



Central Coast  
Regional Monitoring Program  
Water Quality in  
Areas of Special Biological Significance

**Final Report**  
**2013–2016**  
**August 1, 2016**

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2013–2016  
Central Coast Regional Monitoring Program  
Water Quality in Areas of Special Biological Significance**

*Submitted to:*

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## Central Coast Regional ASBS Monitoring Program

### Final Report 2013–2016

#### 1.0 Executive Summary

In the 1970's, 33 Areas of Special Biological Significance (ASBS) were designated by the California State Water Resources Control Board (State Board) to protect valuable or sensitive biological communities. Regulations prohibited discharges of waste to these ASBS. More recently, stormwater was recognized to contain contaminants from anthropogenic sources and enforcement of the waste discharge prohibition was broadened to include storm runoff. Following nearly a decade of dialogue among the Water Board, participants, and other interested parties, the State Board adopted a set of requirements called Special Protections for Areas of Special Biological Significance, Governing Point Source Discharges of Storm Water and Nonpoint Source Waste Discharges (Special Protections).

The Special Protections laid out the requirements to be met by participants in order to qualify for an exception to the prohibition against discharge of wastes carried by stormwater into ASBS. These requirements included collection and reporting of monitoring data using methods and sampling designs prescribed in the Special Protections. The Special Protections at numerous sites required collection of water quality data during a minimum of 6 storms (3 storms per year) from the following types of samples:

1. ASBS stormwater discharges (discharges) in 2 categories,
  - a. Outfalls 18 – 36 inches
  - b. Outfalls >36 inches (Unless otherwise indicated, discharge samples refer to large outfalls)
2. ASBS pre-storm ocean receiving water (pre-storm) collected from near discharges,
3. ASBS storm ocean receiving water (receiving water) collected in knee-deep water at the point where discharges enter the ocean,
4. Reference storm ocean receiving water (reference) at the mouths of coastal reference streams (i.e., streams with <95% human development in their watersheds), and
5. Reference dry weather (reference pre-storm) samples collected at reference sites during the dry season (not following storms).

In the Central California Regional ASBS Monitoring Program, an additional category of sites was sampled. Two background (background) sites were sampled along the shore within Monterey Bay distant from any ASBS in order to determine whether water quality in ASBS receiving water samples was similar to that in non-ASBS receiving water samples, which could indicate that ASBS receiving water quality was affected by water quality problems existing throughout Monterey Bay.

The Special Protections define the 85<sup>th</sup> percentile of constituent concentrations at reference sites as the upper bounds of natural water quality. In order to qualify for an exception to the waste discharge prohibition, storm samples must have contaminant concentrations below the 85<sup>th</sup> percentile threshold or have storm concentrations that do not exceed pre-storm

concentrations. If exceedances of this threshold occur, the Special Protections require the following:

*“Best management practices to control storm water runoff discharges (at the end-of-pipe) during a design storm shall be designed to achieve on average the following target levels: (1) Table B Instantaneous Maximum Water Quality Objectives in Chapter II of the Ocean Plan<sup>1</sup>; or (2) A 90% reduction in pollutant loading during storm events, for the applicant’s total discharges.”*

The Special Protections also require assessments of the condition of biological communities in ASBS through monitoring of rocky intertidal organisms, measurement of contaminants accumulated in the tissues of resident mussels, and the toxicity of stormwater discharges and receiving water to test organisms.

The Special Protections require measurement of a broad list of contaminants in water and biological organisms, with comparison of concentrations in storm samples to concentrations in reference samples. These contaminants include:

1. **Trace metals, arsenic (As), silver (Ag), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), selenium (Se), and zinc (Zn).** Trace metals are sometimes called heavy metals and they can be toxic at elevated concentrations. They are found naturally in rocks and soils and also can be elevated in association with architectural, construction, and automotive sources.
2. **Polynuclear aromatic hydrocarbons (PAHs).** These compounds are included in petroleum and combustion products and can be toxic at elevated concentrations. PAHs can originate from petroleum spills, natural seeps, automobile leakage, and various combustion sources.
3. **Pyrethroid and Organophosphate pesticides.** These pesticides are known to cause toxicity to aquatic organisms in urban streams. Pyrethroid pesticides are a fairly recent introduction to replace organophosphate pesticides, which are noted for causing toxicity in ambient waters. Pyrethroids are widely applied in agricultural and residential land uses.
4. **Bioaccumulation.** Bioaccumulation refers to the accumulation of contaminants into the tissues of living organisms, such as fish or shellfish. If these contaminants reach sufficiently high concentrations, the organisms can be negatively affected and the health of animals or humans that consume them can be at risk.
5. **Toxicity.** To measure toxicity, aquatic organisms are exposed to samples of discharges and receiving water to determine whether the sample water impairs natural biological processes. Using standardized procedures, success of sea urchin egg fertilization, normal development of bivalve embryos, germination and growth of kelp are compared between controls and sample water to determine whether sampled waters are toxic.

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<sup>1</sup> The California Ocean Plan includes various water quality objectives that differ according to contaminant types: 1) Trace metals, ammonia and some pesticides = 6-month median, daily maximum, and instantaneous maximum. 2) Organic contaminants (e.g., petroleum hydrocarbons) = 30-day average.

6. **Nutrients and conventional constituents.** Nutrients include the nitrogen sources nitrate, ammonia and urea, and the phosphorus source orthophosphate, all of which can contribute to the growth of harmful algae. Sources of nutrients include runoff of residential, urban, and agricultural fertilizers, as well as metabolic excretory waste products from animals. Total Suspended Solids (TSS), and Oil and Grease are conventional constituents that can be associated with erosion (reducing water clarity) and improper maintenance of grease traps, respectively.
7. **Fecal Indicator Bacteria (FIBs).** Three FIBs are measured, including Fecal Coliforms, *Enterococcus*, and *E. coli*. They are used as indicators of fecal contamination. FIBs can be elevated due to sewage leakage and domestic animal and wildlife feces.

The Central California Regional ASBS Monitoring Program was implemented to satisfy the monitoring requirements associated with implementation of the ASBS Special Protections. The program includes Duxbury Reef, Fitzgerald, Pacific Grove, and Carmel Bay ASBS, and spans the coast from Marin County to Big Creek, south of Big Sur. Program participants include Marin County, San Mateo County, Monterey County, Monterey Bay Aquarium, Hopkins Marine Station of Stanford University, City of Monterey, City of Pacific Grove, City of Carmel by the Sea, Pebble Beach Company, and Caltrans.

Monitoring began in the fall of 2013. Because it was necessary to sample a minimum of 6 storms over at least 2 years in order to thoroughly characterize water quality conditions at each sampling location, the prevailing drought required that the Central California discharges request a program extension into a third year of monitoring. Permission to extend the program was granted by State Board staff. The extension was particularly helpful for expanding our description of reference conditions, which are the basis of criteria for describing natural water quality.

Program participants have individually submitted Compliance Plans intended to address constituent concentrations in receiving water samples that have been appreciably above the relevant 85<sup>th</sup> percentile threshold. The process of notifying Regional and State Boards of sites that have storm water quality outside of natural water quality thresholds will be directly from participants to the Water Board. Wherever specific discharges are discussed in this report, they are identified by randomly assigned letters. Consequently, this report focuses on whether there are spatial patterns in constituent concentrations in reference and pre-storm samples, and whether there are associations among constituents that would help determine whether discharge constituents have anthropogenic sources and constitute waste. In particular, the following questions are addressed:

1. Are there north-to-south differences in reference conditions?
2. Are there north-to-south differences in pre-storm water quality at ASBS sites?
3. Are storm discharges altering Natural Water Quality, as defined by the 85<sup>th</sup> percentile and higher concentrations in storm samples than in pre-storm samples?
4. Are alterations of Natural Water Quality likely due to anthropogenic waste?
5. Are marine biological resources being measurably affected by ASBS storm discharges?

Major findings are as follows:



### ***Are there north-to-south differences in reference conditions?***

An important consideration in comparisons of reference water quality between northern and southern areas is whether similar storm conditions were sampled throughout the region. If there are north-to-south differences in ambient and reference constituent concentrations, an inability to sample large storms in some areas could bias the calculated 85<sup>th</sup> percentile threshold. In fact, there were several large storms during which safe access was not possible for sites along the Big Sur coast, requiring that smaller storms be sampled in this area when smaller waves and stream flow allowed access. Consequently, effects of these large storms, while they were captured at northern reference sites, were not captured for the Big Sur coast. ANOVA was performed on each constituent to determine whether there were significant differences in concentrations between reference sites grouped for the northern and southern portions of the study area.

There are clear differences between northern and southern sub-regions in constituent concentrations. Every trace metal, except silver, exhibited significant differences between sub-regions, with northern sites having higher concentrations. In the case of the kelp germination toxicity test, there were also higher rates of germination in tests done at northern reference sites than at southern reference sites. There were also differences between northern reference sites and southern reference sites in the associations between total suspended solids (TSS) and various constituents.

These geographic differences in reference water quality should be considered in determining whether a particular ASBS site conforms to natural water quality. The significant associations between TSS and other constituents in reference samples suggest that comparisons using TSS-constituent associations in other sample types (i.e., discharge, pre-storm, receiving water) could help determine whether some constituents in non-reference samples are derived from natural sources, such as native sediments.

### ***Are there north-to-south differences in pre-storm water quality at ASBS sites?***

This question seeks to determine whether non-storm concentrations of constituents at ASBS sites were consistent throughout the region. If north-to-south differences in non-storm ambient conditions exist, such differences could mean that receiving water samples in some areas have a smaller margin between pre-storm concentrations and the overall 85<sup>th</sup> percentile threshold, thus resulting in more values above the threshold than in areas with lower pre-storm concentrations.

Pre-storm samples have significantly higher trace metal and TSS concentrations at ASBS sites in the northern area of the study region than in the southern area. Concentrations of FIBs, nutrients, PAHs, and organophosphate and pyrethroid pesticides were mostly higher in the south than in the north, but none of the differences was significant in both of the statistical tests used. Potential causes are differences in geology, soil erodibility and trace metal concentrations, and differing proximities to anthropogenic sources associated with large urban

areas. These results suggest that, if all discharges were equal, the difficulties of achieving natural water quality would not be the same across the entire study region.

### ***Do storm discharges alter receiving water quality?***

Concentrations of constituents in receiving water samples were usually below overall 85<sup>th</sup> percentile thresholds. For some constituents, the concentrations measured at reference sites were greater than the highest concentrations measured in ASBS receiving water and there were reference samples above the overall 85<sup>th</sup> percentile thresholds. There were generally similar concentrations between sample types and high variability within sample types. Nevertheless, concentrations in discharge samples were usually significantly greater than in other sample types, while receiving water samples were not statistically different from concentrations in pre-storm or reference samples when tested with analysis of variance (ANOVA). When all sites were tested together, matched-pair tests between pre-storm and receiving water concentrations indicated most constituents had higher concentrations in receiving water than in pre-storm samples. When examined site-by-site, with attendant lower sample sizes, these differences were not universally observed and those that were significant did not necessarily correlate with site differences in the percentage of receiving water samples above the overall 85<sup>th</sup> percentile threshold, their magnitude above the threshold or the estimated loads of these constituents.

Selenium and silver are illustrative of these apparent contradictions. Selenium and silver in receiving water were above their respective 85<sup>th</sup> percentile thresholds in 11% and 15% of all samples, respectively. Moreover, 40% and 33% of receiving water samples were above the selenium and silver thresholds, respectively, at 1 site. Nevertheless, their average concentrations in receiving water samples were 88% and 62% below their respective 85<sup>th</sup> percentile thresholds and neither one exhibited significant differences between pre-storm and receiving water samples in matched-pair tests, either across all sites or within any site.

Regressions of estimated constituent loads versus changes in concentrations from pre-storm to receiving water (delta) were mostly significant and explained substantial variation in delta, although this results did not necessarily mean receiving water concentrations were less than overall 85<sup>th</sup> percentile thresholds.

### ***Are alterations of receiving water quality due to anthropogenic waste?***

Determining whether trace metals in discharges are from anthropogenic or natural sources is challenging. Trace metals are ubiquitous in the natural environment and are contained in sediments and geologic formations even in pristine environments. An analysis was performed using the relationships between trace metals and TSS in an effort to distinguish between natural and anthropogenic sources of trace metals. For most trace metals, the concentrations per TSS in discharge samples were elevated above other sample types. Exceptions to this pattern were evident for arsenic and silver, in which the relationship between TSS and arsenic was very similar among all sample types and silver concentrations relative to TSS were often lower in discharge samples than in other sample types. The relationships between trace metals and TSS in reference samples were consistent with concentrations of all trace metals increasing with increasing TSS concentrations, except for silver.

Analysis of variance (ANOVA) revealed that the amounts of various constituents per unit of TSS were similar among all sample types, except for discharges. Discharge samples often had significantly increased constituent concentrations per unit of TSS. Moreover, another ANOVA showed that the relationship of TSS to copper, lead, mercury, and zinc differed among sites. Some sites exhibited relationships between these trace metals and TSS in their discharges that paralleled the positive slopes of these relationships in other sample types, but with elevated trace metals per unit of TSS. Other sites exhibited elevated trace metals in their discharges that had no relationship to TSS concentrations, and which were often accompanied by elevations of the trace metals per unit of TSS in receiving water samples. Discharges of trace metals with high percentages in the dissolved fraction indicate different processes controlling their release into the environment from the processes that controlled reference trace metal concentrations, and suggests anthropogenic sources. Moreover, several other studies have found high loads of dissolved copper, zinc, and lead in runoff from building roofs made of copper, zinc-coated metal and slate.

FIBs and nutrients are also ubiquitous in the environment, but the available data do not allow determinations of sources. Nevertheless, FIBs stand out because their maximum concentrations in receiving water samples were greater than those at reference sites. If not strictly anthropogenic, their concentrations were highest in receiving water samples, although not significantly, and they also exhibited significant associations between estimated loads and changes in receiving water concentrations. Thus, it appears that storm receiving waters at the base of watersheds affected by human development tend to have high concentrations of FIBs, although it is unknown whether these FIBs were from anthropogenic sources.

Nutrients cannot be chemically directly linked to anthropogenic sources. They are present in soil and natural organic matter. Moreover, there were no significant increases in receiving water concentrations over pre-storm concentrations at any site and no relationship between loads and changes in receiving water concentrations.

PAHs are naturally present in the marine environment. Along the California coastline from near San Simeon southward into the Santa Barbara Channel, there are natural seeps that result in tar balls on beaches and rocky intertidal areas. Nevertheless, we are not aware of any natural seeps onshore within the study area. Consequently, PAHs detected in the discharges and receiving water samples are presumed to be from anthropogenic sources, such as motorized vehicles and other types of combustion processes.

Organophosphate and pyrethroid pesticides are exclusively man-made compounds that have no natural sources. Although they were infrequently detected, their presence in any sample, including receiving water, is presumed to derive from an anthropogenic source.

### ***Are marine biological resources being affected by ASBS storm discharges?***

#### **Rocky Intertidal Monitoring**

Rocky intertidal monitoring was performed under the direction of Dr. Peter Raimondi of University of California, Santa Cruz. Methods were identical with those used for regional ASBS

monitoring programs in other parts of California. Sampling was conducted in the fall of 2014 at the following sites:

1. Alder Creek discharge (Duxbury Reef ASBS)
2. Fitzgerald Marine Reserve discharge
3. Año Nuevo discharge
4. Hopkins discharge (Pacific Grove ASBS)
5. Stillwater discharge (Carmel Bay ASBS)
6. Point Lobos discharge (Point Lobos State Marine Reserve)
7. Bolinas Point reference
8. Pigeon Point reference

Data from each site were compared with current and historic data from numerous sites along the central California coast. Sites were selected using broad criteria to ensure adequate similar substrate among sites and safe access. Sessile and mobile organisms were quantified using random quadrats and point contact methods, respectively

Based on the results of these analyses, there is no support for the idea that discharges along the central California coast generate impacts to diversity or community composition in the nearby rocky intertidal habitats. Other attributes such as individual growth and reproduction could be affected with no subsequent impact to diversity or composition.

Some sites stood out as differing substantially from what was expected for biological communities in the region. In particular, Fitzgerald Marine Reserve was an outlier with respect to sessile species composition. It is likely that this difference in community structure is the result of the geomorphology at the site. The intertidal zone at Fitzgerald Marine Reserve is a very wide and flat bench surrounded by sand and subject to considerable scour. In addition, the reef tends to hold water because it is flat and the key mid intertidal species, *Chthamalus* spp., *Mytilus californianus* and *Mastocarpus* spp., which are species that dominate on hard rock surfaces with extended periods of emersion are all uncommon at this site.

## Mussel Bioaccumulation Monitoring

For the past 2 years, the Central California Regional ASBS monitoring program has collaborated with the Central California Long-term Environmental Assessment Program (CCLEAN) on mussel bioaccumulation monitoring. CCLEAN has measured several persistent organic pollutants (POPs) polychlorinated biphenyls (PCBs), the flame retardants polybrominated diphenyl ethers (PBDEs), and chlorinated pesticides in mussels at 5 sites around Monterey Bay for over 15 years and the long database permits analysis for spatial and temporal patterns. This collaboration provided the ASBS program participants with access to a long-term dataset on the condition of an important biological resource in rocky intertidal communities around Monterey Bay, including ASBS.

In the collaboration between this project and CCLEAN a site was added at Point Reyes National Seashore and the list of analytes normally measured by CCLEAN was expanded to include organophosphate pesticides, pyrethroid pesticides and acid-positive pharmaceuticals. None of the organophosphate or pyrethroid pesticides were detected in any of the samples. Acid-positive refers to the type of extraction to recover the compounds from the sample matrix.

Concentrations of POPs in mussels have been declining over recent years around Monterey Bay and have been consistently low at Carmel River Beach. Dieldrin in mussels along the northern shore of Monterey Bay have remained below the USEPA recreational fisher screening value at all sites for the sixth year in a row, although Dieldrin still exceeds the subsistence fisher screening level at several sites. DDTs also remain below human health alert levels. PBDEs also have declined significantly over time at all sites, except for The Hook. Acid-positive pharmaceuticals detected in the mussels consisted entirely of compounds with both human and veterinary or animal husbandry uses, suggesting runoff from pets and livestock operations. More pharmaceuticals were detected at The Hook than at other sites. The broad-spectrum antibiotic Lomefloxacin was detected in more samples than any other pharmaceutical. Concentrations of contaminants measured in mussels from Point Reyes National Seashore were generally lower than at the other CCLEAN sites around Monterey Bay, except for PCBs, which were higher at Point Reyes. The mussels at Carmel River Beach have very low concentrations of contaminants compared to other locations in the Monterey Bay area, which indicates that water quality is sufficient to protect this biological resource in the Carmel Bay ASBS.

## Toxicity Testing

Toxicity tests are widely accepted laboratory procedures that are intended to indicate whether a particular sample of water could cause harm to aquatic organisms. They often rely on measurements of physiological responses, such as egg fertilization, embryonic development, gametophyte germination, and growth that are likely to be more sensitive than survival as a test endpoint. Being conducted in the laboratory, the test conditions, such as temperature, oxygen concentration, and water quality, can be monitored in order to minimize the effects of uncontrolled variables on test outcomes. Bringing samples into the laboratory for testing allows a specific set of organisms to be observed throughout the course of the test, which is very difficult under ambient conditions.

Toxicity was not presumed to be a normal feature of natural water quality (Schiff et al, 2016). Consequently, the occurrence of toxicity failures in <2% of reference samples is notable and indicates that some toxicity could be naturally occurring. The 3 toxicity tests that exhibited failures at reference sites were the kelp growth, mussel embryonic development, and mussel embryo survival tests. These 3 tests also failed in 8%, 2%, and 3% of receiving water samples. The urchin fertilization test exhibited a higher rate of failure in receiving water samples, with 2 samples at 1 site and single samples at 2 other sites failing. Discharge samples tested with the urchin fertilization test failed in 24% of samples overall. The high rates of failure in the discharge samples at several sites were not consistently associated with large numbers of failures in receiving water samples. Discharges smaller than 36 inches failed the urchin fertilization test in 17% of samples.

A statistical test revealed that 39% of the variation in the numerical endpoints of urchin fertilization toxicity tests was accounted for by a combination of trace metals and pesticides. The negative effects of zinc and pyrethroid pesticides accounted for most of the variation, while the apparent positive effects of nickel and PAHs, and the negative effects of arsenic and silver were less important. The results of the stepwise linear regression modeling reveal statistical associations and do not establish causal links between the significant constituents and toxicity. Nevertheless, they provide guidance for any future toxicity identification evaluations

Toxicity measured in receiving water samples suggest that marine biological resources could be affected by ASBS discharges. Toxicity in discharge and receiving water samples has been statistically associated with some trace metals and pyrethroid pesticides. Toxicity associated with dissolved trace metals will be challenging to attribute and control.

### **Nutrient Effects on Algal Blooms**

It is assumed that the measurement of nutrients in this program was required because of their potential effects on algal blooms. Harmful algal blooms have become a global problem. Last year saw an extraordinary bloom along the entire west coast of the United States of *Pseudo-nitzschia*, which is a diatom that produces the neurotoxin domoic acid. Kudela et al (2008) linked seasonal red tides along the northern bight of Monterey Bay to discharges of agricultural nutrients from the Pajaro River.

Annual loads of nitrogen in nitrate, ammonia, and urea from rivers and wastewater discharges average 3,400,000 kg. Average loads of these nutrients from the ASBS discharges monitored in this program were 14.5 kg/site/storm, which amounts to 0.00043% of the annual load from rivers and wastewater. Nutrients discharged into ASBS have had no noticeable effect on algal blooms or nuisance growths.

### **Regulatory Considerations**

Given that monitoring has demonstrated that there are significant geographic differences in natural water quality at reference sites in this study, the overall 85<sup>th</sup> percentile does not necessarily reflect local natural water quality at a given ASBS. The primary water quality threshold for judging whether natural water quality is being achieved in ASBS is the overall 85<sup>th</sup> percentile of values from reference sites in the ocean at the mouths of streams with <5% of their watersheds under human development. This threshold essentially requires ASBS participants to achieve better water quality than is present in the ocean at the mouths of these clean reference streams. It is far from certain that this level of water quality is achievable. It seems a very daunting task to ensure that water quality along a city shoreline be better than the best water quality available along undeveloped shoreline of the state. If we can assume that the water quality at reference sites fully supports sensitive marine life, then requiring the same, and not necessarily better, water quality should provide a robust level of protection for marine life in ASBS.

If this approach were utilized, a more reasonable threshold would be the 95<sup>th</sup> percentile. This would ensure that any value falling outside the bounds of most reference values would become the focus of corrective measures. Such a threshold would have a profound effect on the number of constituents potentially being flagged for mitigation measures, while still leaving plenty of room for improving water quality.

Notwithstanding consideration of a revised threshold for natural water quality, the water quality objectives in the Ocean Plan were specifically developed to protect marine resources and human health. The toxicities of constituents were considered and appropriate safety margins were added to ensure that constituent concentrations falling under Ocean Plan objectives would not cause toxicity. In the case of organic compounds, objectives were set to protect human health based upon assumptions about bioaccumulation of compounds into seafood consumed by people and added health risks. Consequently, these compounds do not

have instantaneous maxima for the protection of marine life. FIB Ocean Plan objectives also were developed to protect human health from diseases transmitted via contact with water. They were established from epidemiological studies that determined the increased risks of becoming infected after swimming in water with increased FIB concentrations and also include built-in safety factors.

A comparison of receiving water data with Ocean Plan objectives reveals sporadic occurrences of concentrations above objectives. There was a single receiving water sample at Site B with a concentration of copper above the Ocean Plan objective. Chromium and nickel Ocean Plan objectives were each exceeded in a single reference sample. Fecal coliform and *Enterococcus* concentrations were above Ocean Plan objectives at most sites, ranging from 17% to 100% of samples. These 2 FIBs were above Ocean Plan objectives in 6% and 22% of reference samples, respectively. PAHs were above the Ocean Plan 30-day average objective for the protection of human health at most ASBS sites, ranging from 17% to 50% of samples per site. Four percent of reference samples were also above the 30-day average objective for PAHs. If an instantaneous maximum is estimated for PAHs using the 10:1 ratio used for instantaneous maximum to 6-month median concentrations for other constituents, an estimated instantaneous maximum for PAHs would approximate 0.088 µg/L and the percentage of samples above the objective would decrease substantially across all ASBS and reference sites. Moreover, if receiving water is not meeting natural water quality according to the Compliance Flowchart of the Special Protections (Figure 1), actions can be required that either bring offending constituents below Ocean Plan objectives or reduce their loads by 90%.

Comparisons of ASBS receiving water data with pertinent thresholds (e.g., 95<sup>th</sup> percentile and Ocean Plan), while reducing the number of samples above the Special Protections 85<sup>th</sup> percentile threshold, have emphasized that identifying sources and reducing anthropogenic loads of FIBs and PAHs into ocean waters should be a high priority, along with determining sources of and reductions in toxicity.

## 2.0 Program Background

### 2.1 Regulatory History

The regulation of stormwater runoff as a discharge of waste has its genesis in the passage of the Porter-Cologne Water Quality Control Act (PCA) in the State of California in 1969. Parallel Federal legislation, known as the Clean Water Act (CWA), was passed in 1972. Under provisions of the CWA, the State of California was given authority to manage federally mandated waste discharge permits within California. The PCA defines waste as follows:

*“..... sewage and any and all other waste substances, liquid, solid, gaseous, or radioactive, associated with human habitation, or of human or animal origin, or from any producing, manufacturing, or processing operation, including waste placed within containers of whatever nature prior to, and for purposes of, disposal.*

Over time, with the recognition that stormwater can contain high concentrations of various pollutants, the CWA has been amended to include requirements for permits to discharge stormwater from point sources (pipes, ditches or channels) into water of the United States (lakes, rivers or oceans). The stormwater permit process has been implemented in a tiered approach, in which larger municipalities were the first to be regulated, followed recently by smaller municipalities.

Also in 1972, the State Water Resources Control Board (State Board) adopted the California Ocean Plan (Ocean Plan), which established numeric and narrative water quality objectives for ocean waters along the coast of California. These water quality objectives are designed to protect the beneficial uses of ocean waters. Beneficial uses include 20 diverse potential uses, such as municipal supply, industrial process supply, agricultural supply, navigation, marine habitat, rare, threatened and endangered species, water contact recreation, commercial and sport fishing, etc. In each case, waters must be of sufficient quality to support the beneficial uses designated for the water body in question.

One of the designated beneficial uses is “Areas of Special Biological Significance” (ASBS), which can be nominated by Regional Water Boards and approved for implementation by the State Board. The definition of the ASBS beneficial use is as follows:

*Areas of Special Biological Significance (ASBS) - are those areas designated by the State Water Resources Control Board as requiring protection of species or biological communities to the extent that alteration of natural water quality is undesirable.*

Numerous Areas of Special Biological Significance were nominated and approved in 1974 and 1975, based upon biological surveys. There currently are 34 coastal areas in California designated as Areas of Special Biological Significance. In 2000, sections were added to the Public Resources Code (PRC) of California that placed ASBS into the general classification of State Water Quality Protection Area, which were defined as “a non-terrestrial marine or estuarine area designated to protect marine species or biological communities from an undesirable alteration in natural water quality, including, but not limited to, areas of special



biological significance that have been designated by the State Water Resources Control Board through its water quality control planning process.” The PRC further states: “In a state water quality protection area point source waste and thermal discharges shall be prohibited or limited by special conditions. Nonpoint source pollution shall be controlled to the extent practicable.” To our knowledge, none of the reports nominating coastal areas for designation as ASBS included water quality data.

In the early 2000s, a not-for-profit environmental advocacy group threatened a suit against the State Water Boards for failure to enforce the prohibition against discharge of waste into ASBS via stormwater. This action prompted issuance of Cease and Desist Orders (CDOs) in 2004 to several municipalities by Regional Water Boards charging violations of the Ocean Plan. The CDOs were subsequently withdrawn and a process was initiated by the State Board, Ocean Division, to engage participants in the development of a regulatory framework for issuing exceptions to the prohibition against the discharge of waste into ASBS. Beginning on January 13, 2005 at Scripps Institution of Oceanography, meetings were held throughout coastal California by State Board staff to engage stakeholders. In 2010, the State Water Board passed Resolution No. 2010-0057, which directed State Board staff “to prioritize ongoing work related to exceptions for current discharges to ASBS ahead of new work related to designation of new ASBS and State Water Quality Protected Areas (SWQPA) until all of the current ASBS discharge issues are resolved through the exception process, and all of the Marine Protected Areas are designated and implemented statewide.” The development of the exception process culminated in the adoption of Resolution 2012-0031 on June 19, 2012, which included the following provisions:

2. *Approves the exceptions to the Ocean Plan prohibition against waste discharges to ASBS for discharges of storm water and nonpoint source waste by the applicants listed in Attachment A to this resolution provided that:*
  - a. *The discharges are covered under an appropriate authorization to discharge waste to the ASBS, such as an NPDES permit and/or waste discharge requirements;*
  - b. *The authorization incorporates all of the Special Protections, contained in Attachment B to this resolution, which are applicable to the discharge; and*
  - c. *Only storm water and nonpoint source waste discharges by the applicants listed in Attachment A to this resolution are covered by this resolution. All other waste discharges to ASBS are prohibited, unless they are covered by a separate, applicable Ocean Plan exception.*

The Special Protections mentioned in Item 2.b. (SWRCB, 2012) included monitoring requirements designed to determine whether stormwater discharges to ASBS are causing an undesirable “alteration of natural water quality.” In support of the development of the Special Protections, the State Water Board provided funding in 2005 to the Southern California Coastal Water Research Project (SCCWRP) to determine the feasibility of defining “natural water quality.” With Water Board participation, SCCWRP convened a working group, which became

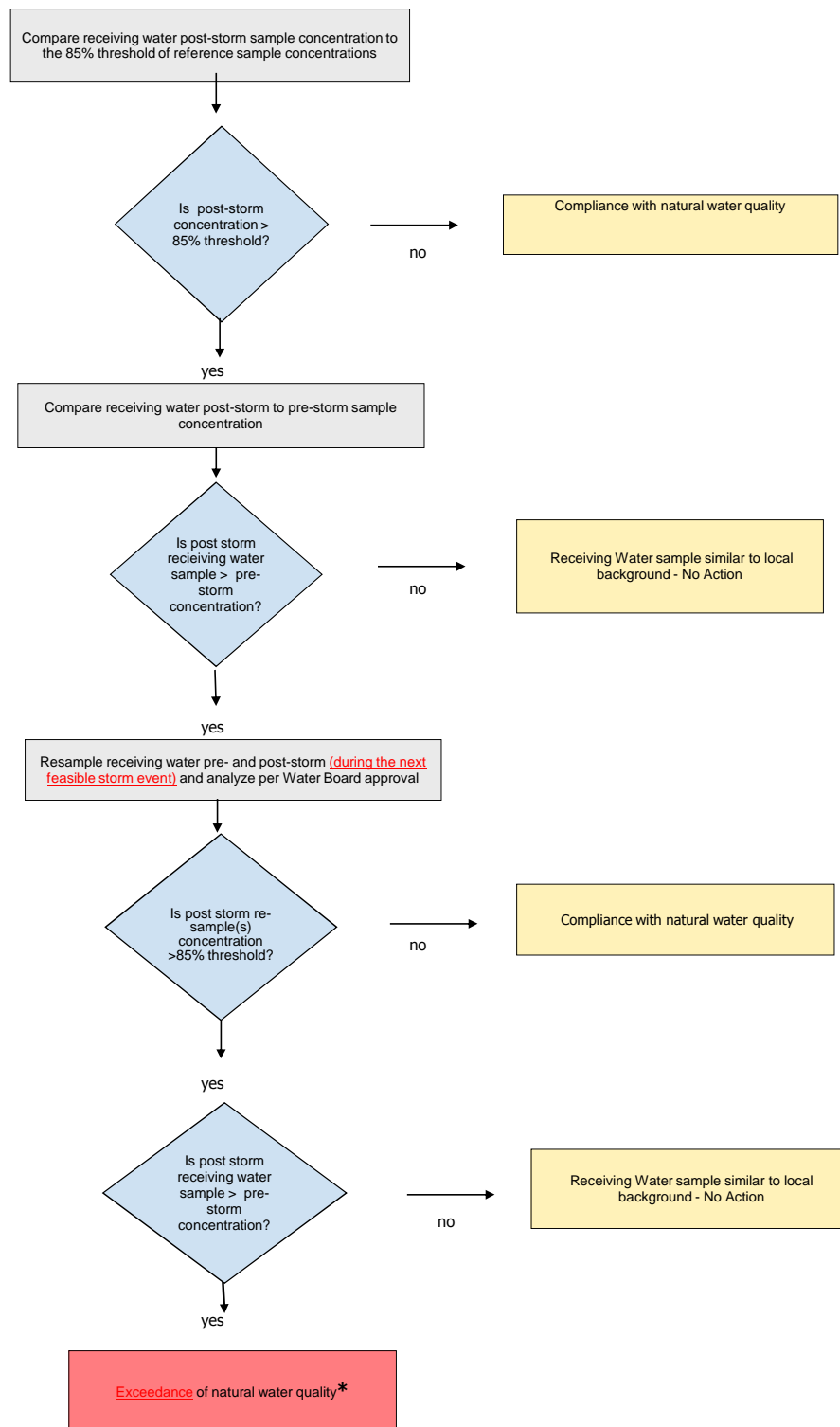
known as the Natural Water Quality Committee. This committee was composed of water quality and ecological experts from southern California. Over several years, the committee met and considered how to define “natural water quality” so that water quality criteria could be created that would enable determinations of whether stormwater discharges to ASBS were causing an undesirable “alteration of natural water quality.”

Ultimately, the Natural Water Quality Committee determined that natural water quality could be generally characterized by an absence of significant amounts of the following:

1. *Man-made constituents (e.g., DDT),*
2. *Other chemical (e.g., trace metals), physical (temperature/thermal pollution, sediment burial) and biological (e.g., bacteria) constituents at levels that have been elevated due to man’s activities above those resulting from the naturally occurring processes that affect the area in question, and*
3. *Non-indigenous biota (e.g., invasive algal bloom species) that have been introduced either deliberately or accidentally by man.*

The Committee also recognized that the oceans are no longer free from man-made constituents with trace contaminants being measureable worldwide. Consequently, it considered that defining natural water quality with specified constituent concentrations was impractical, and recommended comparisons of ASBS water quality to water quality measured at reference sites (i.e., in the ocean at the mouths of streams whose watersheds were >90% undeveloped land) in order to gauge whether stormwater discharges cause “alteration of natural water quality.” Moreover, the Committee established a statistical indicator of natural water quality based on the concentrations of pollutants at reference sites. The Committee recommended that ocean concentrations of a pollutant at a stormwater discharge in an ASBS would be considered to have altered natural water if it exceeded the 85<sup>th</sup> percentile of measurements of that pollutant in reference site samples.

To determine compliance with natural water quality, the Special Protections require measurement of numerous constituents in designated stormwater discharges, pre-storm ocean receiving water at these discharges, storm ocean receiving water at these discharges, and storm ocean receiving water at the mouths of reference streams. A total of six storms were to be sampled over several years during the initial phase of monitoring required by the Special Protections. The decision as to whether ASBS water quality does not conform to natural water quality requires several steps, as indicated in Figure 1 (Attachment 1 to the Special Protections). Because the ASBS beneficial use is for the protection of marine life, the point of compliance was established as the ocean receiving water and not the stormwater discharge.



\* = When an exceedance of natural water quality occurs, the participants must comply with section I.A.2.h. Note, when data are available, end-of-pipe discharge concentrations will be considered by the Water Boards in making this determination.

**Figure 1. Special Protections flowchart to determine compliance with natural water quality.**

The Compliance Flowchart (Flowchart; Figure 1) relies on comparisons between pre-storm ocean concentrations and post-storm (storm) concentrations and comparisons between the storm concentrations and the reference 85<sup>th</sup> percentile threshold. If a constituent in a storm sample exceeds the 85% threshold, the storm concentration is to be compared to the pre-storm concentration. If the storm concentration is greater than the pre-storm concentration, sampling must be repeated during the next feasible storm. If the constituent concentration in the next storm sample still exceeds the 85<sup>th</sup> percentile threshold and is greater than the concentration in the pre-storm sample, an exceedance of natural water quality is declared. Samples with slightly higher concentrations than the 85<sup>th</sup> percentile threshold would apparently be considered to have exceeded natural water quality, even if their concentrations fall within the range of all reference values. Although the role of discharge samples in determining an exceedance (i.e., compliance) is not specified in the flowchart, the footnote to the chart suggests that Water Boards would consider “end-of-pipe effluent concentrations” in making a determination of whether water quality is in compliance with natural water quality.

If an exceedance of natural water quality is determined, corrections must be proposed in a Compliance Plan that each participating entity submitted in September 2015. The Compliance Plan was required to include management practices to ensure that either 1) the identified constituent is reduced below the Ocean Plan instantaneous maximum allowable concentration in storm ocean samples or 2) the load to the ocean of the target constituent is reduced by 90% from all sources under the authority of the responsible party. Due to prevailing drought conditions that limited the available data before the Compliance Plan due date, State Board Staff granted the Central Coast ASBS participants leeway in providing complete details of planned best management practices, and an opportunity to re-submit updated final compliance plans by September 2016.

The Ocean Receiving Water and Reference Area Monitoring Program described in the Special Protections required the collection of at least three samples from each site for each storm season over at least two years (i.e. six samples from each site) in order to characterize the receiving water condition and to establish the 85<sup>th</sup> percentile threshold. For this reason, any determination of exceedance based on single samples before that program was complete and the natural water quality definition was established would have been premature. This final report summarizes the characterization of program ASBS receiving water samples and the full complement of reference data providing the program participants the information needed to complete the flowchart to evaluate exceedances of natural water quality.

In reviewing this final report and the final program data, if a participant determines that their discharge is causing or contributing to an exceedance of natural ocean water quality in the ASBS, they will submit a report to the State and Regional Water Board within 30 days. The individual reports will identify additional management practices to be implemented as outlined in Section I.A.2.h of the Special Protections.

Because the 85<sup>th</sup> percentile thresholds are statistical estimates derived from the available population of reference values, which differ among sub-regions and vary naturally over time, the thresholds also have uncertainty associated with them, as the “true” 85<sup>th</sup> percentile is assumed to fall within a range of estimates (Smith, 2002). Accordingly, a conservative approach to determining exceedances may be justified by focusing on the constituents with significant

associations between discharges and higher corresponding concentrations in receiving water, those with the greatest rates of exceedances (e.g., >15% of samples; see Schiff et al, 2016), those with the greatest magnitudes of exceedances (e.g., >15% above the 85<sup>th</sup> percentile threshold), and those trace metals that diverge from the relationships between suspended sediments and constituent concentrations observed in reference samples. Moreover, an effort has been made to identify those constituents with the most likely anthropogenic sources and that can be characterized as waste following the precedent of Singarella and Richardson (2008).

## **2.2 Central California Regional Program Development**

In 2007 and 2008, ASBS participants on the Monterey Peninsula began meeting to consider options for designing a monitoring program to satisfy anticipated Special Protection requirements. These meetings ultimately included representatives from Marin County, San Mateo County, Monterey County, City of Monterey, City of Pacific Grove, Carmel-by-the-Sea, Monterey Bay Aquarium, Hopkins Marine Station, Pebble Beach Company, California State Parks, Caltrans, US Air Force Pillar Point facility, and National Park Service Point Reyes National Seashore. Support was expressed for a regional approach that would incorporate or leverage other regional monitoring efforts to help address larger water quality management issues of interest to stakeholders other than just ASBS stormwater discharges. State Board staff encouraged a proactive regional approach for developing a monitoring program, implying that there could be more flexibility before the Special Protections were formally adopted.

When the State Board formally adopted the Special Protections they included incentives for participants to organize themselves into regional monitoring groups. A group that ultimately included Marin County, San Mateo County, Monterey County, City of Monterey, City of Pacific Grove, City of Carmel-by-the-Sea, Monterey Bay Aquarium, Hopkins Marine Station, Pebble Beach Company, and Caltrans executed a Memorandum of Agreement to jointly fund a regional monitoring program, and a final Scope of Work for the Central California ASBS monitoring program (Appendix A) was negotiated with the State Board by late November 2012.

In February 2013, the consulting firm Applied Marine Sciences was selected to conduct the monitoring program. Based upon the progress made by the Central California regional ASBS group in organizing themselves and getting a monitoring program approved, as well as the drought conditions that were developing at that time, State Board staff gave permission for sampling to begin with the 2013 – 2014 storm season.

The State Board provided grant funding to support reference site sampling during the first year of the program. This funding came through a grant to Southern California Coastal Water Research Program (SCCWRP), which was then divided among the three regional monitoring efforts (northern, central and southern California). Schiff et al (2016) includes evaluations of reference site water quality in all three regions, with the understanding that some regions had not yet completely characterized reference conditions.

### 3.0 Report Organization and Scope

This report analyzes the results from the 2013–2016 storm seasons. Program participants are in the process of finalizing Compliance Plans intended to address maintenance of natural water quality within their respective ASBS. The notification to State and Regional Water Boards of sites that have receiving water quality outside of natural water quality thresholds will be directly from participants to the Water Board. Accordingly, randomly assigned letter are used to identify specific discharges that are discussed in this report. All data from this program will be delivered digitally to the California Environmental Data Exchange Network (CEDEN) by the end of October 2016, where it will be publically available. This report focuses on whether there are spatial patterns in constituent concentrations in reference and pre-storm samples that could inform discussions of what constitutes natural water quality, whether receiving water is being altered regardless of whether constituent concentrations are above or below 85<sup>th</sup> percentile thresholds, and whether there are associations among constituents that could help determine if discharge constituents have anthropogenic sources and constitute waste. In particular, the following questions are addressed:

1. Are there north-to-south differences in reference conditions?
  - a. The answer to this question could help participants select reference sites that are particularly relevant to the conditions prevailing at their discharge(s).
2. Are there north-to-south differences in Pre-Storm water quality at ASBS sites?
  - a. This question examines conditions at ASBS receiving water sites approximately 24 hours before storm events in order to determine whether different ambient conditions between sub-regions could affect the number of constituent concentrations measured above the 85<sup>th</sup> percentile threshold. If pre-storm concentrations are elevated in an area, participants in that area have a smaller margin in receiving water quality before concentration are >85<sup>th</sup> percentile threshold.
3. Do storm discharges alter receiving natural water quality?
  - a. Answering this question requires comparing water quality conditions at ASBS sites to water quality at reference sites. The answer to this question can help determine whether or not stormwater discharges are directly responsible for increases in receiving water constituent concentrations that fall above the 85<sup>th</sup> percentile threshold.
4. Are alterations of receiving water quality due to anthropogenic waste?
  - a. The answer to this question can help determine whether any alterations to natural water quality identified in Question 3 could be addressed with management practices.
5. Are marine biological resources being affected by ASBS storm discharges?
  - a. The sole aim of the ASBS beneficial use is ensure water quality necessary to protect important marine biological resources.

In order to obtain answers to these questions, this report focuses on analysis and interpretation of data collected at the large stormwater outfalls prescribed in the Scope of Work (SOW; Appendix A) and compares data from those sites with data from the reference sites (Appendix A). The four ASBS included in this program and all associated sampling sites are distributed along the coastline from Marin County to the southern Big Sur coast (Figure 2).

The line demarking the northern and southern sub-regions was placed geographically, in order to help balance the numbers of samples between sub-regions for subsequent statistical analyses. Its placement makes no assumptions about ambient or receiving water conditions on either side of the line. The northern reference sites span the coastline from San Mateo County into Monterey Bay. Also included in the northern sub-region is Año Nuevo ASBS, which was monitored by Caltrans. Those data and data from other sites sampled by Caltrans in the region covered by the Central California Region Monitoring Program were not analyzed in this report. The southern reference sites are distributed along the open coast from Malpaso Creek to Big Creek. The Little Sur River was originally listed as a reference site in the SOW (Appendix A), but access could not be obtained and Soberanes Creek was substituted in its place. The northernmost ASBS included is Duxbury Reef in Marin County (Figure 3). Along the San Mateo County coastline, Fitzgerald Marine Reserve is the next ASBS to the south (Figure 4). The Monterey Peninsula includes the Pacific Grove ASBS (Figure 5, including the Hopkins Marine Life Refuge) and the Carmel Bay ASBS (Figure 6). The sites along the Pacific Grove ASBS shoreline are the regulatory responsibilities of the City of Monterey, City of Pacific Grove, Monterey Bay Aquarium, and Hopkins Marine Station. The sites in Carmel Bay ASBS are the regulatory responsibilities of Pebble Beach Company, City of Carmel-by-the-Sea, and County of Monterey.

As described in Appendix A, different sampling activities occurred at different sites depending on their designated purpose and the size of the stormwater discharge at the site. State Board staff allowed two sites at sandy beaches in Monterey Bay to serve as background sites for gauging the general conditions of nearshore waters in the bay distant from ASBS. These sites at La Selva Beach and Marina State Beach were credited to the monitoring requirements of the Central California regional monitoring effort with the condition that the sites would not be used to calculate 85<sup>th</sup> percentile reference threshold values. Consequently, they are only discussed relative to data from receiving water samples.



Figure 2. Central California regional ASBS study area.





Figure 3. Duxbury Reef ASBS with monitored discharge indicated.



Figure 4. Fitzgerald Marine Reserve ASBS with monitored discharges indicated.



Figure 5. Pacific Grove ASBS with monitoring sites indicated.





Figure 6. Carmel Bay ASBS with monitoring sites indicated.



## 4.0 Monitoring Methods

Collections were made at numerous sites during a minimum of 6 storms from the following types of samples:

1. ASBS stormwater discharges (discharges) in 2 categories,
  - a. Outfalls 18 – 36 inches
  - b. Outfalls >36 inches (Unless otherwise indicated, discharge samples in this report refer to outfalls >36 inches.
2. ASBS pre-storm ocean receiving water (pre-storm) collected from near discharges
3. ASBS storm ocean receiving water (receiving water) collected in knee-deep water at the point where discharges enter the ocean
4. Reference storm ocean receiving water (reference) at the mouths of coastal reference streams (i.e., streams with <95% human development in their watersheds)
5. Reference samples collected during the dry season
6. Background non-urban samples collected outside ASBS during storms

The following numbers of samples are included in the analyses in this report:

1. Large ASBS discharges - 52 samples from 10 sites
2. Small ASBS discharges – 46 samples from 23 sites
3. Pre-storm samples – 48 samples from 8 sites
4. Receiving water samples – 48 samples from 8 sites
5. Reference samples – 54 samples from 9 sites
6. Reference dry samples – 11 samples from 11 sites
7. Background – 12 samples from 2 sites

All sampling and analytical methods were prescribed by a Quality Assurance Program Plan (AMS, 2014), Sampling and Analysis Plan (AMS, 2013), and Standard Operating Procedures approved following review by the State Board QA Officer. All procedures satisfy the State’s Surface Water Ambient Monitoring Program (SWAMP) requirements and include appropriate data quality objectives. Sampling methods include “clean hands, dirty hands” protocols to minimize sample contamination and compositing samples from multiple discrete grabs of sample water to minimize effects of small-scale temporal or spatial variation. Chemical analyses include the following quality assurance samples: field blanks, laboratory blanks, field duplicates, matrix spikes and matrix spike duplicates, and analysis of certified reference materials or laboratory control samples. Data are submitted to the California Environmental Data Exchange Network (CEDEN). All data underwent a thorough QA evaluation (Appendix B).

The following laboratories performed analyses for data presented in this report:

- California Department of Fish and Wildlife Water Pollution Control Laboratory: PAHs, organophosphate pesticides, and pyrethroid pesticides
- Physis: trace metals in saltwater
- Marine Pollution Studies Laboratory: mercury
- Alpha Labs: fecal indicator bacteria (FIBs) for sites in Marin and San Mateo counties
- Monterey Bay Analytical Services: FIBs from all other sites, nutrients, and TSS

- Granite Canyon: toxicity
- Axys Analytical: chlorinated pesticides, PCBs, PBDEs, and acid-positive pharmaceuticals in mussels

One element of the program involved collaboration with the Central Coast Long-term Environmental Assessment Network (CCLEAN). The CCLEAN mussel bioaccumulation program has measured contaminants in resident mussels at 5 locations along the central California coast for 13 years. Initially, samples were collected twice per year, in the wet season and in the dry season. In 2008, sampling frequency was reduced to annually in an index period during the wet season, when the highest concentrations of contaminants had been measured in previous years. As part of this collaboration, State Board staff required addition of a mussel bioaccumulation reference site at Point Reyes and also required the addition of acid-positive pharmaceuticals to the CCLEAN analyte list, based on previous detection of an antibiotic in mussels from Point Reyes.

