Quality Assurance Project Plan

for

CENTRAL COAST LONG-TERM ENVIRONMENTAL ASSESSMENT NETWORK

CCLEAN

Revised July 1, 2013

GROUP A ELEMENTS: PROJECT MANAGEMENT

1. TITLE AND APPROVAL SHEETS

Quality Assurance Project Plan

For

PROJECT NAME: Central Coast Long-term Environmental Assessment Network

Version: 6.1

Date: July 1, 2013

NAME OF RESPONSIBLE ORGANIZATION: Central Coast Long-term Environmental Assessment Network

APPROVAL SIGNATURES

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Chair, CCLEAN Steering Committee	Garrett Haertel		
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4. PROJECT/TASK ORGANIZATION

4.1 Involved parties and roles
The involved parties and their responsibilities are shown in Table 1.

Table 1. CCLEAN personnel responsibilities.

Name	Organizational Affiliation	Title	Contact Information (Telephone number, fax number, email address.)
Dane Hardin	Applied Marine Sciences, Inc.	CCLEAN Program Director	831-426-6326 hardin@amarine.com
Jon Toal	Kinnetic Laboratories	Project Manager, Effluent, Mussels, and Nearshore	808-661-1110 mstevens@kinneticlabs.com
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4.2 Quality Assurance Program Plan (QAPP)
This QAPP consists of the systems and plans necessary to provide adequate confidence that the studies and projects that CCLEAN sponsors and/or executes will meet program and study objectives satisfactorily and efficiently. The goal of quality assurance (QA) is to assure that monitoring, research, and analytical activities are performed in a controlled manner, and maintained according to sound and defensible technical specifications, quality practices that ensure valid and retrievable data. QA also includes the quality control, which comprises all those actions necessary to verify the characteristic features of program elements and the resulting data.

4.3 Persons responsible for QAPP update and maintenance
The Program Director of CCLEAN is responsible for maintaining and updating the QAPP, with the assistance of the CCLEAN QA Officer. Because program data are not generated by Applied Marine Sciences but are instead generated by other entities, including program participants and subcontractors (see Section 4.4), the CCLEAN Program Director and QA Officer are independent from the entities generating the data.
The maintenance activities include:

a. Assuring in concert with the CCLEAN lead agency and chairperson that contracting laboratories implement QA elements consistent with CCLEAN study and program objectives;
b. Coordinating QA elements relevant to CCLEAN projects and studies with contracting laboratories;
c. Overview of relevant quality assurance implementation plans relating to CCLEAN projects by contributing agencies;
d. Verify that QA requirements have been considered in conceptual stages of study plans; assure that project and study costs account for quality assurance and quality control;
f. Assure that corrective actions consistent with CCLEAN QAPP are taken for all flags and other quality control defects; and
g. Provide an annual QA audit for the review of CCLEAN steering committee prior to finalizing annual and/or project reports.

CCLEAN Base Program Contractors are responsible for:

a. Developing and implementing QA programs consistent with CCLEAN study objectives contracted to their organizations;
b. Preparing and producing QA audits of CCLEAN studies contracted to their organizations, when requested by CCLEAN;
c. Performing all corrective actions as indicated by CCLEAN's QAPP for studies and projects under their respective contracts.

4.4 Organizational chart and responsibilities

The organizational chart for the CCLEAN program is shown in Figure 1.

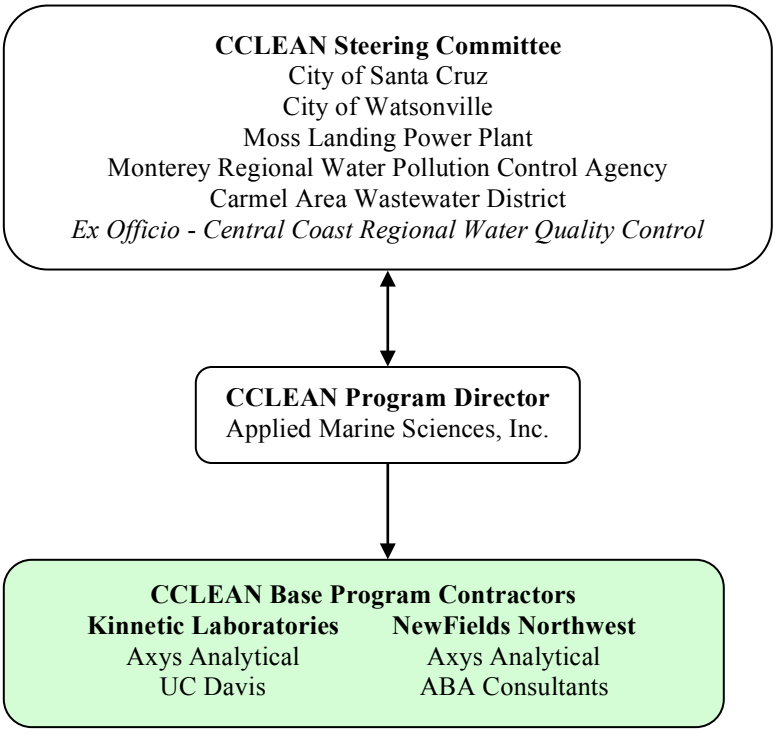

Figure 1. Organizational chart for CCLEAN

5. PROBLEM DEFINITION/BACKGROUND

5.1 Problem statement

The complexity of environmental issues affecting nearshore marine waters today have led to general agreement that their protection is only possible by implementing regional approaches to monitoring and resource management. Nearshore marine waters are affected by point-source discharges, storm runoff, rivers, discharges from ships, and aerial deposition. At the same time, many marine resources are diminishing under pressure from increasing usage. In the late 1990s, multiple agencies in the Monterey Bay area began working toward implementation of a regional approach to monitoring watersheds and marine waters.

The Central Coast Long-term Environmental Assessment Network (CCLEAN) is a long-term monitoring program that has been designed by program participants through a commitment to environmental stewardship in order to fulfill several regulatory objectives. CCLEAN is currently funded by the City of Santa Cruz, the City of Watsonville, Moss Landing Power Plant, Monterey Regional Water Pollution Control Agency, and Carmel Area Wastewater District, under the direction of the Water Board, Central Coast Region (hereafter Water Board). CCLEAN fulfills a significant component of the subscribing agencies' compliance to their NPDES monitoring commitments. In addition, it represents a significant portion of their contributions to their communities' efforts at sustainability of their coastal environments. However, CCLEAN is also the current mechanism by which the Water Board fulfills part of its obligations under a monitoring framework developed to provide an ecosystem-based Water Quality Protection Program for the Monterey Bay National Marine Sanctuary. The monitoring framework evolved to fulfill the Water Board's obligations to the Management Plan for the Sanctuary. The Sanctuary's Management Plan includes a Memorandum of Agreement among eight federal, state, and regional agencies (including the Water Board). The Water Board's framework for partial fulfillment of this Water Quality Protection Program is the Central Coast Ambient Monitoring Program (CCAMP). This multidisciplinary program includes sampling in watersheds that flow into coastal regions, in estuarine coastal confluences, and at coastal sites. The goal of CCAMP is to "collect, assess, and disseminate scientifically based water quality information to aid decision-makers and the public in maintaining, restoring, and enhancing water quality and associated beneficial uses." CCLEAN provides the initial nearshore component of CCAMP. CCLEAN has been underway since 2001 and its QAPP is being revised to incorporate recent program changes, and to retain consistency with the Water Board surface water ambient monitoring program (SWAMP) requirements for data compatibility.

Within the framework of CCAMP, the goal of the CCLEAN program is to assist stakeholders in maintaining, restoring, and enhancing nearshore water and sediment quality and associated beneficial uses in the Central Coast Region. The program's objective is to use high-quality data to address the following questions and objectives:

- What are the status and long-term trends in the quality of nearshore waters, sediments, and associated beneficial uses?
- Do nearshore waters and sediments comply with California Ocean Plan and associated NPDES permits?
- What are the major sources of contaminants to nearshore waters?
- What are the effects of wastewater discharges in nearshore waters?
- Manage the program adaptively to ensure cost effectiveness and response to emerging issues of concern to water quality managers
- Develop a long-term database on trends in the quality of nearshore waters, sediments and associated beneficial uses.
- Ensure that the database is compatible with other regional monitoring efforts and regulatory requirements.
- Ensure that data are presented in ways that are understandable and relevant to the needs of stakeholders.

The questions lend themselves to hypothesis testing, which should be the basis of program decision making, whenever possible. For example, determination of trends in contaminant concentrations in nearshore waters, sediments and associated beneficial uses can be made by testing the null hypothesis to determine if no changes have occurred over time in the concentrations of contaminants or level of impairment by using either linear regression or a Seasonal Kendall Test. Specific examples of how the data will lead to outcomes and the applicable criteria for determining impairments are discussed in sections 5.2 and 5.3.

The CCLEAN program and decision-making process includes a commitment to adaptive management. This ensures the flexibility needed to add or delete program elements in response to previous findings or emerging concerns. For example, the CCLEAN Steering Committee has recently implemented measurements of polybrominated diphenyl ethers (PBDEs), screening for perfluorinated compounds (PFCs) and reproduction disrupting activity in wastewater, while reducing resources allocated to riverine monitoring.

5.2 Decisions or outcomes

Data sets from CCLEAN are made available for scientific research, regulatory purposes, and public awareness. Examples of how the data will be used by CCLEAN are as follows:

- Trend analysis - Data may be used to investigate seasonal, annual, and long-term patterns in pollutants entering nearshore waters by testing with linear regression or Seasonal Kendall Test.
- Objectives and Guidelines - Data may be used to evaluate the status of nearshore waters, sediments and fish and shellfish tissues and whether they achieve various water, sediment, and tissue quality guidelines.
- Integrated Contaminant Measurements - Tissue contaminants and benthic community data may be used to determine time-averaged trends in contaminant concentrations and their effects and for comparison with other trend data.
- Data may be used to assess the relative contributions of point and nonpoint sources of pollutants to Monterey Bay.
- Impairment of beneficial uses can be determined by comparing the number of exceedences to statistical criteria established by the State of California for listing water bodies on the California State Water Resources Control Board (SWRCB) Total Maximum Daily Load (TMDL) 303d list.

5.3 Water quality or other criteria

Data generated through CCLEAN will be used to determine whether nearshore waters and sediments are in compliance with the California Ocean Plan, satisfy the NPDES receiving water monitoring and reporting requirements of program participants, and inform the ongoing TMDL development process. Regulatory criteria and comparative data used by the program include the following:

Water - California Ocean Plan and Basin Plan standards, California Toxics Rule values,
Sediment – National Oceanic and Atmospheric Administration (NOAA) Effects Range Low and Median, California Sediment Quality Objective (when available), San Francisco Bay comparative data, and
Tissue – California State Mussel Watch elevated data levels (for the 85^{th} and 95^{th} percentiles (EDL 85 and 95), US Food and Drug Administration (USFDA) alert levels, USEPA recreational and subsistence fisher screening values, and California Office of Environmental Health Hazard Assessment (OEHHA) screening values, Bodega Head and San Francisco Bay comparative data.

6. PROJECT/TASK DESCRIPTION

6.1 Work statement and produced products
CCLEAN measures inputs of possible water quality stressors and effects in nearshore waters by sampling wastewater effluent, nearshore waters, mussels, sediments, and benthic communities. Effluent for each municipal wastewater discharger is sampled for persistent organic pollutants (POPs), nutrients, and suspended sediments using automated equipment to obtain twice per year 30-day flow-proportioned samples in the wet and dry seasons. Mussels are sampled at five locations that fill geographic gaps in other programs to measure POPs and bacteria. Sediments are sampled for POPs and benthic organisms once a year at two sites within the depositional band that has been identified by U.S. Geological Survey along the 80-meter contour in Monterey Bay and at four sites near presumed contaminant sources. Nearshore background water is sampled twice per year at two sites for concentrations of POPs, nutrients, and bacteria.

The CCLEAN monitoring program is designed to 1) determine the major sources of contaminants that are affecting beneficial uses in marine waters, 2) estimate the loads of those contaminants and 3) determine the effects of those contaminants. During the first six years of the program, the sources contaminants were investigated by sampling the four rivers discharging to the Monterey Bay area, in addition to wastewater. Loads from sampled sources are estimated by multiplying flow-proportioned concentrations times measured or modeled flow during the sampling period. Effects are determined by comparing concentrations of contaminants in water, sediment and mussel tissue to applicable objectives or alert levels and measuring statistical relationships between sediment contaminant concentrations and benthic community composition. An evaluation of five years of data revealed numerous impairments to beneficial uses associated with POPs and pathogen indicators, with the four rivers in the program area discharging much higher loads than the wastewater treatment plants of most contaminants that are impairing beneficial uses. Program directions for the next five years of monitoring are designed to emphasize further characterization of wastewater treatment effluents and the sources of existing receiving water impairments.

6.2. Constituents to be monitored and measurement techniques
The CCLEAN program involves multiple sampling components and measurement techniques (Table 2). Constituents to be monitored are described in detail in Element 11. Measurement techniques are described in Element 13.

Table 2. Overview of sample types and collection techniques.

Sample Type	Sampling Method
Effluent Sampling	Flow-proportioned solid-phase extraction and grab samples.
Receiving Water Sampling	Grab sample
Mussel Sampling	Hand collected
Sediment Sampling	Benthic grab sample
Nearshore Background Sampling	Time-integrated solid-phase extraction and grab sample

6.3 Project schedule
Project schedules for the CCLEAN program are shown in Table 3. CCLEAN reports are submitted annually to the Water Board by January 31 for the previous July–June period (see Section 21). As CCLEAN data for effluent are used for permit compliance, raw data for effluent are available to dischargers within 90 days of sampling.

Table 3. Sampling sites, parameters sampled, frequency of sampling, applicable water-quality stressors, and relevant program objectives for CCLEAN during the 2008–2013 program period.

Sampling Sites	Parameters Sampled at Each Site	Frequency of Sampling	Applicable Water-quality Stressors
Water Sampling Four wastewater discharges (Santa Cruz, Watsonville, Monterey, Carmel) in effluent	30-day flow proportioned samples using automated pumping equipment, solid-phase-extraction techniques for POPs; screen effluent for reproductive endocrine disruption activity	Twice per year (wet season and dry season)	Sources, loads, trends, effects and permit compliance for: POPs
	Grabs of effluent for ammonia and nitrate, turbidity, temperature, conductivity, pH, urea, orthophosphate, dissolved silica and total suspended solids	Monthly	Sources, loads, trends and permit compliance for: Nutrients
	Evaluate satellite imagery for algal blooms	Periodically	Effects of: Nutrients
30-ft contour sites for Santa Cruz, Watsonville and MRWPCA	Grabs for total and fecal coliform, *enterococcus*	At least monthly	Sources, trends, effects and permit compliance for: Pathogen indicators
Two nearshore background sites	30-day time-integrated samples using automated pumping equipment and solid-phase-extraction techniques for: POPs, nitrate, ammonia, urea, orthophosphate and dissolved silica, total suspended solids, temperature, conductivity, pH, total and fecal coliform, *enterococcus*	Twice per year (wet season and dry season)	California Ocean Plan compliance for: POPs Nutrients Pathogen indicators
Sediment Sampling Three depositional sites and three background sites along 80-m contour	Single samples for benthic infauna, POPs, total organic carbon and grain size	Every five years in the fall	Status, effects and alert level comparisons for: POPs
Mussel Sampling Five rocky intertidal sites	One composite of 30-40 mussels for POPs, total and fecal coliform, and *enterococcus*	Annually in the wet season	Status, trends, effects and alert level comparisons for: POPs Pathogen indicators

6.4 Geographical setting

CCLEAN sampling sites span the Monterey Bay area from Scott Creek in the north to Carmel Bay in the south (Figure 2).

