, phytoplankton species, zooplankton or fish over the entire time series. Thus, a clear management strategy is the regulation of effluent N discharge through nitrification and denitrification. Until such reductions occur, other measures, including regulation of water pumping or manipulations of salinity, as has been the current strategy, will likely show little beneficial effect. Without such action, the recovery of the endangered pelagic fish species is unlikely at best.

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## Figure Legends

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

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

Figure 3. CUSUM values (primary axis, filled diamonds) as a function of time for ammonium ( $\text{NH}_4^+$ ) concentrations for A) the upper Sacramento at station C3, B and C) Suisun Bay at stations D8 and D7, and D) the lower San Joaquin at station D28. The secondary axis (open squares) for all panels gives the actual data in  $\mu\text{g L}^{-1}$ . The vertical dashed lines are guides to delineate the major periods discussed in text.

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

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



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

Figure 6. Nutrient concentrations ( $\text{mg L}^{-1}$ ) of the wastewater effluent as a function of time for A)  $\text{NH}_4^+$ , B)  $\text{NO}_3^- + \text{NO}_2^-$ , C)  $\text{PO}_4^{3-}$ , D) the volumetric daily rate of effluent discharge ( $\text{ML day}^{-1}$ ) from the wastewater facility, and E) the molar ratio of dissolved inorganic nitrogen:phosphorus (DIN:DIP) for the major wastewater treatment facility in the upper Sacramento River. Although the plant came on line in 1982, monitoring data are only available from 1992.

Figure 7. (A) Correlation between the CUSUM trend in  $\text{NH}_4^+$  concentration in wastewater discharge and that in the upper Sacramento River for the period of discharge data availability (1992-2005); and (B) Correlation between the CUSUM trend in  $\text{NH}_4^+$  concentration in the upper Sacramento River at station C3 and that in Suisun Bay at station D8 (1984-2005).

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

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

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

Figure 10. Correlations between the CUSUM trends in  $\text{NH}_4^+$  and A) diatoms; B) Cryptophytes; C) Green algae; D) Cyanobacteria; and E) Flagellates

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

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

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

1037

1038 Figure 14. Correlations between the CUSUM trends in A)  $\text{NH}_4^+$  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

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

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

Figure 20. Correlations between the CUSUM trends in  $\text{NH}_4^+$  and DIN:DIP at station D8 in Suisun Bay and CUSUM trends in delta smelt (panels A-B; summer townet index), longfin smelt (panels C-D) and young-of-the-year striped bass (panels E-F). All correlations cover the period 1975-2005.

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

Figure 22. Correlation between the trend in CUSUM in  $\text{NH}_4^+$  concentration in wastewater discharge in the upper Sacramento River and the trend in CUSUM delta smelt, estimated from the summer townet index.

Figure 23. Conceptual diagram of some of the hypothesized changes in the food chain from phytoplankton to fish that have occurred in the Sacramento-San Joaquin Estuary over the past 30 years. Each of these hypothesized food chains has different dominant nitrogen forms or amounts relative to 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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Fig. 1

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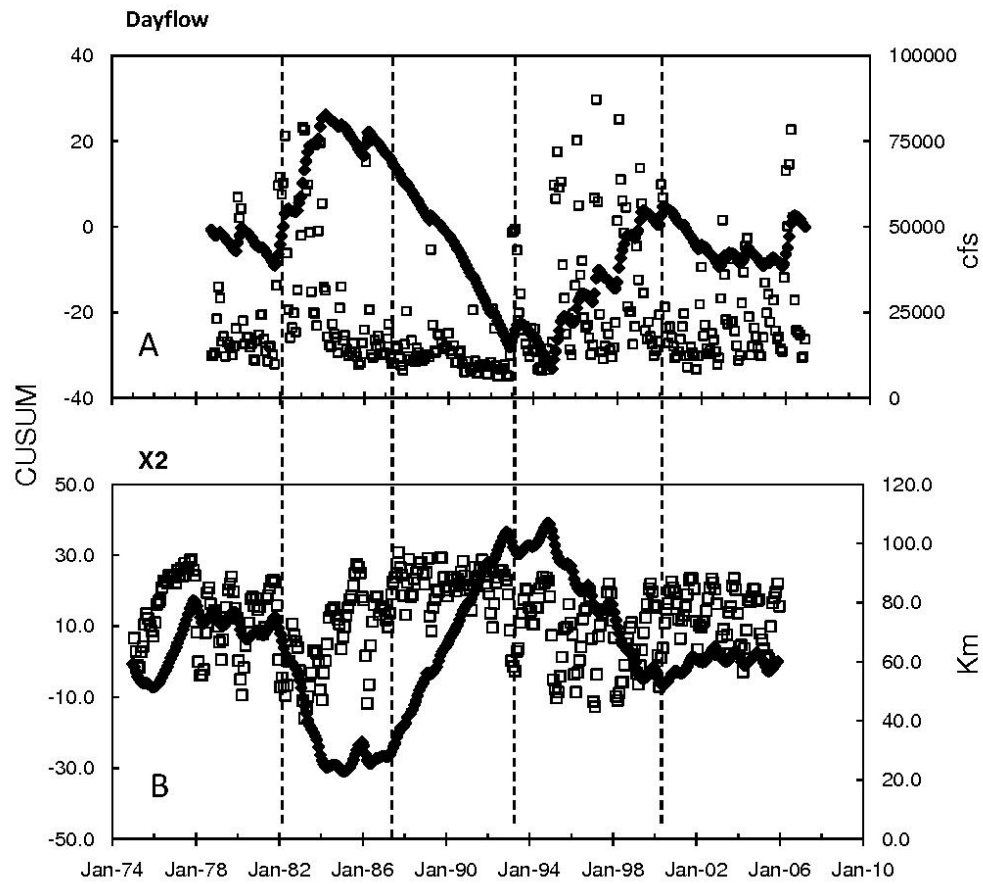


Fig. 2

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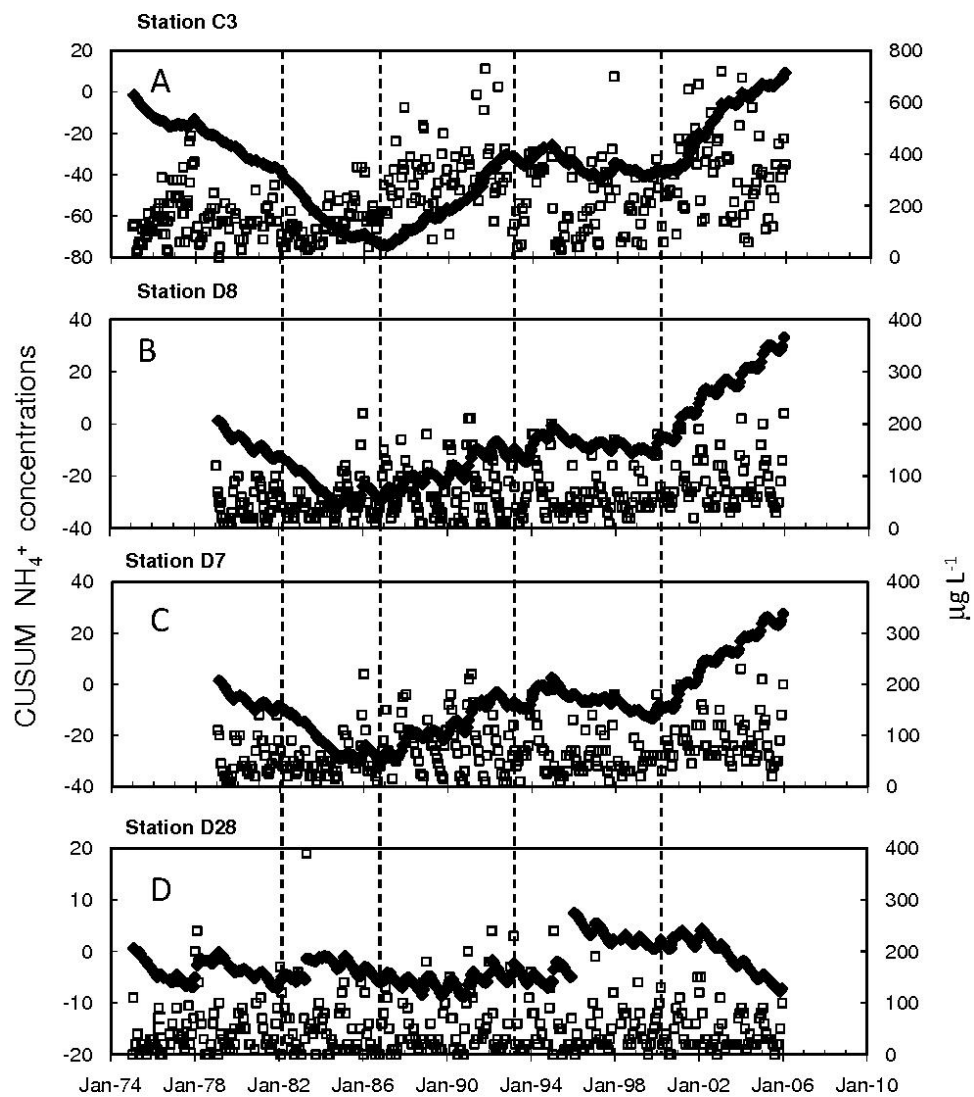


