Technical Memorandum
Nutrient Science Summary

December 21, 2012

Historically, scientists have described primary productivity in the Bay-Delta as not being limited by nutrients (Cloern 2001; Lopez et al. 2006) and not experiencing signs of classic eutrophication (Cloern 2001). However, changes in nutrient loads are affecting ecosystem dynamics in complex ways that extend beyond our historic understanding of the process of eutrophication. Total nutrient load sets the upper limit on total primary production, and ultimately secondary production, and increases in nutrient loading are commonly associated with eutrophication. The most common effects of eutrophication are increased chl-*a* in the water column, development of hypoxia or anoxia (low or no dissolved oxygen, respectively), loss of native submerged aquatic vegetation, increased harmful algal blooms, and changes in biodiversity, including loss of certain fisheries (e.g., Cloern 2001; Anderson et al. 2002).

Nutrient effects on aquatic systems are far more complex and subtle than those normally associated with eutrophication and can occur across the full spectrum of nutrient limitation to nutrient super-saturation (Glibert et al 2012a). Changes in nutrient form (chemical state, oxidized vs. reduced, organic vs. inorganic, dissolved vs. particulate) and the proportion of different elements (including carbon (C), nitrogen (N), phosphorous (P), and silicon (Si), among others) also have effects on ecosystems at both the scale of the primary producers (the algae) and throughout the ecosystem. In the Bay-Delta, the total loads, the forms, and the relative proportions of nutrients have been changing over time. These changes have had profound effects on ecosystem structure of this system, as documented below. This technical memorandum describes the effects of two such changes: the proportion of ammonium to nitrate (NH_4:NO_3) and the proportion of nitrogen to phosphorus (N:P).

Ammonium:Nitrate

For decades, researchers have explored the relative use – or relative preference for – different forms of nitrogen (N) by phytoplankton. Ammonium (NH_4) is generally considered to be the form of nitrogen preferred by phytoplankton due to the more favorable energetics associated with its assimilation compared to that of nitrate (NO_3). It is also well documented that NH_4 can inhibit the uptake of NO_3, but the relative effect of this inhibition is a function of species composition and other environmental factors (Dortch 1990). When NH_4 inhibits the uptake of NO_3 by phytoplankton, it can also exhibit a strong negative control on total productivity (Yoshiyama and Sharp 2006; Dugdale et al. 2007). NH_4 suppression of NO_3 uptake when both nutrients are in ample supply should not be confused with the preferential use of NH_4 by phytoplankton when N is limiting. Under the latter conditions, phytoplankton will use NH_4 preferentially because it requires less energy than NO_3. Under the former conditions, the cells must cope with an excess; and in doing so, their metabolism is less capable of assimilating $NO_{3.}$

Within the Bay-Delta's aquatic ecosystems, Dugdale et al. (2007) show that "bloom levels of chlorophyll-*a* are evident only when NO_3 uptake occurs and that NO_3 uptake only takes place at lower ambient NH_4 concentrations." They conclude that ammonium concentrations greater than 4 μmol L^{-1} (0.056 mg L^{-1}) inhibit nitrate uptake by diatoms and thus suppress bloom formation. This level of NH_4 is in line with other inhibitory level estimates in the Bay-Delta (Wilkerson, *et al.* 2006; Parker *et al.* 2012a, 2012b; Dugdale *et al.* 2012), in the Delaware Estuary (Yoshiyama and Sharp 2006) and in laboratory experiments with Chesapeake Bay phytoplankton (Lomas and Glibert 1999a).

This level of ammonium is exceeded a majority of the time in the Sacramento River and Suisun Bay. For example, water quality monitoring data for the Bay-Delta show that the ammonium concentrations in the lower Sacramento River at Hood consistently exceed the ammonium inhibition threshold of 4 µmol L^{-1} (equivalent to 0.056 mg L^{-1}), as established by data from the Interagency Ecological Program's Environmental Monitoring Program (Figure 1).

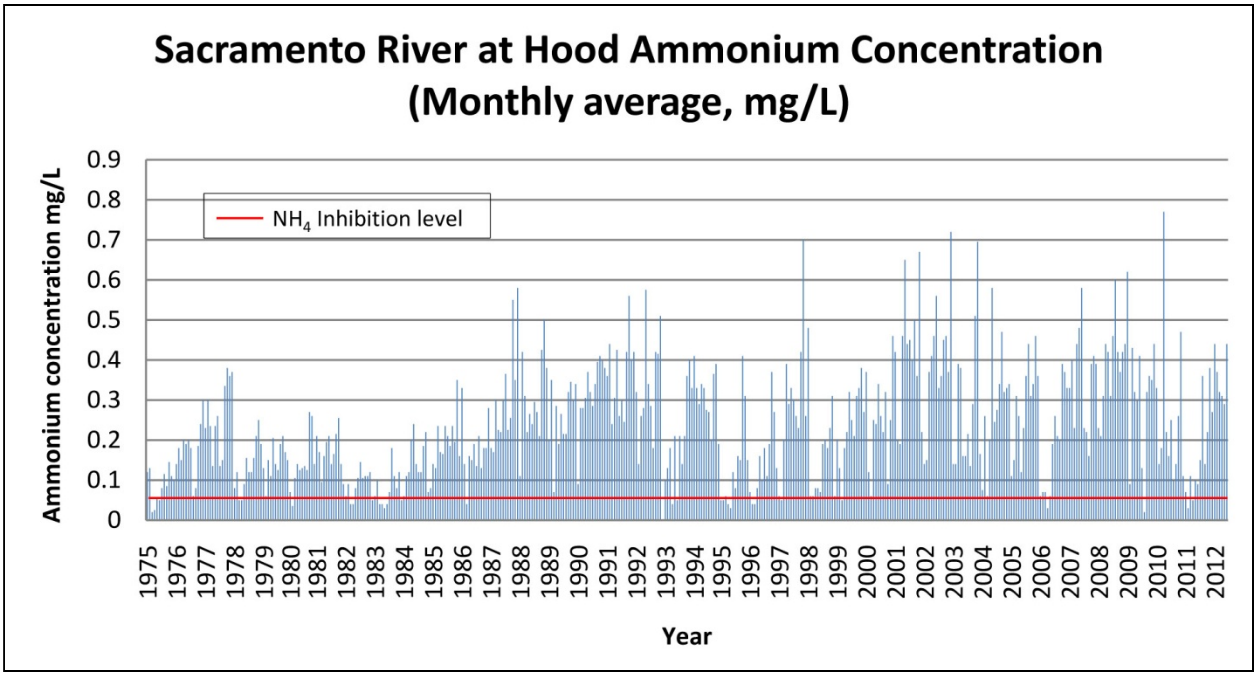

Figure 1. Average monthly ammonium concentration in the lower Sacramento River at Hood. Source: Environmental Monitoring Program data.

The effects of changes in the proportion of NH_4:NO_3 have been shown for the Bay-Delta in both field observations and laboratory experiments. Parker et al. (2012a) observed a 60% decline in primary production in the Sacramento River below the Sacramento Regional Wastewater Treatment Plant, where NH_4 is discharged, compared to production above the Treatment Plant's outfall. Also supporting this finding, Parker et al. (2012b) found that "[b]y tracing both carbon (C) and N uptake we provide clear evidence that high rates of C uptake are linked to phytoplankton NO_3, and not NH_4, use." They conclude that the increased proportion of NH_4 "may help explain some of the reduced primary production and phytoplankton biomass observed [in the San Francisco Estuary] since the 1970s."

In enclosure experiments with samples from Central Bay, Suisun Bay, and the Sacramento River at Rio Vista, representing a gradient of both nutrient concentrations and proportions of different forms of N, Wilkerson et al. (in preparation) observed "a gradient of decreasing phytoplankton physiological rates in the upstream direction as far as Rio Vista." Phytoplankton productivity rates (both carbon and nitrogen uptake) decreased with increasing concentrations of NH_4.