Figure 2. Locations of CCLEAN sampling sites for receiving water, sediment, mussels, and nearshore background water.

6.5 Constraints

CCLEAN program constraints are all reflective of the characteristics of multi-agency projects with broad and evolving focus areas. These focus areas include the development of background and trends data for numerous

conventional and emerging pollutants. The resource pool is limited relative to the range of candidate pollutants and ecological niches to assess. Therefore the most prominent constraints include:

a. Technological resources to assess subtle ecological changes before sustainability is further eroded. This is particularly relevant to the projects to quantify load and concentrations of ultra-trace organic compounds for dischargers and their effects in the nearshore;

b. Paucity of data from other sources to provide evaluative and reference points for CCLEAN generated data in the nearshore;

c. Limited availability of routine analytical and contract laboratories for CCLEAN projects to be delivered in a timely manner; and

d. Budget is a constraint for CCLEAN. The agencies funding the program face financial limitations associated with the general economic condition of their constituents.

7. Quality Objectives and Criteria for Measurement Data

Data quality objectives are driven by the program's commitment to SWAMP data compatibility; and to specific project and study objectives. And because data sets generated by CCLEAN are used in more than one type of analysis, data quality objectives must be rigorous enough to address those analyses with the most stringent detection limits and the greatest needs for accuracy. For example, estimating loads based upon 30-day flow proportioned samples requires modest accuracies and detection limits, whereas comparing measured concentrations to California Toxics Rule or California Ocean Plan objectives requires detection limits at least as low as the applicable objectives. Moreover, many of the compounds being measured by CCLEAN are found in very low concentrations and comparably low detection limits are necessary to give reasonable confidence that undetected compounds are not present.

Data quality objectives for this project will consist of the following:

Field Measurements – Accuracy, Precision, Completeness

Laboratory Analysis of POPs – Accuracy, Precision, Recovery, Sample Integrity; Completeness

Laboratory Analysis of TOC and Grain Size – Accuracy, Precision, Completeness

Laboratory Analysis of Bacteria – Accuracy, Bias and Completeness

Accuracy - Control limit criteria are based on "relative accuracy", which is evaluated for each analysis of the Certified Reference Material (CRM) or Laboratory Control Material (LCM) by comparison of a given laboratory's values to the "true" or "accepted" values. The "true" values are defined as the 95% confidence intervals of the mean. Based on typical results attained by experienced analysts in the past, accuracy control limits have been established both for individual compounds and combined groups of compounds (Tables 7 - 10). There are three combined groups of compounds for the purpose of evaluating relative accuracy for organic analyses: polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pesticides.

Precision - Precision is the reproducibility of an analytical method. Each laboratory is expected to maintain control charts for use by analysts in monitoring the overall precision of the CRM or LCM. Upper and lower control chart limits (e.g., warning limits and control limits) will be continually updated; control limits based on 99% confidence intervals around the mean are recommended. The relative standard deviation (RSD) will be calculated for each analyte of interest in the CRM based on the last 7 CRM analyses. Acceptable precision targets for various analyses are listed in Tables 7 - 10.

Completeness - Completeness is defined as "a measure of the amount of data collected from a measurement process compared to the amount that was expected to be obtained under the conditions of measurement" (Stanley and Verner, 1985). Field and laboratory personnel will always strive to exceed completeness of 95%.

Recovery - A laboratory-fortified sample matrix (a matrix spike, or MS) and a laboratory fortified sample matrix duplicate (a matrix spike duplicate, or MSD) will be used both to evaluate the effect of the sample matrix on the recovery of the compounds of interest and to provide an estimate of analytical precision. A minimum of 5% of the total number of samples submitted to the laboratory in a given year will be selected at random for analysis as matrix spikes and matrix spike duplicates. Recovery data for the fortified compounds ultimately will provide a basis for determining the prevalence of matrix effects in the samples analyzed during the project. Analysis of the MS/MSD is also useful for assessing laboratory precision. The relative percent difference (RPD) between the MS and MSD results should be less than the target criterion listed in Tables 4 - 7 for each analyte of interest.

Field Replicates and Field Split Samples - As part of the quality assurance program of CCLEAN, replicate or split samples will be collected for sediment and mussel samples for subsequent chemical analysis. Field duplicates will be submitted as blind samples to the analytical laboratory. Field splits also will be collected and sent blind to additional laboratories selected to participate in the split sample analysis. One field replicate and one field split will

be collected for analysis from each sample matrix each year (i.e., one field replicate and one field split per six samples for sediment and per five samples for mussels).

Bias - A systematic error due to the experimental method that causes the measured values to deviate from the true value. This quality parameter is particularly important in microbiological analyses involving culturing and dilutions. It is also important in assessing data compiled from analytical work on trace organics and by reference methods.

Representativeness – CCLEAN samples are collected to represent concentrations and loads of contaminants at different locations and the effects of time on those concentrations and loads (i.e., long-term or seasonal patterns). As such, CCLEAN sampling activities are designed to maximize both spatial and temporal representativeness. Spatial representativeness of effluent loads is ensured by sampling all the major wastewater discharges in the program area. Sediment and mussel samples are collected randomly from fixed locations to represent areas distant from and close to sources of contaminants. Because of limited resources, temporal representativeness for effluent and ocean waters is achieved by sampling in the dry season and wet season in order to capture the minimum and maximum effects of rainfall on discharges of contaminants to the ocean. While logistical considerations require that sampling be scheduled well ahead of time, representativeness of wet-season and dry-season periods is improved by using a 30-day sampling period for effluent and ocean waters. Sediment samples are collected in the early fall each year to represent the maximum annual diversity of benthic organisms before winter storms disrupt bottom sediments. Mussel samples are collected in the wet season to represent the maximum likely accumulation of contaminants from winter runoff. Both sediment and mussel samples tend to integrate their exposure to contaminants over time preceding sample collection and those samples represent the antecedent period.

In addition to the above elements of the study design, sample representativeness is ensured by proper collection and handling procedures (see sections 11 and 12). These procedures minimize sample degradation by use of preservatives, cooling and/or keeping the samples in darkness so that analytical results represent the original sample matrix as much as possible.

Table 4. Data quality objectives for laboratory analysis of ammonia, nitrate, urea, orthophosphate, dissolved silica, and TSS in water. The completeness objective for CCLEAN field and laboratory samples is 95%. Program action limit for ammonia is that in the California Ocean Plan, Table A. There are no applicable action limits for the other constituents in either effluent or ocean water.

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	CRITERIA	CORRECTIVE ACTION
Method Blank	Contamination by reagents, laboratory ware, etc.	One per year for every 12 samples	<DL or <10% of lowest sample	Identify and eliminate contamination source. Apply value to the calculated data if quantified ≥DL but < MDL. Reanalyze all samples in batch, when value is ≤ MDL. Qualify data as needed
Certified Reference Material (CRM) or Laboratory Reference Material (LRM) or Standard	Accuracy	Once per year for every 12 samples	Within 95% CI of stated value. If not available then within 80 to 120% of true value.	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, then identify and eliminate source of inaccuracy and reanalyze. Do not begin analysis of field samples until laboratory initial capability is clearly demonstrated.
Replicates: (analytical and/or laboratory) Applies to replicates, CRMs, LRMs, Standards, matrix spike samples, etc.	Precision	One per year for every 12 samples	RPD or RSD < 25%	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, then identify and eliminate source of imprecision and reanalyze.
Matrix Spike	Recovery	1 per batch of 20 or fewer field samples	Recovery 80–120%	Review data reports and chromatographs. Check instruments.

DL = Instrument detection Limit; MDL = method detection limit; RPD = relative percent difference; RSD = relative standard deviation

Table 5. Data quality objectives for laboratory analysis of POPs in water. The completeness objective for CCLEAN field and laboratory samples is 95%. Program action limits for POPs in effluent are those in each participant's NPDES permit, as applicable. Program action limits for POPs in ocean water are those in the California Ocean Plan, Table B, as applicable.

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	CRITERIA	CORRECTIVE ACTION
Method Blank	Contamination by reagents, laboratory ware, etc.	One per batch of six samples (i.e., once in each sampling period)	< DL or < 10% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed
Instrument Blank	Cross contamination	NA	Set by laboratory	NA
Reference Performance Spike	Retention of analytes by sampling media and sampling integrity	Every XAD-2 column	≥80% Report performance for tracking and evaluation	Qualify data within 50% of acceptable range. Otherwise reject and re-analyze. Review with CCLEAN Stakeholders
Certified Reference Material (CRM)	Accuracy	NA for solid-phase extraction	NA for solid-phase extraction	NA for solid-phase extraction
Replicates: (analytical and/or laboratory) Applies to replicates of CRMs, matrix spike samples, etc.	Precision Instrument and/or overall reproducibility of a result.	One per batch of six samples (i.e., once in each sampling period)	RPD or RSD < 25%	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, identify and eliminate source of imprecision and reanalyze.
Matrix Spike	Recovery	1 per batch of 20 or fewer field samples	Recovery 50–150%	Check CRM or LCS recovery. Review chromatograms and raw data quantitation reports. Check instrument response using calibration standard. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed.
Surrogate Spike	Recovery (used to adjust sample results)	One per sample batch of six samples (i.e., once in each sampling period)	Set by analyzing laboratory (Report surrogate recovery and acceptance criteria in final report)	Check CRM or LCS recovery. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed
Continuing Calibration Check solutions	Accuracy & Precision	At least every 12 hours	Known values for 90% of analytes shall not deviate more than ±25% for PAHs, and ±20% for PCBs and Pesticides.	Beginning with last sample before failure, recalibrate and reanalyze. Compare RPD and reanalyze.

MDL = method detection limit; RPD = relative percent difference; RSD = relative standard deviation

Table 6. Data quality objectives for laboratory analysis of POPs in sediment and tissue. The completeness objective for CCLEAN field and laboratory samples is 95%. Program action limits for POPs in sediments are those in either the NOAA sediment quality alert levels (ERLs or ERMs). Program action limits for POPs in mussels are those in either the California Office of Environmental Health Hazard Assessment (OEHHA) or U.S. Food and Drug Administration, as appropriate.

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	CRITERIA	CORRECTIVE ACTION
Method Blank	Contamination by reagents, laboratory ware, etc.	One per batch of five or six samples (i.e., once in each sampling period)	< MDL or < 10% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed
Certified Reference Material (CRM)	Accuracy	1 per 20 field samples	As a group: 70% of the analytes within 35% of the 95% confidence interval. Individually: No analyte outside 30% of 95% confidence interval for 2 consecutive analyses.	Review chromatograms and raw data quantitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat analysis until control limits are met.
Replicates: (analytical and/or laboratory) Applies to replicates of CRMs, matrix spike samples, etc.	Precision	1 per batch of 20 or fewer field samples	RPD <25%	Recalibrate and reanalyze. If problem persists eliminate source of imprecision and reanalyze.
Matrix Spike	Recovery	1 per 20 field samples	>50–150% recovery if no CRM limits apply, otherwise use CRM limits.	Check CRM or LCS recovery. Review chromatograms and raw data quantitation reports. Check instrument response using calibration standard. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed.
Surrogate Spike or Internal Standard	Recovery (used to adjust sample results)	One per sample	Set by analyzing laboratory (reported in QA report). (Report surrogate recovery and acceptance criteria in final report)	Check CRM or LCS recovery. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed.

MDL = method detection limit; RPD = relative percent difference; RSD = relative standard deviation

Table 7. Data quality objectives for laboratory analysis of total organic carbon and grain size in sediment. The completeness objective for CCLEAN field and laboratory samples is 95%.

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	CRITERIA	CORRECTIVE ACTION
Method Blank	Contamination by reagents, laboratory ware, etc.	One per batch of six samples (i.e., once in each sampling period)	<MDL or <10% of lowest measurement at ≤ 0.25 mg/L	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed
Certified Reference Material	Accuracy	TOC: every 15 samples. Grain Size: NA	Within 95% confidence interval of the certified value	Review raw data quantitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat analysis until control limits are met.
Replicates	Precision	One per batch of six samples (i.e., once in each sampling period)	RPD or RSD <20%	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, then identify and eliminate source of imprecision and reanalyze.
Laboratory control material (LCM)	Accuracy & Precision	One per batch of 20 or fewer samples	Within 20–25% consensus value	Review raw data quantitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat analysis until control limits are met.

MDL = method detection limit; RPD = relative percent difference; RSD = relative standard deviation

8. Special Training Needs/Certification

8.1 Specialized training or certifications
CCLEAN requires all program laboratories to demonstrate capability continuously through participation in an on-going series of interlaboratory comparison exercises.

Personnel in any laboratory performing CCLEAN analyses will be well versed in good laboratory practices, including standard safety procedures. It is the responsibility of the particular analytical component project officer, laboratory manager, and/or supervisor to ensure that safety training is mandatory for all laboratory personnel. Each laboratory is responsible for maintaining a current safety manual in compliance with the Occupational Safety and Health Administration (OSHA), or equivalent state or local regulations. The safety manual will be readily available to laboratory personnel. Proper procedures for safe storage, handling, and disposal of chemicals will be followed at all times; each chemical will be treated as a potential health hazard and good laboratory practices will be implemented accordingly.

8.2 Training and certification documentation
Any laboratory performing analysis of bacteria in mussels shall be certified by the State of California Department of Health Services according to the USFDA Shellfish testing program to perform Shellfish meat and Shellfish Growing Waters microbiological testing.

8.3 Training personnel
Each field sampling contractor and analytical laboratory is responsible for training its personnel per relevant standard operating procedures. Periodic audits will be conducted of field sampling activities to confirm adherence to the CCLEAN QAPP.

9. Documents And Records

Field sampling contractors will collect records for sample collection, and will be responsible for developing sampling plans and sampling reports and delivering them to the Program Director. Samples sent to analytical laboratories will include Chain of Custody (COC) forms. Analytical laboratories will collect records for sample receipt and storage, analyses, and reporting.

All records, except lab records, generated by this project will be stored at the responsible contractor's office. All electronic data are backed up weekly on an external hard-drive that is used exclusively for back-up purposes in the Program Director's office in Santa Cruz, CA, in addition to being automatically backed up on the Applied Marine Sciences server in Livermore, CA whenever the Program Director visits that location. All CCLEAN laboratory records pertinent to this project will be maintained the Program Director's office in Santa Cruz, CA.

All analytical records are submitted by Kinnetic Laboratories and NewFields Northwest electronically in Excel® spreadsheets in a format that is specified to make it easier to perform quality assurance checks and submit data to SWAMP via Region 3's online web-checking tool.