Fig. 3

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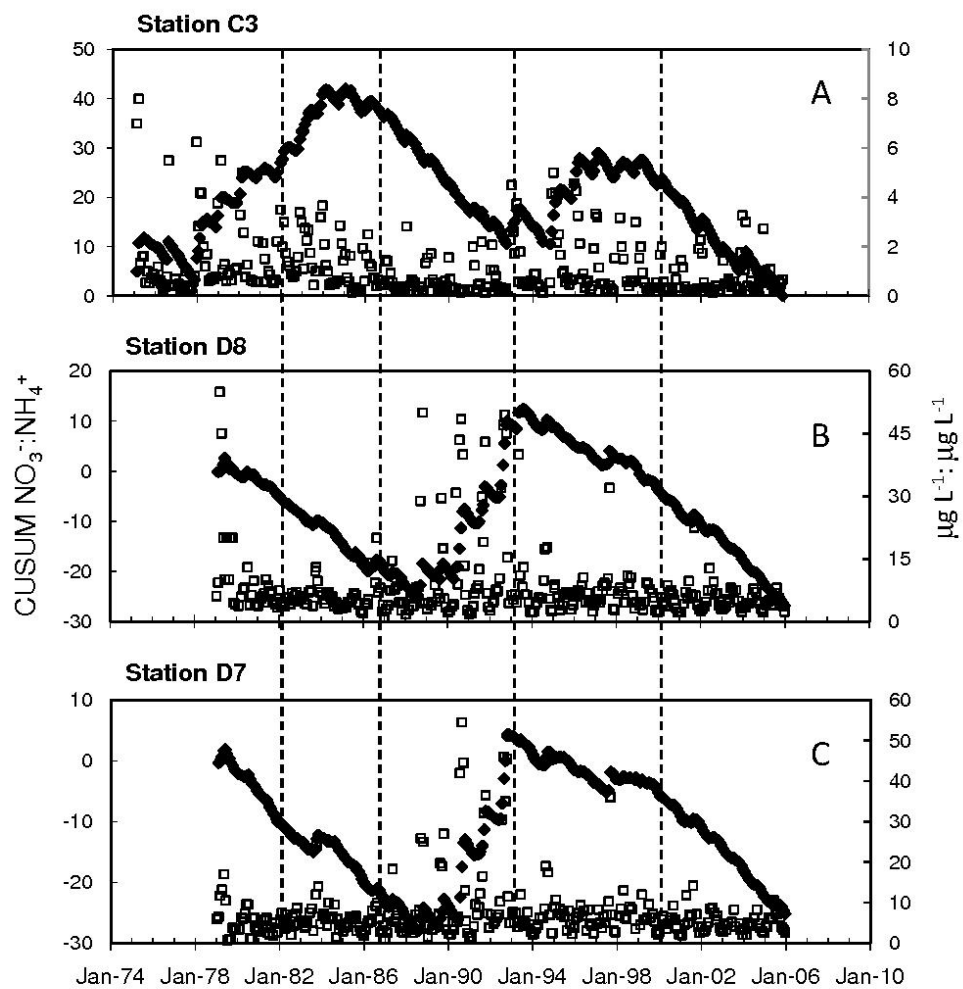


Fig. 4

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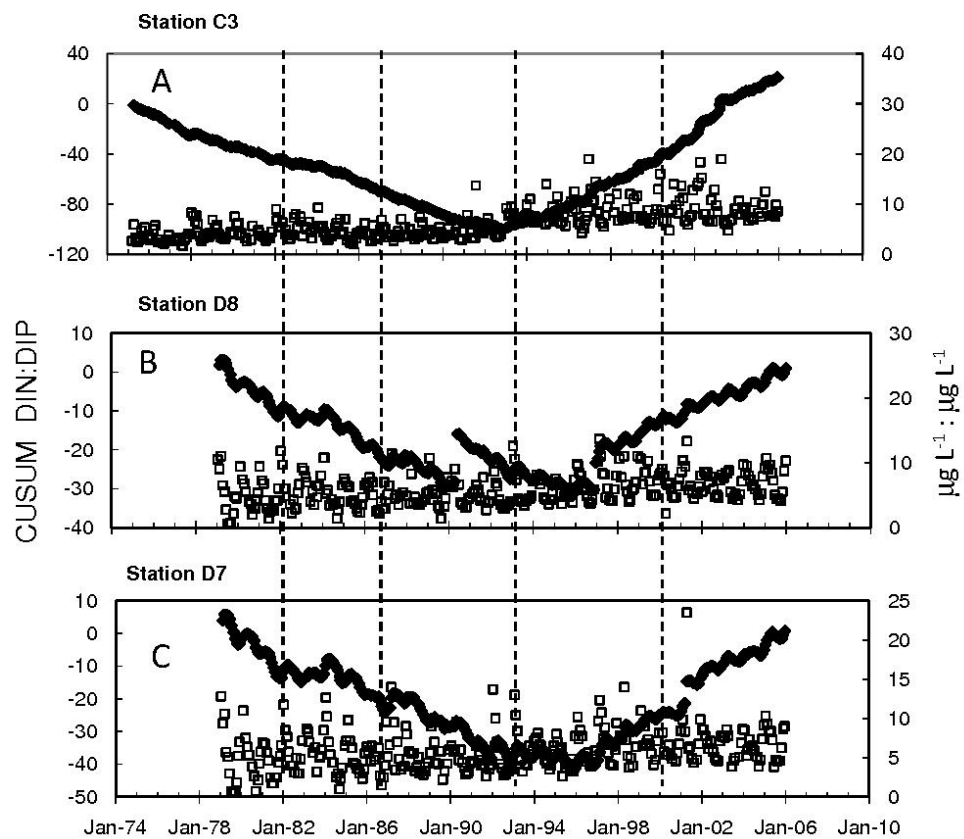