Loads per storm and loads per acre for each storm were calculated for the discharges that were associated with receiving water monitoring. These calculations were made using catchment areas, percentage impervious area in each catchment and rainfall from the nearest available precipitation gauge. The rainfall was multiplied by the amount of impervious area to arrive at an estimate of storm-specific runoff. The runoff volume was then multiplied by the concentration of each constituent measured in the corresponding discharge samples.

Analysis of trace metals presented some problems during the first year of the program. The laboratory that was originally contracted to provide trace metal analyses eventually determined that its high resolution Inductively Coupled Plasma Mass Spectrometry (ICP-MS) machine had become degraded to the point that it could not provide accurate measurements for saltwater samples. This problem was identified in early 2014 when there was sufficient sample material remaining from all samples collected after December 2013 so that those samples could be transferred to another laboratory for analysis. Freshwater samples (i.e., discharges) were not affected and neither was analysis of mercury. Concerns that the degradation of the high resolution ICP-MS could have begun before it was clearly apparent resulted in a decision to disregard saltwater trace metal data from samples collected during October and November 2013, except for mercury, which was analyzed with a different instrument.

Another data presentation issue concerned how to include non-detected concentrations in data analysis and compare them to the 85<sup>th</sup> percentile threshold. There are various conventions for handling non-detected concentrations (Helsel, 2006; Lee and Helsel, 2005; Kayhanian et al, 2002; EPA 2004), including non-detects represented as 0, non-detects represented as ½ the method detection limit, and non-detects represented as the detection limit. Each of these approaches has its proponents and is preferable over the others, depending on the purpose of the sampling program. There are also a number of ways to estimate the mean value of a measurement in a population of samples with non-detected values. The ASBS Special Protections present unique challenges in determining how to handle non-detected values. In particular, it is a regulatory program that determines compliance based on comparisons of single samples to a threshold that is statistically derived from a set of reference values.

A feature of many chemical analyses is that general sample properties, such as the dissolved organic matter, can affect detection limits (Bruzzoniti et al, 2000; Hajšlová and Zrostlíková, 2003; Niessen et al, 2006; Shahin, 2004; Yamamoto et al, 2003), these properties are generally termed “matrix effects.” Matrix effects especially affect the analysis of organic compounds. For example, lower detection limits are often achievable in samples that have less dissolved organic material in them. This means that the reported method detection limit for each analyte is not necessarily a static value. It can vary by location and by sampling event, depending on ambient conditions. If non-detected values were revised to the method detection limit or a fraction thereof, a non-detected concentration could exceed the 85<sup>th</sup> percentile threshold because that particular sample had a higher detection limit. This exact situation arose in this program in the analysis of PAHs. Consequently, it was determined that non-detected values would be set to 0 in order to avoid the situation in which an exceedance is caused by a non-detected concentration. Because individual organophosphate and pyrethroids pesticides were infrequently detected, they were considered as summed concentrations for each type of pesticide.

A number of statistical procedures were used to analyze data. These procedures included matched-pair *t*-tests, linear regressions, correlations, nonparametric tests for differences (Wilcoxon), analysis of variance, and *a posteriori* tests (each pair Student’s *t*-test) to determine between which groups of samples statistically significant differences occurred. Because tests were not performed to confirm that the data satisfied assumptions for parametric statistical tests, the Wilcoxon test was used for confirmation, when available. Nevertheless, studies confirm the robustness of analysis of variance (ANOVA) to violations of the assumption that data have a normal distribution (Schmider et al, 2010). All statistical procedures were run using JMP statistical software (SAS Institute Inc., 100 SAS Campus Drive, Cary, NC 27513-2414, USA).





## 5.0 Findings

### **5.1 Question 1: Are there north-to-south differences in reference conditions?**

An important consideration in comparisons of reference water quality between northern and southern areas is whether similar storm conditions were sampled throughout the region. If there are north-to-south differences in ambient and reference constituent concentrations, an inability to sample large storms in some areas could bias the calculated 85<sup>th</sup> percentile threshold. In fact, there were several large storms during which safe access was not possible for sites along the Big Sur coast, requiring that smaller storms be sampled in this area when smaller waves and stream flow allowed access. Consequently, effects of these large storms, while they were captured at northern reference sites, were not captured for the Big Sur coast. ANOVA was performed on each constituent to determine whether there were significant differences in concentrations between reference sites grouped for the northern and southern portions of the study area.

There were clear differences between northern and southern sub-regions in constituent concentrations (Table 1). Every trace metal, except silver, exhibited significant differences between sub-regions, with northern sites having higher concentrations. The results for lead and zinc were not confirmed by the Wilcoxon test, but both had higher means in the north than in the south. In fact, all constituents had higher mean concentrations in the north than in the south, with unambiguous significant differences also for fecal coliform, *E. coli*, and the numerical endpoint for the kelp germination toxicity test. A higher numerical endpoint equates to a higher percentage of kelp germination. These results indicate that ocean waters sampled during storms at the mouths of reference streams in the northern sub-region have higher concentrations of these constituents than do ocean waters sampled at reference sites in the southern sub-region, as reflected in calculated 85<sup>th</sup> percentiles for each constituent (Table 2). This result could be due to geological differences that manifest as different trace metal concentrations, differences in the vegetation coverage in the reference watersheds that could create different percolation rates for storm runoff or differences in ambient ocean concentrations, or the aforementioned differences in accessibility, therefore excluding large storm events from the southern reference data. Regardless of the reasons for these north-to-south differences, they will inform discussions between participants and the Water Board regarding determinations of the appropriate reference sites for setting the 85<sup>th</sup> percentile threshold. All subsequent comparisons to 85<sup>th</sup> percentile thresholds in this report are based on the overall 85<sup>th</sup> percentiles.

A follow-up ANOVA was performed to determine whether there were north-to-south differences in constituent concentrations in ocean water at reference sites that were not affected by storm runoff (i.e., reference dry weather samples). This test found no differences between sub-regions, although its power was limited by a small sample size (i.e., 3 samples in the north and 6 samples in the south). This result lends credence to the idea that exclusion of large storm data from southern reference sites affected the significant north-south difference in reference site data.

Another important aspect of data from reference sites is the relationships among constituents that could suggest patterns indicative of natural sources, as opposed to anthropogenic sources of measured constituents. This consideration is especially important for trace metals because they are ubiquitous, frequently detected and are found in natural geological formations and soils. Exploration of constituent relationships began with tests to determine whether there were correlations between trace metal concentrations and total suspended solids (TSS) in reference samples.

**Table 1. Results of sub-regional comparisons of constituent concentrations at reference sites using analysis of variance and a non-parametric Wilcoxon test.**

Constituent	ANOVA		Wilcoxon	Result <sup>2</sup>
	$R^2$	$p$	$p^1$	
Arsenic	0.16	0.005	0.013	N > S
Cadmium	0.20	0.001	<0.001	N > S
Chromium	0.09	0.035	0.002	N > S
Copper	0.11	0.019	0.021	N > S
Lead	0.12	0.015	0.172	N ≥ S <sup>3</sup>
Nickel	0.13	0.010	<0.001	N > S
Mercury	0.13	0.009	0.045	N > S
Selenium	0.11	0.018	0.013	N > S
Silver	0.00	0.910	0.476	N = S
Zinc	0.11	0.018	0.136	N ≥ S <sup>3</sup>
TSS	0.10	0.018	0.004	N > S
Oil & Grease	- <sup>4</sup>	-	-	-
Fecal Coliform	0.13	0.009	0.001	N > S
<i>Enterococcus</i>	0.05	0.092	0.008	N ≥ S <sup>3</sup>
<i>E. coli</i>	0.12	0.011	0.024	N > S
Nitrate	0.02	0.370	0.363	N = S
Orthophosphate	0.06	0.084	0.074	N = S
Ammonia	0.00	0.796	0.743	N = S
Urea	0.01	0.457	0.445	N = S
Urchin Fertilization NE <sup>5</sup>	0.04	0.162	0.130	N = S
Kelp Germination NE	0.09	0.023	0.002	N > S
Kelp Growth NE	0.00	0.830	0.420	N = S
Mussel Development NE	0.02	0.338	0.441	N = S
Mussel Survival NE	0.01	0.637	0.628	N = S
Sum of PAHs	-	-	-	-
Sum of OPs	-	-	-	-
Sum of Pyrethroids	-	-	-	-

<sup>1</sup> =  $P \leq 0.05$  is statistically significant.

<sup>2</sup> = N is northern sub-region, S is southern sub-region, sub-region on left has the higher mean.

<sup>3</sup> = One test gave a non-significant result.

<sup>4</sup> = Constituent not detected in any sample.

<sup>5</sup> = Numerical endpoint of the test.

**Table 2. Available Ocean Plan water quality objectives and calculated 85<sup>th</sup> percentiles of constituent concentrations for reference sites grouped over the entire region and grouped by northern and southern sub-regions.**

Constituent	Ocean Plan Objective	Overall 85th percentile	Northern 85th percentile	Southern 85th percentile
Arsenic, µg/L	80	1.6410	4.9504	1.5963
Cadmium, µg/L	10	0.0607	0.2407	0.0427
Chromium, µg/L	20	1.7450	13.2756	0.9686
Copper, µg/L	30	1.1115	11.8123	1.0045
Lead, µg/L	20	0.2194	3.0201	0.1775
Mercury, ng/L	400	4.2275	25.9000	3.1560
Nickel, µg/L	50	1.6666	26.8870	0.7471
Selenium, µg/L	150	0.1135	0.3429	0.0767
Silver, µg/L	7	0.6000	0.3730	0.6160
Zinc, µg/L	200	2.6577	31.7608	1.7507
TSS, mg/L	None	24	560.3	19.8
Fecal Coliform, MPN/100ml	400	143	1023.95	83.9
<i>Enterococcus</i> , MPN/100ml	104	229	476.65	188.55
<i>E. coli</i> , MPN/100ml	None	125.5	670.75	84.35
Nitrate, mg/L	None	0.675	1.145	0.6
Orthophosphate, mg/L	None	0.08	0.1635	0.05
Ammonia, mg/L	6	0	0	0
Urea, µg/L	None	10	10.45	4.5
Sum of PAHs, µg/L	0.0088 <sup>1</sup>	0	0.0037	0
Sum of OPs, µg/L	None	0	0	0
Sum of Pyrethroids, µg/L	None	0	0	0

<sup>1</sup> = Ocean Plan objective for 30-day average concentration

When reference samples from the entire project region were considered, all constituents, except silver and urea, were found to be significantly associated with TSS concentrations (Table 3). This association explained 74–99% of the variation in trace metals concentrations, whereas TSS explained only 23–81% of variation in concentrations of fecal indicator bacteria (FIBs), nutrients and polynuclear aromatic hydrocarbons (PAHs). The same patterns were found for reference sites in the northern sub-region with similar  $R^2$  values, except that the association between TSS and *Enterococcus* was not significant. At the southern reference sites, only copper, lead, mercury, zinc, fecal coliform, *E. coli*, nitrate and ammonia were significantly associated with TSS. These results suggest that silver and urea are nearly exclusively found in the dissolved phase throughout the region and that copper, lead, mercury and zinc are primarily found in the particulate phase, throughout the region. The lower number of significant correlations between TSS and other constituent in the south than in the north is probably due to lower

concentrations of TSS and most other constituents in the south (Table 1). The significant associations between TSS and other constituents suggest a background condition, in which constituents could be derived from native soils in the reference watersheds.

**Table 3. Results of regressions between TSS and constituents in sub-regional groups of reference sites.**

Constituent	Overall		North Sub-region		South Sub-region	
	$R^2$	$p^1$	$R^2$	$p$	$R^2$	$p$
Arsenic	0.89	<0.001	0.96	<0.001	0.00	0.893
Cadmium	0.74	<0.001	0.74	<0.001	0.01	0.588
Chromium	0.92	<0.001	0.98	<0.001	0.01	0.589
Copper	0.93	<0.001	0.99	<0.001	0.19	0.014
Lead	0.97	<0.001	0.97	<0.001	0.65	<0.001
Nickel	0.98	<0.001	0.99	<0.001	0.03	0.352
Mercury	0.94	<0.001	0.94	<0.001	0.51	<0.001
Selenium	0.86	<0.001	0.89	<0.001	0.11	0.07
Silver	0.00	0.939	0.00	0.878	0.00	0.914
Zinc	0.99	<0.001	0.99	<0.001	0.82	<0.001
Oil & Grease	<sup>2</sup>	-	-	-	-	-
Fecal Coliform	0.44	<0.001	0.39	0.006	0.16	0.017
<i>Enterococcus</i>	0.23	<0.001	0.19	0.066	0.10	0.060
<i>E. coli</i>	0.60	<0.001	0.57	<0.001	0.16	0.019
Nitrate	0.26	<0.001	0.62	<0.001	0.55	<0.001
Orthophosphate	0.81	<0.001	0.82	<0.001	0.08	0.100
Ammonia	0.30	<0.001	0.82	<0.001	0.53	<0.001
Urea	0.00	0.673	0.00	0.920	0.00	0.907
Sum of PAHs	0.35	<0.001	0.31	0.017	-	-
Sum of OPs	-	-	-	-	-	-
Sum of Pyrethroids	-	-	-	-	-	-

<sup>1</sup> =  $P \leq 0.05$  is statistically significant.

<sup>2</sup> = Not detected.

### 5.1.1 Conclusion: Are there north-to-south differences in reference conditions?

There are clear differences between northern and southern sub-regions in constituent concentrations. Every trace metal, except silver, exhibited significant differences between sub-regions, with northern sites having higher concentrations. In the case of the kelp germination toxicity test, there were also higher rates of germination in tests done at northern reference sites than at southern reference sites. There were also differences between northern reference sites and southern reference sites in the associations between total suspended solids (TSS) and various constituents.

These geographic differences in reference water quality should be considered in determining whether a particular ASBS site conforms to natural water quality. The significant associations between TSS and other constituents in reference samples suggest that comparisons using TSS-constituent associations in other sample types (i.e., discharge, pre-storm, receiving water) could help determine whether some constituents in non-reference samples are derived from natural sources, such as native sediments.

## **5.2 Question 2: Are there north-to-south differences in Pre-Storm water quality at ASBS sites?**

Question 1 asked whether reference sites throughout the study region responded similarly to storms. Question 2 seeks to determine whether non-storm concentrations of constituents at ASBS sites were consistent throughout the region. If north-to-south differences in non-storm ambient conditions exist, such differences could mean that receiving water samples in some areas have a smaller margin between pre-storm concentrations and an 85<sup>th</sup> percentile threshold, thus resulting in more values above the threshold than in areas with lower pre-storm concentrations.

The analytical approach to this question was identical to that for Question 1. Pre-storm concentrations of all trace metals (except silver) and TSS were higher in the northern part of the study area than in the southern sub-region (Table 4). Conversely, the concentrations of FIBs, nutrients (except urea), PAHs, organophosphate pesticides, and pyrethroid pesticides were higher in the south, although none of the differences was unequivocally significant.

The reasons for these north-to-south differences are unknown. Differences in soil erodibility and trace metal concentrations, and differing proximities to anthropogenic sources associated with large urban areas are potential causes. Moreover, differences between areas in ocean currents and wave action could also affect differences in ambient conditions. Regardless, these differences in ambient conditions suggest that the study region is not homogeneous. They also provide important context for discussions of ways to achieve natural water quality.

### **5.2.1 Conclusion: Are there north-to-south differences in Pre-Storm water quality at ASBS sites?**

Pre-storm samples have significantly higher trace metal and TSS concentrations at ASBS sites in the northern area of the study region than in the southern area. Concentrations of FIBs, nutrients, PAHs, and organophosphate and pyrethroid pesticides were mostly higher in the south than in the north, but none of the differences was significant in both of the statistical tests used. Potential causes are differences in geology, soil erodibility and trace metal concentrations, and differing proximities to anthropogenic sources associated with large urban areas. These results suggest that, if all discharges were equal, the difficulties of achieving natural water quality would not be the same across the entire study region.

**Table 4. Results of sub-regional comparisons of constituent concentrations in pre-storm samples using analysis of variance and a non-parametric Wilcoxon test.**

Constituent	ANOVA		Wilcoxon	Result <sup>2</sup>
	$R^2$	$p^1$	$p$	
Arsenic	0.14	0.001	0.001	N > S
Cadmium	0.36	<0.001	0.002	N > S
Chromium	0.63	<0.001	<0.001	N > S
Copper	0.15	0.007	0.001	N > S
Lead	0.01	0.44	0.013	N ≥ S <sup>3</sup>
Nickel	0.70	<0.001	<0.001	N > S
Mercury	0.28	<0.001	<0.001	N > S
Selenium	0.10	0.031	0.035	N > S
Silver	0.00	0.646	0.779	N = S
Zinc	0.18	0.003	0.003	N > S
TSS	0.39	<0.001	<0.001	N > S
Oil & Grease	-	-	-	-
Fecal Coliform	0.03	0.238	<0.001	S ≥ N <sup>3</sup>
<i>Enterococcus</i>	0.03	0.235	0.177	S = N
<i>E. coli</i>	0.03	0.216	<0.001	S ≥ N <sup>3</sup>
Nitrate	0.00	0.670	0.802	S = N
Orthophosphate	0.01	0.472	0.291	S = N
Ammonia	-	-	-	-
Urea	0.00	0.802	0.539	N = S
Sum of PAHs	0.01	0.591	0.586	S = N
Sum of OPs	-	-	-	-
Sum of Pyrethroids	-	-	-	-

<sup>1</sup> =  $P \leq 0.05$  is statistically significant.

<sup>2</sup> = N is northern sub-region, S is southern sub-region, sub-region on left has the higher mean.

<sup>3</sup> = One test gave a non-significant result.

### **5.3 Question 3: Do storm discharges alter receiving water quality?**

Answering this question requires a detailed evaluation of data from discharge, pre-storm, and receiving water samples at the 8 ASBS discharges monitored in this program. As the stated point of compliance in the Special Protections is the receiving water, those data receive most of the attention. The 85th percentile threshold that is referenced in the following sections is calculated from the full set of program reference sites. Given that monitoring has demonstrated that there are significant geographic differences in natural water quality at reference sites in this study, the overall 85th percentile does not necessarily reflect local natural water quality at a given ASBS.

There was substantial variation in trace metal concentrations among samples types (Figure 7). Discharge samples were above the maximum reference concentrations of copper, lead, mercury, selenium, and zinc. For all other trace metals, the ranges of concentrations

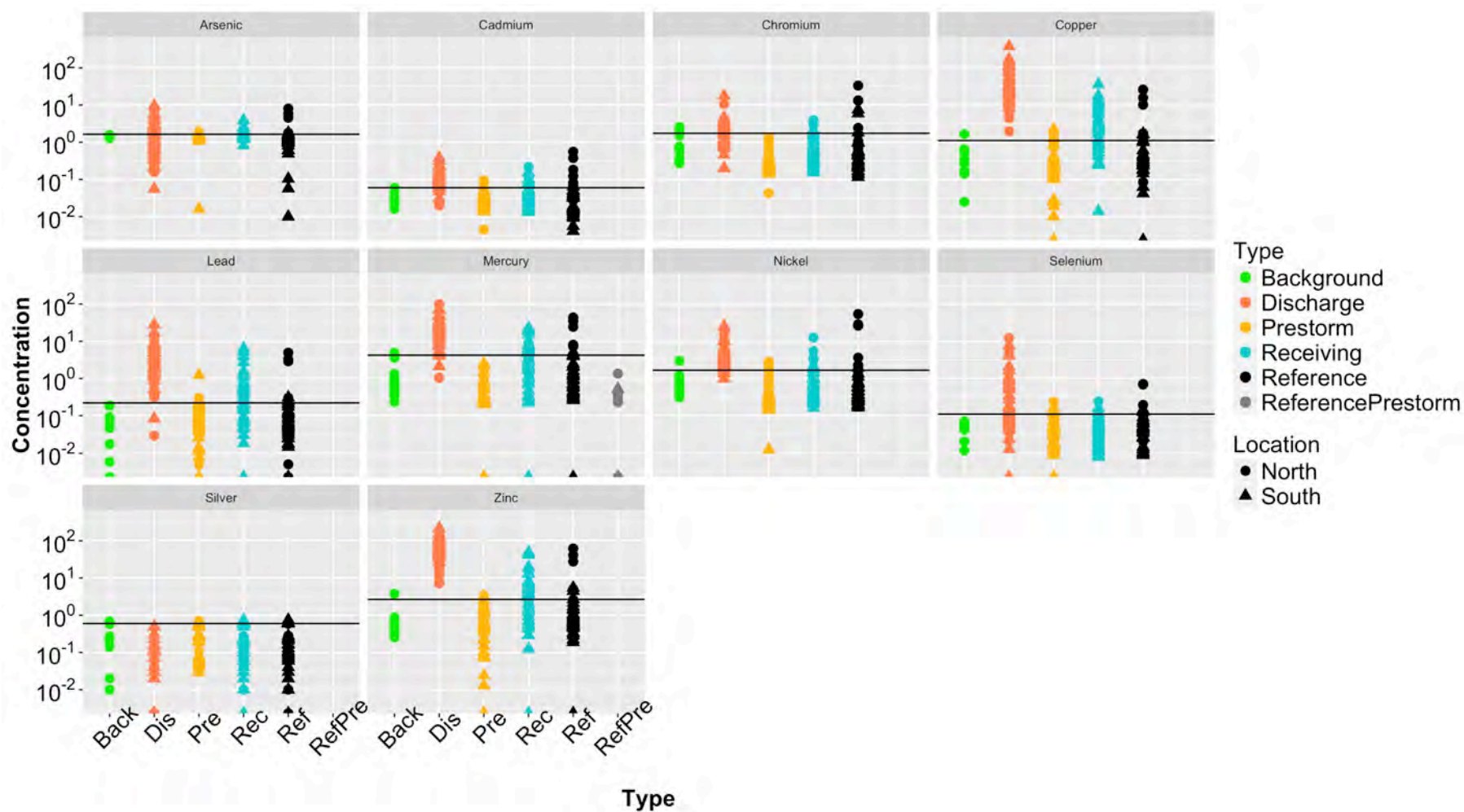


Figure 7. Concentrations of trace metals ( $\mu\text{g/L}$  except for mercury =  $\text{ng/L}$ ) in different sample types. The horizontal line indicates the 85<sup>th</sup> percentile threshold for all reference sites. Circles indicate northern sites and triangles indicate southern sites for each sample type. Reference pre-storm silver samples were collected once in October 2013 and all traces metal data, except mercury, were deleted due to instrumentation problems.



overlapped. In the cases of arsenic, cadmium, chromium, mercury, nickel, and selenium, the maximum reference concentrations were above the maxima for both pre-storm and receiving water samples. Another relevant feature of these data is that numerous reference samples were above the overall 85<sup>th</sup> percentile threshold for all trace metals, except selenium and silver. Maximum concentrations of trace metals at the 2 background sites were usually lower than those at receiving water sites, especially for copper, lead, and zinc, which suggests that the concentrations of these 3 trace metals in ASBS receiving waters were not reflected by storm conditions throughout Monterey Bay nearshore areas.

There was also a large range in FIB concentrations (*E. coli*, fecal coliforms and *Enterococcus* spp.), particularly in discharge and receiving water samples (Figure 8). There was also a large range in bacterial concentrations at the reference sites. Lowest concentrations were detected at the southern reference sites, whereas highest concentrations were detected at the northern reference sites. The highest receiving water concentrations for all bacterial types were greater than concentrations at reference sites. In turn, the highest bacterial concentrations in discharges were substantially above concentrations in receiving waters.

The picture was different with respect to dissolved nutrients (ammonia, nitrate, urea, and orthophosphate) where large numbers of samples had no detectable concentrations within any sample type, including reference sites (Figure 8). Method detection limits were partly responsible for the small number of detections. For example, the method used to analyze ammonia had a high detection limit relative to ambient ammonia concentrations and the 85<sup>th</sup> percentile threshold was zero. Therefore, all receiving water concentrations above zero were above the threshold. For nitrate, urea and orthophosphate, the 85<sup>th</sup> percentiles were above zero. In general, nutrient concentrations in receiving waters were low and within the same range as those measured at the reference sites. With respect to nitrate and orthophosphate, a few of the reference site concentrations were above the highest receiving water concentrations. That was also the case for TSS, where concentrations measured at northern reference sites were above receiving water concentrations and similar to concentrations measured in discharges (Figure 8).

ANOVA was performed using all samples in each sample type to test for differences in constituent concentrations among discharge, pre-storm, receiving water, background, reference pre-storm, and reference samples. Discharge samples had significantly higher concentrations of all chemical constituents, except for arsenic, silver, and TSS (Table 5). In fact, concentrations of silver were significantly lowest in discharge samples. Reference samples had the highest concentrations of TSS, but it was not possible to determine between which sample type differences were significant. Receiving water samples had the second highest concentrations of arsenic, copper, lead, mercury, zinc, FIBs, nitrate, ammonia, and urea, but receiving water samples were not significantly different from reference samples for any constituent.

The numerical endpoints of the 4 toxicity tests also exhibited significant differences among sample types (Table 5), regardless of whether the samples passed or failed. Urchin fertilization was significantly lower in discharge samples than in reference, background, and receiving water samples, although discharge results were not different from reference pre-storm samples. Reference dry weather samples had lower rates of kelp germination than did in background,

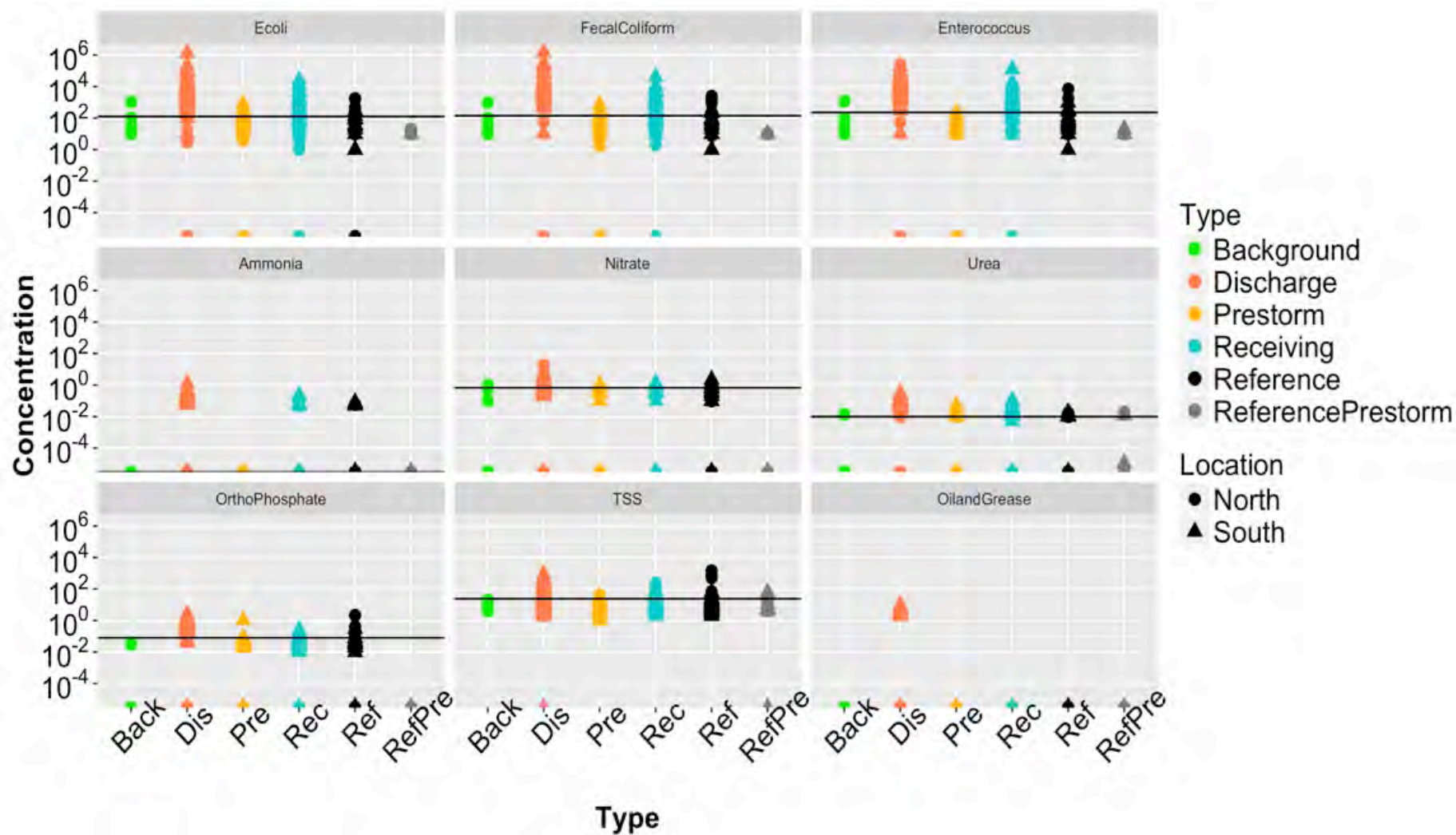


Figure 8. Concentrations of FIBs (MPN/100 ml) and nutrients (mg/L) in different sample types. The horizontal line indicates the 85<sup>th</sup> percentile threshold for all reference sites. Circles indicate northern sites and triangles indicate southern sites for each sample type.

**Table 5. Results from comparisons of constituent concentrations among sample types.**

Constituent	ANOVA		Wilcoxon	<i>A posteriori</i> Result <sup>2</sup>
	$R^2$	$p^1$	$p$	
Arsenic	0.03	0.191	0.053	<u>D Rw Rf P B</u>
Cadmium	0.22	<0.001	<0.001	D <u>Rf Rw P B</u>
Chromium	0.06	0.014	<0.001	<u>D Rf B Rw P</u>
Copper	0.28	<0.001	<0.001	D <u>Rw Rf B P</u>
Lead	0.28	<0.001	<0.001	D <u>Rw Rf P B</u>
Nickel	0.12	<0.001	<0.001	D <u>Rf Rw B P</u>
Mercury	0.42	<0.001	<0.001	D <u>Rw Rf B P Pr</u>
Selenium	0.13	<0.001	<0.001	D <u>Rf Rw P B</u>
Silver	0.13	>0.001	<0.001	<u>B Rf Rw P D</u>
Zinc	0.57	<0.001	<0.001	D <u>Rw Rf B P</u>
TSS	0.03	0.255	<0.001	Rf D Rw Pr P B <sup>3</sup>
Oil & Grease	0.08	0.002	<0.001	D <u>B P Pr Rw Rf</u>
Fecal Coliform	0.07	0.003	<0.001	D <u>Rw Rf B P Pr</u>
<i>Enterococcus</i>	0.12	<0.001	<0.001	D <u>Rw Rf B P Pr</u>
<i>E. coli</i>	0.08	0.001	<0.001	D <u>Rw Rf B P Pr</u>
Nitrate	0.15	<0.001	<0.001	D <u>Rw Rf P B Pr</u>
Orthophosphate	0.21	<0.001	<0.001	D <u>Rf P Rw B Pr</u>
Ammonia	0.19	<0.001	<0.001	D <u>Rw Rf B Pr P</u>
Urea	0.44	<0.001	<0.001	D <u>Rw P Pr Rf B</u>
Urchin Fertilization	0.14	<0.001	<0.001	<u>Rf B Rw Pr D</u>
Kelp Germination	0.26	<0.001	<0.001	<u>B Rw Rf Pr</u>
Kelp Growth	0.03	0.405	0.262	<u>Pr Rf Rw B</u>
Mussel Development	0.07	0.067	0.157	<u>Pr Rf Rw B</u>
Mussel Survival	0.00	0.953	0.805	<u>Rf Rw B</u>

<sup>1</sup> =  $P \leq 0.05$  is statistically significant. If  $p > 0.05$ , there is no statistical difference.

<sup>2</sup> = D is Discharge, P is Pre-storm, Pr is Reference Pre-storm (Dry Weather), and Rf is Reference, and Rw is storm Receiving Water. Sample type on left has the highest mean. There were no results for trace metals in Pr samples. PAHs, organophosphate pesticides and pyrethroid pesticides were detected too infrequently to provide reliable results. Urchin fertilization is the only toxicity test performed in discharge samples and mussel survival was not measured in reference pre-storm samples.

<sup>3</sup> = One test gave a non-significant result

receiving water and reference samples, indicating the presence of toxicity in reference waters in the absence of storm runoff. Neither rates of mussel embryo normal development nor embryo survival differed among reference, receiving water, and background samples.

Differences among sites were observed in the number and percentage of receiving water samples with constituent concentrations above the overall 85<sup>th</sup> percentile threshold (Table 6 and Table 7). There were also several cases in which receiving water concentrations were above the threshold when pre-storm concentrations were equal to or greater than receiving water concentrations, and also cases in which receiving water constituents above the threshold were not detected in the discharge. There were a total of 7 samples across 5 sites whose constituent concentrations in receiving water were above the overall 85<sup>th</sup> percentile threshold and were preceded by higher pre-storm concentrations. Single samples at sites C, F, and G, and 2 samples at site H had higher pre-storm than receiving water concentrations of urea. A single sample at Site D exhibited this pattern for TSS and a single sample at Site F exhibited this pattern for *E. coli*. A single sample at Site A had the same concentrations of nitrate in a pre-storm sample with an equivalent concentration in the receiving water sample. Site H had single receiving water samples that were above the threshold for *Enterococcus* and *E. coli*, with corresponding non-detection in the discharge sample. Site A had 3 samples and Site D had a single sample in which PAHs were detected in receiving water but not in discharge samples. Sites C and D had detections of pyrethroid and organophosphate pesticides, respectively, in single receiving water samples for which there were no detections in the discharge. The sites with the greatest overall percentages of receiving water samples above the overall 85<sup>th</sup> percentile threshold were A (20%), C (19%), D (24%), and F (21%). Site E had the lowest percentage of samples (4%) above the threshold. Across all sites and constituents, 16% of receiving water samples had concentrations of at least 1 constituent above the threshold.

A literal interpretation of the Special Protections flowchart for determining compliance, in which 1 out of 2 samples were above the threshold, suggests that >50% of samples with concentrations above the 85<sup>th</sup> percentile threshold for any given constituent would be interpreted as exceeding natural water quality. Overall, this hypothetical guideline was exceeded for copper, lead, zinc, fecal coliform, *Enterococcus* and PAHs (Table 7). *E. coli* was close to this threshold with 48% of all receiving water samples over the overall 85<sup>th</sup> percentile. Sites A and C had the most constituents (i.e., 11) with ≥50% of values above the overall 85<sup>th</sup> percentile threshold. Next came sites D and F, with 9 constituents with ≥50% of values over the threshold. Sites G, B, H, and E followed with 7, 5, 4, and 0 samples, respectively, over the hypothetical guideline.

In addition to the numbers of receiving water samples with concentrations above 85<sup>th</sup> percentile thresholds, analysis of the relative magnitudes of concentrations above the threshold is informative (Table 8). For example, whereas 39% of all samples were above the 85<sup>th</sup> percentile threshold for arsenic, the average concentration was only 3% above the threshold. Moreover, although 40% of receiving water samples at site H were above the threshold for cadmium, the average concentration of cadmium at that site was 20% below the threshold. Such comparisons can also highlight sites with constituent concentrations very much above 85<sup>th</sup> percentile thresholds. For example, sites D and F had FIB concentrations in receiving water that were above the thresholds in 83–100% of samples (Table 7) and those samples also averaged 2,665–10,598% above the thresholds (Table 8).

**Table 6. Number of samples above overall 85<sup>th</sup> percentile thresholds / number of samples with greater concentrations in receiving water samples than in pre-storm samples.**

Site	Arsenic	Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Selenium	Silver	Zinc	TSS
A	4/4	3/3	3/4	3/4	3/4	2/6	4/5	2/4	0/2	3/5	4/4
B	2/4	1/3	0/5	3/6	3/6	1/5	0/5	1/4	1/4	2/5	1/5
C	4/5	1/6	0/5	4/5	5/6	3/5	0/6	0/2	2/3	5/6	2/6
D	2/4	2/6	1/5	6/6	5/6	4/6	1/3	0/4	1/2	5/6	1/4*
E	0/3	0/1	0/4	0/5	0/5	0/5	0/4	0/2	1/2	0/2	1/5
F	0/2	1/5	1/6	5/6	6/6	2/6	0/5	1/2	1/2	6/6	1/5
G	0/4	1/4	0/5	5/6	1/5	2/5	0/5	0/3	0/0	2/6	1/6
H	1/3	2/4	1/5	1/5	3/4	1/6	2/4	0/3	0/3	2/5	4/6

Site	Fecal Coliform	<i>Enterococcus</i>	<i>E. coli</i>	Nitrate	Orthophosphate	Ammonia	Urea	PAHs	Organophosphate Pesticides	Pyrethroids
A	3/6	3/6	2/4	2/3 <sup>x</sup>	0/1	2/2	0/0	4/4 <sup>+++</sup>	0/0	0/0
B	2/6	4/6	3/6	0/1	1/1	1/1	2/3	2/2	0/0	0/0
C	3/4	3/5	3/4	1/1	0/2	1/1	3/3*	2/2	0/0	2/2 <sup>+</sup>
D	6/6	6/6	6/6	1/3	2/2	1/1	4/4	4/4 <sup>+</sup>	1/1 <sup>+</sup>	1/1
E	0/4	1/5	0/2	1/1	0/1	0/0	0/0	1/1	0/0	0/0
F	6/6	6/6	5/5*	1/1	0/0	1/1	4/4*	3/3	1/1	0/0
G	3/5	4/5	3/5	1/1	3/4	1/1	3/3*	0/0	0/0	2/2 <sup>+</sup>
H	2/5	1/4 <sup>+</sup>	1/4 <sup>+</sup>	0/0	0/2	0/0	1/1 <sup>**</sup>	3/3	0/0	0/0

\* = A single case of a value above the overall 85th percentile threshold being disregarded due to a higher value in the Pre-storm sample.

<sup>+</sup> = A single case of a value above the overall 85th percentile threshold with the constituent not being detected in the discharge sample.

<sup>x</sup> = A single case of a value above the overall 85th percentile threshold with the constituent having equal concentrations in the pre-storm and receiving water samples.

**Table 7. Percentage of samples above overall 85<sup>th</sup> percentile thresholds for constituents in receiving water samples at each ASBS site.**

Site	Arsenic	Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Selenium	Silver	Zinc	TSS
A	80%	80%	60%	60%	60%	33%	80%	40%	20%	60%	67%
B	33%	17%	0%	67%	50%	17%	0%	17%	17%	50%	17%
C	67%	17%	0%	67%	83%	50%	0%	0%	33%	83%	33%
D	33%	33%	17%	83%	83%	67%	33%	0%	17%	83%	17%
E	0%	0%	0%	17%	0%	0%	0%	0%	17%	0%	17%
F	17%	17%	17%	83%	100%	50%	0%	33%	17%	100%	17%
G	0%	0%	0%	83%	17%	33%	0%	0%	0%	50%	17%
H	80%	40%	40%	20%	60%	17%	40%	0%	0%	40%	67%
Overall	39%	23%	17%	60%	57%	33%	19%	11%	15%	58%	31%

Site	Fecal Coliform	<i>Enterococcus</i>	<i>E. coli</i>	Nitrate	Orthophosphate	Ammonia	Urea	PAHs	Organophosphate Pesticides	Pyrethroids	Overall
A	50%	50%	33%	17%	0%	33%	0%	67%	0%	0%	18%
B	33%	67%	50%	0%	20%	20%	40%	33%	0%	0%	12%
C	50%	50%	50%	17%	0%	17%	50%	33%	0%	33%	16%
D	100%	100%	100%	17%	33%	17%	67%	50%	17%	17%	22%
E	0%	17%	0%	17%	0%	0%	0%	17%	0%	0%	3%
F	100%	100%	83%	17%	0%	17%	67%	50%	17%	0%	20%
G	50%	67%	50%	17%	33%	17%	50%	0%	0%	33%	11%
H	33%	17%	17%	0%	0%	0%	17%	0%	0%	0%	11%
Overall	52%	58%	48%	13%	11%	15%	36%	50%	4%	10%	14%

**Table 8. Mean percentage above overall 85<sup>th</sup> percentile thresholds ( $[\text{concentration} - 85^{\text{th}} \text{percentile}] / 85^{\text{th}} \text{percentile}$ ) for constituents in receiving water samples at each ASBS site.**

Site	Arsenic	Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Selenium	Silver	Zinc
A	33%	76%	45%	103%	126%	-17%	196%	3%	-62%	112%
B	4%	-33%	-63%	725%	204%	-43%	-71%	-58%	-62%	51%
C	32%	-3%	-63%	80%	265%	-20%	-68%	-62%	-49%	156%
D	-6%	-20%	-55%	543%	809%	106%	-38%	-65%	-59%	700%
E	-11%	-62%	-89%	-44%	-83%	-93%	-85%	-73%	-56%	-87%
F	-9%	-16%	-59%	307%	617%	46%	-48%	-38%	-56%	468%
G	-17%	-52%	-74%	359%	-28%	35%	-59%	-66%	-87%	9%
H	6%	-20%	-9%	-8%	53%	-25%	-3%	-59%	-80%	-9%
Overall	3%	-18%	-49%	267%	252%	-1%	-27%	-88%	-63%	180%

Site	TSS	Fecal Coliform	<i>Enterococcus</i>	<i>E. coli</i>	Nitrate	Orthophosphate	Urea	PAHs	Organophosphate Pesticides	Pyrethroids
A	240%	156%	158%	303%	-43%	-81%	-100%	NC <sup>1</sup>	0%	0%
B	-26%	276%	336%	292%	-64%	-25%	-10%	NC	0%	0%
C	-38%	656%	119%	414%	-58%	-67%	45%	NC	0%	NC
D	-42%	2895%	2794%	2665%	-28%	-44%	68%	NC	NC	0%
E	-67%	-64%	-53%	-71%	-60%	-92%	-100%	NC	NC	NC
F	-21%	6350%	10598%	5172%	-53%	-69%	298%	NC	0%	NC
G	-39%	4807%	139%	73%	-43%	23%	32%	0%	0%	0%
H	56%	120%	46%	-75%	-65%	-67%	-35%	0%	0%	0%
Overall	8%	1899%	1767%	1097%	-52%	-53%	26%	NC	NC	NC

1 = PAHs detected, but percentage above the threshold is not calculable because 85<sup>th</sup> percentile threshold is 0.

In order to understand the effect that periodically high constituent concentrations can have on the relationship between the percentage of samples above the overall 85<sup>th</sup> percentile threshold and the average magnitude of concentrations above the threshold, examination of data for individual storms is necessary. In the case of arsenic, most values above the threshold were very small in magnitude, with 1 larger excursion above the threshold at each of sites A and C (Figure 9a). Similarly, there were very sporadic receiving water concentrations greater than overall 85<sup>th</sup> percentile thresholds for cadmium, chromium, and mercury (Figure 9b, c, and d) and for nickel, selenium, and silver (Figure 10a, b, and c), with most values below the threshold. Site A had the most samples and highest concentrations above the overall 85<sup>th</sup> percentile threshold for all 7 of these trace metals, except for mercury, which had periodical concentrations much above the threshold at sites D, F, and G (Figure 9d). Site A exhibited high concentrations of arsenic, cadmium, chromium, selenium, and zinc in storm 6 (Figure 9a, b, c, and Figure 10a and b), but no other site had peak concentrations of arsenic, cadmium, chromium, lead, nickel, mercury, selenium or silver in any particular storm.

In contrast to the infrequent occurrence of receiving water concentrations above the overall 85<sup>th</sup> percentile threshold for these 7 trace metals, copper, lead and zinc had frequent and widespread occurrences of concentrations above the threshold (Figure 11a, b, and c). These 3 trace metals have been globally associated with urban storm runoff (Brown and Peake 2006; Göbel et al, 2007; O’Sullivan et al, 2011). The spatial and temporal patterns exhibited by these 3 trace metals were similar to that seen for mercury, with the highest concentrations above the threshold occurring at sites B, D, F, and G for copper and at B, D, and F for lead and zinc. Storm 1 at sites B, D, and F and storm 3 at Site D exhibited peaks for all 3 of these trace metals. None of these peak concentrations appear to be obviously related to the amount of rainfall prior to sampling (Table 9), except perhaps for some trace metals at Site A (Figures 9 and 10).

FIBs also exhibited sporadic receiving water concentrations much above the overall 85<sup>th</sup> percentile threshold at sites D, F, and G (Figure 12). There were also many receiving water samples across all sites that had FIB concentrations near or below the threshold that were essentially invisible compared to the large magnitudes of concentrations above the threshold. The storms with high FIB concentrations at sites D and F corresponded to the same storms that exhibited peaks for copper, lead and zinc.