Copies of this QAPP will be distributed to all parties on the distribution list. Any future amended QAPPs will be held and distributed in the same fashion. All originals of this and subsequent amended QAPPs will be held at the Program Director's office. Copies of versions, other than the most current, will be discarded so as not to create confusion. Current versions of the CCLEAN QAPP are posted on the organization's website to provide access to stakeholders at all times.

Persons responsible for maintaining records for this project are shown in Table 8.

Table 8. Responsibilities for Record Collection and Maintenance.

Name	Organizational Affiliation	Records
Dane Hardin	CCLEAN Program Director	Lab reports, sampling plans, sampling reports
Jon Toal	Kinnetic Laboratories	Lab reports for effluent, nearshore, and mussel sampling
Greg Cotten	Kinnetic Laboratories	Field datasheets, COCs
Susie Watts	NewFields Northwest	Field datasheets, COCs, lab reports for sediment sampling
Candice Navaroli	Axys	Lab records for effluent, nearshore, mussel and sediment POPs
Jim Oakden	ABA	Field datasheets, lab records for benthic sampling
Barbara Byrne	UC Davis	Lab records for pathogens analysis

The Project Director will oversee the actions of these persons and will arbitrate any issues relative to records retention and any decisions to discard records. Copies of all records will be maintained by the applicable field-sampling contractor or analytical laboratory for at least five years after project completion.

GROUP B: DATA GENERATION AND ACQUISITION

10. SAMPLING PROCESS DESIGN

CCLEAN measures inputs to the ocean of the identified possible water quality stressors (i.e., POPs, suspended sediments, nutrients and pathogens in water) and effects in nearshore waters by sampling wastewater effluent, mussels, sediments and benthic communities, and nearshore waters using a judgmental design. Effluent for each of the four municipal dischargers will be sampled twice per year for POPs using automated equipment to obtain 30-day flow-proportioned samples in the wet and dry seasons. During 2009-2010, effluent grab samples also will be collected in the wet and dry seasons for PFCs. Effluent will be screened in the dry season and in the wet season for disruption of reproductive endocrine processes with a fathead minnow assay using daily replacements of 24-hour composite effluent samples. Nutrients in effluent will be sampled monthly using grab samples. Mussels will be sampled annually in the wet season at five locations to fill geographic gaps in other programs to measure POPs and bacteria. Sediment and benthic organisms will be sampled annually for POPs at six sites within the depositional band that has been identified by U.S. Geological Survey in Monterey Bay and near presumed contaminant sources. Nearshore background water will be sampled twice per year at two sites for concentrations of POPs, nutrients, and bacteria. See Figure 2 for locations of sampling sites.

The types, numbers and approximate timing of samples to be collected each year are as follows:

Effluent
250-liter samples collected twice per year for the analysis of POPs, during 30-day periods in the wet season and in the dry season; 4 sites x 2 times per year = 8 samples per year
Monthly samples collected for nutrients; 4 sites x 12 samples = 48 samples per year

Ocean Water
250-liter samples collected twice per year for the analysis of POPs, during 30-day periods in the wet season and in the dry season; 2 sites x 2 times per year = 4 samples per year
Paired grabs for nutrients and bacteria collected from each site at the beginning and end of the buoy deployment period; 2 sites x 8 samples = 16 samples per year

Mussels – 5 sites
Annual collection of single replicates from each site consisting of composites of 30–40 individuals for analysis of POPs and bacteria; 5 sites x 1 sample = 5 samples per year

Sediment – 6 sites
Collection of single replicates every five years from each site for analysis of POPs, sediment quality and benthic infauna; 6 sites x 1 sample = 6 samples every five years

Because CCLEAN has been sampling since 2001, access to all sites is well established, although ocean conditions sometimes limit access. In this case, sampling is rescheduled to a time when conditions are more acceptable.

The approximate schedules for sampling each program element are as follows:

Program Element	Season	Approximate Dates
Effluent	Wet Season	February - March
	Dry Season	June - November
	Monthly	July - June
Ocean Water	Wet Season	February - March
	Dry Season	June - November
Mussels	Wet Season	February - March
Sediment	Every Five Years	September - October

Samples for POP analysis will be shipped to the laboratory for analysis as soon after they are collected from the field as possible, although mussel tissues will be removed from the shells and homogenized before being shipped. Samples for bacteria and nutrient analyses will be delivered to the laboratory for analysis as soon as possible after being collected.

All the data collected by CCLEAN are used to achieve its objectives and there are no data that are collected for informational purposes only.

Potential sources of bias include sampling and analytical methods. In the case of sampling, bias is controlled by using prescribed methods to provide repeatable results. For example, if samples are collected in a systematic way that targets specific types of organisms (e.g., mussels of a certain size), and there is inconsistency in the types of organisms collected in each sampling effort, bias is introduced, insofar as analytical measurements might vary according to organism type. This type of bias also could occur if different sieve mesh sizes were used each time for removing benthic infauna from sediment. These potential sources of bias are controlled by always collecting mussels of approximately the same size from all locations and by using a standardized sieve mesh size for processing all benthic samples. Sampling bias can also be introduced by using sampling methods that do not effectively collect certain types of analytes. For example, the *in situ* solid-phase extraction method used by CCLEAN for sampling POPs does not adequately sample highly polar compounds. This type of bias is controlled by only analyzing non-polar compounds.

Analytical bias is introduced if measurement methods are either more or less accurate under different ambient conditions or if they inherently misrepresent the actual concentration of an analyte. Applying Quality Control limits to measurements of reference performance spikes and laboratory spikes helps control the former type of analytical bias in water samples for analysis of POPs. Control of this type of bias in other samples is done primarily through examination throughout the analytical process for interferences due to matrix effects. Bias due to inherent misrepresentation of analyte concentrations is controlled by requiring analysis of certified reference materials, laboratory reference materials or standards.

Sources of natural variability and how this variability is reconciled with program information is discussed in Section 24.

11. SAMPLING METHODS

The CCLEAN program comprises multiple sampling components as outlined previously. A brief summary of each is provided below. A Sampling Plan for each field sampling effort is submitted to the Program Director two weeks prior to sampling that provides information on sampling dates, procedures and personnel. Any problems that occur during sampling are reported immediately to the Program Director by the respective Field Program Manager and corrective actions are taken, when possible. A Sampling Report is submitted within two weeks following the completion of sampling that provides information on actual sampling dates, duration of sampling efforts, unusual conditions or problems encountered and corrective actions taken.

11. 1 Wastewater Effluent Sampling

Effluent sampling includes collection of 30-day flow-proportioned samples twice per year (i.e., in the wet season and in the dry season) for analysis of POPs, as well as collection of composite samples during each sampling period for the analysis of PFCs, which will occur during the 2008-2009 and 2009-2010 program years. Annual loads of POPs are estimated by calculating the average daily load during each sampling period (average flow multiplied by concentration) and multiplying the average load from both sampling periods by 365. The objective of this sampling component is to estimate the loads to Monterey Bay of POPs from effluent.

Several methods are available for sampling POPs in effluent. The selected method employs an *in situ* solid-phase extraction process that captures contaminants in both the particulate and dissolved phases. This method is discussed in greater detail in Section 11.1.1. Other methods, such as *in situ* use of semi-permeable membrane devices (SPMD) and polar organic chemical integrative samplers (POCIS) are currently being used by some CCLEAN participants to sample their effluent to provide data for a wide range of California Ocean Plan Table B compounds and contaminants of emerging concern, such as personal care products and pharmaceuticals. The constituents measured in effluent by CCLEAN are shown in Table 17. All of these POPs are in the California Ocean Plan Table B, except the PAHs biphenyl, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 2,6-dimehtylnaphthalene, 2,3,5-trimethylnaphthalene, acenaphthene, dibenzothiophene, 1-methylphenanthrene, fluoranthene, benzo(e)pyrene and perylene, and PFCs and PBDEs. Table B constituents not measured in effluent by CCLEAN are shown in Table 9.

11.1.1 Solid-Phase Extraction Sampling

The collection of 30-day flow-proportioned samples of effluent is accomplished by Kinnetic Laboratories using specialized equipment (Figure 3). Off-the-shelf equipment was obtained from suppliers and configured for each sampling location. Programmable ISCO 3700 samplers are used to pump water through glass-fiber particle filters and Teflon™ columns packed with XAD-2 resin beads, which were obtained from Axys Environmental. Handling of the particle filters and XAD-2 columns is performed according to the Axys Infiltrex 300 User's Manual in Appendix B. All sampler tubing is composed of Teflon™, silicone (pump tubing) and stainless steel, which undergoes a thorough cleaning process prior to use. The samplers are programmed to pump 1 liter of effluent through the filter and column in response to electrical signals from the flow meter in each treatment plant. The ISCO pumping rate is controlled so it falls within the optimum range (i.e., 1.25–1.8 L/minute) for efficient capture of POPs by the resin beads. The estimated flow at each site is projected to ensure that the target volume of effluent will be pumped through the filter and column over an approximately 30-day period. Two hundred liters is the target volume to ensure the lowest possible detection limits for POPs. Dry-season effluent samples are collected with the ISCO equipment during the months of June–August and wet-season effluent samples are collected during the months of January–March. An equipment blank sample is collected for each sampling period by pumping ultra-pure water through the equipment.

The SOPs that apply to this sampling task are as follows:

- KLI –WQ-1993001-02 (17 Aug. 2007) for Nitric Acid Neutralization Procedure,
- KLI –WQ-1990004-04 (17 Aug. 2007) for Cleaning Procedures for Miscellaneous Items Related to NPS Sampling,
- KLI –CCL-2006002-02 (28 Oct. 2008) for CCLEAN Solid-Phase Extraction Column and Glass Fiber Filter Handling Procedures and
- KLI –CCL-2006001-02 (28 Oct. 2008) for CCLEAN Teflon7 Sample Tubing, Silicon Peristaltic Tubing, Silicon Tubing, Teflon7 Check Valve, Stainless Steel Glass Fiber Filter Canister, and Nearshore Micropump Cleaning Procedures.

These SOPs from Kinnetic Laboratories, Inc. are proprietary and are available for examination at the Program Director's office in Santa Cruz, CA or the Regional Board office in San Luis Obispo, CA.

11.1.2 Grabs by Plant Personnel

Effluent grab samples are collected by personnel of the program participants and analyzed in their laboratories. The grabs by plant personnel are collected monthly for analysis of urea, dissolved silica orthophosphate, ammonia, nitrate, total suspended solids, temperature, conductivity, and pH. All grabs are taken from the effluent stream at the point where samples are collected for the regular effluent monitoring required under each NPDES permit. Annual loads of these constituents are estimated by calculating the load on each sampling date (flow multiplied by concentration) and multiplying the average load among all samples by 365. The objective of this sampling component is to estimate the loads to Monterey Bay of nutrients from effluent. SOPs for collection of grab samples are based on EPA-approved methods and are on file at each wastewater treatment plant.

Table 9. California Ocean Plan Table B constituents not measured in effluent by CCLEAN.

For the Protection of Marine Aquatic Life
Arsenic
Cadmium
Chromium (Hexavalent)
Copper
Lead
Mercury
Nickel
Selenium
Silver
Zinc
Cyanide
Total Chlorine Residual
Ammonia (expressed as nitrogen)
Chronic Toxicity
Phenolic Compounds (non-chlorinated)
Chlorinated Phenolics
Radioactivity
For the Protection of Human Health - Noncarcinogens
acrolein
antimony
bis(2-chloroethoxy) methane
bis(2-chloroisopropyl) ether
chlorobenzene
chromium (III)
di-n-butyl phthalate
dichlorobenzenes
1,1-dichloroethylene
diethyl phthalate
dimethyl phthalate
4,6-dinitro-2-methylphenol
2,4-dinitrophenol
ethylbenzene
hexachlorocyclopentadiene

isophorone
nitrobenzene
thallium
toluene
1,1,2,2-tetrachloroethane
tributyltin
1,1,1-trichloroethane
1,1,2-trichloroethane

For Protection of Human Health - Carcinogens
acrylonitrile
benzene
benzidine
beryllium
bis(2-chloroethyl) ether
bis(2-ethylhexyl) phthalate
carbon tetrachloride
chloroform
1,4-dichlorobenzene
3,3í-dichlorobenzidine
1,2-dichloroethane
dichloromethane
1,3-dichloropropene
2,4-dinitrotoluene
1,2-diphenylhydrazine
halomethanes
hexachloroethane
N-nitrosodimethylamine
N-nitrosodiphenylamine
tetrachloroethylene
toxaphene
trichloroethylene
2,4,6-trichlorophenol
vinyl chloride

11.2 Receiving Water Sampling

Receiving water sampling consists of monthly or more frequent sampling for pathogen indicators at stations along the 30-foot contour near the wastewater discharges of Santa Cruz, Watsonville, and Monterey Regional. Measurements are made for total coliform, fecal coliform, and *Enterococcus* bacteria. Samples are collected by boat from the top foot of the water column and placed into pre-sterilized Whirlpak® containers or plastic jars. Carmel is required to sample beach sites if their effluent concentration of total coliform exceeds 2,400 Most Probable Number (MPN)/100L three or more times in a 30-day period. Collections are made by treatment plant personnel from Santa Cruz, Watsonville, Monterey Regional, Carmel or their consultants, according to the requirements of their respective NPDES permit monitoring and reporting programs and analyzed in the respective treatment plant laboratories. Locations of receiving water monitoring sites for each agency are described in Table 10. SOPs for collection of receiving water samples are based on EPA-approved methods and are on file at each wastewater treatment plant.

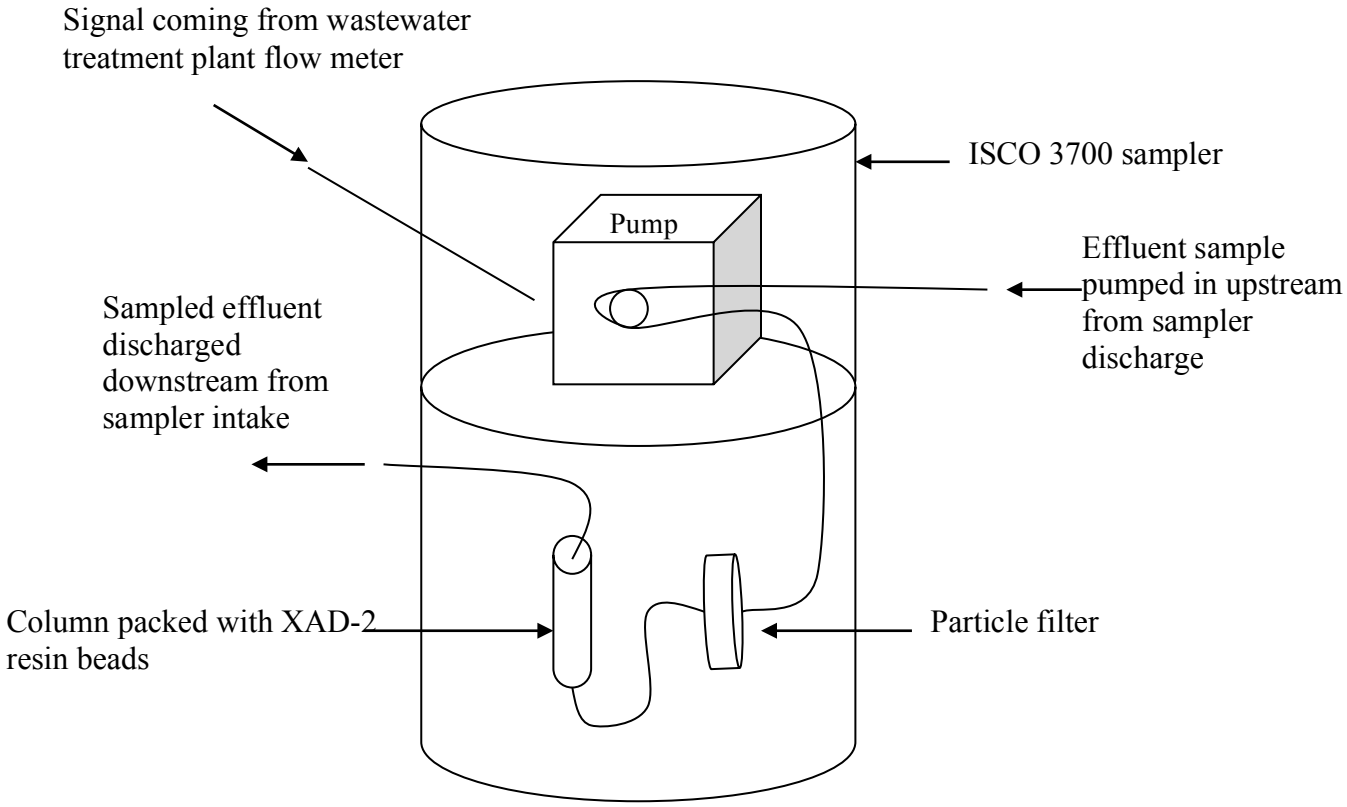

Figure 3. Configuration of ISCO samplers for CCLEAN effluent sampling.

