

Background/Summary of Ammonia Investigations in the Sacramento-San Joaquin Delta and Suisun Bay

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Prepared by: Adam Ballard, Central Valley Regional Water Board
Rich Breuer, CA Department of Water Resources
Frances Brewster, Santa Clara Valley Water District
Cliff Dahm, CALFED Science Program
Cameron Irvine, CH2M HILL
Karen Larsen, Central Valley Regional Water Board
Anke Mueller-Solger, Interagency Ecological Program
Al Vargas, CALFED Science Program

Purpose of this Document

The purpose of this document is to briefly summarize the background and status of studies of the potential impacts of ammonia/ammonium on aquatic species in the Sacramento-San Joaquin Delta (Delta) and Suisun Bay. This document, along with relevant peer reviewed journal articles, sets the stage for discussion at a CALFED Science Program Workshop on 10-11 March 2009. The purpose of the workshop is to develop a research framework to determine the role of ammonium and ammonia within the Delta and Suisun Bay ecosystem. During the workshop, the discussion will be separated into three topic areas: 1) ammonia and ammonium sources, concentrations, fate, and transport, 2) effects of ammonium on the food web, and 3) toxicity of ammonia and ammonium to Delta fish and invertebrates. To be consistent, following the background on the Delta pelagic organism decline, this document also is organized by these topics. Following each section are lists of illustrative outstanding questions that will help guide discussion during the workshop. In addition to these questions, the workshop planning committee will solicit additional questions from stakeholders and local experts.

Pelagic Organism Decline

Monitoring conducted by the Interagency Ecological Program (IEP) in the freshwater and brackish portions of the San Francisco Estuary known as the Delta and Suisun Bay (Figure 1) showed an unexpected decline of four pelagic (open-water) fishes (delta smelt, longfin smelt, juvenile striped bass, and threadfin shad) that began around the beginning of the new millennium. This decline has collectively become known as the Pelagic Organism Decline (POD). In 2005, the IEP formed a multi-agency POD Management Team (MT) tasked with designing and managing a comprehensive study to evaluate the causes of the decline and to synthesize and report the results. The causes under investigation include stock-recruitment effects; flow; a decline in habitat quality; increased mortality rates; and reduced food availability due to invasive species. The POD MT has completed comprehensive progress reports in 2006 and 2008 and

results from many individual POD study elements have been summarized in journal articles and reports (s. http://www.science.calwater.ca.gov/pod/pod_index.html for reports and publications). However, many studies are still under way. A new comprehensive progress report highlighting new results is expected in early 2009 and a final report summarizing and synthesizing all results is planned for late 2010. The ammonia and ammonium summary provided here will be part of the 2009 report, and some aspects are also contained in the 2008 report.

The overall story that is emerging from the POD investigations is that the estuarine ecosystem appears to have undergone a fairly rapid shift from a state that allowed pelagic fishes to thrive or at least persist to a state that appears to be quite hostile to pelagic fishes. This shift likely is caused by a variety of factors related to changes in climate, food webs, land use, and water project operations. It is important to note that no one factor is solely responsible for this shift, and ammonia/ammonium is only one of several potentially important factors.

Status of POD Ammonia/Ammonium Investigations and Brief Summary of Results

POD ammonia/ammonium investigations started in 2006 and include coordinated studies funded by IEP, CALFED, the State Water Resources Control Board, and the State Water Contractors and San Luis & Delta-Mendota Water Authority. Most studies are ongoing or just starting in 2009. The results summarized here are preliminary at this time and most have not yet been published in peer-reviewed journals. All interpretation and application of these preliminary results needs to proceed with caution.

Ammonia/Ammonium Sources, Concentrations, Fate and Transport

In water, ammonia primarily exists in two forms, un-ionized ammonia (NH_3) and ammonium ion (NH_4^+), which are in equilibrium according to $\text{NH}_4^+ \leftrightarrow \text{NH}_3 + \text{H}^+$. The equilibrium between ammonium and un-ionized ammonia depends primarily on pH, and also on temperature and salinity. Collectively, ammonium and un-ionized ammonia are often referred to as total ammonia or sometimes simply ammonia (although this can lead to confusion). Un-ionized ammonia is a gas that is toxic to animals and occurs in the water and in the air. Ammonium ion is an important nutrient for plants and algae that is dissolved in water. Both ammonium and un-ionized ammonia are present in effluent from wastewater treatment plants that employ secondary treatment methods, but also in some types of agricultural run-off from the use of nitrogenous fertilizers and atmospheric depositions. Many hydrodynamic, chemical and biological processes affect the transport, fate, and effects of un-ionized ammonia and ammonium after discharge into waterways.

The IEP Environmental Monitoring Program (EMP) has been monitoring ammonium concentrations at monthly or biweekly intervals at 10 stations in the Delta and Suisun Bay since 1975. Refer to Figure 1 for a map of the sampling locations and Figure 2 for the total ammonia concentrations at stations where ammonia data were available

through 2008. Median concentrations (1975-2006) and annual trend magnitudes of ammonium and other dissolved nutrients monitored simultaneously by the EMP at each location as well as median nitrate to ammonium ratios and their annual trends are provided in Figure 3. Figure 4 shows calculated un-ionized ammonia concentrations at IEP monitoring stations for 1975-1995. The EMP did not collect simultaneous pH measurements after 1995, so it is not possible to calculate un-ionized ammonia and compare ambient levels to United States Environmental Protection Agency (US EPA) (1999) acute and chronic criteria at these stations after 1995. The ambient ammonia concentrations are below the US EPA acute and chronic ammonia criteria.

The Sacramento Regional Wastewater Treatment Plant (SRWTP) is the largest point source of ammonium and ammonia in the Delta. The SRWTP's output has increased with human population growth (Figure 5) and it has contributed to an increase in ammonium concentrations in the Delta downstream of the discharge. The discharge from the SRWTP accounts for 90% of the ammonium load in the Sacramento River at Hood (Jassby 2008). The Central Valley Regional Water Board's current total ammonia requirements for the SRWTP are based on the US EPA (1999) aquatic toxicity guidance that is designed to protect the most sensitive aquatic species. The receiving environment downstream of SRWTP's effluent discharge is in compliance with the US EPA ammonia criteria (Figure 6). When writing a permit, Regional Water Board staff evaluates effluent concentrations, concentrations of total ammonia already in the river and available dilution. Limitations in permits are, therefore, site specific. The SRWTP's permit allows for discharge of relatively high concentrations of total ammonia because the Sacramento River provides considerable dilution. SRWTP uses large storage basins to hold wastewater for short periods of time when there is not sufficient dilution in the river because of reverse tidal flows. Additional sources of ammonium to the Delta and Suisun Bay include other wastewater treatment plants, agricultural run-off, atmospheric deposition, internal cycling, and possibly discharges from wetlands.

In addition to the IEP, several other programs and investigators are collecting ammonium and associated water quality data from around the Delta (e.g., DWR-Municipal Water Quality Investigation stations, USGS monitoring stations, NPDES permit receiving water monitoring stations, and ongoing extensive UC Davis research). Various entities are currently compiling a summary of sources and concentrations of ammonium in the Delta based on readily available data collected by existing monitoring programs. The goals of these compilations are to better characterize sources, trends, and data gaps, and to support development of an ammonium fate and transport model. Additional work may be needed to improve hydrodynamic modeling and conduct more in-depth investigations of chemical, biological, and hydrodynamic conversion and mixing rates downstream of discharge points and throughout the Delta and Suisun Bay.

