Nutrient Studies: Moored Sensor Monitoring Program Development, Algal Biotoxin Monitoring, Stormwater Nutrient Measurements, and Load Quantification

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ESTIMATED COST: $263,000 ($228,000 after applying $35,000 of unused 2012 USGS funds)
OVERSIGHT GROUP: Nutrient Workgroup through the Nutrient SAG

TABLE 1: PROPOSED DELIVERABLES, BUDGET, AND TIMELINE

Deliverable	Budget		Due Date
	RMP	Other	
Task 1 Project management	10k		Jan-Dec 2013
Task 2. Moored sensor monitoring program development	120k	150k	
Task 2.1 Moored sensor platform selection and purchase			Jan-Feb 2013
Task 2.2 Sensor system calibration and basic dockside operation			Apr-May 2013
Task 2.3 Sensor Deployment, operation, and maintenance at Dumbarton Bridge			Jun-Dec 2013
Task 2.4 Data analysis, QA/QC			Jun-Dec 2013
Task 2.5 Develop calibration, operation, and maintenance manual			Nov 2013
Task 2.6 Technical memo: data interpretation and recommendations for next steps with moored sensors			Mar 2014
Task 3 Developing Solid Phase Adsorption Toxin Tracking (SPATT) as a Monitoring Tool for Microcystins and Related Toxins in San Francisco Bay	65k	-	
Task 3.1 Monthly monitoring of algal biotoxins during Bay-wide monthly cruises and at fixed sites			Jan-Dec 2013
Task 3.2 Controlled experiments to calibrate biotoxin field sampling device			Jan-Aug 2013
Task 3.3 Technical memo			Mar 2014
Task 4 Stormwater nutrient monitoring in 6 Bay area catchments	38k	~300k	
Task 4.1 Field sampling and sample analysis			Nov2012-Apr2013
Task 4.2 Data analysis and preparation of technical memo			June-Aug 2013
Task 5 Technical report quantifying nutrient loads to the Bay and identifying data gaps	30k	-	June 2013
Nutrient/phytoplankton biogeochemical modeling (see CFWG modeling proposal			
Total	263k	~450k	

Background and Justification

San Francisco Bay has long been recognized as a nutrient-enriched estuary, but one that has historically proven resilient to the harmful effects of nutrient enrichment, such as excessive phytoplankton blooms and hypoxia. The published literature suggests that the accumulation of phytoplankton biomass in the Bay is strongly limited by tidal mixing, grazing pressure by invasive clams, light limitation from high turbidity, and potentially, in the North Bay, ammonium inhibition of diatom uptake of nitrate. However, evidence is building that, since the late 1990s, the historic resilience of the Bay to the harmful effects of nutrient enrichment is weakening (Cloern et al., 2007; Dugdale et al, 2007).

In response to the apparent changes in the Bay's resilience to nutrient loading, SFEI has been working with the San Francisco Bay Regional Water Quality Control Board and Bay area stakeholders to develop the San Francisco Bay Nutrient Strategy (http://www.waterboards.ca.gov/sanfranciscobay/water_issues/programs/planningtmdls/amendments/estuarynne.shtml). The goal of the Nutrient Strategy is to lay out a well-reasoned and cost-effective program to generate the scientific understanding needed to fully support major management decisions. The Nutrient Strategy has 6 main goals:

1. Define the problem: develop conceptual models for Bay segments that characterize important processes linking nutrient, biological responses, and indicators of adverse effects of nutrient over-enrichment
2. Establish guidelines (water quality objectives; i.e., assessment framework) for nutrients, including ammonium, focusing on the endpoints of eutrophication and other adverse effects of nutrient overenrichment;
3. Implement a monitoring program that supports regular assessments of the Bay;
4. Develop and utilize nutrient-load response models to support nutrient management decisions;
5. Evaluate control strategies to reduce nutrient inputs from wastewater treatment plants and other sources; and
6. Consider alternative regulatory scenarios for how to move forward with nutrient management in SF Bay.

This proposal to the RMP is requesting funds to support technical studies that directly address several goals of the Nutrient Strategy and key management questions, as noted within the description of each task. The Steering Committee provisionally allocated $200,000 in 2013 for nutrient-related projects. In addition, the USGS had a one-time surplus in their other sources of funding, and is requesting $35,000 less from the RMP in 2012, with the request that if possible those funds be allocated toward monitoring program development projects (e.g., Task 2 or Task 3).

