## Reducing Dissolved Organic Carbon and Mercury Export from Subsided Delta Islands with Coagulant–Wetland Treatment Systems

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Water discharged from subsided Delta islands affects water quality in the San Francisco Bay-Delta by contributing dissolved organic carbon (DOC), disinfection byproduct precursors (DBPPs), and mercury (Hg). These constituents of concern (COC) have been identified as key components affecting drinking-water safety and environmental health. From July 2012 to November 2013, we conducted field tests of a treatment system that used in-situ coagulation followed by passage through constructed wetlands to remove COCs from the water column and sequester them in wetland sediments via natural settling of particulate material. The replicated field study on Twitchell Island in the central Delta consisted of nine 4,000 $ft^2$ wetlands comparing COC removal from island drainage waters due to passage through wetlands alone (control), and removal by the addition of iron (Fe)- or aluminum (Al)-based coagulants followed by wetland passage. In the treated inflow waters, both Fe and Al coagulation removed DOC, particularly more humified components, and also significantly decreased DBP precursors, dissolved methyl Hg (MeHg), and dissolved total Hg (THg). The coagulant removal efficiency of both DOC and dissolved MeHg improved with greater inflow concentrations of those constituents. For the study period, concentrations of DOC, DBPPs, and Hg at the Fe and Al treated wetland outflows were significantly lower than in the undosed inflow water, although release of these COCs was observed during wetland passage during summer months. Load calculations, which accounted for losses through seepage and effects of precipitation and ET, confirm that dosed wetland cells were usually sinks for both MeHg and DOC whereas the control wetland cells were usually sources. Coagulation technology could be used at wetlands sited in the Delta to reduce subsidence and improve wildlife habitat; these wetlands could then also serve to reduce DOC and Hg loadings coming off of the islands.

**Keywords:** DOC, methylmercury, mercury, DBPP, chemical dosing, wetland, water treatment

**Poster Topic:** Water and Sediment Quality

## Clues to Physiological Pathways in Diatoms from Stable Isotope Investigations - Influence of Irradiance and Nitrogen Source

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Two species of diatoms common to Suisun Bay, *Entomoneis paludosa* and *Thalassiosira weissflogii*, were grown in a matrix of four different irradiance levels, at three different nitrogen concentrations, using two different sources of nitrogen. The two sources of nitrogen were nitrate and ammonium. While growth rates varied significantly with irradiance level, concentration and type of nitrogen did not have significant effects. Growth rates were lowest at either low or high irradiances, and greatest at the intermediate irradiance, for both species. In addition, the difference in growth rate with N source was greatest at intermediate irradiance, and was twice as large for *T. weissflogii* as it was for *E. paludosa*. Because the difference in growth rate when using ammonium compared with using nitrate was more pronounced in *T. weissflogii*, the impact of growing on ammonium versus nitrate was examined in further detail in this species using the natural abundance of the stable isotopes $^{15}N$ and $^{13}C$. Carbon isotope enrichment in *T. weissflogii* particulate matter differed markedly with irradiance levels whereas enrichment in nitrogen isotopes did not. In contrast, enrichment in nitrogen isotopes differed markedly with concentration and type of nitrogen in the growth medium. These isotope enrichment patterns are interpreted and discussed in the context of the cellular physiology of estuarine phytoplankton.

**Keywords:** *Entomoneis paludosa*, *Thalassiosira weissflogii*, Nutrients, Irradiance, Stable isotopes

**Poster Topic:** Water and Sediment Quality

## Sources and Transformations of Dissolved Organic Matter in the San Francisco Bay Estuary as Indicated by Biomarkers

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Dissolved organic matter (DOM) fuels the microbial loop, and estuarine environments contain some of the most diverse sources, concentrations, and reactivities of DOM in the world. We conducted three transects through the San Francisco Bay Estuary (SFBE) in order to investigate the roles of sources, hydrologic and seasonal changes on the DOM composition. Sampling started with a riverine endmember, with higher density sampling at low salinities and 13 samples taken in total across an axial transect from river to coastal ocean. The winter transect (Dec 2014) at maximum winter discharge allowed the study of DOM dynamics largely in the absence of photodegradation processes and low levels of algal production; the summer transect (June 2015) captured significant photodegradation and algal production; the spring transect revealed the signal of stored DOM from the snowmelt cold water flows. Multiple studies indicate that algal primary production alone cannot support the SFBE foodweb, hence other sources of organic matter must be considered, including autochthonous and allochthonous DOM. Terrestrial DOM export in SFBE were revealed by dissolved lignin dynamics. Dissolved lignin were concentrated using solid phase extraction (Agilent Technologies, Bond Elut PPL), followed by alkaline CuO oxidation. With great improvements in real-time gas chromatograph pressure adjustments that allow Retention Time Locking (Agilent Technologies), and advanced tools in metabolomics (Automated Mass Spectral Deconvolution and Identification System (AMDIS), Metabolomics Ion-based Data Extraction Algorithm (MET-IDEA)), we were able to catalogue every compound other than lignin phenols in the chromatogram resulting from CuO oxidation. This study will provide desperately needed new tools for quantitative sourcing of DOM with biomarkers.