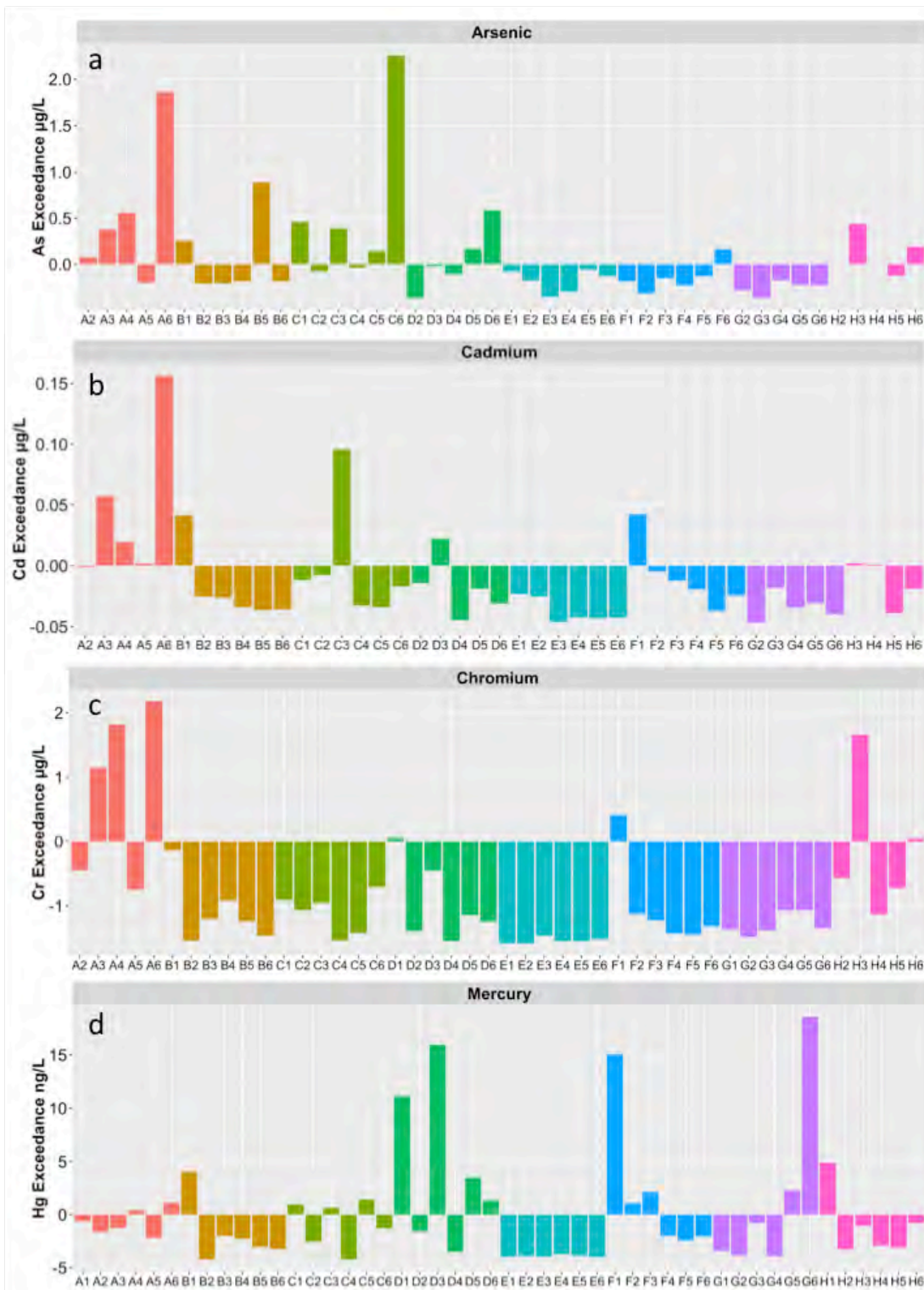
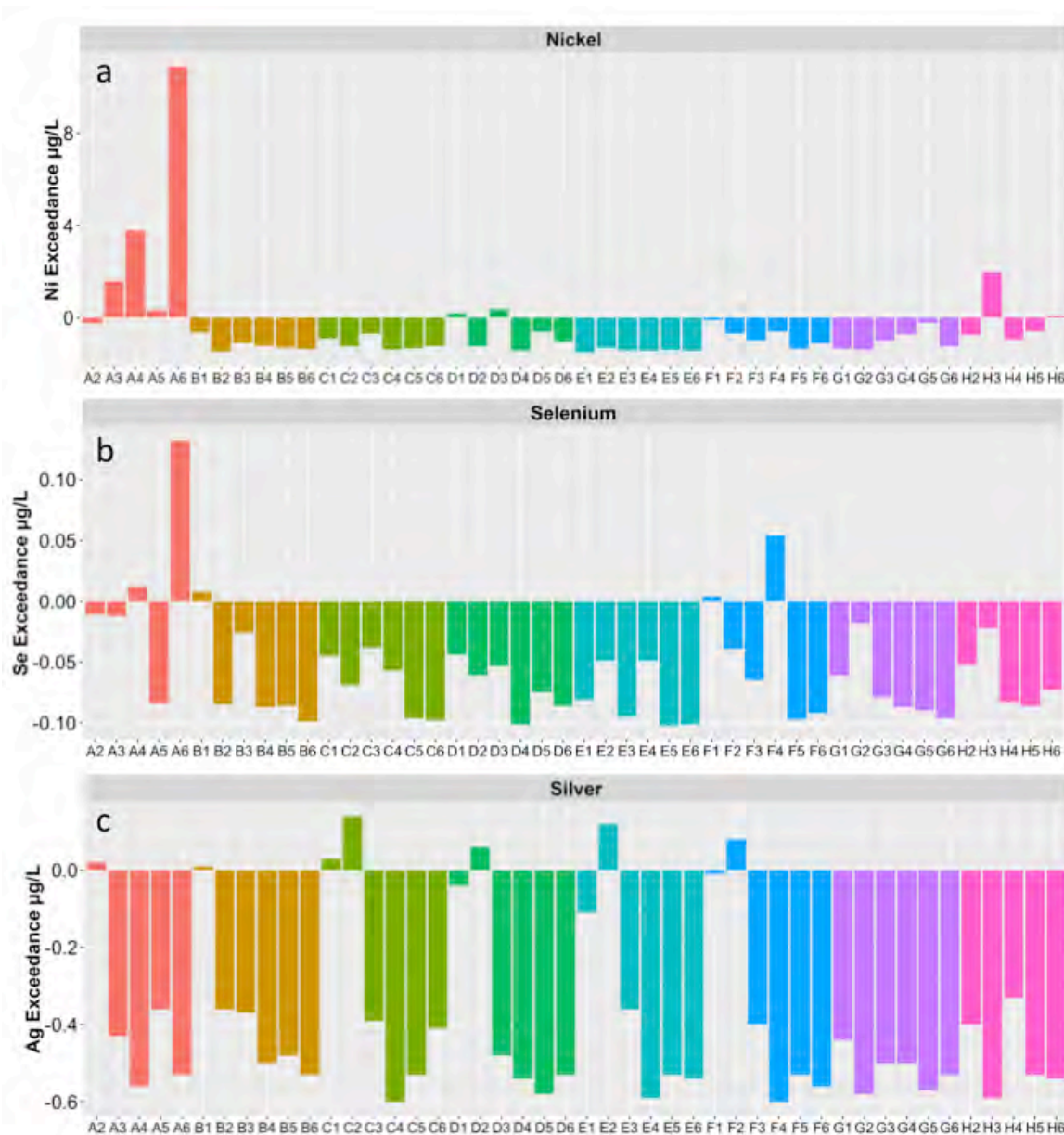


Figure 9. Magnitude of receiving water concentrations for arsenic, cadmium, chromium and mercury above and below the overall 85<sup>th</sup> percentile in receiving water samples during each storm at each site. Letters A–H along the x-axis refer to sites and numbers 1–6 refer to storms. “Exceedance” refers to the concentration above or below the overall 85<sup>th</sup> percentile threshold.



**Figure 10. Magnitude of receiving water concentrations for nickel, selenium, and silver above and below the overall 85<sup>th</sup> percentile in receiving water samples during each storm at each site. Letters A–H refer to sites and numbers 1–6 refer to storms. “Exceedance” refers to the concentration above or below the overall 85<sup>th</sup> percentile threshold.**

Nutrients were also below the overall 85<sup>th</sup> percentile threshold in most receiving water samples (Figure 13). Moreover, there was no apparent coherence among nitrate, orthophosphate, ammonia and urea in their respective temporal patterns of high and low concentrations. Nevertheless, the temporal patterns in TSS at Site A (Figure 13e) closely corresponded to those for arsenic, cadmium, chromium, nickel, and selenium (Figure 9a, b, c, and Figure 10a and b) at that site.

These results reveal no consistent patterns across sites in receiving water concentrations above the overall 85<sup>th</sup> percentile threshold. Moreover, the temporal patterns are inconsistent among constituents and sites, with no obvious relationship to rainfall.

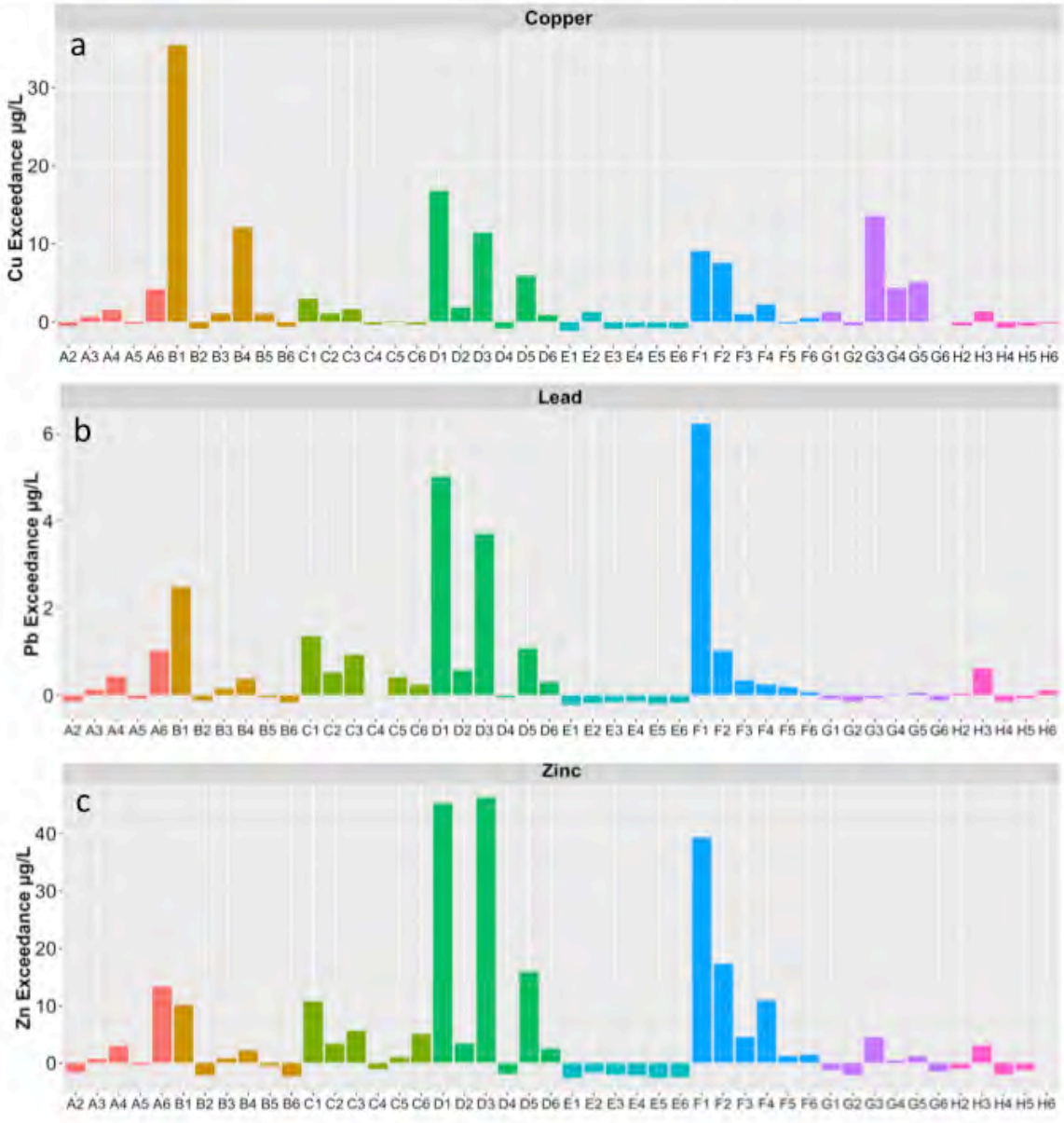
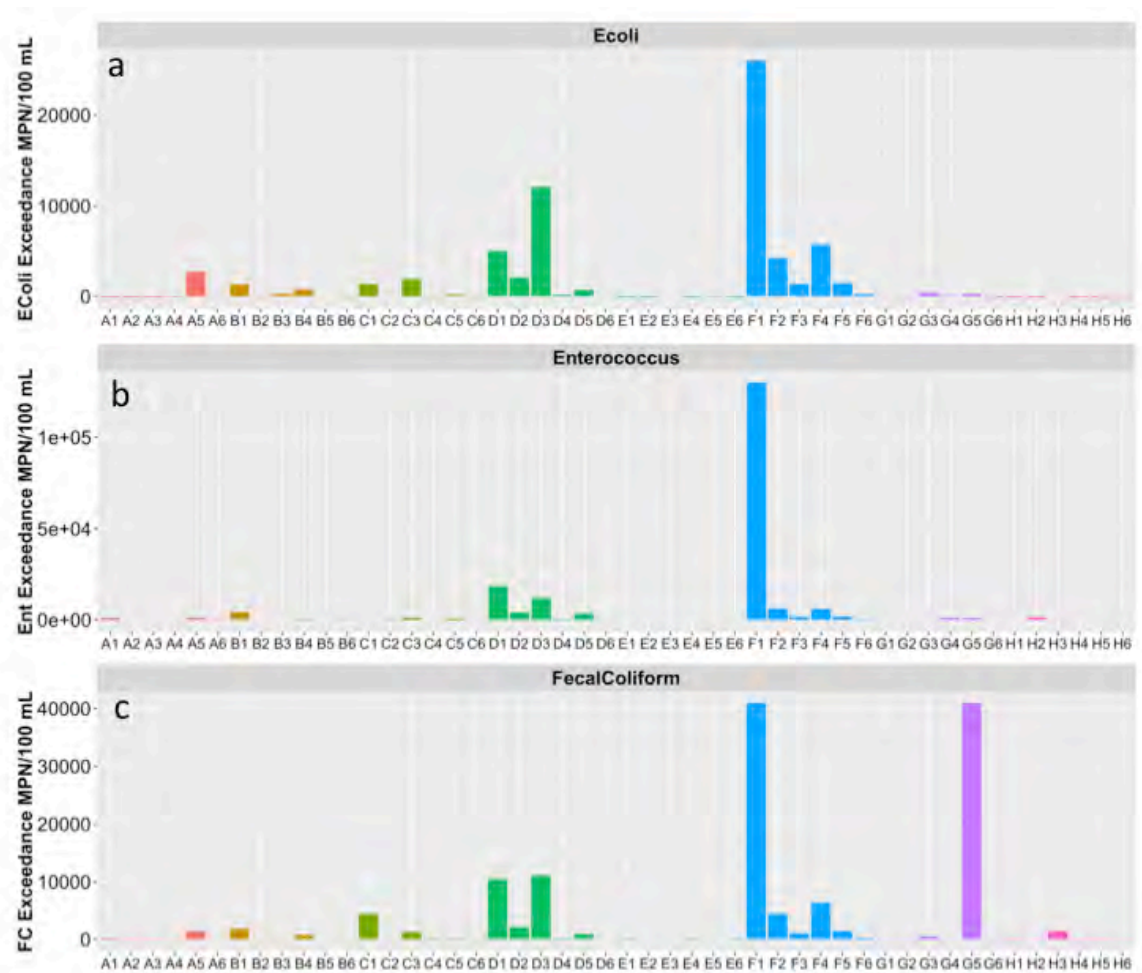


Figure 11. Magnitude of receiving water concentrations for copper, lead and zinc above and below the overall 85<sup>th</sup> percentile in receiving water samples during each storm at each site. Letters A–H along the x-axis refer to sites and numbers 1–6 refer to storms. “Exceedance” refers to the concentration above or below the overall 85<sup>th</sup> percentile threshold.

**Table 9. Rainfall for each storm prior to sample collection at each site (inches).**

Storm	Site							
	A	B	C	D	E	F	G	H
1	0.34	0.3	0.8	0.27	0.37	0.66	0.1	0.29
2	0.2	2.6	0.07	.013	0.1	0.09	0.35	.013
3	0.1	0.42	3.85	3.69	2.25	3.67	0.36	0.17
4	0.85	0.67	0.33	0.69	0.36	0.33	0.36	.063
5	0.64	2.28	0.74	0.93	0.48	0.68	0.69	0.33
6	1.83	0.37	0.94	2.41	2.28	0.89	2.28	1.08



**Figure 12. Magnitude of receiving water concentrations for a) *E. Coli*, b) *Enterococcus* and c) fecal coliform, above and below the overall 85<sup>th</sup> percentile in receiving water samples during each storm at each site. Letters A–H along the x-axis refer to sites and numbers 1–6 refer to storms. “Exceedance” refers to the concentration above or below the overall 85<sup>th</sup> percentile threshold.**



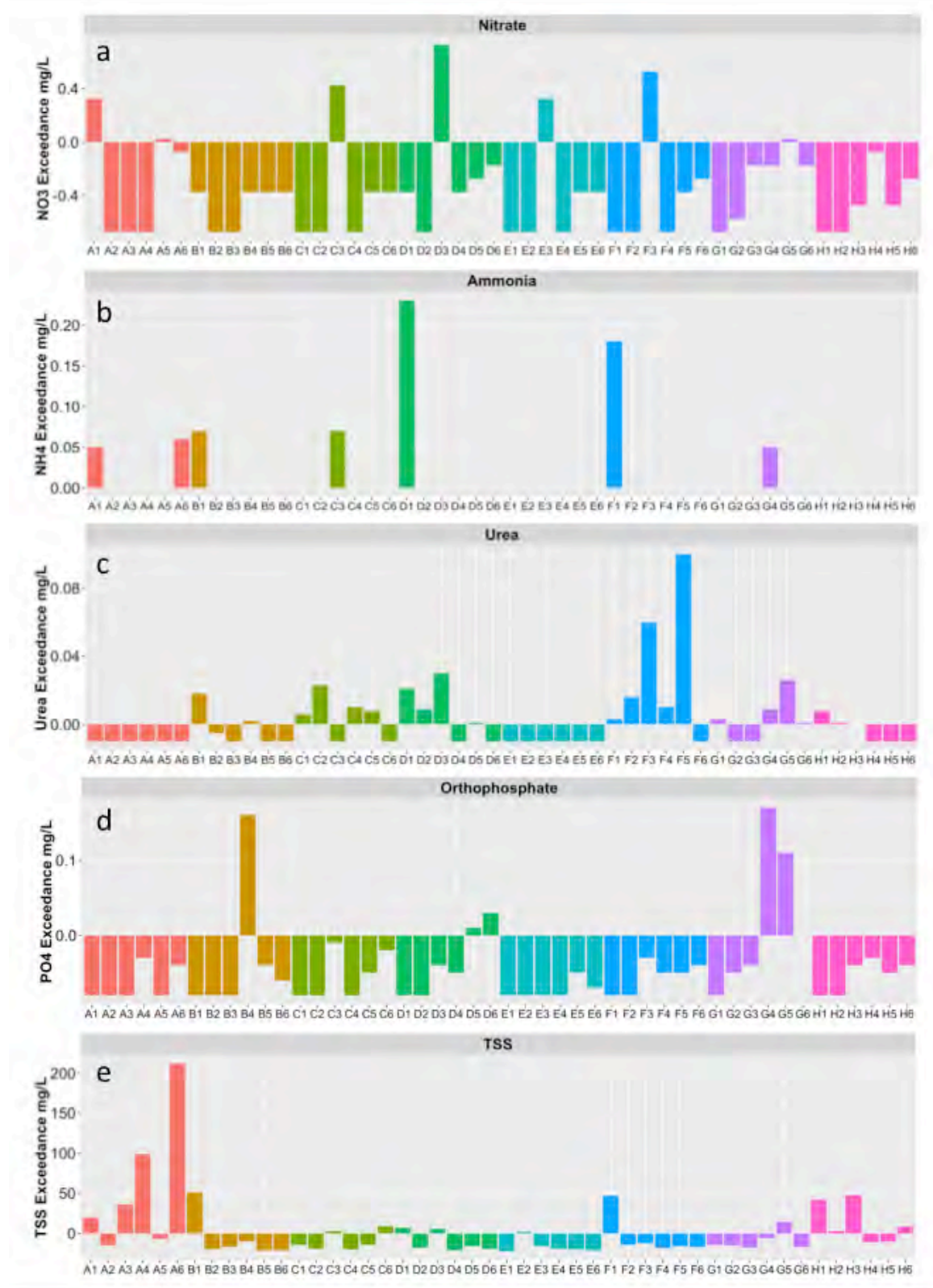


Figure 13. Magnitude of receiving water concentrations for a) nitrate, b) ammonia, c) urea, d) orthophosphate, and e) TSS above and below the overall 85<sup>th</sup> percentile in receiving water samples during each storm at each site. Letters A–H along the x-axis refer to sites and numbers 1–6 refer to storms. “Exceedance” refers to the concentration above or below the overall 85<sup>th</sup> percentile threshold.

ANOVA was used to test for differences among groups of sample types. ANOVA compares the variation within sample types to the variation between sample types. If there is high variation within sample types compared to variation between sample types, ANOVA returns a non-significant result. Consequently, another test was performed to determine whether there were small, but systematic differences between pre-storm and receiving water samples collected in the same storm at each site. The matched-pair test is often performed on test subjects in drug trials in which the ability of a drug to affect a measurable attribute, such as blood pressure or heart rate, is being tested. It compares a before-drug measurement with an after-drug measurement on each subject. In our case, we compared the before-storm with the after-storm constituent concentrations, without considering whether the receiving water concentrations were above or below the 85<sup>th</sup> percentile threshold.

The matched-pair test revealed that there were significant increases in all constituents, except selenium, silver, *Enterococcus*, nitrate, orthophosphate, the sum of pyrethroid pesticides, and the sum of organophosphate pesticides during storms when all sites were tested together (Table 10). Thus, the concentrations of arsenic, cadmium, chromium, copper, lead, nickel, mercury, zinc, TSS, fecal coliform, *E. coli*, ammonia, urea, and PAHs increased in receiving water samples overall during the storms that were sampled.

Another matched-pair test was performed within each site to determine whether sites differed in the constituents that increased in receiving water samples (Table 11). Site B had the fewest constituents with statistically higher concentrations in receiving water samples than in corresponding pre-storm samples; only nickel and *E. coli* exhibited increases at Site B. Sites A and H had significantly higher receiving water concentrations of 3 constituents, cadmium, mercury, and *Enterococcus* and chromium, zinc, and TSS, respectively. Sites E and F each had 4 constituents with higher receiving water concentrations, lead, mercury, fecal coliform, *Enterococcus* and copper, nickel, mercury, and zinc, respectively. Sites C, D, and G each had 8 constituents with significantly higher concentrations in receiving water samples as follows: C) arsenic, chromium, copper, lead, nickel, mercury, zinc, and *Enterococcus*; D) cadmium, chromium, copper, lead, nickel, mercury, zinc, and *Enterococcus*; G) chromium, copper, lead, nickel, zinc, *Enterococcus*, *E. coli*, and orthophosphate.

These results indicate that ASBS sites with high percentages of receiving water constituents above the overall 85<sup>th</sup> percentile threshold do not necessarily exhibit significant increases in receiving water samples from pre-storm samples. For example, a comparison of Table 7 with Table 11 reveals that there is no significant relationship between pre-storm and receiving water concentrations of arsenic at Site A, where 80% of the receiving water samples were above the threshold. At this site there were also no significant increases for cadmium, copper, lead, nickel, or zinc, all of which were above their respective thresholds in 60–80% of samples. Conversely, Site B exhibited significantly increased concentrations of nickel in receiving water samples, but none of its samples were above the overall 85<sup>th</sup> percentile threshold for nickel. The matched-pair results tell us that increased concentrations of some constituents at some sites occur during storms. They do not tell us whether the discharges or some other feature of storms (e.g., resuspension of fine sediment particles and organic material due to wave action) are causing the increases.

**Table 10. Results from matched-pair (pre-storm vs. receiving water) statistical tests to determine whether receiving water concentrations were higher than pre-storm concentrations for each constituent across all ASBS sites.**

Analyte	Mean Difference (in units of measure)	$p^1$
Arsenic, $\mu\text{g/L}$	0.213	0.007
Cadmium, $\mu\text{g/L}$	0.016	0.001
Chromium, $\mu\text{g/L}$	0.541	<0.001
Copper, $\mu\text{g/L}$	3.717	<0.001
Lead, $\mu\text{g/L}$	0.672	<0.001
Nickel, $\mu\text{g/L}$	0.688	0.002
Mercury, $\mu\text{g/L}$	3.549	<0.001
Selenium, $\mu\text{g/L}$	0.007	0.175
Silver, $\mu\text{g/L}$	0.023	0.169
Zinc, $\mu\text{g/L}$	6.72	<0.001
TSS, $\text{mg/L}$	15.92	0.001
Fecal Coliform, MPN/100ml	2813	0.012
<i>Enterococcus</i> , MPN/100ml	4245	0.062
<i>E. coli</i> , MPN/100ml	1452	0.010
Nitrate, $\text{mg/L}$	0.060	0.055
Orthophosphate, $\text{mg/L}$	0.010	0.145
Ammonia, $\text{mg/L}$	0.015	0.013
Urea, $\mu\text{g/L}$	7.447	0.016
Sum PAHs, $\mu\text{g/L}$	0.029	0.006
Sum Pyrethroids, $\mu\text{g/L}$	0.002	0.085
Sum Org. Pesticides, $\mu\text{g/L}$	0.004	0.093

<sup>1</sup> = Probabilities <0.05 are statistically significant. If  $p > 0.05$ , there is no statistical difference.

Constituent loads were estimated for each storm sampled, as another element in the analyses designed to determine whether storm discharges alter receiving water constituent concentrations. Among trace metals, zinc and copper had the highest average loads, nearly 5 and 3 grams per site per storm (Table 12). Silver and cadmium had the lowest average loads, <0.001 g per storm. TSS loads averaged >2 Kg per storm and oil and grease averaged >1 Kg per storm, although it was detected in discharges from only sites B, E, and F.

Estimation of constituent loads from each site also revealed differences among sites that did not always match results from other analyses. For example, average loads of every trace metal from Site B ranked among the top 3 across all sites (Table 12), whereas nickel was the only trace metal that exhibited significant increases in receiving water at that site (Table 11) and the percentages of samples that were above the overall 85<sup>th</sup> percentile threshold for trace metals at site B were generally low, except for copper, lead, and zinc (Table 8). Conversely, average loads from

**Table 11. Results from matched-pair (pre-storm vs. storm) statistical tests for each constituent across individual sites. (con't on next page)**

Analyte	Site							
	A		B		C		D	
	Mean Diff.	$p^1$	Mean Diff.	$p$	Mean Diff.	$p$	Mean Diff.	$p$
Arsenic	0.4754	0.1176	0.173	0.1724	0.9327	0.0337	0.0543	0.4014
Cadmium	0.0341	0.1637	0.0091	0.2592	0.0306	0.0881	0.0226	0.0413
Chromium	1.6055	0.0246	0.4244	0.0593	0.4249	0.0086	0.525	0.0405
Copper	1.2942	0.0805	9.0977	0.0898	1.631	0.0297	6.8838	0.0277
Lead	0.3309	0.1679	0.6628	0.0869	0.6930	0.014	1.7449	0.0387
Nickel	2.9979	0.0895	0.2474	0.0498	0.3391	0.0347	0.7695	0.0228
Mercury	2.0512	0.0028	2.344	0.0516	2.2298	0.0231	8.1222	0.0179
Selenium	0.0424	0.1631	0.0238	0.0736	-0.0005	0.5104	0.006	0.2407
Silver	-0.122	0.8444	0.03	0.0701	0.1	0.1174	0.065	0.2205
Zinc	3.7743	0.1085	3.8816	0.0511	0.0070	0.007	20.52	0.0329
TSS	52.83	0.0808	14.833	0.1317	8.8333	0.0671	1.6667	0.4093
Fecal Coliform	363	0.1059	527	0.0778	1010	0.117	4114	0.0507
<i>Enterococcus</i>	578	0.0439	988	0.1043	487	0.0425	6535	0.0395
<i>E. coli</i>	504	0.1626	482	0.0462	584	0.082	3293	0.0621
Nitrate	0.1667	0.1917	0.02	0.3995	0.0167	0.1816	0.1333	0.0606
Orthophosphate	-0.0083	0.7691	0.034	0.2551	0.0017	0.4655	0.0133	0.2441
Ammonia	0.0183	0.0884	0.014	0.187	0.0117	0.1816	0.0383	0.1816
Urea	-1.6667	0.8184	6.8	0.177	1.6667	0.4195	14.33	0.0712
Sum PAHs	0.0401	0.0668	0.0625	0.1252	0.0060	0.1398	0.0382	0.0833
Sum Pyrethroids	-	-	-	-	0.0027	0.0894	0.0095	0.1816
Sum Org. Pesticides	-	-	-	-	-	-	0.0097	0.1816



**Table 11 (continued). Results from matched-pair (pre-storm vs. storm) statistical tests for each constituent across individual sites.**

Analyte	Site							
	E		F		G		H	
	Mean Diff.	<i>p</i>	Mean Diff.	<i>p</i>	Mean Diff.	<i>p</i>	Mean Diff.	<i>p</i>
Arsenic	-0.0213	0.7113	-0.027	0.8286	0.05567	0.163	0.0838	0.211
Cadmium	-0.005	0.9242	0.0241	0.0503	0.0037	0.1552	0.01408	0.1414
Chromium	0.0013	0.475	0.4788	0.0898	0.2021	0.012	0.9003	0.0301
Copper	0.4892	0.1362	3.9895	0.0392	4.8488	0.0362	0.5774	0.0645
Lead	0.0279	0.0093	1.4571	0.1021	0.1087	0.0106	0.2161	0.0676
Nickel	0.016	0.2732	0.5285	0.0372	0.4118	0.0317	0.5560	0.1145
Mercury	0.2568	0.0112	5.7857	0.0448	5.4523	0.0957	2.1507	0.0682
Selenium	-0.02	0.8582	0.0232	0.1389	0.0037	0.1996	-0.0246	0.766
Silver	0.0517	0.2654	0.0617	0.2154	-0.0533	0.905	0.028	0.2271
Zinc	-0.0104	0.5155	14.19	0.0352	2.2047	0.0485	1.4559	0.0486
TSS	5.1667	0.1155	14.17	0.129	7.5	0.0752	22.33	0.0309
Fecal Coliform	35.8333	0.0403	9144	0.1078	7007	0.1753	302	0.1434
<i>Enterococcus</i>	96.5	0.0274	24418	0.1498	536	0.044	323	0.1463
<i>E. coli</i>	17.83	0.0996	6508	0.0825	207	0.0318	17.5	0.1958
Nitrate	0.15	0.21	-0.05	0.7188	0.05	0.3325	-0.0167	0.8184
Orthophosphate	-0.025	0.965	-0.0217	0.9249	0.0817	0.0471	0.005	0.2075
Ammonia	-	-	0.03	0.1816	0.0083	0.1816	-	-
Urea	-1.6667	0.8184	31.17	0.0944	11.17	0.0608	-2.3333	0.7659
Sum PAHs	0.0009	0.1816	0.0681	0.1651	-	-	0.0137	0.0765
Sum Pyrethroids	-	-	-	-	0.0012	0.0935	-	-
Sum Org. Pesticides	-	-	0.02033	0.1816	-	-	-	-

<sup>1</sup> = Probabilities <0.05 are statistically significant. If *p* >0.05, there is no statistical difference.

**Table 12. Mean loads per storm of constituents from each ASBS sites with discharge >36 inches.**

Site	Arsenic µg	Cadmium µg	Chromium µg	Copper µg	Lead µg	Mercury ng	Nickel µg	Selenium µg	Silver µg	Zinc µg	TSS mg
A	530,183	34,809	378,328	2,420,360	214,473	4,917,557	4,374,025	444,851	1,286	6,215,007	5,314,818
B	16,412,528	945,768	13,005,416	387,530,118	36,422,944	196,600,212	25,461,760	1,944,429	741,669	450,419,834	161,197,354
C	4,343,968	238,213	2,922,933	36,022,503	7,939,545	25,913,887	4,454,268	437,172	74,030	192,625,406	54,850,926
D	55,348,120	1,602,423	25,428,000	280,022,877	62,559,322	449,944,057	47,374,373	4,365,811	861,686	1,085,251,315	363,610,574
E	383,307	9,673	194,899	6,106,999	279,155	2,556,803	488,712	41,316	9,643	4,376,360	2,490,809
F	10,894,319	1,296,434	16,398,804	164,405,793	40,489,232	284,800,398	30,544,077	1,557,180	729,049	727,532,401	252,323,348
G	4,748,518	399,273	8,558,681	122,733,913	4,561,021	111,232,291	21,553,366	934,042	0	93,064,842	41,686,164
H	796,273	42,096	2,518,377	14,125,995	2,209,773	18,316,941	3,359,593	190,124	4,021	35,212,884	36,094,925
Average	10,813,976	530,947	8,094,703	118,325,979	17,924,249	128,573,161	16,057,436	1,171,281	284,736	301,305,320	109,965,666
Load/acre	185,455	9,746	163,431	2,705,170	280,412	2,370,324	396,781	30,277	5,369	4,960,121	2,287,507

Site	O&G mg	Fecal coliform MPN/100 mL x 10 <sup>3</sup>	<i>Enterococcus</i> MPN/100 mL x 10 <sup>3</sup>	<i>E. coli</i> MPN/100 mL x 10 <sup>3</sup>	Nitrate mg	OPhos. mg	Ammonia mg	Urea µg	PAHs µg	OP pest µg	Pyreth. µg
A	0	1,530,485	3,967,756	2,060,600	2,683,734	29,242	0	2,684,735	54	0	0
B	1,175,156	30,804,715	27,345,109	37,629,078	4,116,669	2,848,803	204,358	213,370,294	662,639	0	58,216
C	0	14,628,925	19,962,169	11,320,004	1,779,511	870,644	308,013	161,208,681	175,038	60,190	140,868
D	0	222,402,280	166,479,730	196,948,185	22,669,174	8,164,688	943,636	826,594,940	1,139,509	0	523,753
E	182,786	838,849	2,589,575	522,832	73,582	23,598	2,314	7,824,020	9,739	12,862	3,142
F	8,485,661	357,997,681	302,975,585	236,139,201	21,808,338	3,336,451	1,294,889	1,660,298,390	936,701	410,455	33,367
G	0	5,166,210	3,479,606	888,881	5,928,235	1,679,245	184,658	204,244,622	19,572	0	10,544
H	0	497,651	1,972,353	663,902	641,946	146,786	27,369	32,193,220	87,798	0	2,480
Average	1,166,502	74,357,695	61,593,883	57,242,279	7,089,197	1,996,010	356,153	369,286,198	355,897	55,789	89,737
Load/acre	33,384	1,091,906	1,120,313	880,071	143,840	30,677	6,032	5,688,906	6,477	1,832	1,668
<36" Average	41,112	1,652,277	553,606	1,507,598	-	-	-	-	-	-	-
<36" Load/acre	5,773	139,454	109,361	145,923	-	-	-	-	-	-	-

Site D of every trace metal, except copper, were the highest of any site, which corresponded to the numerous trace metals at that site with significant increases in receiving water samples. Average loads of trace metals from Site F also ranked among the top 3 across all sites and, similar to Site B, it only had 4 trace metals that increased significantly in receiving water samples and the percentage of samples above the threshold was generally low, except for copper, lead and zinc (Table 7).

Loads of FIBs, nutrients and PAHs were more consistent with other indicators than were loads of trace metals. Sites D and F had the highest average loads of FIBs, nutrients, and PAHs. Site F also had the highest loads of oil and grease and organophosphate pesticides (Table 12). Receiving water samples from both Site D and Site F were nearly always above the overall 85<sup>th</sup> percentile threshold for FIBs, although only *Enterococcus* at Site D exhibited significant increases in receiving water samples. Receiving water samples from these 2 sites also exceeded the threshold for ammonia and urea in 50–67% of samples.

A final test was performed to examine the relationship between discharges and the change in concentrations (delta) of constituents from pre-storm to receiving water samples. The estimated load of each constituent was compared to the delta. A significant regression inferred a link between estimated loads of a constituent and changes in its receiving water concentrations (i.e., an effect of load on the change in concentration). Previous comparisons of this type for trace metals, performed on single constituents across all storms, had not revealed consistent relationships between loads and delta. These negative results could be attributed 1) the variation among storms, 2) differences in the point in the storm at which sampling was conducted, or 3) differences among field crew in the location in the receiving where samples were collected, and differences in wave action (i.e., resuspension). Consequently, a different approach was taken for trace metals, in which regressions were performed using the estimated loads and deltas within each storm for all constituents. This method provides more points for each regression than the 6 that would be available if each constituent was plotted for all storms. It also was not limited by differences among storms in loads, storm conditions, or sampling location in the receiving water.

Trace metals exhibited numerous significant regressions for load versus delta, with apparent differences among storms and sites (Table 13 and Figure 14). Slight slope differences in the significant regressions reveal differences among storms in the relationships between loads and deltas, as predicted from previous results. Sites E and A had the fewest significant regressions, with 2 and 3, respectively (i.e., 33% and 50% of storms). These 2 sites, along with Site H, also consistently had the lowest average loads for every trace metal (Table 12). Site B, which consistently had among the top 3 average loads for each trace metal, exhibited only 4 significant regressions, whereas sites C and G, which had much lower average loads of trace metals, had 5 and 6 significant regressions, respectively. Sites D and F, which also had consistently high average trace metal loads, had 6 and 5 significant regressions, respectively. The differences among sites in the correspondence between loads and the number of significant regressions probably reflected differences in site conditions that affected dilution of storm runoff as it entered the ocean, such as beach slope and wave exposure.

**Table 13. Results from regressions of trace metal load vs delta. (continued on next page)**

Site & storm	Date	$R^2$	$p^1$	Y-int
A1	2/6/14	0.2255	0.1655	1.24E-01
A2	2/26/14	0.0596	0.4965	5.55E-01
A3	2/7/15	0.5548	0.0135	5.67E-01
A4	4/7/15	0.6942	0.0028	-1.11E-01
A5	1/5/16	0.5469	0.0145	1.20E+00
B1	2/6/14	0.9543	<0.0001	1.49E-02
B2	2/26/14	0.3222	0.087	-3.12E-02
B3	12/12/14	0.9630	<0.0001	1.26E-01
B4	1/5/16	0.9956	<0.0001	5.36E-02
B5	2/18/16	0.7808	0.0007	2.56E-01
B6	3/6/16	0.3701	0.062	6.06E-02
C1	2/6/14	0.9694	<0.0001	4.68E-01
C2	2/26/14	0.9752	<0.0001	2.42E-01
C3	12/12/14	0.9297	<0.0001	7.29E-01
C4	2/7/15	0.6682	0.0039	-1.59E-02
C5	1/5/16	0.2821	0.1142	6.77E-01
C6	2/18/16	0.7120	0.0021	2.03E-01
D1	2/6/14	0.9920	<0.0001	1.99E-01
D2	2/26/14	0.9207	<0.0001	1.88E-01
D3	12/12/14	0.9988	<0.0001	-2.88E-02
D4	1/5/16	0.6759	0.0035	6.97E-02
D5	2/18/16	0.9607	<0.0001	5.99E-01
D6	3/6/16	0.9728	<0.0001	1.09E-01
E1	2/6/14	0.0051	0.8442	-0.0121
E2	2/26/14	0.5985	0.0087	0.0764
E3	12/12/14	0.0728	0.4508	-3.14E-02
E4	2/7/15	0.0793	0.4306	4.10E-03
E6	1/5/16	0.1771	0.2259	3.49E-02
E6	3/6/16	0.4841	0.0255	1.76E-02
F1	2/6/14	0.9799	<0.0001	6.92E-01
F2	2/26/14	0.9743	<0.0001	3.58E-01
F3	12/12/14	0.8747	<0.0001	1.84E-01
F4	2/7/15	0.9979	<0.0001	7.15E-02
F5	1/5/16	0.9273	<0.0001	1.18E-01
F6	2/18/16	0.4071	0.0471	-4.69E-02
G1	2/26/14	0.8336	0.0002	6.22E-02
G2	2/7/15	0.7907	0.0006	-8.63E-03
G3	4/7/15	0.9783	<0.0001	2.40E-01
G4	1/5/16	0.9106	<0.0001	-2.24E-01
G5	2/18/16	0.7996	0.0005	-9.97E-02
G6	3/6/16	0.7038	0.0024	-1.43E+00

**Table 13. Results from regressions of trace metal load vs delta. (continued)**

Site & storm	Date	$R^2$	$p^1$	Y-int
H1	2/26/14	0.7383	0.0014	1.56E-01
H2	2/6/14	0.6628	0.0041	7.23E-01
H3	4/7/15	0.4895	0.0243	-2.54E-03
H4	12/3/15	0.6454	0.0051	9.96E-03
H5	1/5/16	0.3741	0.0602	1.40E-01

<sup>1</sup> = Probabilities <0.05 are statistically significant.

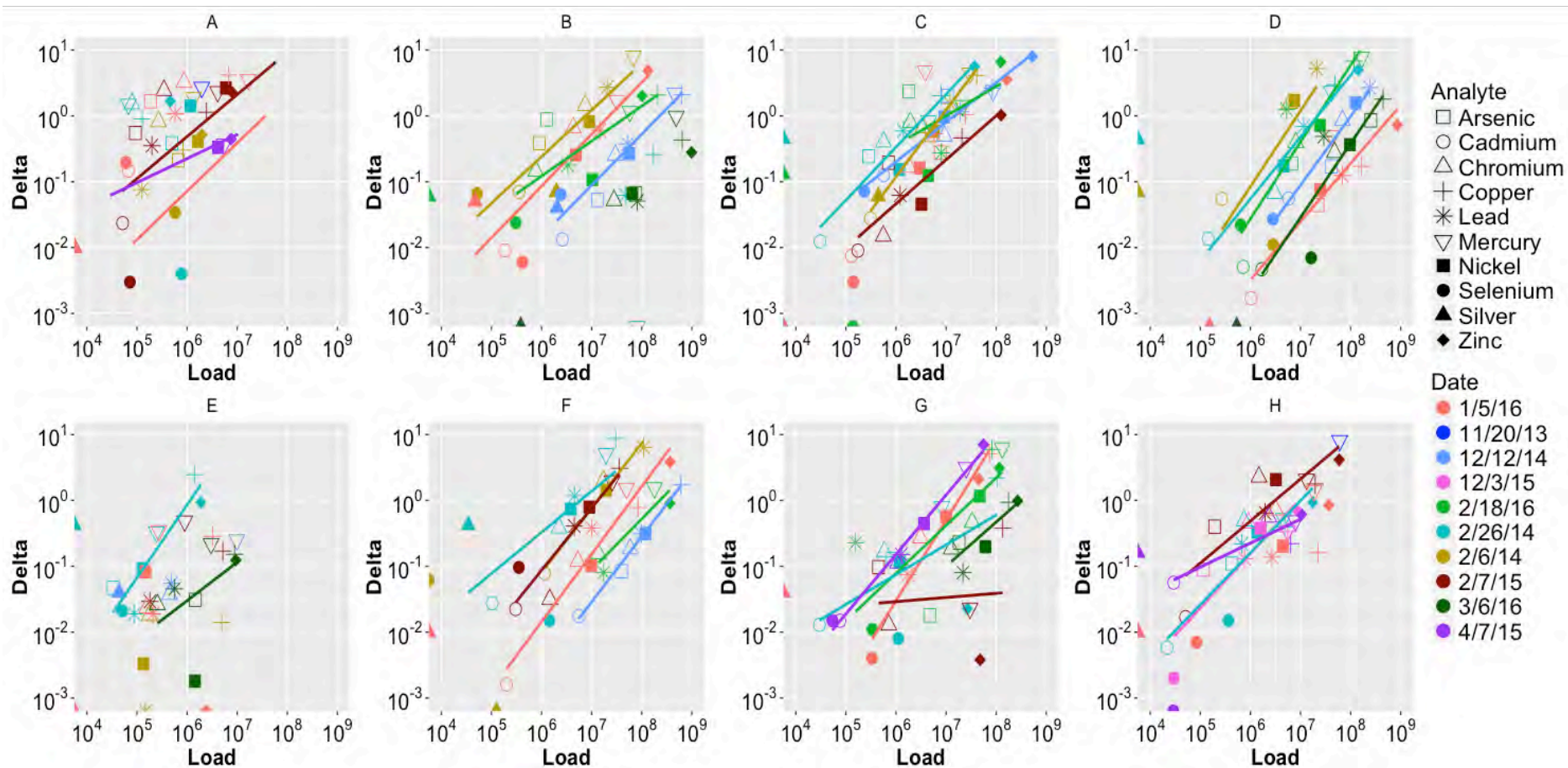
Estimated loads of FIBs for the 3 sites with the greatest magnitude of concentrations above the overall 85<sup>th</sup> percentile threshold across all 3 FIBs (C, D, and F) also were regressed against the delta. The regressions were significant, with estimated load explaining 54%, 84% and 72% of differences between pre-storm and receiving water concentrations of *E. coli*, *Enterococcus*, and fecal coliforms, respectively (Figure 15), suggesting that discharge of bacteria were driving the storm-related increases in receiving water concentrations at these 3 sites.

Examining the correspondence of nutrient load with difference between pre-storm and receiving water concentrations demonstrated that there was no significant relationship for any of the nutrients (Figure 10), suggesting that the increase in nutrient concentrations during storms could be related to factors other than discharge, such as sediment re-suspension.

### 5.3.1 Conclusion: Do storm discharges alter receiving water quality?

Concentrations of constituents in receiving water samples were usually above overall 85<sup>th</sup> percentile thresholds. Nevertheless, for some constituents, the concentrations measured at reference sites were greater than the highest concentrations measured in receiving waters and there were reference samples above overall 85<sup>th</sup> percentile thresholds. Moreover, while ANOVA revealed that concentrations in discharge samples were usually significantly greater than in other sample types, receiving water samples were not statistically different from concentrations in pre-storm or reference samples. When examined with a matched-pair test on all sites combined, an effect of storms was observed in which most constituents had higher concentrations in receiving waters than in pre-storm samples. When examined site-by-site, with attendant lower sample sizes, these differences between pre-storm and receiving water values were not universally observed. Comparisons of estimated loads to changes in receiving water concentrations also indicated that many discharges did alter receiving water quality, although none of them necessarily correlate with site differences in the percentage of receiving water samples above the overall 85<sup>th</sup> percentile threshold, their magnitude above the threshold or the estimated loads of these constituents.

Selenium and silver were illustrative of these apparent contradictions. Selenium and silver in receiving water were above their respective 85<sup>th</sup> percentile thresholds in 11% and 15% of all samples, respectively. Moreover, 40% and 20% of receiving water samples were above the selenium and silver thresholds, respectively, at Site A (Table 7). Nevertheless, their average concentrations in receiving water samples were 88% and 62% below their respective 85<sup>th</sup> percentile thresholds (Table 8) and neither one exhibited significant differences between pre-storm and receiving water samples in matched-pair tests, either across all sites or within any site (Table 11).



**Figure 14. Regressions of changes in receiving water concentrations of all trace metals during storms (delta) against each metal’s estimated respective load within each storm. Lines indicate statistically significant regressions. Note log scale on each axis. All units are consistent with those in Table 12.**

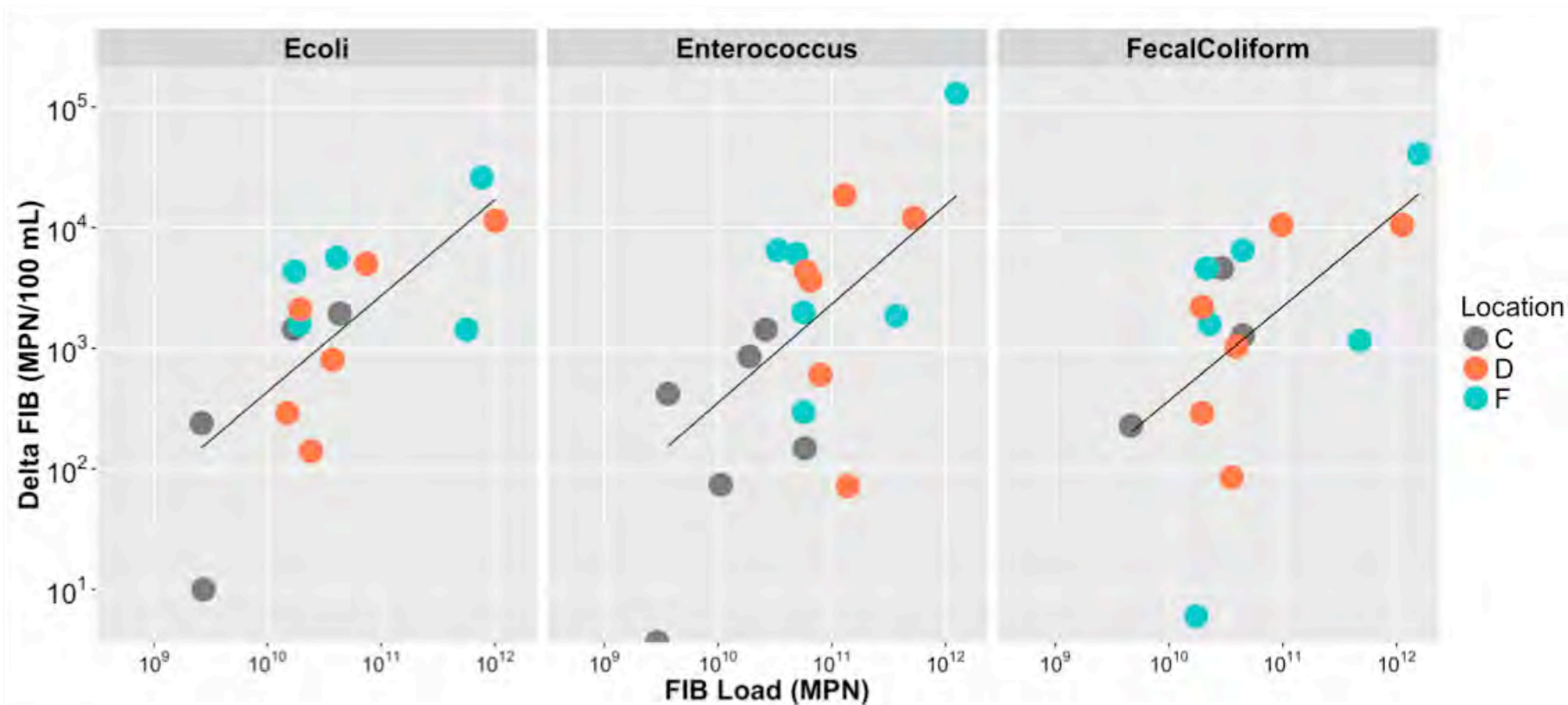


Figure 15. Relationship between A) *E. coli* (circles) delta versus load,  $\text{delta (MPN/100 mL)} = 1.55 \times 10^{-8}(\text{load, MPN}) + 1163$ ,  $r^2 = 0.54$ ,  $p = 4.9 \times 10^{-4}$ ; B) *Enterococcus* (triangles) delta versus load,  $\text{delta (MPN/100 mL)} = 9.1 \times 10^{-8}(\text{Load, MPN}) - 4322$ ,  $r^2 = 0.84$ ,  $p = 1.1 \times 10^{-7}$ ; C) Fecal coliform (squares) delta versus load;  $\text{delta (MPN/100 mL)} = 1.89 \times 10^{-8}(\text{Load, MPN}) + 1012$ ,  $r^2 = 0.72$ ,  $p = 6.9 \times 10^{-6}$ ; at sites C (red symbols), D (green symbols), and F (blue symbols). Note log scale on each axis.