While not discussed in this proposal, the CFWG modeling proposal has direct links to and benefits for nutrient work in the Bay. That proposal, with a requested budget of $200,000 from the RMP and $300,000 from other sources, aims to build the foundation of a Bay-wide modeling program that can support modeling of bioaccumulative contaminants and nutrients/phytoplankton.

RMP Master Plan Priority Questions addressed by study proposal

1. Is there a problem or are there signs of a problem with respect to nutrient enrichment?
2. What are appropriate guidelines for assessing SF Bay health?
3. What is the relative contribution of nutrient loading pathways and how do loads vary seasonally and between Bay segments?

Goals of Nutrient Strategy addressed by study proposal

1. Document our current understanding of nutrient dynamics in the Bay, highlighting what is known and the crucial questions that need to be answered
2. Develop a monitoring program to support regular assessments in the Bay
3. Quantify nutrient loads to and important processes in the Bay

Task 2 Moored Sensor Monitoring Program Development

The indications of decreased Bay resilience to high nutrient loads noted above have come to the fore at a time when the availability of resources to continue assessing the Bay's condition is uncertain. Since 1969, a USGS research program has supported water-quality sampling in the San Francisco Bay. This USGS program collects monthly samples between the South Bay and the lower Sacramento River to measure salinity, temperature, turbidity, suspended sediments, nutrients, dissolved oxygen and chlorophyll a. The USGS data, along with sampling conducted by the Interagency Ecological Program, provide coverage for the entire San Francisco Bay –Delta system. The San Francisco Bay Regional Monitoring Program (RMP) has no independent nutrient-related monitoring program, but instead contributes approximately 20% of the USGS data collection cost. Thus, there is currently an urgent need to lay the groundwork for a locally-supported, long-term monitoring program to provide information that is most needed to support management decisions in the Bay.

While most of the historic and current data being generated by the USGS and IEP research programs are derived from ship-based measurements, there is a growing recognition that moored multi-sensor platforms can provide valuable temporally-intensive data. A number of large estuaries in the US (e.g., Chesapeake Bay, http://mddnr.chesapeakebay.net/eyesonthebay/index.cfm; Columbia River, http://www.stccmop.org/datamart/observation_network; Caloosahatchee Estuary, http://recon.sccf.org/) have well-established moored sensor networks that are integral components of monitoring efforts and provide a strong complement to ship-based monitoring. At a recent RMP-sponsored nutrient conceptual model technical meeting, the technical team recommended that pursuing a pilot project with moored sensors would be a valuable step that should be taken in the early stages of planning the next generation monitoring program for the Bay. This group further advised that the RMP invest sufficiently in person power, beyond the cost of the hardware, to ensure the success of this effort and to allow ample time for sensor platform selection, operation and maintenance, and data analysis, so that the effort contributes to monitoring program development.

Task 2 has been broken down into five subtasks (Table 1). Task 2.1 focuses on sensor platform selection. D Senn has already researched a variety of sensor platforms, and the LOBO system (http://www.satlantic.com/lobo) is our initial recommendation, because of its robust sensors (good track record based on other estuaries), including the considerable attention paid to minimizing biofouling. However other sensor platforms will be considered. The proposed LOBO sensor package includes conductivity, temperature, depth, dissolved oxygen, chl-a, turbidity, and nitrate, and has both logs data and telemeters data via the cellular network to a manufacturer-provided web-interface for real-time data visualization (this will likely be most useful for tracking sensor drift or failure; however it could also be useful for detecting short-lived events, such as blooms, and triggering a focused field sampling campaign). The SUNA nitrate sensor (http://www.satlantic.com/suna) that is part of this package is a state of the art sensor and has sufficiently low detection limits (~1 uM) for Bay conditions (~20-80 uM).

In Task 2.2, the LOBO system will be calibrated and tested in the lab, and then field tested for 0.5-1 month at the Redwood City dock near USGS Menlo Park. In Task 2.3 the system will be deployed on a bridge piling at Dumbarton Bridge in June 2013, in collaboration with D Schoellhamer whose group currently deploys and maintains turbidity, conductivity, temperature, and dissolved oxygen sensors at this site. The overlap in sensor capabilities is helpful because it will allow for continuous and co-located validation during the early stages of this pilot project. We will coordinate our maintenance schedule with Schoelhamer's group; they have agreed to collaborate on maintenance, which will allow both groups to leverage funds from various sources to support field work. Data will be collected continuously from June-December 2013, with on-going QA/QC (Task 2.4). Discreet water samples will be collected periodically (bi-weekly) adjacent to the sensor and measured for the suite of parameters to validate sensor operation. An operation and maintenance manual will be developed (Task 2.5). Finally, a technical memo will be produced that presents initial data analysis and synthesis, and just as importantly describes lessons learned during year 1 and recommendations for next steps with moored sensor applications.