**Keywords:** DOM, San Francisco Bay Estuary, Lignin, biomarker

**Poster Topic:** Water and Sediment Quality

## Predicting the Ecological Implications of Leachates from North Pacific Gyre Plastics from In Vitro and In Vivo Models

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Marine plastics are one of the most common and persistent pollutants in ocean waters and beaches worldwide and are estimated to be present between 60-95% in the marine environment. Plastic marine debris may pose a threat to aquatic life as many plastics contain endocrine-disrupting compounds including nonylphenol, bisphenol A and various phthalates, and have been shown to adsorb common persistent organic pollutants. Plastic samples recovered from the North Pacific Gyre along with UV-irradiated virgin plastic and non-irradiated virgin plastic were extracted and concentrated using solid phase extraction (in methanol) and nitrogen evaporation. *In vitro* assays using luciferase-reporter estrogen receptor-dependent (ER) agonist cells (BG1Luc4E2) revealed significantly higher activity in UV-irradiated virgin plastic leachates than gyre plastics and virgin plastics (EEQ= 159.0, 7.7 and <0.1 ng/L , respectively). Beta-lactamase-reporter GeneBLAzer® CYP1A1-Bla (aryl hydrocarbon-receptor or AhR) assays revealed greater activity in gyre-recovered plastics than in virgin plastic and UV-irradiated virgin plastic (TEQ= 2, <0.1 and <0.1 ng/L, respectively). *Oryzias latipes* (Japanese medaka) fish were used as an endocrine-disruption *in vivo* model for these plastic leachates. To better understand the in vivo responses of plastic leachates and adsorbents, larval Japanese medaka (1-5 dph) were exposed to 0.01% methanol plastic extracts for 5 days. Induction of vitellogenin mRNA (VTG; an estrogen-dependent yolk precursor) and cytochrome P450-1A mRNA (CYP1A; an aryl-hydrocarbon-dependent enzyme) were measured using quantitative real-time polymerase chain reaction (q-RT-PCR). These results indicate the occurrence of AhR and ER ligands on plastics and that UV light may alter the impacts of plastics on biological systems.

**Keywords:** eco-toxicology, plastic, marine debris, endocrine disruption, in vitro

**Poster Topic:** Water and Sediment Quality

## Changes in DOC Concentration, Composition, and Reactivity During Passage Through Constructed Wetlands of the Central Delta: Implications for Drinking Water Quality

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Wetland restoration in the Central Delta would not only provide habitat benefits to fish and wildlife, but would help ameliorate and potentially reverse subsidence. However, wetlands have the potential to add dissolved organic carbon (DOC) to Delta waterways which can negatively impact downstream drinking water quality because a fraction of this DOC pool reacts upon disinfection to form harmful disinfection byproducts (DBPs). In the Central Delta, water pumped off the subsided islands is already high in DOC due to inputs from organic peat soils. We examined whether passage of agricultural drainage waters through constructed wetlands on Twitchell Island altered surface water DOC concentrations, and by examining the chemical composition of the DOC gained insight into its likely source (i.e. peat soils, plants, algae). We also related this to the reactivity of the DOC pool with respect to trihalomethane (THM) and haloacetic acid (HAA) formation. The constructed wetlands were primarily vegetated with cattails, and the hydraulic residence time over the 1-year study period was on average 3 days. Water samples were collected monthly from the inflows and outflows of three replicated cells.
Passage of water through the wetlands increased DOC concentrations from 20% to 55% during summer months, but in the winter there was little change. Despite little to no change in DOC concentration in the winter there was a shift in composition suggesting inputs from degrading plant material. Compositional changes in DOC were less consistent across summer months. There were only minor changes in the reactivity of DOC with respect to THM and HAA formation. Changes in DOC concentration, composition, and reactivity in these constructed wetlands can be compared to adjacent wetlands that were treated with iron- and aluminum-based coagulants to target removal of DOC and DBP precursors while also improving rates of sediment accretion to reverse subsidence.

**Keywords:** Water quality Wetland restoration Dissolved organic carbon

**Poster Topic:** Water and Sediment Quality

## Elevated Se Concentrations in Biological Tissue Occur during Unprecedented Drought in the San Francisco Estuary

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In the San Francisco Estuary, a five-year drought severely diminished the flow of freshwater into the estuary, which correlated with the increase in concentration of selenium (Se), a chemical contaminant from agricultural and industrial sources (e.g. oil refineries), in water and biological tissue. For this study, we examine a 21-year time series of Se concentrations in the estuarine bivalve *Potamocorbula amurensis* collected from two locations throughout the estuary spanning a range of flow conditions and water year classifications. This time series includes wet years (from before and after oil refineries reduced selenium loads), dry years, and critically dry years (i.e drought years). Our objective is to assess how different water year types, especially drought years, and different sources of selenium affect the Se concentration of clams, an important exposure pathway for Se in higher trophic levels. We found that severe drought correlated with clam tissue selenium concentrations rising above Se levels prior to managed reductions of Se in oil refinery effluents. During drought, tissue Se concentrations remain persistently high at levels exceeding toxicological thresholds (they ranged from 2 μg/g to 22 μg/g, with 62% of the 1,271 samples exceeding recommended thresholds) while seasonal variability in tissue Se concentrations decreased. Although the drought correlated with elevated Se concentrations at each site respectively, spatial patterns persisted across water year types where bivalves collected closer to the freshwater delta and the agricultural irrigation drainage sources had lower Se concentrations than those collected near oil refinery effluent discharge points (mean of 8.84 ± 1.00 μg/g near freshwater delta and mean of 13.80 ± 1.03 μg/g near oil refinery discharge). These results suggest that understanding the effects of drought and the significance of different sources of contaminants in estuarine systems will become critical for managing water quality in the face of climate change.

