#### **Quantifying External Nutrient Loads to San Francisco Bay**

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Nutrient loads to and concentrations in subembayments of San Francisco Bay are comparable to or greater than those in other estuaries that experience beneficial use impairment due to nutrient over-enrichment. The combination of high nutrient availability and changes in environmental factors that regulate the Bay's response to nutrients has generated growing concern about whether areas of the Bay are trending toward, or may already be experiencing, nutrient-related impairment. To help inform nutrient management considerations, we estimated external nutrient loads to the Bay from multiple point and non-point sources, evaluated how those loads vary spatially and temporally in magnitude and speciation, and assessed the relative importance of various sources. On an annual-average basis, all considered sources combined for loads of 75000 kg d<sup>-1</sup> dissolved inorganic nitrogen and 6000 kg d<sup>-1</sup> phosphate Bay-wide. Treated wastewater effluent from the 42 publicly-owned treatment works (POTW) that service the Bay Area's 7.2 million people contributed 34000 kg d<sup>-1</sup> ammonium, 12000 kg d<sup>-1</sup> nitrate, and 4000 kg d<sup>-1</sup> phosphate. The dominant sources of N and P loads, and the form of N, varied substantially among subembayments. In southern subembayments, POTWs were the dominant N and P sources. Exchange with the coastal ocean has the potential to be a substantial net source of nutrients, but remains poorly quantified and highly uncertain. Although stormwater loads estimates developed to date are highly uncertain, in most subembayments and during most of the year stormwater nutrient loads were substantially less than POTW loads, with potential exceptions being loads to northern subembayments. The San Joaquin and Sacramento Rivers, which enter the northern Bay through the Delta after draining  $\sim$ 40% of California, deliver approximately 90% of the Bay's freshwater inputs, and have the potential to be large and seasonally-dominant nutrient sources to northern subembayments, potentially constituting 25-30% of annual-average Bay-wide loads.

Keywords: Nutrients, External Loads, Seasonality, Spatial Variability

Poster Topic: Nutrients

# Nutrient Exchange in Northern San Francisco Bay Sediments: Rates, Environmental Controls, and Impacts of Invasive Bivalves

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Algal production in the Northern San Francisco Bay region is sustained by direct inputs of nutrient elements and both water column and sediment nutrient recycling. Differential retention and recycling of sediment nitrogen and phosphorus may lead to changes in nutrient effluxes to the overlying water and have consequences for the productivity and composition of phytoplankton communities. Using core incubations, we have measured the net exchange of nitrogen, phosphorus and oxygen at the sediment water interface of Sacramento-San Joaquin Delta and Suisun Bay tidal environments, including microbial denitrification and benthic microalgal production during late spring and summer. Additional measurements have been made of oxygen penetration, bioirrigation, invasive bivalve biomass, and pore water chemistry. Most sites have moderate rates of sediment metabolism, nutrient efflux and denitrification, with high rates of benthic microalgal photosynthesis in shallow water Delta environments. Sites with invasive bivalves (Corbicula fluminea, Potamocorbula amurensis) have higher rates of sediment metabolism and nutrient exchange. The observed rates of nutrient recycling and denitrification are consistent with low algal biomass. These data suggest that Bay-Delta sediments are important sites for nutrient recycling, transformation and retention. These data will help inform nutrient models and contribute to our growing understanding of sources and fates of nutrients in this system.

**Keywords:** Nutrients, Sediment-Water Exchange, Denitrification, Invasive Bivalves, Sediment, Nitrogen, Phosphorus

Poster Topic: Nutrients

# How Anthropogenic Nutrients from Wastewater Treatment May Contribute to Low Phytoplankton Productivity and Blooms in the San Francisco Estuary

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For the last 20 years, studies of water quality and phytoplankton in the San Francisco Estuary (SFE) focused on measuring nutrient concentrations and chlorophyll with relatively few direct measurements of primary production and virtually no estimates of nutrient uptake. The paradigm was that the elevated inorganic nutrients (mostly anthropogenically derived) had no impact on blooms. However studies suggest that the chemical form of inorganic nitrogen (N) and nitrogen to phosphorus ratio in SFE waters may influence algal production and the occurrence of blooms as well as food web composition. With increasing human population, anthropogenic N loads to estuaries are increasingly in reduced forms (ammonium; urea) resulting from wastewater treatment rather than oxidized forms (nitrate). Ammonium may a) inhibit the potential for phytoplankton blooms (oligotrophication) by preventing access to nitrate and b) shift phytoplankton functional groups away from diatoms to phytoplankton that are more ammonium-tolerant. We evaluated whether N redox state and N:P stoichiometry would influence SFE phytoplankton by measuring nutrient uptake and primary productivity in experimental enrichments with combinations of ammonium, nitrate and P. Added ammonium consistently inhibited nitrate uptake and promoted the growth of cryptophytes. Nitrate enrichment and low N:P conditions favored diatoms. Phytoplankton altered N:P assimilation in response to experimentally manipulated N : P availability. These findings provide a revised view of how changes in estuarine nutrient loading due to wastewater treatment practices can influence eutrophication responses.