The Central Valley Regional Water Board is currently developing an ammonia sampling program for the Delta. The purpose of this study is to collect additional nutrient data, including ammonium and un-ionized ammonia, for the Delta to determine whether ambient concentrations are potentially toxic, and to support development of a fate and transport model. A spatial emphasis is placed on the lower Sacramento River and

northern Delta as ammonia levels from the SRWTP are likely to be highest here. However, other areas of the San Francisco Estuary are also proposed for sampling as SRWTP is not the only source of ammonia/ammonium.

Outstanding Questions

- What are the relative contributions of various ammonia and ammonium sources to the Delta?
- What transport processes affect the distribution of nutrients, including ammonium, within the Delta and Suisun Bay under varying river discharge and tidal forcing?
- What physical, chemical, and biological processes most strongly affect the distribution and concentration of ammonium in the Delta and Suisun Bay?

Ammonium Effects on Delta Food Web

This section includes discussion of potential effects on Delta phytoplankton as well as on the prevalence of harmful algal blooms and invasive aquatic plants. These will be discussed as part of the food web effects during the March 2009 workshop.

Ammonia Effects on Delta Phytoplankton

Primary production rates and standing chlorophyll *a* levels associated with phytoplankton (open water algae) in the Delta and Suisun Bay are among the lowest of all the major estuaries in the world (Table 1, Figure 7) (Cloern and Jassby 2008, Jassby 2008, Boynton et al. 1982, Jassby et al. 2002). Chlorophyll *a* and primary productivity levels in the Delta declined from 1975 to 1995, but have increased significantly from 1996-2005 while Suisun Bay levels remained relatively unchanged over the last decade (Jassby et al. 2002, Jassby 2008).

Table 1. Five-year medians of March–November chlorophyll *a* (Chl-*a*) and suspended particulate matter (SPM) concentrations and for phytoplankton gross primary production (GPP) estimates for Suisun Bay (Stations D6, D7, and D8) and the Delta (Stations C3, D4, C10, P8, D26, MD10, and D28). See Figure 1 for locations. Reproduction of Table 4 in Jassby 2008.

Period	Delta Chl-<i>a</i> ($\mu\text{g L}^{-1}$)	Suisun Chl-<i>a</i> ($\mu\text{g L}^{-1}$)	Delta SPM (mg L^{-1})	Suisun SPM (mg L^{-1})	Delta GPP Index ($\text{mg C m}^{-2} \text{d}^{-1}$)
1976–1980	7.0	5.1	24	32	430
1981–1985	5.4	5.4	18	30	390
1986–1990	4.3	1.9	15	30	340
1991–1995	2.7	1.5	12	27	250
1996–2000	2.8	1.6	13	33	250
2001–2005	3.4	1.6	11	24	330

The composition of the phytoplankton community has generally shifted from diatoms toward green algae, cyanobacteria, and miscellaneous flagellate species (Lehman 2000). Blooms of *Microcystis aeruginosa*, a cyanobacterial harmful algal bloom (CHAB) species that can produce toxic substances, have been observed in Delta waters since 1999 (Lehman et al. 2005). The changes in phytoplankton composition and especially the now regularly occurring *Microcystis* blooms have been implicated as possible factors in the decline of important Delta pelagic fish species including delta smelt (IEP 2008), but the connection with ammonia is not clear.

Low light availability and high grazing rates have been identified as important factors controlling overall phytoplankton production and biomass in the Delta. Much of the interannual variation can be attributed to precipitation and associated river flows (Cloern 2001, Jassby et al. 2002, Lehman 2004). Nutrients are generally thought to be of lesser importance in this turbid, nutrient-rich estuary, although one study (Van Nieuwenhuysse 2007) found an association between an abrupt decline in total phosphorus concentrations due to reductions in urban phosphorus discharges in the mid-1990s and a decline in chlorophyll *a* levels at three Delta stations (D26, D28A, and MD10 in Figure 1).

Ammonium is known as an important, but also “paradoxical” nutrient (Britto and Kronzucker 2002) because it can stimulate plant growth, but also suppress plant uptake of another important nutrient, nitrate, and ultimately suppress growth of some sensitive plants. This type of sensitivity to ammonium is well established for many agricultural crops. Two recently published studies, show that high ammonium levels ($>4 \mu\text{mol L}^{-1}$ or $\sim 0.056 \text{ mg L}^{-1}$) in Suisun Bay, once considered one of the most productive areas of the San Francisco Estuary, can suppress the growth of phytoplankton in this area even when there is sufficient light (Dugdale et al. 2007, Wilkerson et al. 2006). Diatoms appear to be particularly affected by relatively low levels of ammonium in Suisun Bay. It is not known whether the same effect is manifested in the freshwater portions of the Delta.

Pilot level investigations conducted by the Dugdale and Wilkerson Laboratory in 2007 and 2008 have repeatedly shown suppression of phytoplankton growth in the lower Sacramento River near Rio Vista and a site on the lower San Joaquin River downstream of Stockton. However, two tests conducted in 2008 with Sacramento River water collected near the discharge point of the SRWTP showed good phytoplankton growth in spite of high ammonium concentrations. The reasons for different growth responses in the Sacramento River near the SRWTP discharge compared to samples near Rio Vista and from the San Joaquin River stations are unclear and investigations will continue with increased intensity in 2009.

Outstanding Questions

- To what extent, if any, and potentially where and when does nitrate uptake inhibition by ammonium affect algal productivity and/or community composition in the Delta and Suisun Bay?

- How do other factors that affect algal growth and community composition interact with nitrate uptake inhibition by ammonium?
- What are responses of phytoplankton growth rates and community structure to spatial and temporal differences in nutrient concentrations and ratios?

Ammonium Effects on Harmful Algal Blooms and Invasive Aquatic Plants

Elevated ammonium concentrations potentially contribute to harmful algal blooms (e.g., *Microcystis*) that have been occurring with increasing frequency and biomass in some parts of the Delta (Lehman et al. 2005). A recent study in the San Francisco Estuary found that low stream flow and high water temperature were strongly correlated with the seasonal variation of *Microcystis* cell density, total microcystins concentration (cell^{-1}) and total microcystins concentration ($\text{chl } a^{-1}$), while ambient nutrient concentrations and ratios were of secondary importance (Lehman et al. 2008).

As has been shown elsewhere, elevated levels of ammonium and other nutrients may also benefit invasive rooted and floating aquatic plants in the Delta, such as the water hyacinth (*Eichhornia crassipes*) and the Brazilian waterweed (*Egeria densa*) (Reddy and Tucker 1983, Feijó et al. 2002). Both species are now widely distributed across the Delta (Hestir et al. 2008) and are controlled in Delta channels through chemical herbicides and mechanical removal by the California Department of Boating and Waterways.

Outstanding Questions

- To what extent, if any, and potentially where and when does ammonium contribute to harmful algal blooms in the Delta and Suisun Bay?
- To what extent, if any, and potentially where and when does ammonium contribute to the spread of invasive aquatic plants in the Delta and Suisun Bay?