Table 10. Locations of receiving water-monitoring sites for each CCLEAN discharger.

Agency	Site	Location
Santa Cruz	RW(A)	Point Santa Cruz
	RW(C)	Old outfall
	RW(E)	610 m upcoast of old outfall
	RW(F)	Natural Bridges
	RW(G)	Terrace Point
	RW(H)	1180 m upcoast of Terrace Point
	RW(I)	2080 m upcoast of Terrace Point
Watsonville	A	2000 m north of outfall
	B	1500 m north of outfall
	C	300 m north of outfall
	D	Adjacent to outfall
	E	300 m south of outfall
	F	1500 m south of outfall
	G	2000 m south of outfall
	ZID	Edge of zone of initial dilution
Monterey Regional	A	900 ft north of outfall
	B	Adjacent to outfall
	C	900 ft south of outfall
	D	1800 ft north of outfall
Carmel Area	K-4	Mission Point
	K-5	North Shore Carmel River Mouth
	K-6	Point at North end of Monastery Beach

11.3 Mussel Sampling

Mussel sampling consists of collecting mussels from five sites (Table 11) once a year, during the wet season, for analysis of POPs and bacteria. The objective of this program element is to determine the extent to which humans and sea otters might be exposed to POPs and pathogens from consumed components of the food web. Mussel sampling is being performed by KLI, with POP analyses analyzed by Axys and bacteria analyzed by UC Davis. Seventy mussels, 40-60 mm in shell length, are collected at each site. A sixth sample is collected at one of the five sites. This will be submitted to the laboratories as a blind field duplicate for QA/QC purposes. Mussel collection and processing will be consistent with the California Department of Fish and Game's most recent Standard Operating Procedures[1]. Collection and processing of mussels for this task is performed according to SOP KLI –CCL-2006003-01. This proprietary SOP is available for examination at the Program Director's office in Santa Cruz, CA or the Regional Board office in San Luis Obispo, CA. Samples and equipment are handled with polyethylene-gloved hands only. In addition, gloves will be changed between the handling of different samples. Mussels will be collected from the rocks by gloved hands.

Mussels collected from each site will be stored in two separate pre-cleaned heavy-duty aluminum foil bags. The heavy-duty aluminum foil is cleaned with Micro detergent, rinsed with tap water (to ensure removal of the detergent), rinsed with deionized water, and then rinsed with either methanol or petroleum ether. Mussels will only contact the dull side of the foil bags. Forty mussels will be placed in one bag for the chemical analysis of POPs. Thirty mussels will be placed in the second bag for the microbiological samples to be analyzed for pathogen indicator organisms by UC Davis. Both will be labeled with a water-proof marking pen. Each foil bag will then be double-bagged in two Ziploc bags. Both samples will be placed in an ice chest with double-bagged blue ice packets and maintained at 2-4°C for transfer to the laboratories. The sample for microbiological analysis will be immediately transferred to UC Davis for initiation of the testing prior to expiration of the 24-hour holding time. In order to prevent the mussels collected for chemical analysis of POPs from gaping, resections will be conducted

immediately or the next day in order to avoid the need to initially freeze the samples.

Resections will be performed at Kinnetic Laboratories in cleaned glove boxes. Equipment used to remove the tissues will be washed in a hot Micro detergent solution, rinsed thoroughly with tap water (to ensure removal of the detergent) and then rinsed with deionized water. This will be followed by a methanol rinse and a petroleum ether rinse. Mussels will be individually removed from the bag and cleaned of epiphytic organisms under running deionized water. Mussels will be allowed to thaw, if frozen, on a precleaned sheet of heavy-duty aluminum foil. Resection will be performed on pre-cleaned Teflon™ cutting boards. A pre-cleaned stainless steel scalpel will then be used to sever the adductor mussel and remove the byssal threads. The remaining tissue, including the gonads will then be placed in certified clean glass jars and frozen at or below -20°C until ready for homogenization, extraction and analysis. Samples will be homogenized using a Brinkman™ homogenizer (PT 10 35) with a titanium generator (PT20 STI). The Brinkman™ homogenizer is designed to prevent contamination during homogenization by ensuring that sample material only contacts titanium or Teflon™ parts. The generator is cleaned at the onset of homogenization and between stations. The generator is cleaned with a hot Micro™ detergent solution, rinsed two times with tap water, rinsed three times with deionized water, and once with MilliQ water. Water used for cleaning is changed between samples. The homogenizer is operated at the lowest speed possible to avoid heating the sample or spattering. The tissue is homogenized to a paste-like consistency with no chunks of clearly defined tissue left in the homogenate. Samples are delivered to UC Davis for testing by experienced laboratory staff in accordance with the American Public Health Association (1970) procedures. Sterile, protective gloves are worn during the processing. Extraneous material will be removed from the shell with a sterile brush and sterile water. Byssal fibers are removed at this time. Before removing the tissue, the analyst dons new sterile gloves that are rinsed in alcohol or iodophor solution and sterile water. A sterile knife is used to enter the mussel at the byssal opening, sever the adductor muscle and letting the liquor drain into the sterile test container. Tissue is then removed and added to the test container.

1 Sampling and Processing Trace Metal and Synthetic Organic Samples of Marine Mussels, Freshwater Clams, Marine Crabs, Marine and Freshwater Fish and Sediments (DFG SOP 102), July 21, 2001

Table 11. Site names and coordinates for CCLEAN mussel sampling locations.

Site Name	Latitude	Longitude
Scott Creek	37.042°	-122.234°
Laguna Creek	36.984°	-122.159°
The Hook	36.959°	-121.965°
Fanshell Overlook	36.584°	-121.972°
Carmel River Beach	36.539°	-121.932°

11.4 Sediment Sampling

The objectives of this program component are to measure concentrations of POPs in sediments where the sediments are most likely to be deposited after washing off the land and out of rivers, and the effects of POPs on benthic infauna. Site coordinates and depths are shown Table 12. Sediment sampling is conducted by NewFields, with support from other consultants. Benthic infauna are analyzed by ABA Consultants, POPs are analyzed by Axys and total organic carbon (TOC) and grain size are analyzed by NewFields.

Table 12. Names and locations of CCLEAN sediment sampling sites.

Site Name	Depth, m	Latitude	Longitude
SedRef 02	80	36° 56.615’	-122° 12.610’
SedRef 03	80	36° 55.490’	-122° 10.640’
SedRef 04	80	36° 54.745’	-122° 09.370’
SedDep 01	80	36° 51.800’	-122° 02.366’
SedDep 02	80	36° 50.245’	-121° 55.910’
SedDep 03	80	36° 45.670’	-121° 52.290’

Sediment samples are collected every five years from six sites along the 80-m contour in Monterey Bay. The 80-m contour is where the U.S. Geological Survey (USGS) has identified the thickest layer of Holocene sediments around Monterey Bay, which represents the area where sediments washing off the land and out of the rivers have been deposited (Eittreim et al. 2002). Sampling sites were located in this area because it is where contaminants adsorbed to sediment particles are most likely to be deposited and where possible contaminant effects on benthic infauna most likely would be observed.

Sediment samples are collected with a 0.1 m^2 Smith-McIntyre grab sampler or a modified 0.1 m^2 van Veen grab sampler. Two samples are taken at each station. One sample is collected for benthic infauna while the second provides the sediment for chemistry and physical grain size analyses. These samples are not composited but retained separately.

There are several quality control procedures employed in the field. Prior to each sampling event the grab is scrubbed and rinsed with seawater, air-dried and again rinsed with site seawater. The grab sampler is opened and loaded prior to moving over the water, and then the device is lowered slowly through the water column in order for it to impact the sediment surface without a bow wave. Samples will be accepted based on a minimum penetration depth of 10 cm for the biological samples and at least 7 cm for the chemistry. There should be little to no visible leakage upon recovery to the vessel, no over- penetration, and little to no visible signs of surface disturbance when the doors are opened to view the surface of the grab.

The benthic grab sample used for biological analyses will be sieved through a 0.5 mm screen in the field, retained in glass containers with sea water and $MgCl_2$ to relax the organisms and then preserved in seawater formalin mixtures of approximately 10%. These samples will be retained in the formalin solution for at least 48 hrs prior to transfer to 70% ethyl alcohol. The fixed and preserved samples will then be archived in the benthic lab at the Moss Landing Marine Laboratory until sorted.

The same acceptability criteria apply to the sample used for chemistry evaluation. The sampler is placed on a support table on deck where the overlying water can be removed. The upper 2 cm of the sediment surface will then be removed using stainless steel implements and then stored in either amber glass containers or Ziploc plastic bags. Glass containers will be <~70% of capacity in order to minimize potential for breaking during the storage process. Once filled, the samples will be labeled, packaged in bubble wrap, stored in plastic coolers containing blue ice, sealed with chain-of-custody information contained in the container and sent by FedEx to Axys Laboratories for analysis of persistent organic pollutants. Sediment also are be placed in two Ziploc plastic bags for determination of grain size and total organic carbon. One of these samples remains with ABA as a QC check while the other is sent in coolers with blue ice and chain-of-custody information to NewFields Northwest in Port Gamble, Washington.

11.5 Nearshore Background Water Sampling

The objective of this program component is to determine the status and trends of contaminants in background waters of Monterey Bay and whether ocean waters comply with the California Ocean Plan.

Buoys are deployed twice per year for 30-day periods at a site in northern Monterey Bay and at a site in southern

Monterey Bay (Table 13). The buoys contain sampling equipment that collects time-integrated samples of POPs using the same particle filters and columns packed with XAD-2 resin as used in the wastewater sampling. Duplicate grabs are collected from each site at buoy deployment and buoy retrieval for analysis of total coliform, fecal coliform, enterococcus, NO_3-N, NH_3-N, urea-N, and O-PO_4, SiO_2 and TSS.

The SOPs that apply to this sampling task are as follows:

- KLI –WQ-1993001-02 (17 Aug. 2007) for Nitric Acid Neutralization Procedure,
- KLI –WQ-1990004-04 (17 Aug. 2007) for Cleaning Procedures for Miscellaneous Items Related to NPS Sampling,
- KLI –CCL-2006002-02 (28 Oct. 2008) for CCLEAN Solid-Phase Extraction Column and Glass Fiber Filter Handling Procedures and
- KLI –CCL-2006001-02 (28 Oct. 2008) for CCLEAN Teflon7 Sample Tubing, Silicon Peristaltic Tubing, Silicon Tubing, Teflon7 Check Valve, Stainless Steel Glass Fiber Filter Canister, and Nearshore Micropump Cleaning Procedures.

These SOPs from Kinnnetic laboratories, Inc. are proprietary and are available for examination at the Program Director's office in Santa Cruz, CA or the Regional Board office in San Luis Obispo, CA. Collection of bacteria, nutrient and TSS samples are according to EPA-approved protocols.

Table 13. Locations of sites for sampling nearshore background water in Monterey Bay.

Site	Latitude	Longitude
North Monterey Bay	36.890	121.924
South Monterey Bay	36.711	121.911

12. Sample Handling and Custody

In the field, all samples will be packed in wet ice or frozen ice packs (blue ice) during shipment, so that they will be kept at approximately 4°C. Samples will be shipped in insulated containers. All caps and lids will be checked for tightness prior to shipping. All samples will be handled, prepared, transported and stored in a manner so as to minimize bulk loss, analyte loss, contamination, or biological degradation. Sample containers will be clearly labeled with an indelible marker. Where appropriate, samples may be frozen to prevent biological degradation. Water samples will be kept in Teflon™ , glass, or polyethylene bottles and kept cool at a temperature of 4°C until analyzed. Maximum holding times for specific analyses are listed in Tables 14, 15 and 16 on the following pages. Ice chests are sealed with tape before shipping. Samples are placed in the ice chest with enough ice and appropriate packing material to completely fill the ice chest.

Because of the importance of program samples and analytical data, sample Chain-of-Custody (COC) must be controlled and documented in the laboratory. Sample custody and document control procedures function to identify and document tracking and handling of samples and documents. Chain-of-custody (COC) procedures require that possession of samples be traceable from the time the samples are collected until completion and submittal of analytical results. Each sampling contractor provides its own COC. A complete COC form is to accompany the transfer of samples to the analyzing laboratory. COC forms are placed in an envelope and taped to the top of the ice chest or they may be placed in a plastic bag and taped to the inside of the ice chest lid. It is assumed that samples in tape-sealed ice chests are secure whether being transported by staff vehicle, by common carrier, or by commercial package delivery. The receiving laboratory has a sample custodian who examines the samples for correct documentation, proper preservation and holding times during the sample login process. Contract laboratories will follow sample custody procedures outlined in their QA plans. At a minimum, the login documentation will indicate the sample identification, including dates collected and received, identity of the sampler, the analyses requested, as well as the use of proper containers and preservatives. Any deviations from required sampling techniques (e.g. wrong container type, not enough sample) are noted on the sample log form. Contract laboratory QA plans are on file with the respective laboratory. All samples remaining after successful completion of analyses will be held by the analytical laboratory until authorized by the Program Director to dispose of them properly. It is the responsibility of the personnel of each analytical laboratory to ensure that all applicable regulations are followed in the disposal of samples or related chemicals.

Table 14. Sample handling and custody for CCLEAN aqueous samples.