Regressions of estimated constituent loads versus changes in concentrations from pre-storm to receiving water (delta) were mostly significant and explained substantial variation in delta, although this results did not necessarily mean receiving water concentrations were less than overall 85<sup>th</sup> percentile thresholds.

#### ***5.4 Question 4: Are alterations of receiving water quality due to anthropogenic waste?***

Determining whether trace metals in discharges are from anthropogenic or natural sources is challenging. Trace metals are ubiquitous in the natural environment and are contained in sediments and geologic formations in pristine environments. In an effort to distinguish between natural and anthropogenic sources of trace metals, the relationships between concentrations of trace metals and TSS were compared among sample types (Figure 16). For most trace metals, the concentrations per TSS in discharge samples were elevated above other sample types. Exceptions to this pattern were evident for arsenic and silver, in which the relationship between TSS and arsenic was very similar among all sample types and silver concentrations relative to TSS were often lower in discharge samples than in other sample types. The consistent relationships between trace metals and TSS in reference samples shown in Table 3 are also evident in Figure 16, in which concentrations of all trace metals, except silver, increase with increasing TSS concentrations.

Systematic differences among sample types in the concentrations of constituents per unit of TSS could help differentiate between natural and anthropogenic sources, at least for trace metals. The concentrations of constituents per unit of TSS were calculated and tested with ANOVA, the Wilcoxon nonparametric test and Student's t test between each pair of samples. All trace metals, except arsenic, chromium, selenium, and silver were significantly enriched relative to TSS in discharge samples (Table 14), suggesting a geologic source. Examination of site-specific data suggested that patterns of elevated of trace metals relative to TSS were not uniform.

To test whether there were significant differences among sites in relationships between TSS and trace metals, a 2-way ANOVA was performed to test for the effects of site, TSS, and interactions between site and TSS on trace metal concentrations in discharge samples. If a significant interaction occurred between site and TSS, it meant that the effect of TSS differed among sites, which was equivalent to testing for differences among sites in the slope of TSS versus trace metal. Only copper, lead, mercury, and zinc exhibited significant interactions (Table 15).

To determine whether there were systematic differences among sites that could account for the significant interactions for copper, lead, mercury, and zinc, plots of these 4 trace metals versus TSS were made for each site and arranged together (Figures 17 and 18). For all four metals, and especially copper and zinc, there were 2 basic patterns. One pattern, illustrated by sites A, E, and H, exhibited trace metal concentrations in the discharge samples that were elevated above all other samples, but fell along a rough line whose slope approximated that for all the other samples types combined. The other 5 sites tended to have much more elevated discharge trace metal concentrations that were accompanied by substantially elevated concentrations in receiving water. In the discharge samples at these 5 sites, there also was no apparent relationship between trace metal concentrations and TSS. While these patterns were less consistent from site to site for lead and mercury, sites A and H always exhibited positive



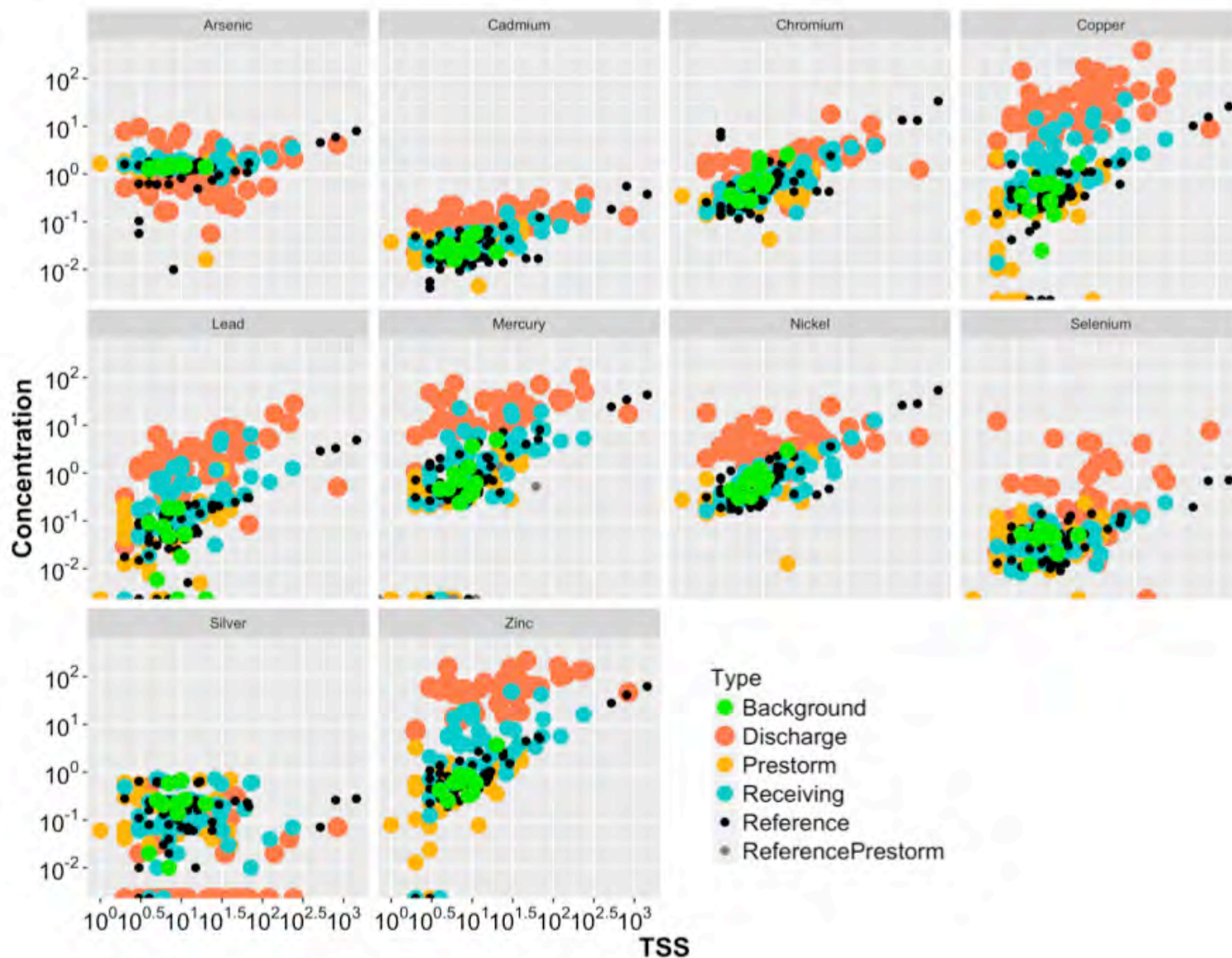


Figure 16. Relationships between trace metal concentration ( $\mu\text{g/L}$  except mercury= $\text{ng/L}$ ) and TSS concentrations ( $\text{mg/L}$ ) across all stations by sample type.

slopes for TSS versus trace metal and no elevation of receiving water concentrations above the other sample types. The relationship between TSS and lead was more indicative of a positive slope at all sites, except G.

**Table 14. Results from comparisons among sample types of constituent concentrations per TSS.**

Constituent	ANOVA		Wilcoxon	<i>A posteriori</i> Result <sup>2</sup>
	R <sup>2</sup>	p <sup>1</sup>	p	
Arsenic	0.0512	0.019	<0.001	P <u>D</u> <u>Rw</u> <u>Rf</u>
Cadmium	0.0816	0.001	0.003	<u>D</u> <u>P</u> <u>Rw</u> <u>Rf</u>
Chromium	0.0253	0.183	<0.001	D P <u>Rw</u> <u>Rf</u> <sup>3</sup>
Copper	0.1536	<0.001	<0.001	D <u>Rw</u> <u>P</u> <u>Rf</u>
Lead	0.3136	<0.001	<0.001	D <u>Rw</u> <u>P</u> <u>Rf</u>
Nickel	0.0966	<0.001	<0.001	D <u>P</u> <u>Rw</u> <u>Rf</u>
Mercury	0.1842	<0.001	<0.001	D <u>Rw</u> <u>Rf</u> <u>P</u> <u>Pr</u>
Selenium	0.0218	0.2436	<0.001	D P <u>Rw</u> <u>Rf</u> <sup>3</sup>
Silver	0.1101	>0.001	<0.001	P <u>Rf</u> <u>Rw</u> <u>D</u>
Zinc	0.2840	<0.001	<0.001	D <u>Rw</u> <u>P</u> <u>Rf</u>
Oil & Grease	0.0585	0.012	<0.001	D <u>P</u> <u>Pr</u> <u>Rw</u> <u>Rf</u>
Fecal Coliform	0.0493	0.030	<0.001	D <u>Rw</u> <u>Rf</u> <u>B</u> <u>P</u> <u>Pr</u>
<i>Enterococcus</i>	0.0730	0.003	<0.001	D <u>Rw</u> <u>P</u> <u>Rf</u> <u>Pr</u>
<i>E. coli</i>	0.0136	0.5705	<0.001	Rf D <u>Rw</u> <u>P</u> <u>Pr</u> <sup>3</sup>
Nitrate	0.0136	0.574	<0.001	Rf D P <u>Rw</u> <u>Pr</u> <sup>3</sup>
Orthophosphate	0.1013	<0.001	<0.001	D <u>P</u> <u>Rw</u> <u>Rf</u> <u>Pr</u>
Ammonia	0.1173	<0.001	<0.001	D <u>Rw</u> <u>Rf</u> <u>P</u> <u>Pr</u>
Urea	0.1808	<0.001	<0.001	D <u>P</u> <u>Rw</u> <u>Pr</u> <u>Rf</u>
PAHs	0.3827	<0.001	<0.001	D <u>Rw</u> <u>P</u> <u>Rf</u> <u>Pr</u>
Orthophosphate Pesticides	0.0218	0.323	0.183	D <u>Rw</u> <u>P</u> <u>Rf</u> <u>Pr</u>
Pyrethroid Pesticides	0.1502	<0.001	<0.001	D <u>Rw</u> <u>Pr</u> <u>P</u> <u>Rf</u>

<sup>1</sup> =  $P \leq 0.05$  is statistically significant. If  $p > 0.05$ , there is no statistical difference.

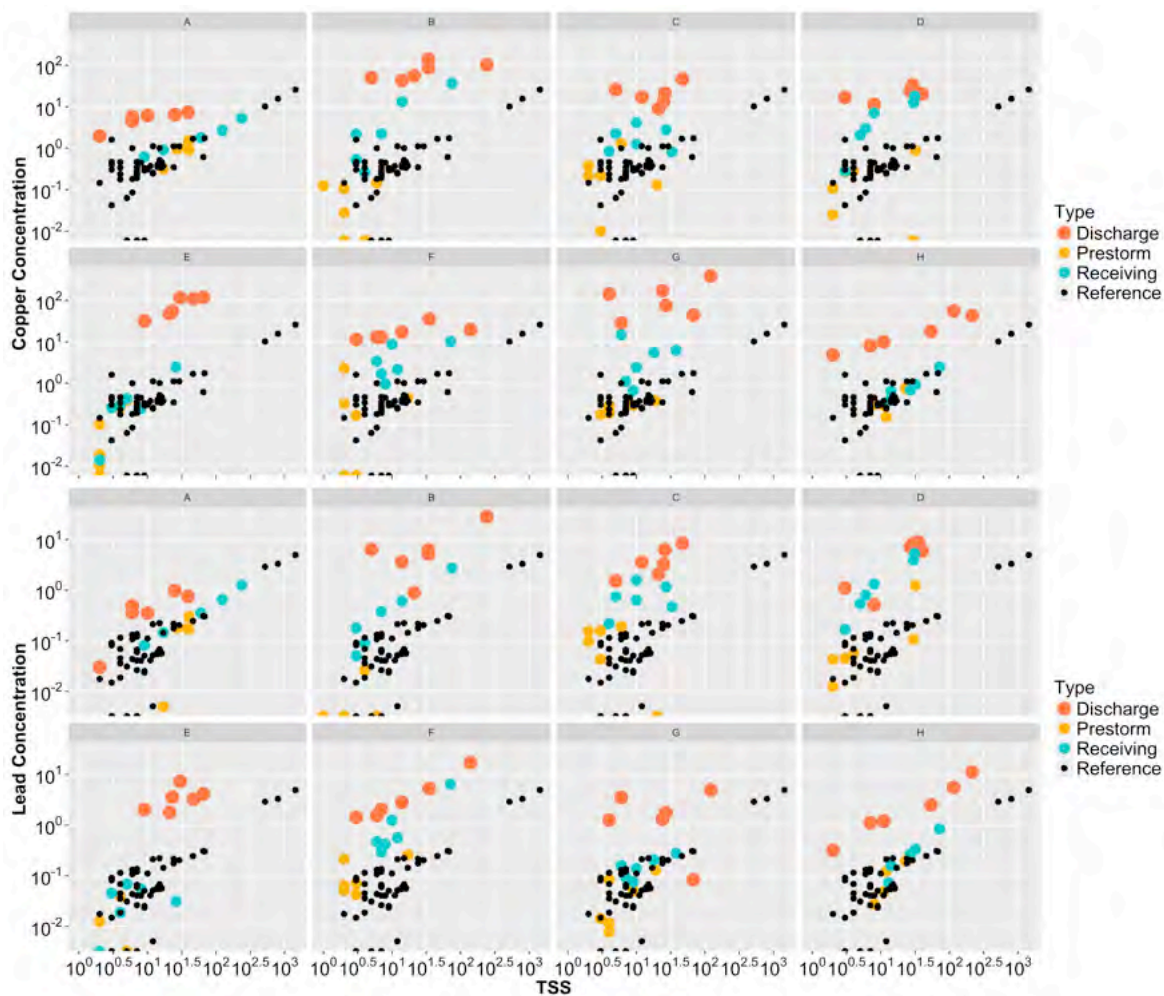
<sup>2</sup> = D is Discharge, P is Pre-storm, Pr is Reference Dry Weather, and Rf is Reference, and Rw is storm Receiving Water. Sample type on left has the highest mean.

<sup>3</sup> = One test gave a non-significant result

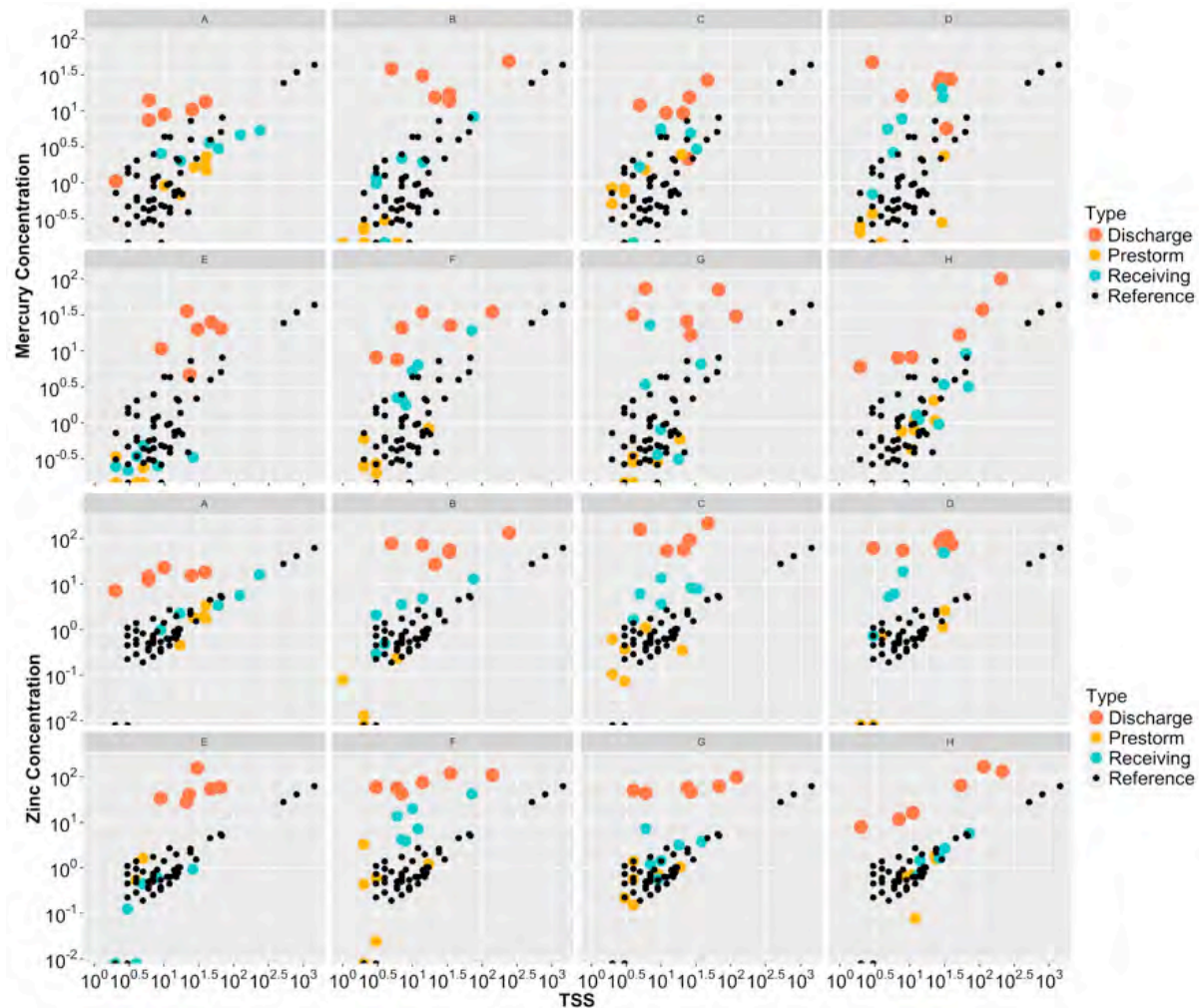
**Table 15. Results from 2-way ANOVA to test for the effects of site, TSS and interactions of site and TSS on trace metal concentrations in discharge samples.**

Constituent	Model		Site	TSS	Interaction
	R <sup>2</sup>	p <sup>1</sup>	p	p	p
Arsenic	0.363	0.528	0.920	0.312	0.433
Cadmium	0.558	0.029	0.146	0.692	0.089
Chromium	0.437	0.244	0.745	0.409	0.223
Copper	0.738	<0.001	<0.001	0.171	0.005
Lead	0.927	<0.001	<0.001	<0.001	<0.001
Nickel	0.611	0.007	0.120	0.956	0.734
Mercury	0.689	<0.001	0.193	0.791	<0.001
Selenium	0.521	0.064	0.991	0.808	0.541
Silver	0.470	0.155	0.184	0.029	0.195
Zinc	0.627	0.005	0.112	0.047	0.037

<sup>1</sup> = P ≤ 0.05 is statistically significant. If p > 0.05, there is no statistical difference.



**Figure 17. Plots of a) copper concentration (µg/L) versus TSS concentration (mg/L) and b) lead concentration (µg/L) versus TSS concentration (mg/L) by site (A – H).**



**Figure 18. Plots of a) mercury concentration (ng/L) versus TSS concentration (mg/L) and b) zinc concentration (µg/L) versus TSS concentration (mg/L) by site (A – H).**

There was evidence that trace metals discharged at some sites were mostly in the dissolved fraction, rather than associated with particulate material. During 2 storms in 2016, discharges from the sites that were sampled were analyzed for total and dissolved concentrations of all trace metals, except mercury (Table 16). There were substantial differences among sites and trace metals in the percentages measured in the dissolved fraction. For those trace metals exhibiting a strong affinity for TSS in reference samples across the entire study area (i.e., copper, lead, mercury and zinc), discharges of high percentages in the dissolved fraction indicate different processes controlling their release into the environment from the processes that controlled reference trace metal concentrations, and suggests anthropogenic sources. Moreover, several studies have found high loads of dissolved copper, zinc, and lead in runoff from building roofs made of copper, zinc-coated metal and slate (Bannerman et al, 1993; Barron 2006; Gromaire et al, 2001; Lye 2009; O’Sullivan et al, 2011; Pitt et al, 2004; Wicke et al, 2014).

While trace metals have been amenable to inferences regarding anthropogenic versus natural sources, FIBs and nutrients are also ubiquitous in the environment, but the available data do



**Table 16. Percent of metals in the dissolved fraction from discharge samples collected during 2 storms in 2016. Values over 100% indicate higher concentrations measured in aliquots for dissolved metals than in aliquots for total metals. Silver was not detected in any of these samples**

February 18, 2016

Site	Arsenic	Cadmium	Chromium	Copper	Lead	Nickel	Selenium	Zinc	All metals
B	72.8%	44.7%	17.7%	66.3%	19.2%	75.2%	47.6%	62.6%	42.3%
C	122.2%	33.3%	28.2%	77.4%	13.6%	76.1%	59.0%	64.3%	48.9%
D	118.2%	55.1%	24.3%	76.7%	22.3%	75.7%	85.5%	78.0%	55.7%
F	146.7%	49.1%	79.2%	80.1%	30.7%	81.5%	70.8%	59.4%	62.9%
G	8.0%	7.6%	3.2%	57.5%	0.6%	18.4%	49.2%	5.7%	15.1%
All sites	99.7%	39.4%	32.3%	72.4%	17.5%	67.1%	65.8%	56.1%	

March 6, 2016

B	85.0%	64.6%	65.2%	76.9%	28.2%	91.9%	85.5%	53.6%	61.5%
D	95.2%	50.1%	61.1%	87.0%	33.9%	93.4%	73.9%	68.4%	60.9%
E	101.0%	100.4%	66.9%	37.1%	7.9%	96.1%	144.9%	7.9%	57.1%
G	83.4%	65.7%	40.3%	87.8%	18.8%	66.1%	75.9%	54.1%	52.2%
All sites	91.1%	70.2%	58.4%	72.2%	22.2%	86.9%	95.0%	46.0%	

Mean for 2 events

B	78.9%	54.7%	41.4%	71.6%	23.7%	83.6%	66.5%	58.1%	51.9%
D	106.7%	52.6%	42.7%	81.8%	28.1%	84.5%	79.7%	73.2%	58.3%
G	45.7%	36.6%	21.7%	72.6%	9.7%	42.2%	62.5%	29.9%	33.7%

not allow determinations of sources. Nevertheless, FIBs stand out because their maximum concentrations in receiving water samples were greater than those at reference sites. If not strictly anthropogenic, their concentrations were highest in receiving water samples, although not significantly, and they exhibited significant associations between estimated loads and changes in receiving water concentrations. Thus, it appears that storm receiving waters at the base of watersheds affected by human development tend to have high concentrations of FIBs, although it is unknown whether these were from anthropogenic sources.

Nutrients cannot be chemically directly linked to anthropogenic sources. They are present in soil and natural organic matter. Moreover, there were no significant increases in receiving water concentrations over pre-storm concentrations at any site and no relationship between loads and changes in receiving water concentrations.

PAHs are naturally present in the marine environment. Along the California coastline from near San Simeon southward into the Santa Barbara Channel, there are natural seeps that result in tar balls on beaches and rocky intertidal areas. Nevertheless, we are not aware of any natural seeps onshore within the study area. Consequently, PAHs detected in the discharges and receiving water samples were presumed to be from anthropogenic sources, such as motorized vehicles and other types of combustion processes.

Organophosphate and pyrethroid pesticides are exclusively man-made compounds that have no natural sources. Although they were infrequently detected, their presence in any sample, including receiving water, was presumed to derive from an anthropogenic source.

#### **5.4.1 Conclusion: Are alterations of receiving water quality due to anthropogenic waste?**

Determining whether trace metals in discharges are from anthropogenic or natural sources is challenging. Trace metals are ubiquitous in the natural environment and are contained in sediments and geologic formations even in pristine environments. An analysis was performed using the relationships between trace metals and TSS in an effort to distinguish between natural and anthropogenic sources of trace metals. For most trace metals, the concentrations per TSS in discharge samples were elevated above other sample types. Exceptions to this pattern were evident for arsenic and silver, in which the relationship between TSS and arsenic was very similar among all sample types and silver concentrations relative to TSS were often lower in discharge samples than in other sample types. The relationships between trace metals and TSS in reference samples were consistent with concentrations of all trace metal concentrations increasing with increasing TSS concentrations, except for silver.

Analysis of variance (ANOVA) revealed that the amounts of various constituents per unit of TSS were similar among all sample types, except for discharges. Discharge samples often had significantly increased constituent concentrations per unit of TSS. Moreover, another ANOVA showed that the relationship of TSS to copper, lead, mercury, and zinc differed among sites. Some sites exhibited relationships between these trace metals and TSS in their discharges that paralleled the positive slopes of these relationships in other sample types, but with elevated trace metals per unit of TSS. Other sites exhibited elevated trace metals in their discharges that

had no relationship to TSS concentrations, and which were often accompanied by elevations of the trace metals per unit of TSS in receiving water samples. Discharges of trace metals with high percentages in the dissolved fraction indicate different processes controlling their release into the environment from the processes that controlled reference trace metal concentrations, and suggests anthropogenic sources. Moreover, several other studies have found high loads of dissolved copper, zinc, and lead in runoff from building roofs made of copper, zinc-coated metal and slate.

FIBs and nutrients are also ubiquitous in the environment, but the available data do not allow determinations of sources. Nevertheless, FIBs stand out because their maximum concentrations in receiving water samples were greater than those at reference sites. If not strictly anthropogenic, their concentrations were highest in receiving water samples, although not significantly, and they also exhibited significant associations between estimated loads and changes in receiving water concentrations. Thus, it appears that storm receiving waters at the base of watersheds affected by human development tend to have high concentrations of FIBs, although it is unknown whether these have anthropogenic sources.

Nutrients cannot be chemically directly linked to anthropogenic sources. They are present in soil and natural organic matter. Moreover, there were no significant increases in receiving water concentrations over pre-storm concentrations at any site and no relationship between loads and changes in receiving water concentrations.

PAHs are naturally present in the marine environment. Along the California coastline from near San Simeon southward into the Santa Barbara Channel, there are natural seeps that result in tar balls on beaches and rocky intertidal areas. Nevertheless, we are not aware of any natural seeps onshore within the study area. Consequently, PAHs detected in the discharges and receiving water samples are presumed to be from anthropogenic sources, such as motorized vehicles and other types of combustion processes.

Organophosphate and pyrethroid pesticides are exclusively man-made compounds that have no natural sources. Although they were infrequently detected, their presence in any sample, including receiving water, is presumed to derive from an anthropogenic source.

### ***5.5 Question 5: Are marine biological resources being affected by ASBS storm discharges?***

As the purpose of the ASBS beneficial use is to ensure protection of water quality needed to support important biological resources, the answer to this question requires consideration of ASBS biological resources or their surrogates. There are 5 components of the Central California Regional Monitoring Program that are particularly pertinent to this consideration.

1. Rocky Intertidal Monitoring. The purpose of this component was to determine whether stormwater discharges in ASBS could be affecting biological communities.
2. Mussel Bioaccumulation Monitoring. The purpose of this component was to determine whether harmful contaminants are accumulating in resident organisms in ASBS.

3. Toxicity Testing. This purpose of this component was to determine whether receiving waters in ASBS are toxic by integrating all constituents, even those that were not measured and regardless of the concentrations of measured constituents.
4. Measurement of Nutrients. This component was included due to the known relationship between harmful algal blooms and excess nutrients.

### **5.5.1 Rocky Intertidal Monitoring**

Rocky intertidal communities were sampled by Dr. Pete Raimondi using methods that have been applied in ASBS rocky intertidal monitoring programs in other parts of California (Appendix C). Sampling was conducted in the fall of 2014 at the following sites:

1. Alder Creek discharge (Duxbury Reef ASBS)
2. Fitzgerald Marine Reserve discharge
3. Año Nuevo discharge
4. Hopkins discharge (Pacific Grove ASBS)
5. Stillwater discharge (Carmel Bay ASBS)
6. Point Lobos discharge (Point Lobos State Marine Reserve)
7. Bolinas Point reference
8. Pigeon Point reference

Data from each site were compared with current and historic data from numerous sites along the central California coast. Sites were selected using broad criteria to ensure similar substrate among sites and safe access. Sessile and mobile organisms were quantified using random quadrats and point contact methods, respectively. The following null hypotheses were tested:

1. Species richness will not vary as a function of site type (Discharge, Reference)
2. Community composition of sessile species will not vary as a function of site type
3. Community composition of mobile species will not vary as a function of site type
4. An assessment of both mobile and sessile species will not identify particular sites as being substantially different from the expectation based on all sites. This is a way to look at specific sites rather than site types.

There were no differences found between sample types for species richness, community composition of sessile species, or community composition of mobile species and null hypotheses 1, 2, and 3 were not rejected. Null hypothesis 4 was rejected, as the composition of sessile organisms at Fitzgerald Marine Reserve differed substantially from what was expected for other rocky intertidal communities in the region, likely due to natural factors.

#### **5.5.1.1 Rocky Intertidal Conclusions**

Based on the results of these analyses, there is no support for the idea that discharges along the central California coast generate impacts to diversity or community composition in the nearby rocky intertidal habitats. This does not ensure that there are no impacts to organisms in the communities. Other attributes such as individual growth and reproduction could be affected with no subsequent impact to diversity or composition.

Some sites stood out as differing substantially from what was expected for biological



communities in the region. In particular, Fitzgerald Marine Reserve was an outlier with respect to sessile species composition. It is likely that this difference in community structure is the result of the geomorphology at the site. The intertidal zone at Fitzgerald Marine Reserve is a very wide and flat bench surrounded by sand and subject to considerable scour. In addition, the reef tends to hold water because it is flat and the key mid intertidal species, *Chthamalus* spp., *Mytilus californianus* and *Mastocarpus* spp., which are species that dominate on hard rock surfaces with extended periods of emersion are all uncommon at this site.

### 5.5.2 Mussel Bioaccumulation Monitoring

The bioaccumulation monitoring originally included analysis of resident mussels from Lovers Point in Pacific Grove. This expectation assumed collaboration with California State Mussel Watch, which had been funded the Central Coast regional Water Board to sample Lovers Point and other sites for contaminants in mussel tissues. Unfortunately, the collaboration could not be arranged and that site was not sampled for the Central California regional ASBS program. Instead, the bioaccumulation studies relied on collaboration with the Central Coast Long-term Environmental Assessment Network (CCLEAN).

CCLEAN has measured several persistent organic pollutants (POPs) polychlorinated biphenyls (PCBs), the flame retardants polybrominated diphenyl ethers (PBDEs), and chlorinated pesticides in mussels at 5 sites around Monterey Bay (Figure 19) for over 13 years and the long database permits analysis for spatial and temporal patterns. This collaboration provided the ASBS program participants with access to a long-term dataset on the condition of an important biological resource in rocky intertidal communities around Monterey Bay, including ASBS.

In the collaboration between this project and CCLEAN a site was added at Point Reyes National Seashore and the list of analytes normally measured by CCLEAN was expanded to include organophosphate pesticides, pyrethroid pesticides and acid-positive pharmaceuticals. None of the organophosphate or pyrethroid pesticides were detected in any of the samples. Acid-positive refers to the type of extraction to recover the compounds from the sample matrix.

The acid-positive pharmaceuticals include a broad range of drugs, such as antibiotics, antihistamines, mood stabilizers, replacement hormones, calcium channel blockers, cardiac glycosides and caffeine. Only 8 of these acid-positive compounds were detected in mussels from any site (Table 17) out of the 45 that were analyzed. The detected pharmaceuticals were mostly those with both human and animal (veterinary or livestock) uses. Seven out of the 8 compounds detected have veterinary or animal husbandry uses and 6 have human applications. Two of the antibiotics, Enrofloxacin and Virginiamycin M1, have exclusively animal uses. The fluoroquinolone antibiotic Lomefloxacin was the most widely detected pharmaceutical, having been measured at 5 out of 6 sites and in 10 out of 12 samples. Moreover, Lomefloxacin concentrations were substantially higher in 2015 than in 2014 at all but 1 of the sites where it was detected in either year. Caffeine was also detected at 5 out of 6 sites, having been measured in 7 out of 12 samples. Caffeine comes exclusively from humans along the Central Coast. The only non-human source of caffeine in the continental USA is from a holly plant native only to the southeastern USA. The strongest human signature occurred over the 2 years of pharmaceutical analyses at The Hook in Capitola where 6 drugs with veterinary and/or human

applications were detected. While there are no human health alert levels for pharmaceuticals in shellfish, the ubiquitous occurrence of them is an indicator of the extent to which they have been released into the environment. The site in Carmel Bay ASBS (Carmel River Beach) had among the lowest rates of pharmaceutical occurrence of any site.

Concentrations of several POPs in mussels along the Monterey Bay area coastline have exceeded or nearly exceeded various alert levels for the protection of human health. EPA and the California Office of Environmental Health Hazard Assessment (OEHHA) have published several applicable human health alert levels. USEPA has published risk-based alert levels that are based on the relative amount of tissue that is predicted to be eaten, which are called the subsistence and recreational fisher alert levels (EPA 2000). OEHHA has published a variety of alert levels (Klasing and Brodberg 2008, 2011). These include the Fish Contaminant Goal (FCG), which represents the concentration below which there are no significant health risks from eating a single 8-ounce serving of fish per week, for life. OEHHA also published several levels of Advisory Tissue Level (ATL), which differ in the amount of fish that can be eaten at minimal health risk, from three servings per week down to no consumption recommended. These alert levels are indicated in the following figures, as appropriate.

Concentrations of several POPs in mussels have declined over time at some sites. Consistent with providing data on the effects of POPs on beneficial uses, data have been presented on a wet-weight basis, as human health alert levels are based on wet-weight concentrations because they are developed using assumptions about human consumption. Because most POPs are lipid-soluble, tracking trends of contaminant concentrations in organisms is often based on concentrations normalized to lipid content (i.e., ng POP per g of lipid), which gives a better estimate of the actual burden of POPs being carried by the organisms. Consequently, lipid normalizations were performed for concentrations of Dieldrin, Chlordanes, PCBs, and DDTs in mussels to parallel those POPs that are most problematic on Monterey Bay waters and are presented side-by-side with the wet-weight data (Figures 20, 21, 22, and 23). PBDEs are also considered here (Figure 24) because they are chemically very similar to PCBs, they have serious consequences for human health (Windham et al, 2015), and a 2006 ban of certain forms in California has resulted in declines in some areas (Sutton et al, 2014). In addition, exceptionally high concentrations were measured in women's breasts in the San Francisco Bay area (Windham et al, 2010), which is not far from Monterey Bay.

Overall trends of Dieldrin, Chlordanes, PCBs, DDTs, and PBDEs have been mostly downward at all sites. The legacy pesticide Dieldrin has been detected above the USEPA recreational fisher screening value at two sites between 2002 and 2008 (Figure 20a). While the legacy pesticide Dieldrin has exceeded the USEPA recreational fisher screening level at 2 sites in 2002 and 2008 and it continues to be broadly detected at concentrations near or slightly above the EPA subsistence fisher screening level (Figure 20a), there have been downward trends at some sites, with similar trends in lipid-weight concentrations (Figure 20b). Wet-weight concentrations of Chlordanes, another legacy pesticide, have not exceeded any human health alert level in any mussel samples (Figure 21a). Nevertheless, concentrations of Chlordane at The Hook were just below the OEHHA Fish Contamination Goal in 2002 and have been consistently higher there than at the other sites (Figure 21a). Concentrations at Laguna Creek were intermediate

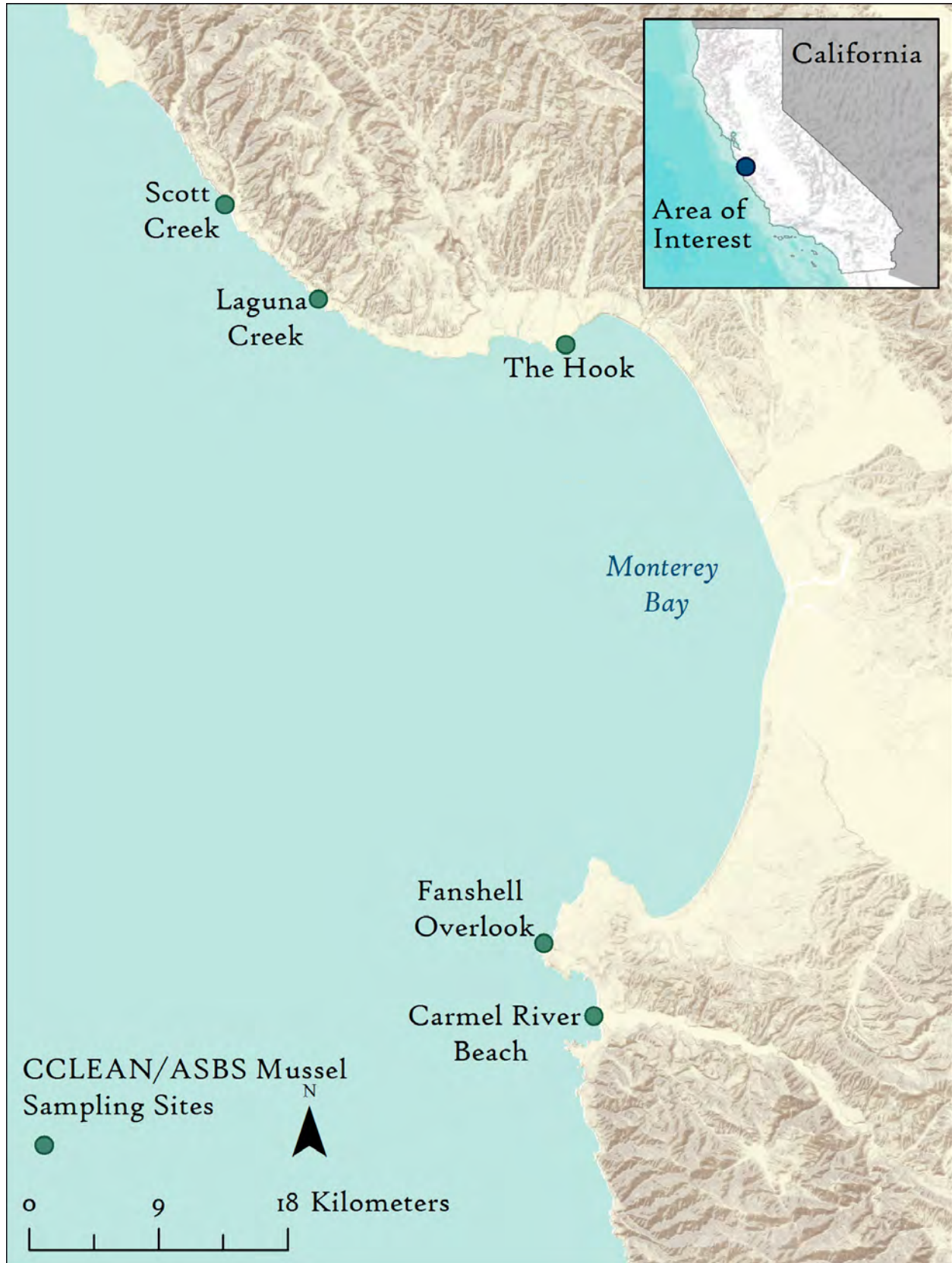


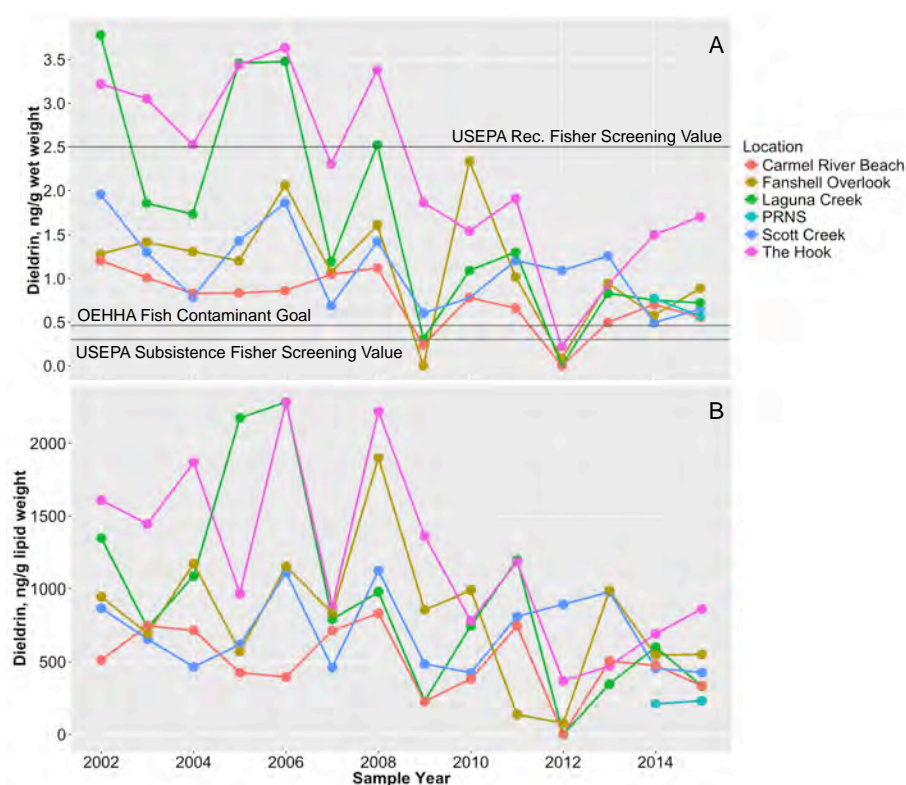
Figure 19. Locations of mussel bioaccumulation monitoring sites.

**Table 17. Acid-positive pharmaceuticals detected in mussels in 2014 and 2015. All compounds reported in ng/g dry weight.**

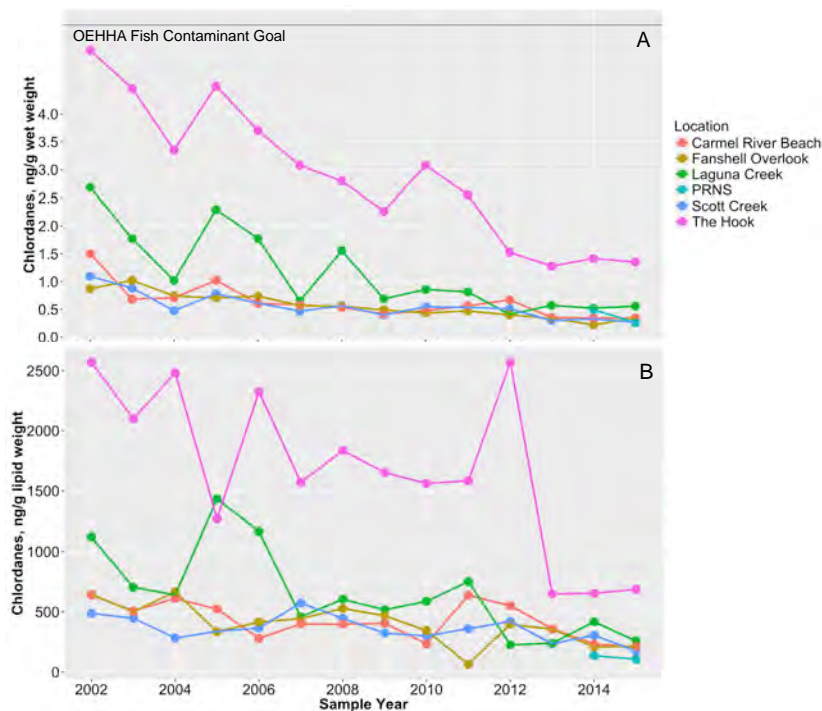
Compound	Site Uses	PRNS <sup>1</sup>		Scott		Laguna		Hook		Fanshell		Carmel R	
		2014	2015	2014	2015	2014	2015	2014	2015	2014	2015	2014	2015
Caffeine	Constituent in coffee	ND <sup>2</sup>	61.8	61.2	47.9	50.4	271	117	ND	ND	122	ND	ND
Diltiazem	Calcium channel blocker for heart failure in pets and humans	ND	ND	ND	ND	ND	ND	0.719	ND	ND	ND	ND	ND
Diphenhydramine	Antihistamine for pets, horses and humans	1.44	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Enrofloxacin	Broad-spectrum veterinary antibiotic	ND	ND	ND	ND	ND	ND	7.16	ND	ND	59.3	ND	ND
Erythromycin-H2O	Broad-spectrum human and veterinary antibiotic	ND	ND	ND	ND	ND	5.73	ND	6.51	ND	ND	ND	ND
Lomefloxacin	Broad-spectrum human and veterinary antibiotic	ND	ND	42.6	103	58	44.2	58.6	228	89.5	233	46.3	130
Penicillin V	Narrow-spectrum human and veterinary antibiotic	ND	ND	ND	8.97	ND	ND	ND	ND	ND	ND	ND	ND
Virginiamycin M1	Growth-enhancing livestock antibiotic	11.4	ND	ND	ND	17	ND	32.7	ND	18.6	ND	24.8	ND

<sup>1</sup> = Point Reyes National Seashore<sup>2</sup> = Not Detected

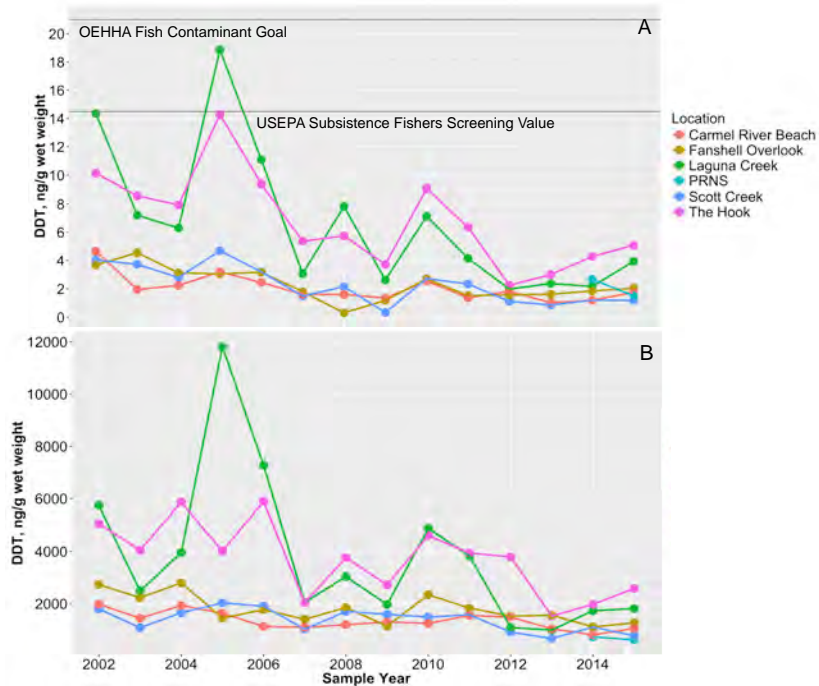
between The Hook and other sites in 2002, but declined to concentrations very similar to the other sites by 2009. DDTs have been detected at wet-weight concentrations near or above the USEPA subsistence fishers screen value at Laguna Creek and The Hook between 2002 and 2005 (Figure 22a). Wet-weight concentrations of DDTs were also similar at Laguna Creek and The Hook, with Laguna Creek often exceeding The Hook during this period. Wet-weight concentrations of PCBs in mussels have remained substantially below any human health alert level (Figure 23). As with Chlordanes, wet-weight concentrations of PCBs at The Hook have remained substantially above those at the other sites, except for Point Reyes, which exhibited a greater concentration than any of the other sites (Figure 23a). In all cases, the POP concentrations in mussels at Carmel River Beach have been among the lowest of any site, and near or below those at Point Reyes National Seashore.