In a series of recent experiments conducted with natural samples from the Sacramento River, the effects of altered proportions of NH_4:NO_3 were also apparent (Glibert et al. 2012b). In these experiments, the proportions of these nutrients were manipulated, and both short-term N uptake rates and longer-term N production rates were assessed. Two findings are of note. First, when 20 µmol NH_4 was added to the sample, a concentration commonly observed in the Sacramento River, and the rate of NO_3 uptake was measured across a concentration gradient, the rate of uptake of NO_3 decreased significantly compared to unamended rates measured over a period of < 1 hour (Figure 2). Second, when samples were enriched with NH_4, NO_3, or urea (at the molar equivalent dose) for a period of 24-48 hours, and then rates of uptake of all N forms measured, the summed rate of N uptake in the NH_4-added treatment was significantly lower than that in the NO_3-added or urea-added treatments (Figure 3).

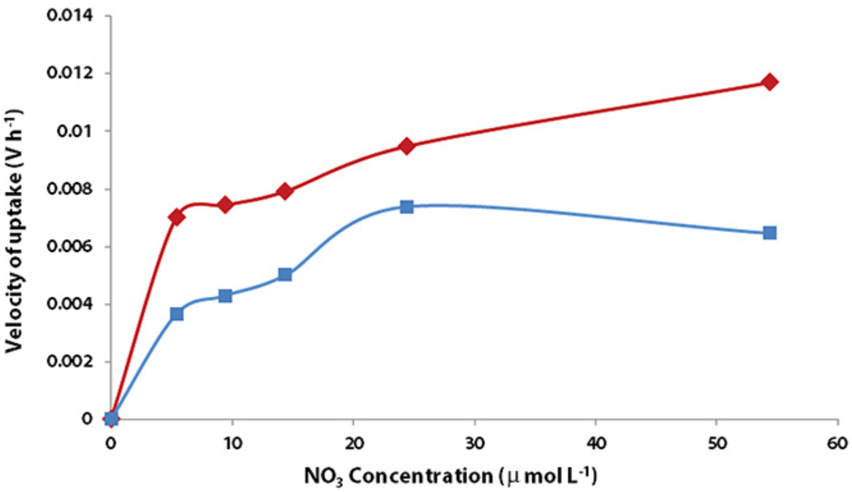

Figure 2. Velocity of uptake of NO_3 as a function of added NO_3 enrichment (red curve), and the same relationship but with a constant addition of 20 µmol L^{-1} NH_4 (blue curve). Nitrate uptake is reduced when NH_4 is added. Experiment was conducted with water collected from the Sacramento River. Data from Glibert et al. (2012b).

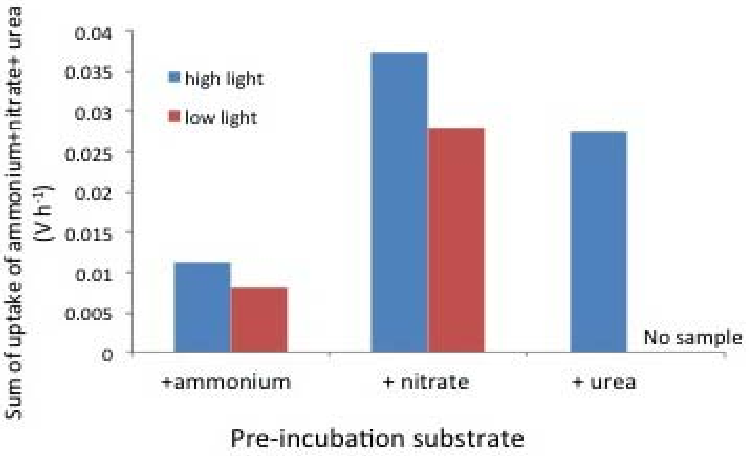

Figure 3. Summed rate of uptake of nitrate+ ammonium+ urea for samples collected from the Sacramento River and pre-incubated with the substrate indicated, after which short-term uptake rates were measured using ^{15}N tracer techniques**.** The experiment was conducted under both high (blue bars) and low (red bars) irradiance levels. The summed rate of N uptake in the NH_4-added treatment was significantly lower than that in the NO_3-added or urea-added treatments. From Glibert et al. (2012b).

This finding is further supported by the 37 years of data collected by the Environmental Monitoring Program in the Bay-Delta. When monthly data of chlorophyll-a and diatom cell count are plotted against ammonium levels for the period 1975 to 2012 there is a marked decreasing trend in both as ammonium levels rise, with an increasing effect around the 0.056 mg L^{-1} (4 µmol L^{-1}) inhibition level (Figures 4 and 5).

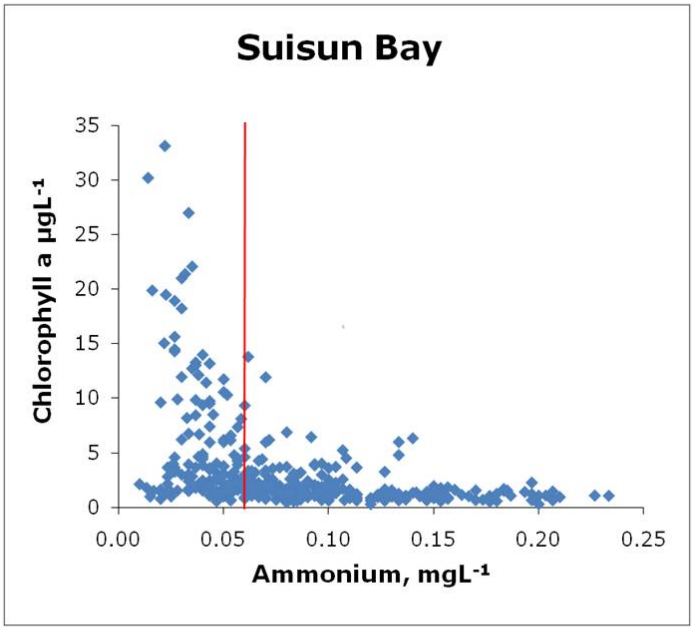

Figure 4. Chlorophyll-*a* concentration plotted with ammonium concentration in Suisun Bay. As NH_4 concentration increases above the level where inhibition is observed (red line at 0.056 mg L^{-1} NH_4), chl-*a* levels decline. (Source: Environmental Monitoring Program data)

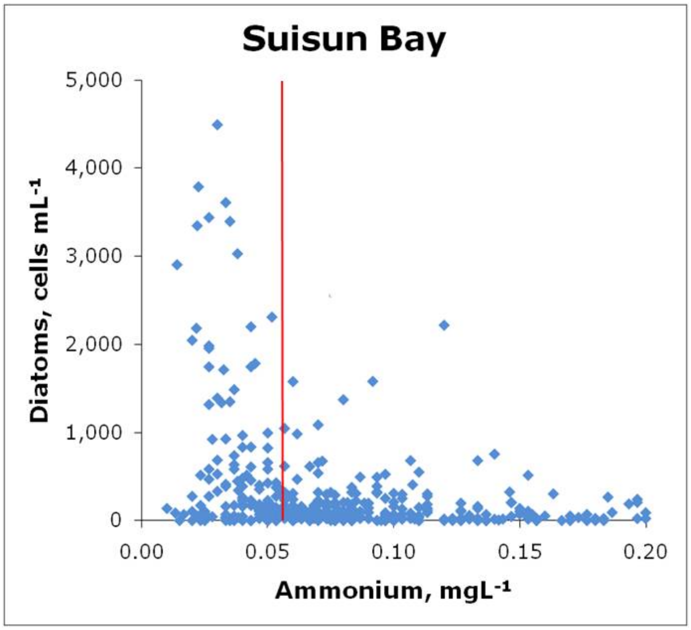

Figure 5. Diatom cell count plotted with ammonium concentration in Suisun Bay**.** As NH_4 concentration increases above the level where inhibition is observed (red line at 0.056 mg L^{-1} NH_4), diatom abundance declines. (Source: Environmental Monitoring Program data)

