

*SWAMP Monitoring Plan*

2011-12

## **SAN FRANCISCO BAY REGION WORKPLAN**

### **MONITORING SPRING PHYTOPLANKTON BLOOM PROGRESSION IN SUISUN BAY**

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**FINAL SWAMP WORKPLAN  
SAN FRANCISCO BAY REGION (FY 2010-11 & 2011-12)**

**I. MONITORING SPRING PHYTOPLANKTON BLOOM PROGRESSION IN  
SUISUN BAY**

**II. BACKGROUND**

There is evidence that primary productivity is inhibited in Suisun Bay, and that  $\text{NH}_4$  may be causing that inhibition. The main purpose of this study is to measure nutrients, primary production, nutrient uptake by phytoplankton and, phytoplankton biomass and species composition in Suisun Bay in the spring to determine if there is inhibition, and if so, to determine what is causing the inhibition. Suisun Bay is an area identified as critical habitat for the threatened Delta Smelt (Hobbs et al., 2006). Several important changes in the pelagic food web of this area have been documented over the last two decades indicating that food for Delta Smelt and other threatened fishes is in short supply (Müller-Solger et al. 2002; Sommer et al. 2007). One of the most striking changes in Suisun Bay is the decline in phytoplankton between 1975 - 1995 (Jassby et al. 2002) and the shift from large accumulations of phytoplankton biomass ( $>40 \mu\text{g L}^{-1}$  chlorophyll) during the summer (Cloern 1979) to much smaller phytoplankton blooms ( $<10 \mu\text{g L}^{-1}$  chlorophyll) that occur infrequently during spring (Wilkerson, et al. 2006; Kimmerer et al., in prep). Wilkerson et al (2006) studied phytoplankton and nutrient dynamics in the northern estuary from 1999-2003 and observed only a single phytoplankton bloom in Suisun Bay ( $30\mu\text{g L}^{-1}$ ) during the entire study period. During an intensive study of the Suisun Bay foodweb, made during 2006 and 2007, phytoplankton blooms were largely absent (Kimmerer et al in prep). During spring 2010, the San Francisco Bay Regional Water Quality Control Board (SFBRWQCB) and the Romberg Tiburon Center (RTC) monitored Suisun Bay phytoplankton weekly during the spring and observed two localized phytoplankton bloom events ( $>30 \mu\text{g L}^{-1}$ ) providing evidence that while large spring phytoplankton blooms are (or have recently been) rare in Suisun Bay, the ecosystem does have the potential to support large populations of phytoplankton and increase its carrying capacity for higher trophic levels. The study results also suggest that monthly monitoring programs at limited locations within Suisun Bay may be insufficient to fully capture the dynamics of phytoplankton blooms.

Prior studies of phytoplankton in Suisun Bay have attributed low rates of primary productivity (Cole and Cloern, 1984; Cloern, 1996) to turbidity (Cloern, 1987, 1991) resulting in light limitation (Alpine and Cloern, 1988). In fact, the relationship between light availability and primary production is robust enough that most estimates of primary production in the San Francisco Estuary (SFE) made since the mid 1980s rely on measurements of chlorophyll-a and solar irradiance rather than direct (e.g.  $^{14}\text{C}$ -tracer based) measurements of autotrophic carbon fixation (Cole and Cloern 1987, Jassby et al. 2002, Parker et al in prep). Low standing stocks of phytoplankton have been attributed to benthic grazing (Nichols and Thompson, 1985, Kimmerer and Orsi, 1996, Lehman 2000) especially by the invasive *Corbula amurensis*. Seasonal phytoplankton blooms in the SFE have been observed following periods of high freshwater flow, when stratification reduces both the effects of benthic grazing and light limitation (Cloern 1982, 1984, 1991;

Cloern et al. 1983; Lucas et al. 1998).

Nutrient limitation had been largely dismissed as a driver of phytoplankton dynamics in the northern SFE, as nutrients are generally found in sufficient supply to meet phytoplankton needs (Hager and Schemel, 1996). While there are a large number of point source inputs of nutrients to the northern SFE, the dominant source of ammonium upstream appears to come from the Sacramento Regional Wastewater Treatment Plant (ca. 90% of loading) which discharges into the Sacramento River approximately 65 km upstream of Suisun Bay. An additional potentially important source of  $\text{NH}_4$  to Suisun Bay is the Central Contra Costa Wastewater Treatment Plant that discharges into western Suisun Bay near the Carquinez Strait. As a result, nutrient concentrations, including  $\text{NH}_4$ , are higher in Suisun Bay compared to other subembayments (i.e. San Pablo and Central Bay) of the northern SFE, where phytoplankton blooms are more frequent.

Wilkerson et al. (2006) and Dugdale et al. (2007) hypothesized that nutrients, particularly the availability of inorganic nitrogen in the form of nitrate ( $\text{NO}_3$ ) and  $\text{NH}_4$  may play a role in controlling phytoplankton dynamics in the northern SFE. Their research suggested that while the northern estuary is primarily light limited due to high turbidity and turbulence, differences in rates of primary productivity and chlorophyll-a accumulation that occur during spring phytoplankton blooms may be dependent on the form of available dissolved inorganic nitrogen (DIN), either as  $\text{NO}_3$  or  $\text{NH}_4$  and that relative concentrations of  $\text{NH}_4$  and  $\text{NO}_3$  act together as a secondary control (limitation) on primary production after irradiance.