Fig. 5

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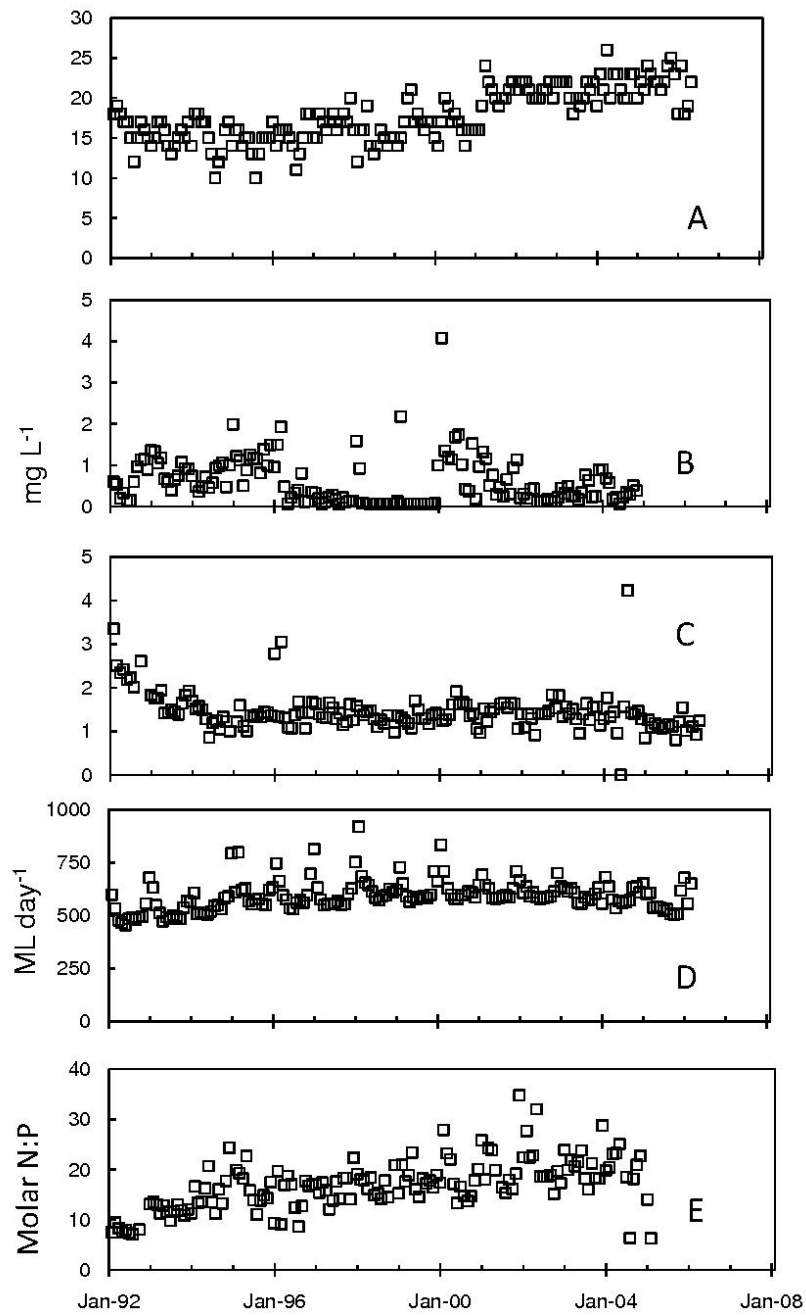
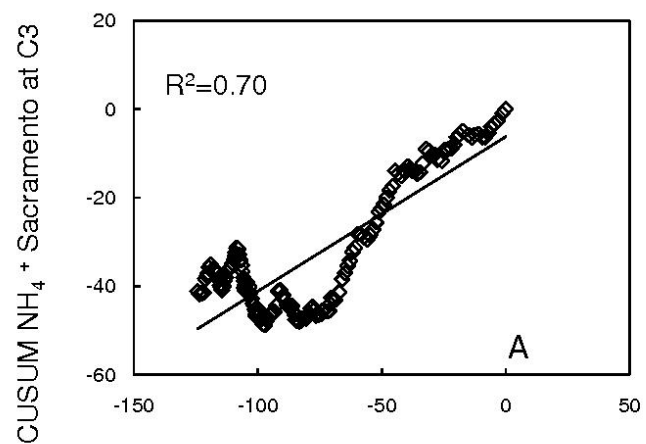


Fig. 6

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CUSUM  $\text{NH}_4^+$  wastewater discharge

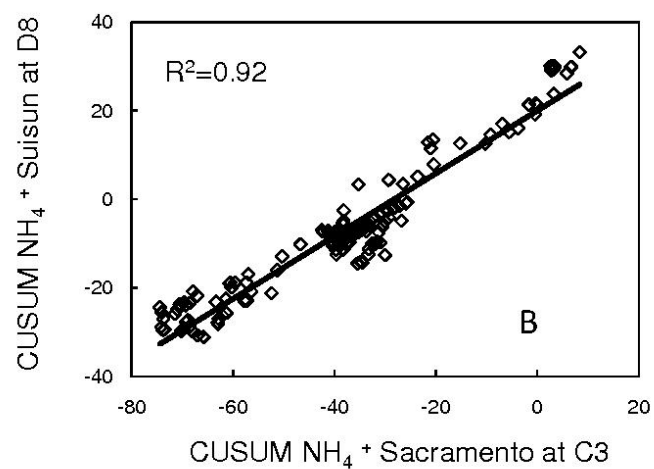


Fig. 7

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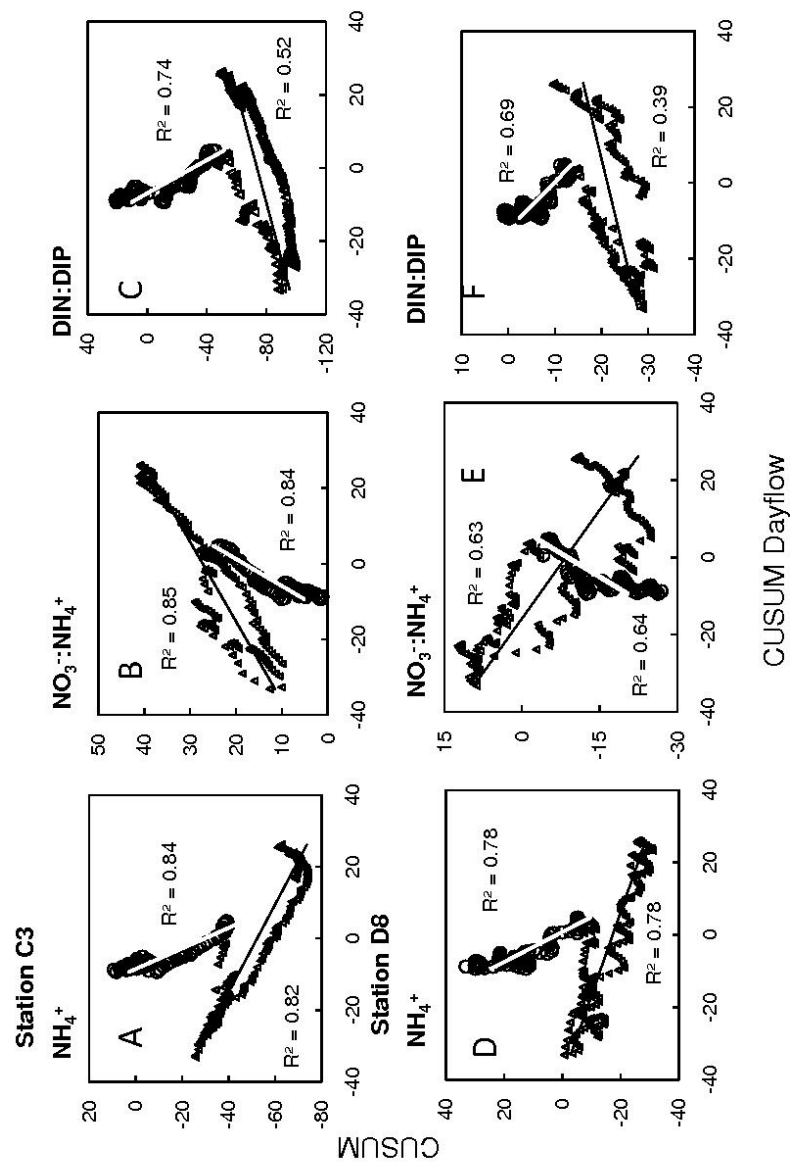