These observations of NH_4 suppression are not new in or unique to the Bay-Delta. A large body of scientific research describes NH_4 suppression of algae productivity (*e.g.* Ludwig 1938; Harvey 1953). Some of the early field demonstrations of this phenomenon were carried out by MacIsaac and Dugdale

(1969, 1972), followed by research in the Chesapeake Bay by McCarthy et al. (1975). Maestrini et al. (1982) showed that only after NH_4 concentrations were reduced to < 7 µmol L^{-1} (0.098 mg L^{-1}) was NO_3 uptake sufficient to match that of NH_4 uptake. Price et al. (1985) showed that the rate of NO_3 uptake was reduced ~50% in samples that also received an NH_4 spike compared to those receiving a NO_3 spike. Lomas and Glibert (1999a) described the threshold for inhibition of NO_3 uptake at NH_4 levels of approximately 1 µmol L^{-1} (0.014 mg L^{-1}). Yoshiyama and Sharp (2006) saw a "striking decline in production at NH_4 levels above a low threshold (around 10 µmol L^{-1})" (0.14 mg L^{-1}). The importance of NH_4 inhibition of NO_3 uptake was considered to be a necessary interaction to include in a recent model of the emergent phytoplankton community in the California Current System (Goebel et al. 2010). In recent experiments conducted in the tidal freshwater estuarine zone of the Guadiana Estuary (Spain and Portugal), it was also found that NO_3 consumption decreased with increasing NH_4 uptake, and these findings were most pronounced during the most productive period. Total primary productivity was suppressed as a result (Domingues et al. 2011). This is particularly problematic for the Bay-Delta as it is already a comparatively low producing estuary (Jassby *et al.,* 2002; Kimmerer *et al.*, 2012). Laboratory experiments suggest that Delta-wide chl-a levels are now low enough to limit zooplankton abundance (Müller -Solger *et al*., 2002).

The form of N available to a phytoplankton community affects more than just rates of uptake and productivity. Their proportions also affect phytoplankton species composition. The physiological literature strongly supports the concept that different algal communities use different forms of N. Diatoms, once the dominant algal group in the Bay-Delta, generally have a preference for NO_3; dinoflagellates and cyanobacteria generally prefer more chemically reduced forms of N (NH_4, urea, organic nitrogen) (e.g., Berg et al. 2001; Glibert et al. 2004, 2006; Brown 2009). Under some circumstances, diatoms have a physiological requirement for NO_3 (Lomas and Glibert 1999a,b). Moreover, diatoms usually show no evidence of NO_3 uptake saturation under very high NO_3 conditions (Collos et al. 1992, 1997; Lomas and Glibert 1999a), in contrast to the generally accepted saturating uptake kinetic relationships that are used to describe the relationship between nutrients and uptake rate. Cyanobacteria have been shown to preferentially use chemically reduced forms of N, like NH_4, over NO_3. Evidence comes from measurements of enzyme activities in the cells (Solomon et al. 2010), directly determined rates of N uptake using isotope tracer techniques (Glibert et al. 2004; Kendall et al. 2011), direct growth studies (Berman and Chava 1999; citations within Meyer et al. 2009), and observations of changes in community composition with enrichment with different forms of N (Domingues et al. 2011).

There is also evidence that the increase in aerial coverage by the invasive aquatic plant *Egeria densa* may be attributed to the ratio of nutrient inputs to the system. Feijoo, et al. (2002) experimentally found that *E. densa* absorbed more nitrogen from water when it was present in the form of NH_4 than when it occurred as NO_3.

Thus, although there are many factors that regulate the relative contribution of a nutrient source to different phytoplankton groups, and even species-specific differences within groups, it has generally been established that NO_3 disproportionately contributes to diatoms' uptake and production, while reduced forms of N (both NH_4 and urea) disproportionately contribute to the uptake and growth of cyanobacteria. As stated by Domingues et al. (2011), "…increased inputs of N as NH_4 due to urban waste effluents may result in a shift in phytoplankton community composition, towards a dominance of cyanobacteria and green algae." And, as stated by Lehman et al. (2010), "Recent increases in NH_4 concentration in the western delta may give a competitive advantage to Microcystis which rapidly assimilates NH_4 over NO_3." The phytoplankton community composition in the Bay-Delta estuary has shifted in just this manner.

The shift in algal community composition in the Bay-Delta has been far more extensive than just the recent increase in annual blooms of *Microcystis.* The Delta's algal species composition has shifted from diatoms to smaller and lower quality food species such as flagellates, cryptophytes and cyanobacteria (Lehman, 2000*;* Lehman *et al*., 2005*;* Lehman et al., 2010; Jassby *et al*., 2002; Sommer *et al*., 2007*;* Glibert, 2010; Glibert et al., 2011; Winder and Jassby, 2010) and to invasive macrophytes such as *Egeria densa* (Sommer, *et al*., 2007; Nobriga et al., 2005; Glibert et al., 2011). Jassby (2008) states:

> *A decrease in percentage of diatom biovolume occurred during 1975–1989, caused by both a decrease in diatoms and an increase in green algae, cyanobacteria, and flagellate species biovolume (Kimmerer 2005; Lehman 1996), i.e., probably in the direction of declining nutritional value per unit biomass. In principle, the total nutritional value of a community could decrease even as its biomass increases. Moreover, changes in size, shape, and motility of species comprising the phytoplankton community could also affect their availability as food particles for crustacean zooplankton and other consumers*.

Total Ammonia Toxicity

In addition to altering phytoplankton community structure, growth rates and abundance, total ammonia is also toxic to some higher trophic level organisms. Scientists at UC Davis have investigated the effects of total ammonia to the calanoid copepod *Pseudodiaptomus forbesi* using a full life-cycle bioassay approach (Teh et al. 2011). *P. forbesi* is an important prey item for the young of many fish species in the Bay-Delta including delta smelt and longfin smelt (Nobriga 2002; Hobbs et al. 2006; Feyrer et al. 2003). Teh et al. (2011) found that total NH_4 at 0.36 mg L^{-1} (25.7 µmol L^{-1}) significantly affects the recruitment of new adult copepods and total NH_4 at 0.38 mg L^{-1} (27. 1 µmol L^{-1}) significantly affects the number of newborn nauplii surviving to 3 days (Teh et al. 2011). For comparison, monthly water samples collected between 2009-2010 from the Sacramento River between Hood and Isleton, approximately 30 miles downstream from the point of discharge, exceeded this level of NH_4 44% of the time (Figure 6).