Wilkerson et al (2006) described how phytoplankton growth during most of the year is supported by  $\text{NH}_4$  at relatively low growth rates (e.g.  $0.013 \text{ h}^{-1}$  for Central Bay during summer). However over much of the year phytoplankton cannot use  $\text{NO}_3$  as  $\text{NH}_4$  concentrations (in excess of ca.  $4 \mu\text{mol L}^{-1}$  or  $0.056 \mu\text{g L}^{-1}$ ) in the SFE inhibit  $\text{NO}_3$  uptake (e.g. Dortch, 1990). The authors concluded that increased rates of primary production and chlorophyll biomass accumulation only occurs in the northern SFE with: 1) an improved light field, 2) phytoplankton uptake of  $\text{NH}_4$  to reduce  $\text{NH}_4$  concentrations to below inhibitory levels and, 3) utilization of  $\text{NO}_3$  by phytoplankton. Because Suisun Bay generally has the highest concentrations of  $\text{NH}_4$ , the inhibition of  $\text{NO}_3$  uptake (and primary production) may be most pronounced in Suisun Bay compared to other locations in the northern SFE. In enclosure experiments that controlled for light and eliminated the effects of stratification and benthic grazing, Dugdale et al (2007) observed that compared to phytoplankton in San Pablo and Central Bay locations, phytoplankton  $\text{NH}_4$  uptake rates in Suisun Bay were relatively low. In San Pablo and Central Bays increasing  $\text{NH}_4$  concentrations were related to increasing phytoplankton  $\text{NH}_4$  uptake rates. In Suisun Bay, phytoplankton  $\text{NH}_4$  uptake rates were relatively low and unchanging in response to  $\text{NH}_4$  concentration. The reason for this finding has not been resolved, but will be investigated in the proposed study.

Phytoplankton community composition may also be an important determinant of the relative importance of the  $\text{NH}_4$  inhibition hypothesis on chlorophyll-a accumulation. Diatoms thrive in high  $\text{NO}_3$  environments and have inherently high growth rates. In SFE

the dominant diatoms include *Skeletonema costatum*, *Chaetoceros* species, *Thalassiosira* species *Coscinodiscus* (Cloern and Dufford, 2005) and *Entomoneis* (Lidstrom, 2008, Kimmerer et al in prep). Historically, diatoms were the dominant group making up the chlorophyll-a in Suisun Bay. Since the 1980's there has been a shift in phytoplankton community composition in Suisun Bay from diatoms to flagellates and cyanobacteria (Lehman, 1996; Glibert 2010) which has been attributed to climate change (Lehman, 1996), size-selected grazing by clams (Werner & Hollibaugh, 19) and most recently by changes in nutrient loading (primarily  $\text{NH}_4$ ) and shifts in N:P ratio (Glibert 2010).

While there is strong evidence for the role that *Corbula* played on the decline in summer chlorophyll accumulation in Suisun Bay after 1987, the long term decline in chlorophyll-a in Suisun Bay began prior to the 1986 invasion of *Corbula* suggesting that other factors were likely also important. Clam grazing rates vary seasonally and are at their lowest during spring in Suisun Bay, minimizing their impact on phytoplankton biomass. Interannual clam abundance in Suisun Bay was similar in 2010 to previous years, however, a large difference in chlorophyll-a accumulation occurred during 2010, weakening the bivalve grazing hypothesis during the spring period and suggesting that additional factors likely dictate the accumulation of chlorophyll-a. The *Corbula* population may hold ambient chlorophyll concentrations at relatively low values, but the phytoplankton present are held to low growth rates by other factors. The combination ensures low primary production rates and low biomass during much of the time.

During 2010 the SFBRWQCB and the RTC monitored phytoplankton in Suisun Bay with 10 sampling events at 7 stations over the period of March to July (Fig 1). These stations are also monitored monthly by USGS or DWR which provide valuable additional data for analysis. Two blooms were observed with chlorophyll concentrations of  $30 \mu\text{g L}^{-1}$  or greater. The first was measured on April 14th and the second on May 24th. Analysis of the conditions and possible causes of the 2010 blooms is in a preliminary stage, although  $\text{NH}_4$  likely plays an important role.  $\text{NH}_4$  concentrations at the landward end of Suisun Bay (Station D4) fell from  $10.31 \mu\text{mol L}^{-1}$  in mid-March to  $5.5 \mu\text{mol L}^{-1}$  (close to the inhibitory level of  $4 \mu\text{M}$ ; Wilkerson et al. 2006) on April 14 and remained below that value through June 21. Loading of  $\text{NH}_4$  to the Bay from upstream, calculated from Delta Outflow and the  $\text{NH}_4$  concentrations at D4 (Table 1), were as high as  $3.04 \text{mmol m}^{-2}\text{d}^{-1}$  (normalized to the area of Suisun Bay) pre-bloom, and reduced by about 50% or more for the remainder of the monitoring period. At the central location of the bloom,  $\text{NH}_4$  concentrations fell to as low as  $0.5 \mu\text{mol L}^{-1}$ . Upstream events, not analyzed in detail, apparently resulted in both reduced loadings and reduced ambient  $\text{NH}_4$  concentrations that along with other favorable environmental conditions, e.g. irradiance, water column stability and flow rate, allowed the phytoplankton to take control of the  $\text{NH}_4$  inputs (reducing the concentrations below inhibitory levels), to access the  $\text{NO}_3$  pool and result in blooms (Dugdale et al., ms in prep). Both blooms occurred as flow was increasing with a decrease in both loading and concentration at D4. An analysis of the conditions at the Sacramento Regional WWTP outfall area in 2009 (non-bloom year) and 2010 revealed a decrease in loading and  $\text{NH}_4$  concentration from mid-March to mid-April. These changes were reflected in the reduced loading and  $\text{NH}_4$  concentration in Suisun Bay and may be the major event enabling the 2010 blooms (Dugdale et al, in prep)

However, in this study an additional  $\text{NH}_4$  signal was detected in the western part of Suisun that may play a role in controlling phytoplankton blooms in Suisun Bay. Central Contra Costa Sanitation District discharges an average of approximately 7,000 lbs/day of ammonia to western Suisun Bay close to station 207SNB007 (Fig. 2).