Toxicity of Ammonia to Delta Fish and Invertebrates

Ammonia Effects on Delta Smelt

In 2008, UC Davis Aquatic Toxicology Laboratory (UCD ATL) conducted a pilot study to assess the potential acute toxicity of ammonia and treated wastewater effluent from the SRWTP to larval delta smelt. The bioassay results suggest that ammonia concentrations present in the Sacramento River below the SRWTP were not acutely toxic to 55-day old delta smelt (Werner et al. 2009). The results from this study were consistent with total ammonia and un-ionized ammonia effect concentrations established for 50-day old delta smelt using filtered hatchery water (UCD ATL, unpublished data; Werner et al. 2009). The delta smelt 96-hour no observed effect concentration (NOEC), lowest observed effect concentration (LOEC), lethal concentration-50 (LC50), and LC10 for total ammonia and un-ionized ammonia are presented in Table 2. At 50 days old, delta smelt are about as sensitive to total ammonia and un-ionized ammonia as salmonid species, and about >5-fold more sensitive than larval fathead minnow (UCD ATL, unpublished data; Werner et al. 2009),

a common toxicity test species used by the SRWTP and other dischargers in accordance with their discharge permits.

Table 2. Delta smelt 96-hour NOEC, LOEC, LC50, and LC10 for total ammonia and un-ionized ammonia (pH 7.9, T=16°C)¹

Ammonia Species	Toxicological Endpoints (mg/L)			
	NOEC	LOEC	LC10	LC50
Total ammonia-nitrogen	5.0	9.0	4.0	12.0
Un-ionized ammonia	0.066	0.105	0.067	0.147

¹ Sources: Werner et al. 2008a, Werner et al. 2009

Ammonia may contribute to the POD if its concentrations in Delta waters are high enough to cause direct toxicity to the POD fishes or their food organisms. It is well known that salmonids are particularly sensitive to ammonia (US EPA 1999). In general, un-ionized ammonia levels in the Delta appear to be too low to cause acute mortality of even the most sensitive species.

Questions remain about the potential for chronic (i.e., long-term, sub-lethal) impacts from ammonia as well as the impacts in sensitive delta smelt spawning areas (e.g., Cache Slough). Un-ionized ammonia concentrations in the Delta do exceed levels where histopathological effects have been observed (US EPA 1999); however, it is unclear whether these effects translate to effects on survival, growth or reproduction. In addition, there is some evidence that actively swimming and unfed fish may be several times more sensitive to ambient un-ionized ammonia levels than these laboratory exposures indicate (Eddy 2005).

There may be a potential for toxic ammonia levels to be reached in very productive areas in the southern Delta or smaller productive sloughs or shallow areas throughout the Delta, when high concentrations of un-ionized ammonia coincide with warm temperatures and elevated pH (phytoplankton productivity increases pH that influences how much un-ionized ammonia is present). The relatively few ammonium, temperature, and pH data available in many of these areas are currently being compiled and evaluated.

In addition, the potential for combined effects of un-ionized ammonia with other toxicants and stressors, and differences in fish sensitivity depending on health status, age, and physiological state add uncertainty to data analyses. While un-ionized ammonia interactions with other toxicants and variable sensitivity have been demonstrated for a variety of species (e.g., Eddy 2005, Camargo and Alonso 2006), similar studies for the POD fishes are in their initial stage. Much more work is needed to reduce the many uncertainties about chronic toxicity effects of ammonia on the POD fishes in various Delta regions and discern population level effects.

Ammonia Effects on Delta invertebrates

Invertebrates are generally considered less acutely sensitive to un-ionized ammonia toxicity than fish (US EPA 1999), and direct toxicity effects are thus not very likely at the current un-ionized ammonia levels throughout most of the Delta. A recent review article by Camargo and Alonso (2006), however, does show that juvenile mollusks are sensitive at levels below sensitivity levels for salmonids. The US EPA (1999) derived Genus Mean Chronic Values (GMCVs) show that *Hyalella azteca*, a resident amphipod species in the Delta, is the most sensitive species in that assessment. The UCD ATL performs 10-day *Hyalella azteca* bioassays with waters collected from the Delta and Suisun Bay on a bi-weekly basis. Site-specific water quality parameters also are monitored in the field at the time of sampling and provide a valuable database for which to evaluate the conditions and effects of ambient surface waters (Werner et al. 2008b). *Hyalella azteca* toxicity tests will continue in 2009.

Outstanding Questions

- To what extent, if any, does ammonia cause acute, chronic, or sub-lethal effects to Delta fish and invertebrate species in sensitive Delta habitats?
- To what extent, if any, do significant interactive effects between ammonia and other toxicants or stressors occur that affect Delta fish or invertebrate species?
- Do ambient total ammonia concentrations ever exceed the US EPA (1999) chronic or acute ammonia criteria?
- Are the US EPA (1999) chronic and acute ammonia criteria adequately protective for Delta and Suisun Bay species?
- How can biomarkers be incorporated into monitoring programs to assess sub-lethal effects?