BUDGET – Task 2

USGS-Menlo Park will provide in-kind support equivalent to 20% of one FTE focused on sensor maintenance and calibration. USGS-Menlo Park will also contribute other in-kind salary support for project guidance, and in-kind support for analysis of discrete water samples for relevant parameters to validate sensor performance. USGS-Sac (Schoelhammer) will be providing in-kind support related to shared costs for maintenance/field work. A request will be made to Nutrient Strategy stakeholders to cover the cost of the instrument purchase. The proposal to the RMP is directed toward funding engineering costs for mounting the sensor system, field costs, and personnel costs.

	RMP	Nutrient Strategy	USGS-Menlo Park	USGS-Sac	**Total**
hardware and shipping		80k			80k
personnel					
SFEI 50% FTE	89k				89k
5% Senn	16k				16k
5% Cloern (USGS)			14k		14k
5% Schraga (USGS)			10k		10k
USGS technicians			21k (20% FTE)	10k (10% FTE)	31k
Field/logistics	5k			10k	15k
Machining/engineering of deployment/retrieval of system	10k				10k
Sample analysis			5k		3k
Totals	120k	80k	50k	20k	270k

Task 3 Developing Solid Phase Adsorption Toxin Tracking (SPATT) as a Monitoring Tool for Microcystins and Related Toxins in San Francisco Bay

Task 3 is also related to monitoring program development, focused on the detection of algal toxins produced by harmful algal blooms (HABs). There was broad agreement within the conceptual model technical team that increased frequency and magnitude of algal toxin monitoring measurements are one likely outcome of elevated nutrient loads to the Bay and Delta. The group further concurred that the development of sensitive tools for measuring phytotoxins should be a high priority for the Bay monitoring program.

Cyanobacterial blooms and their associated toxins have become increasingly problematic globally (Chen et al. 1993, Domingos et al. 1999, Lehman et al. 2005, Guo 2007, Paerl & Huisman 2008). *Microcystis aeruginosa* in particular is considered a cyanobacterial harmful algal bloom (CyanoHAB) organism because it can impede recreational use of waterbodies, reduce aesthetics, lower dissolved oxygen concentration, and cause taste and odor problems in drinking water, as well as produce microcystins, powerful hepatotoxins associated with liver cancer and tumors in humans and wildlife (Carmichael 2001). Extensive *Microcystis* blooms with toxin production occur during summer and fall in impaired waterways in Washington, Oregon and California (Gilroy et al. 2000, Johnston & Jacoby 2003) and *Microcystis* contamination has been documented at the marine outflows of the Klamath and San Francisco estuaries (Lehman et al. 2005, Fetcho 2007) as well as from river inputs to Monterey Bay (Miller et al. 2010). More recently, a SCCWRP study detected microcystins and/or anatoxin-a in thirty-nine of forty freshwater lakes and intermittently closed coastal lagoons tested within the coastal watersheds of 5 Southern California counties (Magrann, 2011). The recently documented direct impact to the threatened California Sea Otter (*Enhydra lutris*) has also promoted these blooms and toxins from predominantly a freshwater issue to potentially a land-sea problem, with concomitant risk because of the lack of monitoring in brackish and marine waters (Miller et al. 2010).

Until recently, *Microcystis* (and associated Cyanobacterial Harmful Algal Bloom (CyanoHAB) genera) blooms and microcystin intoxication were considered a public health issue solely of freshwater ponds, lakes, reservoirs, public water supplies and rivers; this assumption is reflected in the vast body of scientific literature available on potential public health risks from microcystin exposure in freshwater habitat. By comparison, monitoring of the freshwater-marine interface for similar ecological or public health risks has remained a low priority until very recently, despite observation of outflows of *Microcystis* and microcystin-contaminated fresh water to the ocean (Lehman *et al.* 2005; Tonk *et al.* 2007). Given the severe and ubiquitous nature of this problem in freshwater habitats and potentially coastal marine systems, surveillance and monitoring is critical. Traditional monitoring programs for phycotoxins typically rely on discrete sampling (“grab” samples) from a particular site or sites, sometimes augmented with automated sampling systems. Such methods are inherently biased if the sampling does not capture the spatial and temporal variability of the system due to (e.g.) behavioral adaptations of the algae such as vertical migration, hydrologic or circulation effects, and ephemeral or episodic events. Furthermore, grab sampling may underestimate the presence of low levels of toxins if the sampling protocol does not include pre-concentration and/or if the toxin concentrations are below the analytical limit of detection.