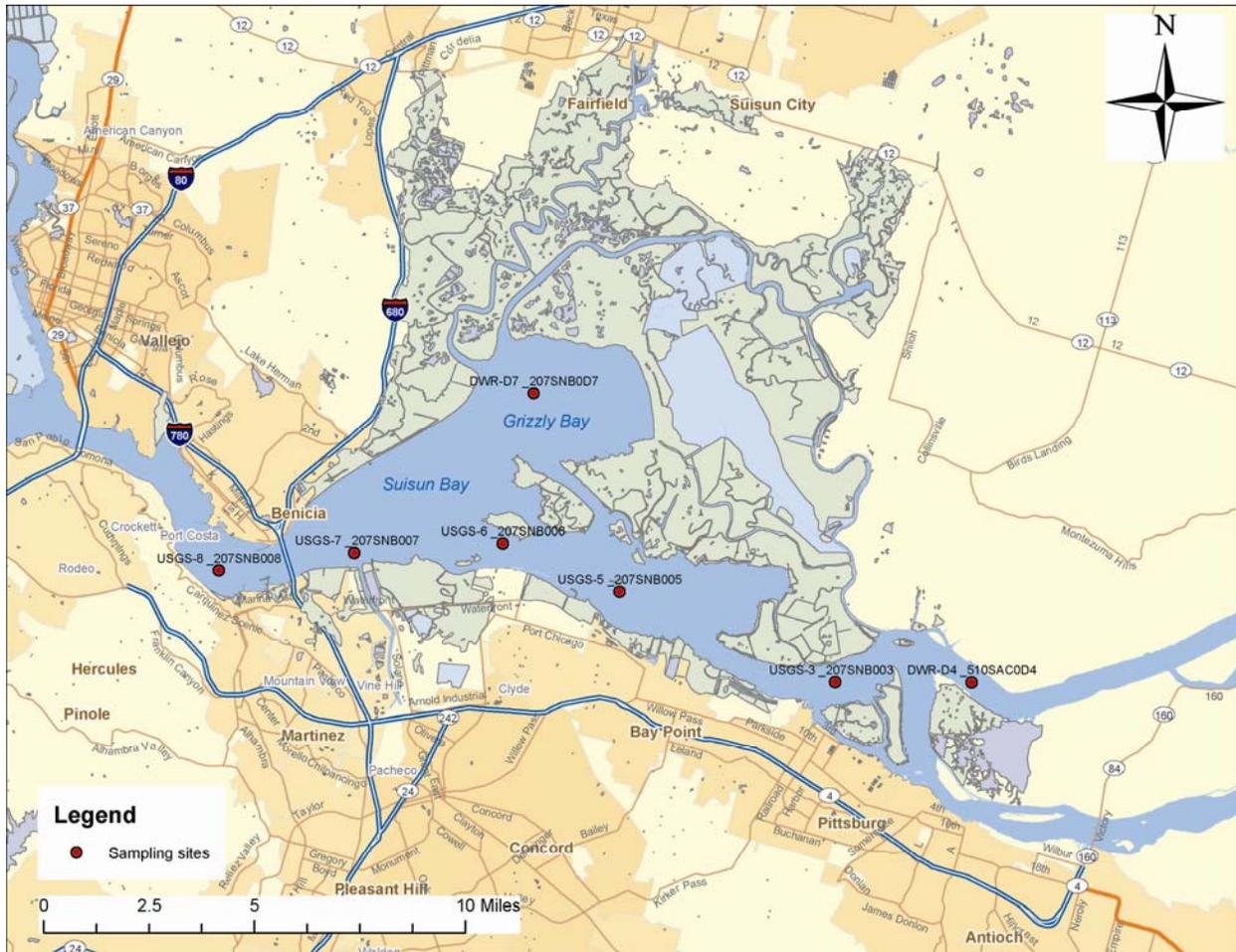


Figure 1: Station locations for 2010 SFRWQCB/RTC study of phytoplankton in Suisun Bay

An additional sampling run was conducted for the SWAMP study on September 1, 2010 using the types of sampling and analyses proposed in this study. Results will be made available in the winter 2011.

	Delta Outflow, $m^3 s^{-1}$	$NH_4$ conc $mmol m^{-3}$	$NH_4$ loading, $mmol m^{-2} d^{-1}$
17-Mar	496.9	10.31	2.61
24-Mar	283.3	6.97	1.01
7-Apr	616.9	9.66	3.04
14-Apr	633.5	5.5	1.77
26-Apr	765.3	5.18	2.02
12-May	617.3	4.43	1.39
24-May	639.7	3.56	1.16
16-Jun	595.5	4.29	1.30
21-Jun	280.9	2.69	0.38
mean			1.63
sd			0.82

Table 1: Calculated  $NH_4$  loading to Suisun Bay based on Delta Outflow and  $NH_4$  concentrations at Station D4 (from Dugdale et al, in prep)