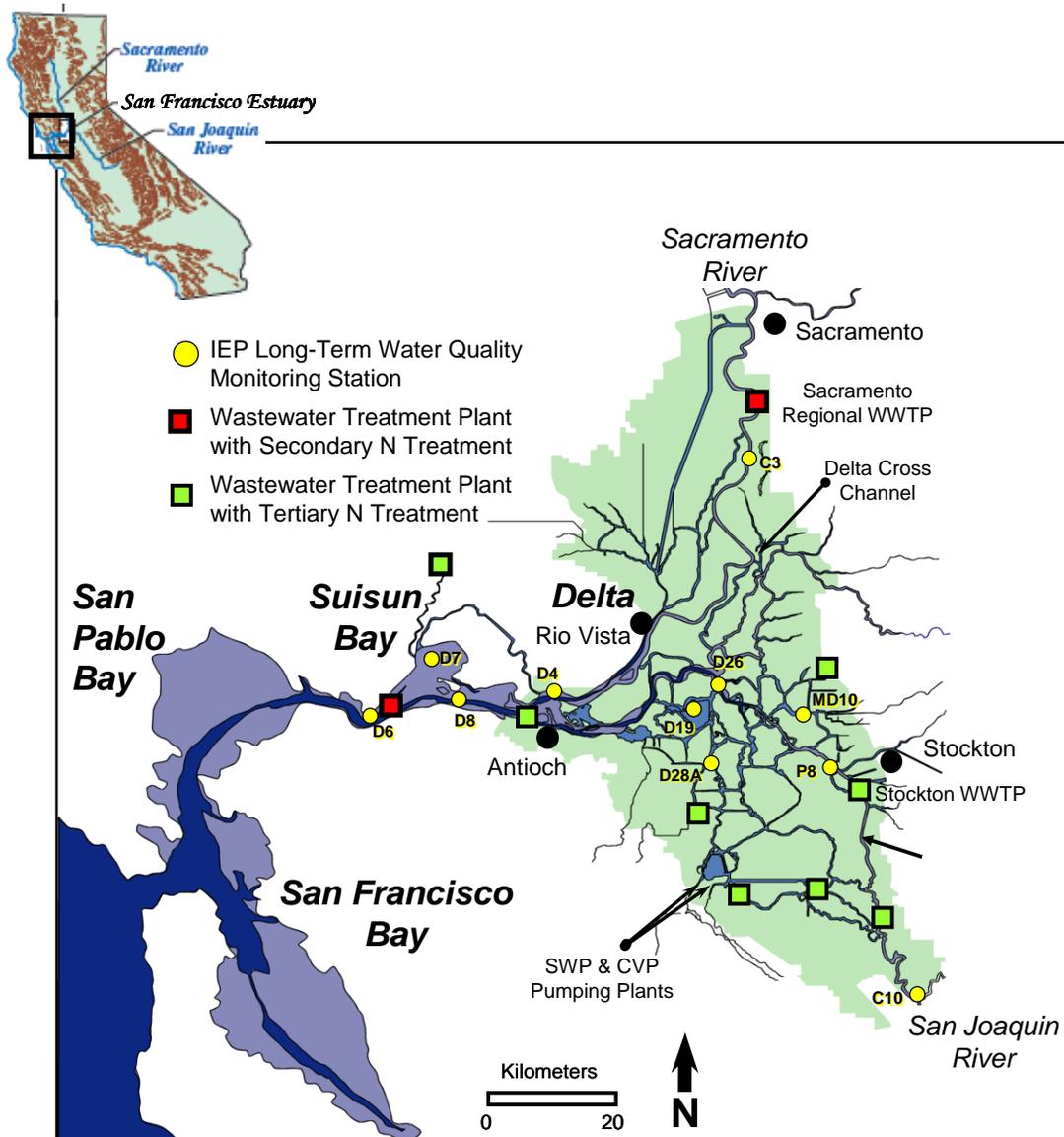


Figure 1. Map of the San Francisco Estuary showing the Delta region (green) and Bays as well as long-term IEP water quality monitoring stations and wastewater treatment plant discharge locations in the Delta and Suisun Bay regions.

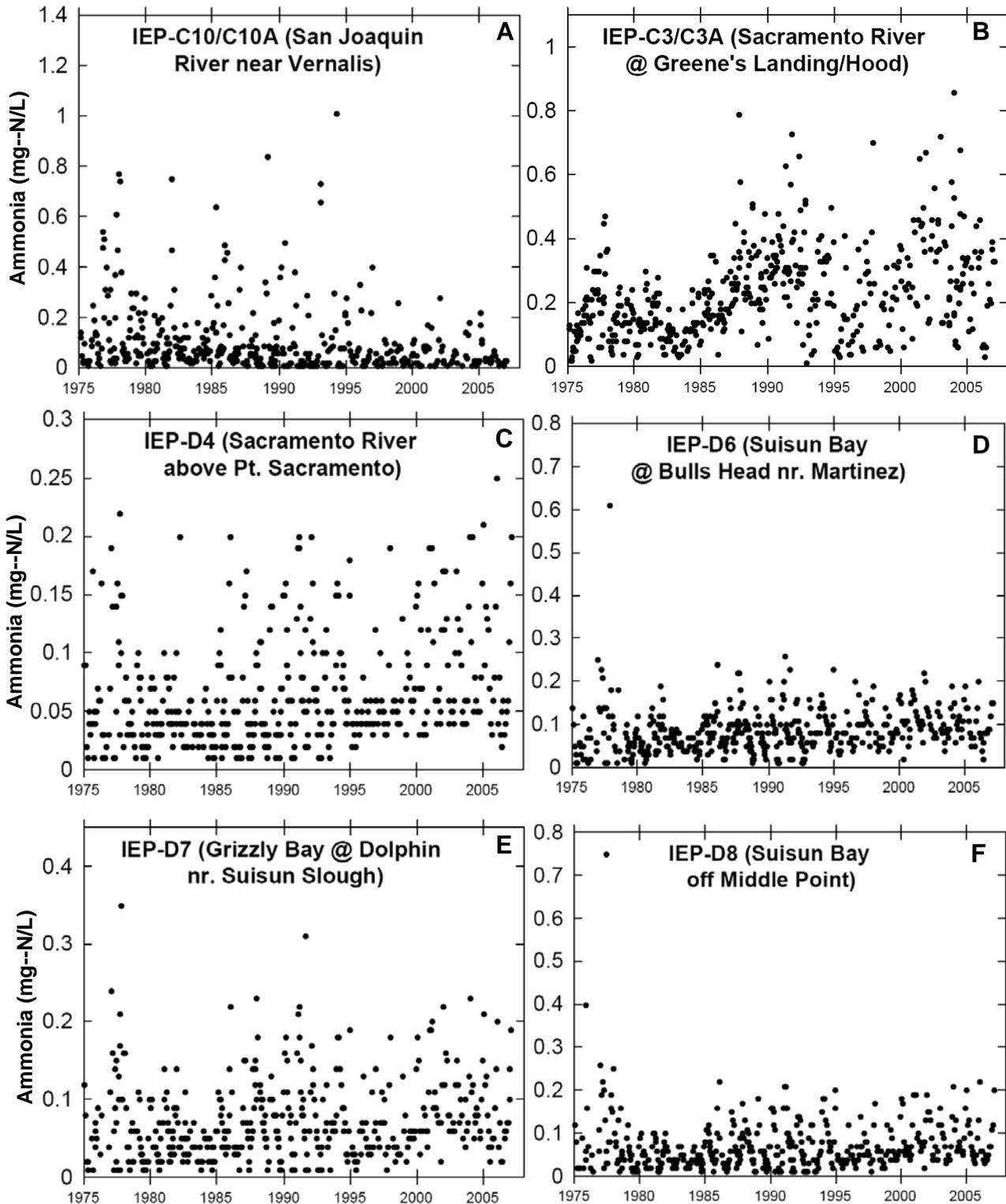


Figure 2. Ambient total ammonia concentrations (mg-N/L) from surface water grab sample (3 ft depth) at the IEP Environmental Monitoring Program (EMP) locations for which data are available through 2008. IEP reported these values as total ammonia from 1975-1978 using method EPA 350.2. 1979-2008 values were reported as dissolved ammonia using method EPA 350.1. Note the variable scales of each y-axis.