In response to this challenge, Kudela and colleagues at UCSC have been investigating the use of a passive sampling method, Solid Phase Adsorption Toxin Tracking (SPATT), to monitor microcystin (and other toxin) levels in seawater. SPATT was first proposed for HAB monitoring by MacKenzie et al. (2004), who developed developed this passive sampling device by placing SPATT resin, which binds an array of lipophilic algal toxins, within a polyester mesh bag. Over the last several years UCSC researchers have been further developing and applying SPATT for HAB detection in both marine and freshwater environments. Their results indicate that the sensitivity of this system is extremely high, which greatly facilitates source-tracking efforts. They researchers routinely detect biotoxins using SPATT when simultaneous point-sampling of water fails to detect the same toxins in a given waterway (Lane et al., 2010; Kudela, 2012).

Kudela and colleagues have conducted limited SPATT and grab-sampling within the Bay Delta and surrounding environment. Those data demonstrate that microcystins are present at moderate to high concentrations in source waters of the Bay (particularly the Delta, but also the ponds in the South Bay region; Figure 1). They have also tested SPATT in "flow-through" mode aboard the R/V Polaris during USGS cruises (Figure 2). Of particular concern, they have identified microcystins throughout the Bay during autumn, suggesting that toxins (but not necessarily cells) are being physically transported throughout the ecosystem.

Proposed Work Plan

Task 3 is divided into three subtasks. In Task 3.1, it is proposed to continue deployment of SPATT during USGS monthly cruises. As in past cruises (Figure 2), one SPATT will be deployed per basin in the surface-sampling flow-through system on the Polaris, totaling 5 SPATT per cruise. In other watersheds, UCSC has successfully deployed SPATT from fixed platforms such as moorings (this has been done in the Delta, Alviso Slough and Pond A6, and throughout the Monterey Bay region). SPATT can easily be deployed up to 30 days, and require minimal handling for field personnel. SPATT can be stored indefinitely in the freezer (-80°C) and are routinely shipped through common carriers (including US Postal Service). In Task 3.1, SPATT will be deployed at both the Dumbarton Bridge and Benicia Bridge for periods of ~1 month, taking advantage of existing fixed monitoring programs. A similar effort in Pinto Lake, CA for a year was sufficient to develop statistical models relating toxin concentrations to environmental conditions (Kudela, 2012).

SPATT has now been extensively tested and applied for microcystin detection by UCSC, and there is widespread interest from the research and management community in deploying SPATT as part of existing monitoring programs. As part of the move toward more routine use of SPATT in monitoring programs, several issues related to SPATT deployment and interpretation need to be addressed, such as how SPATT compare to ambient concentrations (calibration relative to in situ conditions), best practices for deployment/recovery and analysis of SPATT (i.e. length of deployment, analytical methods for toxin detection), and how SPATT compare with more mature passive samplers to quantify the partitioning coefficients and kinetics, and effects of flow and surface area. Some of these preliminary lab measurements have been conducted already (Kudela 2012) but UCSC has not extensively tested longer deployments or the partitioning in flow-through versus controlled volume situations.

In Task 3.2, controlled experiments will be conducted in the laboratory to better characterize partitioning of phytotoxins out of solution and into the SPATT during exposure in ship-board flow-through systems. Specifically, experiments will be carried out in simulated flow-through systems in which SPATT will be exposed to brackish water and seawater containing varying concentrations of a microcystin-RR. Microcystin-RR uptake will be quantified as a function of both dissolved concentration and exposure time. This “calibration” information will allow for more accurate back-calculations of average ambient concentrations in natural systems. In addition, a time-series of “bottle” experiments will be conducted during which SPATT will be exposed in containers holding seawater with known concentrations of microcystin-RR. SPATT will be removed at several time points and microcystin-RR uptake will be measured. This information will aid in characterizing the uptake kinetics of microcystin under conditions simulating longer term deployments at a single site.