Fig. 8

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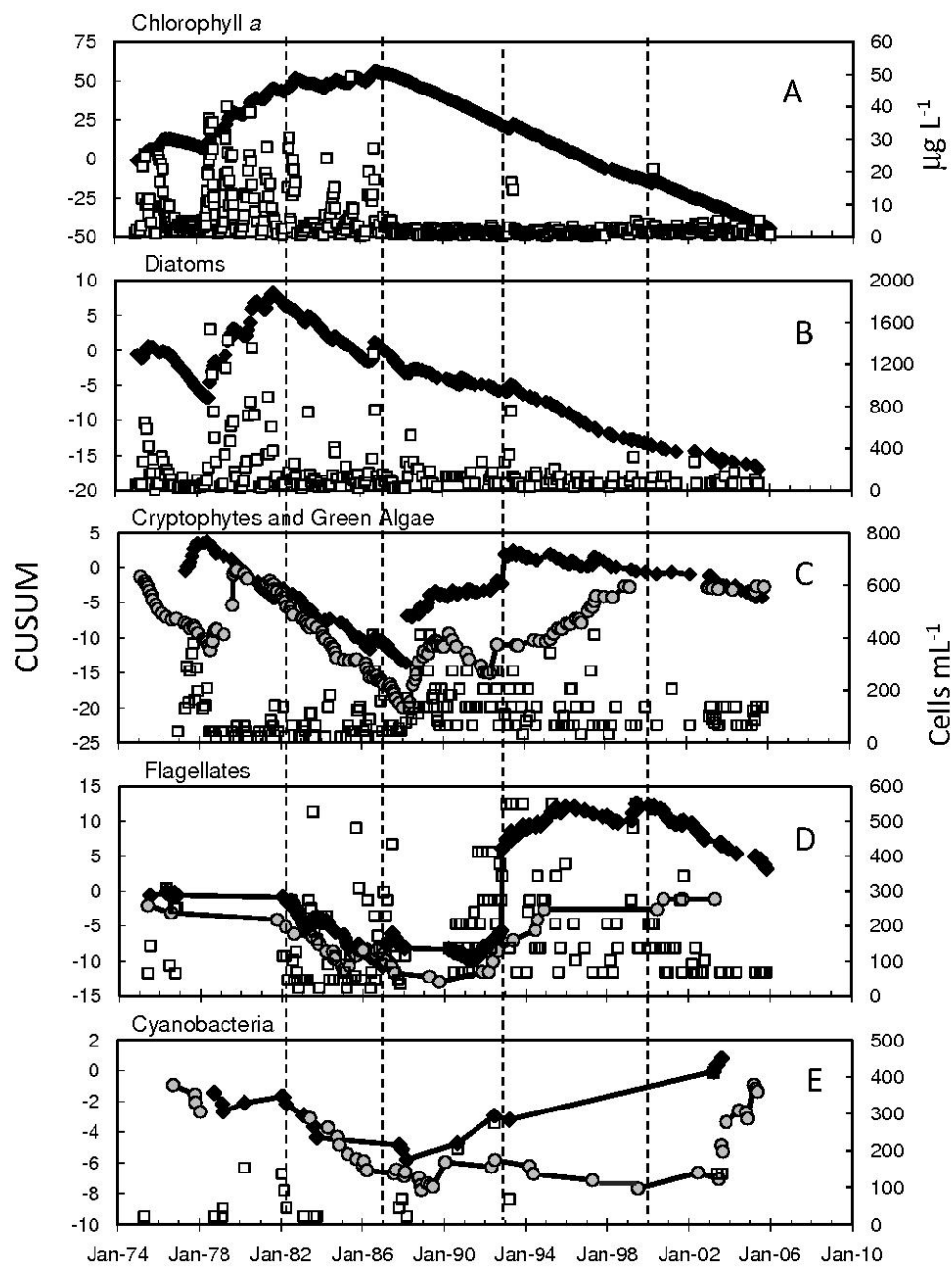


Fig. 9

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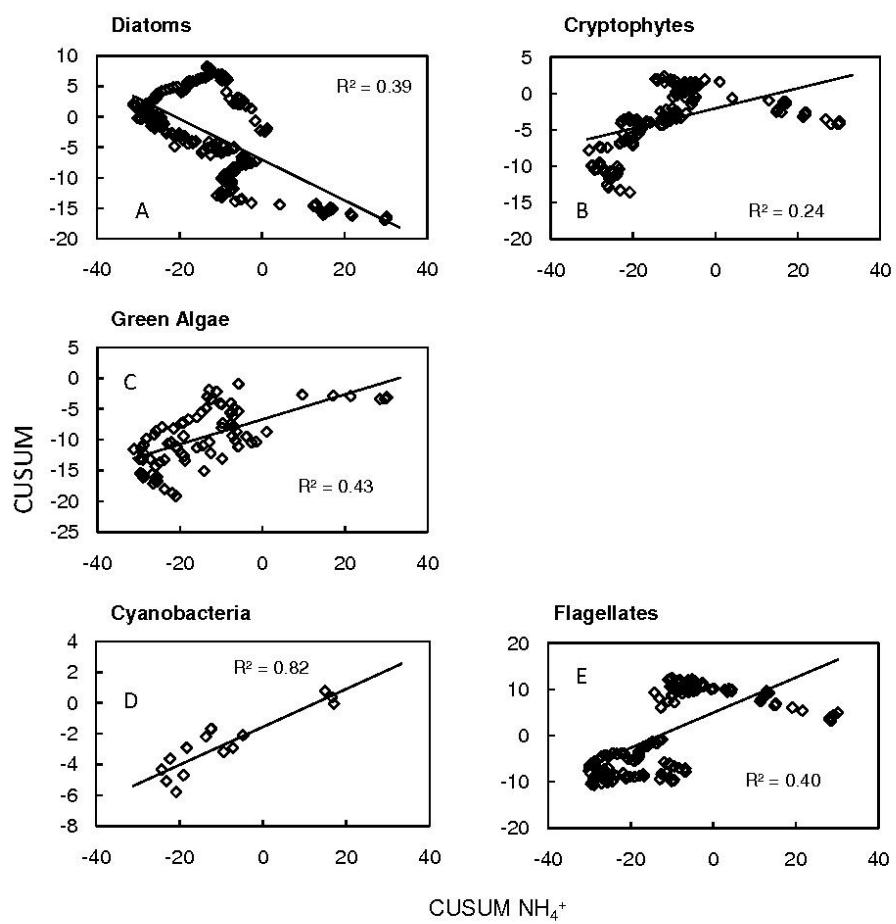