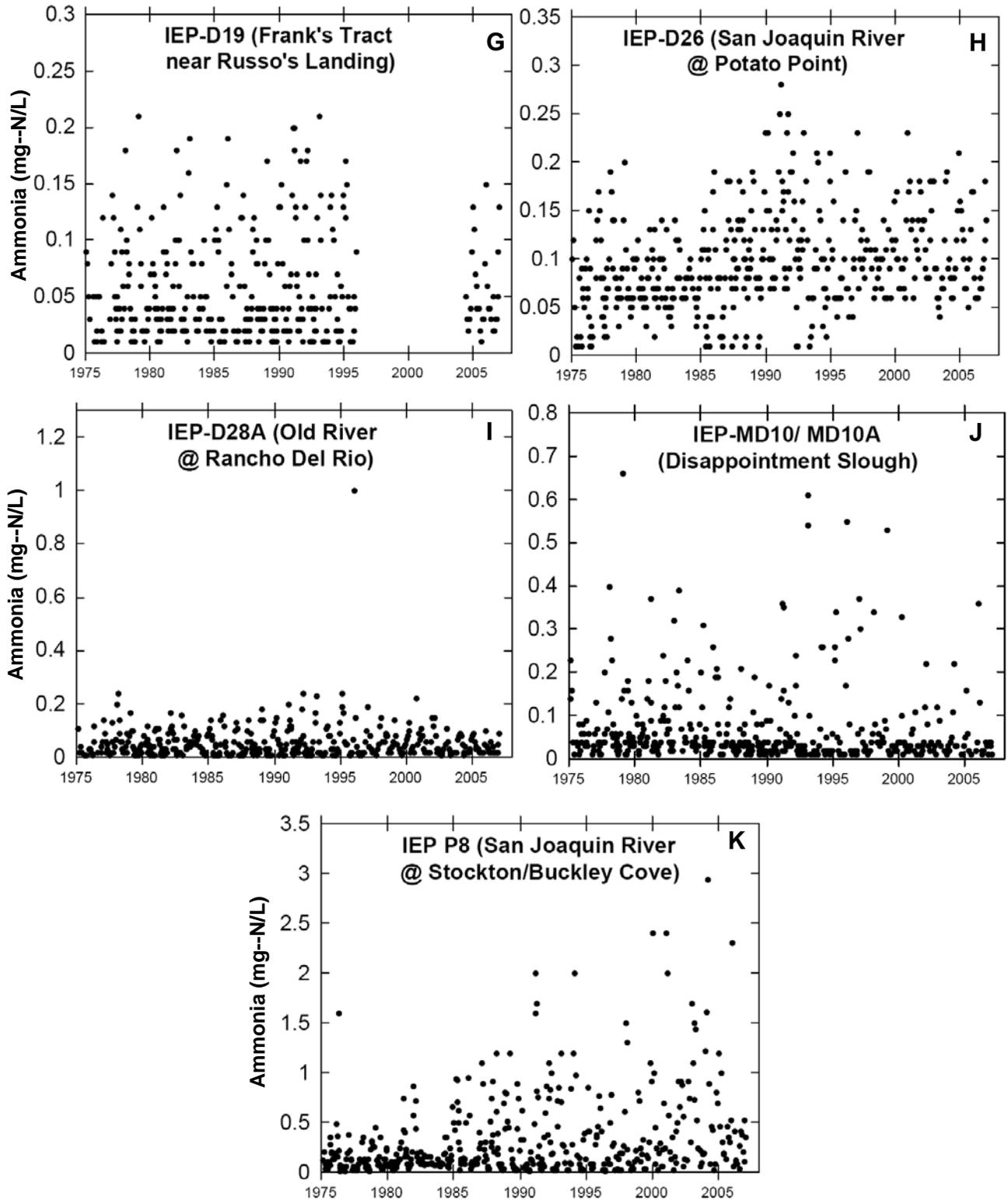


Figure 2 (continued). Ambient total ammonia concentrations (mg-N/L) from surface water grab sample (3 ft depth) at the IEP Environmental Monitoring Program (EMP) locations for which data are available through 2008. IEP reported these values as total ammonia from 1975-1978 using method EPA 350.2. 1979-2008 values were reported as dissolved ammonia using method EPA 350.1. Note the variable scales of each y-axis.

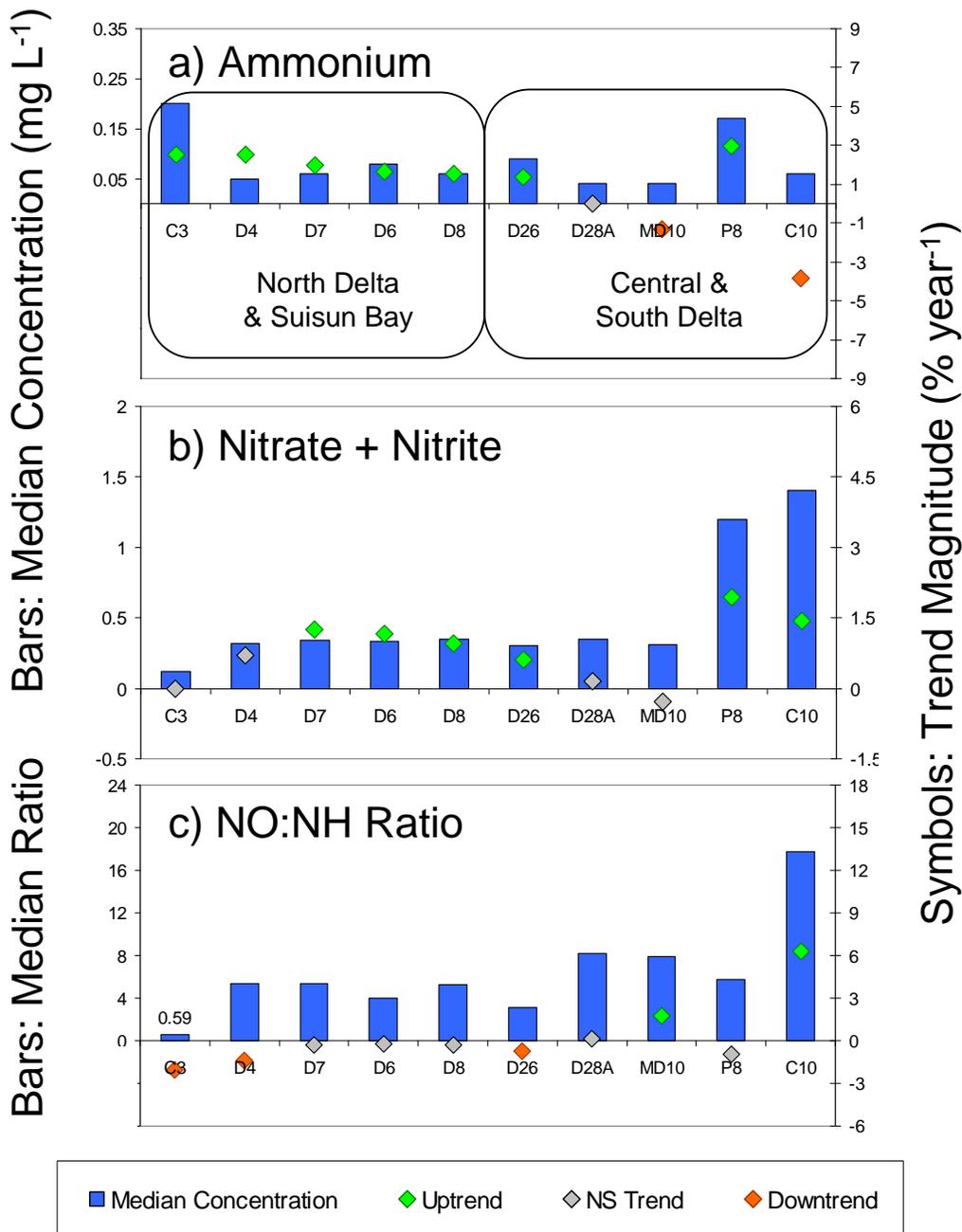


Figure 3. Median magnitudes (columns) and annual trends (symbols) for concentrations of a) ammonium, b) nitrate + nitrite, c) the ratios of nitrate + nitrite (NO) to ammonium (NH) at long-term IEP EMP monitoring stations throughout the lower Sacramento River, Suisun Bay, and Delta regions of the San Francisco Estuary from 1975 to 2006. Trends were estimated and tested with USGS "Estrend" for S-plus using seasonal Kendall tests with months as seasons and no flow adjustment (because actual concentrations were of interest here). For station locations see Figure 1. Data and metadata are available at <http://www.baydelta.water.ca.gov/emp/>.