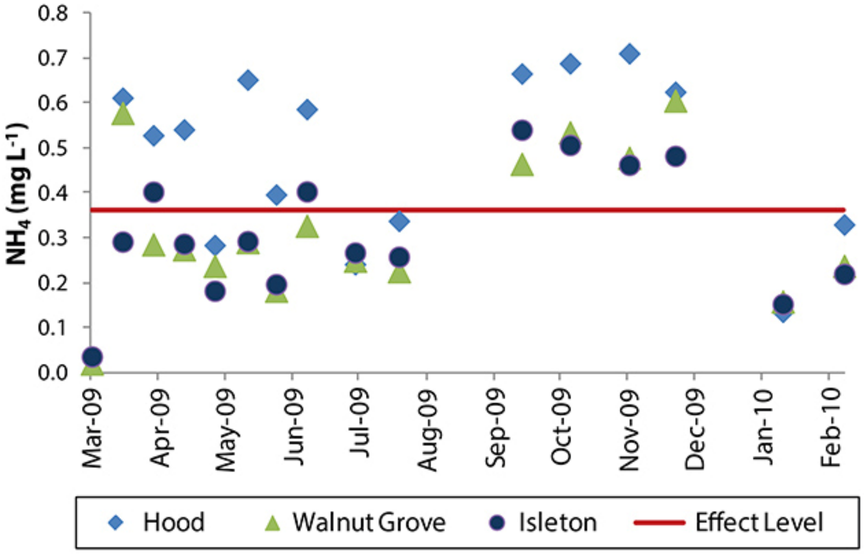

Figure 6. Ammonium concentrations in the Sacramento River measured at Hood, Walnut Grove, and Isleton between 2009 and 2010. Hood and Isleton are approximately 8 and 30 miles downstream of the discharge, respectively. The horizontal line at 0.36 mg L^{-1} is the level at which significant toxicity to copepods is observed. Data from Foe et al. (2010).

The Teh et al. (2011) study was recently cited in the U.S. Fish and Wildlife Service 12-month finding on the petition to list the Bay-Delta longfin smelt as threatened or endangered under the ESA. (77 Fed. Reg. 19755, 19776 [April 12, 2012].) The proposed rule states that "[a]quatic insects on which the longfin smelt relies upon for food have been shown to be sensitive to ammonia." (77 Fed. Reg. 19776.) The proposed rule states that "[a]mmonia also can be toxic to several species of copepods important to larval and juvenile fishes." (*Id.*) The toxic effect of total ammonia is a major stressor on aquatic life that has a pervasive impact across the Bay-Delta estuary.

Further, the U.S. Environmental Protection Agency's (USEPA) recently published Bay-Delta Action Plan highlights concerns with aquatic life toxicity caused by total ammonia nitrogen and identifies total ammonia levels as one of the suspected contributors to the pelagic organism decline in the Bay Delta (USEPA 2012). USEPA also proposed updated Ammonia Aquatic Life Criteria in 2009, which are more stringent than existing criteria promulgated in 1999 and consider ammonia toxicity to freshwater mussels (USEPA 2009). In the Bay Delta Action Plan USEPA states that they will finalize the new national ammonia aquatic life criteria and they encourage the Regional Boards to consider adopting the criteria and using the criteria to develop effluent limitations for ammonia.

Nitrogen:Phosphorus

Extensive research has found that the N:P ratio also has profound effects on community structure. The N:P ratio of nutrients has doubled in the Bay-Delta estuary over the last 35 years as is apparent from the data on Figure 7. These increases are a result not only of the increasing total N load (due to increasing effluent as well as other sources), but also as a function of declining P loads (Van Niewenhuyse 2007; Glibert 2010, Glibert et al. 2011).

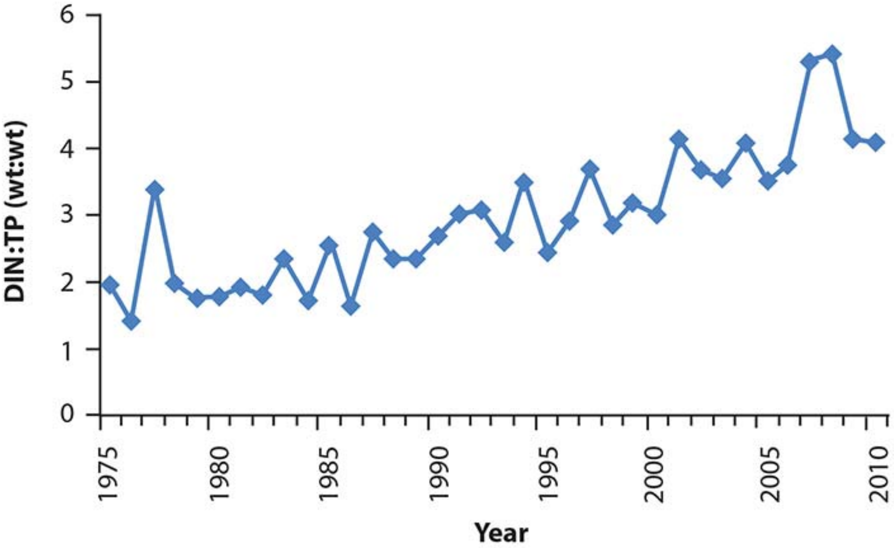

Figure 7. Average annual (March-November) ratio of dissolved inorganic nitrogen to total phosphorus has doubled in the Bay-Delta**.** (Source: IEP monitoring data from stations in Suisun Bay and the confluence (D4, D6, D7, D8)).

There are a number of strategies available to different types of phytoplankton for coping with an environment where nutrient ratios are not in proportion to their internal requirements (Glibert and Burkholder 2011). For example, cell size is an important determinant of elemental composition (Harris 1986; Finkel et al. 2010). Small cells have a lower requirement for P due to the smaller need for structural components in the cell (Finkel et al. 2010). In comparison to diatoms, very small cyanobacteria such as *Synechococcus* have a much larger cellular ratio of carbon to phosphorus (C:P), on average (Finkel et al. 2010). This explains why small cells, such as *Synechococcus*, have been found to thrive in waters that are comparatively P poor, as is the case in Florida Bay (Glibert et al. 2004).

There is strong support in the scientific literature for the proposition that the N:P ratio influences phytoplankton community composition. For example, in the Seto Inland Sea of Japan, removal of phosphorus also led to a shift in phytoplankton community structure from "nonharmful diatoms to harmful raphidophytes…and then finally to harmful/toxic dinoflagellates" (Yamamoto 2002). In this case the reduction in phosphorus which increased N:P, led to a change in phytoplankton community composition and was suggested to be "the major cause of the reduction in fishery production" (Yamamoto 2002).

In a retrospective analysis of 30 years of data from the Bay-Delta estuary, Glibert et al. (2011) found that the variation in these nutrient concentrations and ratios is highly correlated to variations in the total amount and composition of phytoplankton. This analysis revealed relationships between biological parameters and nutrients and/or nutrient ratios using both the original data and data that were adjusted for autocorrelation. At the phytoplankton level, as described earlier, there has been a decline in total chl-a and a decline in total diatoms over the past several decades in proportion to the increase in total inorganic N to total P (Figure 8). The change in chl-a with N:P is apparent in different regions of the Bay Delta; as N:P increases, chl-a declines (Figure 9).

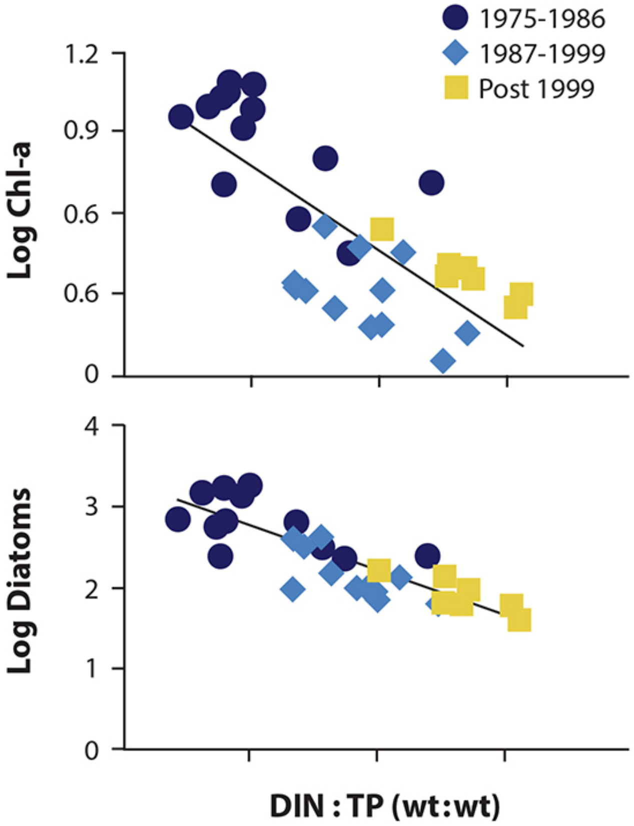

Figure 8. Change in the concentration of chl-*a* (µg L^{-1}) and abundance of diatoms (Bacillariophyceae, cells mL^{-1}) as a function of dissolved inorganic N to total phosphorus. A loss of total chl-*a* and a loss of total diatoms in the phytoplankton community have occurred over the past several decades in

proportion to the change in total inorganic N to total P. The relationship is significant at $p<0.05$. Different periods of time are represented by different symbols: 1975-1986, filled circles; 1987-1999, diamonds; post-1999- filled squares. Data shown are for the years 1975-2005 and cover the region from the confluence to Suisun Bay. All data log-transformed. Data from Glibert et al. (2011).