Keywords: Phytoplankton, Nitrogen, Ammonium

Poster Topic: Nutrients

# Reinventing Water Infrastructure in the Face of Uncertainty: An Integrative Approach to Nitrogen Management in the San Francisco Bay

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Recent data suggest that the San Francisco Bay is at a growing risk of eutrophication. As a result, protection of the ecosystem may require reducing the mass of nitrogen released to the Bay. Stakeholders have expressed interest in new approaches for controlling nitrogen discharges that realize co-benefits, such as habitat restoration, protection from sea-level rise and simultaneous removal of other contaminants. There is currently considerable uncertainty about the cost and efficacy of such innovative control strategies. In contrast, the performance of traditional approaches to managing nitrogen by controlling point sources (i.e., adding additional unit process to existing wastewater treatment plants), which tend to be energy intensive and vulnerable to climate change impacts, are known with a high degree of certainty. To assess the merits of investing in new types of urban water infrastructure that achieve both nitrogen reduction and co-benefits that are important to key stakeholders, a multi-criteria decision-making approach was used for assessing different scenarios relevant to the Bay. The analysis compares the use of engineered wetlands for treatment of municipal wastewater effluent, riparian buffer strips for treatment of nitrogen in agricultural runoff and green infrastructure on the eastern side of the city of San Francisco for treatment of urban runoff and minimization of combined sewer overflows with conventional forms of nitrogen control at municipal wastewater treatment plants. The analysis identifies the need for additional data to decrease uncertainty and give decision-makers confidence in investments in new forms of infrastructure. Pilot projects can serve as laboratories to fill data gaps while simultaneously familiarizing the community with the co-benefits associated with new forms of urban water infrastructure.

Keywords: Nutrients, Nitrogen, Stormwater, Decision-Making, Wetlands

# Nitrogen Pollution in Tilden Park's Lakes and Ponds

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Nitrogen is one of the major nutrients for plant growth. Through this project I hoped to understand the effects that nitrogen pollution from humans and cows has on lakes and ponds in the Bay Area watersheds, specifically evaluating surface waters in Tilden Park, a 2,079 acre regional park. I sampled four ponds: a pond off of the Nimitz way trail, an area which is used to graze cattle; Jewel Lake, which is below the little farm; Lake Anza a bathing area; as well as Wildcat Creek which runs between Lake Anza and Jewel Lake. I hypothesized that the pond off of Nimitz Way would be most affected by nitrogen pollution as it would be contaminated with cow manure, followed by Jewel Lake as it would gather run off from the livestock, Lake Anza would be next as the urine from the bathers contains urea and therefore nitrogen, the cleanest would be Wildcat Creek as it is a protected stream whose bacteria would filter the nitrogen. In addition, to find out how nitrogen pollution from outside sources affected the algae within the ponds, I incubated test tubes of surface water with different sources of nitrogen in the laboratory. To measure nitrate in ponds, I prepared a cadmium reduction column and used a spetrophometer to measure the colorimetric changes. Concentrations of nitrate in these surface waters ranged from 0.5 to 6.5 x 10<sup>-6</sup> M, with the highest concentrations observed at Wildcat Creek. Based on the results of this experiment, I found that nitrogen pollution from humans and livestock in Tilden Park can result in an increase in algae growth.

Keywords: Nutrients, Nitrate, Watersheds, Tilden Park

### Nitrogen Removal and Energy Recovery with the Coupled Aerobic-Anoxic Nitrous Decomposition Operation (CANDO)

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The <u>C</u>oupled <u>A</u>erobic-anoxic <u>N</u>itrous <u>D</u>ecomposition <u>O</u>peration (CANDO) is a new wastewater treatment process that removes and recovers renewable energy from reactive nitrogen  $(NH_4^+)$ . The process consists of three steps: (1)  $NH_4^+$  oxidation to  $NO_2^-$  (2)  $NO_2^-$  reduction to  $N_2O$ , and (3)  $N_2O$  conversion to  $N_2$  with energy recovery by using  $N_2O$  as an oxidant in biogas combustion.