Fig. 10

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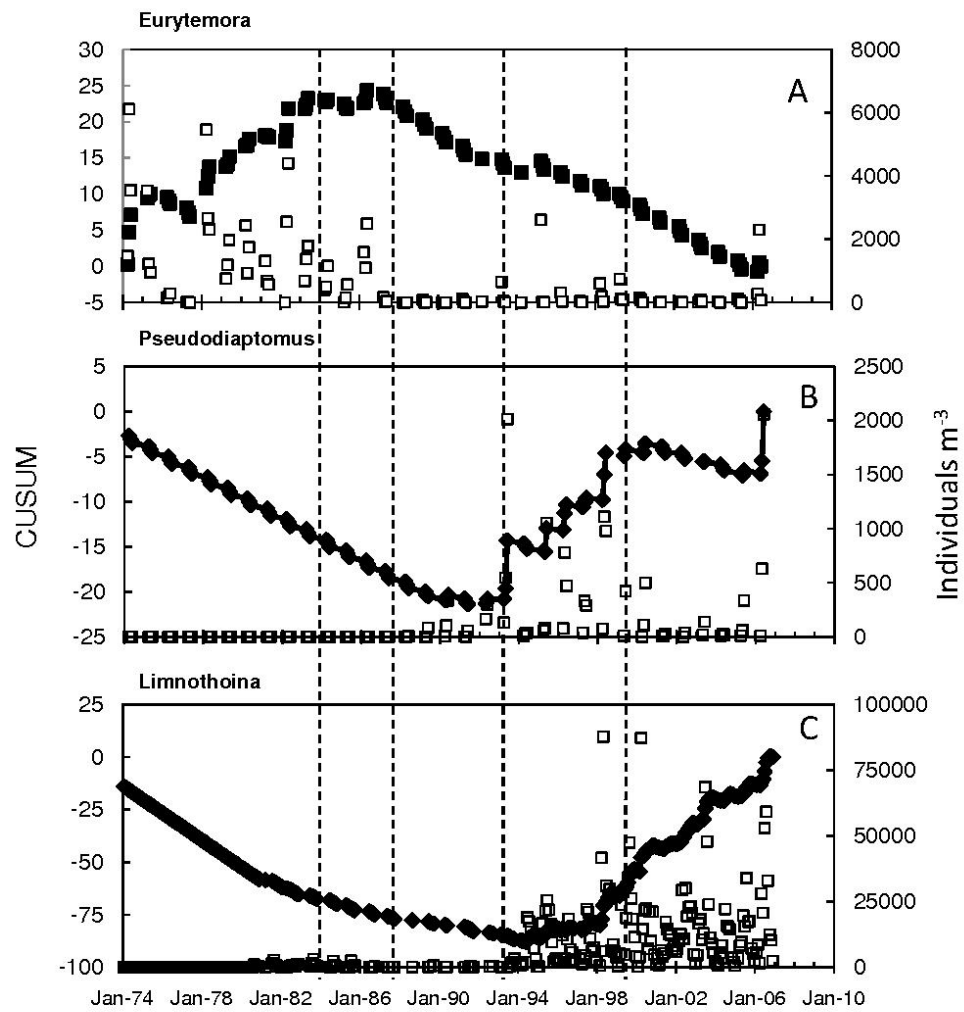


Fig. 11

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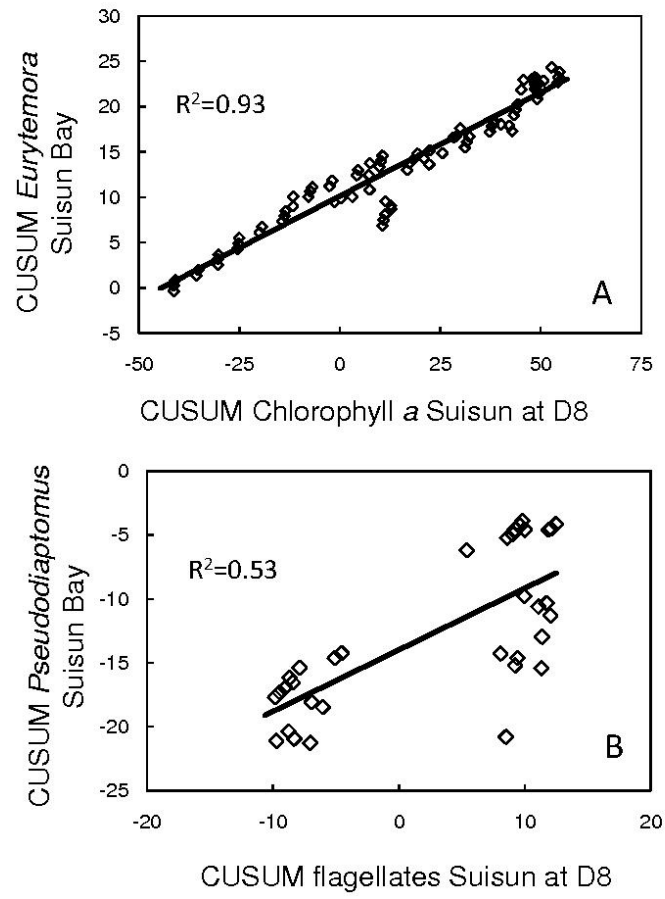


Fig. 12

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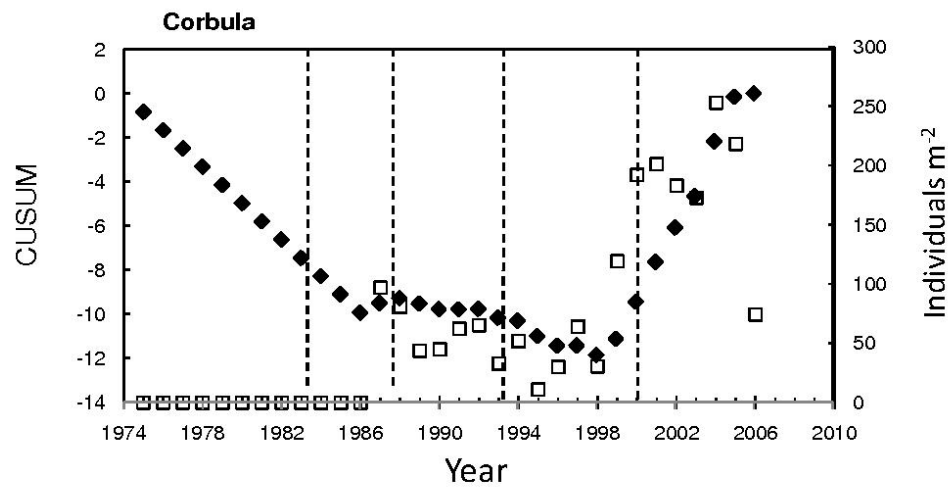


Fig. 13

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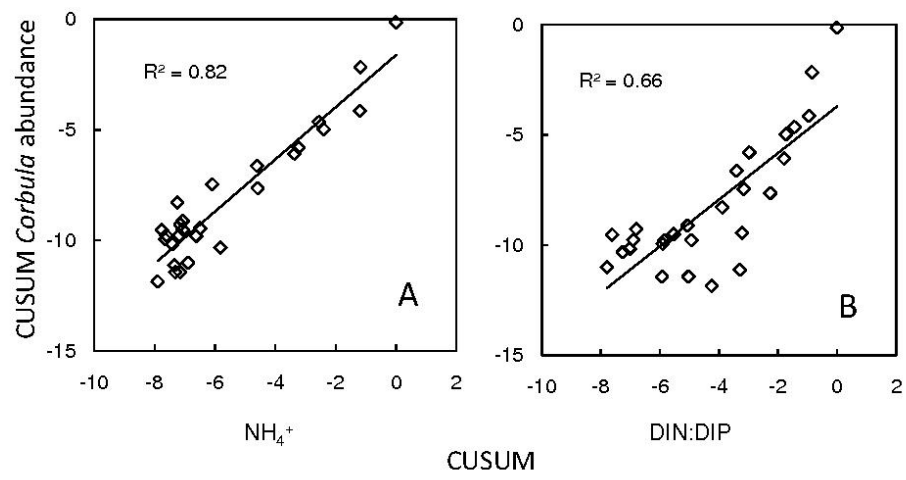