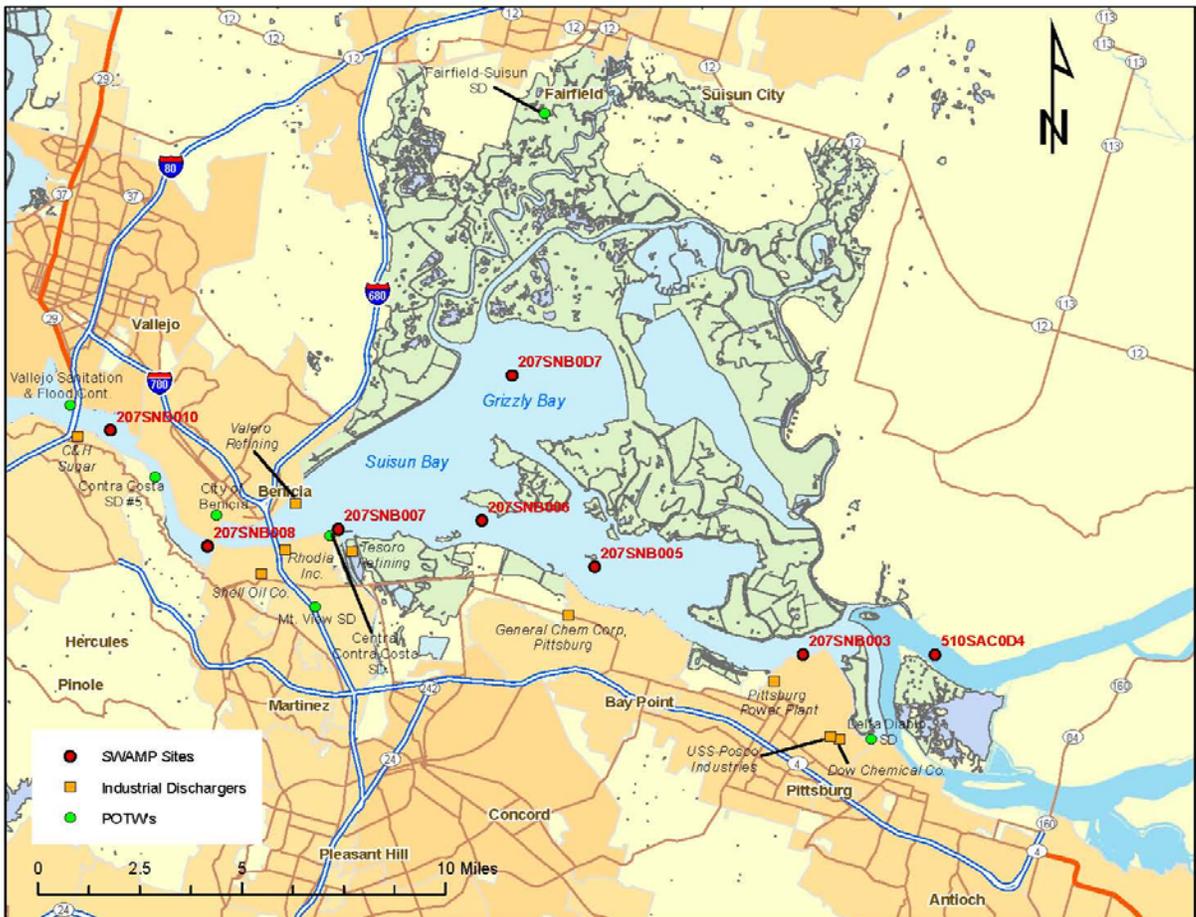


Figure 2. SWAMP 2011 sampling stations with point discharges of ammonium in Suisun Bay.

DWR and USGS conduct ongoing monthly monitoring in Suisun Bay. However, since the specific conditions that favor spring phytoplankton blooms in Suisun Bay are not clear, and initiation of bloom events is temporally variable, more frequent, spatially

intensive monitoring is needed to capture the initiation of blooms and the specific conditions associated with the event. In addition, a more intensive spatial scale is needed to identify the source(s) of contaminant(s) causing inhibition.

Although there is evidence that primary productivity in Suisun Bay may be inhibited by  $\text{NH}_4$ , other contaminants in the water of Suisun Bay may be contributing to this inhibition. By using Toxicity Identification Evaluation (TIE) methods, the cause(s) of toxicity may be able to be identified. In a study conducted by AQUA-Science for CALFED and the Central Valley RWQCB, diuron was identified as the cause of phytoplankton toxicity (growth inhibition) in the Sacramento-San Joaquin watershed and Delta through the use of TIEs (Miller et al 2002). As part of this study we will use TIEs to attempt to identify the cause of primary production inhibition in Suisun. Some R&D will be required to adapt TIEs to diatoms that would occur in Suisun and to target the most likely causes of growth inhibition (ammonium, pesticides/herbicides and copper). In addition, several years of monitoring/studies will probably be necessary to accomplish all of the objectives below. If TIEs are able to identify the cause of inhibition, and that cause includes contaminants other than  $\text{NH}_4$ , that contaminant will be measured in future sampling runs. In addition, samples will be archived for retrospective analysis. Therefore, this is a multi-year study plan.

#### Monitoring Objectives and Questions

The seven objectives and associated research questions of this project are:

1) Background: Previous studies in Suisun Bay have measured the relationships between nutrients and phytoplankton biomass. An enclosure incubation study conducted by Dugdale et al (2007) measured low  $\text{NH}_4$  uptake rates by phytoplankton from Suisun Bay compared to Central and San Pablo Bays. Carbon uptake (=primary productivity) in Suisun Bay enclosures was only 30% of that in the Central Bay enclosures and was related in part to a lower rate of  $\text{NH}_4$  uptake, but especially to a reduced  $\text{NO}_3$  uptake in the Suisun enclosures (Wilkerson, unpublished data). There has been some controversy as to whether a decline in  $\text{NH}_4$  uptake results in a decline in primary productivity. Studies conducted in the Sacramento River have shown reduced  $\text{NH}_4$  uptake at high  $\text{NH}_4$  concentrations accompanied by reduced carbon uptake (Parker et al, 2010 in prep) By measuring both phytoplankton nitrogen ( $\text{NO}_3$  and  $\text{NH}_4$ ) uptake and primary production, as well as nutrient concentrations in the water column this relationship can be confirmed and quantified for Suisun Bay.