**Figure 20. Wet-weight (A) and lipid-weight (B) concentrations of Dieldrin measured in mussels during the wet season from 5 CCLEAN sites in the Monterey Bay area and 1 site at Point Reyes National Seashore.**

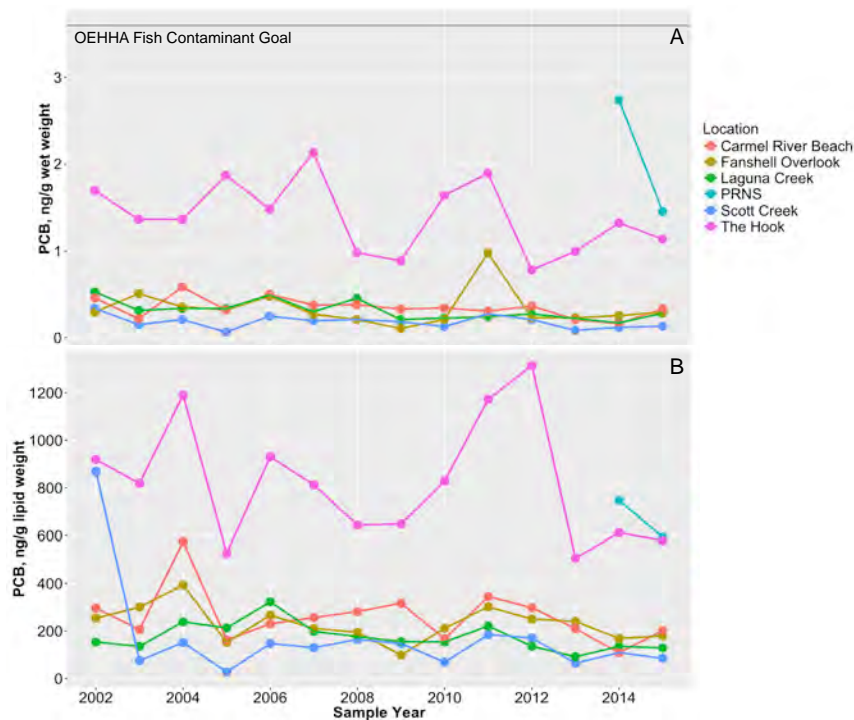


**Figure 21. Wet-weight (A) and lipid-weight (B) concentrations of Chlordanes measured in mussels during the wet season from 5 CCLEAN sites in the Monterey Bay area and 1 site at Point Reyes National Seashore.**

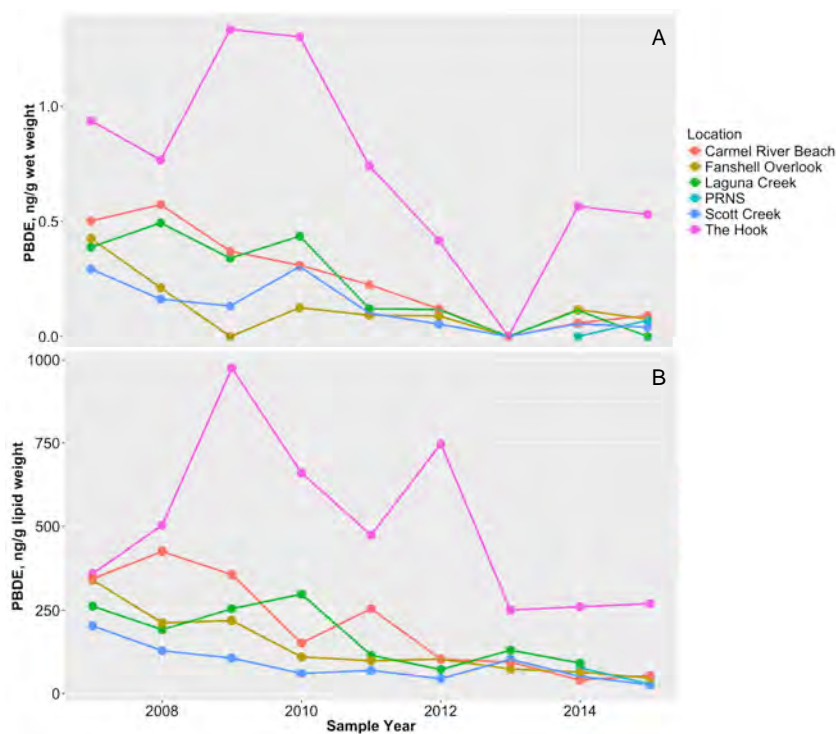


**Figure 22. Wet-weight (A) and lipid-weight (B) concentrations of DDTs measured in mussels during the wet season from 5 CCLEAN sites in the Monterey Bay area and 1 site at Point Reyes National Seashore.**





**Figure 23. Wet-weight (A) and lipid-weight (B) concentrations of PCBs measured in mussels during the wet season from five CCLEAN sites in the Monterey Bay area and 1 site at Point Reyes National Seashore.**



**Figure 24. Wet-weight (A) and lipid-weight (B) concentrations of PBDEs measured in mussels during the wet season from five CCLEAN sites in the Monterey Bay area and 1 site at Point Reyes National Seashore.**

### 5.5.2.1 Mussel Bioaccumulation Conclusions

Concentrations of POPs in mussels have been declining over recent years around Monterey Bay and have been consistently low at Carmel River Beach. Dieldrin in mussels along the northern shore of Monterey Bay have remained below the USEPA recreational fisher screening value at all sites for the sixth year in a row, although Dieldrin still exceeds the subsistence fisher screening level at several sites. DDTs also remain below human health alert levels. PBDEs also have declined significantly over time at all sites, except for The Hook. Acid-positive pharmaceuticals detected in the mussels consisted entirely of compounds with both human and veterinary or animal husbandry uses, suggesting runoff from pets and livestock operations. More pharmaceuticals were detected at The Hook than at other sites. The broad-spectrum antibiotic Lomefloxacin was detected in more samples than any other pharmaceutical. Concentrations of contaminants measured in mussels from Point Reyes National Seashore were generally lower than at the other CCLEAN sites around Monterey Bay, except for PCBs, which were higher at Point Reyes. There is no evidence contaminants from stormwater are accumulating or causing adverse effects on mussels in the Carmel Bay ASBS.

### 5.5.3 Toxicity Testing

Toxicity tests are widely accepted laboratory procedures that are intended to indicate whether a particular sample of water could cause harm to aquatic organisms. They often rely on measurements of physiological responses, such as egg fertilization, embryonic development, gametophyte germination, and growth that are likely to be more sensitive than survival as a test endpoint. Being conducted in the laboratory, the test conditions, such as temperature, oxygen concentration, and water quality, can be monitored in order to minimize the effects of uncontrolled variables on test outcomes. Bringing samples into the laboratory for testing allows a specific set of organisms to be observed throughout the course of the test, which is very difficult under ambient conditions. Conversely, while toxicity tests do not mimic natural conditions and no direct conclusions can be drawn about biological effects in ambient waters, they are effective screening tools (Chapman, 2000). In the case of the ASBS monitoring program, toxicity tests can be indicators of potential effects on biological resources.

Toxicity is not a normal feature of natural water quality and anthropogenic constituents are assumed to be the cause of toxicity tests in ocean waters. Consequently, the occurrence of toxicity at reference sites, even in <2% of reference samples (Table 18) is surprising. The 3 toxicity tests that exhibited failures at reference sites were the kelp growth, mussel embryonic development, and mussel embryo survival tests. These 3 tests also failed in 8%, 2%, and 3% of receiving water samples. Kelp growth failures occurred at sites B, C, E, and H. Single failures of mussel development and survival occurred at Site A. The urchin fertilization test exhibited a higher rate of failure in receiving water samples, with 1/3 of samples at Site C and single samples at sites B and F failing. Discharge samples tested with the urchin fertilization test failed in 24% of samples overall. Two-thirds of the samples at Site D and half the samples at sites C, F, and G also failed. Discharges smaller than 36 inches failed the urchin fertilization test in 17% of samples. The high rates of failure in the discharge samples from sites C, D, F, and G were not consistently associated with large numbers of failures in receiving water samples. In fact, sites



D and G, which had failure rates of 67% and 50%, respectively, in discharge samples, had no failures in receiving water samples.

**Table 18. Percentage of failed toxicity tests at each ASBS and all Reference Sites.**

Site	Discharge	Receiving Water					Receiving Water Overall
	Urchin Fertilization	Urchin Fertilization	Kelp Germination	Kelp Growth	Mussel Development	Mussel Survival	
A	0%	0%	0%	0%	17%	17%	8%
B	17%	17%	0%	17%	0%	0%	8%
C	50%	33%	0%	17%	0%	0%	13%
D	67%	0%	0%	0%	0%	0%	0%
E	17%	0%	17%	17%	0%	0%	8%
F	50%	17%	0%	0%	0%	0%	4%
G	50%	0%	0%	0%	0%	0%	0%
H	17%	0%	0%	17%	0%	0%	4%
Overall	24%	8%	2%	8%	2%	3%	5%
Mean <36 inches	17%	-	-	-	-	-	-
Overall Ref	-	0%	0%	0.4%	0.4%	0.4%	1.2%
North Ref	-	0%	0%	0%	0%	0%	0%
South Ref	-	0%	0%	0.6%	0.6%	0.6%	1.8%

A statistical procedure was used to examine potential causes of toxicity. A step-wise linear regression was performed in an effort to determine whether toxicity numerical endpoints were significantly associated with certain constituents. The toxicity test endpoints were the dependent variables and the chemical constituents were the independent variables. All independent variables were put into the model and it was run backward until only variable with statistically significant ( $p < 0.05$ ) associations with toxicity remained. All sites, including discharge, receiving water, and reference, were combined for this test.

Thirty-nine percent of the variation in the numerical endpoints of urchin fertilization toxicity tests was accounted for by a combination of trace metals and pesticides (Table 19). The results suggest that the negative effects of zinc and pyrethroid pesticides accounted for most of the variation, while the positive effects of nickel and PAHs, and the negative effects of arsenic and silver were less important.

**Table 19. Results of step-wise linear regression of urchin fertilization numerical endpoints versus constituent concentrations in all samples.**

$R^2$	$p$	Model
0.3856	<0.0001	Tox endpoint = $-2.03(\text{arsenic})^6 + 0.57(\text{nickel})^5 - 14.5(\text{silver})^4 - 0.24(\text{zinc})^1 + 27.5(\text{sum of PAHs})^3 - 151(\text{sum of pyrethroids})^2 + 99.3$

<sup>1-6</sup> = Order of variable importance as determined by partial correlations.

While 61% of the variation in urchin fertilization results is unaccounted for in this model, the results are surprising. Previous studies of storm runoff in the area have indicated trace metals as a major contributor to toxicity (Phillips et al, 2004). When the summed concentrations of the trace metals that were found to have negative associations with urchin fertilization (i.e., arsenic, silver and zinc; Table 19) are plotted versus the percent of successful fertilization, there is no apparent relationship between the summed concentrations of these trace metals and the samples with failed toxicity tests (Figure 16). This suggests that constituents in the water, other than the trace metals, are ameliorating the toxic effects. Numerous authors have reported reductions in toxicity of trace metals in aquatic samples related to concentrations of dissolved organic carbon and compounds that tend to bind the metals (Cao et al 1995, Meador 1991, Tatara et al 1997). Consequently, the samples that failed the toxicity tests indicated in Figure 25 could have been “cleaner” with less dissolved organic material in them than the samples with higher concentrations of trace metals that passed the toxicity test.

Effects of pyrethroids (permethrin) on urchin fertilization have recently been reported (Erkmen, 2015). Inhibitory concentrations for  $IC_{25}$  and  $IC_{50}$  were 0.58  $\mu\text{g/L}$  and 0.94  $\mu\text{g/L}$ , respectively. This author also reported toxicity to urchin embryos as concentration-dependent inhibition of normal development, with  $IC_{25}$  and  $IC_{50}$  of 0.195  $\mu\text{g/L}$  and 0.346  $\mu\text{g/L}$ , respectively. Maximum concentrations of pyrethroids detected in the discharges from ASBS sites did not reach the fertilization IC values (Table 20), but summed permethrin (i.e., cis + trans) concentrations approached the  $IC_{25}$  in some samples and could have affected fertilization success.

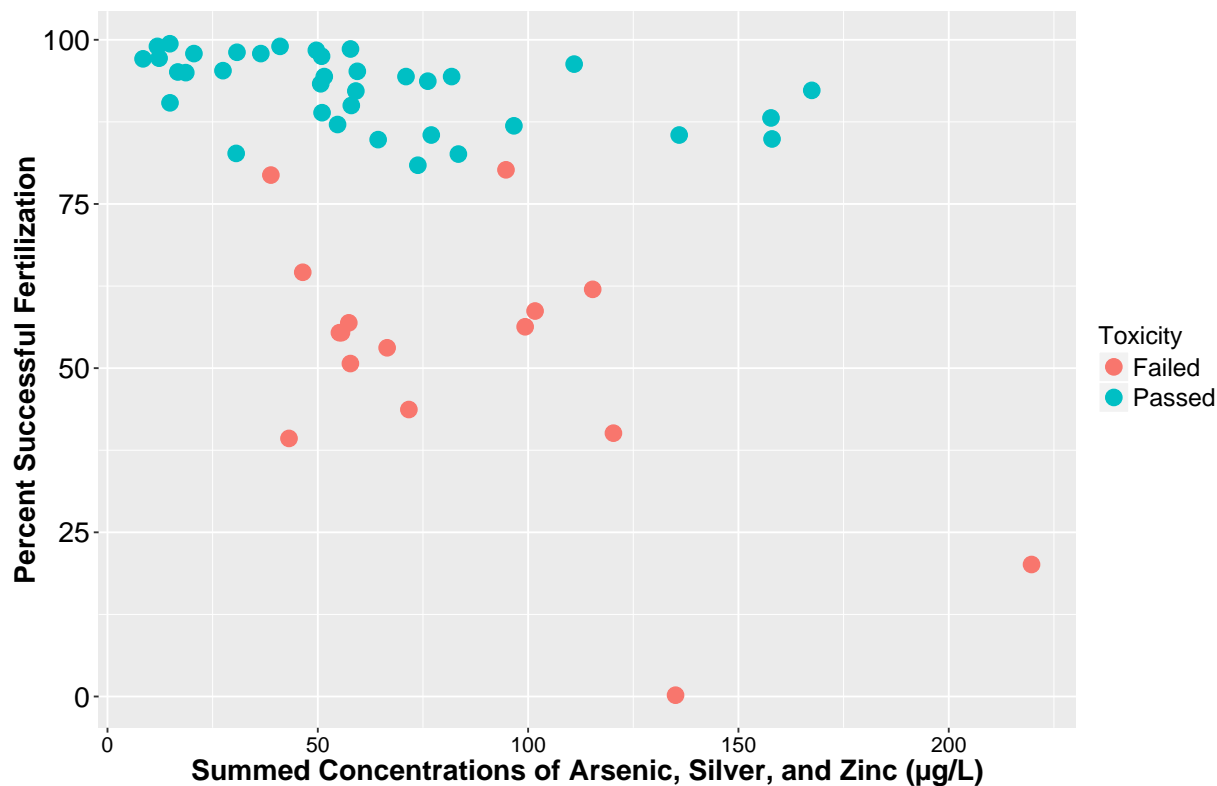


Figure 25. The relationships between summed concentrations of the trace metals that exhibited significant negative associations with numerical endpoints for urchin fertilization success (see Table 18) for tests that passed and failed the toxicity test.

Table 20. Maximum concentrations (µg/L) of pyrethroid pesticides detected in discharge samples.

Site	Bifenthrin	Cyfluthrin total	Cyhalothrin Total lambda	Cypermethrin total	Deltamethrin/ Tralomethrin	Esfenvalerate/ Fenvalerate total	Fenpropathrin	Sum of Permethrin
A	0	0	0	0	0	0	0	0
B	0.0087	0.007	0	0	0.0105	0	0	0.438
C	0.0066	0.069	0.0109	0	0.012	0.0023	0	0
D	0.005	0.018	0	0	0	0	0	0.135
E	0.0117	0.011	0	0	0	0	0	0.106
F	0.03	0.0066	0	0	0	0	0	0
G	0	0.154	0	0	0.0061	0	0	0
H	0.0115	0	0	0	0	0.006	0	0

The results of the stepwise linear regression modeling reveal statistical associations and do not establish causal links between the significant constituents and toxicity. Nevertheless, they provide guidance for any future toxicity identification evaluations.

Trace metals in the dissolved fraction are more likely to be taken up and cause toxicity to aquatic organisms than those in the particulate fraction (Lorenzo et al, 2002; Rainbow 1995, Bellas et al 2001). It is primarily these dissolved trace metals, with apparent non-natural sources, that account for high concentrations in some discharge samples and are potentially contributing to toxicity. The high percentages of trace metals in the dissolved fraction in discharges at some sites (Table 16) suggest it could be challenging to control toxicity caused by trace metals. Moreover, the influence of other constituents in the water on the bioavailability of trace metals provides an additional complication for reducing trace metal toxicity.

#### **5.5.3.1 Toxicity Testing Conclusions**

Toxicity measured in receiving water samples suggests that marine biological resources could be affected by ASBS discharges. Toxicity in discharge and receiving water samples has been statistically associated with some trace metals and pyrethroid pesticides. Toxicity associated with dissolved trace metals will be challenging to control (Barron 2006; Dierkes et al, 2005).

#### **5.5.4 Nutrient Effects on Algal Blooms**

It is assumed that the measurement of nutrients in this program was required because of their potential effects on algal blooms. Harmful algal blooms have become a global problem (Hallegraeff 1993, Anderson et al. 2002, Paerl and Huisman 2008). Last year saw an extraordinary bloom along the entire west coast of the United States of *Pseudonitzschia*, which is a diatom that produces the neurotoxin domoic acid. Kudela et al (2008) linked seasonal red tides along the northern bight of Monterey Bay to discharges of agricultural nutrients from the Pajaro River.

Concentrations of nutrients near-shore in Monterey Bay are mainly affected by riverine inputs and wastewater discharges, whereas concentrations offshore are principally affected by upwelling (CCLEAN 2016). Dr. Raphael Kudela of UCSC studied the effects of nutrients from rivers and streams, and municipal wastewater discharges for CCLEAN. Loads from rivers and streams averaged 1,100,000 kg N/year, whereas wastewater averaged 1,300,000 kg N/year over 7 years. Annual loads from each wastewater discharge ranged from 26,000 kg to 614,000 kg. Using satellite imagery to measure sea-surface chlorophyll, Dr. Kudela noted significant ( $p < 0.05$ ) positive correlations between discharges of nitrogen from wastewater and increased sea-surface chlorophyll at all wastewater sites. Compared with these constant river and wastewater sources, the transient loads of nitrogen from nitrate, ammonia, and urea into ASBS receiving waters during storms (averaging approximately 14.5 kg total N/storm/site; see Table 12) are insignificant (i.e., 0.00043% of combined annual loads from rivers and wastewater) and do not affect nutrient concentrations in Monterey Bay, which despite the large sources of nutrients mentioned above, are low year-round. For example, concentrations of ammonia are typically below 0.5  $\mu\text{moles N/L}$  (0.007  $\mu\text{g N/L}$ ) and concentrations of nitrate vary between 1-5  $\mu\text{moles N/L}$  (0.014-0.07  $\mu\text{g N/L}$ ) (Kudela and Dugdale 2000). Moreover, we are not aware of any nuisance growths or algal blooms being reported in nearshore areas of ASBS during or following

storms. The relatively small loads compared to riverine inputs and the nearshore turbulence both prevent buildup of nutrients to the point of causing algal blooms.

#### **5.5.4.1 Nutrient Effects on Algal Blooms Conclusion**

Annual loads of nitrogen in nitrate, ammonia, and urea from rivers and wastewater discharges average 3,400,000 kg. Average loads of these nutrients from the ASBS discharges monitored in this program were 14.5 kg/site/storm, which amounts to 0.00043% of the annual load from rivers and wastewater. Nutrients discharged into ASBS have had no noticeable effect on algal blooms or nuisance growths.

#### **5.5.5 Conclusion: Are marine biological resources being affected by ASBS storm discharges?**

Effects of stormwater discharges on resident biological communities in ASBS monitored by this program have not been observed. Rocky intertidal communities and mussels sampled for bioaccumulation have shown no demonstrable effects of stormwater discharges. Rocky intertidal communities have been similar to communities at reference sites, although sessile species at Fitzgerald Marine Reserve are different from what would be expected at other similar sites. This difference is more likely due to the effects of sand that surrounds and scours the site, as well as the tendency of the rocky bench to retain water. The concentrations of various contaminants in resident mussels have been declining over the past 13 years throughout the Monterey Bay area, with lower concentrations at the site in Carmel Bay ASBS than at other sites. There is no evidence contaminants from stormwater are accumulating or causing adverse effects on mussels in the Carmel Bay ASBS. Loads of nutrients from stormwater discharges into ASBS are multiple orders of magnitude lower than those from rivers and municipal wastewater and there is also no evidence that they are causing nuisance growth or blooms of algae in ASBS.

Toxicity tests exhibited a small number of failures with greater numbers of discharge samples failing than receiving water samples. The urchin fertilization test was most sensitive. Toxicity could be affecting sensitive life stages of some organisms and sources should be determined and reduced, wherever possible.

## 6.0 Regulatory Considerations

This monitoring program has documented significant geographic differences in reference area natural water quality. This fact means that it may be more appropriate to compare receiving water samples from a particular ASBS to an 85th percentile threshold calculated from relevant reference site(s). The primary water quality threshold for judging whether natural water quality is being achieved in ASBS is the 85<sup>th</sup> percentile of values from reference sites in the ocean at the mouths of streams with <5% of their watersheds under human development. This threshold essentially requires ASBS participants to achieve better water quality than is present in the ocean at the mouths of these clean reference streams. It is far from certain that this level of water quality is achievable. It seems a very daunting task to ensure that water quality along a city shoreline be better than the best water quality available along undeveloped shoreline of the state. If we can assume that the water quality at reference sites fully supports sensitive marine life, then requiring the same, and not necessarily better, water quality should provide a robust level of protection for marine life in ASBS.

If this approach were utilized, a more reasonable threshold would be the 95<sup>th</sup> percentile. This would ensure that any value falling outside the bounds of most reference values would become the focus of corrective measures. Such a threshold would have a profound effect on the number of constituents potentially being flagged for mitigation measures, while still leaving plenty of room for improving water quality (Table 21).

Notwithstanding consideration of a revised threshold for natural water quality, the water quality objectives in the Ocean Plan were specifically developed to protect marine resources and human health. The toxicities of constituents were considered and appropriate safety margins were added to ensure that constituent concentrations falling under Ocean Plan objectives would not cause toxicity. In the case of organic compounds, objectives were set to protect human health based upon assumptions about bioaccumulation of compounds into seafood consumed by people and added health risks. Consequently, these compounds do not have instantaneous maxima for the protection of marine life. FIB Ocean Plan objectives also were developed to protect human health from diseases transmitted via contact with water. They were established from epidemiological studies that determined the increased risks of becoming infected after swimming in water with increased FIB concentrations and also include built-in safety factors.

A comparison of receiving water data with Ocean Plan objectives reveals sporadic occurrences of concentrations above objectives (Table 22). There was a single receiving water sample at Site B with a concentration of copper above the Ocean Plan objective. Chromium and nickel Ocean Plan objectives were each exceeded in a single reference sample. Fecal coliform and *Enterococcus* concentrations were above Ocean Plan objectives at most sites, ranging from 17% to 100% of samples. These 2 FIBs were above Ocean Plan objectives in 6% and 22% of reference samples, respectively. PAHs were above the Ocean Plan 30-day average objective for the protection of human health at most ASBS sites, ranging from 17% to 50% of samples per site. Four percent of reference samples were also above the 30-day average objective for PAHs. If an instantaneous maximum is estimated for PAHs using the 10:1 ratio used for instantaneous maximum to 6-month median concentrations for other constituents, an estimated instantaneous maximum for PAHs would approximate 0.088 µg/L and the percentage of

samples above the objective would decrease substantially across all ASBS and reference sites. Moreover, if receiving water is not meeting natural water quality according to the Compliance Flowchart of the Special Protections (Figure 1), actions can be required that either bring offending constituents below Ocean Plan objectives or reduce their loads by 90%.

Comparisons of ASBS receiving water data with pertinent thresholds (e.g., 95<sup>th</sup> percentile and Ocean Plan), while reducing the number of samples above the Special Protections 85<sup>th</sup> percentile threshold, have emphasized that identifying sources and reducing anthropogenic loads of FIBs and PAHs into ocean waters should be a high priority, along with determining sources of and reductions in toxicity.

**Table 21. Percentage of samples above a reference 95<sup>th</sup> percentile threshold for constituents in receiving water samples at each ASBS site.**

Site	Arsenic	Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Selenium	Silver	Zinc	TSS
A	0%	0%	0%	0%	0%	0%	0%	40%	0%	0%	0%
B	0%	0%	0%	33%	0%	0%	0%	17%	0%	0%	0%
C	0%	0%	0%	0%	0%	0%	0%	0%	17%	0%	0%
D	0%	0%	0%	17%	33%	0%	0%	0%	17%	33%	0%
E	0%	0%	0%	0%	0%	0%	0%	0%	17%	0%	0%
F	0%	0%	0%	0%	17%	0%	0%	33%	17%	17%	0%
G	0%	0%	0%	17%	0%	0%	0%	0%	0%	0%	0%
H	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
Overall	0%	0%	0%	8%	6%	0%	0%	11%	8%	6%	0%

Site	Fecal Coliform	<i>Enterococcus</i>	<i>E. coli</i>	Nitrate	Orthophosphate	Ammonia	Urea	PAHs	Organophosphate Pesticides	Pyrethroids	Overall
A	17%	33%	17%	0%	0%	33%	0%	50%	0%	0%	4%
B	17%	17%	33%	0%	0%	20%	20%	33%	0%	0%	4%
C	33%	17%	33%	0%	0%	17%	67%	17%	0%	33%	6%
D	50%	67%	67%	0%	0%	17%	50%	50%	17%	17%	10%
E	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	1%
F	83%	83%	83%	0%	0%	17%	67%	33%	17%	0%	10%
G	17%	33%	0%	0%	0%	17%	33%	0%	0%	33%	3%
H	17%	17%	0%	0%	0%	0%	17%	50%	0%	0%	3%
Overall	29%	33%	29%	0%	0%	15%	32%	26%	4%	10%	5%



**Table 22. Number of samples above Ocean Plan water quality objective for instantaneous maximum. PAHs have no instantaneous maximum objective and one was estimated at 10x the 30-day average ( $10 \times 0.0088\mu\text{g/L} = 0.088\mu\text{g/L}$ ).**

Site	Chromium	Copper	Nickel	Fecal Coliform	<i>Enterococcus</i>	PAHs	
						30-day average	Estimated Instantaneous Maximum
A	0%	0%	0%	17%	33%	17%/50%*	0%/33%*
B	0%	17%	0%	33%	67%	33%	17%
C	0%	0%	0%	33%	67%	17%	0%
D	0%	0%	0%	67%	100%	33%	17%
E	0%	0%	0%	0%	33%	0%	0%
F	0%	0%	0%	83%	100%	33%	17%
G	0%	0%	0%	33%	67%	0%	0%
H	0%	0%	0%	17%	33%	50%	0%
Reference	2%	0%	2%	6%	22%	4%	0%

\* = Percentage of discharge samples with PAHs detected / percentage of receiving water samples above the objective.

## 6.0 References Cited

- Anderson, D.M., Glibert, P.M., and J.M. Burkholder. 2002. Harmful algal blooms and eutrophication: nutrient sources, composition, and consequences. *Estuaries* 25:704-726.
- Applied Marine Sciences. Sampling and Analysis Plan: The Central Coast Areas of Special Biological Significance Regional Monitoring Program and Reference Site Monitoring. AMS-201301108. November 8, 2013.
- Applied Marine Sciences. Quality Assurance Project Plan: The Central Coast Areas of Special Biological Significance Regional Monitoring Program and Reference Site Monitoring. AMS-2014-00313. March 13, 2014.
- Bannerman. R.T., D.W. Owens, R.B. Dodds, N.J. Hornewer. 1993. Sources of pollutants in Wisconsin stormwater. *Water Science and Technology*. 28(3-5):241–259.
- Barron, T.S. 2006. Architectural uses of copper, an evaluation of stormwater pollution loads and best management practices. Report to Palo Alto Regional Water Quality Control Plant.
- Bellas, J., E. Vazquez, R. Beiras. 2001. Toxicity of Hg, Cu, Cd, and Cr on early development stages of *Ciona intestinalis* (Chordata, Ascidiacea) with potential application in marine water quality assessment. *Water Research*. 35(12):2905–2912.
- Birch, G.F., M.S. Fazeli, and C. Matthai. 2005. Efficiency of an infiltration basin in removing contaminants from urban stormwater. *Environmental Monitoring and Assessment*. 101:23–38.
- Bradford, G.R., A.C. Change, A.L. Page, D. Bakhtar, J.A. Frampton, and H. Wright. 1996. Background Concentrations of Trace and Major Elements in California Soils. Kearney Foundation of Soil Science Special Report, University of California at Riverside, Division of Agriculture and Natural Resources. Riverside, CA. 32 p.
- Bruzzoniti, M.C., C. Sarzanini, E. Mentasti. 2000. Preconcentration of contaminants in water analysis. *Journal of Chromatography A*. 902(1):289–309.
- Bubb, J.M., and J.N. Lester. 1994. Anthropogenic heavy metals inputs to lowland river systems, a case study The river Stour U.K. *Water, Air and Soil Pollution*. 78:279–296.
- Cao, Y., M. Conklin, E. Betterton. 1995. Competitive complexation of trace metals with dissolved humic acid. *Environmental Health Perspectives*. 103(Suppl 1):29–32.
- Central Coast Long-term Environmental Assessment Network. 2016. Regional Monitoring program Annual Report 2014–2015. January 31, 2016. 911 Center Street, Santa Cruz, CA 95060.
- Chapman, P.M. 2000. Whole effluent toxicity testing – usefulness, level of protection, and risk assessment. *Environmental Toxicity and Chemistry*. 19(1):3–13.

- Dierkes, C., P. Göbel, M. Lohmann, W.G. Coldewey. 2005. Development and investigation of a pollution control pit for treatment of stormwater from metal roofs and traffic areas. 10<sup>th</sup> International Conference on Urban Drainage, Copenhagen/Denmark, 21-26 August 2005.
- Erkmen, B. 2015. Spermiotoxicity and embryotoxicity of permethrin in the sea urchin *Paracentrotus lividus*. *Bulletin of Environmental Contamination and Toxicity*. 94(4):419–424.
- Gromaire, M.C., A. Garnaud, M. Saad, G. Chebbo. 2001. Contribution of different sources to the pollution of wet weather flows in combined sewers. *Water Research*. No. 2 521–533.
- Gustavsson, N., B. Bølviken, D.B. Smith, and R.C. Severson. 2001. Geochemical. Landscapes of the Conterminous United States—New Map Presentations for 22 Elements, U.S. Geological Survey Professional Paper 1648. 44 p.
- Hallegraeff, G.M. 1993. A review of harmful algal blooms and their apparent global increase. *Phycologia* 32:79-99.
- Hasajšlová, J., and J. Zrostlíková. 2003. Matrix effects in (ultra)trace analysis of pesticide residues in food and biotic matrices. *Journal of Chromatography A*. 1000(2003)181–197.
- Helsel, D.R. 2006. Fabricating data: How substituting values for nondetects can ruin results, and what can be done about it. *Chemosphere* 65; 2434-2439.
- Kayhanian, M., A. Singh, and S. Meyer. 2002. Impact of non-detects in water quality data on estimation of constituent mass loading. *Water Science and Technology* 45(9); 219-225.
- Klasing, S. and R. Brodberg (2008). Development of Fish Contaminant Goals and Advisory Tissue Levels for Common Contaminants in California Sport Fish: Chlordane, DDTs, Dieldrin, Methylmercury, PCBs, Selenium, and Toxaphene. California Office of Environmental Health Hazard Assessment, Sacramento, CA.
- Klasing, S. and R. Brodberg (2011). Development of Fish Contaminant Goals and Advisory Tissue Levels for Common Contaminants in California Sport Fish: Polybrominated Diphenyl Ethers (PBDEs). California Office of Environmental Health Hazard Assessment, Sacramento, CA.
- Kudela, R.M., R.C. Dugdale. 2000. Nutrient regulation of phytoplankton productivity in Monterey Bay, California. *Deep-Sea Res II* 47:1023-1053
- Kudela, R.M., J.P. Ryan, M.D. Blakely, J.Q. Lane, and T.D. Peterson. 2008. Linking physiology and ecology of *Cochlodinium* to better understand harmful algal bloom events: a comparative approach. *Harmful algae*. 7:278–292.
- Lee, L., and D. Helsel. 2005. Statistical analysis of water-quality data containing multiple detection limits: S-language software for regression on order statistics. *Computer & Geoscience*. 31; 1241-1248.

Lorenzo, J.I., O. Nieto, R. Beiras. 2002. Effect of humic acids on speciation and toxicity of copper to *Paracentrotus lividus* larvae in seawater. *Aquatic Toxicity*. 58: 21–41.

Lye, D.J. 2009. Rooftop runoff as a source of contamination: A review. *Science of the Total Environment*. 407:5429–5434.

Meador, J.P. 1991. The interaction of pH, dissolved organic carbon, and total copper in the determination of ionic copper and toxicity. *Aquatic Toxicity*. 19:13–32.

Niessen, W.M.A, P. Manini, and R. Andreoli. 2006. Matrix effects in quantitative pesticide analysis using liquid chromatography-mass spectrometry. *Mass Spectrometry Reviews*. 25: 881-899.

Paerl, H.W., and J. Huisman. 2008. Blooms like it hot. *Science*. 320:57-58.

Phillips, B.M., B.S. Anderson, J.W. Hunt, R. Tjeerdema, C. Beegan, F.H. Palmer. 2004. Marine Bioassay Project, Twelfth Report. University of California, Davis, Marine Pollution Studies Laboratory at Granite Canyon. Report to California State Water Resources Control Board, Division of Water Quality, Oceans Unit. 34 pp.

Pitt, R., R. Bannerman, S. Clark, D. Williamson. 2004. Sources of pollutants in urban areas (Part 2) – Recent sheetflow monitoring. *Effective Modeling of Urban Water Systems*. Monograph 13. Pp 485–506.

Rainbow, P.S. 1995. Physiology, physicochemistry and metal uptake – a crustacean perspective. *Marine Pollution Bulletin*. 31(1–2):55–59.

Schiff, K., J. Brown, S. Trump, and D. Hardin. 2015. *Near-Coastal Water Quality at Reference Sites Following Storm Events*. *Marine Pollution Bulletin* 103(1-2):294–300.

Schmider, E., M. Ziegler, E. Danay, L. Beyer, and M. Bühner. 2010. Is it really robust? Reinvestigating the robustness of ANOVA against violations of the normal distribution assumption. *Methodology*, 6(6): 147–151.

Shahin, L. 2004. Analysis of some chlorinated pesticides in Jordanian ground- and surface-waters by solid-phase extraction and mass spectrometric detection – a method development. Submitted in partial fulfillment of the requirements for the degree of Master in Water Resources and Livelihood Security, Department of Water and Environmental Studies, Linköping University, Sweden. 58pp.

Singarella, P.N. and K.E. Richardson. 2008. When water becomes a waste: A call for a practical approach to regulating stormwater discharges. *Environs, Environmental Law and Policy Journal* University of California, Davis. 31(2):125–154.

Smith, R.W. 2002. The use of Random-Model Tolerance Intervals in Environmental Monitoring and Regulation. *Journal of Agricultural, Biological, and Environmental Statistics*. 7(1): 74-94.

State Water Resources Control Board. 2012. State Water Resources Control Board Resolution No. 2012-0012; *Approving Exceptions to the California Ocean Plan for Selected Discharges into Areas of Biological Significance, Including Special Protections for Beneficial Uses, and Certifying a Program Environmental Impact Report*. Environmental Protection Agency, State Water Resources Control Board, Sacramento, CA. March 20, 2012. 27p.

Sutton, R., M.D. Sedlak, D. Yee, J.A. Davis, D. Crane, R. Grace, N Arsem (2014). Declines in polychlorinated biphenyl contamination of San Francisco Bay following production phase-outs and bans. *Environmental Science and Technology*. 49: 777–784.

Tatara, C.P., M.C. Newman, J.T. McCloskey, P.L. Williams. 1997. Predicting relative metal toxicity with ion characteristics: *Caenorhabditis elegans* LC50. *Aquatic Toxicity*. 39:279–290.

U.S. Environmental Protection Agency (2000). *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 1 Fish Sampling and Analysis, Third Edition*. Office of Science and Technology, Office of Water, U.S. Environmental Protection Agency, EPA 823-B-00-007, Washington, D.C.

U.S. Environmental Protection Agency. 2004. *Revised Assessment of Detection and Quantitation Approaches*. Office of Science and Technology, Office of Water, U.S. Environmental Protection Agency, EPA-821-B-04-005.

Wicke, D., T.A. Cochrane, A.D. O’Sullivan, S. Cave, M. Derksen. 2014. Effect of age and rainfall pH on contaminant yields from metal roofs. *Water Science and Technology*. 69(10):2166–2173.

Windham, G.C., S.M. Pinney, A. Sjödin, R. Lum, R.S. Jones, L.L. Needham, F.M. Biro, R.A. Hiatt, L.H. Kushi (2010). Body burdens of brominated flame retardants and other persistent organohalogenated compounds and their descriptors in U.S. girls. *Environmental Research* 110(3): 251–257.

Windham, G.C., S.M. Pinney, R.W. Voss, A., A. Sjödin, F.M. Biro, L.C. Greenspan, S. Stewart, R.A. Hiatt, L.H. Kushi. 2015. Brominated flame retardants and other persistent organohalogenated compound in relation to timing of puberty in a longitudinal study of girls. *Environmental Health Perspectives*. 123(10):1046–1052.

Yamamoto, H., H.M. Liljestrand, Y. Shimzu, and M. Morita. 2003. Effects of physical-chemical characteristics on the sorption of selected endocrine disruptors by dissolved organic matter surrogates. *Environmental Science and Technology*. 37(12): 2646–2657.

## Appendix A. Scope of Work

### Central California Areas of Special Biological Significance Storm Water Monitoring to Satisfy Special Protections Scope of Work

#### I. Introduction

The Central Coast ASBS Regional Monitoring Program will be implemented during the 2012–2013 and 2013–2014 storm seasons and includes all ASBS responsible parties<sup>2</sup> on the Central Coast, covering an area from Big Sur, in Monterey County, to Pt. Reyes, in Marin County. This Scope of Work for the Central Coast ASBS Regional Monitoring Program has been developed through discussions with staff from State and Regional Water Boards, as well as the responsible parties discharging storm water into Areas of Special Biological Significance (ASBS).

#### II. Technical Program

In all specifications for storm water and receiving water monitoring that follow, the minimum requirement for a storm shall satisfy the criteria specified in the Special Protections (i.e., >0.10 inches of rainfall resulting in runoff, >72 hours from the previous storm). Moreover, every attempt shall be made to satisfy the criteria for storm runoff monitoring conducted by the Monterey Bay National Marine Sanctuary (i.e., sheeting water on roadways, heavy flow through the storm drain system and conductivity levels less than 1000 micro Siemens ( $\mu\text{S}$ ) and declining) and ensure sufficient time after the initiation of rainfall to allow for time of concentration to include flow runoff from all parts of the catchment or watershed.

This Scope of Work covers monitoring requirements specified in the Special Protections for 12 participants<sup>1</sup> designated as Responsible Parties, as follows:

- National Park Service, Point Reyes National Seashore
- Marin County
- San Mateo County
- Monterey Bay Aquarium
- Hopkins Marine Station
- City of Monterey
- City of Pacific Grove
- Carmel by the Sea
- Pebble Beach Company
- Monterey County
- California Department of Parks and Recreation
- Caltrans

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<sup>2</sup> It should be noted that three participants, Caltrans, National Park Service and California Department of Parks and Recreation, have not yet committed to full participation in the Central Coast regional program. These State and Federal Agencies may contract separately to implement their monitoring requirements, but with a commitment that they use the same monitoring design, laboratories for sample analysis and provide their data for analysis with the other participants.

While the City of Monterey is a Responsible Party, it does not operate any storm runoff outfalls of its own that drain into an ASBS. It does, however, contribute runoff to an ASBS outfall operated by the City of Pacific Grove. Storm water, sediment, receiving water and reference site monitoring will be performed under this Scope of Work for Monterey Bay Aquarium and Hopkins Marine Station in compliance with the individual Draft Mitigated Negative Declaration documents issued to each. These two participants have other monitoring requirements for seawater discharges that are being performed outside this Scope of Work.

## **A. Core Monitoring**

### **1. Runoff Flow Measurements**

Total annual storm runoff from each participant shall be estimated (modeled) by using measured rainfall and the amount of impervious area (to be provided by each participant) in each catchment. Targeted ground-truth measurements will be made to calibrate the model. This runoff modeling will permit estimates of total annual and event-specific loads for each participant.

### **2. Discharge Monitoring**

All outfalls  $\geq 18$  inches shall be sampled, as follows:

- a. 1 storm in each of 2 years, except for discharges at receiving water sites, which shall be sampled in the same 3 storms sampled for receiving water;
- b. Each sample shall be analyzed for oil and grease, total suspended solids and fecal indicator bacteria;
- c. Annual samples (1 storm in each year) shall be analyzed for critical life stage chronic toxicity with a sea urchin using salted-up water.

All samples from outfalls  $\geq 36$  inches shall be sampled, as follows:

- a. 1 storm in each of 2 years, except for discharges at receiving water sites, which shall be sampled in the same 3 storms each year that are sampled for receiving water;
- b. Each sample shall be analyzed for oil and grease, total suspended solids and fecal indicator bacteria, California Ocean Plan trace metals, polynuclear aromatic hydrocarbons, organophosphorous pesticides, pyrethroid pesticides and nutrients (ammonia, nitrate, urea and phosphate);
- c. Annual samples (1 storm in each year) shall be analyzed for critical life stage chronic toxicity with a sea urchin test using salted-up discharge water.

## **B. Receiving Water and Reference Monitoring**

### **1. Receiving Water Monitoring**

Receiving water (receiving water = in the surf zone at the point of contact between runoff and the ocean) at 11 large storm water outfalls selected to represent worst-case conditions shall be sampled as follows:

- a. Samples shall be collected before and during 3 storms in each of 2 years;
- b. Each sample shall be analyzed for oil and grease, total suspended solids, fecal indicator bacteria, California Ocean Plan trace metals, polynuclear aromatic

- hydrocarbons, organophosphorous pesticides, pyrethroid pesticides and nutrients (i.e., nitrate, ammonia, urea, orthophosphate);
- c. Samples collected during storms shall be analyzed for critical life stage chronic toxicity with 3 marine species (sea urchin, mussel and giant kelp).

## 2. Reference Site Monitoring

Ocean water at 11 selected reference sites (reference site = in the surf zone at the mouth of a watershed with >90% open space and no listed water quality impairments) shall be sampled as follows:

- Samples shall be collected during 3 storms in each of 2 years;
- Each sample shall be analyzed for oil and grease, total suspended solids, fecal indicator bacteria, California Ocean Plan trace metals, polynuclear aromatic hydrocarbons, organophosphorous pesticides, pyrethroid pesticides and nutrients;
- Each sample shall be analyzed for of critical life stage chronic toxicity with 3 marine species (sea urchin, mussel and giant kelp).

The proposed locations for reference sites span the study region. One reference site described below is not part of this Scope of Work, but is included because State Water Board staff requested that the Central Coast regional program determine the location of that reference site. Locations of sites south of Point Lobos were selected based upon a reconnaissance survey made on November 19, 2012. Several of these southern sites involve either substantial hikes, permission from property owners or special permission for vehicle access. Consequently, adjustments to site locations may be necessary. Moreover, access to at least one site will require crossing a creek to reach the beach at the creek mouth and extreme precautions will be necessary during storm events. The proposed reference locations for water quality monitoring are as follows:

Region	Specific Site
North of Point Reyes	Salmon Creek (USAF responsibility, not covered by this Scope of Work))
San Mateo County	Tunitas Creek
	Gazos Creek
South of Año Nuevo	Scott Creek
Non-urban shoreline in Monterey Bay	La Selva Beach
	Marina State Beach
South of Point Lobos	Malpaso Creek <sup>a</sup>
	Doud Creek
	Soberanes Creek
Big Sur coast <sup>a</sup>	Big Sur River
	Sycamore Creek
	Big Creek
Total covered by the Scope of Work	11

<sup>a</sup> = Beach access to ocean requires crossing the creek.