Fig. 14

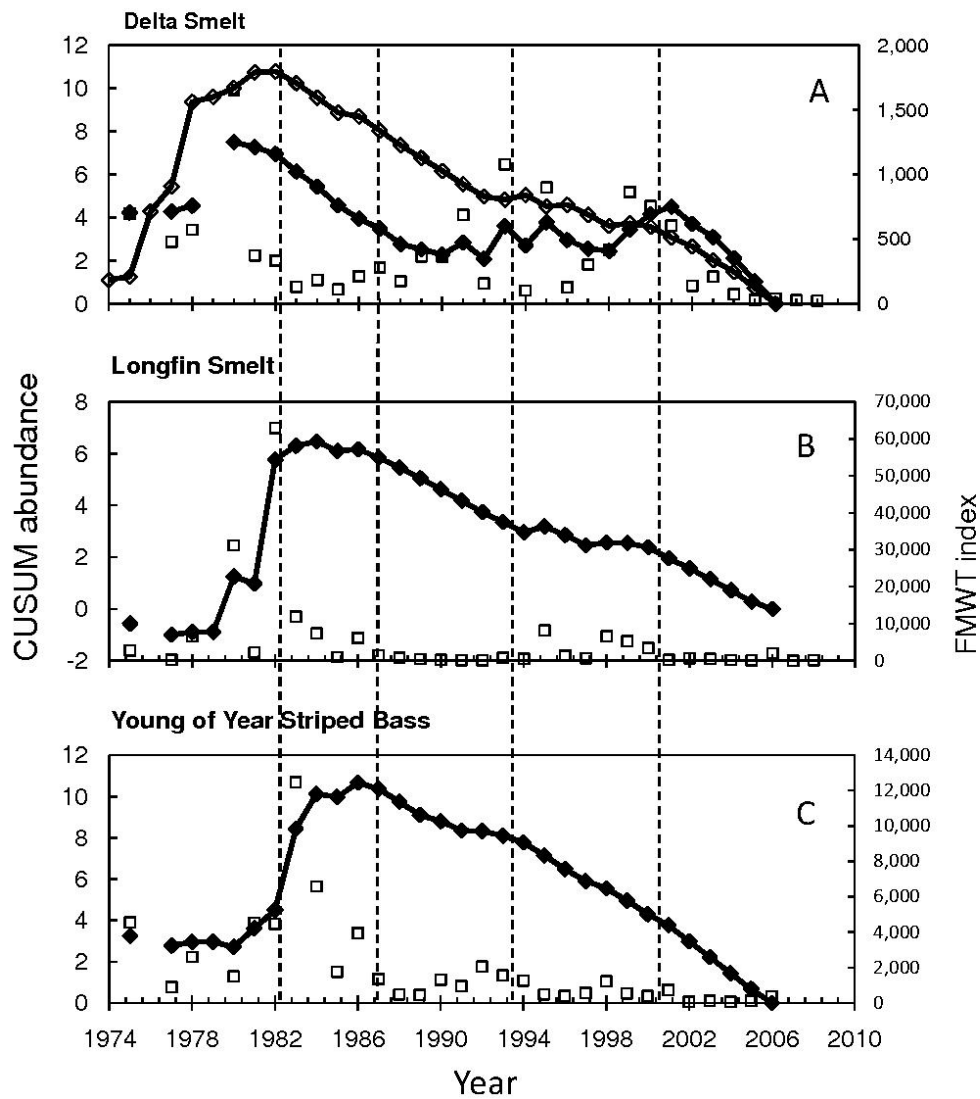


Fig. 15

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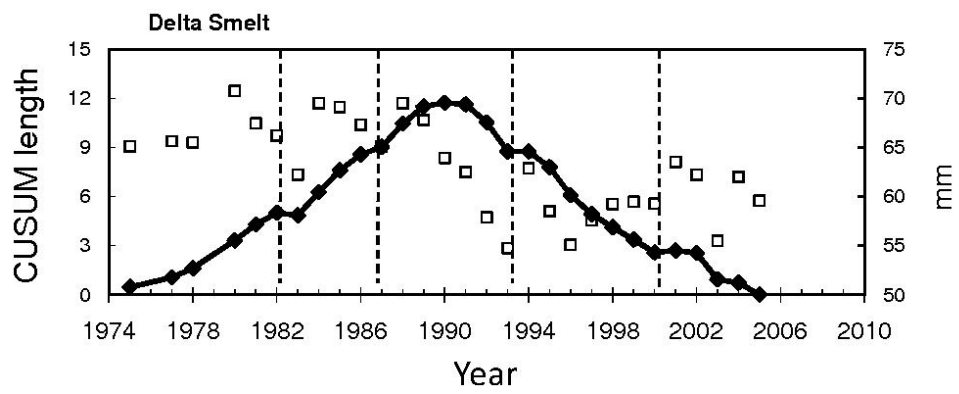


Fig. 16

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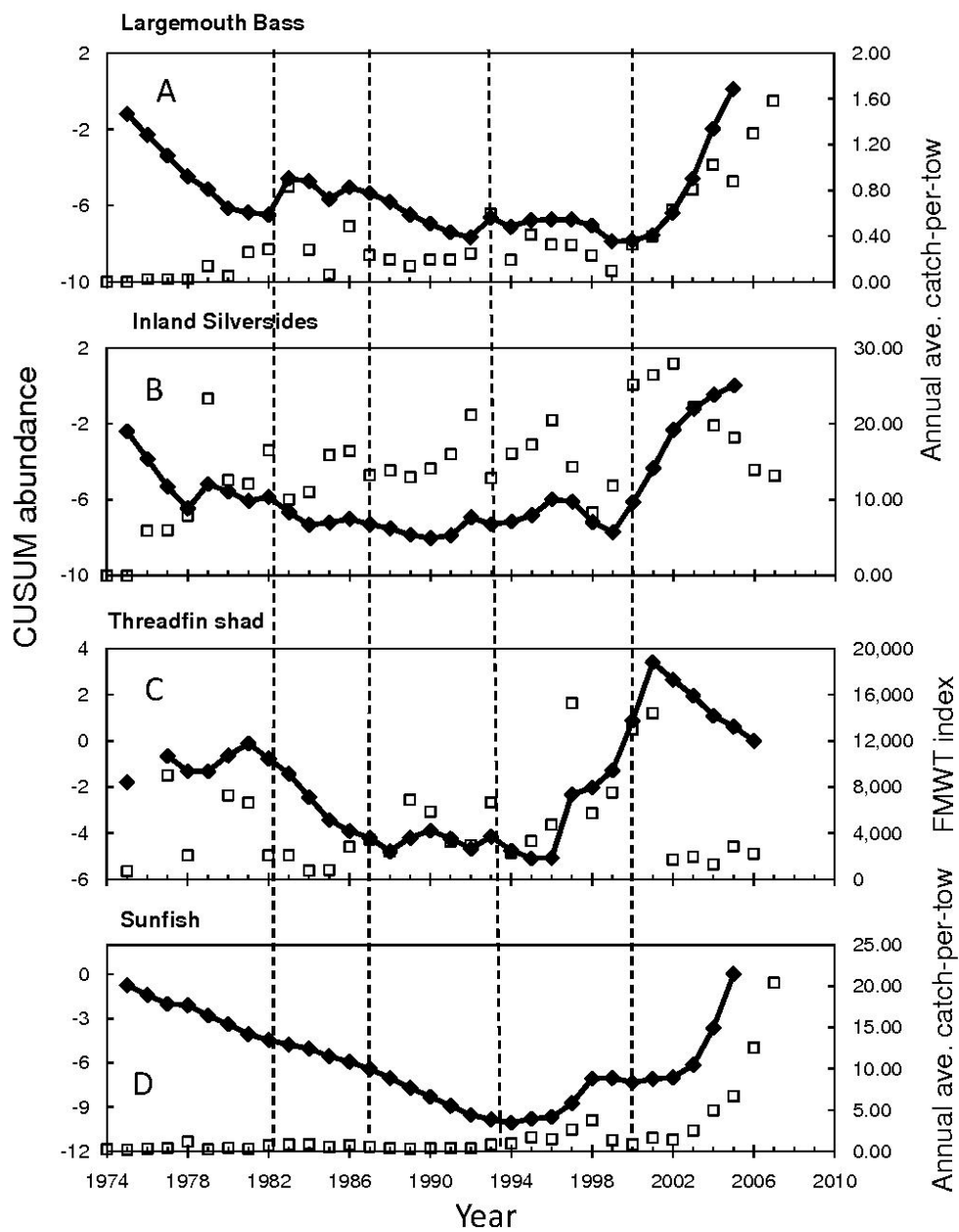