This work demonstrates steps (1) and (2) at the bench-scale treating synthetic and real anaerobic digester supernatant, and step (3) at full-scale on a biogas-fed internal combustion engine. Step (1) is demonstrated by a continuous flow partial nitrifying reactor that oxidizes >85% NH<sub>4</sub><sup>+</sup> to NO<sub>2</sub><sup>-</sup>. Step (2) is demonstrated by two strategies: (1) a biological strategy favoring microorganisms that store polydroxybutyrate, then oxidize it to reduce  $NO_2^-$  to  $N_2O$ , and (2) an abiotic strategy where carbonate green rust reduces  $NO_2^-$  to  $N_2O$ . For the biological strategy,  $NO_2^{-}$  supplied from the partial nitrifying reactor is reduced to  $N_2O$ , with acetate as the electron donor, achieving 60-80% conversion over multiple cycles. For the abiotic strategy, a closed loop Iron cycle couples carbonate green rust oxidation with  $NO_2^-$  to  $N_2O$  reduction, and then regenerates the oxidized Iron back to carbonate green rust with Fe(II) from an acetate-fed microbial community, achieving >90% N<sub>2</sub>O conversion. Step (3) is demonstrated by N<sub>2</sub>O injections in a full-scale biogas engine that increase power output by 4-8% (7-14%  $N_2O$  by volume). Many processes recover energy from waste COD as CH<sub>4</sub>; but none recovers energy from waste nitrogen. As compared to conventional nitrification/denitrification, CANDO is expected to decrease oxygen demand, decrease biosolids production, increase organic matter for biogas production, and recover energy from nitrogen waste.

Keywords: CANDO, Wastewater, Nutrients, Energy Recovery

### Is Urea of Water Quality Concern in the San Francisco Estuary?

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Increasing anthropogenic sources of nitrogen as urea from agriculture and wastewater have resulted in elevated urea concentrations in many estuarine and coastal environments. This has the potential to adversely affect coastal and estuarine environments. The San Francisco Estuary (SFE) is strongly influenced by agriculture and a large metropolitan area. However, little data is currently available regarding urea concentrations in the SFE or the potential ecological effects of increased urea to the estuary. Nearly one thousand discrete measurements of urea concentration, along with other water quality data (macro-nutrients and chlorophyll-*a*) have been made throughout the northern SFE for the past six years. In contrast to some other estuaries, urea is generally less than  $1\mu$ M-N urea, representing a small percentage of the nitrogen pool. Additionally, a preliminary set of urea uptake measurements (using 15N-labeled urea) suggest that both ammonium and nitrate are larger contributors to phytoplankton nitrogen uptake in the estuary. These results suggest a limited role for urea in phytoplankton-nutrient dynamics in the SFE.

Keywords: Urea, Phytoplankton, Nitrogen, Estuary

# Measurements and Potential Significance of Urea as a Nitrogen Source for HAB Species in San Francisco Bay, California: A One Year Pilot Study

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Since 1968 the U.S. Geological Survey has maintained a program of research and observation in San Francisco Bay. The program includes measurements of dissolved inorganic nutrients, but organic forms of nutrients including urea are not regularly measured and their concentrations are unknown. Urea is important because it can promote growth and toxicity of harmful algal bloom (HAB) phytoplankton species. We conducted a one-year study of monthly sampling in 2011 to measure urea concentrations at five stations chosen to represent the major subembayment of varying hydrography and nutrient chemistry: South Bay, Central Bay, San Pablo Bay, Suisun Bay and the Sacramento River. Each station had maximum urea concentrations in February. The South Bay, Central Bay and San Pablo Bay stations saw urea concentrations above a threshold (1.5  $\mu$ M) that promotes growth of some HAB-forming dinoflagellates and flagellates. South Bay concentrations exceeded the threshold in December, February, August, and September (1.5-2.5  $\mu$ M) and maintained the greatest overall mean concentration (1.3  $\mu$ M). Samples were above the threshold in Central Bay in January and February (1.7 and 3.0  $\mu$ M respectively) and San Pablo Bay in February (2.0 µM); both stations sustained low values during the other months (0.1-1.2 µM). The Suisun Bay and Sacramento River stations always had low concentrations (0.2-1.3 μM). Based on previous studies and these new findings, we conclude that urea is a potentially significant nitrogen source for phytoplankton in marine-influenced regions of San Francisco Bay. The urea concentrations measured in South Bay, Central Bay and San Pablo Bay are comparable to those seen in research linking urea to HAB species. These results warrant inclusion of urea in monitoring programs and further studies to identify the sources of urea in San Francisco Bay.