Parameter	Container	Volume	Initial Preservation	Holding Time
Total coliform, *E. coli*, *Enterococcus*,	2 Whirl-Pak bags per site	125 ml	Sodium thiosulfate	Bacteria 8 hrs
Nitrate, orthophosphate	Nalgene high-density polyethylene	60 ml	Vacuum-filtered (0.45 mm), cool to 4°C	48 hrs at 4°C in the dark
Urea	Sterile polypropylene centrifuge tube	50 ml	Cool to 4°C	30 days frozen
Ammonia	I-Chem high-density polypropylene	125 ml	Sulfuric acid	28 days at 4°C
Total suspended solids, dissolved silica	Nalgene high-density polypropylene	250 m	None	7 days at 4°C
Conductivity, pH	Nalgene high-density polyethylene	125 ml	Cool to 4°C	8 hrs

Parameter	Container	Volume	Initial Preservation	Holding Time
PAHs, PCBs, PBDEs, Dioxins, Furans, Pesticides	Axys Teflon column packed with XAD-2 resin beads and Axys glass-fiber particle filter	≈250 liters	Cool to 4°C with blue ice	Keep at 4°C, dark, no limits on holding time prior to extraction (ADDITIONAL JUSTIFICATION NEEDED)

Table 15. Sample handling and custody for CCLEAN sediment samples.

Parameter	Container	Volume	Initial Preservation	Holding Time
Conventional (Grain Size, TOC)	Plastic Ziploc bag	125 ml	Cool to 4°C, dark	Keep at 4°C up to 6 months for grain size, keep frozen up to 1 year for TOC
Benthic samples	Glass jars	Various	Relax with $MgCl_2$, fix with 10% formalin/sea water, preserve with 70% ethyl alcohol	Indefinite
PAHs, PCBs, Pesticides	Pre-cleaned, certified glass jar, with Teflon lid-liner	500 ml	Cool to 4°C, dark	Keep at 4°C, dark, up to 14 days for extraction and 40 days for analysis (1 year if frozen)

Table 16. Sample handling and custody for mussel samples.

Parameter	Container	Volume	Initial Preservation	Holding Time
Mussels, POPs	Pre-cleaned aluminum foil bags (1/site), double wrapped in Ziploc bags	40 mussels	Stored on blue ice	24 hours before resection, then frozen at -20°C
Mussels, pathogen indicators	Pre-cleaned aluminum foil bags (1/site), double wrapped in Ziploc bags	30 mussels	Stored on blue ice	24 hours

13. ANALYTICAL METHODS

CCLEAN incorporates a performance-based measurement system (PBMS) approach for measurements of contaminants at low concentrations involving continuous laboratory evaluation through the use of accuracy, and precision-based materials (e.g., CRMs; OPR), laboratory matrix spikes, laboratory reagent blanks, calibration standards, laboratory-and field-duplicated blind samples, and others as appropriate. Under the performance-based CCLEAN QA program, laboratories are not required to use a single, standard analytical method for each type of analysis. Rather, they are free to choose the best or most feasible method within the constraints of cost and equipment that is suitable for meeting CCLEAN's Data Quality Objectives (DQO). Nevertheless, validated methods are used whenever possible and each laboratory will continuously demonstrate proficiency and data comparability through routine analysis of performance evaluation samples, split samples, and reference materials representing actual sample matrices. In cases where validated methods might not be available, methods from the peer-reviewed scientific literature are favored. Recommended methods for analysis of POPs are EPA methods and those used in the NOAA NS&T Program (Lauenstein and Cantillo, 1993), but equivalent methods may be used where appropriate with approval of the Program Director. Suggested methods and target method detection limits (MDLs) for non-POP constituents in ocean water, sediment, and tissue are shown in Table 17. The target MDLs are not prescriptive because it is recognized that many factors can affect the actual MDL, such as variations in sample volume and unforeseen matrix interferences. Target MDLs for non-POP constituents in effluent are not specified because, while they vary widely among CCLEAN program participants, QC checks of effluent data indicate that these constituents are consistently measured in all effluent samples. The MDLs prescribed in this document for nitrate and orthophosphate are higher than those required by SWAMP due to the analytical capabilities of the participant laboratories. While concentrations of these nutrients in ocean samples are often below the stated MDLs, there are no ocean criteria to guide selection of MDLs and efforts to lower the achievable MDLS are not warranted. Similarly, higher MDLs in this QAPP than those required by SWAMP for Enterococcus, E. coli, fecal coliform, total coliform and sediment total organic carbon are sufficiently low to determine whether Ocean Plan objectives and NOAA sediment quality alert levels are being met and there is no compelling need to reduce the MDLs. Target MDLs and suggested methods for POPs in water, sediment and mussel tissue are shown in Table 18. Laboratory turnaround times for effluent data are specified in Section 6.3. All other data for the period July 1 to June 30 shall be delivered to the Program Director no later than the following November 1.

There are numerous SOPs that apply to analysis of samples in this program, as follows:

- MLA-007 Rev 13.05 (06 Jun. 2013) for analysis of PCBs and pesticides using low resolution mass spectroscopy,
- MLA-010 Rev 11.03 (05 Dec. 2012) for analysis of chlorinated biphenyl congeners in water, soil, sediment, biosolids, and tissue by HRGC/HRMS, according to EPA Method 1668
- MLA-013 Rev 9.02 (03 Jun. 2011) for analysis of polychlorinated dibenzodioxins and furans, polybrominaqted diphenyl ethers, PCB congeners, chlorinated pesticides and toxaphene,
- MLA-017 Rev 20.06 (13 Jul. 2012) for analysis of polychlorinated dibenzodioxins and dibenzofurans by EPA Method 1613B, EPA Method 8290/8290A,
- MLA-021 Rev. 10.08 (23 May 2013) for analysis of PAHs,
- MLA-028 Rev 06.06, (16 Apr. 2013) for analysis of organochlorine pesticides by isotope dilution high resolution gas chromatography and high resolution mass spectroscopy
- MLA-033 Rev 6, (23 Nov. 2009) for analysis of brominated diphenyl ethers by EPA Method 1614
- SLA-011 Rev 3, (17 Feb. 2006) for compositing samples,
- SLA-013 Rev 7, (13 May 2013) for homogenization of solids and tissues,
- SLA-015 Rev 7, (19 Jan. 2012) for moisture determination
- SLA-020 Rev 2, (14 Apr. 2004) for gravimetric lipid determination by weight of extract,
- SLA-037 Rev 9, (12 Mar. 2010) for cleaning of sample preparation equipment used for preparing metals and organic samples,
- SLA-043 Rev 4, (25 May 2010) for removing sample media from field sampling equipment,
- SLA-048 Rev 4, (09 Dec. 2005) for cleaning of bulk resin,
- SLA-049 Rev 6, (12 Jul. 2010) for cleaning and packing of sample columns,

These SOPs from Axys Analytical are proprietary and are available for examination at the Program Director's office in Santa Cruz, CA or the Regional Board office in San Luis Obispo, CA.

Although there are no *in situ* instruments used for ambient monitoring, measurement probes used for *in situ* measurements of wastewater effluent are calibrated according to approved EPA methods with SOPs on file at each wastewater treatment plant.

If failures of analytical DQOs occur, the first person to be notified will be the QA officer of each respective laboratory. If a resolution cannot be achieved internally, the problem will be discussed with the Program Director to arrive at an acceptable solution. If failures involve matrix interferences that could be resolved with method revisions, additional analyses may be approved by the Program Director with concurrence of the CCLEAN Steering Committee. All failures and corrective actions taken will be documented in the narrative analytical report submitted to the Program Director with each batch of data.

CCLEAN samples will be archived by the respective analytical laboratory until disposal is approved by the Program Director. Disposal of any samples will be according to applicable environmental regulations.

In addition to the chemical analytical methods described below, the program is employing a pilot fish assay to screen wastewater effluent for disruption of reproductive endocrine processes in 2009 - 2010. The test involves continuous 21-day flow-through exposures of adult fathead minnows to 24-hour composites from each wastewater treatment plant diluted to concentrations predicted at the edge of the zone of initial dilution for each diffuser. Temperature, pH, dissolved oxygen and conductivity are also regularly measured. Measured assay endpoints are survival, length and weight, development of secondary sexual characteristics, reproductive and nest-guarding behavior, fecundity, fertilization success, vitellogenin in blood of males and gonadal-somatic index. The QAPP and SOPs for these fish assays are included in Appendix B.

Table 17. Methods and Target MDLs for non-POP Constituents in Ocean Water, Sediment, and Tissue.

Analysis	Matrix	Reporting Units	Suggested Analytical Methods	MDL
AMMONIA (as N)	water (dissolved)	mg/L	EPA 350.3 EPA 350.2 SM 4500-NH_3 F	0.02
CONDUCTIVITY	water	mS/cm	SM 2510B EPA 120.1	10
NITRATE (as N)	water (dissolved)	mg/L	EPA 300.1 SM 4110 SM 4500-NO_3 D	0.1
ORTHO-PHOSPHATE (as P)	water (dissolved)	mg/L	EPA 365.1	0.02
PATHOGEN INDICATORS ***Enterococcus***	water	colonies/100 ml	SM 9230B, SM 9230C or Enterolert	10
E. coli	water	MPN/100 ml	SM 9221E, SM 9222D (25-tube dilution) or Colilert[1]	10
Fecal Coliform	water	MPN/100 ml	SM 9221E, SM 9222D (25-tube dilution) or Colilert	10
Total Coliform	water	MPN/100 ml	SM 9221B, SM 9222B (25-tube dilution) or Colilert[1]	10

Analysis	Matrix	Reporting Units	Suggested Analytical Methods	MDL
SILICA	water (dissolved)	mg/L	EPA 370.1 SM 4500-Si D	0.1
TOTAL SUSPENDED SOLIDS	water	mg/L	EPA 160.2 SM 2540D	0.5
TEMPERATURE	water	°C	EPA 0170.1	0.1
pH	water	units	EPA 150.1 SM 4500HB	0.1
UREA	water	mg/L	Mulvenna and Savidge (1992) Goeyens, et al (1998)	0.1
SEDIMENT GRAIN SIZE ANALYSIS	sediment (4 fractions)	% gravel+shell (>2mm) % sand (63μm) % silt (4-63μm) % clay (<4μm)	Puget Sound Estuary Program (1986)	1%
SEDIMENT TOTAL ORGANIC CARBON	sediment	%OC (dry weight)	EPA 9060, and (13) EPA 1986 (Kahn Method)	0.1
MOISTURE	sediment, mussel tissue	%	Lauenstein and Cantillo (1993)	0.1
LIPID	mussel tissue	%	Lauenstein and Cantillo (1993)	0.1
PATHOGEN INDICATORS **Enterococcus**	tissue (mussels)	MPN/100 g	American Public Health Association (1970)	20
Fecal Coliform	tissue (mussels)	MPN/100 g	American Public Health Association (1970)	20
Total Coliform	tissue (mussels)	MPN/100 g	American Public Health Association (1970)	20
SPECIES IDENTIFICATION	Organism (benthics)	taxon	Lab SOP	lowest possible

[1] = Colilert may not be used in marine water samples.

Table 18. Target MDLs for POPs in Water, Sediment, and Mussel Tissue.

Matrix	Parameter & Analyte	Units	Suggested Analytical Methods	Target MDL
Water	**PAHs**			
	Methylnaphthalene, 1-	ng/L	EPA 8270 & 1625 modified	0.91
	Trimethylnaphthalene, 2,3,5-	ng/L	EPA 8270 & 1625 modified	1.10
	Dimethylnaphthalene, 2,6-	ng/L	EPA 8270 & 1625 modified	1.05
	Methylnaphthalene, 2-	ng/L	EPA 8270 & 1625 modified	0.90
	Biphenyl	ng/L	EPA 8270 & 1625 modified	1.23
	Naphthalene	ng/L	EPA 8270 & 1625 modified	0.94
	Methylphenanthrene, 1-	ng/L	EPA 8270 & 1625 modified	1.34
	Acenaphthene	ng/L	EPA 8270 & 1625 modified	1.45
	Acenaphthylene	ng/L	EPA 8270 & 1625 modified	1.05
	Anthracene	ng/L	EPA 8270 & 1625 modified	0.94
	Fluorene	ng/L	EPA 8270 & 1625 modified	1.03
	Phenanthrene	ng/L	EPA 8270 & 1625 modified	0.88
	Benz(a)anthracene	ng/L	EPA 8270 & 1625 modified	1.03
	Chrysene	ng/L	EPA 8270 & 1625 modified	1.19
	Fluoranthene	ng/L	EPA 8270 & 1625 modified	0.92
	Pyrene	ng/L	EPA 8270 & 1625 modified	0.84
	Benzo(a)pyrene	ng/L	EPA 8270 & 1625 modified	1.11
	Benzo(b)fluoranthene	ng/L	EPA 8270 & 1625 modified	0.97
	Benzo(e)pyrene	ng/L	EPA 8270 & 1625 modified	1.00
	Benzo(k)fluoranthene	ng/L	EPA 8270 & 1625 modified	1.09
	Dibenz(a,h)anthracene	ng/L	EPA 8270 & 1625 modified	1.12
	Perylene	ng/L	EPA 8270 & 1625 modified	0.92
	Benzo(g,h,i)perylene	ng/L	EPA 8270 & 1625 modified	0.92
	Indeno(1,2,3-c,d)pyrene	ng/L	EPA 8270 & 1625 modified	1.00
	Dibenzothiophene	ng/L	EPA 8270 & 1625 modified	0.78
	Pesticides			
	Cyclopentadienes			
	Aldrin	ng/L	EPA 608, 8081, & 1625 modified	3.7
	Dieldrin	ng/L	EPA 608, 8081, & 1625 modified	0.20
	Endrin	ng/L	EPA 608, 8081, & 1625 modified	0.29
	Chlordanes			
	Chlordane, cis-	ng/L	EPA 608, 8081, & 1625 modified	1.5
	Nonachlor, cis-	ng/L	EPA 608, 8081, & 1625 modified	1.4
	Chlordane, trans-	ng/L	EPA 608, 8081, & 1625 modified	1.1
	Heptachlor	ng/L	EPA 608, 8081, & 1625 modified	3.3