Specific locations of outfalls to be monitored are as follows:

>18"	>36"	Responsible Party	Location	Longitude	Latitude	Nearest SWRCB Site		
						ID	Longitude	Latitude
	X <sup>a</sup>	Marin County	Trailhead at Agate Beach	-122.71059	37.89749	DUX009	-122.71058	37.89757
X		San Mateo County	Maritime Walk	-122.517537	37.531153	FIT012	-122.51756	37.53115
X		San Mateo County	Juliana	-122.516679	37.529092	FIT015	-122.51667	37.52915
X		San Mateo County	Distillery	-122.513269	37.517706	FIT028	-122.51355	37.51789
X		San Mateo County	Madrone	-122.511592	37.514237	FIT029	-122.51067	37.51246
	X <sup>a</sup>	San Mateo County	Weinke Way	-122.516958	37.528645	FIT016	-122.5173	37.5282
X		California State Parks	Año Nuevo	-122.32181	37.11666	ANO012	-122.32181	37.11666
	X	California State Parks	Point Lobos	-121.93812	36.5187	PTL004	-121.93812	36.5187
	X <sup>a</sup>	California State Parks	Año Nuevo	-122.33662	37.13245	ANO027	-122.33662	37.13245
	X	California State Parks	Point Lobos	-121.94775	36.51524	PTL034	-121.94775	36.51524
	X	California State Parks	Julia Pfeiffer Burns	-121.68885	36.17192	PFE008	-121.68885	36.17192
	X	California State Parks	Julia Pfeiffer Burns	-121.68629	36.17072	PFE011	-121.68629	36.17072
	X	California State Parks	Julia Pfeiffer Burns	-121.68281	36.16924	PFE012	-121.68281	36.16924
	X	California State Parks	Julia Pfeiffer Burns	-121.6773	36.16634	PFE015	-121.6773	36.16634
	X	California State Parks	Julia Pfeiffer Burns	-121.6764	36.16569	PFE016	-121.6764	36.16569
	X	California State Parks	Julia Pfeiffer Burns	-121.66883	36.1553	PFE026	-121.66883	36.1553
	X	California State Parks	Julia Pfeiffer Burns	-121.66781	36.15469	PFE027	-121.66781	36.15469
	X <sup>a</sup>	Pacific Grove	Lover's at Ocean View	-121.91614	36.6246	PCG120	-121.91613	36.6246
X		Pacific Grove	Ocean View between Fountain Avenue and 15th Street	-121.914835	36.62381	PCG215	-121.91484	36.62378
	X <sup>a b</sup>	Pacific Grove	Ocean View between 12th Street and 13th Street	-121.913831	36.622873	PCG219	-121.91381	36.62281
	X	Pacific Grove	Ocean View at 15th Street	-121.91472	36.62339	PCG217	-121.91472	36.62339
X		Pacific Grove	Ocean View between Clyte Street and Naiad Street	-121.919561	36.627369	PCG069	-121.91955	36.62735
X		Pacific Grove	Northwest corner of Lover's Point Park at Ocean View Boulevard	-121.916596	36.626648	PCG098	-121.91657	36.6266
X		Pacific Grove	Grand Avenue at Ocean View	-121.914835	36.62381	PCG215	-121.91484	36.62378
X		Pacific Grove	8th Street at Ocean View	-121.910348	36.621624	PCG229	-121.91036	36.62162
X	X <sup>a c</sup>	Pacific Grove	Ocean View at the Hopkins Marine Laboratory Stanford University	-121.90305	36.61897	PCG257 PCG258	-121.90305	36.61897
X		Pacific Grove	At Ocean View between 7th Street and	-121.909634	36.621125	PCG230	-121.90995	36.62115

>18"	>36"	Responsible Party	Location	Longitude	Latitude	Nearest SWRCB Site		
						ID	Longitude	Latitude
			5th Street					
	X <sup>a</sup>	County of Monterey	TBD (12")	-121.93286	36.54439	CAR029	-121.93286	36.54439
	X <sup>a</sup>	Carmel	4 <sup>th</sup> Avenue	-121.93075	36.55610	CAR062	-121.93075	36.55605
X		Carmel	Ocean Avenue	-121.93030	36.55502	CAR061	-121.93033	36.55501
X		Carmel	8 <sup>th</sup> Avenue	-121.92940	36.55250	CAR059	-121.92933	36.55275
X		Carmel	10 <sup>th</sup> Avenue	-121.92898	36.55007	CAR050	-121.92904	36.55003
X		Carmel	11 <sup>th</sup> Avenue	-121.92877	36.54883	CAR046	-121.92877	36.54881
X		Carmel	13 <sup>th</sup> Avenue	-121.92903	36.54641	CAR037	-121.9291	36.5464
X		Carmel	parking lot at Del Mar near Ocean Avenue	-121.93003	36.55442	CAR060	-121.93006	36.55439
X		Carmel	9 <sup>th</sup> Avenue	-121.92890	36.55117	CAR055	-121.92891	36.55117
X		Carmel	Scenic Road & Santa Lucia Avenue	-121.92962	36.54552	CAR093	-121.92968	36.54547
X		Carmel	12 <sup>th</sup> Avenue	-121.92857	36.54765	CAR044	-121.92854	36.54767
X		Pebble Beach Company	Stillwater Pier	-121.942739	36.566625	CAR279	-121.94274	36.56655
X		Pebble Beach Company	18 <sup>th</sup> Fairway PBGL	-121.948014	36.567247	CAR299	-121.94803	36.5672
X		Pebble Beach Company	18 <sup>th</sup> Green PBGL / Lodge	-121.950131	36.567372	CAR221	-121.9501	36.56738
	X <sup>a</sup>	Pebble Beach Company	18 <sup>th</sup> Green PBGL / Lodge	-121.950097	36.567383	CAR220	-121.95001	36.56741
	X	Pebble Beach Company	9 <sup>th</sup> Green PBGL	-121.933397	36.560394	CAR076	-121.93337	36.5603
X <sup>a</sup>		Caltrans	Fitzgerald	-122.51771	37.53154	FIT011	-122.51771	37.53154
	X	Caltrans	Año Nuevo	-122.29297	37.10714	ANO035	-122.29297	37.10714
	X	Caltrans	Año Nuevo	-122.297	37.11084	ANO034	-122.297	37.11084
	X	Caltrans	Año Nuevo	-122.29764	37.1113	ANO032	-122.29764	37.1113
	X <sup>a</sup>	Caltrans	Año Nuevo	-122.29881	37.11202	ANO033	-122.29881	37.11202
	X	Caltrans	Año Nuevo	-122.30121	37.11334	ANO030	-122.30121	37.11334
	X	Caltrans	Carmel Bay	-121.9247	36.52453	CAR007	-121.9247	36.52453
X		Caltrans	Carmel Bay	-121.92457	36.52469	CAR026	-121.92457	36.52469

<sup>a</sup> = Sites selected for discharge receiving water monitoring

<sup>b</sup> = Monitoring of this site will be shared between the cities of Pacific Grove and Monterey

<sup>c</sup> = Monitoring of this site will be shared among Pacific Grove, Monterey Bay Aquarium and Hopkins Marine Station

### 3. Biological Monitoring

Recent studies have examined whether rocky intertidal communities vary in response to storm water discharges. Initial results from southern California suggest that 2 out of 11 discharge sites exhibited community composition and abundances that could be consistent with storm water discharges (Raimondi *et al*, 2012). Consequently, monitoring of rocky intertidal communities shall be part of this program. The community structure in rocky intertidal habitats shall be measured once at 6 sites near ASBS storm water discharges and at 2 reference sites. Sampling shall involve point-contact estimates of substrate coverage by species along transects from the high intertidal zone to the low intertidal zone. Biological monitoring sites have been selected in consultation among permittees and regulatory agencies with consideration for the locations of sites with existing data.

Rocky intertidal communities will be sampled at the following sites:

ASBS	Sampling Site Name
Año Nuevo Point and Islands ASBS	Año Nuevo
Carmel Bay ASBS	Stillwater
Duxbury Reef ASBS	Bolinas Point
James V. Fitzgerald Marine Reserve ASBS	Fitzgerald Marine Reserve
Pacific Grove ASBS	Hopkins
Point Lobos Ecological Reserve ASBS	Point Lobos
Reference	Santa Maria Creek
Reference	Pigeon Point

### 4. Bioaccumulation Monitoring

California mussels are known to accumulate concentrations of pollutants in their tissues to concentrations much higher than found in the surrounding water. Consequently, they have been widely applied in studies of water quality status and trends (e.g., CCLEAN, 2012; Davis *et al*, 1999). Consequently, concentrations of contaminants shall be measured in resident mussels from sites near ASBS storm water discharges and from reference sites distant from urbanized ASBS areas utilizing existing programs, wherever possible, as follows:

- a. Population composites of mussels of roughly uniform shell length shall be collected from each of 7 sites.
- b. Each composite shall be thoroughly homogenized and analyzed for polynuclear aromatic hydrocarbons, polychlorinated biphenyls, polybrominated diphenyl ethers, chlorinated pesticides, pyrethroid pesticides and Lomefloxacin. These analytes are slightly different from those measured in sections A and B and, except for pyrethroids and Lomefloxacin, are consistent with those measured by CCLEAN.

The following sites will be sampled for bioaccumulation:

Sites
Point Reyes
Scott Creek
Laguna Creek
41 <sup>st</sup> Avenue, Capitola
Lovers Point
Fanshell Overlook, 17-Mile Drive
Carmel River Beach
Total = 7

### C. Mooring Field Operations (Pebble Beach Company only)

#### 1. Receiving Water

Ocean receiving water at the mooring facility shall be sampled as follows:

- a. Samples shall be collected monthly from May through October on a high use weekend in each month.
- b. Samples shall be analyzed for Ocean Plan indicator bacteria, residual chlorine, copper, zinc, grease and oil, methylene blue active substances (MBAS), and ammonia nitrogen.

#### 2. Sediments

Subtidal sediment shall be sampled, as follows:

- a. Samples shall be collected annually from within the mooring field and below the pier.
- b. Samples shall be analyzed for Ocean Plan Table 1 metals (for marine aquatic life beneficial use), acute toxicity (using *Eohaustorius estuaries*), PAHs, and tributyltin.

### D. General Requirements

#### 1. Ensure Data Quality

- a. All sampling and analysis shall conform to a Sampling and Analysis Plan (SAP) and to a Quality Assurance Program Plan (QAPP) that are consistent with requirements of the State of California Surface Water Ambient Monitoring Program (SWAMP). At a minimum, sampling shall be conducted so as to ensure that samples are representative of the site and matrix being sampled and to minimize the introduction of extraneous contamination into samples. Ultra-clean techniques shall be used for collection samples to be analyzed for organic contaminants and trace metals.
- b. Samples of the same type shall all be performed by the same laboratory and shall include appropriate lab blanks, certified reference materials, matrix spikes and matrix spike duplicates and reporting limits shall equal or be lower than those required by SWAMP.

- c. An audit will be prepared describing laboratory performance relative to data quality objectives prescribed in the QAPP.
2. Ensure data availability  
All chemical data will be uploaded to the California Environmental Data Exchange Network annually.
  3. Reporting  
Annual reports shall be delivered within 6 months of the completion of laboratory analyses. At a minimum, annual reports shall include a complete description of sampling methods, sites and analytical methods and analysis of data, including comparison of data from discharges and their respective receiving water sites with those from reference sites and the California Ocean Plan and shall be comparable to Schiff *et al* (2011). The annual report for the second year will be cumulative, including analysis of all data from both years to provide a characterization of storm water discharges and their effects on receiving water quality in Areas of Special Biological Significance.
  4. Areas of Special Biological Significance Included  
Storm runoff from program participants flows into the following ASBS:
    - National Park Service, Point Reyes National Seashore
      - Point Reyes Headlands ASBS
      - Double Point ASBS
      - Duxbury Reef ASBS
    - County of Marin
      - Duxbury Reef ASBS
    - County of San Mateo
      - James V. Fitzgerald ASBS
    - California State Department of Parks and Recreation
      - Año Nuevo ASBS
      - Point Lobos ASBS
      - Julia Pfeiffer Burns ASBS
    - Monterey Bay Aquarium
      - Pacific Grove ASBS
    - Hopkins Marine Station
      - Pacific Grove ASBS
    - City of Monterey
      - Pacific Grove ASBS
    - City of Pacific Grove
      - Pacific Grove ASBS
    - City of Carmel-by-the-Sea
      - Carmel Bay ASBS
    - Pebble Beach Company
      - Carmel Bay ASBS
    - County of Monterey
      - Carmel Bay ASBS
    - Caltrans

- James V. Fitzgerald ASBS
- Año Nuevo ASBS
- Carmel Bay ASBS

**Literature Cited**

- CCLEAN. 2012. Central Coast Long-term Environmental Assessment Network Annual Report, 2010–2011.
- Davis, JA, Stephenson M, Hardin, D, Gunther AJ, Sericano J, Bell D, Scelfo GH, Gold J, Crick J. 1999. Long term bioaccumulation monitoring with transplanted bivalves in San Francisco Bay. *Marine Pollution Bulletin*. 38:170–181.
- Raimondi, P., K. Schiff and D. Gregorio. 2012. Characterization of the rocky intertidal ecological communities associated with southern California Areas of Special Biological Significance. Southern California Coastal Water Research Project Technical Report 703 – May 2012. Costa Mesa, CA.
- Schiff, K.C., B. Luk, D. Gregorio and S. Gruber. 2011. Southern California Bight 2008 Regional Monitoring Program: II. Areas of Special Biological Significance. Southern California Coastal Water Research Project. Costa Mesa, CA.



## **Appendix B. Laboratory QA Summaries**

### **The Central Coast Areas of Special Biological Significance Regional Monitoring Program and Reference Site Monitoring: Water Year 2014**

June 15, 2015

**Submitted to:**  
**Monterey Regional Water Pollution Control Agency**

**Submitted by:**

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## List of Terms

AMS	Applied Marine Sciences, Inc.
CRM	Certified Reference Material
FB	Field Blank
FIB	Fecal Indicator Bacteria
FD	Field Duplicate
LCS/LCSD	Lab Control Sample / Lab Control Sample Duplicate
LPM	Laboratory Project Manager
MBAS	Monterey Bay Analytical Services
MDL	Method Detection Limit
MPSL	Marine Pollution Studies Laboratory
MQO	Measurement Quality Objective
MS/MSD	Matrix Spike / Matrix Spike Duplicate
ND	Non Detect
O&G	Oil & Grease
QA	Quality Assurance
QAO	Quality Assurance Officer
QAPP	Quality Assurance Project Plan
QC	Quality Control
RL	Reporting Limit
RPD	Relative Percent Difference
SWAMP	Surface Water Ambient Monitoring Program
TM	Trace Metal
TSS	Total Suspended Solids
WY	Water Year

## List of QA Codes

BRK	No concentration sample container broken
ERV	Exceeds reference control limits
EUM/VEUM	LCS is outside of control limits
GB/VGB	Matrix spike recovery not within control limits
GN	Surrogate recovery is outside of control limits
IL/VIL	RPD exceeds laboratory control limit
IP/VIP	Analyte detected in field or lab generated blank
PG	Calibration verification outside control limits
VFDP	Field duplicate RPD above QC limit; flagged by QAO
VREL	Target RLs not achieved due to change in lab capabilities
VQCP	QA/QC protocols were not met for precision, flagged by QAO
VRVQ	Based on professional judgment QA/QC protocols were not met, flagged by QAO

## Introduction

Below are narrative summaries of reviews of QA/QC samples analyzed with reported field samples for WY2014. QA/QC samples were evaluated using the procedures and measurement quality objectives (MQOs) described in the project QAPP (AMS 2013). WY2014 monitoring activities included within this review incorporated the following components: (1) water quality monitoring, (2) sediment quality monitoring; and (3) bioaccumulation monitoring. Each of these components is described in detail in the following sections.

## Water Quality Monitoring

WY2014 monitoring was conducted between October 14, 2013 and March 26, 2014. Monitoring included both pre-storm sampling and post-storm sampling associated with each precipitation event. With one notable exception (discussed in more detail below in Section 0), QA/QC results generally met project MQOs, with some minor deviations.

Results of individual analytes, or groups of analytes, are described in more detail below, along with the laboratory responsible for its analysis. The groupings of individual analytes follow the convention of SWAMP<sup>3</sup> where applicable.

### *Hg*

Hg was analyzed by the Marine Pollution Studies Laboratory at Moss Landing (MPSL). MPSL analyzed both freshwater samples (i.e., discharge samples) and marine samples (i.e., receiving water and reference samples), using the same method but diluting the marine samples before processing. Consistent with Project MQOs (AMS 2013), QC checks reported by the lab included laboratory blanks, Laboratory Control Samples (LCSs) or Certified Reference Materials (CRMs), Matrix Spike / Matrix Spike Duplicate (MS/MSD) pairs, and laboratory duplicates.

### **Sensitivity**

MPSL achieved target RL for Hg for all WY2014 analyses. Approximately 13% of samples (including analysis of field samples and lab duplicates) were reported as Non Detect (ND).

### **Lab Blanks**

Reported results for all analyses of TMs are blank corrected. Lab blank contamination was identified in only one batch of samples in WY2014, lab batch MPSL-DFG\_Hg13-044w\_W\_Hg associated with the 10/15/13 sampling event. For this batch, one of the three method blanks reported slightly exceeded the RL and was flagged by the lab with an “IP” qualifier. Data associated with this lab batch (with detectable concentrations) were flagged with a “VIP” qualifier but were not censored because, consistent with MPSL protocols, the average result of the blanks is below MDL. All other method blanks processed in WY2014 were reported as ND.

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<sup>3</sup> Available at <http://checker.swamp.mpsl.mlml.calstate.edu/QAPRP/QAPrPTableReferenceToC.php>.

## **Recovery**

MPSL analyzed and reported CRM results with each lab batch; the CRM was a freshwater sample, which raises uncertainty for its usage with marine samples. Recovery results were good, with all recoveries within the 92% to 99% range, well within QAPP MQO of 75 to 125%. MPSL also analyzed MS samples with each batch. Recoveries for these samples ranged from 85 to 107%, well within the QAPP MQO of 75 to 125%.

## **Precision**

Precision was calculated only for field sample / lab duplicate and MS/MSD sample pairs where an analyte was detected in both samples. Reported Relative Percent Difference (RPD) for field samples ranged from 0 to 17%; RPDs for MS samples ranged from 0 to 22%, both within the Project MQO of <25%.

## **Field QA Samples**

Six Field Blank (FB) results were collected and analyzed blind, each of which reported by the laboratory as ND. Six Field Duplicate samples were collected and analyzed blind. Five of the six were within control limits (<25% RPD). The RPD for the remaining sample pair was reported as 73%, and affected samples from this batch were flagged with a VFDP qualifier.

## **Trace Metal Suite**

Initially, the trace Metals (TMs) As, Cd, Cr, Cu, Ni, Pb, Se, Ag, and Zn were analyzed by MPSL. Due to reliability and quality assurance concerns that arose over the course of the season, AMS made the decision with consent of MPSL to transfer marine samples to Physis for ongoing analyses. Consistent with Project QAPP, QC checks reported by the lab included laboratory blanks, Laboratory Control Samples (LCSs) or Certified Reference Materials (CRMs), Matrix Spike / Matrix Spike Duplicate (MS/MSD) pairs, and laboratory duplicates.

## **Sensitivity**

MPSL and Physis achieved QAPP target RLs for all TMs for all analyses conducted.

## **Lab Blanks**

For MPSL analyses, lab blank contamination was identified in one lab batch associated with analyses of Cu (batch MLML-TM\_HiResICP112213\_W\_TM for 11/22/13 samples), one lab batch associated with analyses of Zn (batch MLML-TM\_HiResICP112213\_W\_TM for 11/22/13 samples), and three lab batches associated with analyses of Ag (MPSL-DFG\_WTM031314\_W\_TM for 3/13/14 sampling, MPSL-DFG\_WTM040814\_W\_TM for 4/8/14 sampling, and MPSL-DFG\_WTM041414AMS\_W\_TM for 4/14/14 sampling). Affected data are flagged with either IP, if qualified by the lab, or VIP, if qualified by the Quality Assurance Officer (QAO).

For Physis analyses, all lab blanks were reported as ND.

## **Recovery**

MPSL analyzed and reported CRM results with each lab batch. Recovery results were good, with all recoveries within QAPP MQO of 75 to 125%. MPSL also analyzed MS samples with each batch.

Recoveries for these samples were generally good (i.e., within QAPP MQO of 75 to 125%), with the exception that some MS recovery results for Ag (66% to 73% recovery in batch MLML-TM\_HiResICP112213\_W\_TM) were outside of the control limits and flagged by the laboratory with a “GB” qualifier. This is not unexpected, as native concentrations of silver within the spiked samples were below detection limits. Affected samples within the lab batch were flagged with “VGB” qualifier.

Physis analyzed and reported LCS results with each lab batch. Recovery results were good for each trace metal analyzed, with all recoveries within QAPP MQO of 75 to 125%. Physis did not analyze and report MS/MSD pairs, instead reporting LCS/LCSD pairs for analysis of precision consistent with their laboratory quality control protocols, so no additional measurement of recovery can be made.

### **Precision**

For MPSSL results, precision was calculated only for field sample / lab duplicate and MS/MSD sample pairs where an analyte was detected in both samples. In general, reported RPDs for all results fell within Project MQO of <25% for most pairs. Reported RPD for one MS/MSD pair for analysis of Zn within lab batch MPSSL-DFG\_WTM040814\_W\_TM fell just outside of control limits (25.5% RPD); this result was associated with a non-project sample (flagged with an “IL” qualifier by the lab) that was identified by the laboratory as containing sand in the aqueous sample, which contributed to sample heterogeneity. Data that were potentially affected by the MS/MSD results were in this case not qualified because of the noted issue with non-project sample heterogeneity and the other measures of precision associated with this batch that exhibit laboratory control of the process, namely that one lab duplicate and two field duplicates each exhibited very low RPDs (0 to 4%).

For Physis results, precision was calculated only for field sample / lab duplicate and LCS/LCSD sample pairs where an analyte was detected in both samples. In general, reported RPDs for field sample / lab duplicate pairs fell within Project MQO of <25%. The following lab duplicates fell outside the QAPP control limits: (1) Cd and Se within lab batch Physis\_E-7146\_W\_TM; (2) Ag and Se within lab batch Physis\_E-7122\_W\_TM; and (3) Cu and Se within lab batch Physis\_E-7120\_W\_TM. Five of the six results were flagged by the lab with an “IL” qualifier, and the sixth was flagged by the QAO with “VIL” qualifier as it was reported as exactly 25%, which falls within the lab control limits, but does not meet the QAPP MQO. Affected data were flagged with “VIL” qualifier. For LCS/LCSD pairs, all reported RPDs fell within QAPP control limits (75 to 125%).

### **Field QA Samples**

Two FB samples were collected for each analyte and analyzed blind by MPSSL. There was minor blank contamination present in at least one result reported for As, Cr, Cu, Pb, and Se within batch MPSSL-DFG\_WTM040814\_W\_TM; affected samples were flagged with a “VIP” qualifier.

Two FD samples were collected and analyzed blind by MPSSL. Field RPDs ranged from 0% to 14%, within QAPP MQOs.

Three FB samples were collected for each analyte and analyzed blind by Physis. There was minor blank contamination present in one result reported for Zn within batch Physis\_E-7122\_W\_TM and all three results associated with analysis of Ag (batches Physis\_E-7120\_W\_TM, Physis\_E-7121\_W\_TM, and Physis\_E-7122\_W\_TM); affected samples were flagged with a “VIP” qualifier.

## **General**

During WY2014, MPSSL had ongoing difficulty with the reliability of the laboratory equipment used to analyze TMs in marine samples. This often caused delays in analyzing and reporting, and eventually contributed to the decision to transfer analyses of TMs to a different lab for WY2015, Physis. In general, the data quality of the reported analytes is considered good and results are acceptable for Project purposes.

## **Nutrients**

Nutrients, including Ammonia as N, Nitrate as N, and Orthophosphate as P, were analyzed by Monterey Bay Analytical Services (MBAS). Consistent with Project MQOs, QC checks reported by the lab included laboratory blanks, Laboratory Control Samples (LCSs), Matrix Spike / Matrix Spike Duplicate (MS/MSD) pairs, and laboratory duplicates.

## **Sensitivity**

For ammonia, MBAS achieved target MRLs for all analyses of nutrients with the exception of ammonia. For two field samples collected on 11/18/13, MBAS employed an alternative distillation method for analysis (SM4500 NH<sub>3</sub> B,C), which resulted in two samples exceeding target MRL. As there was no appropriate qualifier to match this situation, AMS applied the recently-added "VREL" qualifier, which is more related to lab capabilities, and added a LabResultComment to indicate that the elevated RL is associated with the use of alternate method.

## **Blanks**

All laboratory blanks were reported as ND.

## **Recovery**

MBAS analyzed and reported LCS results with each lab batch. Recovery results were good, with all recoveries within QAPP MQO of 80 to 120% (ranging from 90 to 106% for Ammonia, 95 to 104% for Nitrate, and 86 to 110% for Ortho-P).

MBAS also analyzed MS samples with each batch. Recoveries for these samples in several cases (four analyses of Ortho-P associated with batches MBAS\_20131015\_W\_PO4P and MBAS\_20140228\_W\_PO4P, and two analyses of Ammonia associated with batches MBAS\_20140311\_W\_NH<sub>3</sub> and MBAS\_20140321\_W\_NH<sub>3</sub>) fell outside of QAPP MQO of 80 to 120% recovery. Each of the results outside of control limits was associated with analysis of non-project media. Affected samples within the various lab batches were flagged with "VGB" qualifier.

## **Precision**

MBAS reported precision based upon results of MS/MSD samples. Reported RPDs ranged from 0 to 11% for the three nutrients analyzed, all within the QAPP MQO of <25%.

## **Field QA Samples**

Seven FB samples were collected for each analyte and analyzed blind. All results were reported as ND.

Six FD samples were collected and analyzed blind. Field RPDs ranged from 0% to 22%, all within QAPP MQOs. For the majority of samples, no RPD could be calculated as one or both samples were reported below RLs.

### ***Fecal Indicator Bacteria***

Fecal Indicator Bacteria (FIB) analyses included measurement of Fecal Coliform, *E. coli*, and *Enterococcus*. QC checks required by the Project QAPP in place during WY2014 include reporting on laboratory controls, laboratory duplicates (when a sufficient number of duplicates have been analyzed), and laboratory blanks (if samples are diluted).

The majority of FIB samples were analyzed by MBAS. A small number of samples, collected from sampling locations within Marin County south to Tunitas Creek, were sent to Alpha Labs (Alpha) in order to achieve QAPP hold time requirements.

### **Sensitivity**

Both MBAS and Alpha achieved target MRLs for all analyses.

### **Controls**

Both laboratories indicated that results of all required positive and negative controls were acceptable.

### **Blanks**

For MBAS samples, all associated lab blanks were reported below detection and reporting limits.

For Alpha samples, no lab blank information was reported. All results were flagged with “VRVQ” qualifier, indicating that overall QA protocols were not met. The data was not rejected outright, as discussions with the Laboratory Project Manager (LPM) indicated that the analyses were in control throughout Project implementation. Data should, however, be reviewed in context with what was reported.

### **Precision**

For MBAS samples, precision was calculated only for two field sample / lab duplicate pairs where the analyte was detected in both samples. Both RPDs for field sample and duplicate pairs for analysis of Fecal Coliform within batch MBAS\_20140206\_W\_FC exceeded Project MQO of <25% (66 and 70%, respectively). Affected samples within this lab batch were flagged with “VIL” qualifier. All other field samples were flagged with a “VQCP” qualifier, indicating that QAPP protocols for precision were not achieved / reported by lab.

For Alpha samples, precision was not reported. Per above, all data flagged with “VVQ” qualifier.

### **Field QA Samples**

Field Blanks are not required by Project QAPP.

For MBAS samples, six to seven FD samples were collected for each FIB analyte and analyzed blind. MBAS reported RPDs for each FIB analyte generally fell within the Project QAPP control limits of 75 to 125%. One of six Fecal Coliform samples (17%) and one of seven *Enterococcus* samples (14%) exceeded

control limits, and were flagged with the “VFDP” qualifier. No additional qualification was required as, per above, all FIB field samples were flagged with the “VQCP” qualifier.

Field duplicate samples were not submitted to Alpha during WY2014.

### **General**

Based upon the inadequacy of QA data reporting associated with WY2014 analyses reported by Alpha, AMS reviewed the QA issues with the Alpha LPM. Alpha informed AMS that the required QA data had been conducted, but it was not worth the effort to compile and report for such a small number of analyses. Based upon this discussion, AMS decided to identify and use an alternate lab for the required FIB analyses for WY2015 monitoring.

After reviewing options, AMS determined that there were no labs in close enough proximity to the monitoring locations to meet hold time requirements. Therefore, AMS made the decision to continue to work with Alpha, but with requirements in place, and additional funding, to support the additional effort required to fully document performance against MQOs.

Per the above discussion, WY2014 analyses of FIB did not report performance relative to all QAPP MQOs. The data for these analytes are qualified, but not censored for use, based upon two factors: (1) current ELAP certifications held by the two labs; and (2) discussions with Laboratory Project Managers that indicated that analyses were conducted consistent with laboratory protocols and were in control. Regarding future usage of the FIB results, all WY2014 FIB data should be viewed within the context of the above discussion. AMS is pursuing corrective actions with each laboratory in hopes of obtaining future analytical results more in line with QAPP requirements.

### ***Conventional Parameters.***

Any analytes not listed within specific SWAMP groupings of analytes were analyzed per the MQOs associated with conventional parameters, including Urea, which is often grouped with Nutrients. Conventional ASBS parameters include the following:

- Oil & Grease (O&G)
- Total Suspended Solids (TSS)
- Urea

All conventional parameters were analyzed by MBAS. Consistent with Project MQOs, QC checks reported by the lab included laboratory blanks, lab dups, LCSs (not applicable for TSS), and Matrix Spike / Matrix Spike Duplicate (MS/MSD) pairs (not applicable for TSS).

### **Sensitivity**

For all three conventional parameters, MBAS achieved target MRLs. For O&G, approximately 5% of samples were of detectable concentration. For TSS, 98% of samples were detectable. And for Urea, 43% of samples were detectable.

### **Blanks**

All laboratory blanks were reported as ND associated with each of the three conventional parameters.

## **Recovery**

For analysis of Urea, MBAS reported recoveries associated with analysis of CRM and LCS samples alternately. Recoveries ranged between 79 and 121%, with the majority of results reported within Project MQO of 80 to 120%. CRM / LCS results outside of the control limits were flagged by the lab with an “ERV” qualifier; affected samples within the lab batch were flagged with “VEUM” qualifier. MBAS also reported recoveries associated with analyses of MS/MSD samples. Three of fifteen recoveries reported fell outside of Project MQO of 80 to 120%, each associated with lab batch MBAS\_20140218\_W\_Urea. Affected samples were flagged with a “VGB” qualifier.

For analysis of O&G, MBAS reported recoveries associated with analysis of LCS. Recoveries ranged between 73 and 99%, with the two analyses outside the Project MQO control limits flagged by the laboratory with the “ERV” qualifier. Affected data within the same lab batch were flagged with the “VEUM” qualifier. MBAS reported MS/MSD information on a subset of lab batches; for each, recoveries fell within MQO control limits.

## **Precision**

For analysis of Urea, MBAS reported precision based upon results of MS/MSD samples. Reported RPDs ranged from 0 to 3%, all within the QAPP MQO of <25%.

For analysis of O&G, MBAS reported precision based upon results of MS/MSD samples. Reported RPDs ranged from 5 to 9%, all within the QAPP MQO of <25%.

For analysis of TSS, MBAS reported precision based upon results of lab duplicate analyses. Reported RPDs ranged from 0 to 29%, with a single result falling outside of the QAPP MQO of <25%. Affected data associated with the 29% RPD (lab batch MBAS\_20140210\_W\_TSS) were flagged with a “VGB” qualifier.

## **Field QA Samples**

Seven and six field blank samples were submitted blind to the laboratory for analysis of O&G and Urea, respectively. All results were reported as ND, with the exception of one O&G sample that was broken in the lab, and flagged with a “BRK” qualifier.

Six Urea FD samples were collected and analyzed blind. For three of the samples, no RPD could be calculated as one or both samples were reported below RLs. Field RPDs for remaining field sample / field duplicate pairs ranged from 4% to 27%, with a single result falling outside of QAPP MQO (<25%). The field duplicate result of 27% was flagged with a “VFDP” qualifier, but remaining samples within the batch were not qualified as three of the four FD samples analyzed associated with this batch met QAPP MQOs.

Seven TSS FD samples were collected and analyzed blind. For one of the samples, no RPD could be calculated as one or both samples were reported below RLs. Field RPDs for remaining field sample / field duplicate pairs ranged from 0% to 31%, with a single result falling outside of QAPP MQO (<25%). Affected data associated with the 31% field RPD were flagged with a “VFDP” qualifier.

## **General**

Data quality assurance is generally good, and all data are considered acceptable for reporting purposes.



## ***Organophosphorus Pesticides.***

Organophosphorus (OP) Pesticides were analyzed by California Department of Fish and Wildlife's Water Pollution Control Laboratory (WPCL). Consistent with Project MQOs, QC checks reported by the lab included laboratory blanks, Laboratory Control Samples (LCSs), Matrix Spike / Matrix Spike Duplicate (MS/MSD) pairs, laboratory duplicates, and surrogate recoveries.

### **Sensitivity**

The majority of OP pesticide analyses achieved QAPP target RLs. For those analyses that exceeded RLs and resulted in ND, data were flagged with the "VREL" qualifier, indicating that lab capabilities had changed over time from what was originally quoted for the project.

It should be noted that, in general, there were very few field samples that generated results at detectable concentrations (<3% for all analytes). Therefore, estimation techniques used to quantify the ND results may greatly influence interpretation.

### **Blanks**

All laboratory blanks were reported as ND.

### **Recovery**

WPCL analyzed and reported LCS results with each lab batch. Recovery results were generally good, with only one recovery reported outside of the QAPP MQO of 50 to 150% for LCS samples, an analysis of chlorpyrifos, methyl for which a second reported LCS fell within the MQO control limits. The affected datapoint was flagged with the "EUM" qualifier by the laboratory.

WPCL also analyzed MS samples on a subset of lab batches. In all cases, recoveries fell within QAPP MQO of 50 to 150% recovery.

WPCL also reported surrogate recoveries associated with each lab batch. With one exception, recoveries fell within the QAPP MQO standard range of 50 to 150% - for lab batch WPCL\_L-088-14\_B1\_W\_OP, one surrogate result fell slightly outside of control limits (155%), and was flagged with "GN" qualifier.

### **Precision**

WPCL reported precision based upon results of LCS/LCSD or MS/MSD analyses. Reported RPDs ranged from 0 to 15% for all OP pesticides analyzed, all within the QAPP MQO of <25%.

### **Field QA Samples**

Six FB samples were collected for each analyte and analyzed blind. All results were reported as ND.

Five FD samples were collected and analyzed blind. In each case, no RPD could be calculated as one or both samples within the field sample / field duplicate pair was reported below RLs.

### **General**

WPCL reported several instances of Continuing Calibration Verification (CCV) exceeding acceptance criteria. These exceedances are flagged with a "PG" qualifier. In each case, the results for associated

field samples all were reported as ND; according to the lab, high CCV results do not adversely affect ND results, and data quality is therefore not considered to be affected.

### ***Pyrethroid Pesticides***

Pyrethroids were analyzed by WPCL. Consistent with Project MQOs, QC checks reported by the lab included laboratory blanks, Laboratory Control Samples (LCSs), Matrix Spike / Matrix Spike Duplicate (MS/MSD) pairs, laboratory duplicates, and surrogate recoveries.

#### **Sensitivity**

The majority of Pyrethroid analyses achieved QAPP target RLs. A total of four analyses of Trans-Permethrin slightly exceeded the target RL (0.11 µg/L actual vs. 0.1 µg/L target). For these four analyses, each of which was reported as ND, data were flagged with the “VREL” qualifier.

It should be noted that, in general, there were relatively few field samples that generated results at detectable concentrations, ranging from a low of 2% for Cypermethrin to a high of 21% for Cyfluthrin. Therefore, estimation techniques used to quantify the ND results may greatly influence interpretation.

#### **Blanks**

All laboratory blanks were reported as either ND or DNQ (for results between DL and RL).

#### **Recovery**

WPCL analyzed and reported LCS results with each lab batch. Recovery results were generally good, with a total of four LCS recoveries reported outside of the QAPP MQO of 50 to 150%; each of these qualified data points is associated with analysis of Deltamethrin/Tralomethrin (within lab batches WPCL\_L-573-13\_W\_PYD, WPCL\_L-057-14\_B2\_W\_PYD, and WPCL\_L-057-14\_B3\_W\_PYD). Affected data was flagged with either the “EUM” or “VEUM” qualifier, depending on whether the flag was added by the laboratory or QAO. The low recoveries, which were not considered unusual for WPCL analyses of Deltamethrin/Tralomethrin, may indicate a potential low bias in results.

WPCL also analyzed MS samples with each lab batch. Recoveries generally fell within QAPP MQO of 50 to 150% recovery. The major exception to this was associated with analysis of lab batch WPCL\_L\_633\_13\_PYD, in which MS/MSD results from a re-extraction and re-analyses were reported with several Pyrethroid compounds above 150% recovery (152 to 181% recoveries). All affected data were flagged with either “GB” or “VGB” qualifier, depending on whether the flag was applied by the lab or QAO.

WPCL also reported surrogate recoveries associated with each lab batch. With one major exception, surrogate recoveries were generally good - recoveries reported by WPCL associated with lab report WPCL\_L-057-14 (lab batches WPCL\_L-057-14\_B2\_W\_PYD and WPCL\_L-057-14\_B3\_W\_PYD) were low and outside of QAPP control limits (50 – 150%). The laboratory investigated and determined that the surrogate solution had degraded over time, and, combined with other QA measures reviewed, are not indicative of low quality data. The affected surrogate recoveries were flagged with a “GN” qualifier by WPCL; a LabResultComment was added to affected data to clarify the cause of the low recoveries.

## **Precision**

WPCL reported precision based upon results of LCS/LCSD and/or MS/MSD analyses. Reported RPDs for LCSDs ranged from 0 to 89% for all Pyrethroid pesticides analyzed. Two results fell outside of the QAPP MQO of <25% (analyses of Deltamethrin/ Tralomethrin in lab batches WPCL\_L-057-14\_B2\_W\_PYD and WPCL\_L-573-13\_W\_PYD; affected samples were flagged by the laboratory with an “IL” qualifier. All reported RPDs for MSDs fell within QAPP MQO of <25%.

## **Field QA Samples**

Six FB samples were collected for Pyrethroids analysis and analyzed blind. All results were reported as ND.

Five FD samples were collected and analyzed blind. In the vast majority of cases, no RPD could be calculated as one or both samples within the field sample / field duplicate pair was reported below RLs. For the four pairs for which RPDs could be calculated, RPDs ranged from 1 to 15%, within the Project QAPP MQO of <25%.

## **General**

WPCL reported several instances of Continuing Calibration Verification (CCV) exceeding acceptance criteria. These exceedances are flagged with a “PG” qualifier. In the vast majority of cases, the results for associated field samples were reported as ND; according to the lab, high CCV results do not adversely affect ND results, and data quality is therefore not considered to be affected. Where field sample results are quantified within affected lab batches, there may be a slight high bias in reported results.

## **PAHs**

PAHs were analyzed by WPCL. Consistent with Project MQOs, QC checks reported by the lab included laboratory blanks, Laboratory Control Samples (LCSs), Matrix Spike / Matrix Spike Duplicate (MS/MSD) pairs, laboratory duplicates, and surrogate recoveries.

## **Sensitivity**

All analyses of PAHs achieved QAPP target RLs.

## **Blanks**

All laboratory blanks were reported as ND.

## **Recovery**

WPCL analyzed and reported LCS results with each lab batch. Recovery results were generally good, with all LCS recoveries falling within the QAPP MQO of 50 to 150%.

WPCL also analyzed MS samples with each lab batch. Recoveries generally fell within QAPP MQO of 50 to 150% recovery. The exception to this was associated with analysis of lab batch WPCL\_L-088-14\_B1\_W\_PAH, in which MS/MSD recovery results for several PAH compounds were reported outside of control limits on both the high and low end. All affected data were flagged with either “GB” or “VGB” qualifier, depending on whether the flag was applied by the lab or QAO.

WPCL also reported surrogate recoveries associated with each lab batch. Surrogate recoveries were generally good; six total surrogate results fell outside of QAPP control limits (50 to 150%) – affected data were flagged with “GN” qualifier.

### **Precision**

WPCL reported precision based upon results of both LCS/LCSD and MS/MSD analyses. Reported RPDs for LCSDs ranged from 0 to 10% for all PAH compounds analyzed, all within the Project MQO of <25%.

RPDs for MS/MSD sample pairs ranged from 0 to 62%. Each of the eleven PAH compound RPDs reported outside of Project QAPP control limits (0 to 25%) were associated with lab batch WPCL\_L-088-14\_B1\_W\_PAH. Affected samples were flagged with either an “IL” or “VIL” qualifier depending on whether it was applied by the lab or QAO.

### **Field QA Samples**

Six FB samples were collected for analysis of PAH compounds and analyzed blind. Only Naphthalene (detected in four of six field blanks) and Pyrene (detected in two of six field blanks) were reported at detectable concentrations. Affected samples were flagged with “VIP” qualifier. These findings suggest that it may be difficult to obtain a “true” concentration of Naphthalene using existing techniques.

Five FD samples were collected and analyzed blind. In the vast majority of cases, no RPD could be calculated as one or both samples within the field sample / field duplicate pair were reported below RLs. For the remaining pairs for which an RPD could be calculated, the reported RPDs associated with sample 203PAC010-DIS-36 collected on 2/26/14 exhibited high RPDs (ranging from 24 to 67%), which may indicate a difference between the two samples in water sampled, sampling technique, laboratory process, or other. Affected samples were flagged with a “VFDP” qualifier.

### **General**

WPCL reported a major lab error in analysis of PAHs in lab batch L-088-14 and L-089-14. A surrogate solution added to all samples contained the following target compounds:

- Methylfluorene, 1-,
- Fluorenes, C1,
- Methyl dibenzothiophene, 4-,
- Dibenzothiophene, C1,
- Dimethylphenanthrene, 3,6-,
- Phenanthrenes/Anthracenes, C2,
- Methylfluoranthene, 2-,
- Fluoranthene/Pyrenes, C1

Concentrations of the above PAH compounds were quantified by the laboratory using an alternative extract (from Pyrethroids analysis), but was reported only as a screening type value due to potential loss that might have occurred through that process. Data were flagged with a “VRVQ” qualifier and “Rej” compliance code by the QAO to indicate their rejection based upon QA concerns. The affected PAH compounds are not among those regulated by the California Ocean Plan and did not affect reported

total PAHs or interim exceedances of the preliminary 85<sup>th</sup> percentile threshold. All other PAH results are considered acceptable for Project usage.

### **Toxicity**

All toxicity testing was conducted by UC Davis Marine Pollution Studies Laboratory at Granite Canyon (Granite Canyon). The toxicity of discharge samples was assessed with the purple sea urchin (*Strongylocentrotus purpuratus*) fertilization test. Receiving water samples were tested with the sea urchin fertilization test, as well as the mussel larval development test with *Mytilus galloprovincialis*, and the giant kelp germination and growth test with *Macrocystis pyrifera*. QC checks required by the Project QAPP in place during WY2014 include laboratory controls (positive, negative, and brine, where applicable) and checks on water quality parameters and test conditions.

### **Controls**

Results of all laboratory controls were acceptable.

### **Water Quality Parameters**

For MBAS samples, all associated lab blanks were reported below detection and reporting limits.

### **Field QA Samples**

Required water quality measurements (i.e., Ammonia, Dissolved Oxygen, pH, Salinity, Temperature) were reported associated with each lab batch. The vast majority of reported water quality parameters fell within recommended ranges listed within QAPP, where applicable. Those falling outside of the recommended ranges are not thought to affect test results or interpretation.

### **General**

Toxicity summary results for two lab batches processed by Granite Canyon for the mussel development test are flagged with an "H" qualifier, indicating the analyses were conducted beyond recommended hold time. In both cases, control organisms used did not meet initial test acceptability criteria. Batches and GC\_ASBSMG4\_W\_TOX and GC\_ASBSMG4\_W\_TOX were analyzed five and six days after collection, respectively, consistent with laboratory protocols. All toxicity results are considered acceptable for Project usage.

### **References**

AMS, 2013. *Quality Assurance Project Plan: The Central Coast Areas of Special Biological Significance Regional Monitoring Program and Reference Site Monitoring, Version 1.0*. Prepared by Applied Marine Sciences, Inc. April 15, 2013.

# Laboratory QA Summary

## The Central Coast Areas of Special Biological Significance Regional Monitoring Program and Reference Site Monitoring: Water Years 2015 and 2016

June 23, 2016

Submitted to:  
Monterey Regional Water Pollution Control Agency

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## List of Terms

AMS	Applied Marine Sciences, Inc.
CRM	Certified Reference Material
FB	Field Blank
FIB	Fecal Indicator Bacteria
FD	Field Duplicate
GC	Granite Canyon
LCS/LCSD	Lab Control Sample / Lab Control Sample Duplicate
LPM	Laboratory Project Manager
MBAS	Monterey Bay Analytical Services
MDL	Method Detection Limit
MPSL	Marine Pollution Studies Laboratory
MQO	Measurement Quality Objective
MS/MSD	Matrix Spike / Matrix Spike Duplicate
ND	Non Detect
O&G	Oil & Grease
PR	Percent Recovery
QA	Quality Assurance
QAO	Quality Assurance Officer
QAPP	Quality Assurance Project Plan
QC	Quality Control
RL	Reporting Limit
RPD	Relative Percent Difference
SWAMP	Surface Water Ambient Monitoring Program
TM	Trace Metal
TSS	Total Suspended Solids
WPCL	Water Pollution Control Lab
WY	Water Year

## List of QA Codes

BRK	No concentration sample container broken
BY/VBY	Sample received at improper temperature, flagged by QAO
CVH	Continuing calibration verification high, no bias
CS/VCS	QC criteria not met due to analyte concentration near RL
DF	Reporting limits elevated due to matrix interferences
ERV	Exceeds reference control limits
EUM/VEUM	LCS is outside of control limits
GB/VGB	Matrix spike recovery not within control limits
GN/VGN	Surrogate recovery is outside of control limits
IL/VIL	RPD exceeds laboratory control limit
IP/VIP	Analyte detected in field or lab generated blank
PG/VPG	Calibration verification outside control limits
RE/VRE	Elevated reporting limits due to limited sample volume
TW/VTW	Water quality parameters outside recommended test method

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	ranges
VFDP	Field duplicate RPD above QC limit; flagged by QAO
VREL	Target RLs not achieved due to change in lab capabilities
VQCP	QA/QC protocols were not met for precision, flagged by QAO
VRVQ	Based on professional judgment QA/QC protocols were not met, flagged by QAO



## 1. Introduction

Below are narrative summaries of the QA/QC review of WY2015 and WY2016 ASBS monitoring results. These assessments were made using the procedures and measurement quality objectives (MQOs) described in the project QAPP (AMS 2014). Monitoring activities included within this review incorporated the following components: (1) water quality monitoring and (2) sediment quality monitoring. These components are described in detail in the following sections.

## 2. Water Quality Monitoring

WY2015 water quality monitoring was conducted between December 9, 2014 and April 8, 2015. WY2016 water quality monitoring was conducted between December 2, 2015 and March 9, 2016. QA/QC results generally met project MQOs, with some minor deviations.

Results of individual analytes, or groups of analytes, are described in more detail below, along with the laboratory responsible for its analysis. The groupings of individual analytes follow the convention of SWAMP<sup>4</sup> where applicable.

### 2.1. Hg

Hg was analyzed by the Marine Pollution Studies Laboratory at Moss Landing (MPSL). MPSL analyzed both freshwater samples (i.e., discharge samples) and marine samples (i.e., receiving water and reference samples), using the same method but diluting the marine samples before processing. Consistent with Project MQOs (AMS 2013), QC checks reported by the lab included laboratory blanks, Certified Reference Materials (CRMs), Matrix Spike / Matrix Spike Duplicate (MS/MSD) pairs, and Laboratory Duplicates.

#### 2.1.1. Sensitivity

MPSL achieved target RL for Hg for all WY2016 analyses. Approximately 5% of samples (9 of 170 samples)<sup>5</sup> were reported as Non Detect (ND).

#### 2.1.2. Lab Blanks

All method blanks processed in WY2015 and WY2016 were reported as ND.

#### 2.1.3. Recovery

MPSL assessed recovery based upon analysis of CRM samples. Recovery results were good, with all recoveries meeting the QAPP MQO of 75 to 125%. MPSL also analyzed MS samples with each batch. Recoveries for these samples also fell within the QAPP MQO of 75 to 125% for each batch.

#### 2.1.4. Precision

Precision was calculated for field sample / lab duplicate and MS/MSD sample pairs where an analyte was detected in both samples. For one sample within batch MPSL-DFG\_20160204\_W\_Hg, the laboratory failed to report an RPD in the EDD; it was therefore calculated manually by QA Officer (QAO) and

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<sup>4</sup> Available at <http://checker.swamp.mpsl.mlml.calstate.edu/QAPRP/QAPrPTableReferenceToC.php>.

<sup>5</sup> Including field samples and field duplicate samples.

entered into the data deliverable as part of the review process. In all cases, reported Relative Percent Difference (RPD) for both field and MS sample pairs achieved the Project MQO of <25%.

### 2.1.5. Field QA Samples

One Field Blank (FB) sample was collected and analyzed blind. The result was reported as ND.

There were no field duplicates analyzed during this period.

## 2.2. Trace Metal Suite

For the various monitoring events, all or a subset of Trace Metals (TMs) Al, As, Cd, Cr, Cu, Fe, Ni, Pb, Se, Ag, and Zn were analyzed by Physis. Consistent with Project QAPP, QC checks reported by the lab included laboratory blanks, Laboratory Control Samples (LCSs) or Certified Reference Materials (CRMs), Lab Control Sample / Lab Control Sample Duplicate (LCS/LCSD) pairs, and Laboratory Duplicates.

### 2.2.1. Sensitivity

Physis achieved QAPP target RLs for all TMs for all analyses conducted. With the exception of Silver (29% NDs), analyses of trace metals generally resulted in detectable concentrations. The relative proportion of field samples and field duplicate samples that were reported at detectable concentrations is summarized in **Error! Reference source not found.**

**Table 1. Proportion of WY2015 and WY2016 Trace Metal Samples Reported as Non Detects**

Analyte	Total NDs	Total Analyses	% ND
Aluminum	0	23	0%
Arsenic	0	176	0%
Cadmium	0	176	0%
Chromium	2	176	1%
Copper	0	176	0%
Iron	0	23	0%
Lead	7	176	4%
Nickel	0	176	0%
Selenium	1	176	1%
Silver	51	176	29%
Zinc	9	176	5%

### 2.2.2. Lab Blanks

All lab blanks were reported as ND.

### 2.2.3. Recovery

Physis analyzed and reported LCS results with each lab batch. Recovery results generally were good for each trace metal analyzed, with the great majority of all reporting recoveries falling within QAPP MQO of 75 to 125%.