Keywords: Nutrients, Urea, Harmful Algal Bloom Species, San Francisco Bay

# Nitrogen and Chlorophyll A Flux Between a Restored Tidal Wetland (Blacklock Marsh) and an Adjacent Bay in Suisun Marsh

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Large-scale wetland restoration has been proposed for the northern San Francisco Estuary and Delta as a means to improve water quality by mitigating anthropogenic nutrient loads and to increase organic matter production as food resources for zooplankton and planktivorous fish. Presently, few studies exist that demonstrate such improvements will occur with wetland restoration in the SFE. The goal of this ongoing study is to quantify nutrient and chlorophyll-a exchange between a recently restored wetland (Blacklock Marsh) and the adjacent open water habitat (Little Honker Bay) within the Suisun Marsh complex. In June 2013, we began testing the hypothesis that Blacklock Marsh acts as a sink for dissolved inorganic nutrients and as a source of chlorophyll-a for Little Honker Bay. Samples of surface water were collected hourly over a tidal cycle at a breach in a levee surrounding the marsh. Preliminary data show higher nitrate concentrations in samples taken on flood tides than those taken during ebb tides, suggesting that biological and/or physical processes within the marsh decrease nitrate. Additional analysis of measurements made in summer 2013 will be used to quantify nutrient and chlorophyll-a flux in Blacklock Marsh to better constrain nutrient and organic matter budgets. Budgetary findings from this study may assist management in making decisions about future wetland restoration projects.

**Keywords:** Wetland Restoration, Water Quality, Organic Matter Production, Nitrogen, Chlorophyll A

# The Oro Loma Ecotone Project: Nitrogen Removal in a Constructed Wetland Habitat on San Francisco Bay

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Results from recent studies of San Francisco Bay suggest that it may be necessary to reduce the mass of nitrogen discharged by municipal wastewater treatment plants. Conventional approaches for nitrogen control, such as biological nutrient removal, tend to be energy intensive and expensive. As an alternative, it may be possible to use managed natural systems to remove nitrogen from wastewater while simultaneously obtaining co-benefits including improvement of wetland habitat and adaptation of coastal systems to the effects of sea-level rise. To assess the potential for achieving nitrogen removal in a managed natural system, the Oro Loma Sanitary District plans to build a demonstration project at its treatment plant in San Lorenzo on the East Bay. The Oro Loma Ecotone Project will employ a sub-surface constructed wetland to remove nitrate from wastewater effluent through denitrification and plant uptake on a 180-meter wide sloped surface adjacent to the treatment plant. Experiments will be conducted in a series of test-strips to determine the effects of fill material and plant species on nitrogen removal and habitat creation. Data collected as part of the project will also provide information needed to assess the costs and benefits of applying this approach in other coastal systems located along the Bay.

Keywords: Nitrogen, Nutrients, Wetlands, Sea-Level Rise, Ecotone, Habitat Restoration

# Does Nitrogen Form Make a Difference in the Amount of Nitrogen Algae Take Up? Some Forms are More Equal than Others

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One of the common assumptions in nutrient ecology is that algae will use the same total amount of nitrogen (N) whether the N is provided in chemically oxidized (e.g. nitrate) or reduced (e.g., ammonium, urea) form. Indeed, when cells are growing under conditions of balanced or acclimated growth, and when cells are growing at maximal growth rates (set by culture conditions of light, temperature, etc.), it is fully expected that the total N taken up by cells will be the same regardless of the form provided (assuming that species has the necessary transporters and other physiology). On the other hand, uptake and growth are more typically uncoupled in natural conditions. Under those conditions, there is evidence that at elevated concentrations of NH<sub>4</sub><sup>+</sup>, inhibition of NO<sub>3</sub><sup>-</sup> uptake can result in an actual decrease in total N uptake and in primary productivity. Using data from nutrient-enriched mesocosms, with samples collected from both the Sacramento River and Suisun Bay at different seasons, we show that total N uptake indeed differs on time times from hours to days when cells are provided nitrate, ammonium or a combination and whether those treatments were balanced in phosphate availability. These results show that total N uptake does vary with the form of N substrate, a finding that has relevance to the discussion over nitrification of wastewater effluent.