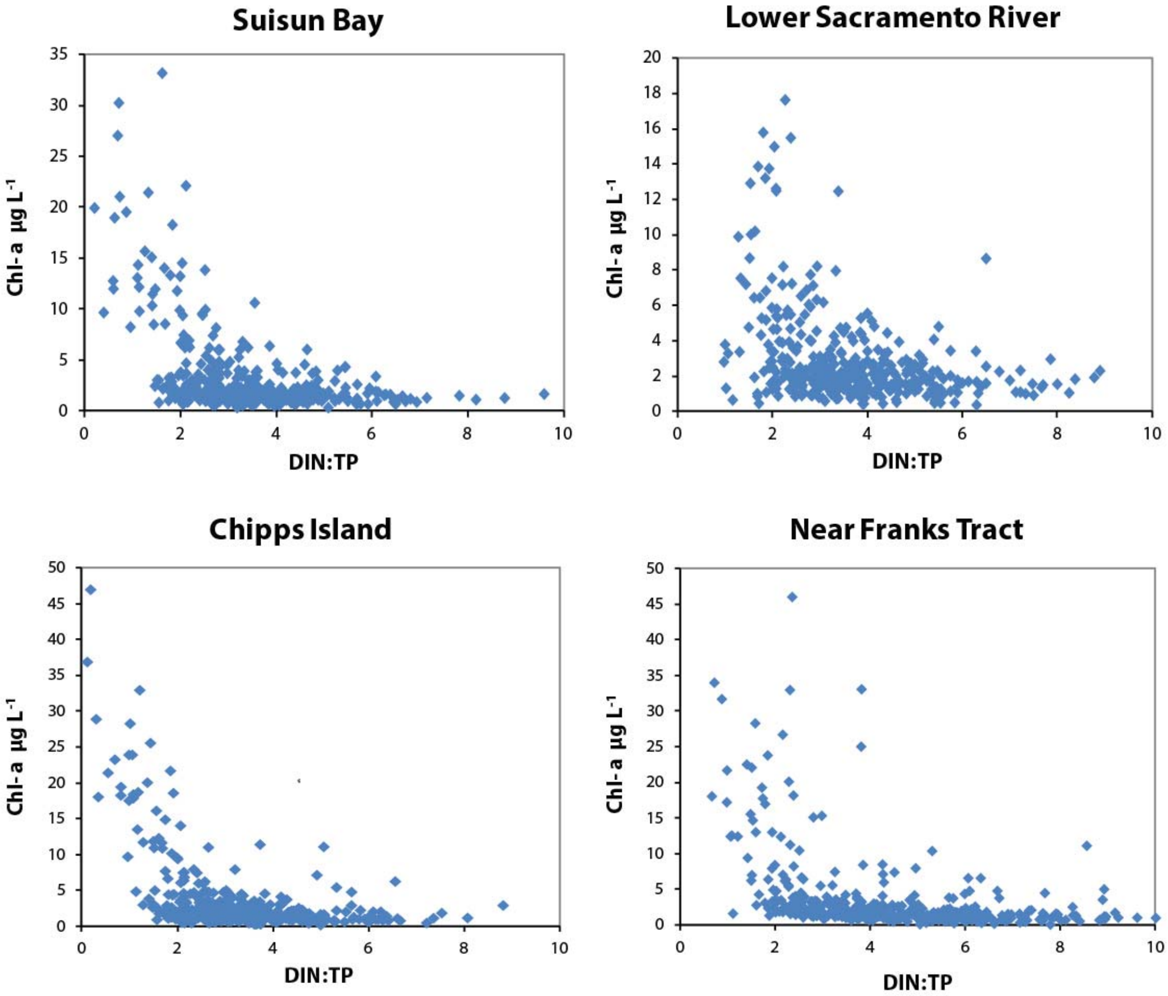

Figure 9. Chl-*a* concentration plotted against DIN:TP for subregions of the Delta, 1975-2011**.** As DIN:TP increases, there is a loss of chl-*a*. (Source: Environmental Monitoring Program data).

Fast-growing phytoplankton require proportionately more P to satisfy metabolic demands. Diatoms are typically fast-growing, and thus require proportionately more P to meet this metabolic demand. In ecological terms, they are considered a *r*-selected group, would be expected to have a low N:P biomass ratio (due to the high P cellular demand), and thus would be expected to be outcompeted if N:P in the environment increases. So-called *r*-selected species are out-competed when the environment changes (e.g., Heckey and Kilham 1988). In contrast, many cyanobacteria are considered to be *k*-selected, implying a slower growth rate and a higher metabolic N:P. In fact, “Reynolds (1984) singled out *Microcystis* as an example of a *k*-selected phytoplankter because it grows slowly in nature” (Heckey and Kilham 1988).

The balance of N:P can also affect other metabolic aspects of phytoplankton besides growth, including toxin production, cell membrane thickness, and other chemical constituents that have been considered to turn good food “bad” (Mitra and Flynn 2005). For example, toxin production by numerous harmful algae has been shown to increase when the cells are grown under nutrient-imbalanced conditions and when there is a change in N or P availability (Flynn et al. 1994; Johansson and Granéli 1999; Granéli and Flynn 2006). In Daechung Reservoir, Korea, researchers found that toxicity of cyanobacteria was related not only to an increase in N in the water, but to the cellular N content as well (Oh et al. 2000). A recent report by van de Waal (2009) demonstrated in chemostat experiments that under high carbon dioxide and high N conditions, microcystin (an algal toxin) production was enhanced in *Microcystis*. Similar relationships were reported for a field survey of the Hirosawa-no-ike fish pond in Kyoto, Japan, where the strongest correlations with microcystin were high concentrations of NO_3 and NH_4 and the seasonal peaks in *Microcystis* blooms were associated with extremely high N:P ratios (Ha et al. 2009). Thus, not only is *Microcystis* abundance enhanced under high N:P, but its toxicity appears to be as well (Oh et al. 2000).

It is well accepted that the nutritional value of phytoplankton differs from one species to another. Toxin production can inhibit grazing. Some phytoplankton species are rejected by grazers due to their size. Others vary in their nutritional quality. For example, some diatom species produce certain highly unsaturated fatty acids that are essential for zooplankton reproduction (reviewed by Kilham et al. 1997) while flagellates generally produce different fatty acids than diatoms (Olsen 1999). Many trophic interactions, such as rates of growth or fecundity, are dependent on the acquisition of particular fatty acids, as a measure of the food quality of algae (e.g., Ahlgren et al. 1990; Coutteau and Sorgeloos 1997; Weers and Gulati 1997; Brett and Müller-Navarra 1997). In feeding experiments, Ger et al. (2010) observed reduced survival of the copepods, *Pseudodiaptomus* and *Eurytemora*, even when *Microcystis* was only a small portion of their available diet. Brett and Müller-Navarra (1997) developed a food quality rank for 10 species from 5 major phytoplankton groups based on the average of the observed change in the abundance of individual zooplankters that preyed upon these phytoplankton in growth bioassays. They and others (see Park et al. 2003) have applied a 0-1 scale of phytoplankton food quality in which cyanobacteria ranks at 0.2; green algae, 0.525; diatoms, 0.7; and cryptomonads, 0.95. Thus, a trend of decreasing diatoms and increasing cyanobacteria in the Bay-Delta would suggest, based on these rankings, a decrease in food quality for higher trophic levels.