**Keywords:** Drought, Selenium, bioaccumulation, water quality, climate change, invasive species, bivalves

**Poster Topic:** Water and Sediment Quality

## The Sensitivity of a Resident California Freshwater Mussel (*Anodonta oregonensis*) to Ammonia and Possible Regulatory Implications

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USEPA published final revised freshwater national recommended water quality criteria for ammonia in 2013. The inclusion of new toxicity data for freshwater unionid mussels in USEPA's 2013 recommended criteria resulted in substantially reduced revised criteria for ammonia; however, the mussel genera included in USEPA's dataset are not indigenous to California, or the western United States. Nevertheless, species of indigenous unionid mussels (*Anodonta*, *Margaritifera*, and *Gonidea* genera) are historically widely distributed throughout California, including the Sacramento-San Joaquin Delta and associated watersheds, yet little is known as to the sensitivity of these indigenous mussels to ammonia. In order to explore this question, acute toxicity testing of juvenile *Anodonta oregonensis*, a species historically present in California, was conducted. While significantly more sensitive than other invertebrate and vertebrate animals, *Anodonta oregonensis* appears to be substantially less sensitive than many of the non-resident mussels included in USEPA's toxicity dataset for ammonia. The regulatory implications of this result are explored through a hypothetical recalculation of USEPA's ammonia criteria.

**Keywords:** ammonia, toxicity, regulatory implications, mussels

**Poster Topic:** Water and Sediment Quality

## Net Ecosystem Fluxes of Methyl Halides from a Coastal Salt Marsh with Invasive Pepperweed

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Terrestrial emissions of methyl bromide ($CH_3Br$) and methyl chloride ($CH_3Cl$) are believed to constitute the 'missing' source of these compounds to the atmosphere, but the variability of emission rates from natural ecosystems has led to large uncertainties in scaling up. Since April 2016, surface-atmosphere fluxes for methyl halides have been measured at Suisun Marsh, a coastal salt marsh in northern California, USA. Flux measurements are performed in two ways: tower based relaxed eddy accumulation (REA) for net ecosystem fluxes and static flux chamber measurements for plant-scale fluxes. The study site is invaded by perennial pepperweed (*Lepidium latifolium*), a methyl halide emitting species, covering a significant part of the flux source area. Both, REA and chamber samples are analyzed for methyl chloride ($CH_3Cl$) and methyl bromide ($CH_3Br$) using gas chromatography with electron capture detector (GC-ECD). The analytical precision [ppt] and REA flux detection limits [$\mu mol\ m^{-2}\ d^{-1}$] are on the order of 3.9/0.6 for $CH_3Cl$ and 0.01/0.2 for $CH_3Br$.

Chamber measurements confirmed that methyl halide emissions of pepperweed are large, but that the native alkali heath (*Frankenia salina*) is a much stronger emitter, when normalized by biomass. REA measurements show that during the summer, the studied marsh is a substantial methyl halide source with net fluxes of ~20 $\mu mol\ m^{-2}\ d^{-1}$ ($CH_3Cl$) and ~1 $\mu mol\ m^{-2}\ d^{-1}$ ($CH_3Br$). Notably, these fluxes are comparable with reported chamber based emissions from southern California salt marshes. Furthermore, a positive response to light and temperature was found. The presentation will also expand on the diurnal variability and seasonality of the measured fluxes.

**Keywords:** terrestrial emissions, methyl bromide, methyl chloride, Suisun Marsh, perennial pepperweed

**Poster Topic:** Water and Sediment Quality

## Drivers of Phytoplankton in the Sacramento River: Comparing Phytoplankton Abundance and Composition in the Presence and Absence of Treated Wastewater Effluent

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Ammonium in treated wastewater effluent entering rivers and estuaries has been implicated as a stressor on phytoplankton growth and a factor responsible for declines in diatom populations, but much of this evidence comes from controlled laboratory incubations and enclosure studies and has not been explicitly evaluated in-situ. In the Bay Delta, ammonium from the Sacramento Regional wastewater treatment plant (WWTP) discharges to the Sacramento River, the main source of water entering the estuary. To assess immediate effects of effluent on phytoplankton at the whole-river scale, in October 2013 and June 2014 we diverted WWTP discharges from the river to create a ~15 km segment of effluent-free (-EFF) river and used a Lagrangian approach to compare changes in -EFF water parcels to effluent containing (+EFF) water parcels as they transited downstream from Sacramento to Isleton. Changes in phytoplankton chlorophyll-*a*, species composition, and productivity were tracked, along with nutrients, zooplankton, and benthic grazer abundances. Over the 5 days of travel down the study reach, chlorophyll-*a* concentrations declined from 15–25 µg L-1 to ~2.5 µg L-1, with the greatest decline occurring upstream of the WWTP. There was no statistical difference in phytoplankton chlorophyll-*a* nor species composition between the +EFF and -EFF parcels during either experiment, indicating that declines in phytoplankton observed were not attributable to effluent inputs alone. Estimated grazing losses to zooplankton and clams could not account for the measured declines. This result, together with the prevalence of benthic and facultative planktonic diatoms, suggest that along the study reach hydrodynamic factors may play an underappreciated role in phytoplankton losses through settling in the tidally affected downstream stretch of the river. These results highlight the advantages of in situ, whole-river scale, Lagrangian experiments to understand the dynamic and complex interplay between physical, chemical, and biological factors that control phytoplankton populations.