Objective: Determine if  $\text{NH}_4$  concentrations, specific nutrient ratios or phytoplankton nitrogen uptake rates are related to lower rates of primary production in spring in Suisun Bay.

- i. What is the relationship between phytoplankton nitrogen uptake rates and primary production?
- ii. Do high  $\text{NH}_4$  concentrations in Suisun Bay correlate with low primary production?

2) Background: Based on relationships between the introduction of *Corbula* and the

accumulation of phytoplankton biomass, there has been the assumption that the grazing effect of *Corbula* limits the accumulation of phytoplankton biomass regardless of the rate of primary production. However, in the 2010 SWAMP study a bloom did occur when *Corbula* were present and in the same concentrations as previous years.

Objective: Determine if stations with high primary productivity can accumulate high phytoplankton biomass despite the presence of *Corbula*.

- i. Can locations with elevated primary productivity accumulate elevated phytoplankton biomass, despite the presence of *Corbula* ?

3) Background: There has been the assumption that the Sacramento Regional WWTP is the primary and most important source of  $\text{NH}_4$  to Suisun Bay. However, in the 2010 SWAMP study concentrations of  $\text{NH}_4$  dropped from east to west but then became elevated again in the western edge of Suisun.

Objective: Identify sources of  $\text{NH}_4$  to Suisun Bay in the spring.

- i) Do spatial and temporal patterns in  $\text{NH}_4$  indicate a single upstream source to Suisun Bay?
- ii Are there indications of additional sources of  $\text{NH}_4$  west of or within Suisun Bay and if so, where are these sources?

4) Background: Previous data in Suisun Bay has shown that phytoplankton blooms usually start in shoals rather than in channels. However, in the 2010 SWAMP study, the blooms were more pronounced in the channels than in the shoals.

Objective: Compare spatial patterns in inorganic nutrient concentrations, chlorophyll-a, primary production and phytoplankton nitrogen uptake to determine if a detected bloom originates in shoals or channels during spring in Suisun Bay.

- i.) Do phytoplankton blooms in the spring in Suisun Bay originate in the shoals or channels?

5) Background: Phytoplankton community composition in Suisun Bay has changed from diatoms to flagellates and other phytoplankton species. Nutrient concentrations and ratios may have changed in Suisun to select for certain species over others.

Objective: Compare phytoplankton community composition during phytoplankton blooms and non-blooms in Suisun Bay and with different nutrient concentrations and ratios.

- i.) Is elevated  $\text{NH}_4$  associated with a different phytoplankton community composition compared to elevated  $\text{NO}_3$ ?

6) Background: Historically, primary production in the SF Estuary has been light limited, rather than nutrient limited. However, concentrations of suspended sediments are declining in the estuary increasing light available for phytoplankton growth.

Objective: Evaluate the role that water column stratification and an improved light field play in promoting phytoplankton bloom initiation in Suisun Bay.

- i) Does  $\text{NH}_4$  inhibition of  $\text{NO}_3$  uptake and primary production hold in highly turbid (i.e. low light) conditions?
- ii) Can phytoplankton blooms occur under high light AND elevated  $\text{NH}_4$ ?

7) Background: There is a great deal of controversy whether  $\text{NH}_4$  is causing the inhibition of primary production in Suisun Bay. In addition, some data suggest that there may be other contaminants that may be contributing to the inhibition of primary production in Suisun Bay. In order to regulate contaminants that may be causing impacts on the food web, a higher level of certainty is desired regarding the cause of inhibition. Objective: Determine if  $\text{NH}_4$ , copper and/or pesticides/herbicides, are causing the inhibition of primary production in Suisun Bay in the spring.

i. Are  $\text{NH}_4$ , copper and/or pesticides/herbicides inhibiting primary production in Suisun Bay in the spring?

### Benefits and Outcomes

The proposed monitoring program for FY10-11 (and planned monitoring in future years) will provide the following benefits and outcomes:

- Conduct controlled studies to determine if contaminants, including ammonium ( $\text{NH}_4$ ), are inhibiting primary production in Suisun in the spring.
- Evaluate whether point sources (POTWs) influence nutrient concentrations, or the concentrations of other contaminants, that limit primary production in Suisun Bay.
- Provide detailed characterization of phytoplankton blooms, including primary production and nutrient uptake rates in addition to biomass measurements in Suisun Bay, a critical habitat for food limited species.
- Provide a comparison of phytoplankton parameters in shoal and channel habitats.
- Further test the "  $\text{NH}_4$  inhibition" hypothesis for phytoplankton,

### **III. Study Methods and Materials**

a. Monitoring design, spatial and temporal scale, and frequency of sampling

The monitoring program will be based on the sampling plan completed from March – July 2010 by the SFBRWQCB and RTC and will be comprised of 10 cruises completed from March to June 2011 and 2012. Sampling will be conducted at 8 stations between the Sacramento River and Carquinez Straits. Most of these samples will be collected in the channel except for one station in the shoals of Suisun Bay (207SNB0D7). These stations will be the same 7 stations as in 2010 (Fig 1). However, an additional station will be included to the west of station 207SNB008 at the western end of Carquinez Strait to bracket the input of  $\text{NH}_4$  from sources in the western part of Suisun (Fig. 2). In order to extend the results obtained during 2010 and address the objectives described above, sampling for some parameters, i.e. phytoplankton C and N uptake rates will be added and samples will be incubated at 4 light intensities (e.g. 50%, 25%, 10% 5% of surface solar irradiance) equivalent to 4 depths within the photic zone (typically the top 1.5m in Suisun Bay) during all cruises. These results will provide depth-integrated phytoplankton C and N uptake for the spring bloom progression. Because of the significant number of cancelled cruises in 2010 due to weather, during 2011 and 2012 sampling will be conducted using the 38-ft RV Questuary. The Questuary is outfitted with a vertically deployed conductivity, temperature and depth (CTD) profiler and a rosette system

carrying six, 3-L Niskin bottles for sampling the water column at discrete depths. In addition, the Questuary is outfitted with an underway data acquisition system (UDAS) for geo-referenced, continuous measurements of temperature, salinity and *in vivo* fluorescence for greater spatially resolution of water characteristics and phytoplankton biomass within Suisun Bay. The RV Questuary has been used extensively for studies in Suisun Bay and can operate under inclement weather and is able to access all the stations to be sampled.