Cloern and Dufford (2005) state, “[t]he efficiency of energy transfer from phytoplankton to consumers and ultimate production at upper trophic levels vary with algal species composition: diatom-dominated marine upwelling systems sustain 50 times more fish biomass per unit of phytoplankton biomass than cyanobacteria-dominated lakes.”

For species that prey on phytoplankton (e.g., zooplankton), stoichiometry affects all aspects of behavior, such as growth rate, fecundity, and ultimately the success of different populations (Jeyasingh and Weider 2005, 2007), but may affect various life stages differently (Moe et al. 2005, p.31): “[a]n organism’s requirements for different elements may vary throughout its life cycle, and thus certain life stages may be more sensitive than others to variation in the stoichiometry of its resource.” For example, copepod juveniles have a relatively high demand for C, N, and P, but at a later stage, while C is still needed for metabolism, more P must be allocated to eggs. Therefore, P-poor food sources can disproportionately affect egg production while not affecting survival (Faerovig and Hessen 2003; Laspoumaderes et al. 2010). In a laboratory study where *Acartia tonsa* was fed diatoms grown on different N concentrations, Kiørboe (1989), confirmed that this zooplankter changes its feeding rate in response to phytoplankton of different chemical composition – thus, in response to food quality. Moreover, egg production followed the variation in algal N content and increased with increasing algal N. In the Bay-Delta, Slaughter and Kimmerer (2010) observed lower reproductive rates and lower growth rates of the copepod, *Acartia* sp. in the low salinity zone compared to taxa in other areas of the estuary. Their observation may be due to differences in nutrient stoichiometry between these areas.

In a review of field and laboratory-based research on stoichiometry in food webs, Hessen (1997) showed that a shift from copepods to *Daphnia* tracked N:P; copepods retain proportionately more N, while *Daphnia* are proportionately more P rich. Often, those organisms that are most able to retain the nutrient in limited supply, in this case P, have the competitive advantage in an unbalanced system. Glibert et al. (2011) illustrated a finding similar to Hessen's, that the decline in calanoid copepods in the Bay-Delta, and the invasion of cyclopoids tracked N:P over time. Variation in proportional densities of the calanoid copepod *Eurytemora* with the cyclopoid copepod *Limnoithona* over time has followed changes in the DIN:TP (dissolved inorganic nitrogen to total phosphorus) ratio (Figure 10), a pattern consistent with these grazers being responsive to changes in elemental stoichiometry and maintenance of altered dynamic equilibria on a long-term scale. In fact, Glibert et al. (2011) found relationships between many zooplankton species and nutrient composition. Results from whole-lake experimentation suggest that the N:P ratio is linked to alterations in zooplankton size, composition, and growth rate, as those animals with increased RNA allocation (more P available for growth) will grow at higher rates due to increased protein synthesis rates (Sterner and Elser 2002, Schindler 1974). Similar findings were reported from annual studies in the Baltic Sea (Walve and Larsson 1999).

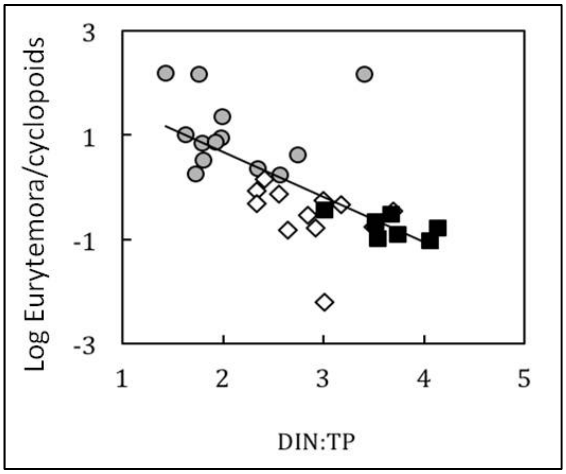

Figure 10. Change in the ratio of Eurytemora to cyclopoid copepods (all data log transformed) as a function of DIN:TP for annually averaged data from 1975-2005 for samples collected between the confluence and Suisun Bay**.** As DIN:TP increases, the proportion of Eurytemora to Cyclopoids decreases. Different periods of time are represented by different symbols: 1975-1986, filled circles; 1987-1999, diamonds; post-1999 filled squares. The correlation for these and for data that were detrended (not shown) are significant ($p<0.05$). From Glibert et al. 2011.

Superimposed on these empirical observations is consideration of whether substrate quality or food quality is altered on an episodic basis, or whether changes are long-term and sustained. As conceptualized by Hood and Sterner (2010), a change in predator growth rate depends on the extent to which a diet is sustained or switches between low-quality food and high-quality food as defined by the relative P content.

Higher Trophic Level Effects

Disproportionate N and P loads are now recognized to have effects at all scales, from genomic to ecosystems that need further empirical resolution (Peñuelas et al. 2012). When N:P availability changes, food webs change, biogeochemical cycling can change, and these changes can be positively reinforcing. Sterner and Elser (2002) state: "[s]toichiometry can either constrain trophic cascades by diminishing the chances of success of key species, or **be a critical aspect of spectacular trophic cascades with large shifts in primary producer species and major shifts in ecosystem nutrient cycling**" [emphasis added]. Just as different elemental ratios may affect the composition of the primary producers, different nutrient requirements of organisms occupying higher trophic levels will have an impact on their ability to thrive as community composition changes at the base of the food web. At the ecosystem scale, the total load and balance of nutrient elements have effects that propagate through the food web, with the potential of transforming ecosystems to new stable states. Although the shift in algal community composition in terms of diatoms and cyanobacteria has been emphasized above, this shift in the Bay-Delta estuary has been far more complicated. With the decline in water column chl-*a* and an increase in light availability, other primary producers have increased in abundance, including invasive macrophytes such as *Egeria densa* (Sommer et al. 2007; Nobriga et al. 2005; Glibert et al. 2011). *E. densa* may be particularly well suited to the low DIP:DIN environment of the Bay-Delta since it is able to access sediment bound phosphorus through its roots. In fact, similar increases in macrophytes were observed in many other systems in which N:P increased following N enrichment and P reduction, including the Potomac River, Chesapeake Bay, Ebro River in Spain, and the Rhine River in Germany (Glibert et al. 2011; Glibert 2012). Such macrophyte invasions can have profound impacts on ecosystems, not only because they alter the flow of C and the overall productivity of the system, but they also serve as “ecological engineers,” decreasing nutrients through uptake, reducing turbidity by trapping sediments, and providing refuge for zooplankton and habitat for other species, including fish (Yarrow et al. 2009; Glibert 2012).