**Keywords:** phytoplankton, ammonium, effluent, wastewater, nutrients, foodweb, hydrodynamics, Sacramento River

**Poster Topic:** Water and Sediment Quality

## Spatial Patterns of Phytoplankton, Nutrients, and Cell Health From the Sacramento River to Suisun Bay: Are There Biological Hotspots?

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Several hypotheses have been put forward to explain the "bad Suisun" hypothesis, the observation that Suisun Bay is less productive than other parts of the San Francisco Estuary. Factors that have been invoked include the loading of ammonium from wastewater treatment plants, the salinity gradient, presence of other contaminants, the role of benthic grazing by clams, and light-limitation. As part of an IEP and Bureau of Reclamation funded project, we completed four surveys of the Sacramento River and Suisun Bay in August, October, January, and May (2014-2015). Strong gradients in phytoplankton species composition were observed, as well as persistent "hotspots" of low phytoplankton health, as derived from variable fluorescence, as well as gradients in the subsurface light field and nutrient concentrations. Phytoplankton isolated from these cruises were used in a series of physiological experiments to directly test the role of nitrogen source (ammonium versus nitrate) and irradiance. Here we present the field data, with a summary of the laboratory experimental results presented within the context of the environmental conditions, to answer the first-order question of whether there is a persistent gradient in phytoplankton health/abundance related to physical or chemical factors. Consistent with the laboratory results, we find weak evidence for a direct response to ammonium concentration, and strong evidence for light-limitation embedded within physical gradients driven by salinity, with persistent "hotspot" locations of lower phytoplankton health consistent with localized changes in the environment.

**Keywords:** Bad Suisun Phytoplankton Ammonium Nitrate Light Limitation Variable Fluorescence

**Poster Topic:** Water and Sediment Quality

## Using Multivariate Analysis to Understand the Yolo - Cache Slough Complex's Water Quality Variability

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Tidal wetland restoration in the Yolo Bypass - Cache Slough Complex (YBCS) has the potential to increase dissolved organic matter concentrations. This could possibly increase disinfection by-products in municipally treated water, posing public health risks. California Department of Water Resources (DWR) is monitoring water quality conditions at eleven discrete sampling locations in the YBCS. These sampling locations were selected to evaluate drinking water quality in an existing tidal marsh habitat that surrounds ecologically-driven restoration projects. Data was collected bimonthly during two critically dry water years. It was categorized and assessed by 'all', 'wet', and 'dry' months for interannual variability. The purpose of this project was to evaluate baseline water quality conditions and provide a sound basis for post-restoration comparisons. Multivariate statistics identified which stations, and which of the six key water quality constituents accounted for a majority of the temporal and spatial variability. Although it was hypothesized that the temporal and spatial variations in the watershed were affected by tidal influences, preliminary results indicate hydrodynamics from Lisbon Weir and Sacramento River inflows from Miner Slough had a greater effect on the constituents' concentrations. However, additional influences such as natural biological processes, and anthropogenic point and non-point source discharges, also contributed to the variation. Across sampling locations, these additional influences were seen within DIN:DOP and DOC:ON ratios, and NO3-N to ON concentrations. The project's preliminary results showed that phosphorus and nitrate concentrations were not limiting, suggesting light limitation similar to that found in other parts of the Delta. Results also suggested anthropogenic influences through the stoichiometry of the monitored analytes. Agriculture is the primary land use surrounding YBCS, in addition to being located near two wastewater treatment facilities. Therefore variability in NH4-N, and NO3-N concentrations greater than ON concentrations, were used as potential signals demonstrating anthropogenic influences.

**Keywords:** Water Quality, Anthropogenic, Cache Slough Complex, Interannual Variability

**Poster Topic:** Water and Sediment Quality

## South Bay Salt Ponds Restoration: Tracking Changes in Surface Water Mercury Contamination in Response to Reconnecting Tidal Flow to Historic Wetlands