Matrix	Parameter & Analyte	Units	Suggested Analytical Methods	Target MDL
Water	Heptachlor Epoxide	ng/L	EPA 608, 8081, & 1625 modified	0.59
	Oxychlordane	ng/L	EPA 608, 8081, & 1625 modified	1.2
	Nonachlor, trans-	ng/L	EPA 608, 8081, & 1625 modified	1.1
	DDTs			
	DDD(o,p')	ng/L	EPA 608, 8081, & 1625 modified	0.35
	DDE(o,p')	ng/L	EPA 608, 8081, & 1625 modified	0.48
	DDT(o,p')	ng/L	EPA 608, 8081, & 1625 modified	0.65
	DDD(p,p')	ng/L	EPA 608, 8081, & 1625 modified	0.56
	DDE(p,p')	ng/L	EPA 608, 8081, & 1625 modified	0.54
	DDT(p,p')	ng/L	EPA 608, 8081, & 1625 modified	0.27
	HCH			
	HCH, alpha	ng/L	EPA 608, 8081, & 1625 modified	1.4
	HCH, beta	ng/L	EPA 608, 8081, & 1625 modified	0.80
	HCH, delta	ng/L	EPA 608, 8081, & 1625 modified	0.51
	HCH, gamma	ng/L	EPA 608, 8081, & 1625 modified	0.92
	Other			
	Dacthal	ng/L	EPA 608, 8081, & 1625 modified	NA
	Endosulfan I	ng/L	EPA 608, 8081, & 1625 modified	0.15
	Endosulfan II	ng/L	EPA 608, 8081, & 1625 modified	0.29
	Endosulfan Sulfate	ng/L	EPA 608, 8081, & 1625 modified	0.15
	Oxadiazon	ng/L	EPA 608, 8081, & 1625 modified	NA
	Mirex	ng/L	EPA 608, 8081, & 1625 modified	0.66
	Hexachlorobenzene	ng/L	EPA 608, 8081, & 1625 modified	1.0
	Toxaphene	ng/L	EPA 608, 8081, & 1625 modified	NA
	Hexachlorobutadiene	ng/L	EPA 608, 8081, & 1625 modified	NA
	PCB congeners			
	CL1-PCB-1	pg/L	EPA 1668A	3.9
	CL1-PCB-2	pg/L	EPA 1668A	2.5
	CL1-PCB-3	pg/L	EPA 1668A	3.8
	CL2-PCB-4	pg/L	EPA 1668A	2.8
	CL2-PCB-5	pg/L	EPA 1668A	3.0
	CL2-PCB-6	pg/L	EPA 1668A	2.5
	CL2-PCB-7	pg/L	EPA 1668A	2.5
	CL2-PCB-8	pg/L	EPA 1668A	3.6
	CL2-PCB-9	pg/L	EPA 1668A	2.5
	CL2-PCB-10	pg/L	EPA 1668A	2.5
	CL2-PCB-11	pg/L	EPA 1668A	36.4
	CL2-PCB-12/13	pg/L	EPA 1668A	5.3

Matrix	Parameter & Analyte	Units	Suggested Analytical Methods	Target MDL
Water	CL2-PCB-14	pg/L	EPA 1668A	2.5
	CL2-PCB-15	pg/L	EPA 1668A	4.0
	CL3-PCB-16	pg/L	EPA 1668A	3.2
	CL3-PCB-17	pg/L	EPA 1668A	3.7
	CL3-PCB-30/18	pg/L	EPA 1668A	7.5
	CL3-PCB-19	pg/L	EPA 1668A	3.3
	CL3-PCB-28/20	pg/L	EPA 1668A	5.8
	CL3-PCB-21/33	pg/L	EPA 1668A	5.0
	CL3-PCB-22	pg/L	EPA 1668A	3.1
	CL3-PCB-23	pg/L	EPA 1668A	3.2
	CL3-PCB-24	pg/L	EPA 1668A	2.8
	CL3-PCB-25	pg/L	EPA 1668A	2.5
	CL3-PCB-26/29	pg/L	EPA 1668A	5.0
	CL3-PCB-27	pg/L	EPA 1668A	3.5
	CL3-PCB-31	pg/L	EPA 1668A	4.5
	CL3-PCB-32	pg/L	EPA 1668A	2.5
	CL3-PCB-34	pg/L	EPA 1668A	2.5
	CL3-PCB-35	pg/L	EPA 1668A	3.6
	CL3-PCB-36	pg/L	EPA 1668A	2.5
	CL3-PCB-37	pg/L	EPA 1668A	2.5
	CL3-PCB-38	pg/L	EPA 1668A	2.5
	CL3-PCB-39	pg/L	EPA 1668A	2.5
	CL4-PCB-41/40/71	pg/L	EPA 1668A	8.5
	CL4-PCB-42	pg/L	EPA 1668A	4.7
	CL4-PCB-43	pg/L	EPA 1668A	5.0
	CL1-PCB-1	pg/L	EPA 1668A	3.9
	CL1-PCB-2	pg/L	EPA 1668A	2.5
	CL1-PCB-3	pg/L	EPA 1668A	3.8
	CL2-PCB-4	pg/L	EPA 1668A	2.8
	CL2-PCB-5	pg/L	EPA 1668A	3.0
	CL2-PCB-6	pg/L	EPA 1668A	2.5
	CL2-PCB-7	pg/L	EPA 1668A	2.5
	CL2-PCB-8	pg/L	EPA 1668A	3.6
	CL2-PCB-9	pg/L	EPA 1668A	2.5
	CL2-PCB-10	pg/L	EPA 1668A	2.5
	CL2-PCB-11	pg/L	EPA 1668A	36.4
	CL2-PCB-12/13	pg/L	EPA 1668A	5.3
	CL2-PCB-14	pg/L	EPA 1668A	2.5

Matrix	Parameter & Analyte	Units	Suggested Analytical Methods	Target MDL
Water	CL2-PCB-15	pg/L	EPA 1668A	4.0
	CL3-PCB-16	pg/L	EPA 1668A	3.2
	CL3-PCB-17	pg/L	EPA 1668A	3.7
	CL3-PCB-30/18	pg/L	EPA 1668A	7.5
	CL3-PCB-19	pg/L	EPA 1668A	3.3
	CL3-PCB-28/20	pg/L	EPA 1668A	5.8
	CL3-PCB-21/33	pg/L	EPA 1668A	5.0
	CL3-PCB-22	pg/L	EPA 1668A	3.1
	CL3-PCB-23	pg/L	EPA 1668A	3.2
	CL3-PCB-24	pg/L	EPA 1668A	2.8
	CL3-PCB-25	pg/L	EPA 1668A	2.5
	CL3-PCB-26/29	pg/L	EPA 1668A	5.0
	CL3-PCB-27	pg/L	EPA 1668A	3.5
	CL3-PCB-31	pg/L	EPA 1668A	4.5
	CL3-PCB-32	pg/L	EPA 1668A	2.5
	CL3-PCB-34	pg/L	EPA 1668A	2.5
	CL3-PCB-35	pg/L	EPA 1668A	3.6
	CL3-PCB-36	pg/L	EPA 1668A	2.5
	CL3-PCB-37	pg/L	EPA 1668A	2.5
	CL3-PCB-38	pg/L	EPA 1668A	2.5
	CL3-PCB-39	pg/L	EPA 1668A	2.5
	CL4-PCB-41/40/71	pg/L	EPA 1668A	8.5
	CL4-PCB-42	pg/L	EPA 1668A	4.7
	CL4-PCB-43	pg/L	EPA 1668A	5.0
	CL4-PCB-44/47/65	pg/L	EPA 1668A	10.4
	CL4-PCB-45/51	pg/L	EPA 1668A	5.0
	CL4-PCB-46	pg/L	EPA 1668A	2.6
	CL4-PCB-48	pg/L	EPA 1668A	3.3
	CL4-PCB-69/49	pg/L	EPA 1668A	8.1
	CL4-PCB-50/53	pg/L	EPA 1668A	5.0
	CL4-PCB-52	pg/L	EPA 1668A	5.6
	CL4-PCB-54	pg/L	EPA 1668A	3.1
	CL4-PCB-55	pg/L	EPA 1668A	2.5
	CL4-PCB-56	pg/L	EPA 1668A	3.1
	CL4-PCB-57	pg/L	EPA 1668A	2.5
	CL4-PCB-58	pg/L	EPA 1668A	2.5
	CL4-PCB-59/62/75	pg/L	EPA 1668A	8.4
	CL4-PCB-60	pg/L	EPA 1668A	2.5

Matrix	Parameter & Analyte	Units	Suggested Analytical Methods	Target MDL
Water	CL4-PCB-61/70/74/76	pg/L	EPA 1668A	10.0
	CL4-PCB-63	pg/L	EPA 1668A	2.8
	CL4-PCB-64	pg/L	EPA 1668A	3.5
	CL4-PCB-66	pg/L	EPA 1668A	4.9
	CL4-PCB-67	pg/L	EPA 1668A	3.1
	CL4-PCB-68	pg/L	EPA 1668A	3.0
	CL4-PCB-72	pg/L	EPA 1668A	2.5
	CL4-PCB-73	pg/L	EPA 1668A	3.1
	CL4-PCB-77	pg/L	EPA 1668A	2.5
	CL4-PCB-78	pg/L	EPA 1668A	2.5
	CL4-PCB-79	pg/L	EPA 1668A	2.5
	CL4-PCB-80	pg/L	EPA 1668A	2.5
	CL4-PCB-81	pg/L	EPA 1668A	2.5
	CL5-PCB-82	pg/L	EPA 1668A	4.3
	CL5-PCB-83/99	pg/L	EPA 1668A	10.6
	CL5-PCB-84	pg/L	EPA 1668A	3.8
	CL5-PCB-117/116/85	pg/L	EPA 1668A	8.7
	PCB-108/119/86/97/125/87	pg/L	EPA 1668A	22.8
	CL5-PCB-88/91	pg/L	EPA 1668A	6.6
	CL5-PCB-89	pg/L	EPA 1668A	4.3
	CL5-PCB-113/90/101	pg/L	EPA 1668A	19.6
	CL5-PCB-92	pg/L	EPA 1668A	4.6
	L5-PCB-95/100/93/102/98	pg/L	EPA 1668A	19.2
	CL5-PCB-94	pg/L	EPA 1668A	3.7
	CL5-PCB-96	pg/L	EPA 1668A	3.6
	CL5-PCB-103	pg/L	EPA 1668A	2.7
	CL5-PCB-104	pg/L	EPA 1668A	3.2
	CL5-PCB-105	pg/L	EPA 1668A	3.4
	CL5-PCB-106	pg/L	EPA 1668A	4.1
	CL5-PCB-107/124	pg/L	EPA 1668A	5.0
	CL5-PCB-109	pg/L	EPA 1668A	2.5
	CL5-PCB-110/115	pg/L	EPA 1668A	13.2
	CL5-PCB-111	pg/L	EPA 1668A	4.4
	CL5-PCB-112	pg/L	EPA 1668A	5.1
	CL5-PCB-114	pg/L	EPA 1668A	2.5
	CL5-PCB-118	pg/L	EPA 1668A	6.0
	CL5-PCB-120	pg/L	EPA 1668A	3.1
	CL5-PCB-121	pg/L	EPA 1668A	4.7

Matrix	Parameter & Analyte	Units	Suggested Analytical Methods	Target MDL
Water	CL5-PCB-122	pg/L	EPA 1668A	2.5
	CL5-PCB-123	pg/L	EPA 1668A	2.5
	CL5-PCB-126	pg/L	EPA 1668A	2.5
	CL5-PCB-127	pg/L	EPA 1668A	2.5
	CL6-PCB-128/166	pg/L	EPA 1668A	5.0
	CL6-PCB-138/163/129/160	pg/L	EPA 1668A	16.1
	CL6-PCB-130	pg/L	EPA 1668A	2.5
	CL6-PCB-131	pg/L	EPA 1668A	2.7
	CL6-PCB-132	pg/L	EPA 1668A	3.5
	CL6-PCB-133	pg/L	EPA 1668A	3.0
	CL6-PCB-134/143	pg/L	EPA 1668A	5.0
	CL6-PCB-151/135/154	pg/L	EPA 1668A	15.8
	CL6-PCB-136	pg/L	EPA 1668A	3.3
	CL6-PCB-137	pg/L	EPA 1668A	2.9
	CL6-PCB-139/140	pg/L	EPA 1668A	5.0
	CL6-PCB-141	pg/L	EPA 1668A	5.2
	CL6-PCB-142	pg/L	EPA 1668A	2.5
	CL6-PCB-144	pg/L	EPA 1668A	3.6
	CL6-PCB-145	pg/L	EPA 1668A	3.8
	CL6-PCB-146	pg/L	EPA 1668A	3.8
	CL6-PCB-147/149	pg/L	EPA 1668A	20.8
	CL6-PCB-148	pg/L	EPA 1668A	3.2
	CL6-PCB-150	pg/L	EPA 1668A	3.2
	CL6-PCB-152	pg/L	EPA 1668A	3.5
	CL6-PCB-153/168	pg/L	EPA 1668A	19.9
	CL6-PCB-155	pg/L	EPA 1668A	3.0
	CL6-PCB-156/157	pg/L	EPA 1668A	5.0
	CL6-PCB-158	pg/L	EPA 1668A	2.5
	CL6-PCB-159	pg/L	EPA 1668A	2.5
	CL6-PCB-161	pg/L	EPA 1668A	2.5
	CL6-PCB-162	pg/L	EPA 1668A	2.9
	CL6-PCB-164	pg/L	EPA 1668A	3.4
	CL6-PCB-165	pg/L	EPA 1668A	2.5
	CL6-PCB-167	pg/L	EPA 1668A	2.7
	CL6-PCB-169	pg/L	EPA 1668A	2.9
	CL7-PCB-170	pg/L	EPA 1668A	4.7
	CL7-PCB-171/173	pg/L	EPA 1668A	6.3
	CL7-PCB-172	pg/L	EPA 1668A	3.8

Matrix	Parameter & Analyte	Units	Suggested Analytical Methods	Target MDL
Water	CL7-PCB-174	pg/L	EPA 1668A	5.7
	CL7-PCB-175	pg/L	EPA 1668A	4.1
	CL7-PCB-176	pg/L	EPA 1668A	3.6
	CL7-PCB-177	pg/L	EPA 1668A	4.7
	CL7-PCB-178	pg/L	EPA 1668A	5.0
	CL7-PCB-179	pg/L	EPA 1668A	4.8
	CL7-PCB-180/193	pg/L	EPA 1668A	12.7
	CL7-PCB-181	pg/L	EPA 1668A	4.3
	CL7-PCB-182	pg/L	EPA 1668A	4.5
	CL7-PCB-183/185	pg/L	EPA 1668A	8.4
	CL7-PCB-184	pg/L	EPA 1668A	2.8
	CL7-PCB-186	pg/L	EPA 1668A	5.3
	CL7-PCB-187	pg/L	EPA 1668A	11.7
	CL7-PCB-188	pg/L	EPA 1668A	2.5
	CL7-PCB-189	pg/L	EPA 1668A	2.5
	CL7-PCB-190	pg/L	EPA 1668A	2.5
	CL7-PCB-191	pg/L	EPA 1668A	3.4
	CL7-PCB-192	pg/L	EPA 1668A	2.5
	CL8-PCB-194	pg/L	EPA 1668A	2.5
	CL8-PCB-195	pg/L	EPA 1668A	2.7
	CL8-PCB-196	pg/L	EPA 1668A	4.0
	CL8-PCB-197/200	pg/L	EPA 1668A	7.7
	CL8-PCB-198/199	pg/L	EPA 1668A	5.1
	CL8-PCB-201	pg/L	EPA 1668A	2.8
	CL8-PCB-202	pg/L	EPA 1668A	3.5
	CL8-PCB-203	pg/L	EPA 1668A	2.5
	CL8-PCB-204	pg/L	EPA 1668A	3.1
	CL8-PCB-205	pg/L	EPA 1668A	2.5
	CL9-PCB-206	pg/L	EPA 1668A	2.5
	CL9-PCB-207	pg/L	EPA 1668A	2.5
	CL9-PCB-208	pg/L	EPA 1668A	3.3
	CL10-PCB-209	pg/L	EPA 1668A	2.6
	PBDE congeners			
	BR2-DPE-10	pg/L	EPA 1614	5.4
	BR2-DPE-7	pg/L	EPA 1614	8.8
	BR2-DPE-8/11	pg/L	EPA 1614	10.5
	BR2-DPE-12/13	pg/L	EPA 1614	17.0
	BR2-DPE-15	pg/L	EPA 1614	5.5