There were two exceptions to the above. For lab batch Physis\_E-10059\_W\_TM, the PR reported for analysis of Ag fell outside of QAPP control limits and for lab batch Physis\_E-10138\_W\_TM, the PR

reported for Fe did as well. In both cases, the laboratory flagged the data with the qualifier “Q” to indicate that, while results fell outside of QAPP control limits they did meet laboratory acceptance criteria. A qualifier of “VEUM” was added to the LCS results and affected field samples to indicate the disagreement with the QAPP control limits.

#### **2.2.4. Precision**

Physis calculated precision for field sample / lab duplicate and LCS/LCSD sample pairs where an analyte was detected in both samples. In general, reported RPDs for field sample / lab duplicate pairs fell within Project MQO of <25%, with the following exceptions:

- Analysis of Ag in lab batch Physis\_E-10059\_W\_TM;
- Analysis of Se in lab batch Physis\_E-10107\_W\_TM;
- Analysis of Zn in lab batch Physis\_E-10116\_W\_TM;
- Analysis of Pb, Se, and Zn in lab batch Physis\_E-10138\_W\_TM.

In each case, the QA samples and affected field samples were flagged with the “VIL” qualifier indicating results fell outside QAPP MQO control limits.

In the case of LCS/LCSD pairs analyzed, reported RPDs all achieved the Project MQO of <25%.

#### **2.2.5. Field QA Samples**

Four FD samples were collected and analyzed blind by MPSL in WY2015 and WY2016. Field RPDs ranged from 0% to 105%. Of the 36 sample pairs analyzed, eight (22%) did not achieve the QAPP MQO of an RPD <25%. Those pairs not meeting QAPP MQOs were flagged with a “VFDP” qualifier.

Three FB samples were collected for each analyte and analyzed blind by Physis in WY2015 and WY2016. There was blank contamination present in results reported for Ni and Zn within batch Physis\_E-10138\_W\_TM and Cu and Zn within batch Physis\_E-10116\_W\_TM. Affected field blanks and field samples (i.e., analytes with results <5x the concentration reported for the field blank) were flagged with a “VIP” qualifier.

### **2.3. Nutrients**

Nutrients, including Ammonia as N, Nitrate as N, Orthophosphate as P, and Urea, were analyzed by Monterey Bay Analytical Services (MBAS). Consistent with Project MQOs, QC checks reported by the lab included laboratory blanks, Laboratory Control Samples (LCSs), Matrix Spike / Matrix Spike Duplicate (MS/MSD) pairs, and Laboratory Duplicates.

#### **2.3.1. Sensitivity**

MBAS achieved target MRLs for all analyses of nutrients with the exception of ammonia. Intermittently in WY2015, as in prior years, the MRL reported for ammonia analyses exceeded the target MRL (within lab batches MBAS\_20150824\_W\_NH3 and MBAS\_20150720\_W\_NH3). As in prior years, this change in lab capabilities was not attributable to any issue with the media or analysis, and AMS applied the “VREL” qualifier to those data that had elevated RLs and non-detectable data.

Consistent with prior years, in WY2015 and WY2016 for all nutrients analyzed, a sizable proportion of field samples analyzed resulted in NDs. The relative proportion of field samples and field duplicate samples that were reported at detectable concentrations is summarized in Table 2.

**Table 2. Proportion of WY2015 and WY2016 Nutrient Samples Reported as Non Detects**

Analyte	Total NDs	Total Analyses	% ND
Ammonia	108	132	82%
Nitrate as N	19	125	15%
OilandGrease; HEM	152	160	95%
Orthophosphate as P	15	125	12%
Total Suspended Solids	5	166	3%
Urea	67	125	54%

### 2.3.2. Blanks

For analysis of Ortho-P in lab batch MBAS\_20160219\_W\_PO4P, one of the two lab blanks analyzed showed minor contamination resulting in the lab blank result being reported at the MRL. The blank in question, along with all field samples analyzed that were reported at less than 5 times the blank result, were flagged with the “VIP” qualifier indicating blank contamination. All remaining laboratory blanks, for Ortho-P and all other nutrients analyzed, were reported as ND.

### 2.3.3. Recovery

MBAS analyzed and reported LCS / CRM results with each lab batch. Recovery results were generally good, with the great majority of all recoveries for all analytes falling within QAPP MQO of 80 to 120%. The exceptions falling outside of QAPP control limits are as follows:

- Analysis of two Nitrate LCS samples in lab batch MBAS\_20160106\_W\_NO3N fell outside of control limits (135% and 140% recovery, respectively). The affected LCS samples were flagged with the “VEUM” qualifier, but associated field samples were not qualified as the laboratory also ran MS/MSD analyses, which remained in control.
- Analysis of six Nitrate LCS samples associated with lab batches MBAS\_20160217\_W\_NO3, MBAS\_20160218\_W\_NO3, MBAS\_20160219\_W\_NO3, MBAS\_20160307\_W\_NO3, MBAS\_20160307\_W\_NO3, and MBAS\_20160309\_W\_NO3 also fell outside of control limits (ranging from 135 to 140% recoveries for each). The affected LCS samples were flagged with the “VEUM” qualifier, but associated field samples were not qualified as the laboratory also ran MS/MSD analyses, which again remained in control.

MBAS also analyzed MS samples with each batch. Recoveries for each of these analyses fell within QAPP control limits of 80 to 120%.

### 2.3.4. Precision

MBAS reported precision based upon results of lab duplicate, LCS/LCSD, and/or MS/MSD samples. For all nutrients analyzed, all reported RPDs met the QAPP MQO of <25%.

### **2.3.5. Field QA Samples**

For the two-year period, a total of five FB samples were collected for each analyte and analyzed blind. For the analysis of Nitrate in batch MBAS\_20160104\_W\_NO3N, Nitrate in the FB was reported at a concentration above MRL; the FB and all associated field samples that were reported at a concentration less than 5X the FB concentration were flagged with the “VIP” qualifier. All remaining FB results were reported as ND.

Six FD samples were collected and analyzed blind over this period. Field RPDs ranged from 0% to 67%, with approximately 13% of total sample / duplicate pairs failing to meet QAPP MQO of less than 25% RPD; these pairs were flagged with the “VFDP” qualifier. For just under half of the sample pairs collected (45%), no RPD could be calculated as one or both samples were reported below RLs.

## **2.4. Fecal Indicator Bacteria**

Fecal Indicator Bacteria (FIB), including measurement of Fecal Coliform, *E. coli*, and *Enterococcus*, were analyzed by MBAS. QC checks required by the Project QAPP include reporting on Laboratory Controls, Laboratory Duplicates (when a sufficient number of duplicates have been analyzed to calculate precision), and laboratory blanks (if samples are diluted).

### **2.4.1. Sensitivity**

MBAS achieved target MRLs for all analyses.

### **2.4.2. Controls**

MBAS indicated that results of all required positive and negative controls were acceptable.

### **2.4.3. Blanks**

The QAPP requires analysis of blank water associated with FIB analyses only when sample dilution is required as part of the analysis. With one exception, the results of all lab blanks run on dilution water were reported below detection and reporting limits, and no additional qualification was required. For one batch that required sample dilution (i.e., analysis of *Enterococcus* associated with lab batch MBAS\_20151204\_W\_Enterococcus), no lab blank data was reported. Therefore, *Enterococcus* field sample results within this batch were flagged with the qualifier “VQCA” indicating the results are lacking QA data needed to assess accuracy of results.

### **2.4.4. Precision**

Consistent with QAPP requirements, MBAS assessed precision through calculation of Rlog from a running mean of the prior 15 positive samples generated by the laboratory<sup>6</sup>. In each case reported, precision results achieved the QAPP MQO ( $R_{log}$  of the sample pair  $\leq 3.27 * R_{log}$  of the running mean).

### **2.4.5. Field QA Samples**

Neither Field Blank nor Field Duplicate samples are required by Project QAPP.

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<sup>6</sup> Protocol available at [http://www.swrcb.ca.gov/water\\_issues/programs/swamp/docs/mqo/updated\\_ind\\_bact\\_water.pdf](http://www.swrcb.ca.gov/water_issues/programs/swamp/docs/mqo/updated_ind_bact_water.pdf)

## **2.5. Solids**

Solids-type ASBS parameters, analyzed by MBAS, include the following:

- Total Suspended Solids (TSS)

Consistent with Project MQOs, QC checks reported by the lab included laboratory blanks and lab dups.

### **2.5.1. Sensitivity**

MBAS achieved target MRLs. For TSS, 98% of samples were of a detectable concentration.

### **2.5.2. Blanks**

All laboratory blanks were reported as ND.

### **2.5.3. Recovery**

Not required by QAPP.

### **2.5.4. Precision**

For analysis of TSS, MBAS assessed precision based upon results of lab duplicate analyses. Reported RPDs all met the QAPP MQO of <25%.

### **2.5.5. Field QA Samples**

Collection of field Blanks is not a QAPP requirement.

Over the two-year period, nine FD samples were collected and analyzed blind for TSS. All results were reported above RLs, with five of the nine samples achieving the QAPP MQO of <25% RPD. The field duplicates exceeding 25% RPD were flagged with a "VFDP" qualifier.

## **2.6. Conventional Parameters**

Conventional ASBS parameters, analyzed by MBAS, include the following:

- Oil & Grease (O&G)

Consistent with Project MQOs, QC checks reported by the lab included laboratory blanks, lab dups, Laboratory Control Samples (LCSs), and Matrix Spike / Matrix Spike Duplicate (MS/MSD) pairs.

### **2.6.1. Sensitivity**

MBAS achieved target MRLs. For O&G, approximately 5% of samples were of a detectable concentration.

### **2.6.2. Blanks**

All laboratory blanks were reported as ND.

### **2.6.3. Recovery**

For analysis of O&G, MBAS reported recoveries associated with analysis of LCS. Recovery results were good, with all recoveries within QAPP MQO of 80 to 120%.

MBAS also reported MS/MSD information on a subset of lab batches; for each, recoveries fell within MQO control limits of 80 to 120%. For a subset of batches (MBAS\_20150910\_W\_O&G and MBAS\_20150929\_W\_O&G), no MS/MSD data was reported and affected data were flagged with the "VQCA" qualifier, indicating a lack of QA accuracy data as required by the QAPP.

#### **2.6.4. Precision**

For analysis of O&G, MBAS reported precision based upon results of field sample / field dup or MS/MSD pairs. Reported RPDs all met the QAPP MQO of <25%.

#### **2.6.5. Field QA Samples**

Five field blank samples were submitted blind to the laboratory for analysis of O&G. All results were reported as ND.

Over the two-year period, six FD samples were collected and analyzed blind for O&G. RPDs could not be calculated for five of the six pairs due to one or both results falling below the RL. For the remaining sample pair, the RPD met the QAPP MQO of <25%. No qualification of data was therefore required.

### **2.7. Organophosphorus Pesticides**

Organophosphorus (OP) Pesticides were analyzed by California Department of Fish and Wildlife's Water Pollution Control Laboratory (WPCL). Consistent with Project MQOs, QC checks reported by the lab included laboratory blanks, Laboratory Control Samples (LCSs), Matrix Spike / Matrix Spike Duplicate (MS/MSD) pairs, Laboratory Duplicates, and surrogate recoveries.

#### **2.7.1. Sensitivity**

The majority of OP pesticide analyses achieved QAPP target RLs. The exception to this occurred in a subset of WY2016 batches (WPCL\_L-096-16\_W\_OP) for which RLs were elevated due to sample containers received that contained slightly less than the required 1L volume. For those analyses that exceeded RLs and resulted in ND, data were flagged with the "VRE" qualifier, indicating that the higher RLs were associated with delivery of a limited sample volume rather than any change in lab capabilities.

It should be noted that, in general, there were very few field samples that generated results at detectable concentrations. Therefore, estimation techniques used to quantify the results falling below detection limits may greatly influence interpretation.

#### **2.7.2. Blanks**

All laboratory blanks were reported as ND.

#### **2.7.3. Recovery**

WPCL analyzed and reported LCS results with each lab batch. LCS recovery results associated within a subset of OP analytes measured within batch WPCL\_L-166-15\_BS052\_W\_OP fell below control limits, ranging from 0 to 49% recovery compared with control limits of 50 to 150%. The laboratory attributed this to lower molecular weight compounds being lost in the extraction process for the LCS analysis. Based upon results of the LCSD and field sample surrogate analyses, the laboratory considers the results acceptable for reporting; affected LCS and field samples were flagged with the "EUM" / "VEUM" qualifier depending on whether the laboratory or QAO qualified a specific result.

WPCL also experienced intermittent trouble achieving QAPP MQOs for recovery of the Chlorpyrifos, methyl LCS. In WY2015, five total batches failed to meet the MQO (WPCL\_L-066-15\_BS022\_W\_OP, WPCL\_L-066-15\_BS023\_W\_OP, WPCL\_L-066-15\_BS024\_W\_OP, WPCL\_L-662-14\_BS227\_W\_OP, and WPCL\_L-662-14\_BS228\_W\_OP). Associated data were flagged with the “EUM” / “VEUM” qualifier as described previously.

Recovery results for remaining LCS samples fell within the QAPP MQO of 50 to 150% for percent recovery.

Where sufficient sample volume allowed, WPCL also analyzed recovery of MS samples. Similar to the case for LCS samples, WPCL again experienced issues with recovery of Chlorpyrifos, methyl. In batches WPCL\_L-066-15\_BS022\_W\_OP, WPCL\_L-066-15\_BS023\_W\_OP, WPCL\_L-066-15\_BS024\_W\_OP, and WPCL\_L-662-14\_BS227\_W\_OP, MS recoveries fell below QAPP MQOs. Affected MS samples and field samples were flagged either “GB” or “VGB”, respectively, depending on whether the qualification was performed by the lab or QAO.

WPCL also reported surrogate recoveries associated with each lab batch. In general recoveries met QAPP MQO of 50 to 150% recovery with the following exceptions:

- For lab batch WPCL\_L-066-15\_BS022\_W\_OP, surrogate recovery for Triphenyl Phosphate (Surrogate) was reported as 157%.
- For lab batch WPCL\_L-066-15\_BS024\_W\_OP, surrogate recovery for Triphenyl Phosphate (Surrogate) was reported as 255%.

In each case, affected data were flagged with “GN” qualifier by the laboratory.

#### **2.7.4. Precision**

WPCL reported precision based upon results of MS/MSD analyses, where sufficient sample volume allowed for its analysis, and LC/LCSD analyses. Reported RPDs all met the QAPP MQO of <25%.

#### **2.7.5. Field QA Samples**

Ten FB samples were collected and analyzed blind. All results were reported as ND.

Seven FD samples were collected and analyzed blind. No field RPD could be calculated for OP samples as one or both results within the field sample / field duplicate pair was reported below RLs in each case.

#### **2.7.6. General**

WPCL reported several instances of Continuing Calibration Verification (CCV) exceeding acceptance criteria. These exceedances are flagged with either a “PG” or “CVH” qualifier.<sup>7</sup> In most cases, the results for associated field samples all were reported as ND. Per the lab narrative, high CCV results do not adversely affect ND results (i.e., a potential high bias is not reflected in data), and data quality is therefore not considered to be affected. In the cases for 2016 and beyond where this situation occurs, the new CEDEN QA qualifier “CVH” is applied by the laboratory to indicate no bias in the data. Where

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<sup>7</sup> The CVH qualifier was added to the CEDEN data dictionary between WY2015 and WY2016 with the intent of more easily distinguishing between CCV results that can potentially bias results and those that don't.



potential bias does exist (i.e., detectable concentrations), data beginning with 2016 results are qualified with the “PG” or “VPG” qualifier. Data reported WY2015 and prior will need to be reviewed on a case-by-case basis to determine if a potential bias is present.

## **2.8. Pyrethroid Pesticides**

Pyrethroids were analyzed by WPCL. Consistent with Project MQOs, QC checks reported by the lab included laboratory blanks, Laboratory Control Samples (LCSs), Matrix Spike / Matrix Spike Duplicate (MS/MSD) pairs, Laboratory Duplicates, and surrogate recoveries.

### **2.8.1. Sensitivity**

The majority of OP pesticide analyses achieved QAPP target RLs. The exception to this occurred in one batch (WPCL\_L-096-16\_W\_PYD) for which RLs were elevated due to sample containers received that contained slightly less than the required 1L volume. For those analyses that exceeded RLs and resulted in ND, data were flagged with the “VRE” qualifier, indicating that the higher RLs were associated with delivery of a limited sample volume rather than any change in lab capabilities.

It should be noted that, in general, there were very few field samples that generated results at detectable concentrations. Therefore, estimation techniques used to quantify the results falling below detection limits may greatly influence interpretation.

### **2.8.2. Blanks**

All laboratory blanks were reported as ND.

### **2.8.3. Recovery**

WPCL analyzed and reported LCS results with each lab batch. Recovery results were generally good, with all results achieving the QAPP MQO of 50 to 150%.

WPCL also analyzed MS samples with each lab batch where sufficient sample volume allowed. Recovery results were generally good, with all results achieving the QAPP MQO of 50 to 150%.

WPCL also reported surrogate recoveries associated with each lab batch. Surrogate recoveries were generally good – over the two-year period a total of five surrogate analyses fell below QAPP control limits (50% to 150% recovery), ranging from 39% to just below 50%. The affected surrogate recoveries were flagged with a “GN” qualifier by WPCL.

### **2.8.4. Precision**

WPCL reported precision based upon results of MS/MSD analyses, where sufficient sample volume allowed for its analysis, and LC/LCSD analyses. All reported RPDs for analysis of MSDs and LCSDs achieved QAPP MQO of <25%.

### **2.8.5. Field QA Samples**

Ten FB samples were collected and analyzed blind. All results were reported as ND.

Seven FD samples were collected and analyzed blind. In the vast majority of cases, no RPD could be calculated as one or both samples within the field sample / field duplicate pair were reported below RLs. Only sample 205SAN030-DIS-36 collected on February 6, 2016 resulted in measurable concentrations of

individual Pyrethroid compounds that would allow calculation of RPD. For this sample, one Pyrethroid compound was quantified in both the field sample and field duplicate, with resultant RPD of 14%, achieving the QAPP MQO of <25% RPD. Therefore, no qualification was required.

### **2.8.6. General**

As discussed previously under the analysis of OP pesticides, WPCL reported several instances of Continuing Calibration Verification (CCV) exceeding acceptance criteria. These exceedances are flagged with either a "PG" or "CVH" qualifier. In most cases, the results for associated field samples all were reported as ND. Per the lab narrative, high CCV results do not adversely affect ND results (i.e., a potential high bias is not reflected in data), and data quality is therefore not considered to be affected. In the cases for 2016 and beyond where this situation occurs, the new CEDEN QA qualifier "CVH" is applied to indicate no bias in the data. Where potential bias does exist (i.e., detectable concentrations), data beginning with 2016 results are qualified with the "PG" or "VPG" qualifier (e.g., WY2016 analyses of Permethrin, Trans and Cyfluthrin, Total in lab batch WPCL\_L-096-16\_W\_PYD), depending on whether the qualification is done by the lab or QAO. Data reported WY2015 and prior will need to be reviewed on a case-by-case basis to determine if a potential bias is present.

## **2.9. PAHs**

PAHs were analyzed by WPCL. Consistent with Project MQOs, QC checks reported by the lab included laboratory blanks, Laboratory Control Samples (LCSs), Matrix Spike / Matrix Spike Duplicate (MS/MSD) pairs, Laboratory Duplicates, and surrogate recoveries.

### **2.9.1. Sensitivity**

The majority of PAH analyses achieved QAPP target RLs. The exception to this occurred in a subset of WY2016 batches (WPCL\_L-096-16\_W\_PAH) for which RLs were elevated due to sample containers received that contained slightly less than the required 1L volume. For those analyses that exceeded RLs and resulted in ND, data were flagged with the "VRE" qualifier, indicating that the higher RLs were associated with delivery of a limited sample volume rather than any change in lab capabilities.

It should be noted that, in general, there were very few field samples that generated results at detectable concentrations. Therefore, estimation techniques used to quantify the results falling below detection limits may greatly influence interpretation.

### **2.9.2. Blanks**

All laboratory blanks were reported as ND.

### **2.9.3. Recovery**

WPCL analyzed and reported LCS results with each lab batch. LCS recovery results associated with a subset of PAH analytes measured within WY2015 batch WPCL\_L-166-15\_BS052\_W\_PAH fell well below control limits, ranging from 0 to 24% recovery compared with control limits of 50 to 150%. The laboratory attributed this to lower molecular weight compounds being lost in the extraction process for the LCS analysis. Based upon results of the LCSD and field sample surrogate analyses, the laboratory considers the results acceptable for reporting; affected LCS and field samples were flagged with the "EUM" / "VEUM" qualifier depending on whether the laboratory or QAO qualified a specific result.

Recovery results for remaining batches were generally good, with all LCS recoveries falling within the QAPP MQO of 50 to 150%.

WPCL also analyzed MS samples with each lab batch where sufficient sample volume allowed. Recoveries generally fell within QAPP MQO of 50 to 150% recovery. The exception to this was associated with analysis of WY2015 lab batch WPCL\_L-662-14\_BS227\_W\_PAH, in which MS/MSD recovery results for several PAH compounds were reported outside of control limits on the low end (35% to 41% recoveries). All affected data were flagged with either "GB" or "VGB" qualifier, depending on whether the flag was applied by the lab or QAO.

WPCL also reported surrogate recoveries associated with each lab batch. Surrogate recoveries were generally good; with results of intermittent individual PAH compounds falling outside of QAPP control limits (50 to 150%) in both WY2015 and WY2016. Affected data were flagged with "GN" qualifier by the laboratory. These exceptions were typically identified by WPCL as falling outside of control limits due to matrix effects.

#### **2.9.4. Precision**

WPCL reported precision based upon results of MS/MSD analyses, where sufficient sample volume allowed for its analysis, and LC/LCSD analyses. In general, the reported RPDs for LCSDs met the the Project MQO of <25%. The main exception to this is associated with the loss of lower molecular weight compounds within the analysis of the LCS for lab batch WPCL\_L-088-14\_B1\_W\_PAH discussed previously. Due to the losses experienced while extracting the LCS, the resultant RPDs all exceeded QAPP MQO of <25%. Affected data were flagged "IL" by the laboratory.

WPCL reported precision based upon results of MS/MSD analyses, where sufficient sample volume allowed for its analysis, and LC/LCSD analyses. All reported RPDs for analysis of MSDs and LCSDs achieved QAPP MQO of <25%.

#### **2.9.5. Field QA Samples**

Five FB samples were collected and analyzed blind over the two-year period. Only Naphthalene collected and analyzed in lab batch WPCL\_L-659-14\_BS226\_W\_PAH exceeded the RL, and was flagged with VIP. As all field samples associated with this FB were reported as ND, no additional qualification of field data was required.

Seven FD samples were collected and analyzed blind. In the vast majority of cases, no RPD could be calculated as one or both samples within the field sample / field duplicate pair were reported below RLs. Only sample 205SAN030-DIS-36 collected on February 6, 2016 resulted in measurable concentrations of individual Pyrethroid compounds that would allow calculation of RPDs. For this sample, 13 PAH compounds were quantified in both the field sample and field duplicate, with resultant RPDs ranging from 0 to 21%, achieving the QAPP MQO of <25% RPD. Therefore, no qualification was required.

### **2.10. Toxicity**

All toxicity testing was conducted by UC Davis Marine Pollution Studies Laboratory at Granite Canyon (Granite Canyon). The toxicity of discharge samples was assessed with the purple sea urchin (*Strongylocentrotus purpuratus*) fertilization test. Receiving water samples were tested with the sea urchin fertilization test, as well as the mussel larval development test with *Mytilus galloprovincialis*, and

the giant kelp germination and growth test with *Macrocystis pyrifera*. QC checks required by the Project QAPP in place during WY2015 and WY2016 include Laboratory Controls (positive, negative, and brine, where applicable) and checks on water quality parameters and test conditions.

### **2.10.1. Controls**

Tox summary results for three of the four WY2016 lab batches processed by Granite Canyon for the mussel development test did not meet initial test acceptability criteria for control organisms and required re-testing consistent with laboratory protocols.<sup>8</sup> For two of these sampling events, associated with lab batches GC\_ASBSMG22\_W\_TOX and GC\_ASBSMG20\_W\_TOX, appropriate data are flagged with a "VH" qualifier as the re-tests were initiated outside of QAPP hold times (seven to eight days and six days, respectively). For the remaining lab batch that failed initial test acceptability criteria (GC\_ASBSMG25\_W\_TOX), the tests were re-initiated within the 48-hr hold time, and therefore require no additional qualification. In each case that a re-test was required, follow-on test results met acceptability requirements and all toxicity results are considered acceptable for Project usage.

### **2.10.2. Water Quality Parameters**

Required water quality measurements (i.e., Ammonia, Dissolved Oxygen, pH, Salinity, Temperature) were reported associated with each lab batch. All measurements fell within QAPP MQO recommended ranges.

## **3. Sediment**

WY2016 sediment sampling was conducted on August 5, 2015. Monitoring included collection of subtidal soft bottom sediments from the mooring field and below the pier in Stillwater Cove at Pebble Beach.

Results of individual analytes, or groups of analytes, are described in more detail below, along with the laboratory responsible for its analysis. The groupings of individual analytes follow the convention of SWAMP where applicable.

### **3.1. Organotins**

Organotins (Butyltin, Dibutyltin, Tributyltin, and Tetrabutyltin) in sediment were analyzed by ALS Global (ALS). Consistent with Project QAPP, QC checks reported by the lab included laboratory blanks, Laboratory Control Samples (LCSs), Matrix Spike / Matrix Spike Duplicate (MS/MSD) pairs, and surrogate recoveries.

#### **3.1.1. Sensitivity**

ALS achieved QAPP target RLs for all analyses.

#### **3.1.2. Lab Blanks**

All lab blanks were reported as ND.

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<sup>8</sup> Problems with mussel gamete quality is an ongoing issue that was first identified by Granite Canyon beginning with the WY2015 storm season, and is unrelated to the ASBS monitoring conducted.

### **3.1.3. Recovery**

ALS analyzed and reported LCS results with each lab batch. Reported recovery results achieved the QAPP MQO of 50 to 150%.

ALS also reported recoveries associated with analysis of MS samples. Reported recovery results achieved the QAPP MQO of 50 to 150%.

ALS also reported surrogate recoveries associated with organotin analyses. Surrogate recoveries were generally good; with all reported results achieving QAPP MQO control limits (50 to 150%).

### **3.1.4. Precision**

ALS calculated precision for MS/MSD sample pairs where an analyte was detected in both samples. In all cases, reported RPDs for MS/MSD samples met the Project MQO of <25%.

### **3.1.5. Field QA Samples**

No field duplicate samples were collected in either WY2015 or WY2016.

## **3.2. Mercury**

Hg in sediment was analyzed by MPSL. Consistent with Project QAPP, QC checks reported by the lab included laboratory blanks, Certified Reference Materials (CRMs), Matrix Spike / Matrix Spike Duplicate (MS/MSD) pairs, and Laboratory Duplicates.

### **3.2.1. Sensitivity**

MPSL achieved QAPP target RLs for all analyses.

### **3.2.2. Lab Blanks**

All lab blanks were reported as ND.

### **3.2.3. Recovery**

MPSL analyzed and reported CRM results with each lab batch. Reported recovery results achieved the QAPP MQO of 75 to 125%.

MPSL also reported recoveries associated with analysis of MS samples. Reported recovery results achieved the QAPP MQO of 75 to 125%.

### **3.2.4. Precision**

MPSL calculated precision for field sample / lab duplicate and MS/MSD sample pairs where an analyte was detected in both samples. In both cases, reported RPDs for field sample / lab duplicate pairs and MS/MSD samples fell within Project MQO of <25%.

### **3.2.5. Field QA Samples**

No field duplicate samples were collected in either WY2015 or WY2016.

### **3.3. Trace Metal Suite**

Trace Metals (TMs) As, Cd, Cr, Cu, Ni, Pb, Se, Ag, and Zn in sediment were analyzed by MPSL. Consistent with Project QAPP, QC checks reported by the lab included laboratory blanks, Laboratory Control Samples (LCSs) or Certified Reference Materials (CRMs), Matrix Spike / Matrix Spike Duplicate (MS/MSD) pairs, and Laboratory Duplicates.

#### **3.3.1. Sensitivity**

MPSL achieved QAPP target RLs for all TMs for all analyses conducted.

#### **3.3.2. Lab Blanks**

All lab blanks were reported as ND.

#### **3.3.3. Recovery**

MPSL analyzed and reported LCS (for Se only) or CRM (for all remaining analytes) results with each lab batch. In each case, reported recovery results achieved the QAPP MQO of 75 to 125%.

MPSL also reported recoveries associated with analysis of MS samples. Analyses of percent recoveries for either the MS or MSD sample for Ag (127%), Cd (133%), and Se (151%) all fell outside of QAPP MQO control limits of 75 to 125%. These samples were flagged with the "GB" qualifier by the lab and affected field samples were flagged with the "VGB" qualifier by the QAO.

#### **3.3.4. Precision**

MPSL calculated precision for field sample / lab duplicate and MS/MSD sample pairs where an analyte was detected in both samples. Reported RPDs for field sample / lab duplicate pairs fell within Project MQO of <25%.

The sole MS/MSD sample not achieving the QAPP MQO of <25% RPD was that of Se. Both the QA samples and affected field samples associated with analysis of Se were flagged with the "VIL" qualifier indicating results fell outside QAPP MQO control limits.

#### **3.3.5. Field QA Samples**

No field duplicate samples were collected in either WY2015 or WY2016.

### **3.4. Toxicity**

All toxicity testing was conducted by UC Davis Marine Pollution Studies Laboratory at Granite Canyon (Granite Canyon). Sediment samples were tested with the amphipod *Eohaustorius estuarius*, QC checks required by the Project QAPP in place during WY2015 and WY2016 include Laboratory Controls (positive, negative, and brine, where applicable) and checks on water quality parameters and test conditions.

#### **3.4.1. Controls**

Results of all Laboratory Controls were acceptable.

### **3.4.2. Water Quality Parameters**

Required water quality measurements (i.e., Ammonia, Dissolved Oxygen, pH, Salinity, Temperature) were reported associated with each lab batch. Most reported water quality parameters fell within recommended ranges listed within QAPP, where applicable. The one exception to this is that for lab batch GC\_ASBSSEE19\_S\_TOX, the salinity of overlying water was measured up to 3ppt above the recommended criteria (ranging from 23 to 26 ppt), but still well within the tolerance range of the organisms. These datapoints were flagged with the “VTW” qualifier, but did not affect toxicity test result data quality.

## **4. References**

AMS, 2014. *Quality Assurance Project Plan: The Central Coast Areas of Special Biological Significance Regional Monitoring Program and Reference Site Monitoring, Version 1.4*. Prepared by Applied Marine Sciences, Inc. May 19, 2014.

## **Appendix C. Characterization of the rocky intertidal ecological communities associated with Central California Areas of Special Biological Significance**

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## Introduction

### *The regulatory environment*

The California Ocean Plan defines water quality objectives for State waters and is the basis of regulation of discharges to the marine environment. In 1972, there was recognition that certain areas had biological communities with ecological value or that were fragile. These areas were deemed to deserve enhanced protection to preserve and maintain natural (not affected by anthropogenic influences) water quality. These areas were designated Areas of Special Biological Significance (ASBS). As a result, regulations were enacted to prohibit discharges into ASBS as well as to any nearby waters that could affect the natural water quality in ASBS. In 1974, the State Water Board (SWB) designated 33 ASBS. An additional area was designated in 1975; there have been no subsequent designations.

ASBS have been designated to protect marine species or biological communities from an undesirable alteration in natural water quality. Furthermore, ASBS provide intrinsic value or recognized value to man for scientific study, commercial use, recreational use, or esthetic reasons. Consistent with previous versions of the Ocean Plan, the 2009 Ocean Plan states: “Waste shall not be discharged to areas designated as being of special biological significance. Discharges shall be located a sufficient distance from such designated areas to assure maintenance of natural water quality conditions in these areas.” This absolute waste discharge prohibition in the Ocean Plan stands unless an “exception” is granted. The requirements for an exception are included in the Ocean Plan. When granting exceptions, the State Water Board must determine that the public interest is served, and that protections of beneficial uses are not compromised. Despite the prohibition against waste discharges to ASBS, in 2003, there were approximately 1,658 outfalls to these marine water quality protected areas (SCCWRP 2003). As a result, the State Water Board has initiated regulatory actions, establishing special protections through the Ocean Plan’s exception process.

The key attribute that underlies the ASBS water quality regulations is the standard of “natural water quality”. The logic of the standard is that natural water quality is attainable using limited spatial regulations (prohibition of discharges in some areas) and essential for certain biological communities. Unfortunately for California ASBS, coastal waters may no longer be pristine, even in areas distant from discharges, making “natural water quality” more difficult to define.

Since a definition of natural water quality did not exist, a committee of scientists, termed the ASBS Natural Water Quality Committee, was formed to provide such a definition for the State Water Board. In 2010 the ASBS Natural Water Quality Committee provided the State Water Board with its findings (Dickson 2010), including an operational definition of natural water quality with the following criteria. These criteria address the two tenets of ASBS protections.

- 1) It should be possible to define a *reference* area or areas for each ASBS that currently approximate *natural water quality* and that are expected to exhibit the likely natural variability that would be found in that ASBS.
- 2) Any detectable human influence on the water quality must not hinder the ability of marine life to respond to natural cycles and processes. Such criteria will ensure that the beneficial uses identified by the Ocean Plan are protected for future generations.

This operational definition of natural water quality allows for the assessment of biological impacts related to water quality in ASBS and it provides the basic design elements for the assessment. In particular, the use of reference areas for each ASBS allows for control of natural and temporal variability in biological communities.

### ***The ecological environment***

Because most discharges are into intertidal areas (defined as that area between low and high tides), there has been concern that impacts would be primarily manifested in ecological communities in sandy beach and rocky intertidal systems. Ecological communities in sandy beach habitats are extraordinarily dynamic (McLachlan 1993, Defeo 2008) and attribution of change to anthropogenic causes is quite difficult, mainly due to low statistical power. Species associated with rocky intertidal areas are also dynamic, but much less so than those in or on sandy beaches. As a result, attribution of the cause of change is easier for species or communities associated with rocky intertidal habitats (Littler and Murray 1975, Minchinton and Raimondi 2005, Conway-Cranos and Raimondi 2007, Pinedo et al. 2007, Arevalo et al. 2007).

Within rocky intertidal communities, species have a variety of life histories that affect the assessment of potential causes of change. Shorter lived species like *Chthamalus*, *Ulva*, and *Porphyra* often are associated with disturbance, while longer lived species like *Balanus*, fucoid algae, and mussels tend to be associated with more stable environments. Hence, communities with higher cover of the more ephemeral species are often considered to be indicative of recent or ongoing perturbation. Clearly, perturbations can be due to both natural and anthropogenic causes and hence the design of the sampling program is critical for separating these two general mechanisms of change.

Here we report on a project designed to: (1) characterize the ecological community living on rocky intertidal habitats near discharges inside central California ASBS and at reference areas far from discharges and, (2) use the comparison between ASBS discharge and reference areas as a means to assess the likelihood that differences in ecological community structure could be due to water quality degradation within ASBS. The methods used are consistent with those used in phase I and II assessments for ASBS in southern and northern California (Raimondi et al. 2012, Raimondi 2014, Raimondi et al 2015).

### **Methods**

Comprehensive sampling of ecological communities on rocky intertidal habitats was done using protocols developed by the coastal biodiversity surveys ([www.pacificrockyintertidal.org](http://www.pacificrockyintertidal.org)). The general approach is described below.

**Site selection: Discharge and Reference** – Based on the operational definition of natural water quality described above, along with the regulations prohibiting discharge in ASBS, we selected sites as follows. Sites were selected within ASBS that (1) had sufficient rocky intertidal habitat to be suited for sampling (as described below) and, (2) were located near an active discharge. Reference areas were selected such that they met criterion 1 (above) and were not near an active discharge. For this analysis we also included sites sampled from our Marine Protected

Area (MPA) and regular biodiversity sampling from the central coast to provide a large set of reference sites. This approach provided a large number of reference sites and also allowed us to account for biogeographic effects on the community.

The sampling procedure used was identical to that used by the coastal biodiversity survey (CBS) program housed at UCSC and administered by Peter Raimondi. In order to be cost-efficient, data from sites previously sampled by the CBS program were used in the analyses. New sampling was done to supplement existing data.

**Selecting an appropriate location within a site** - Within a site, the ideal location to do a CBS is on a bench that 1) is at least 30m wide, 2) gently slopes from the high to low zone and most importantly, 3) contains a representative sample of the intertidal community of the entire site. If it is not possible to find a contiguous 30m stretch of coastline, the survey can be done on a 20 m bench or split between two adjacent benches. When this is done, the survey should be divided as evenly as possible between the two benches.

**Set-Up** - Once an appropriate area of shoreline was selected, it was sampled using a series of parallel transect lines extending from the high zone to the low zone. To facilitate the setup of these lines, two permanent 30m horizontal baselines (parallel to the ocean) were first established. The upper baseline was placed in the high zone above the upper limit of the organisms, while the lower baseline was placed in the mid-intertidal zone, parallel to the upper baseline. Depending on the amount of beach traffic or site regulations, the ends of these lines were permanently marked with either hex or carriage bolts.

Once these two baselines were established, parallel transect lines were run down the shore every three meters along the upper base line (or every 2m if a 20m bench was selected). To ensure that transect lines were parallel, samplers made sure to intersect upper and lower base lines at the same meter mark (e.g. transect began at the upper baseline at meter mark 6 and crossed the lower baseline at meter mark 6). In general, the transect lines were allowed to follow the contours of the bench. When necessary, rocks were placed along the lines to prevent them from being shifted by heavy winds. To ensure repeatability of the layout of each parallel transect, the meter mark where each transect crossed the lower baseline was noted. To facilitate resurveys of the site, a map was drawn showing the location of the bolts relative to notable landmarks or other pre-existing permanent plot markers (from other survey types). Photographs were also taken that included prominent visual reef characteristics for orientation (e.g. a large crack or tidepool). The distance and bearing between the baseline endbolts were measured. When possible, measurements were also taken between the endbolts and any pre-existing permanent plot markers. Other pertinent information, such as the compass heading of the vertical transects, the sampling interval along the transects, weather conditions, site complications, and challenges with taxonomic identification, was also recorded. All such information was used to make the mapping of the site more spatially explicit and repeatability more straightforward.

In addition to the spatial information described above, we recorded descriptive information about the site including bench rock type, relief, slope, extent of habitat, and characteristics of the surrounding coast. This information was used to provide spatial context for the site.

**Point-Contact Surveys** - Each vertical transect was sampled using the point intercept method. An average of 100 points were sampled on each transect line. For example, the interval between points would be 20cm for a 20m long transect, and 10cm for a 10m long transect. The

basis of this design was to ensure that there was a similar density of sampled points per vertical unit of tidal elevation for all sites. For each point, two types of data were collected: data that were used to determine relative abundance (% cover), and data that were used to describe spatial distributions. The relative abundance data were collected by identifying all taxa that fell directly under each point, including rock, sand, and tar. If there was layering of species, the taxa occupying the different layers were identified and assigned a letter; A for the top layer, B for the second layer, and C for the third. (Note: each layer must be a different taxon). If the point fell on an epibiont living on a host species, the epibiont was noted. Also recorded was whether the species under the point was in a pool, on cobble, or on boulders. A total of up to three taxa were identified per point.

If fewer than three taxa were recorded under a point, then the next one or two species closest to that point were also noted. These 'nearby' species had to differ from those found under the point, and had to occur within a circle centered over the point with a radius half the length of the sampling interval.

**Mobile Invertebrate Surveys** - Although point-contact surveys are good at determining the abundance of spatially common species, particularly sessile species, they do not sample rare or spatially uncommon species very well. Because most mobile species are not spatially common, their abundances were sampled in 50 x 50 cm quadrats placed at three locations along each transect. Each transect was first divided into three zones; the low zone (below the mussel and rockweed zone), the mid-zone (typically dominated by mussels and rockweeds, and the high zone (above mussels/rockweeds; usually dominated by barnacles and littorines). Within each zone a quadrat was randomly placed adjacent to the transect and all mobile species found within the quadrat were identified and counted. Sub-sampling was used when there were more than one hundred individuals of one species in a quadrat. If a quadrat landed in a deep pool or in an area dominated by sand, a new location within the defined zone was randomly selected.

**Vouchers** - We collected field vouchers for all species that could not be identified in the field. Voucher samples were labeled with the date, site, name of sampler, and transect line on which it was found.

**Specific hypotheses tested** - The general goal of this project was to compare the ecological communities in discharge and reference locations. To do this we developed the following specific (null) hypotheses:

- 1) Species richness will not vary as a function of site type (Discharge, Reference)
- 2) Community composition of sessile species will not vary as a function of site type
- 3) Community composition of mobile species will not vary as a function of site type
- 4) An assessment of both mobile and sessile species will not identify particular sites as being substantially different from the expectation based on all sites. This is a way to look at specific sites rather than site types.

For hypotheses 1-3 our model looked at the relationship between type of site (near to a discharge in an ASBS vs a reference site) and the response variable, species richness or community composition. Point contact (mainly sessile or sedentary organisms) and quadrat data (mobile organisms) were evaluated using a PERMANOVA approach to compare communities between discharge and reference sites. Species richness was assessed using ANOVA. For hypotheses 1-3 we set the critical p-value at 0.05 (null hypothesis not rejected unless  $p < 0.05$ ). Prior to either type of assessment, we clustered sites so as to identify biogeographical regions. All comparisons (discharge vs reference) were done separately for each region having discharge sites.

The results for hypotheses 1-3 could indicate no systemic difference between discharge and reference sites for community composition or species richness. We were concerned that particular discharge sites might be compromised and that these single site impacts would be masked in a general analysis. Hence, we also determined whether particular sites were outliers relative to other sites, which could indicate the effects of compromised water quality (hypothesis 4). To do this, we generated site similarity matrices (using Bray Curtis values) then calculated quasi Mahalanobis distances using values from the two matrices. These distances are the distance from a multivariate centroid (for each biogeographic region) accounting for the covariance structure among variables. Small values indicate that a given site is similar to a hypothetical typical site, while large distances indicate sites very different from the hypothetical typical site. Prediction limits were used to assess the likelihood of inclusion of samples. For example, an 80% prediction limit would contain 80% of samples drawn from a pool of samples coming from the same population. This differs from confidence limits, which are used to assess the inclusion likelihood of means of samples from a population.

## **Results**

**Sites sampled and site attributes** - Sampling locations are shown in Figure 1 (a-c). Description of site metadata and site characteristics are in tables 1 and 2 respectively. Also see Appendix 1 for detailed site descriptions.



Figure 1a: Map of sampling locations. Color of symbol represents site type: Red = Discharge site in ASBS, Blue = reference site. Note that on this map the symbol for Alder Creek is red but hidden beneath Bolinas Pont. Yellow boxes are inset in figures 1b and 1c.





Figure 1b: Map (inset in figure 1a) of sampling locations. Color of symbol represents site type: Red = Discharge site in ASBS, Blue = reference site.



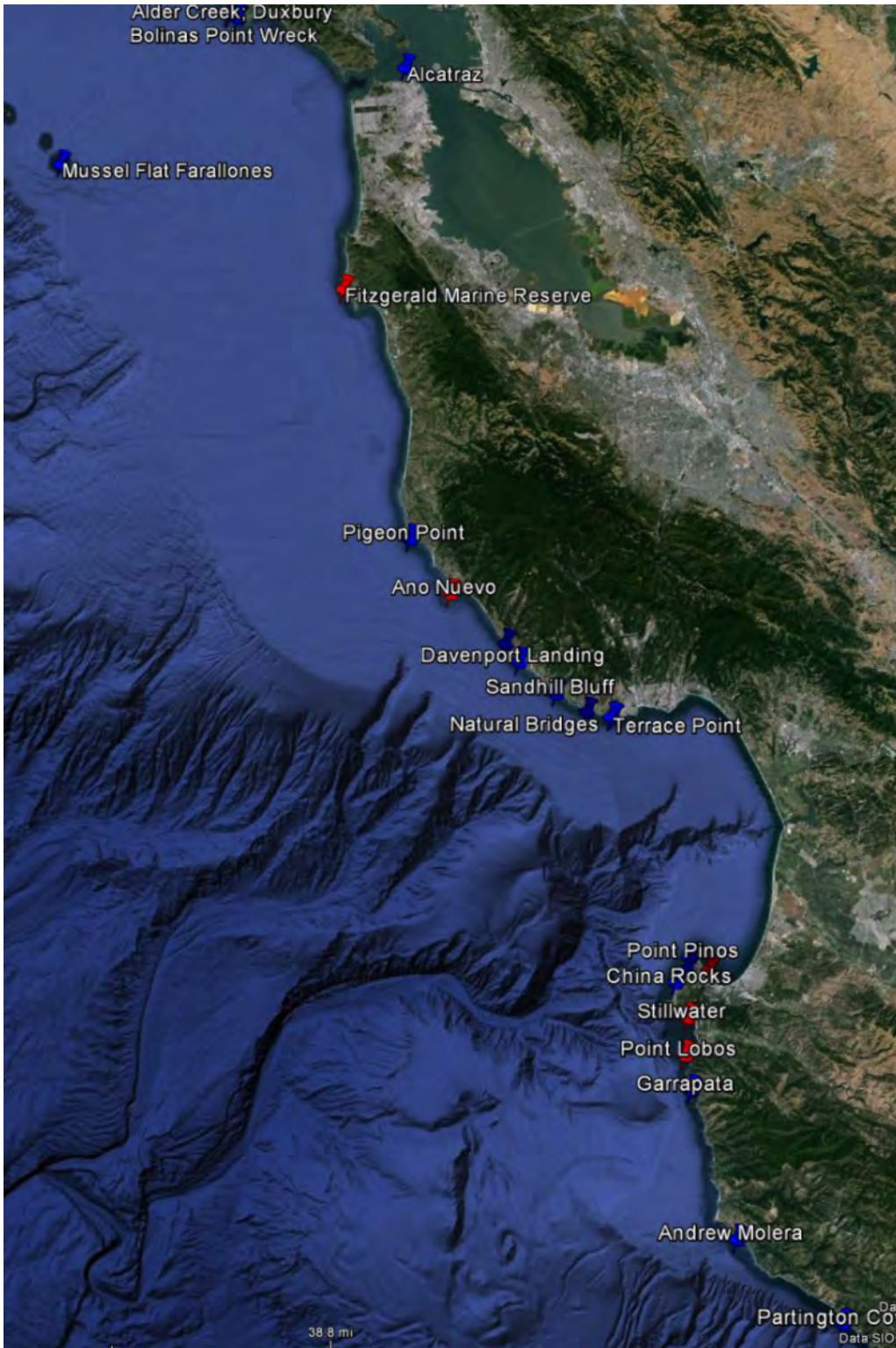


Figure 1c: Map (inset in figure 1a) of sampling locations. Color of symbol represents site type: Red = Discharge site in ASBS, Blue = reference site.