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The drainage basin of the Guadalupe R. includes the New Almaden Mining area, which was the largest historic mercury (Hg) mining region in North America. The Guadalupe R. ultimately drains into South San Francisco Bay via Alviso Slough, one of the most mercury contaminated waterways in the San Francisco Bay region. The lower portion of Alviso Slough is bordered by former salt production ponds that are currently being restored to wetland or managed pond habitat. Concerns about Hg remobilization and enhanced bioaccumulation, potentially resulting from current restoration management actions, have driven numerous Hg investigations in this area for the last decade. In December 2010, the first pond (A6) along Alviso Slough was reconnected to full tidal flushing via multiple levee breaches. In June 2011, a larger Pond complex (A5/A7/A8) was restored to muted tidal flushing via an adjustable notch structure. This opening of this adjustable notch (maximum opening of 40 ft) was incrementally increased from 5 ft. in 2011 to currently 25 ft in 2016. This presentation documents changes in surface water total mercury and the more toxic methylmercury, in both Alviso Slough and the A5/A7/A8 complex, from 2006 thru 2016 (discontinuous), in response to these management actions. Results indicate a significant and sustained decrease in both total Hg and methylmercury (particulate + dissolved) within the pond complex since the initial opening of the adjustable notch. Conversely, total Hg increased in Alviso Slough modestly but significantly during the same period, with most of the change attributable to the Pond A6 breach. Methylmercury in Alviso Slough exhibited a short lived spike in concentration after the opening of the notch, which had decreased to pre-notch levels by 2015 (2016 data pending). This study exemplifies how adaptive management strategies can be employed to support ecosystem restoration goals.

**Keywords:** salt ponds, mercury, methylmercury, adaptive management

**Poster Topic:** Water and Sediment Quality

## A Change in Character: Agricultural Sediments Release Compositionally Distinct Dissolved Organic Matter

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Agricultural practices increase sediment export to surface waters through soil erosion. The release of organic matter (OM) from mineral particles via desorption is a critical component of OM cycling since dissolved OM (DOM) fuels aquatic ecosystems and is a precursor for disinfection by-products formation. This study assessed the elemental and molecular composition of DOM released during abiotic desorption experiments from sediments and soils of an irrigated agricultural watershed of northern California (Willow Slough). Relative to mineral-bound OM, desorbed DOM was nitrogen-poor (lower carbon:nitrogen ratios) and depleted in amino acids and lignin phenols (lower carbon-normalized yields). Water-extracted DOM appeared substantially more degraded than its parent particulate OM with increased molar contributions of acidic amino acids, non-protein amino acids, and acidic lignin phenols, all molecular indicators of a more extensively processed OM pool. Lignin compositional ratios were significantly altered during desorption, which affects their use as biomarkers for vascular-plant sources of DOM. Specific optical parameters, including spectral slope, specific UV absorbance at 254 nm ($SUVA_{254}$), and fluorescence index (FI), did not constitute useful proxies for the desorbed DOM pool, while absorption coefficients and fluorescence peak intensities were strongly correlated with extracted DOM concentrations and composition. This study highlights the profound impact of desorption on DOM composition which, if not accounted for, could lead to misinterpretations of common biomarkers and optical proxies used to predict the composition and quality of DOM. In the agricultural Sacramento and San Joaquin watersheds, sediment mobilization is enhanced. Our findings suggest that sediment inputs to the Bay-Delta ecosystem contribute a biogeochemically distinct source of DOM to the Bay-Delta, with potential impacts on aquatic health and drinking water quality.

**Keywords:** dissolved organic carbon, desorption, biomarkers, amino acids, lignin, absorbance, fluorescence

**Poster Topic:** Water and Sediment Quality

## Optimizing Sampling Methods for Monitoring Pollutant Trends in San Francisco Bay Urban Stormwater

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The Small Tributaries Loading Strategy (STLS) focuses on urban stormwater loadings from small tributaries. Since 2002, the STLS has monitored seven watersheds in the Bay Area to determine annual loadings of PCBs and Hg, in coordination with the San Francisco Bay Municipal Regional Permit (MRP). To-date, STLS monitoring has primarily been geared towards determining concentrations and annual loads from representative watersheds across the Bay Area. The sampling approach has yet to be fully optimized for detecting trends over time. In this study, we evaluated the variability and statistical power for detecting trends in PCBs (concentrations and particle-ratios) based on baseline STLS data from four of the seven watersheds. First, the influence of three climatic factors (low flow, storm stage, and season) on within-year and among-year estimates of variability (standard deviations, SDs) of PCBs was assessed. Subsequently, three variability scenarios (low, moderate, and high variation) were developed for power analysis. The goal of the power analysis was to determine the optimal sample size and revisit frequency that would be required to observe declining exponential trends in PCBs with > 80% power in 25 years. Results indicated that removal of low flow samples had little influence on variability estimates. However, storm stage and season reduced both within-year and among-year SDs for certain watersheds. The power analysis revealed that only under the low variability scenarios would it be possible to achieve >80% power with less than 8 sampled storms per year. This study provides insight into the variability of pollutant concentrations in Bay Area urban stormwater. A preliminary sampling design that could be used to track trends in response to future best management practices for stormwater will be presented.