Matrix	Parameter & Analyte	Units	Suggested Analytical Methods	Target MDL
Water	BR3-DPE-30	pg/L	EPA 1614	9.6
	BR3-DPE-32	pg/L	EPA 1614	5.5
	BR3-DPE-17/25	pg/L	EPA 1614	12.7
	BR3-DPE-28/33	pg/L	EPA 1614	9.2
	BR3-DPE-35	pg/L	EPA 1614	9.7
	BR3-DPE-37	pg/L	EPA 1614	5.5
	BR4-DPE-75	pg/L	EPA 1614	7.8
	BR4-DPE-51	pg/L	EPA 1614	4.8
	BR4-DPE-49	pg/L	EPA 1614	7.3
	BR4-DPE-71	pg/L	EPA 1614	6.2
	BR4-DPE-47 [1]	pg/L	EPA 1614	16.5
	BR4-DPE-79	pg/L	EPA 1614	6.7
	BR4-DPE-66	pg/L	EPA 1614	4.7
	BR4-DPE-77	pg/L	EPA 1614	5.6
	BR5-DPE-100	pg/L	EPA 1614	6.6
	BR5-DPE-119/120	pg/L	EPA 1614	4.6
	BR5-DPE-99 [1]	pg/L	EPA 1614	18.6
	BR5-DPE-116	pg/L	EPA 1614	14.9
	BR5-DPE-85	pg/L	EPA 1614	6.2
	BR5-DPE-126	pg/L	EPA 1614	4.0
	BR5-DPE-105	pg/L	EPA 1614	8.2
	BR6-DPE-155	pg/L	EPA 1614	5.3
	BR6-DPE-154	pg/L	EPA 1614	8.3
	BR6-DPE-153	pg/L	EPA 1614	6.7
	BR6-DPE-140	pg/L	EPA 1614	10.0
	BR6-DPE-138/166 [1]	pg/L	EPA 1614	8.9
	BR6-DPE-128	pg/L	EPA 1614	9.8
	BR7-DPE-183	pg/L	EPA 1614	7.7
	BR7-DPE-181	pg/L	EPA 1614	8.5
	BR7-DPE-190	pg/L	EPA 1614	10.1
	BR8-DPE-203	pg/L	EPA 1614	14.9
	BR9-DPE-206	pg/L	EPA 1614	100
	BR9-DPE-207	pg/L	EPA 1614	100
	BR9-DPE-208	pg/L	EPA 1614	100
	BR10-DPE-209	pg/L	EPA 1614	569
	Dioxins and Furans[1]			
	TCDD, 2,3,7,8-	pg/L	EPA 1613b & 8290	0.60
	PeCDD, 1,2,3,7,8-	pg/L	EPA 1613b & 8290	0.98

Matrix	Parameter & Analyte	Units	Suggested Analytical Methods	Target MDL
Water	HxCDD, 1,2,3,4,7,8-	pg/L	EPA 1613b & 8290	1.78
	HxCDD, 1,2,3,6,7,8-	pg/L	EPA 1613b & 8290	1.74
	HxCDD, 1,2,3,7,8,9-	pg/L	EPA 1613b & 8290	1.20
	HpCDD, 1,2,3,4,6,7,8-	pg/L	EPA 1613b & 8290	1.55
	OCDD, 1,2,3,4,6,7,8,9-	pg/L	EPA 1613b & 8290	2.67
	TCDF, 2,3,7,8-	pg/L	EPA 1613b & 8290	0.44
	PeCDF, 1,2,3,7,8-	pg/L	EPA 1613b & 8290	0.74
	PeCDF, 2,3,4,7,8-	pg/L	EPA 1613b & 8290	0.60
	HxCDF, 1,2,3,4,7,8-	pg/L	EPA 1613b & 8290	1.12
	HxCDF, 1,2,3,6,7,8-	pg/L	EPA 1613b & 8290	0.61
	HxCDF, 1,2,3,7,8,9-	pg/L	EPA 1613b & 8290	1.02
	HxCDF, 2,3,4,6,7,8-	pg/L	EPA 1613b & 8290	2.00
	HpCDF, 1,2,3,4,6,7,8-	pg/L	EPA 1613b & 8290	2.47
	HpCDF, 1,2,3,4,7,8,9-	pg/L	EPA 1613b & 8290	1.08
	OCDF, 1,2,3,4,6,7,8,9-	pg/L	EPA 1613b & 8290	4.21
Sediment[2]	**PAHs**			
	Methylnaphthalene, 1-	µg/kg	EPA 8270 & 1625 modified	0.66
	Trimethylnaphthalene, 2,3,5-	µg/kg	EPA 8270 & 1625 modified	0.47
	Dimethylnaphthalene, 2,6-	µg/kg	EPA 8270 & 1625 modified	0.57
	Methylnaphthalene, 2-	µg/kg	EPA 8270 & 1625 modified	0.80
	Biphenyl	µg/kg	EPA 8270 & 1625 modified	0.56
	Naphthalene	µg/kg	EPA 8270 & 1625 modified	0.87
	Methylphenanthrene, 1-	µg/kg	EPA 8270 & 1625 modified	0.22
	Acenaphthene	µg/kg	EPA 8270 & 1625 modified	0.51
	Acenaphthylene	µg/kg	EPA 8270 & 1625 modified	0.40
	Anthracene	µg/kg	EPA 8270 & 1625 modified	0.36
	Fluorene	µg/kg	EPA 8270 & 1625 modified	0.34
	Phenanthrene	µg/kg	EPA 8270 & 1625 modified	0.19
	Benzo(a)anthracene	µg/kg	EPA 8270 & 1625 modified	0.22
	Chrysene	µg/kg	EPA 8270 & 1625 modified	0.17
	Fluoranthene	µg/kg	EPA 8270 & 1625 modified	0.25
	Pyrene	µg/kg	EPA 8270 & 1625 modified	0.16
	Benzo(a)pyrene	µg/kg	EPA 8270 & 1625 modified	0.18
	Benzo(b)fluoranthene	µg/kg	EPA 8270 & 1625 modified	0.27
	Benzo(e)pyrene	µg/kg	EPA 8270 & 1625 modified	0.21
	Benzo(j,k)fluoranthenes	µg/kg	EPA 8270 & 1625 modified	0.22
	Dibenz(a,h)anthracene	µg/kg	EPA 8270 & 1625 modified	0.24

Matrix	Parameter & Analyte	Units	Suggested Analytical Methods	Target MDL
Sediment[2]	Perylene	µg/kg	EPA 8270 & 1625 modified	0.17
	Benzo(g,h,i)perylene	µg/kg	EPA 8270 & 1625 modified	0.25
	Indeno(1,2,3-c,d)pyrene	µg/kg	EPA 8270 & 1625 modified	0.17
	Dibenzothiophene	µg/kg	EPA 8270 & 1625 modified	0.25
	Pesticides			
	Cyclopentadienes			
	Aldrin	µg/kg	EPA 608, 8081, & 1625 modified	0.12
	Dieldrin	µg/kg	EPA 608, 8081, & 1625 modified	0.037
	Endrin	µg/kg	EPA 608, 8081, & 1625 modified	0.031
	Chlordanes			
	Chlordane, cis-	µg/kg	EPA 608, 8081, & 1625 modified	0.033
	Nonachlor, cis-	µg/kg	EPA 608, 8081, & 1625 modified	0.068
	Chlordane, trans	µg/kg	EPA 608, 8081, & 1625 modified	0.020
	Heptachlor	µg/kg	EPA 608, 8081, & 1625 modified	0.038
	Heptachlor Epoxide	µg/kg	EPA 608, 8081, & 1625 modified	NA
	Oxychlordane	µg/kg	EPA 608, 8081, & 1625 modified	0.068
	Nonachlor, trans-	µg/kg	EPA 608, 8081, & 1625 modified	0.015
	DDTs			
	DDD(o,p')	µg/kg	EPA 608, 8081, & 1625 modified	0.014
	DDE(o,p')	µg/kg	EPA 608, 8081, & 1625 modified	0.015
	DDT(o,p')	µg/kg	EPA 608, 8081, & 1625 modified	0.021
	DDD(p,p')	µg/kg	EPA 608, 8081, & 1625 modified	0.014
	DDE(p,p')	µg/kg	EPA 608, 8081, & 1625 modified	0.019
	DDT(p,p')	µg/kg	EPA 608, 8081, & 1625 modified	0.017
	HCH			
	HCH, alpha	µg/kg	EPA 608, 8081, & 1625 modified	0.048
	HCH, beta	µg/kg	EPA 608, 8081, & 1625 modified	0.032
	HCH, delta	µg/kg	EPA 608, 8081, & 1625 modified	0.024
	HCH, gamma	µg/kg	EPA 608, 8081, & 1625 modified	0.073
	Dacthal	µg/kg	EPA 608, 8081, & 1625 modified	NA
	Other			
	Endosulfan I	µg/kg	EPA 608, 8081, & 1625 modified	0.020
	Endosulfan II	µg/kg	EPA 608, 8081, & 1625 modified	0.022
	Endosulfan Sulfate	µg/kg	EPA 608, 8081, & 1625 modified	0.027
	Mirex	µg/kg	EPA 608, 8081, & 1625 modified	0.026
	Oxadiazon	µg/kg	EPA 608, 8081, & 1625 modified	NA

Matrix	Parameter & Analyte	Units	Suggested Analytical Methods	Target MDL
Sediment[2]	Hexachlorobenzene	µg/kg	EPA 608, 8081, & 1625 modified	0.018
	Toxaphene	µg/kg	EPA 608, 8081, & 1625 modified	NA
	Hexachlorobutadiene	µg/kg	EPA 608, 8081, & 1625 modified	NA
	PCB congeners			
	PCB-8/5	µg/kg	EPA 625, 8270C modified	0.012
	PCB-18	µg/kg	EPA 625, 8270C modified	0.021
	PCB-28	µg/kg	EPA 625, 8270C modified	0.025
	PCB-31	µg/kg	EPA 625, 8270C modified	0.065
	PCB-33/20/21	µg/kg	EPA 625, 8270C modified	0.024
	PCB-44	µg/kg	EPA 625, 8270C modified	0.032
	PCB-49/43	µg/kg	EPA 625, 8270C modified	0.066
	PCB-52/73	µg/kg	EPA 625, 8270C modified	0.075
	PCB-56/60	µg/kg	EPA 625, 8270C modified	0.021
	PCB-66/80	µg/kg	EPA 625, 8270C modified	0.040
	PCB-70/76	µg/kg	EPA 625, 8270C modified	0.045
	PCB-74/61	µg/kg	EPA 625, 8270C modified	0.049
	PCB-87/115/116	µg/kg	EPA 625, 8270C modified	0.097
	PCB-95/93	µg/kg	EPA 625, 8270C modified	0.033
	PCB-97/86	µg/kg	EPA 625, 8270C modified	0.037
	PCB-99	µg/kg	EPA 625, 8270C modified	0.021
	PCB-90/101/89	µg/kg	EPA 625, 8270C modified	0.030
	PCB-105/127	µg/kg	EPA 625, 8270C modified	0.059
	PCB-110	µg/kg	EPA 625, 8270C modified	0.017
	PCB-118/106	µg/kg	EPA 625, 8270C modified	0.022
	PCB-128	µg/kg	EPA 625, 8270C modified	0.018
	PCB-132/168	µg/kg	EPA 625, 8270C modified	0.045
	PCB-138/163/164	µg/kg	EPA 625, 8270C modified	0.055
	PCB-141	µg/kg	EPA 625, 8270C modified	0.017
	PCB-149/139	µg/kg	EPA 625, 8270C modified	0.060
	PCB-151	µg/kg	EPA 625, 8270C modified	0.037
	PCB-153	µg/kg	EPA 625, 8270C modified	0.026
	PCB-156	µg/kg	EPA 625, 8270C modified	0.015
	PCB-158/160	µg/kg	EPA 625, 8270C modified	0.069
	PCB-170/190	µg/kg	EPA 625, 8270C modified	0.026
	PCB-174/181	µg/kg	EPA 625, 8270C modified	0.025
	PCB-177	µg/kg	EPA 625, 8270C modified	0.024

Matrix	Parameter & Analyte	Units	Suggested Analytical Methods	Target MDL
Sediment[2]	PCB-180	µg/kg	EPA 625, 8270C modified	0.011
	PCB-183	µg/kg	EPA 625, 8270C modified	0.022
	PCB-187/182	µg/kg	EPA 625, 8270C modified	0.031
	PCB-194	µg/kg	EPA 625, 8270C modified	0.039
	PCB-195	µg/kg	EPA 625, 8270C modified	0.021
	PCB-201	µg/kg	EPA 625, 8270C modified	0.017
	PCB-196/203	µg/kg	EPA 625, 8270C modified	0.032
	PBDE congeners			
	BR2-DPE-7	ng/kg	EPA 1614	1.3
	BR2-DPE-8/11	ng/kg	EPA 1614	1.5
	BR2-DPE-10	ng/kg	EPA 1614	0.8
	BR2-DPE-12/13	ng/kg	EPA 1614	2.6
	BR2-DPE-15	ng/kg	EPA 1614	0.5
	BR3-DPE-17/25	ng/kg	EPA 1614	1.2
	BR3-DPE-28/33	ng/kg	EPA 1614	1.4
	BR3-DPE-30	ng/kg	EPA 1614	1.8
	BR3-DPE-32	ng/kg	EPA 1614	0.8
	BR3-DPE-35	ng/kg	EPA 1614	0.6
	BR3-DPE-37	ng/kg	EPA 1614	0.6
	BR4-DPE-47	ng/kg	EPA 1614	2.8
	BR4-DPE-49	ng/kg	EPA 1614	0.8
	BR4-DPE-51	ng/kg	EPA 1614	0.8
	BR4-DPE-66	ng/kg	EPA 1614	1.0
	BR4-DPE-71	ng/kg	EPA 1614	0.8
	BR4-DPE-75	ng/kg	EPA 1614	1.7
	BR4-DPE-77	ng/kg	EPA 1614	0.8
	BR4-DPE-79	ng/kg	EPA 1614	1.3
	BR5-DPE-85	ng/kg	EPA 1614	0.5
	BR5-DPE-99	ng/kg	EPA 1614	2.6
	BR5-DPE-100	ng/kg	EPA 1614	0.9
	BR5-DPE-105	ng/kg	EPA 1614	1.3
	BR5-DPE-116	ng/kg	EPA 1614	1.4
	BR5-DPE-119/120	ng/kg	EPA 1614	1.3
	BR5-DPE-126	ng/kg	EPA 1614	0.7
	BR6-DPE-128	ng/kg	EPA 1614	1.3
	BR6-DPE-138/166	ng/kg	EPA 1614	1.6
	BR6-DPE-140	ng/kg	EPA 1614	1.0
	BR6-DPE-153	ng/kg	EPA 1614	0.6