Fig. 17

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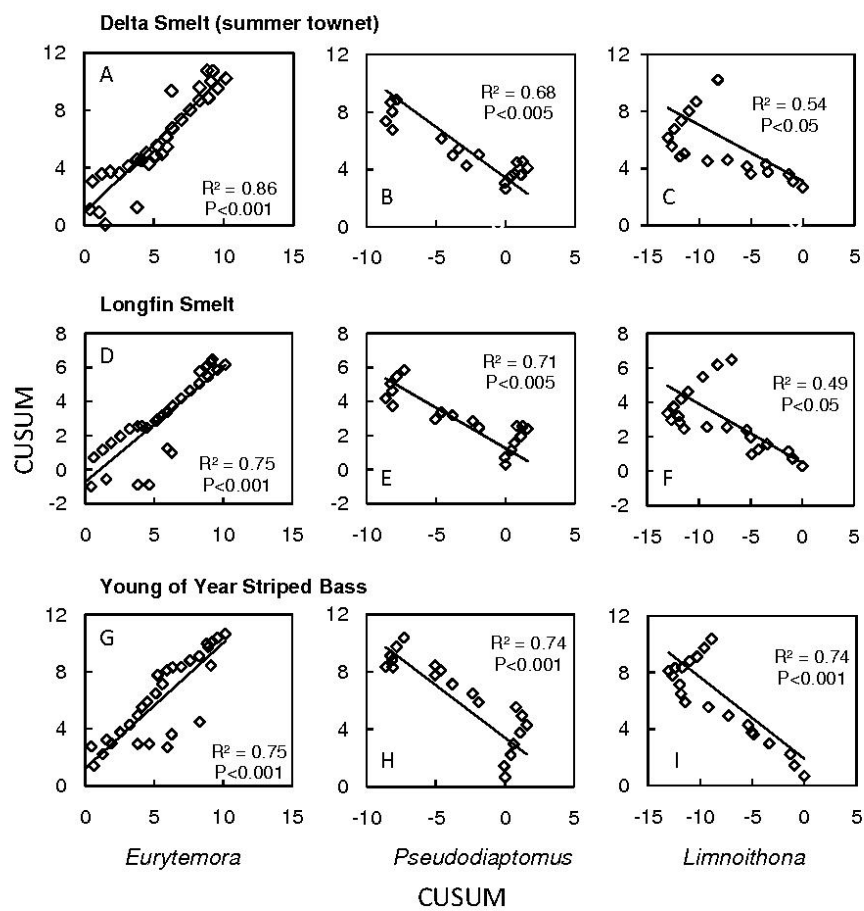


Fig. 18

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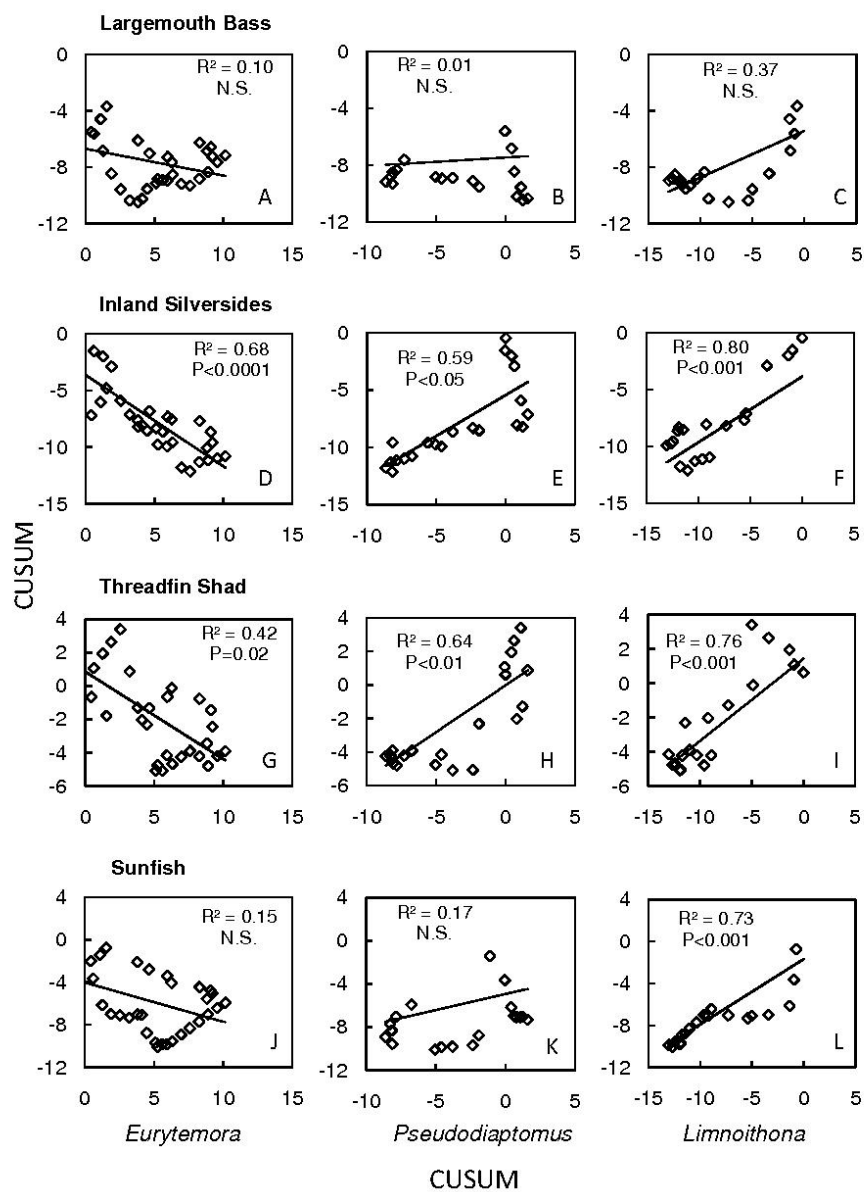