In Task 3.3 a technical memo will be prepared that interprets the results from 2013 field sampling and the controlled experiments. The results of the field and laboratory studies are expected to inform future monitoring approaches in the Bay, and ultimately provide information to support management decisions related to HABs and biotoxins. It is anticipated that results will also be published as a journal article, to be submitted in the first half of 2014.

BUDGET – Task 3

	RMP
personnel	46.5k
analyses, shipping, local travel, materials, misc.	18.5
Total	65k

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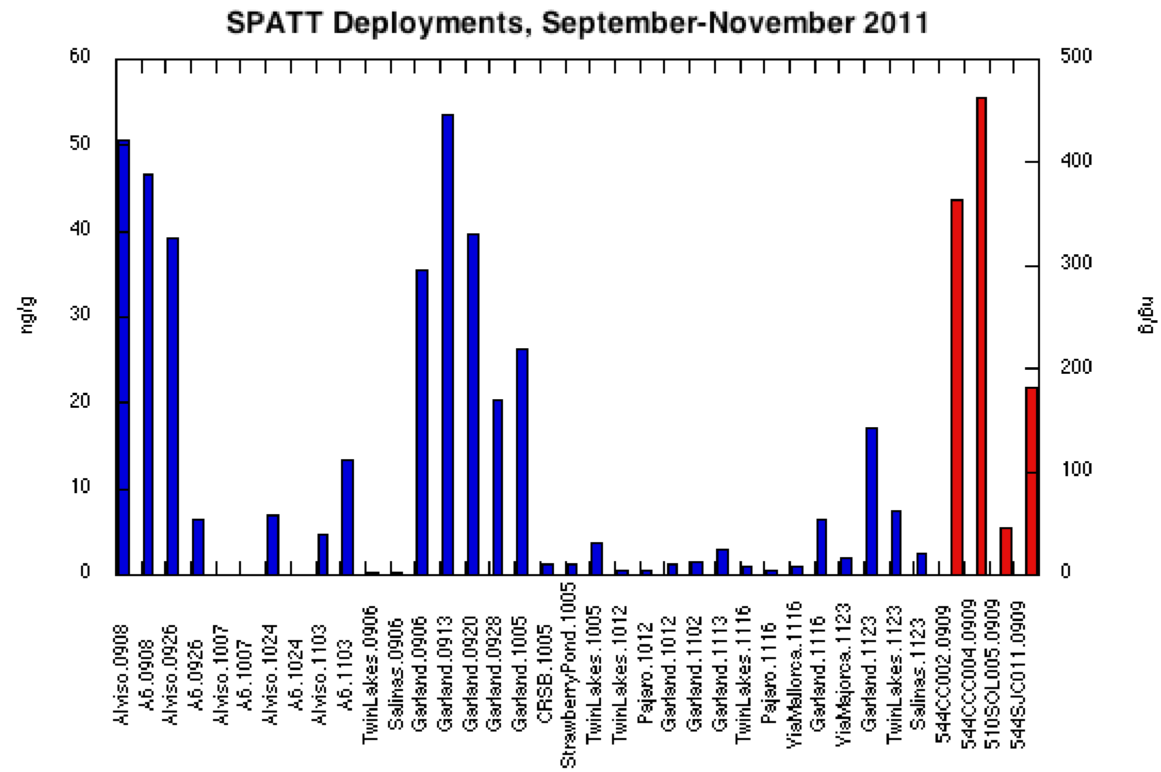

Figure 1. SPATT results from the South Bay region (left) and Monterey Bay (middle) in blue, and from the Delta (right; red) for microcystin-LR. While the Delta has orders of magnitude more toxin for equivalent sampling intervals, there are easily detected toxins throughout the other watersheds. The Monterey Bay toxin loads have been associated with California otter deaths, highlighting the negative impacts of these toxin levels.