**Keywords:** Stormwater, Water Quality, Trends, Power Analysis, PCBs

**Poster Topic:** Water and Sediment Quality

## Ammonium and Nitrate Sources and Patterns in the Bay Delta Using Stable Isotope Techniques

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The Sacramento River is a unique and complicated system. Understanding it through ongoing monitoring is an essential way to gauge its health and identify nutrient sources that impact its biogeochemistry. The USGS Isotope Tracers Project uses stable isotopes as a tool to better understand this system. During this study, water samples were collected on a monthly basis by the Isotope Tracers Project as part of an ongoing research project with the USGS Water Quality of San Francisco Bay Program. Samples were collected at established monitoring stations beginning near the Golden Gate Bridge and ending in Rio Vista. This presentation focuses on water samples collected for $\delta^{15}N$ of ammonium and nitrate from August 2011 to May 2014. $\delta^{15}N$ ammonium observations suggest that as ammonium moves from the Sacramento River into the bay, nitrification alters the $\delta^{15}N$ of the ammonium pool. This is suggested by the increasing $\delta^{15}N$ ammonium signature as water moves from Rio Vista into the North Bay. When $\delta^{15}N$ ammonium comparisons were made between years and between seasons, overall trends remain consistent across a wide range of flow conditions. Nitrate concentrations from the bay also suggest nitrification as water moves into the bay. The main sources of nitrogen are from agricultural and waste water treatment plants; however, concentrations and isotopic composition do vary based on location, time of season, tidal conditions, and biological activity. Nitrogen stable isotope analysis provides valuable insight into sources of ammonium and nitrogen cycling that concentration measurements alone do not provide. Since multiple variables play different and unique roles in the concentration and dynamic movement of these two crucial nitrogen sources, understanding the stable isotope biogeochemistry can give us better insight into overall health and behavior of the bay, and especially behavior in drought conditions.

**Keywords:** ammonium, nitrate, isotope, nitrification, Sacramento river

**Poster Topic:** Water and Sediment Quality

## Targeted and Non-Targeted Analysis of Aqueous Film Forming Foam (AFFF)-Related PFAS in a Wastewater Treatment Plant

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Recently, poly- and perfluoroalkyl substances (PFASs) derived from aqueous film forming foams (AFFF) were measured at relatively high levels in effluent in some San Francisco Bay Area wastewater treatment plants. A follow-up study was commissioned to investigate the fate of PFASs at an airport wastewater treatment plant before, during, and after a major AFFF introduction event. In addition to routine analysis of PFASs by LC-MS/MS, additional transformation products were identified using high resolution quadrupole time of flight mass spectrometry (QTOF/MS). Using a combination of targeted and non-targeted approaches, molecular features that were extracted from the raw total scan chromatography were tentatively identified with compounds from an in-house PFAS database. For compounds without a database match, chemical formulas were generated based on exact mass, isotope distribution, isotope spacing, and retention time (if available). We preliminarily identified the presence of various PFASs in AFFF formulations, such as 6:2 fluorotelomermercaptoalkylamido sulfonate (FtTAoS), 6:2 fluorotelomer sulfonamide alkylbetaine (FTAB), and two transformation products from the biological oxidation of 6:2 FtTAoS. The integrity of the analysis was validated by standardized sample analysis procedures using Agilent MassHunter Qual and Mass Profiler Professional (MPP) software for multivariate analysis, and high match scores (>90) for the assignments. Available isotope labeled and natural PFAS standards were used as positive controls. This is the first study to examine real time, microbially-mediated transformation reactions in a full scale system. The use of unknowns analysis is critical in establishing transformation reactions and their rates because there are only a few commercially available analytical standards that are applicable to the PFASs present in AFFF.

The views expressed herein are those of the authors and do not necessarily reflect those of the California Department of Toxic Substances Control.

**Keywords:** poly- and perfluoroalkyl substances (PFASs), aqueous film forming foams (AFFF)

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## Management Implications for Small Urban Reservoirs Based on a Multi-Year Study of Three East Bay Watershed-Reservoir Pairs

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Watersheds and associated reservoirs in the urban San Francisco Bay (SFB) area are severely stressed due to the recent California drought. Small reservoirs in the SFB provide a variety of services including flood control, recreation, and irrigation water storage; however, major freeways, historic mines, and continued development are changing contaminant loads. Approximately 200 upstream urban reservoirs are directly connected to the SFB-Delta.

We investigated three SFB watershed/reservoir systems to assess how reservoir management may mitigate or exacerbate contaminant discharge to coastal urban environments impacted by acid mine drainage, freeways and development, and natural parklands. Study sites include Lion Creek/Lake Aliso, San Lorenzo Creek/Don Castro Reservoir, and Wildcat Creek/Lake Anza. We collected water quality data (including standard geochemistry, nutrients, and trace element levels) from reservoir inlets and outlets at each of these systems bimonthly. We also measured depth profiles of pH, conductivity, temperature, and dissolved oxygen within each lake bimonthly. We collected and analyzed sediments from each lake for nutrient and trace element concentrations.

Results suggest urban reservoirs are important controls on pollutant cycling in urban watersheds and downstream water quality. Reservoir stratification varies over the course of a year and leads to reducing conditions prevailing during warm summer months and oxidizing conditions dominating during cool winter months. The redox state of these reservoirs determines whether metals and nutrients are mobilized or retained by sediments.

With drought lowering flows, reducing conditions are expected to expand during summer months. Because reducing conditions mobilize many metals and retain nutrients, summertime reservoir management style is most critical for downstream bay water quality, particularly for reservoirs with large acid mine drainage loads. Trade-offs will have to be made between in situ watershed/reservoir water supply for recreation or irrigation and downstream water quality for Bay health.