Keywords: Nitrogen, Ammonium Inhibition, N Productivity

# Nitrogen Uptake by the Bloom-Forming Blue-Green Alga, *Microcystis aeruginosa*, in the San Francisco Estuary Delta

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In the last decade there has been an apparent increase in frequency and intensity of the harmful cyanobacterial bloom-former Microcystis aeruginosa in the San Francisco Estuary Delta (Delta), the heart of California's water infrastructure. It has been suggested that anthropogenic nitrogen, specifically ammonium and urea, may promote these blooms. Currently, little is known about which chemical forms of nitrogen are used by *M. aeruginosa* in the Delta. Nitrogen uptake kinetic experiments with field-collected *M. aeruginosa* were conducted using four <sup>15</sup>N-labeled substrates (nitrate, ammonium, urea and glutamic acid). Maximum biomassspecific uptake rates were highest for ammonium (up to 74.3 x  $10^{-3}$  h<sup>-1</sup>) and lowest for glutamic acid (<  $2.0 \times 10^{-3} h^{-1}$ ). *M. aeruginosa* showed preference (i.e. greater uptake) for nitrogen in the following order: ammonium, urea, nitrate, glutamic acid. M. aeruginosa does not appear to be nutrient-saturated at ambient field concentrations of ammonium, urea or nitrate, indicating a potential for enhanced growth with future increases in nitrogen. Uptake parameters (Ks and Vmax) obtained from this study were compared to published values for other phytoplankton taxa and indicated that *M. aeruginosa* has a competitive advantage for ammonium uptake over other phytoplankton. The preference by this fairly recent newcomer to the Delta for reduced forms of nitrogen may explain its success in an environment influenced by a growing human population and the accompanying increased anthropogenic nitrogen loading from waste water treatment and agricultural practices. Understanding which forms of nitrogen M. aeruginosa utilizes most efficiently will be useful for informing management to mitigate these blooms, which may have negative effects on the Delta food web.

**Keywords:** *Microcystis aeruginosa*, Nutrient Uptake Kinetics, Increased Nitrogen, Ammonium, Cyanobacterial Bloom

# Do Ammonium/Nitrate Conditions Play a Role in the Initiation of Spring Blooms in South San Francisco Bay?

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Recent studies of nutrient conditions and phytoplankton bloom initiation in the northern San Francisco Estuary (SFE) reveal a predictable pattern: 1) with improved irradiance, algal ammonium uptake causes a decline in ammonium concentration, enabling 2) a larger pool of DIN, nitrate to be assimilated by phytoplankton that results in 3) rapid chlorophyll accumulation that outpaces dispersive or grazing losses leading to a phytoplankton bloom. Do spring blooms in South SFE (South Bay) follow a similar sequence? South Bay is different from the northern SFE in at least two respects: 1) a lagoon type circulation resulting in longer residence time and 2) a discharge of advanced secondary treated effluent with high nitrate concentrations. In 2008, the spring bloom in South Bay followed the pattern observed for the northern SFE. Ammonium declined (~15  $\mu$ mol L<sup>1</sup> to <1  $\mu$ mol L<sup>1</sup>), along with nitrate (~50  $\mu$ mol L<sup>1</sup> to zero) and chlorophyll increased (5 to >40  $\mu$ g L<sup>-1</sup>). Silicate declined from 85  $\mu$ mol L<sup>1</sup> to zero signifying substantial diatom production. Contouring the nutrient and chlorophyll concentrations on location and time axes showed the progression of the bloom from south to north with the declines in silicate and nitrate and increase in chlorophyll tracking the contour where ammonium = 1  $\mu$ mol L<sup>-1</sup>. Nitrogen uptake rates measured using 15N showed the same inhibition of NO<sub>3</sub> uptake by NH<sub>4</sub> observed in the northern SFE. The keys to large spring blooms in South Bay are, in addition to favorable irradiance conditions, a high ratio of nitrate to ammonium and long residence time allowing ammonium to be reduced to low levels that enable rapid uptake and full utilization of the large  $NO_3$  and  $Si(OH)_4$  pools by diatoms.

Keywords: Phytoplankton, Ammonium, Silicate, Diatom, South Bay