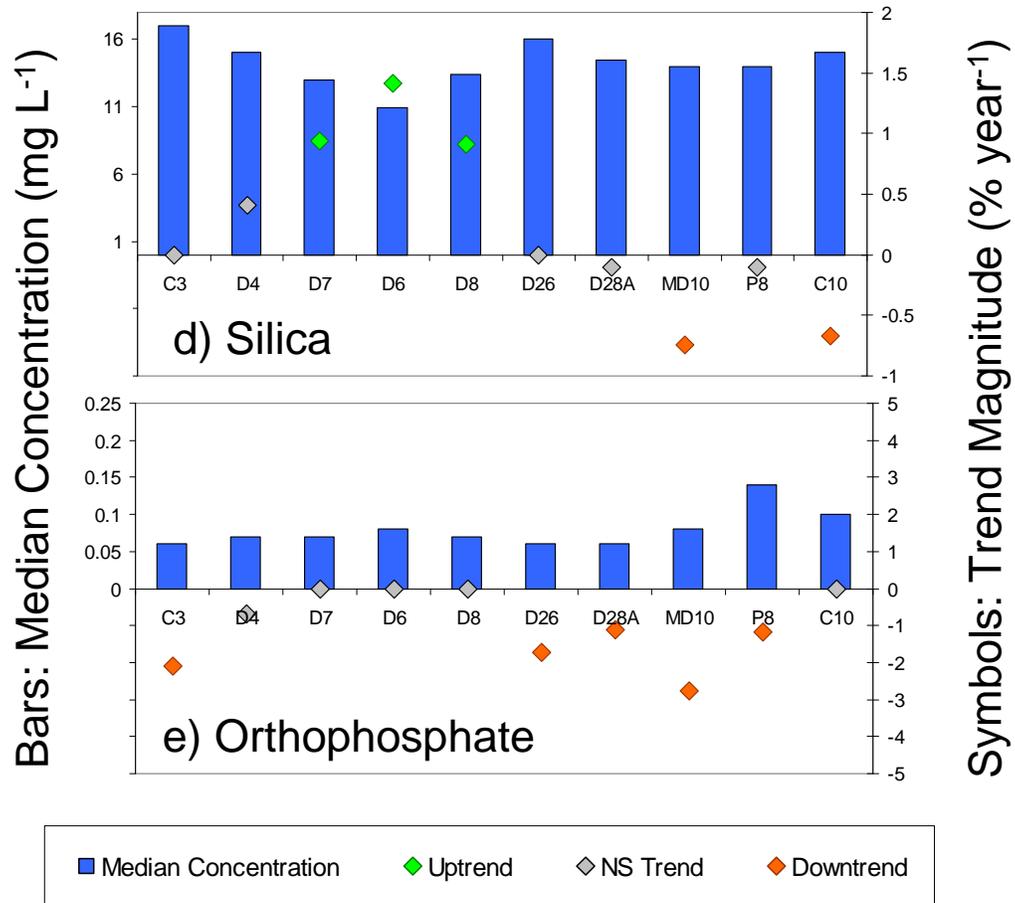


Figure 3 (continued). Median magnitudes (columns) and annual trends (symbols) for concentrations of d) silica and e) orthophosphate.

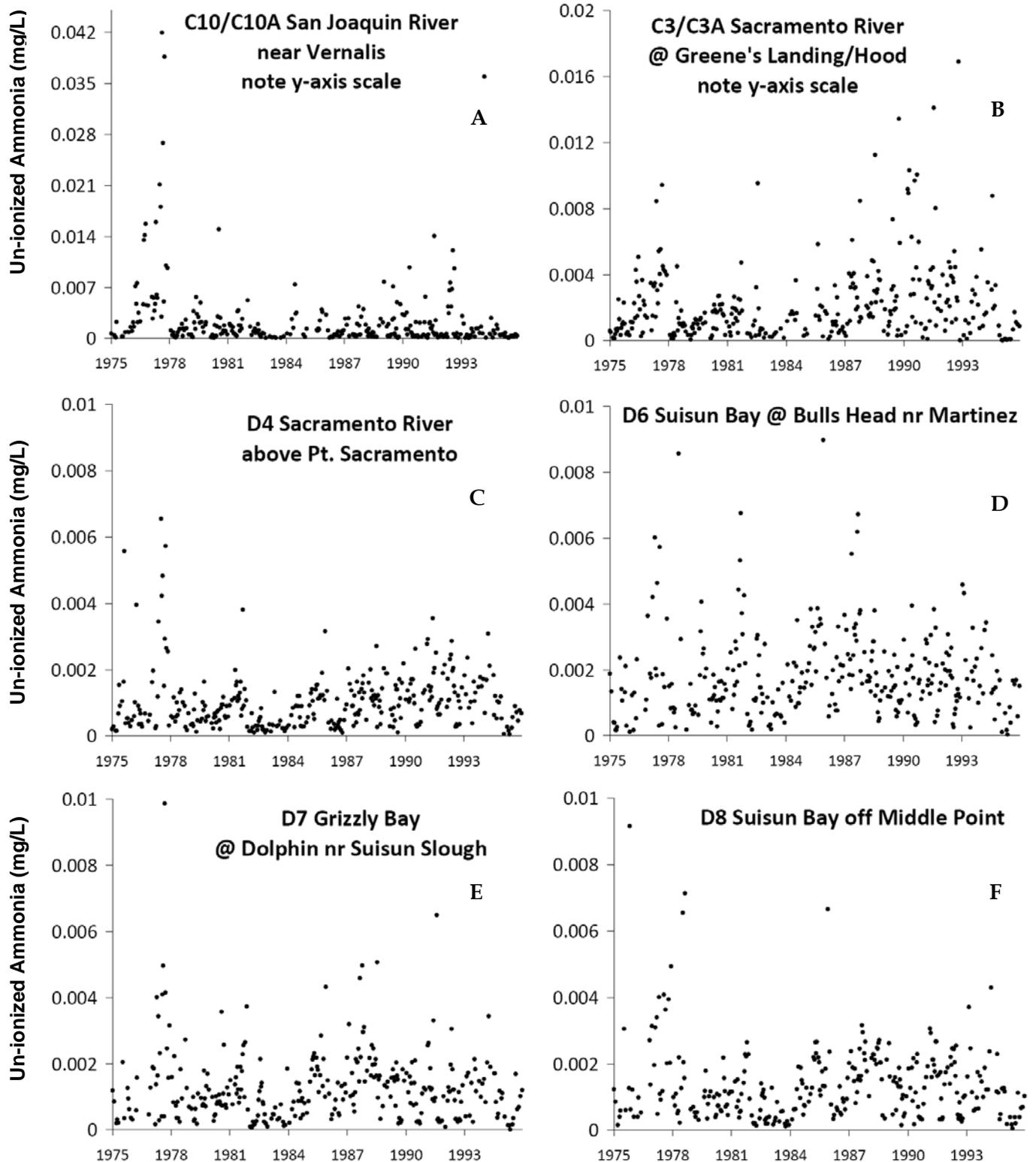


Figure 4. Calculated ambient un-ionized ammonia concentrations (mg/L) from surface water grab samples (3 ft depth) at the IEP Environmental Monitoring Program (EMP) locations for which concurrent pH and temperature data were available through 1995. Note that concentrations were not adjusted for salinity which could lower values up to 15% at 32 ppt (almost seawater). Also note the variable scales of each y-axis.