**Keywords:** reservoir, nutrients, metals, watersheds, East Bay, redox, management, water, sediment

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## Nutrient Budget Study of Nitrogen Related Constituents in the Sacramento River at Hood

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Nutrients composed of nitrogen and phosphorus are a necessary part of a thriving ecosystem. However, when concentrations of these constituents increase beyond background levels, it can cause issues for ecosystem health and drinking water quality. In aquatic habitats, excess nutrients can result in an increase in biomass production. These increases in biomass can clog waterways, block sunlight to lower levels in the water column, and decrease the oxygen availability for aquatic species.

This study is the first step in a greater limnology project of the SWP to understand the sources, transformations, and sinks of nutrients in the SWP. The project entails the assembly of an extensive dataset of nutrients and flow data at key stations throughout the Delta and SWP system, from which nutrient budgets and additional analyses are being developed. The focus of this study is reviewing and analyzing the nutrients at key stations throughout the Delta and SWP, and developing a nitrogen dataset for in-depth analysis sources and processes effecting concentrations and loads of nitrogen compounds in the Sacramento River at Hood.

The study objectives include:

- Develop a comprehensive dataset of flow and the nutrient constituents;
- Understand the sources of nitrogen nutrients contributing to constituents;
- Analyze the data for flow, concentration and loads relationships; and
- Analyze the data to determine long term trends of the nitrogen constituents and loads at Hood, and develop conclusions about those trends to aid in improved management of water quality for the SWP Urban Water Contractors.

The nutrients included in the analysis are Ammonia, Nitrate, Nitrate+Nitrite, Total Kjeldahl Nitrogen, Total Nitrogen, Nutrient data was obtained from DWR's Water Data Library, Interagency Ecological Program (IEP), and United States Geological Survey (USGS). Flow data for the load was obtained from DWR Water Operations Office and the Metropolitan Water District of California.

**Keywords:** Nutrient, nitrogen, nitrate, nitrate+nitrite, ammonia, total kjeldahl nitrogen, concentration, load

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## Coagulant and Sorbent Efficacy in Removing Mercury from Surface Waters in Cache Creek

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Cache Creek, located in California's Coast Range, is an important source of mercury (Hg) to the Sacramento-San Joaquin Delta. Cache Creek is contaminated with Hg from several sources including historical Hg and gold mines, native Hg in the soils, and active hot and cold springs high in dissolved Hg concentrations. We investigated the use of coagulants and sorbents to immobilize Hg from priority sources within the Cache Creek watershed. Three sites were selected, representing both particulate and dissolved sources of Hg: a suspended particulate Hg source sample from the Cache Creek Settling Basin (CCSB) collected during storm flow and two contrasting dissolved Hg source samples collected during base flow from downstream of a geothermal spring and at the emergence point of a connate water spring. Both dissolved samples had similarly high dissolved Hg concentrations (ca. 500 ng/L) but differed in other chemical characteristics. Three coagulants were chosen for testing with the particulate sample: (i) ChitoVanTM HV 1.5% (shell-based); (ii) FerralyteTM 8131 (ferric sulfate-based); and (iii) UltrionTM 8186 (aluminum-based). The initial turbidity of the particulate sample was ~350 Formazin Nephelometric Units (FNU). At optimum dose rates, ChitoVan reduced turbidity by 73-82%, Ferralyte reduced turbidity by 94-97%, and Ultrion reduced turbidity by 99%. The dissolved source samples were passed through three sorbents: (i) chitosan flakes, (ii) coconut shell-based activated carbon, and (iii) coal-based activated carbon. In-line columns were packed with each material and untreated sample was passed through each column at three different flow rates (1.0 L/min, 0.5 L/min, and 0.1 L/min). If sorbent results are as effective as those for coagulation, these materials could be used as cheap and readily available products to aid in Hg removal from Cache Creek, thus decreasing Hg loads to the Sacramento-San Joaquin Delta.

**Keywords:** mercury removal, Cache Creek watershed, coagulation, sorbents,

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## Sediment Accretion in Constructed Wetlands of the Central Delta: Comparisons between Untreated Cells and Those Treated with Iron and Aluminum Based Coagulants

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Subsidence of organic rich soils in the Sacramento-San Joaquin Delta threatens levee stability and freshwater supply. One of the main causes of subsidence is oxidative loss of organic matter that began with the reclamation of wetlands for agricultural use. There is great interest in land management approaches–including constructed wetlands–that will halt or reverse subsidence. Another issue related to these subsided lands is the export of drainage waters high in dissolved organic carbon (DOC), which negatively impacts drinking water quality. We examined the feasibility of using constructed wetlands receiving drainage water treated with metal-based coagulants to not only sequester DOC, but also accrete the organo-metal material along with wetland biomass, thereby providing additional subsidence mitigation benefits. Nine wetlands were constructed on Twitchell Island, each which received local drainage water that was either untreated (Co), or treated with polyaluminum chloride (Al) or ferric sulfate (Fe) coagulants. The wetlands were flooded for 26 months, and treatments were added continuously to inflow waters for the last 14 months. Following this period, sediment samples were collected from near the inlet, center, and outlet of each cell to determine sediment composition and the height of newly deposited material. The Al cells had the greatest accretion at about 14 cm across the length of the cells. While similar accretion rates were measured at the inlet of the Fe cells, at the center and outlet locations accretion was below 3 cm. Accretion in the Control cells was markedly lower at about 3.5 cm near the inlet and less than 1 cm near the outlet. There were differences in sediment composition (C, N, P, Fe and Al) both between treatments and by location within the treatments. Overall, this study shows that constructed wetlands which receive coagulants can store carbon and accrete material at rates exceeding untreated wetlands.