1. **Primary Bench Type:** describes the dominant geology of the site
  - a. **bedrock:** the primary bench type is consolidated bedrock at this site
  - b. **bedrock/boulders:** the primary bench type is a mixture of consolidated bedrock and boulder fields at this site
  - c. **bedrock/sand:** the primary bench type is a mixture of consolidated bedrock and sandy beach at this site
  - d. **bedrock/boulders/sand:** the primary bench type is a mixture of consolidated bedrock, boulder fields, and sandy beach at this site
  - e. **boulders:** the primary bench type is boulder fields at this site
2. **Slope:** describes the slope of the coastline at the site
  - a. **0-5 degrees:** the slope of this site is between 0-5 degrees
  - b. **5-15 degrees** the slope of this site is between 5-15 degrees
3. **Relief:** describes the rugosity of the site
  - a. **high:** the relief of the site consists of extremely uneven terrain, containing many deep cracks and folds, such as in some mixed consolidated bedrock and boulder fields
  - b. **moderate:** the relief of the site consists of moderately uneven terrain, containing few cracks and folds, such as in boulder or cobble fields and some consolidated bedrock
  - c. **low:** the relief of the site consists of flat terrain, such as a sandy beach
4. **Extent:** describes the length of the intertidal area at the site, from the land to the ocean
  - a. **long:** the extent of the site is greater than 15 meters
  - b. **intermediate:** the extent of the site is between 5-15 meters
  - c. **short:** the extent of the site is less than 5 meters
5. **Surrounding Coast:** describes the geology of the area surrounding the site
  - a. **bedrock:** the surrounding coast is consolidated bedrock at this site
  - b. **bedrock/boulders:** the surrounding coast is a mixture of consolidated bedrock and boulder fields at this site
  - c. **bedrock/sand:** the surrounding coast is a mixture of consolidated bedrock and sandy beach at this site
  - d. **bedrock/boulders/sand:** the surrounding coast is a mixture of consolidated bedrock, boulder fields, and sandy beach at this site
  - e. **bedrock/boulders/cobble:** the surrounding coast is a mixture of consolidated bedrock, boulder fields, and cobble beach at this site
  - f. **boulders/sand:** the surrounding coast is a mixture of boulder fields and sandy beach at this site
  - g. **boulders/cobble/sand:** the surrounding coast is a mixture of boulder fields, cobble beach, and sandy beach at this site
  - h. **boulders:** the surrounding coast is boulder fields at this site
  - i. **sand:** the surrounding coast is sandy beach at this site
6. **Species Richness:** a count of the total number of species found at a given site, using existing protocols.

Table 1: Metadata for site attributes.

<b>Attributes of Site</b>	<b>Alder Creek</b>	<b>Bolinas Point</b>	<b>Fitzgerald Marine Reserve</b>	<b>Pigeon Point</b>
Site Type	<b>Discharge</b>	<b>Reference</b>	<b>Discharge</b>	<b>Reference</b>
Primary Bench Type	bedrock/sand	bedrock/boulders	bedrock/sand	bedrock/boulders
Slope	0-5 degrees	0-5 degrees	0-5 degrees	0-5 degrees
Relief	moderate	low	low	high
Extent	long	long	long	long
Surrounding coast	bedrock/sand	bedrock/boulders/sand	sand	bedrock/boulders/sand
Species Richness	68	77	70	66
<b>Species of Special Interest (P for present)</b>				
Haliotis spp				P
Lottia gigantea				P
Phyllospadix spp	P	P	P	P
<b>Invasive species</b>				
Sargassum muticum				
Sargassum agardhianum				
Caulacanthus ustulatus				
<b>Attributes of Site</b>	<b>Año Nuevo</b>	<b>Hopkins</b>	<b>Stillwater</b>	<b>Point Lobos</b>
Site Type	<b>Discharge</b>	<b>Discharge</b>	<b>Discharge</b>	<b>Discharge</b>
Primary Bench Type	bedrock/sand	bedrock/boulders	bedrock	bedrock
Slope	0-5 degrees	5-15 degrees	0-5 degrees	0-5 degrees
Relief	moderate	high	moderate	high
Extent	long	long	intermediate	long
Surrounding coast	bedrock/sand	bedrock/boulders/cobble	bedrock/boulders/sand	bedrock/boulders/cobble
Species Richness	78	82	80	82
<b>Species of Special Interest (P for present)</b>				
Haliotis spp		P	P	P
Lottia gigantea			P	P
Phyllospadix spp	P	P		P
<b>Invasive species</b>				
Sargassum muticum				
Sargassum agardhianum				
Caulacanthus ustulatus				

Table 2: Site characteristics. See table 1 for attribute descriptions. P indicates presence. Sites shown in table 2 represent the sampling funded by this study. Many other sites were also included in the evaluation of the potential discharge impacts (figure 1). Attributes for these sites can be found at [www.pacificrockyintertidal.org](http://www.pacificrockyintertidal.org)

**Biogeographic patterns – sessile species from the point contact surveys**

Results of the cluster analysis are shown in figure 2.

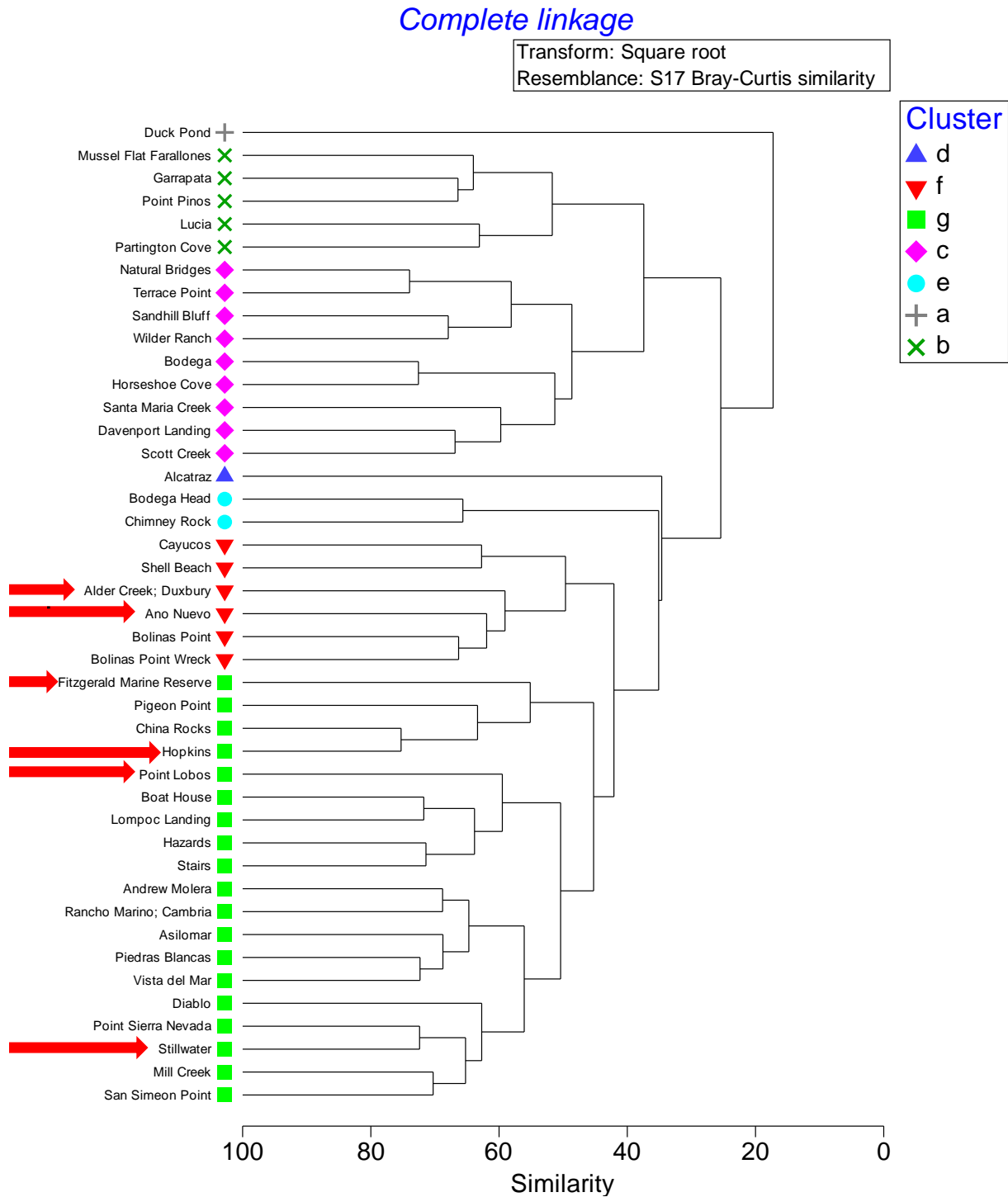


Figure 2: Biogeography of the sessile community from the point contact surveys. Seven clusters were defined. All discharge sites are indicated with red arrows and occur in two clusters: f and g.

**Biogeographic patterns – mobile species from the quadrat surveys**

Results of the cluster analysis are shown in figure 3.

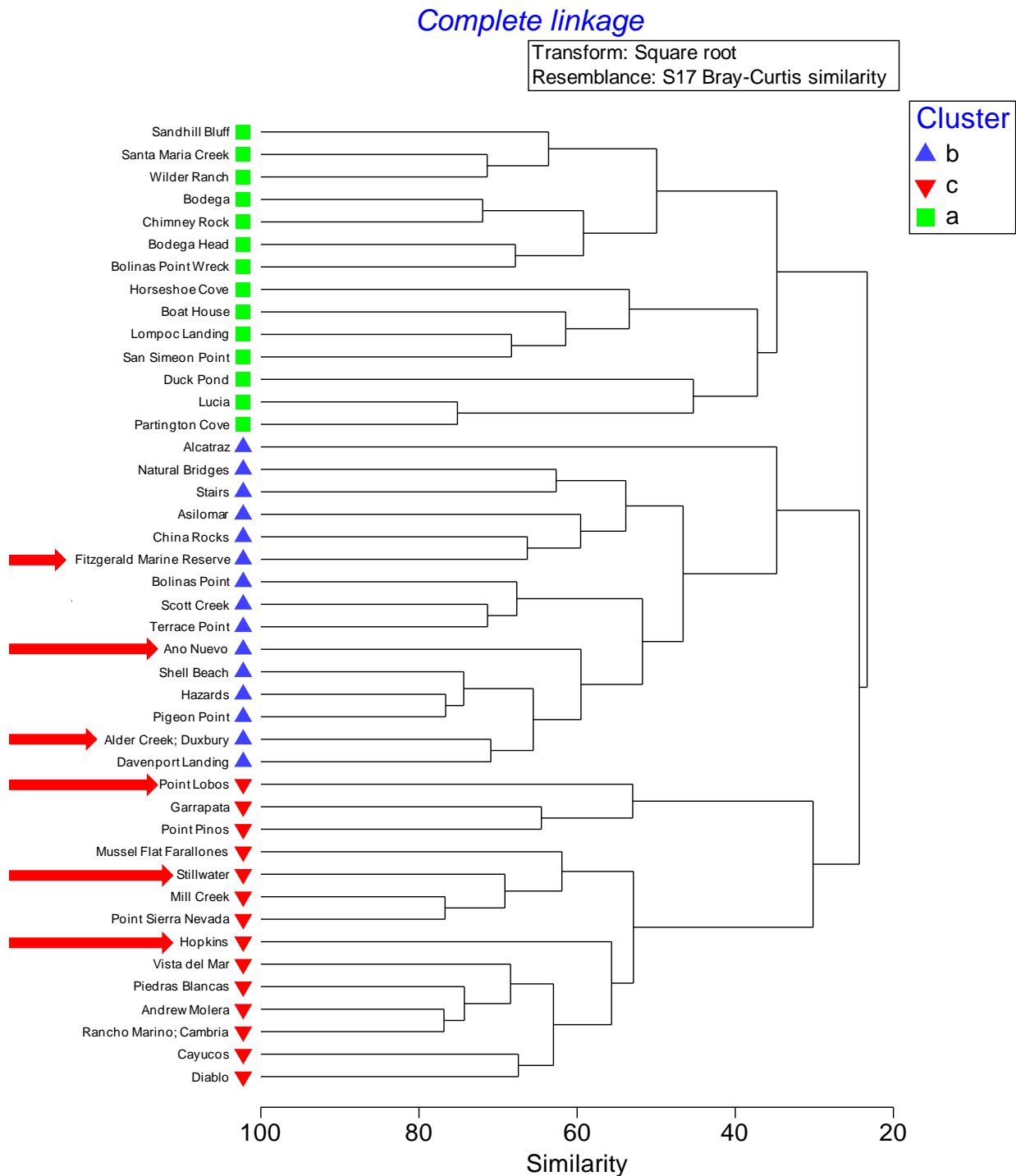


Figure 3: Biogeography of the mobile community from the quadrat surveys. Three clusters were defined. All Discharge sites are indicated with red arrows and occur in two clusters: b and c.

**Species Richness Analysis**

For sessile species, there was no effect on species richness that was associated with Site Type for either biogeographic region containing discharge sites (figure 2, clusters f and g), indicating no difference between discharge and reference sites (Table 3 and Figure 4).

Cluster F					
Source	DF	SS	MS	F	P
Model	1	70.08333	70.0833	0.8527	0.408
Error	4	328.75	82.1875		
Total		5	398.8333		

Cluster G					
Source	DF	SS	MS	F	P
Model	1	133.4211	133.421	2.5922	0.1258
Total	17	875	51.471		
C.		18	1008.421		

Table 3: ANOVA results for species richness: sessile species.

For mobile species, there was no effect on species richness that was associated with Site Type for either biogeographic region containing discharge sites (figure 3, clusters b and c), indicating no difference between discharge and reference sites (Table 4 and Figure 5).

Cluster B					
Source	DF	SS	MS	F	P
Model	1	56.06667	56.0667	2.2612	0.1566
Error	13	322.3333	24.7949		
Total	14	378.4			

Cluster C					
Source	DF	SS	MS	F	P
Model	1	122.6061	122.606	2.557	0.1358
Error	12	575.3939	47.949		
Total	13	698			

Table 4: ANOVA results for species richness: mobile species

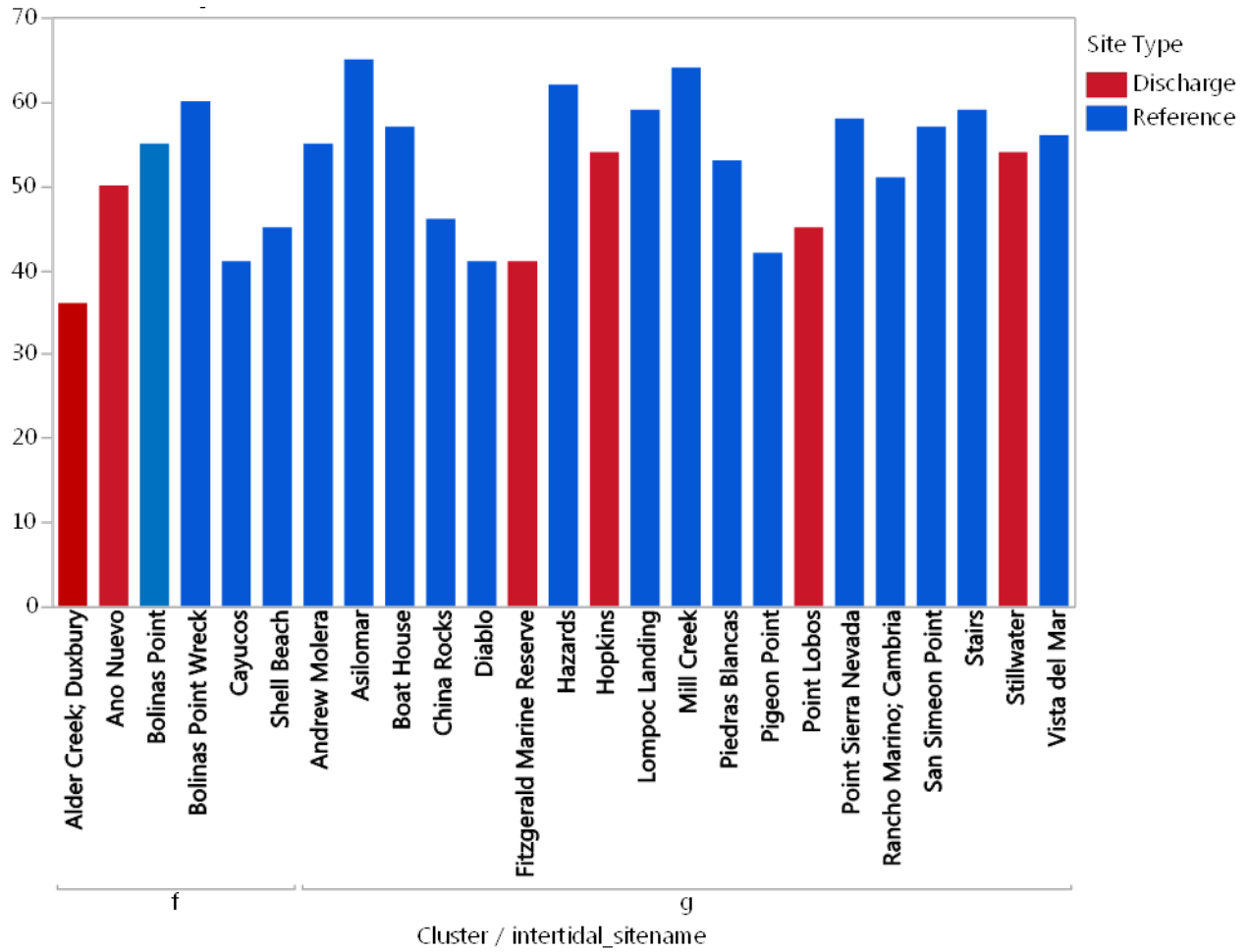


Figure 4: Species richness as a function of Site Type for sessile species. Note the two clusters (f and g).

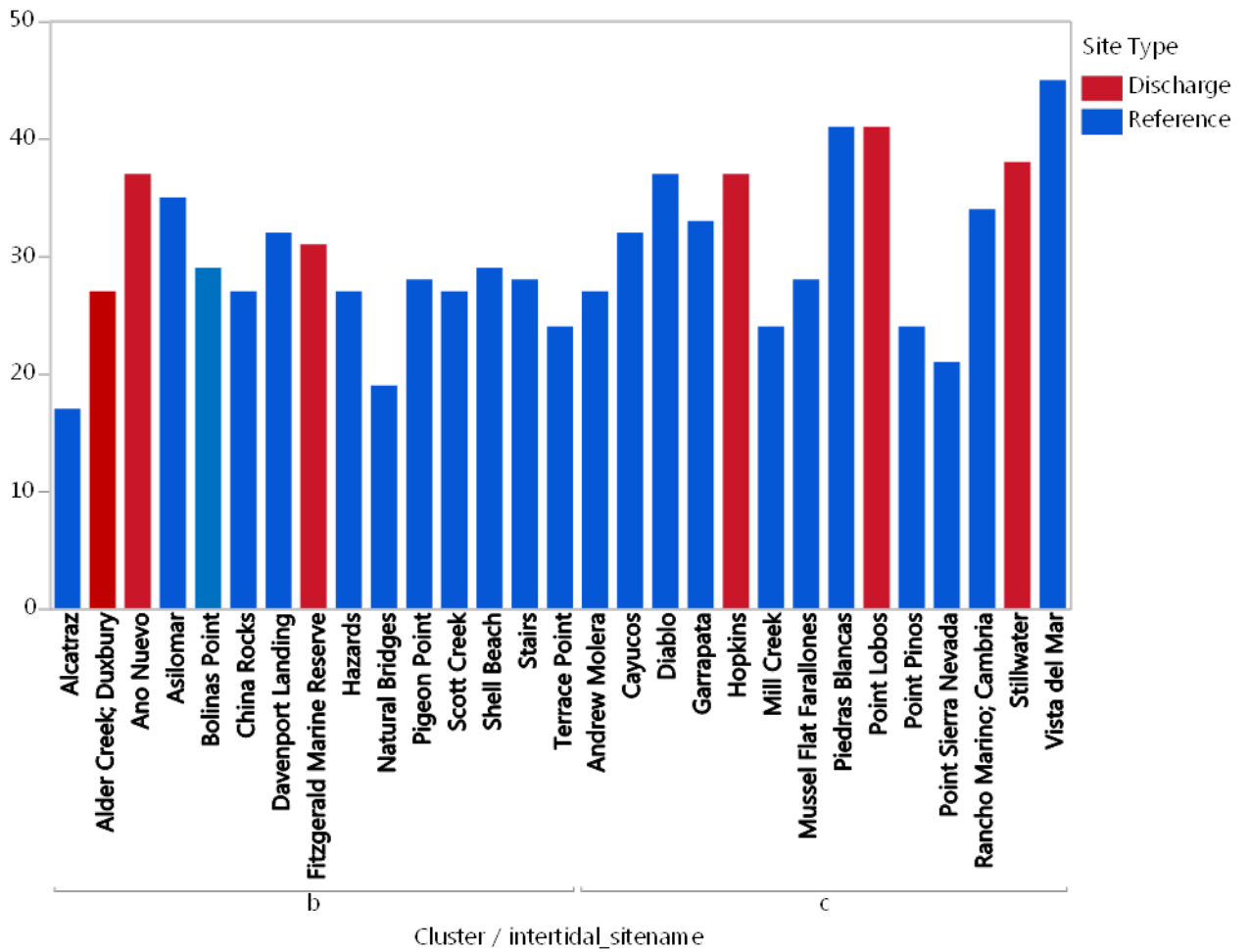


Figure 5: Species richness as a function of Site Type for mobile species. Note the two clusters (b and c).



**Community composition of sessile species**

There was no significant effect of Site Type indicating no difference between ASBS discharge and reference sites (Table 5). The results are shown below in the PERMANOVA tables for both clusters containing discharge sites.

Cluster F					
Source	df	SS	MS	Pseudo-F	P(perm)
Site Type	1	836.9	836.9	0.88129	0.606
Residual	4	3798.5	949.63		
Total	5	4635.4			

Cluster G					
Source	df	SS	MS	Pseudo-F	P(perm)
Site Type	1	990.49	990.49	1.2938	0.182
Residual	17	13015	765.57		
Total	18	14005			

Table 5: PERMANOVA table for effect of site type on the community composition of sessile species.

**Community composition of mobile species**

There was no significant effect of Site Type indicating no difference between ASBS discharge and reference sites (Table 6). The results are shown below in the PERMANOVA tables for both clusters containing discharge sites.

Cluster B						
Source	df	SS	MS	Pseudo-F	P(perm)	perms
Site Type	1	1165.3	1165.3	1.3388	0.177	404
Res	13	11316	870.47			
Total	14	12482				

Cluster C						
Source	df	SS	MS	Pseudo-F	P(perm)	perms
Site Type	1	1094.9	1094.9	1.3353	0.186	336
Res	12	9839.4	819.95			
Total	13	10934				

Table 6: PERMANOVA table for effect of site type on the community composition of mobile species.

**Outlier assessment of both mobile and sessile species**

The results above indicate that there was no systemic difference between discharge and reference sites for community composition or species richness for either sessile or mobile species. The results of the outlier analyses indicate that the general pattern of no discharge effects is also true for specific sites (figure 6 for sessile species and figure 7 for mobile species). Two prediction limits are shown: 80 and 95%. Values beyond these limits indicate communities at specific sites that differ from expected (at the 80 or 95% level).

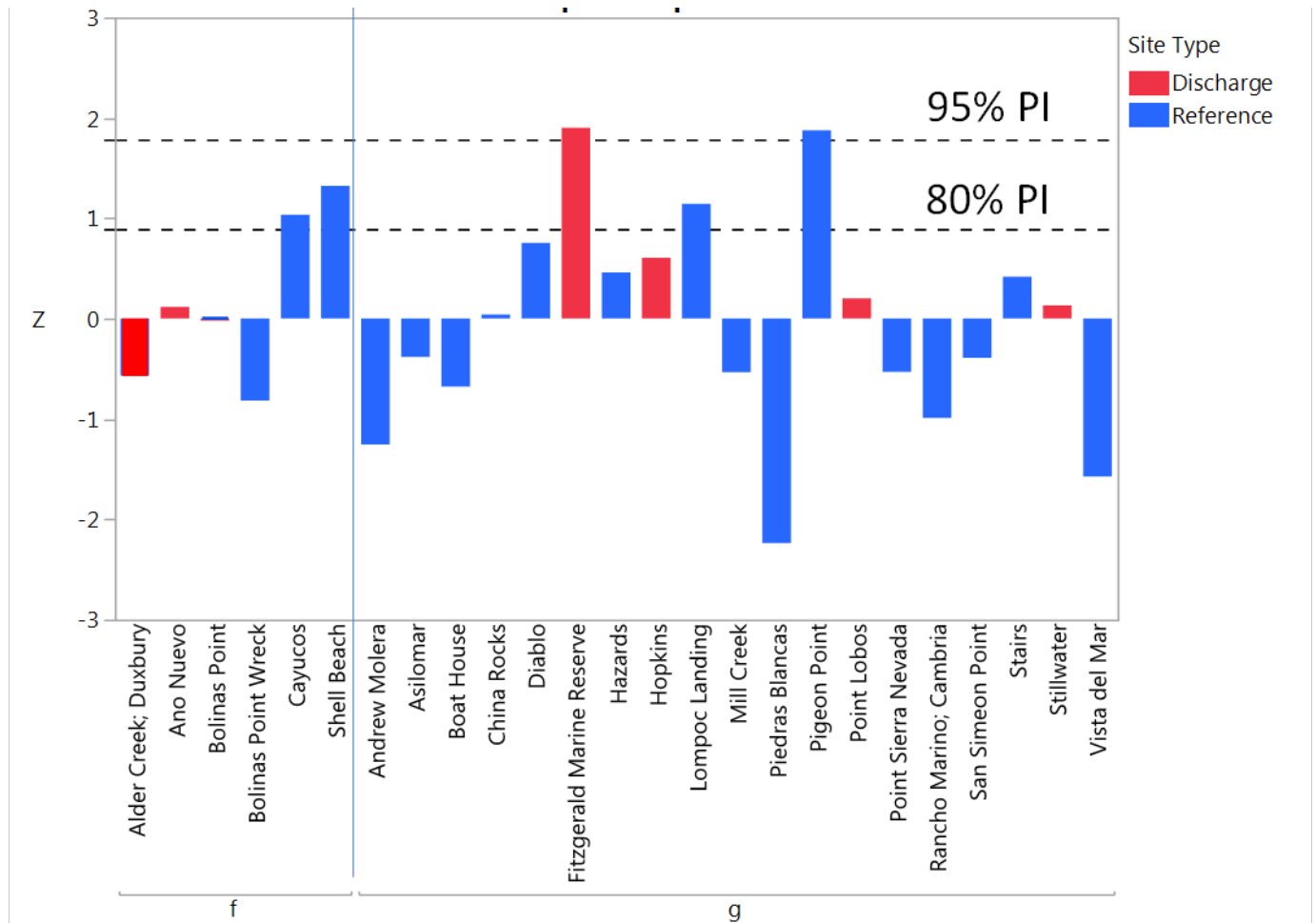


Figure 6: Outlier distances (Z distance from multidimensional centroid) for sessile species for all sample sites. 80 and 95% prediction limits are also shown. Note both clusters are shown (f and g).

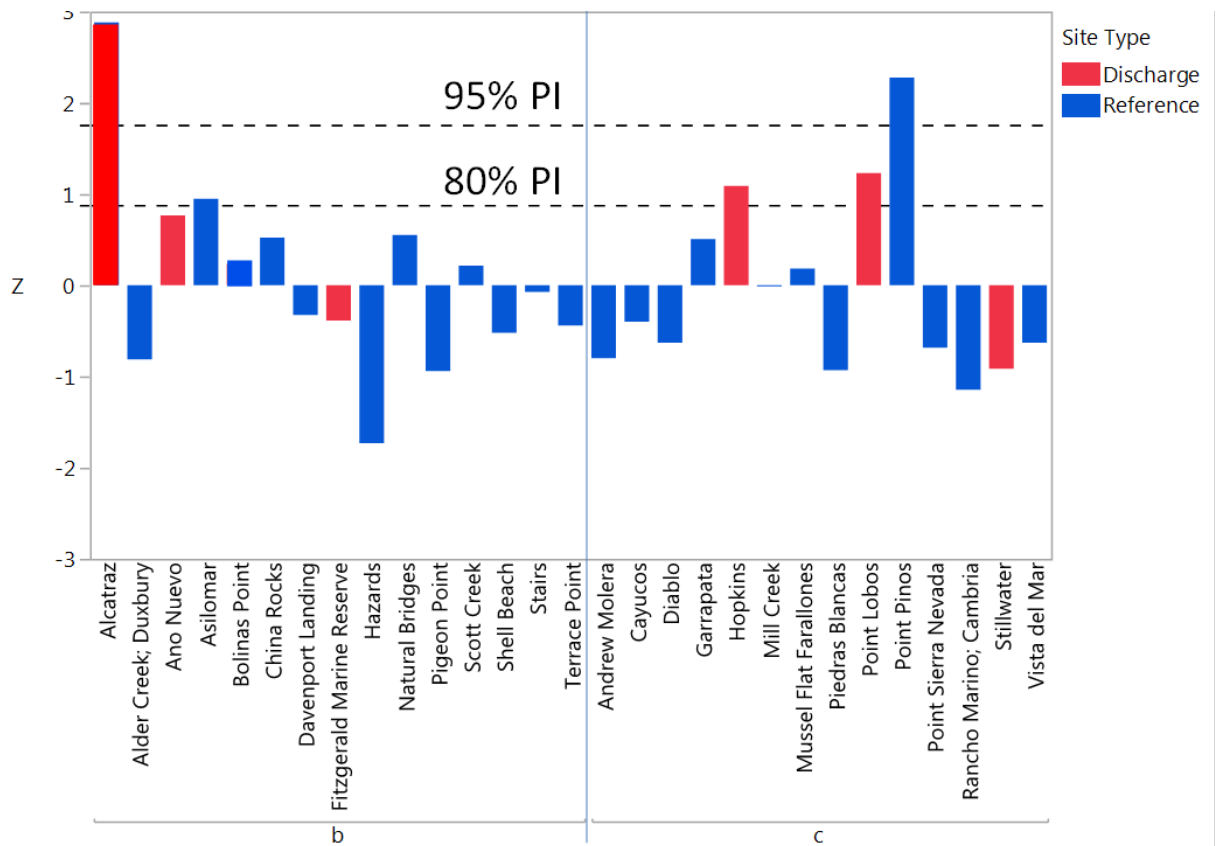


Figure 7: Outlier distances (Z distance from multidimensional centroid) for mobile species for all sample sites. 80 and 95% prediction limits are also shown. Note both clusters are shown (b and c).

The results for sessile species suggest that Fitzgerald Marine Reserve (a discharge site) and Pigeon Point (a reference site) had significantly different communities than expected based on their biogeographic clusters. Figure 8 shows the pattern of difference in species cover between Fitzgerald and the average value for each species. This pattern is consistent with low lying, flat reefs that are exposed to sand.

The results for the mobile species suggest that Alcatraz and Point Pinos (both reference sites) had significantly different communities than expected based on their biogeographic clusters.

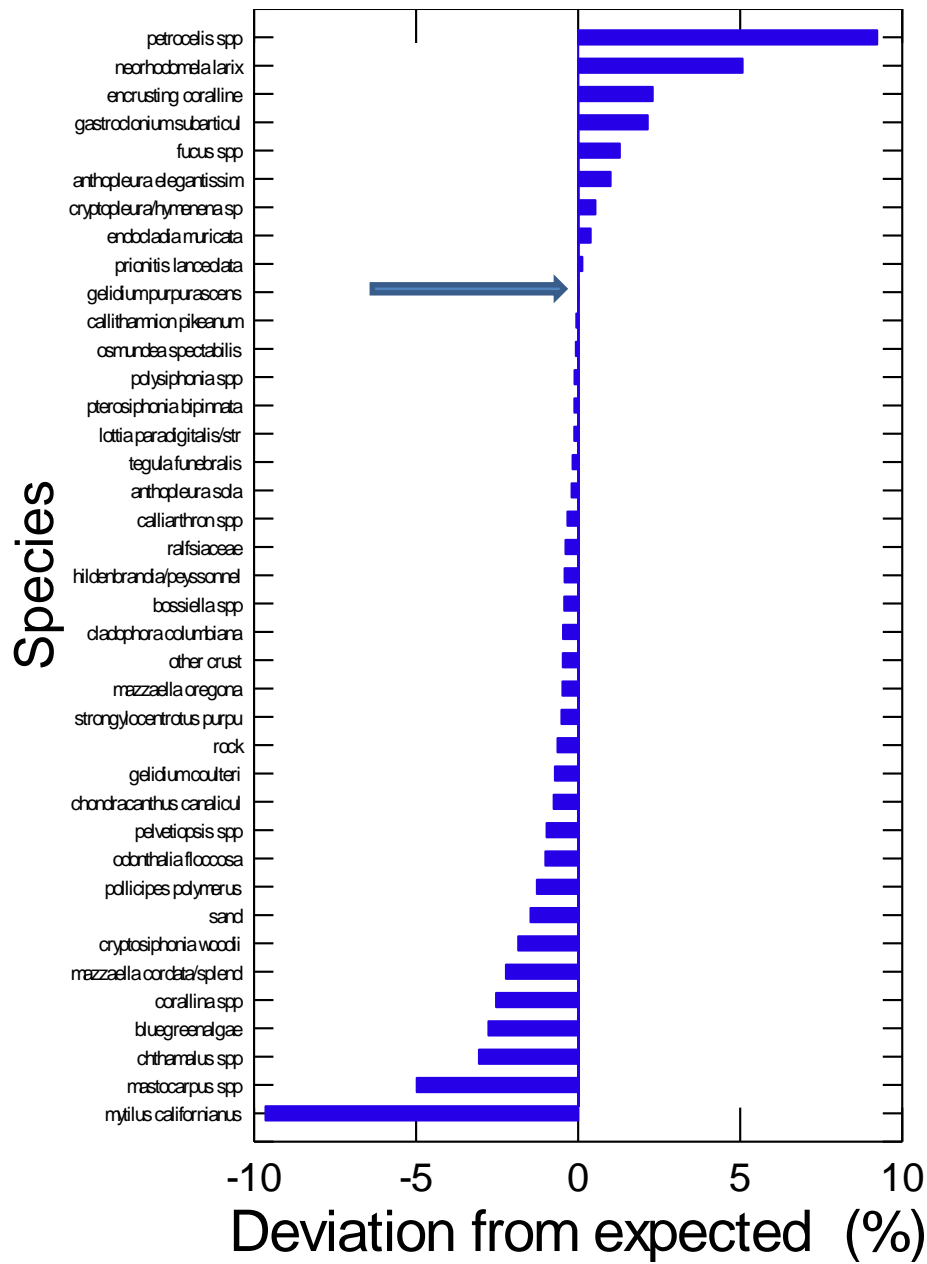


Figure 8: Deviation from expected cover at Fitzgerald Marine Reserve (FMR). Values shown are the differences in cover between FMR and the average value for the species. The arrow shows the transition change from species being more common at FMR to being less common.

## Discussion

There are many natural local (site scale) drivers of community structure including rock type, bedding orientation, sand influence, orientation of the rock surface to the prevailing swell direction, local swell height and period, and upwelling. There are also many local human-induced drivers of community structure that are not related to discharges. These include collecting, trampling, and non-point source pollution. The integration of these factors is the background driver of community structure against which the effect of discharge is measured. In this study, we used a sampling program designed to minimize this integrated driver. We found that there was no general difference in species richness or biological communities at discharge versus reference sites.

In this study we examined whether actual species composition differed from the expected species composition, and if such deviation was associated with whether the site was near or far from a discharge. The general questions are whether the biological community is affected by discharge of water and associated components, and if so, in what way? If a difference is found, then specific expectations need to be evaluated. Here, the specific expectations consistent with an impact due to compromised water quality are (Arevalo et al. 2007, Pineda et al. 2007):

- 1) Generally decreased abundance of species at discharge sites compared to reference sites. This was not the case for any sampled discharge site.
- 2) Communities at discharge sites are characterized by disturbance-associated species. There is not strong support for this general prediction.
  - a. There is support for the idea that specific sites are outlier sites. With respect to discharge sites, one site, Fitzgerald Marine Reserve (FMR) was quite different from expected (figures 6 and 8). There are three general hypotheses for differences seen at FMR: (1) Geomorphology at FMR produces a wide and flat reef that differs from many reefs in the region, (2) Human visitation which likely leads to trampling, (3) Stormwater discharge. All three could independently or jointly yield the type of community seen at FMR, which has lower than expected cover of longer-lived sessile species. Resolving this may require a follow-up study based on a spatial gradient design (as we proposed for sites in southern CA ASBS with substantial community deviations). In such a design transects are arranged in a gradient away from putative perturbations. Geomorphology does not vary enough spatially at FMR to create a meaningful gradient. However, distance from a parking lot and distance from discharge are meaningful spatial gradients that could be taken advantage of. In particular distance from a parking lot is a proxy for trampling and unlikely to be directional, while distance from the discharge is a proxy for discharge impacts and likely to be directional due to prevailing nearshore currents.

In summary, this project provides the first comprehensive condition report for the rocky intertidal zone in central California Areas of Special Biological Significance and serves as a good basis and trigger for focused additional work. The use of standardized sampling consistent with the primary intertidal monitoring program along the West Coast (PISCO/MARINE see [www.pacificrockyintertidal.org](http://www.pacificrockyintertidal.org)) allows for the results of earlier sampling to be incorporated

into the study (because the monitoring uses identical methodologies) and gives context for the ASBS sampling. This approach was used previously in the southern California ASBS assessments, which was a two phase approach (Raimondi et al. 2012, Raimondi 2014) and in the more recent northern California assessment (Raimondi et al. 2015). Phase 1 was identical to the current central California assessment. In southern California, there was a second phase where all sites were evaluated a second time. The goal of the second assessment was to determine how temporal variation in community dynamics might affect the results of the assessment of discharge impacts. In that study, we found that results from repeated surveys were generally in agreement, and as a result, there was a regulatory conclusion that the evaluated discharges *did not hinder the ability of marine life to respond to natural cycles and processes* and were therefore not inconsistent with ASBS goals.

## Conclusions and recommendations

### 1) Conclusions

- a. Based on the results of these analyses, there is no support for the idea that discharges in the North Coast generate region-wide impacts to diversity or community composition in the nearby rocky intertidal sites. This does not mean that there are no impacts to species in the communities. Other attributes such as individual growth and reproduction could be affected with no subsequent impact to diversity or composition.
- b. Some sites stood out as differing substantially from what was expected for biological communities in the region. In particular, Fitzgerald Marine Reserve was an outlier with respect to sessile species composition. It is likely that this difference in community structure is the result of the geomorphology at the site. The intertidal zone at Fitzgerald Marine Reserve is a very wide and flat bench surrounded by sand and subject to considerable scour. In addition, the reef tends to hold water because it is flat and the key mid intertidal species, *Chthamalus spp*, *Mytilus californianus* and *Mastocarpus spp*, which are species that dominate on hard rock surfaces with extended period of emersion are all uncommon at this site (see figure 8).

### 2) Recommendations

- a. The protocols used in this ASBS assessment are identical to those used in Southern California. Because the analytical approach used for these assessments can incorporate geographic effects on community composition (e.g. biogeography), it would be possible to conduct a comprehensive statewide meta-assessment that could be much more powerful (able to detect impacts) than regionally-based assessments.
- b. With respect to the Central Coast Assessment, one discharge site was an outlier: Fitzgerald Marine Reserve. A second year of sampling was used in southern California to confirm impacted sites and increase confidence in statements about deviations in natural water quality for other sites. It is likely that the results presented here reflect the geomorphology and or the effects of trampling by visitors at the site, however there should be considered for a phase two assessment modeled after the southern California ASBS approach.

## References

- Arevalo R., S. Pinedo, E. Ballesteros. 2007. Changes in the composition and structure of Mediterranean rocky-shore communities following a gradient of nutrient enrichment: Descriptive study and test of proposed methods to assess water quality regarding macroalgae. *Marine Pollution Bulletin*, Volume 55, Issues 1-6. Pages 104-113
- Conway-Cranos and Raimondi. 2007. Spatial and temporal variation in recruitment to rocky shores: Relationship to recovery rates of intertidal communities. Coastal Research Center, Marine Science Institute, University of California, Santa Barbara, California. MMS Cooperative Agreement Number 14-35-0001-30758
- Defeo O., A. McLachlan, D. Schoeman, T. Schlacher, J. Dugan, A. Jones, M. Lastra, F. Scapin. 2009. Threats to sandy beach ecosystems: A review. *Estuarine, Coastal and Shelf Science*, Volume 81, Issue 1, Pages 1-12
- Dickson A., R. Gossett, D. Gregorio, B. Jones, S. Murray, B. Posthumus and K. Schiff. 2010. Summation of Findings Natural Water Quality Committee 2006-2009. Technical Report 625. Southern California Coastal Water Research Project, Costa Mesa, CA
- Littler, M. and S. Murray. 1975. Impact of sewage on the distribution, abundance and community structure of rocky intertidal macro-organisms. *Marine Biology*, Volume 30, Number 4, 277-291.
- McLachlan, A. 1993. Sandy beach macrofauna communities and their control by the physical environment: a geographical comparison. *Journal of Coastal Research* 15: 27-38
- Minchinton T. and P. Raimondi. 2007. Effect of Temporal and Spatial Separation of Samples on Estimation of Impacts. MMS OCS Study 2005-002. Coastal Research Center, Marine Science Institute, University of California, Santa Barbara, California. MMS Cooperative Agreement number 14-35-0001-30758. 85 pages
- Raimondi P., K. Schiff, D. Gregorio. 2012. Characterization of the rocky intertidal ecological communities associated with southern California Areas of Special Biological Significance. SCCWRP Technical Report. 80 pages
- Raimondi, P. T. 2014. Characterization of the Rocky Intertidal Ecological Communities Associated with Southern California Areas of Special Biological Significance: Phase II
- Raimondi, P. T., M. George, M. Redfield, S. Worden, R. Williams, N. Fletcher, L. Anderson, D. Lohse, R. Gaddam. 2015. Characterization of the Rocky Intertidal Ecological Communities Associated with Northern Southern California Areas of Special Biological Significance. 33 pages
- Pinedo S., M. Garcia, M. Paola Satta, M. de Torres, E. Ballesteros. 2007. Rocky-shore communities as indicators of water quality: A case study in the Northwestern Mediterranean. *Marine Pollution Bulletin*, Volume 55, Issues 1-6. Pages 126-135
- Southern California Coastal Water Research Project . 2005. California Ocean Plan. Sacramento, CA



# Appendix 1: Site locations, descriptions, pictures and site specific cover and density of species

Sites shown in Appendix 1 represent the sampling funded in this survey. Many other sites were also included in the evaluation of the potential discharge impacts (figure 1). Attributes for these sites can be found at [www.pacificrockyintertidal.org](http://www.pacificrockyintertidal.org).

### ***Bolinas Point***

Bolinas Point is located in the North Central Coast region of California, within the Gulf of the Farallones National Marine Sanctuary and Point Reyes National Seashore. This site is located in an Area of Special Biological Significance (Duxbury Reef Reserve and Extension ASBS), within the Duxbury Reef State Marine Conservation Area established by the State of California, and is 1.4 mi northwest of the Duxbury Reef Point Mussel Watch site.



The site is northwest of the town of Bolinas. This gently sloping site consists of relatively flat terrain. The survey plots are located on the outermost intertidal bench and consist primarily of sedimentary rock outcrops with folded layers oriented in a NW-SE direction. This site receives low visitation by tidepoolers.

The Biodiversity Survey grid encompasses one section that is approximately 30 meters (along shore) x 150 meters (seaward).

## Alder Creek; Duxbury

Alder Creek; Duxbury is located in the North Central Coast region of California, within the Gulf of the Farallones National Marine Sanctuary.



This site is located within the Duxbury Reef State Marine Conservation Area and Agate Beach County Park. This site is also located in an Area of Special Biological Significance (Duxbury Reef Point ASBS). This gently sloping site consists of relatively flat terrain. Alder Creek; Duxbury is dominated by sand and the area surrounding the site is comprised of sandy beach. The primary coastal orientation of this site is southwest.

The Biodiversity Survey grid encompasses one section that is approximately 30 meters (along shore) x 80 meters (seaward).

### ***Fitzgerald Marine Reserve***

Fitzgerald Marine Reserve is located in the North Central Coast region of California, within the Monterey Bay National Marine Sanctuary. This site is located within the Montara State Marine Reserve and San Mateo County Park. This site is also located in an Area of Special Biological Significance (James V. Fitzgerald Marine Reserve ASBS). This gently sloping site consists of relatively flat terrain. This is a site that receives the greatest number of tide-poolers in all of central California.



Fitzgerald Marine Reserve is dominated by a mixture of consolidated bedrock and sandy beach and the area surrounding the site is sandy beach. The primary coastal orientation of this site is west/southwest.

The Biodiversity Survey grid encompasses one section that is approximately 30 meters (along shore) x 40 meters (seaward).

### ***Pigeon Point***

Pigeon Point is located in the Central Coast region of California, within the Monterey Bay National Marine Sanctuary. This site is located within Pigeon Point Lightstation State Historic Park. This site receives high visitation by tidepoolers and is often visited by school groups. This gently sloping site consists of extremely uneven terrain, containing many deep cracks and folds.



Pigeon Point is dominated by a mixture of consolidated conglomerate rock and boulder fields, and the area surrounding the site is comprised of a mixture of consolidated conglomerate rock, boulder fields, and sandy beach. The primary coastal orientation of this site is south/southwest. The Biodiversity Survey grid encompasses one section that is approximately 33 meters (along shore) x 33 meters (seaward).



### ***Año Nuevo***

Año Nuevo is located in the Central Coast region of California, within the Monterey Bay National Marine Sanctuary. This site is located within the Año Nuevo State Marine Reserve and Año Nuevo State Park. This site is also located in an Area of Special Biological Significance (Año Nuevo Point and Islands ASBS), and is near the Año Nuevo Island Mussel Watch site. This gently sloping site consists of moderately uneven terrain, containing few cracks and folds and is essentially not visited by tide-poolers.



Año Nuevo is dominated by a mixture of consolidated sedimentary rock and sandy beach, and the area surrounding the site is comprised of a mixture of consolidated bedrock and sandy beach. The primary coastal orientation of this site is west.

The Biodiversity Survey grid encompasses one section that is approximately 30 meters (along shore) x 40 meters (seaward).

## ***Hopkins***

Hopkins is located in the Central Coast region of California, within the Monterey Bay National Marine Sanctuary. This site is located within the Lovers Point State Marine Reserve. This site is also located in an Area of Special Biological Significance (Pacific Grove Marine Gardens Fish Refuge and Hopkins Marine Life Refuge ASBS), and is 0.6 miles southeast of the Pacific Grove/Lovers Point Mussel Watch site. This site is part of Hopkins Marine Reserve. There is an abundance of historical and ongoing research at this site, and this site has moderate visitation by researchers. This moderately sloping site consists of extremely uneven terrain, containing many deep cracks and folds.



Hopkins is dominated by a mixture of consolidated granite and boulder fields, and the area surrounding the site is comprised of a mixture of consolidated granite, boulder fields, and cobble beach. The primary coastal orientation of this site is north/northwest. The Biodiversity Survey grid encompasses one section that is approximately 30 meters (along shore) x 20 meters (seaward).

### ***Stillwater***

Stillwater is located in the Central Coast region of California, within the Monterey Bay National Marine Sanctuary. This site is located within the Carmel Bay State Marine Conservation Area. This site is also located in an Area of Special Biological Significance (Carmel Bay ASBS), and is near the Carmel Bay/Arrowhead Point Mussel Watch site. This site is accessed through the 17 Mile Drive toll road. This site is directly below Pebble Beach Golf Course and receives low visitation by tidepoolers. This gently sloping site consists of moderately uneven terrain, containing few cracks and folds.



Stillwater is dominated by consolidated bedrock, and the area surrounding the site is comprised of a mixture of consolidated bedrock, boulder fields, and sandy beach. The primary coastal orientation of this site is south/southwest.

The Biodiversity Survey grid encompasses one section that is approximately 30 meters (along shore) x 10 meters (seaward).



### ***Point Lobos***

Point Lobos is located in the Central Coast region of California, within the Monterey Bay National Marine Sanctuary. This site is located within the Point Lobos State Marine Reserve and Point Lobos State Park. This site is also located in an Area of Special Biological Significance (Point Lobos Ecological Reserve ASBS), and is 0.3 mi northwest of the Point Lobos/Weston Beach Mussel Watch site. This site receives high visitation by tidepoolers and is often visited by school groups. This gently sloping site consists of extremely uneven terrain, containing many deep cracks and folds.



Point Lobos is dominated by consolidated conglomerate rock and sandstone, and the area surrounding the site is comprised of a mixture of consolidated conglomerate rock and sandstone, boulder fields, and cobble beach. The primary coastal orientation of this site is southwest.

The Biodiversity Survey grid encompasses two sections that are approximately 8.4 meters (along shore) x 20 meters (seaward), and 12 meters (along shore) x 20 meters (seaward).