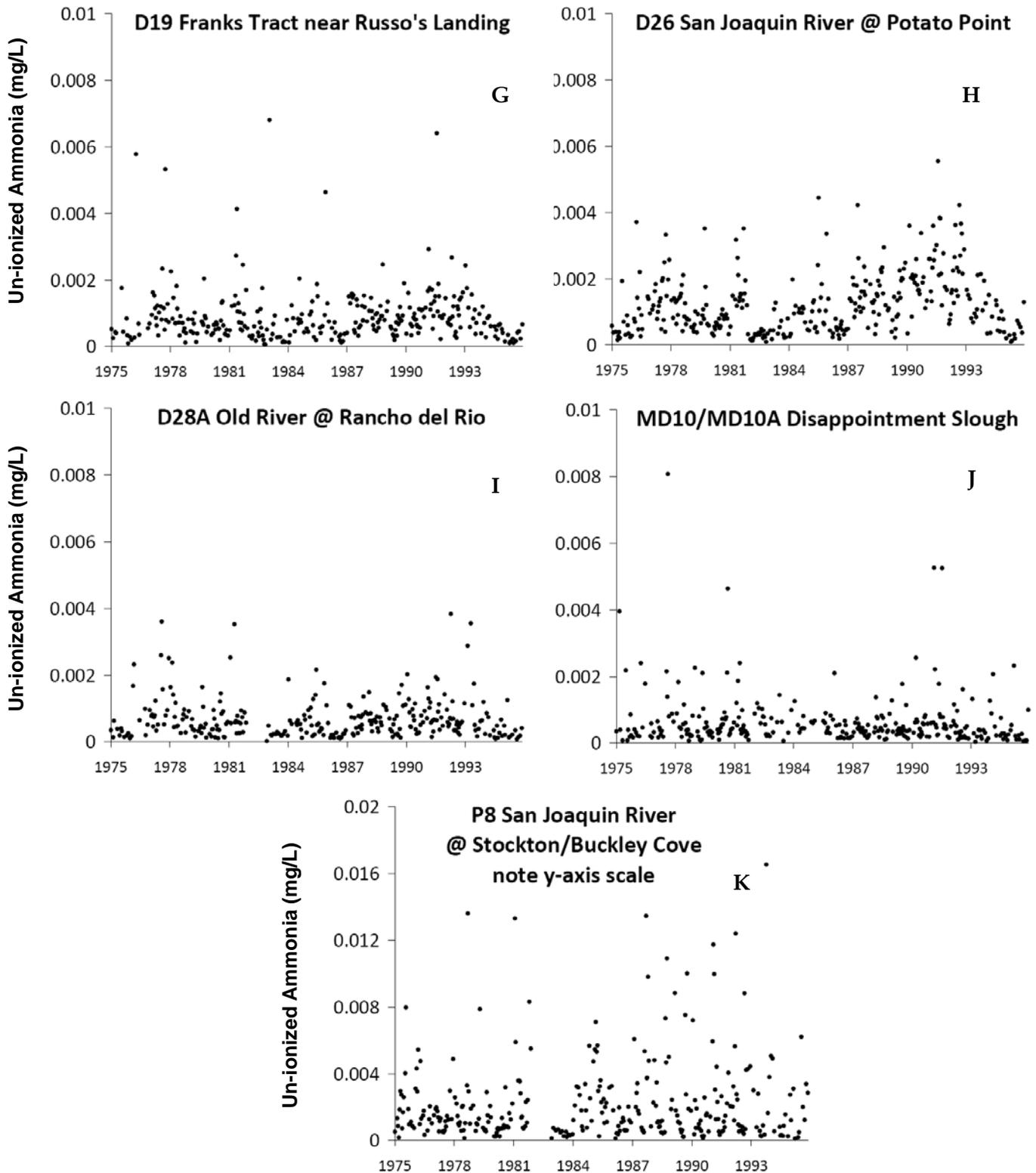


Figure 4 (continued). Calculated ambient un-ionized ammonia concentrations (mg/L) from surface water grab samples (3 ft depth) at the IEP Environmental Monitoring Program (EMP) locations for which concurrent pH and temperature data were available through 1995. Note that concentrations were not adjusted for salinity which could lower values up to 15% at 32 ppt (almost seawater). Also note the variable scales of each y-axis.

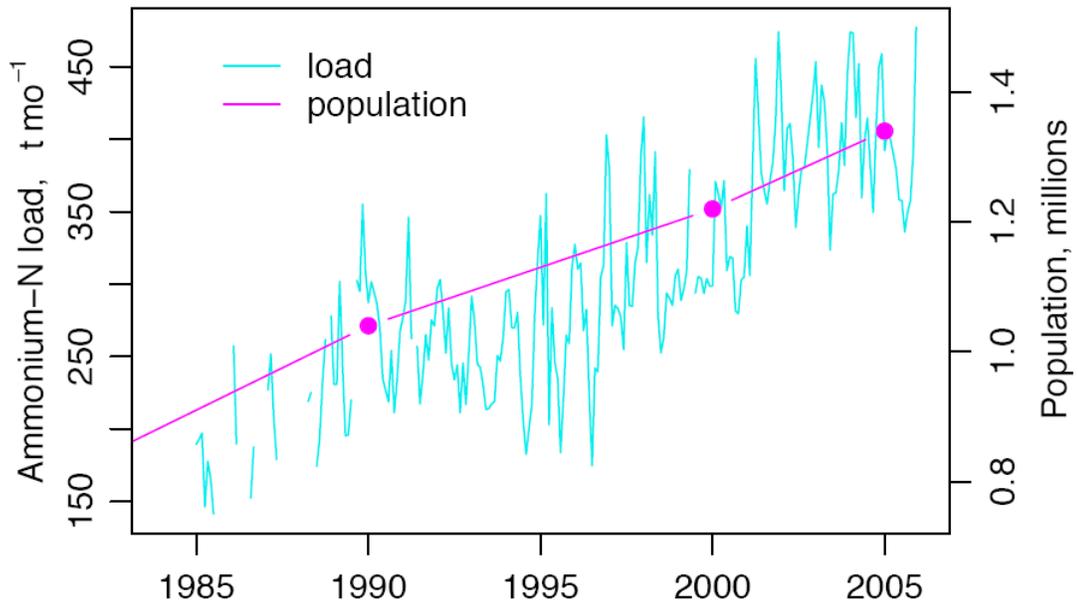


Figure 15. Monthly load of ammonium-N in wastewater from the County of Sacramento Regional Wastewater Treatment Plant. County population is also shown for comparison.

Figure 5. Reproduction of Figure 15 from Jassby (2008).