**Keywords:** constructed wetlands, sediment accretion, subsidence mitigation, metal-based coagulants

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## Non-targeted Analysis of Water-soluble Compounds in Ambient Bay Water and Wastewater to Identify Emerging Contaminants

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Non-targeted analysis is a novel set of techniques designed to identify new potential contaminants of emerging concern without *a priori* knowledge of their occurrence in the environment. It is a key element of the strategy that guides monitoring for emerging contaminants conducted by the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP).The RMP previously conducted a non-targeted analysis of fat-soluble compounds in bivalve tissue and seal blubber, and is now conducting a non-targeted analysis of water-soluble, polar organic contaminants in ambient San Francisco Bay water and wastewater. The San Francisco Bay will be the first ecosystem to be studied via non-targeted methods for both water- and fat-soluble contaminants.

In 2016, Polar Organic Chemical Integrative Samplers (POCIS) were deployed at three locations in the San Francisco Bay watershed influenced by different contaminant pathways: urban stormwater runoff (San Leandro Bay), agricultural runoff (Napa River), and wastewater effluent (Lower South Bay). These passive samplers were used to provide an integrated, semi-quantitative assessment of pollutants entering the Bay over the course of approximately three weeks. Grab samples were collected before and after deployment to provide a quantitative snapshot of contaminants for comparison. 24-hour composite samples of wastewater effluent were also collected from several wastewater dischargers.

Samples were analyzed using cutting-edge Orbitrap liquid chromatography high resolution mass spectrometry (LC-HRMS). Compounds identified through this method may include, but are not limited to, detergents and other surfactants, pesticide and pharmaceutical breakdown products, and plastic additives. Preliminary results from this non-targeted analysis will be presented.

**Keywords:** emerging contaminants, non-targeted analysis, passive sampling, polar organic compounds

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## Record-High Observations of Water Temperature and Specific Conductance, San Francisco Bay, CA

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The U.S. Geological Survey (USGS) operates a network of eight stations in San Francisco Bay at which water quality is monitored. All of these stations are equipped with specific conductance and water temperature sensors; many also report turbidity and dissolved oxygen levels. Many feature sensors at more than one altitude above the bay floor. In each case, observations are made every fifteen minutes, telemetered in near-real-time, and made available via USGS's NWIS online database: http://waterdata.usgs.gov/nwis.

The period of record varies by parameter and site; the oldest station, at the San Mateo Bridge, dates from 1989. Analysis of Water Year 2014 and 2015 data revealed that most stations saw record-high values of water temperature and specific conductance during these years, which fell within a significant drought period. While there are numerous factors that likely contributed to the records being broken, low inflow of freshwater from the Sacramento-San Joaquin Delta appears to be one contributor, as there is clear inverse correlation between annual inflow from the Delta and annual mean specific conductance. There is also a clear spatial variation in the significance of this effect, with stations closer to the Delta impacted more significantly by changes in Delta outflow than those closer to the Golden Gate.

Reference:

Downing-Kunz, M.A., Work, P.A., and Shellenbarger, G.G., 2015, Record-high specific conductance and temperature in San Francisco Bay during water year 2014 (ver. 1.1, December 28, 2015): U.S. Geological Survey Open-File Report 2015–1213, 4 p.

**Keywords:** Water temperature, salinity, specific conductivity, San Francisco Bay

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## Simple Mass Budget Model to Evaluate Long Term PCB Fate in the Emeryville Crescent Sub-embayment

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PCB concentrations in the open waters and sediments of San Francisco Bay have shown some evidence of decline since the phase-out and ban of PCBs in the 1970s. However, during the same period, PCB concentrations in the tissues of sport fish have not changed. A hypothesis for the apparent lack of response in fish tissue PCB concentrations is the presence of ongoing loads and legacy deposits of PCBs in enclosed shallow subtidal and intertidal habitats at the edges of the Bay where prey fish spend much of their lives. In order to examine the potential for load reductions to improve PCB concentrations in these shallow habitats, we applied a simple mass budget for one such area in Emeryville Crescent, a small semi-enclosed sub-embayment with known past PCB source areas just north of the San Francisco-Oakland Bay Bridge. There are large uncertainties and gaps in much of the available data, but our initial assessment suggests the ambient PCB concentrations of the area could potentially recover quickly, reaching within 10% of a new steady state in 10 to 15 years with declines in PCB loading. Sediment and biota surveys are planned to test some of these expectations. Despite the uncertainties, the simple mass budget has proven a valuable tool for prioritizing future data collection and identifying critical areas for future, more detailed, mechanistic or empirical model development. Similar applications of simple models in other areas of the Bay and Delta may be useful for synthesizing available information and prioritizing future pollutant management and monitoring plans.

**Keywords:** PCB fate, load reductions, shallow habitats

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