Sigma autosamplers will be deployed at the DWR Hood sampling facility and at Chipps Island and programmed to obtain a daily composite sample (4 sub-samples/day). The Sigma units are expected to be provided and operated by Central Valley RWQCB. Analyses will be made by RTC. These data on source region  $\text{NH}_4$  concentrations in the 5-7 day period preceding any observed bloom in Suisun Bay will aid in understanding the connection between source  $\text{NH}_4$  and inputs to the Bay.

#### b. Indicators and measurement parameters

##### *Water column light / stability by CTD profiling*

The monitoring program in 2011 and 2012 will be enhanced over 2010 sampling with vertical profiles of temperature, salinity, optical backscatter (OBS), photosynthetically active radiation (PAR) and *in vivo* chlorophyll-a collected at the 8 discrete stations. Temperature and salinity measurements will allow for the evaluation of water column stratification and the ability to estimate vertical water column turnover and the potential for benthic - pelagic coupling. Estimates of PAR will provide insight into the role of light availability on primary production, phytoplankton N uptake and resulting phytoplankton biomass in Suisun Bay. Additional measures of water column clarity, OBS and *in vivo* chlorophyll-a, will provide information about the role of both inorganic particles and phytoplankton in the attenuation of light. The RV Questuary is outfitted with a Seabird Electronics SBE-32 Carousel water sampler and a SBE-19plus CTD which makes continuous measurements of conductivity, temperature, and pressure with depth. Additionally, a LiCOR photosynthetically active radiation (PAR) sensor, Wetlabs fluorometer and D&A optical backscatter sensor are deployed as part of the CTD package. The underway data acquisition system (UDAS) is equipped with a Seabird Electronics SBE-19 CTD and a Wetlabs fluorometer.

##### *Nutrient and dissolved organic carbon and nitrogen concentrations*

A principal objective of the 2011/12 monitoring program is an evaluation of the temporal and spatial trends in inorganic nutrients ( $\text{NO}_3$ ,  $\text{NO}_2$ ,  $\text{NH}_4$ ,  $\text{PO}_4$ ,  $\text{Si}(\text{OH})_4$ ) and organic nutrients (bulk DOC, bulk DON, urea) within habitats of Suisun and Grizzly Bays. Assessment of conservative behavior of nutrients (i.e. nutrient concentrations versus salinity, e.g. Wilkerson et al. 2006) will provide an indication of nutrient sources to Suisun Bay. Finally, the impact of nutrient concentration on primary production, phytoplankton N uptake and phytoplankton biomass is a primary objective of the project. Samples of nutrients will be collected at all 8 stations during each sampling event.

The following nutrient protocols developed in the laboratory of R. Dugdale are SWAMP comparable. Water samples for inorganic nutrients will be collected in polycarbonate vials, filtered and processed within 24 hours according to the SWAMP QAPrP (2008). Water chemistry (nutrients and carbonate system) will be analyzed at the Romberg Tiburon Center. Concentrations of nitrate, nitrite, phosphate, and silicate will be analyzed with a Bran and Luebbe AutoAnalyzer II according to the procedures of Whitledge et al. (1981) for all but silicate which will use Bran and Luebbe (1999). Ammonium will be measured using the Solorzano (1969) method using a 10-cm pathlength cell.

Bulk dissolved organic carbon and total dissolved nitrogen (TDN) will be measured using a Shimadzu TOC-V; Dissolved organic nitrogen will be determined by subtracting dissolved inorganic nitrogen (nitrate, nitrite, and  $\text{NH}_4$ ) from TDN measurements.

#### *Phytoplankton biomass and community composition*

Phytoplankton biomass will be assessed in four ways, *in vivo* chlorophyll-a, size fractionated extracted chlorophyll-a, flow cytometry, and direct microscopic counts. *In vivo* chlorophyll-a measurements from surface water and with depth will provide a high resolution assessment of phytoplankton abundance in Suisun Bay. Size fractionated (all cells and cells with diameter  $> 5 \mu\text{m}$ ) extracted chlorophyll-a measurements will be collected at the discrete stations and will be used for absolute measurements of chlorophyll-a and for comparison with previous phytoplankton monitoring completed in Suisun Bay. Flow cytometry will provide estimated counts of red-fluorescing particles (i.e. phytoplankton) for comparison with chl-a, and direct microscopic counts will provide phytoplankton community structure.

*In vivo* chlorophyll-a will be measured on the CTD and using the UDAS system by a Wetlabs Fluorometer. Calibration of underway data will be made for each cruise using the extracted chlorophyll-a obtained in parallel. Size fractionated extracted chlorophyll (for cells with diameters  $< 5 \mu\text{m}$  or  $> 5 \mu\text{m}$ ) will be determined using the extraction protocol of Arar & Collins (1992) and a Turner Designs Model 10 fluorometer. Size distribution of fluorescent particles will be made using a CytoSense flow cytometer in 20 ml samples (Dubelaar and Gerritsen, 2000). Phytoplankton identification on preserved (with Lugols solution) samples will be completed under a subcontract with EcoAnalysts to be consistent with other phytoplankton taxonomy data collected by the California Department of Water Resources.