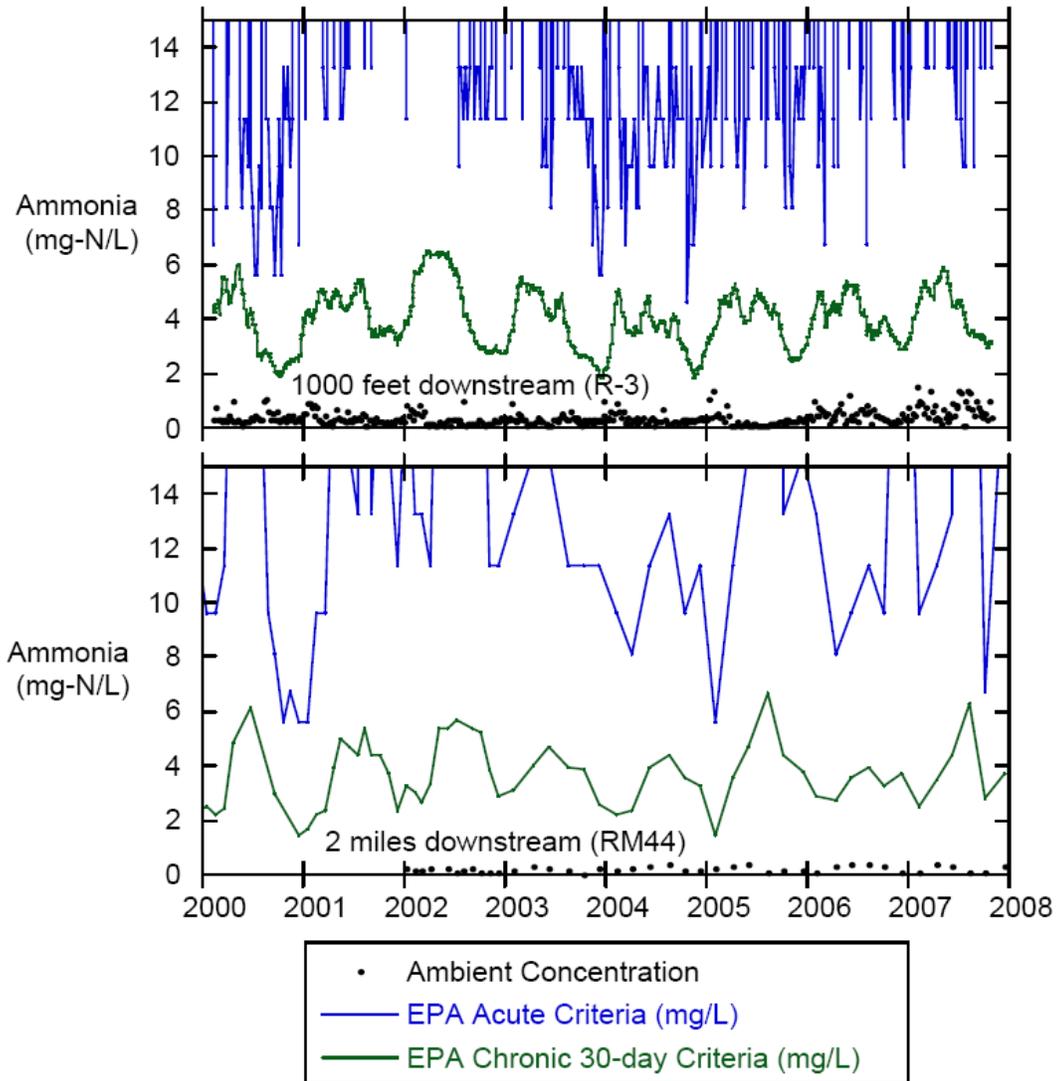


Figure 6. Ambient concentrations of total ammonia (mg-N/L) in the Sacramento River downstream from the SRWTP outfall compared to the EPA acute and chronic toxicity criteria. Ambient concentrations are from surface grab samples at monitoring stations of the Sacramento Regional County Sanitary District (SRCSD) Ambient Monitoring Program (R-3, weekly) or Coordinated Monitoring Program (RM44, monthly). The acute criterion for both stations was calculated using the field pH and water temperature associated with each grab sample. The chronic criteria for R-3 were calculated for each sampling event using 30-day running averages for field pH and temperature. The chronic criteria for RM44 were calculated using the field pH and temperature associated with the monthly grab samples.

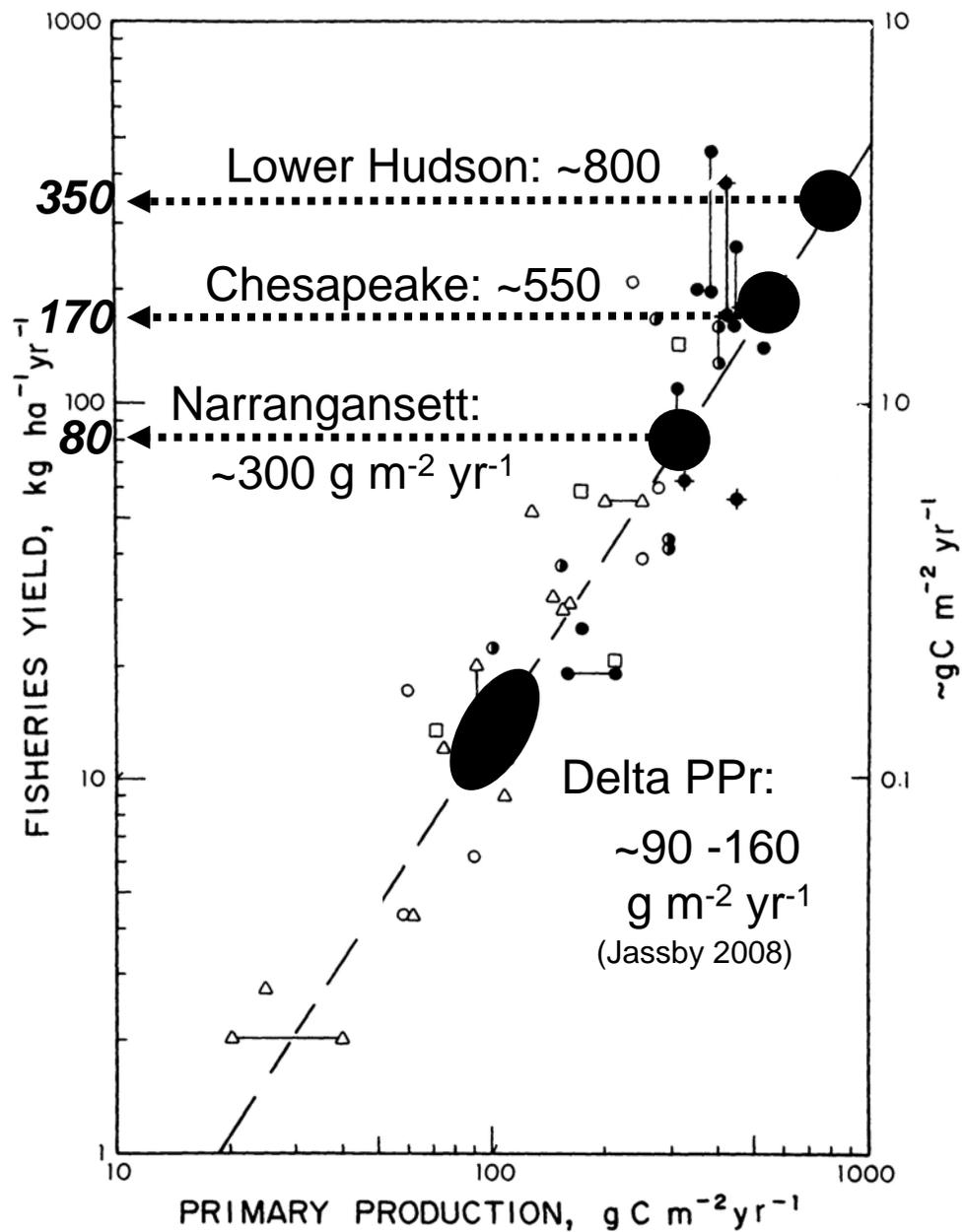


Figure 7. Primary production in the Delta and Suisun Bay plotted on the relationship of fishery yield to primary production from other estuaries around the world (modified from Nixon 1988, using data provided in Jassby 2008).

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