Fig. 19

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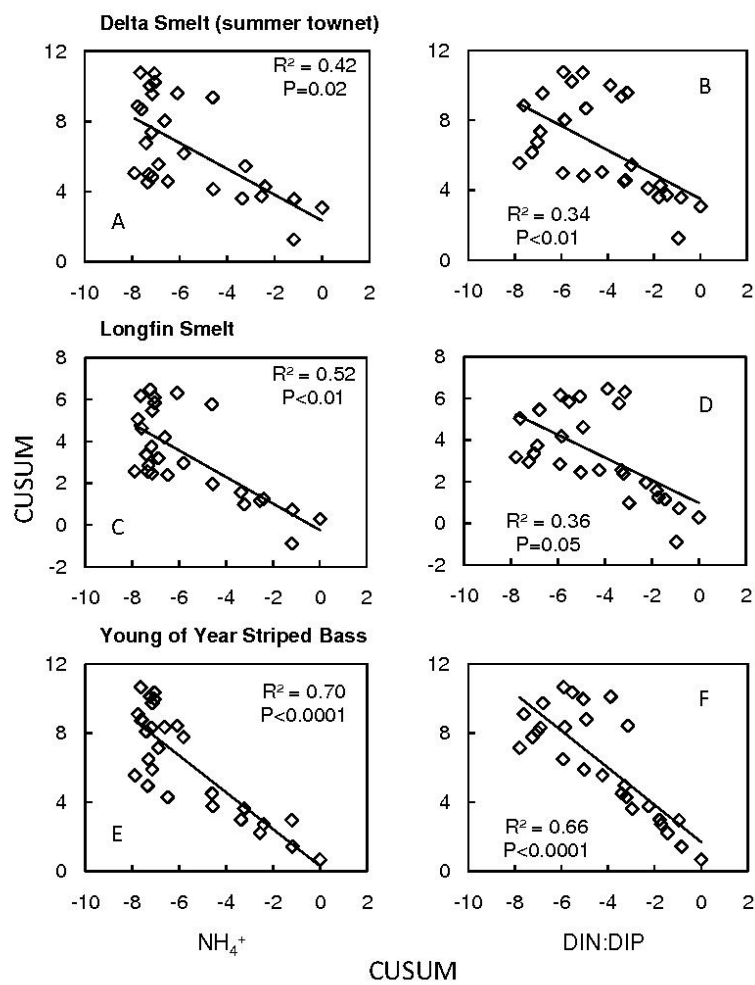
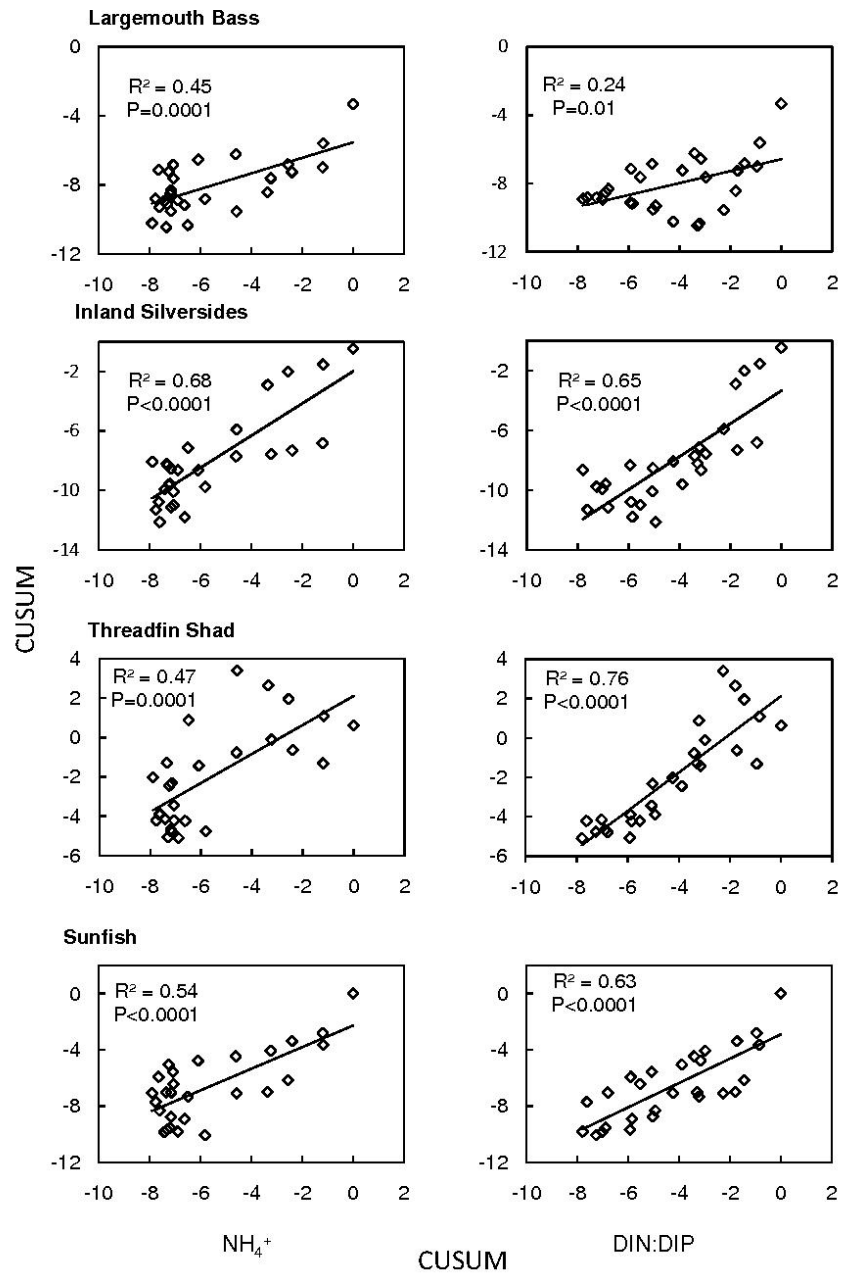


Fig. 20

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1126 Fig. 21.

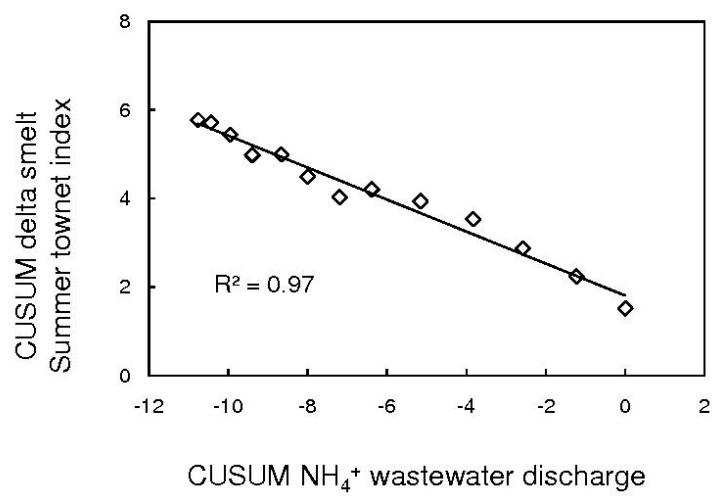
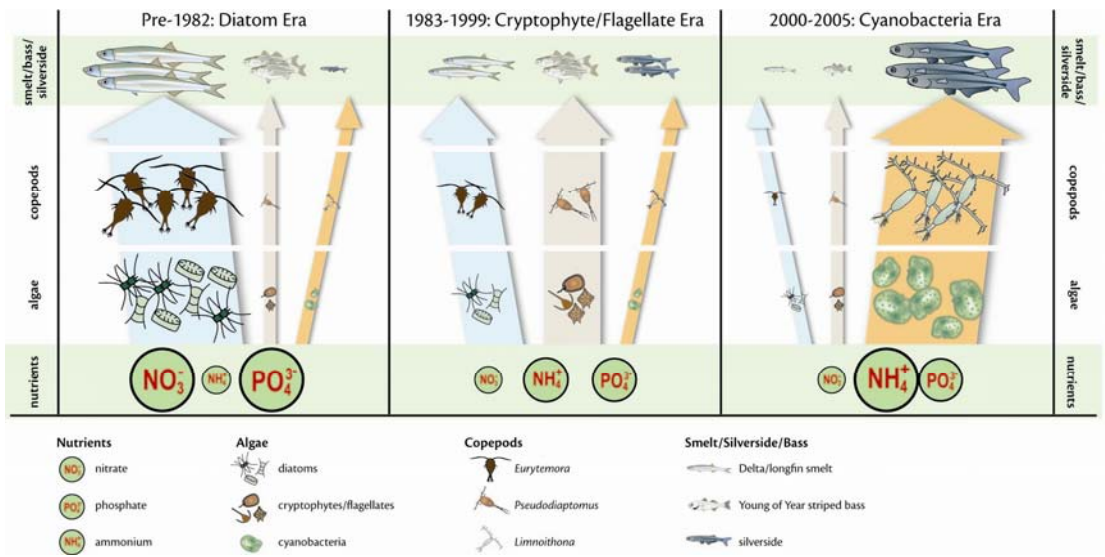


Fig. 22

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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 <sup>2</sup>
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