#### *Primary production and phytoplankton nitrogen uptake*

Estimates of primary production (carbon uptake) and phytoplankton nitrogen uptake ( $\text{NO}_3$  and  $\text{NH}_4$ ) will provide insight into the specific mechanisms responsible for phytoplankton bloom initiation in Suisun Bay. Specifically, it is hypothesized that rates of primary production are lower when phytoplankton grow on  $\text{NH}_4$ . In contrast, when phytoplankton use  $\text{NO}_3$  (i.e. phytoplankton  $\text{NO}_3$  uptake is observed) it is hypothesized to lead to elevated primary production rates and may favor specific groups of fast-growing

phytoplankton (i.e. diatoms). Measurements of depth integrated primary production, using simulated *in situ* methodology will allow for an evaluation of the  $\text{NH}_4$  inhibition hypothesis under varying light limitation conditions and an improved estimate of the capacity of Suisun Bay phytoplankton to absorb the loading of  $\text{NH}_4$ .

Uptake of C,  $\text{NO}_3$ ,  $\text{NH}_4$ , will be made on water sampled from four depths (equivalent to 100%, 50%, 25% and 5% of surface PAR i.e. simulated *in situ* incubations) at all of the 8 discrete stations. Uptake rates will be determined using dual labeled  $^{13}\text{C}/^{15}\text{N}$  stable isotope tracer techniques (Slawyk et al., 1977, Legendre and Gosselin, 1996) to yield simultaneous C and N uptake rates from a single sample. Water will be dispensed into 160 ml incubation bottles and inoculated with either  $\text{Na}^{13}\text{CO}_3$  and  $\text{K}^{15}\text{NO}_3$  or  $\text{Na}^{13}\text{CO}_3$  and  $^{15}\text{NH}_4\text{Cl}$  (99 at%). Additions will be made to approximately 10% of ambient concentration to avoid substrate enhancement effects; Dissolved inorganic carbon will be measured according to Friederich et al. (2002) using a Monterey Bay Research Institute-clone DIC analyzer. Immediately following inoculation, one sample will be filtered onto a precombusted GF/F filter (450°C, 4-hr) by gentle vacuum to determine the initial PON and POC concentration and isotopic filter blank. Incubations will be performed at ambient temperature for 24 hours (Cole and Cloern, 1984) and terminated by gentle vacuum filtration onto precombusted GF/F. C and N concentration and isotopic composition will be determined using a Europa 20/20 mass spectrometer. C and N uptake rates will be calculated based on isotopic enrichment according to Dugdale and Wilkerson (1986) and Parker (2005). Depth integrated primary production and phytoplankton nitrogen uptake estimates will be computed using trapezoidal approach (Cole & Cloern, 1984).

#### *Toxicity Identification Evaluations (TIEs)*

TIEs have the potential of identifying the cause of diatom growth inhibition in Suisun Bay. In the past, correlations or spiking experiments have provided the relationships between ammonium and, nutrient uptake or chl-a. TIEs can identify a cause and effect relationship between diatom growth inhibition and the contaminant(s) that cause(s) the inhibition. TIEs will be conducted using EPA methods (USEPA 1988) adapted to target ammonium, pesticides/herbicides and copper, the mostly likely causes of diatom growth inhibition in Suisun Bay. Pesticides/herbicides will be selected based on use in the watershed and toxicity of the compound. The diatom species that will be used in the TIEs will be selected in consultation with the TIE contractor. The species will probably be a readily available laboratory species (ex. *Thalassiosira* sp.) that may be found in Suisun or diatoms from Suisun collected in this study. If conducive to the salinity tolerance of the chosen diatom, water collected from Central Bay and San Pablo Bay will be used as references during initial toxicity testing.

#### c. Data analysis and assessment

Data collected as part of the Suisun Bay surveys will be analyzed for spatial and temporal

trends and correlation between nutrient concentration and phytoplankton biomass. Primary production and phytoplankton nitrogen uptake will be computed from simulated in situ incubations using a trapezoidal integration approach. 2011/12 results will be compared with results for Suisun Bay collected by the USGS and DWR monthly monitoring program, EPA dataset (Wilkerson et al 2006,) CALFED Foodweb Program (Kimmerer et al, in prep.) and results collected by this group in 2010 (Dugdale et al, in prep). Below are data analysis and assessment methods for each objective:

**Objective #1:** Determine if  $\text{NH}_4$  concentrations, specific nutrient ratios or nitrogen uptake rates are related to lower rates of primary production during spring in Suisun Bay.

Phytoplankton carbon uptake rates will be plotted vs. phytoplankton  $\text{NO}_3$  uptake,  $\text{NH}_4$  uptake,  $\text{NO}_3$  uptake plus  $\text{NH}_4$  uptake and the ratio of  $\text{NO}_3$  uptake to  $\text{NH}_4$  uptake. Parker (2004) obtained a linear relationship between phytoplankton C uptake and phytoplankton N uptake, in enclosure experiments but the slope was almost twice as high for  $\text{NO}_3$  uptake as for  $\text{NH}_4$  uptake. Phytoplankton carbon uptake would be expected to increase as the ratio of  $\text{NO}_3$  uptake to  $\text{NH}_4$  uptake increases in response to decreasing  $\text{NH}_4$  concentrations.

**Objective #2:** Determine if stations with high primary productivity can accumulate high phytoplankton biomass despite the presence of *Corbula*.