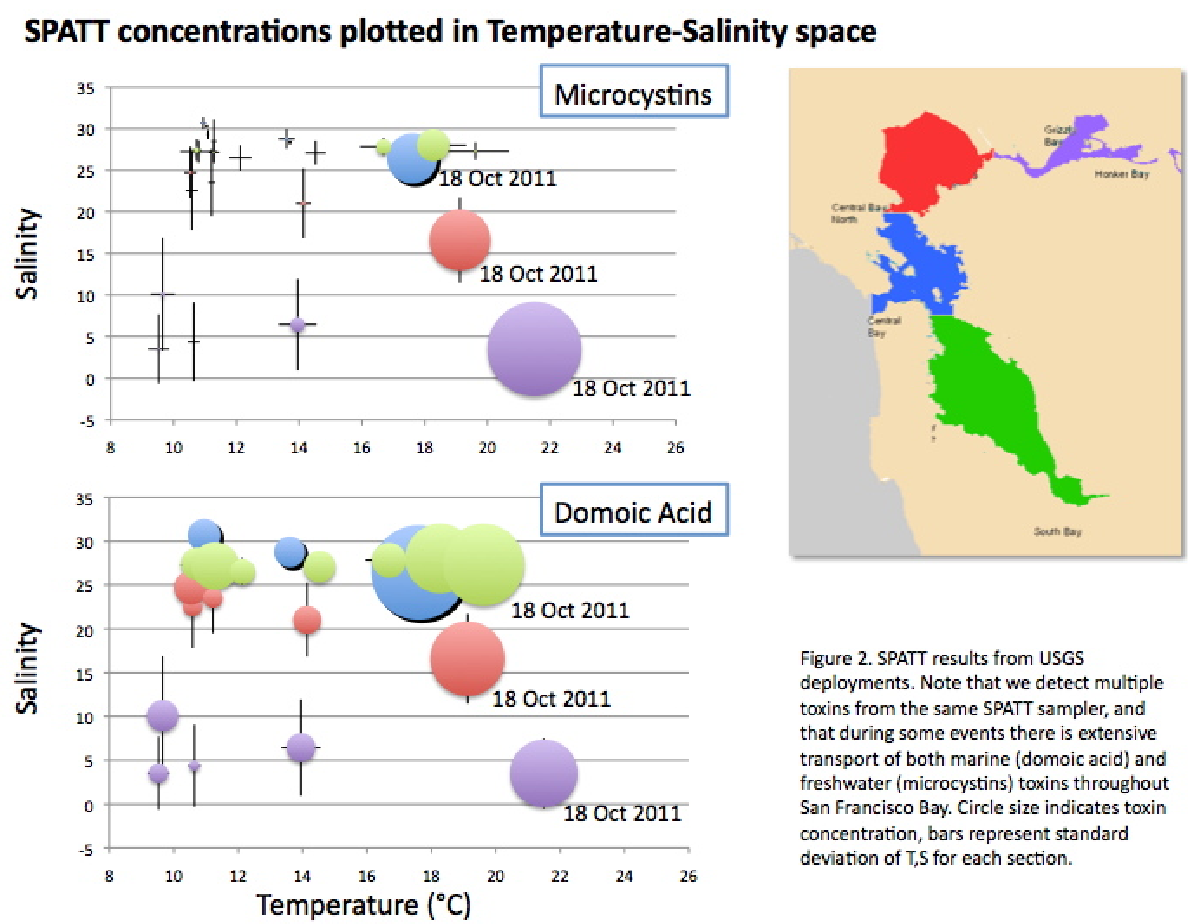

Figure 2. SPATT results from USGS deployments. Note that we detect multiple toxins from the same SPATT sampler, and that during some events there is extensive transport of both marine (domoic acid) and freshwater (microcystins) toxins throughout San Francisco Bay. Circle size indicates toxin concentration, bars represent standard deviation of T,S for each section.

Task 4 Nutrient stormwater sampling in 6 Bay area watersheds

Among the key objectives outlined in the March 2012 Draft Nutrient Strategy is the quantification of nutrient loads from main potential sources. Currently limited data exists to support the quantification of nutrient loads from storm water runoff. Developing accurate estimates for regional watershed loads to the Bay requires both acquiring empirical data from representative watersheds (for calibration/validation) and developing models to quantify loads across the region.

The Small Tributary Loading Strategy (STLS) led to monitoring of watersheds to quantify concentrations and loads of priority pollutants to the Bay during wet weather events. Study watersheds have been selected to represent the range of land use and land cover characteristics of the diverse watersheds draining to the Bay. The STLS is a multi-year effort, which studied 4 watersheds for up to 4 storms in 2011-2012 (3 watersheds monitored by SFEI, one by consultant), and 6 watersheds are proposed for monitoring in 2012-2013. Empirical data on flow and concentration will be collected and used to compute loads, and to calibrate spreadsheet models to estimate loads across the region. Development of the spreadsheet model is underway (Lent and McKee, 2011), but this model does not yet have capacity to predict nutrient loads. Although nutrients are not the main focus of the STLS, three nutrient analytes (nitrate, total phosphorous, dissolved orthophosphate) are among the current list of analytes because they are required as part of the Municipal Regional

Stormwater Permit. However, other important nutrient analytes that are needed to provide a fuller picture of nutrient loads to the Bay are not funded because the permit does not require them (NH4, total Kjeldahl nitrogen (TKN)).