The interplay between nutrient stoichiometry and biogeochemistry is well illustrated when a system is driven to higher macrophyte productivity. Macrophytes can be highly productive, which can result in elevation of pH due to carbon drawdown in the process of photosynthesis. As noted by Glibert (2012), once pH is elevated, the fundamental physical–chemical relationships related to P adsorption–desorption in sediments change, as does N biogeochemistry (Jordan et al. 2008; Gao et al. 2012). Moreover, under increased pH conditions, the biogeochemistry of calcification is altered, increasing the potential for calcification and the growth of calcifying organisms. Thus, the change in the abundance of the clam *Potamocorbula amurensis* from the time of its introduction in the mid-1980s to 2005 has been shown to be highly and positively correlated to the increase in total N:total P ($r^2 = 0.46$; $n = 20$; $p < 0.01$; all data log transformed), and the average annual abundance of this species has also been found to be highly and positively correlated with mean annual average pH in the estuary ($r^2 = 0.64$; $n = 19$; $p < 0.01$; species abundance data log transformed) (Glibert et al. 2011). Interestingly, the Potomac River, Rhine River and the Ebro River have had similar invasions of macrophytes and *Corbicula* clams that relate to increases in N:P loading (Ibanez et al. 2008; Glibert et al. 2011; Glibert 2012).

In the Bay-Delta estuary, data show top-down grazing of phytoplankton by the clam *P. amurensis* exerts a strong control on phytoplankton biomass, as is also the case for other systems when invaded by bivalve mollusks. Prior interpretations, emphasizing stochastic invasions largely via ballast water exchange imply that the invasive event was the ultimate cause of the change in top-down control of phytoplankton. The ecological stoichiometric interpretation does not preclude strong top-down control of selected component organisms, nor ballast water exchange as the mechanism of introduction. The distinction is that, at the overall ecosystem level, the structuring of species is affected by alterations in nutrients and ecosystem biogeochemistry.

The arguments presented here make the case that bottom-up control contributed to the conditions that allowed *P. amurensis* to become a dominant regulator of phytoplankton production. In other words, invasive species effects and nutrient effects are interrelated. This interpretation is consistent with Ware and Thompson’s (2005) insights from a broad survey of the relative contributions of “bottom-up” vs. “top-down” factors that potentially control fish catch in the coastal waters of the western U.S.; they, too, reported that bottom-up factors were more important.

Several recent reviews have investigated the stoichiometry of fish (Sterner and George 2000; Hendrixson et al. 2007; McIntyre and Flecker 2010). Not only does a strong shift in body N:P occur with growth stage (Pilati and Vanni 2007), but strong differences between taxonomic families also occur. In fact, Hendrixson et al. (2007) demonstrated, for 20 families of fish, that a phylogenic tree could be developed based on the body nutrient composition.

In the Bay-Delta estuary, numerous changes in fish community composition occurred in relation to phytoplankton and zooplankton changes, and to N:P (Glibert 2010; Glibert et al. 2011) (Figure 11). Glibert et al. (2011) also found that total P “explained at least as much of the variability in delta smelt as did the [Feyrer et al. 2011] habitat index, and dinoflagellate abundance explained even more.” Unlike correlations with Bay-Delta outflow or with the location of the 2 practical salinity unit isohaline, where the underlying mechanisms driving the correlations are largely unknown, the nutrient relationships have a strong mechanistic explanation in ecological stoichiometry and stable state principles. For this reason, there is relatively low uncertainty that changes in nutrient stoichiometry in the Bay-Delta estuary, achieved through both external forces (altered land-based nutrient loads) and internal, organism-driven, assimilative and dissimilative processes, are related to community compositional changes (Glibert et al. 2011; Glibert 2012).

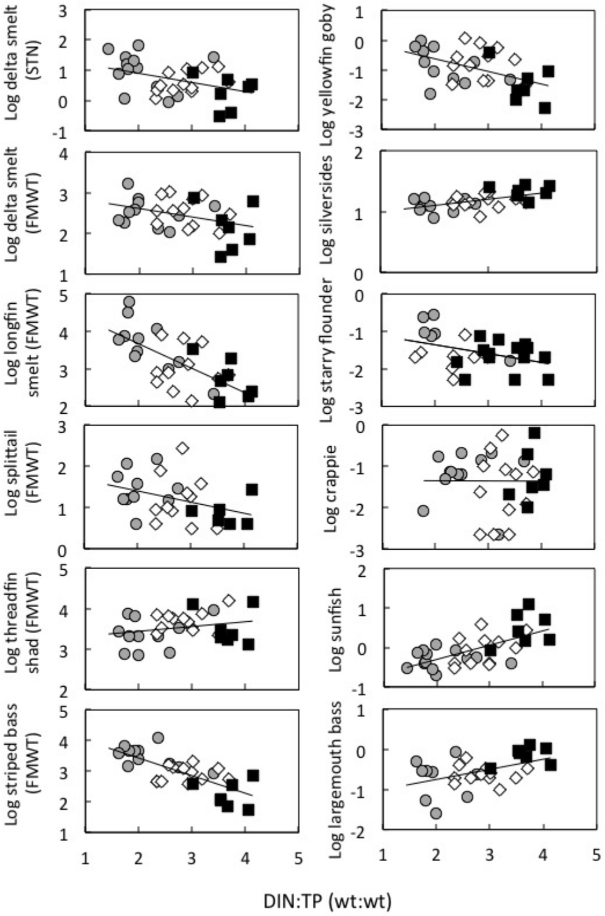

Figure 11. Changes in the abundance of major fishes in relation to ratio of dissolved inorganic nitrogen to total phosphorus from 1975-2005**.** Different periods of time are represented by different symbols: 1975-1986, filled circles; 1987-1999, diamonds; post-1999 filled squares. All data were log-transformed. The correlations for all fish except crappie were significant ($p<0.05$) in these data as well as in data that were detrended. Source: Glibert et al. (2011).

Total Nutrient Loads

Total nutrient load sets the upper limit on total primary production, and increases in nutrient loading are commonly associated with eutrophication. Nutrient levels in water diverted from the Delta are at concentrations that can produce nuisance algal and aquatic weed growth and adversely affect drinking water beneficial uses in downstream conveyance facilities and reservoirs. Algal and aquatic plant growth in the SWP conveyance facilities and downstream reservoirs is neither light limited nor inhibited by high ammonium concentrations since most of the ammonium from the Delta has been nitrified to nitrate. Elevated levels of nutrients (phosphorus and nitrogen compounds) stimulate nuisance algal and aquatic weed growth that includes production, by specific cyanobacteria, of noxious taste and odor compounds and algal toxins. In addition to algal produced taste and odor and algal toxin concerns, increases in algal and aquatic weed biomass can impede flow in conveyances, shorten filter run times and increase solids production at drinking water treatment plants, and add to organic carbon loading.

Frequently annual phosphorus concentrations at Clifton Court Forebay have averaged 0.11 mg/L and total nitrogen has averaged 0.87 mg L^{-1}. Phosphorus is significantly higher than the 0.020 to 0.042 mg L^{-1} that has been associated with a high risk of nuisance growth and eutrophication (USEPA 1980, 2001a). Levels of both nutrients exceed USEPA Ecoregion I phosphorus and total nitrogen reference conditions of 0.047 mg $L^{-1}$and 0.31 mg L^{-1}, respectively (USEPA 2001b)[1]. Ecoregion I includes the Central Valley.

Literature values and USEPA's ecoregion reference conditions[2] provide a starting point for determining whether nutrient concentrations in Delta waters are at levels that could cause water quality impairments, such as algal production of compounds that produce noxious tastes and odors. More importantly, there is already significant evidence of nutrient-related adverse impacts from Delta water. Through 2006, the Department of Water Resources (DWR) has applied algicide treatments to Clifton Court Forebay for aquatic weeds and algae multiple times each summer. This practice was halted in 2007, however, over concerns of potential impacts to listed fish species. DWR has also treated the South Bay Aqueduct (SBA) to control algae that are stimulated by nutrient-rich Delta water. Including preventative treatments, DWR has treated the SBA for algal control between 10 and 16 times per year in recent years. Periodic treatment of the California Aqueduct and State Water Project (SWP) terminal reservoirs is also necessary for the same reason. Given the increasing environmental concerns about the use of copper-based algaecides, it is likely that effective control will become increasingly more difficult and reduce the ability of downstream users to manage algae-related problems in the future.