DWR collects monthly benthic samples in Suisun Bay. This data will be analyzed to determine the presence and concentrations of *Corbula* during our period of sampling. DWR data collected during our sampling period will then be compared to historical data in the DWR database to determine if *Corbula* was present at the same concentrations during our sampling period as at the same time period (spring) in the past when blooms were or were not present.

**Objective #3:** Identify sources of  $\text{NH}_4$  to Suisun Bay in the spring.

Analysis of the spatial distribution of  $\text{NH}_4$  at the stations sampled will indicate the presence of  $\text{NH}_4$  sources in addition to the upstream source from the Sacramento and San Joaquin Rivers. Assessment of conservative behavior of nutrients (i.e. nutrient concentrations versus salinity, e.g. Wilkerson et al. 2006) will provide an indication of nutrient sources to Suisun Bay. This data will be analyzed to evaluate the elevated  $\text{NH}_4$  concentrations often observed at 207SNB007 (Fig 2), and presumed to be from the Central Contra Costa Sanitation District outfall.

**Objective #4:** Compare spatial patterns in inorganic nutrient concentrations, chlorophyll-a, primary production and phytoplankton nitrogen uptake to determine if a detected bloom originates in shoals or channels during spring in Suisun Bay.

Nutrient concentrations, chlorophyll a, depth integrated phytoplankton  $\text{NO}_3$  uptake,  $\text{NH}_4$  uptake and C uptake (primary production) rates at shoal stations will be compared with

channel stations to detect any systematic differences between habitats. Previous studies (Kleckner m.s. thesis) found no differences in nutrient concentrations between shoal and channel stations in Suisun Bay, however, there has been the assumption that blooms originate in the shoals. The bloom of 2010 was initiated in the channel and propagated to the shoal. The 2011/2012 time series will be examined for channel/shoal progressions.

Objective #5: Compare phytoplankton community composition during phytoplankton blooms and non-blooms in Suisun Bay and with different nutrient concentrations and ratios.

The spatial and temporal distribution of the phytoplankton species abundances will be compared with the spatial and temporal distribution of ammonium uptake,  $\text{NO}_3$  uptake, carbon uptake (primary production) and the nutrient distributions to reveal patterns of community composition and the relative effect of the environmental variables measured in addition to nutrients, e.g. temperature, salinity, turbidity, PAR.

Objective #6: Evaluate the role that water column stratification and an improved light field play in promoting phytoplankton bloom initiation in Suisun Bay.

The vertically integrated uptake rates of  $\text{NH}_4$ ,  $\text{NO}_3$  and carbon (primary productivity) will be related to the water column irradiance field, ie. turbidity and PAR (photosynthetically active irradiance) fields obtained from the CTD data. This assessment is important in evaluating how phytoplankton in the water column are reducing ambient  $\text{NH}_4$  concentrations and enabling  $\text{NO}_3$  uptake to initiate a bloom, i.e. elevated irradiance will enhance  $\text{NH}_4$  uptake and aid in reducing ambient  $\text{NH}_4$  concentrations to enable bloom initiation.

Objective 7): Determine if  $\text{NH}_4$ , copper and/or pesticides/herbicides, are causing the inhibition of primary production in Suisun Bay in the spring.

The results of the TIE effort will be used to contribute to the understanding of the cause of the potentially low primary productivity in Suisun compared to Central and San Pablo Bays. Methods will be developed to remove ammonium, copper and targeted herbicides/pesticides from Suisun Bay water. Each method will have a control so that the method itself does not cause diatom toxicity (inhibition). An attempt will be made to conduct phase I and II TIEs and, if successful, phase III if copper or an herbicide/pesticide seems to be the cause of toxicity. Data will be analyzed according to EPA methods for TIEs (U.S.EPA 1988).

#### d. Data Management

Nutrient analysis and chlorophyll-a analysis are all SWAMP comparable with regular assessment of certified reference and spiked field samples. Quality assurance for dissolved organic carbon and nitrogen measurements are made using certified reference material from the laboratory of D. Hansell (U. Miami). Certified reference material for dissolved inorganic carbon measurements are provided by the laboratory of A. Dickson

(Scripps Inst.). RTC will submit data to the SWAMP DMT in SWAMP format and stored in the SWAMP database.

#### **IV. COORDINATION AND REVIEW STRATEGY**

This study will be funded by both the SF Bay regional SWAMP and the State and Federal Contractors Water Agency (SFCWA). Monitoring and laboratory analysis will be funded by SWAMP and be conducted by the SFSU Romberg Tiburon Laboratory. The Central Valley RWQCB will provide and operate the Sigma autosamplers. The SFCWA will fund toxicity identification evaluations and phytoplankton taxonomy. For consistency, EcoAnalysts will conduct the taxonomic analysis for phytoplankton. The project workplan was reviewed through the SWAMP peer review process. However, since TIE protocols need extensive R & D and because the funding is not through SWAMP, the TIE portion of this study design is conceptual rather than descriptive.

#### **V. QUALITY ASSURANCE**

This monitoring study will be consistent with the SWAMP Quality Assurance Program Plan (QAPrP) (2008) for parameters that are part of that plan. MQOs for nutrients and chlorophyll-a will be consistent with the QAPrP.

#### **VI. REPORTING**

Data from this project will be in the SWAMP database and CEDEN. The results of this study will be a peer reviewed journal article written by RTC contractors. There will also be a separate report on TIEs to be funded by the SFCWA.

#### **VII. PROJECT SCHEDULE**

March – June 2011 – Sampling  
July – December 2011 – Data analysis and review  
March – June 2012 - Sampling  
July – December 2012 - Data analysis and review  
March 2012 – Draft paper due to RWQCB  
April 2012 – Respond to RWQCB comments  
May 2012 - Draft paper due to peer reviewed journal

The final paper is a publication of a peer reviewed journal article.

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