At the October 2011 RMP *Sources, Pathways, and Loadings Workgroup* meeting there was general agreement that the current suite of analytes should be augmented to include a full set of nutrient analytes, funds permitting. Adding these nutrient analytes, when teams are already mobilizing for the other contaminant sampling, is a wise investment, leveraging current funds being invested in this effort. NH4 and TKN were added to the list of analytes for the 2011-2012 sites, and that data has just become available and will be analyzed during Summer 2012 to inform potential sampling in 2013

We propose to collect samples for additional nutrient parameters at the six watersheds being sampled during the 2012-2013 rainy season. The proposed additional analytes are again NH4 and TKN. The combined suite of nutrient analytes matches the type of information being collected in the USGS monthly Bay surveys, and data being collected by POTWs over the next two years. Funds are also being requested for data analysis and preparation of a technical memo on all the nutrient data (including those already being measured by STLS), which will describe initial findings and make recommendations for field work in 2013-2014 and beyond. To the extent possible given budget constraints, a compilation of existing data on land use-specific runoff concentrations of nutrient forms will be compiled for a range of land uses through a collaboration with SCCWRP. The results from 2011-2012 and 2012-2013 rainy seasons will provide important information for quantifying nutrient loads to the Bay from urban runoff. It is roughly estimated that this proposed work is leveraging more than $300,000 of field work and logistical support.

BUDGET – Task 4

	# of sites	# of samples per site per storm	# of storms	Total # of samples including QA/QC	Cost per analysis	Total per analyte
NH_4^+ and TKN analysis	6	4	4	110	$130*	$14300
High turbidity filters –110 @$13 each + shipping						1430
Additional sampling effort						3000
Contracting, project management						2000
Data Management, QA/QC						2500
Data analysis and preparation of technical memo						15000
					Total	**$38,300**

*TKN = $70/sample; NH_4^+ = $60/sample

Task 5 Quantifying External Nutrient Loads and Data Gaps Analysis

Quantifying external nutrient loads to San Francisco Bay was identified as a high-priority funding item in the draft Bay Nutrient Strategy. Given that nitrogen (and to a lesser extent phosphorous) can experience multiple potential fates once entering an estuary, accurate load estimates are a pre-requisite for eventually developing reliable mass budgets and quantifying internal-Bay processes. In 2012, we proposed to develop spatially- and temporally-explicit estimates of nutrient loads to the Bay, and identify critical data gaps that contribute most to current uncertainty in total loads, speciation of those loads, and the relative importance of various sources. We proposed that this work would be distributed 40% and 60% between 2012 ($20k) and 2013 ($30K), respectively. Task 5 in this 2013 request is for the continuation and completion of that work.

A summary of external loads to the South Bay has already estimated by SFEI through funding from BACWA (McKee and Gluchowski, 2011). Task 5 (2012 and 2013) expands that loading work into the Central, San Pablo, and Suisun Bays, developing monthly, seasonal and annual load estimates, and exploring the importance of uncertainties in loading and nutrient speciation. The nutrient sources considered will include: POTW discharges; stormwater discharges; flows from the San Joaquin and Sacramento Rivers entering through the Delta; exchange across the Golden Gate; and direct atmospheric deposition. Unlike the South Bay, where loads from POTWs appear to dominate input of nutrients, other sources (flux through the Golden Gate; discharge through the Delta) likely contribute substantial proportions of the overall loads in the Central and North Bay. Loads from the Delta to the North Bay may be reasonably well-constrained, due to intensive monitoring in the region. Some of the funding in 2013 can be applied toward incorporating the historic and new discharge effluent data required under the Regional Water Board's March 2012 13267 Order to wastewater dischargers; that data will begin becoming available in the second half of 2012.

As part of identifying major uncertainties and data gaps, Task 5 will identify high-priority monitoring activities and special studies designed to better constrain nutrient load estimates.

BUDGET – Task 5

	RMP
on-going data analysis, report preparation	30k