Eutrophication, ecological stoichiometry and alternate stable state theories combine to serve as a unifying framework for understanding the complexity of responses not only in the Bay-Delta estuary but also, more generally, in many comparative systems. This interpretation does not negate the importance of ecological invasions, habitat changes, multiple stressors and food-web complexities, but adds an explanatory mechanism to those interpretations through biogeochemistry and organismal stoichiometry. Ecological stoichiometry affects systems by setting elemental constraints on the growth of organisms. This, in turn, affects food quality and the relationships between predators and prey.

Examples of Responses to Nutrient Load Reductions

A growing body of literature documents improvements in ecosystem functions where nutrient loading is reduced and stoichiometric balance is restored. Reducing nutrient loading in the Chesapeake Bay, Tampa Bay, and coastal areas of Denmark has proven to be effective at reversing the harmful effects of previously undertreated discharges and restoring the native food webs. For example, within several years of increasing nutrient removal at the Blue Plains treatment plant in Washington D.C., N:P ratios in the

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[1] The reference condition is the 25th percentile of the nutrient data for sites within the ecoregion and is meant to represent the nutrient concentrations in minimally impacted water bodies.

[2] Significant questions have been raised about the use of reference conditions to establish regulatory criteria for nutrients. Nevertheless, they provide a starting point for evaluating water quality.

Potomac River declined, the abundance of the invasive *Hydrilla verticillata* and *Corbicula fluminea* began to decline (Figure 12 showing *Corbicula Fluminea* and other relationships with N:P), and the abundance of native grasses increased (Ruhl and Rybicki 2010).

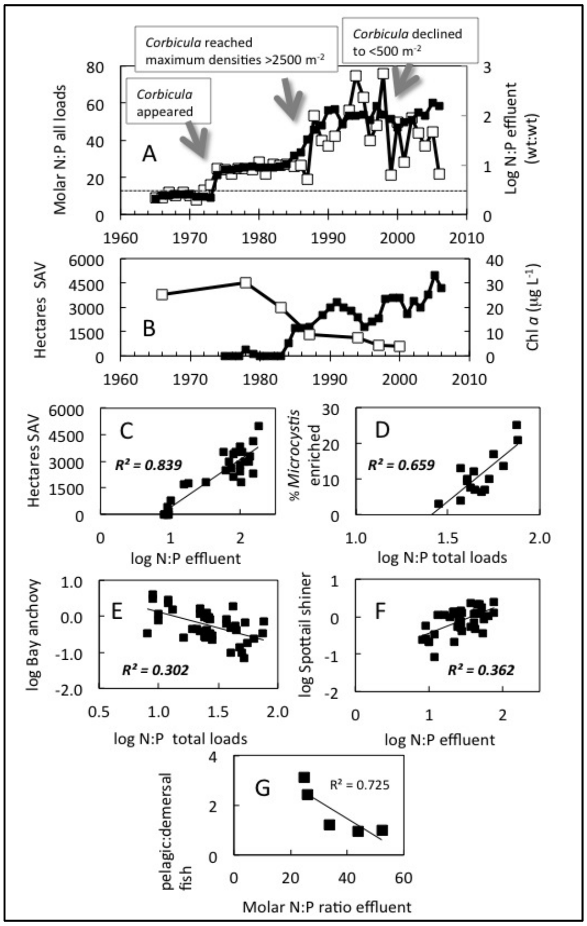

Figure 12. Comparative relationships for the Potomac River. Panel A shows the change in effluent N loading and the relative abundance of the invasive clam, *Corbicula fluminea***.** *C. fluminea* appeared coincident with a sharp increase in N:P and increased in abundance as N:P increased. When N:P decreased sharply around 1999, *C. fluminea* abundance also declined sharply from >2500 m^{-2} to <500 m^{-2} Data derived from Dresler and Cory (1980), Jaworski et al. (2007), and Cummins et al. (2010). Figure reproduced from Glibert et al. (2011).

Tampa Bay provides another important example. Eutrophication problems in Tampa Bay were severe in the 1970s, with N loads approximating 24 tons per day, about half of which was due to point source effluent (Greening and Janicki 2006). Several years after nitrogen and phosphorus reductions were achieved, native seagrass began to increase. Lower nutrient discharges also had positive effects on the coastal waters around the island of Funen, Denmark (Rask et al. 1999). Since the mid 1980s, there has been a roughly 50% reduction in the loading of N and P in the region due to point source reductions. Again, native grasses returned and low oxygen problems were reversed.

Cloern (2001) provides additional examples of recovery following reductions in nutrient and waste inputs. Citing other researchers, Cloern (2001) shows improvements in dissolved oxygen levels in the Forth Estuary in Scotland following improvements in wastewater treatment. Citing a second study, Cloern

(2001) shows increases in fish diversity in the Thames Estuary following improvements in wastewater treatment there (Figure 13).

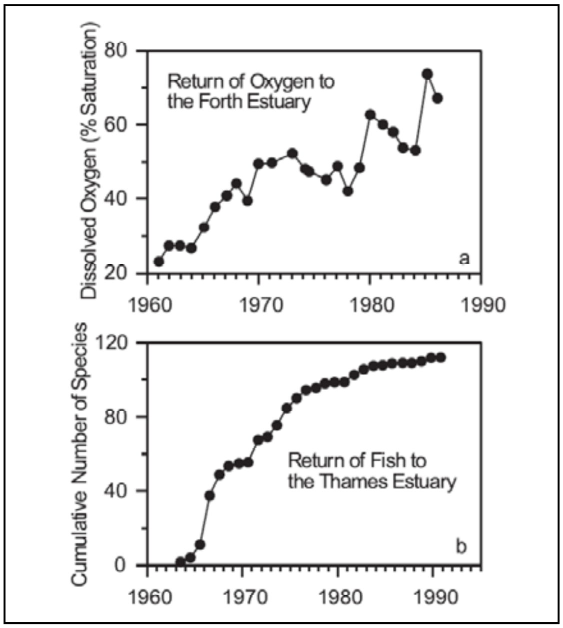

Figure 13. Two examples of recovery following actions to restore water quality in estuaries impacted by nutrient and waste inputs**:** (a) trend of increasing dissolved oxygen concentration (summer months) in the Forth Estuary, Scotland, following Improvements in wastewater treatment; (b) trend of increasing diversity of fishes in the Thames Estuary following implementation of advanced wastewater treatment and increases in oxygen concentrations (Source: Figure 20 from Cloern 2001).

Moreover, there is recent evidence that diatom blooms may be restored in the Bay-Delta estuary if NH_4 loading is reduced. In Suisun Bay, an unusual diatom bloom in Spring 2000 reached chl-*a* concentrations of 30 µg L^{-1} when NH_4 concentrations declined to 1.9 µmol L^{-1} (0.027 mg L^{-1}) (Wilkerson et al. 2006). Similarly, chl-*a* concentrations in Suisun Bay reached 35 µg L^{-1} during spring 2010 when NH_4 concentrations declined to 0.5 µmol L^{-1} (0.007 mg L^{-1}) (Dugdale et al. 2011, 2012). These blooms are comparable to spring chl-*a* levels from 1969 to 1977 (Ball and Arthur 1979) when NH_4 concentrations were 1.8 µmol L^{-1} (0.025 mg L^{-1}) during summer and 4.0 µmol L^{-1} (0.056 mg L^{-1}) during winter (Cloern and Cheng 1981).

Additionally, as Glibert (2010) reported, "[s]upporting 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 NH_4 levels and higher ratios of NO_3:NH_4 than the main Sacramento River [citations removed]."

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