Matrix	Parameter & Analyte	Units	Suggested Analytical Methods	Target MDL
Sediment[2]	BR6-DPE-154	ng/kg	EPA 1614	0.8
	BR6-DPE-155	ng/kg	EPA 1614	0.7
	BR7-DPE-181	ng/kg	EPA 1614	1.0
	BR7-DPE-183	ng/kg	EPA 1614	0.5
	BR7-DPE-190	ng/kg	EPA 1614	1.4
	BR8-DPE-203	ng/kg	EPA 1614	2.0
	BR9-DPE-206	ng/kg	EPA 1614	12.3
	BR9-DPE-207	ng/kg	EPA 1614	11.0
	BR9-DPE-208	ng/kg	EPA 1614	8.8
	BR10-DPE-209	ng/kg	EPA 1614	124
	Pyrethroids			
	Allethrin	µg/kg		0.74
	Bifenthrin	µg/kg		1.36
	Cyfluthrin	µg/kg		0.98
	Cypermthrin	µg/kg		0.45
	Delta/Tralomethrin	µg/kg		1.50
	Fenpropathrin	µg/kg		0.71
	Fenvalerate	µg/kg		0.60
	Flucythrinate	µg/kg		0.40
	L-Cyhalothrin	µg/kg		0.17
	Permethrin	µg/kg		0.16
	Phenothrin	µg/kg		0.37
	Piperonyl-butoxide	µg/kg		0.34
	Prallethrin	µg/kg		0.68
	Pyrethrin	µg/kg		0.34
	Resmethrin	µg/kg		0.31
	Tetramethrin	µg/kg		0.27
Mussel Tissue[2]	**Pesticides**			
	Cyclopentadienes			
	Aldrin	µg/kg	EPA 608, 8081, & 1625 modified	0.037
	Dieldrin	µg/kg	EPA 608, 8081, & 1625 modified	0.029
	Endrin	µg/kg	EPA 608, 8081, & 1625 modified	0.017
	Chlordanes			
	Chlordane, cis-	µg/kg	EPA 608, 8081, & 1625 modified	0.037
	Nonachlor, cis-	µg/kg	EPA 608, 8081, & 1625 modified	0.045
	Chlordane, trans	µg/kg	EPA 608, 8081, & 1625 modified	0.024

Matrix	Parameter & Analyte	Units	Suggested Analytical Methods	Target MDL
Mussel Tissue[2]	Heptachlor	µg/kg	EPA 608, 8081, & 1625 modified	0.019
	Heptachlor Epoxide	µg/kg	EPA 608, 8081, & 1625 modified	0.084
	Oxychlordane	µg/kg	EPA 608, 8081, & 1625 modified	0.137
	Nonachlor, trans-	µg/kg	EPA 608, 8081, & 1625 modified	0.030
	DDTs			
	DDD(o,p')	µg/kg	EPA 608, 8081, & 1625 modified	0.009
	DDE(o,p')	µg/kg	EPA 608, 8081, & 1625 modified	0.014
	DDT(o,p')	µg/kg	EPA 608, 8081, & 1625 modified	0.025
	DDD(p,p')	µg/kg	EPA 608, 8081, & 1625 modified	0.018
	DDE(p,p')	µg/kg	EPA 608, 8081, & 1625 modified	0.014
	DDT(p,p')	µg/kg	EPA 608, 8081, & 1625 modified	0.021
	HCH			
	HCH, alpha	µg/kg	EPA 608, 8081, & 1625 modified	0.030
	HCH, beta	µg/kg	EPA 608, 8081, & 1625 modified	0.029
	HCH, delta	µg/kg	EPA 608, 8081, & 1625 modified	0.077
	HCH, gamma	µg/kg	EPA 608, 8081, & 1625 modified	0.074
	Other			
	Dacthal	µg/kg	EPA 608, 8081, & 1625 modified	NA
	Endosulfan I	µg/kg	EPA 608, 8081, & 1625 modified	0.027
	Endosulfan II	µg/kg	EPA 608, 8081, & 1625 modified	0.031
	Endosulfan Sulfate	µg/kg	EPA 608, 8081, & 1625 modified	0.031
	Mirex	µg/kg	EPA 608, 8081, & 1625 modified	0.031
	Oxadiazon	µg/kg	EPA 608, 8081, & 1625 modified	NA
	Hexachlorobenzene	µg/kg	EPA 608, 8081, & 1625 modified	0.013
	Toxaphene	µg/kg	EPA 608, 8081, & 1625 modified	NA
	Hexachlorobutadiene	µg/kg	EPA 608, 8081, & 1625 modified	NA
	PCB congeners			
	PCB-8/5	µg/kg	EPA 625, 8270C modified	0.036
	PCB-18	µg/kg	EPA 625, 8270C modified	0.022
	PCB-28	µg/kg	EPA 625, 8270C modified	0.014
	PCB-31	µg/kg	EPA 625, 8270C modified	0.027
	PCB-33/20/21	µg/kg	EPA 625, 8270C modified	0.044
	PCB-44	µg/kg	EPA 625, 8270C modified	0.017
	PCB-49/43	µg/kg	EPA 625, 8270C modified	0.029
	PCB-52/73	µg/kg	EPA 625, 8270C modified	0.049
	PCB-56/60	µg/kg	EPA 625, 8270C modified	0.068

Matrix	Parameter & Analyte	Units	Suggested Analytical Methods	Target MDL
Mussel Tissue[2]	PCB-66/80	µg/kg	EPA 625, 8270C modified	0.050
	PCB-70/76	µg/kg	EPA 625, 8270C modified	0.037
	PCB-74/61	µg/kg	EPA 625, 8270C modified	0.027
	PCB-87/115/116	µg/kg	EPA 625, 8270C modified	0.113
	PCB-95/93	µg/kg	EPA 625, 8270C modified	0.042
	PCB-97/86	µg/kg	EPA 625, 8270C modified	0.036
	PCB-99	µg/kg	EPA 625, 8270C modified	0.013
	PCB-90/101/89	µg/kg	EPA 625, 8270C modified	0.040
	PCB-105/127	µg/kg	EPA 625, 8270C modified	0.025
	PCB-110	µg/kg	EPA 625, 8270C modified	0.028
	PCB-118/106	µg/kg	EPA 625, 8270C modified	0.020
	PCB-128	µg/kg	EPA 625, 8270C modified	0.025
	PCB-132/168	µg/kg	EPA 625, 8270C modified	0.039
	PCB-138/163/164	µg/kg	EPA 625, 8270C modified	0.046
	PCB-141	µg/kg	EPA 625, 8270C modified	0.018
	PCB-149/139	µg/kg	EPA 625, 8270C modified	0.039
	PCB-151	µg/kg	EPA 625, 8270C modified	0.028
	PCB-153	µg/kg	EPA 625, 8270C modified	0.015
	PCB-156	µg/kg	EPA 625, 8270C modified	0.017
	PCB-158/160	µg/kg	EPA 625, 8270C modified	0.062
	PCB-170/190	µg/kg	EPA 625, 8270C modified	0.048
	PCB-174/181	µg/kg	EPA 625, 8270C modified	0.033
	PCB-177	µg/kg	EPA 625, 8270C modified	0.018
	PCB-180	µg/kg	EPA 625, 8270C modified	0.021
	PCB-183	µg/kg	EPA 625, 8270C modified	0.018
	PCB-187/182	µg/kg	EPA 625, 8270C modified	0.053
	PCB-194	µg/kg	EPA 625, 8270C modified	0.023
	PCB-195	µg/kg	EPA 625, 8270C modified	0.025
	PCB-201	µg/kg	EPA 625, 8270C modified	0.021
	PCB-196/203	µg/kg	EPA 625, 8270C modified	0.036
	PBDE congeners			
	BR2-DPE-7	ng/kg	EPA 1614	0.61
	BR2-DPE-8/11	ng/kg	EPA 1614	0.42
	BR2-DPE-10	ng/kg	EPA 1614	2.3
	BR2-DPE-12/13	ng/kg	EPA 1614	0.81
	BR2-DPE-15	ng/kg	EPA 1614	0.70

Matrix	Parameter & Analyte	Units	Suggested Analytical Methods	Target MDL
Mussel Tissue[2]	BR3-DPE-17/25	ng/kg	EPA 1614	1.1
	BR3-DPE-28/33	ng/kg	EPA 1614	1.2
	BR3-DPE-30	ng/kg	EPA 1614	1.0
	BR3-DPE-32	ng/kg	EPA 1614	0.60
	BR3-DPE-35	ng/kg	EPA 1614	1.4
	BR3-DPE-37	ng/kg	EPA 1614	0.82
	BR4-DPE-47	ng/kg	EPA 1614	3.9
	BR4-DPE-49	ng/kg	EPA 1614	1.4
	BR4-DPE-51	ng/kg	EPA 1614	0.68
	BR4-DPE-66	ng/kg	EPA 1614	0.98
	BR4-DPE-71	ng/kg	EPA 1614	0.85
	BR4-DPE-75	ng/kg	EPA 1614	0.86
	BR4-DPE-77	ng/kg	EPA 1614	0.56
	BR4-DPE-79	ng/kg	EPA 1614	1.5
	BR5-DPE-85	ng/kg	EPA 1614	0.91
	BR5-DPE-99	ng/kg	EPA 1614	4.2
	BR5-DPE-100	ng/kg	EPA 1614	0.89
	BR5-DPE-105	ng/kg	EPA 1614	1.8
	BR5-DPE-116	ng/kg	EPA 1614	1.9
	BR5-DPE-119/120	ng/kg	EPA 1614	1.3
	BR5-DPE-126	ng/kg	EPA 1614	0.89
	BR6-DPE-128	ng/kg	EPA 1614	4.0
	BR6-DPE-138/166	ng/kg	EPA 1614	1.7
	BR6-DPE-140	ng/kg	EPA 1614	0.94
	BR6-DPE-153	ng/kg	EPA 1614	0.93
	BR6-DPE-154	ng/kg	EPA 1614	0.91
	BR6-DPE-155	ng/kg	EPA 1614	0.98
	BR7-DPE-181	ng/kg	EPA 1614	1.8
	BR7-DPE-183	ng/kg	EPA 1614	1.5
	BR7-DPE-190	ng/kg	EPA 1614	3.4
	BR8-DPE-203	ng/kg	EPA 1614	1.4
	BR9-DPE-206	ng/kg	EPA 1614	4.5
	BR9-DPE-207	ng/kg	EPA 1614	7.9
	BR9-DPE-208	ng/kg	EPA 1614	6.3
	BR10-DPE-209	ng/kg	EPA 1614	23

[1] = Analyzed in effluent only.
[2] = Sediment and mussel tissue persistent organic pollutants are reported on a dry-weight basis.
Note: Organochlorines analyzed by GC-ECD will be determined using two columns of differing polarity (e.g., DB-5 and DB-17) in order to separate co-eluting congeners and reduce the influence of interferences.

14. QUALITY CONTROL

14.1 Field Performance Measurements, General

Following is a list of definitions of field performance measurements that are frequently included in sampling protocols. Some of these measurements only need to be taken when an established procedure is changed, while others should be taken at various intervals throughout the sampling process.

Source Solution Blanks - account for any pre-existing contamination in the water or preservatives used to prepare the sample containers as well as the field or travel blanks.

Bottle Blanks - account for contamination in sampling containers, in addition to any contamination due to the source solution.

Reference Performance Spikes - spiked onto XAD-2 resin to determine retention of POPs during field sampling.

Travel Blanks - account for contaminants introduced during the transport process between the laboratory and field site, in addition to any contamination from the source solution and container.

Equipment Blank - account for contamination introduced by the field sampling equipment.

Field Duplicates - account for variability in the field and laboratory.

Field Blanks - account for all of the above sources of contamination that might be introduced to a sample as well as that which would be due to the sampling equipment and the immediate field environment. Field blanks are generated under actual field conditions and are subjected to the same aspects of sample collection, field processing, preservation, transport, and laboratory handling as the environmental samples. Field blanks for water generally consist of ultra-pure water and those for sediment analyses generally consist of ultra-pure sand. True field blanks for biological tissue samples do not exist.

14.2 Field Performance Measurements Used by CCLEAN

Routine preparation, collection, and analysis of all the blanks and duplicates mentioned above would be redundant and inefficient. Since POPs in effluent and environmental water samples are orders of magnitude lower than in sediments or tissues, extreme care must be taken in the handling and analysis of effluent or water samples. Ultra-pure solvents and materials will be used in all aspects of cleaning, storage, and analysis. The solid-phase extraction columns and pre-filters will be cleaned and the cleaning process will be verified by analytical results of final solvent rinses. Contamination of solvents and source solutions will be routinely checked, and corrective steps taken whenever contamination is indicated. Certified clean borosilicate glass containers will be used for sediment and tissue samples.

Although travel blanks are not routinely used for water, sediment, or tissue samples, they may be implemented in the future. In the meantime, the possibility of contamination during the transport between the laboratory and field site will be mitigated by the measures taken to keep the sample bottles in an enclosed clean environment.

Deuterated compounds are spiked onto the XAD-2 resin beads before deployment for sampling. These compounds are analyzed in the laboratory to determine retention of captured contaminants during field sampling. Low recoveries of these deuterated compounds could indicate losses during the sampling period.

An equipment blank for POP water samples is collected once per sampling effort from a randomly selected sampling apparatus. Two-hundred liters of Milli-Q water (or equivalent) will be pumped through the sample tubing connected to solid-phase extraction (SPE) columns and filters. The sample will be exposed to the interior of the sampler tubing and all fittings, all of which will have been rigorously cleaned with ultra-pure solvents. Sediments will be collected with grab sampler coated with a chemically-inert coating, but equipment blanks will not be taken. Since bivalves will be hand collected, equipment blanks are not relevant for tissue samples.

Field duplicates will be collected for mussel sampling. Duplicate samples will be used to evaluate sampling precision and environmental variability.

True field blanks are not routinely collected in this field and are not routinely reported in the literature. Instead, samples will be collected and handled in ways that minimize contamination. For POP sampling, containers will be routinely checked for contamination, and plastic material for storage, transport, and protection of samples will be avoided. Only ultra-pure solvents will be used in the preparation of the XAD resin and filters. The XAD resin and filters will remain enclosed and inaccessible to aerial contamination until deployed for sampling.

Collection of true sediment field blanks also has been deemed unnecessary due to use of precautions that minimize contamination of the samples. All surfaces of sediment sampling and processing instruments coming into contact with the sample will be made of inert materials, such as Teflon ® or stainless steel coated with Dykon ® (or equivalent), and will be thoroughly cleaned prior to field use. Equipment also will be cleaned with Alconox (or equivalent) detergent between stations and rinsed with hydrochloric acid, followed by methanol, to avoid any carryover contamination from one station to another. Sampling will be conducted on board ship with gloved hands and the sample will be placed into pre-cleaned certified glass jars with Teflon ® -lined lids for POP analyses.

Bivalves will be handled in the field according to established protocols of the California State Mussel Watch Program designed to minimize sample contamination. Bivalves destined for POP analysis will be wrapped in aluminum foil, placed on dry ice, and kept frozen until homogenization and analysis.

14.3 Laboratory Performance Measurements

Laboratory performance measurements are designed to determine whether data quality criteria are met, as defined below. These types of samples serve to check if errors are introduced during the analysis process and at what step(s) and at what magnitude(s).

Method Blanks (also called laboratory reagent blanks or preparation blanks). These account for contaminants present in the solvents, preservatives, and analytical solutions used during the quantification of the parameter.

Injection Internal Standards - account for error introduced by the analytical instrument.

Replicate Samples - replicates of the raw material that are extracted and analyzed to measure laboratory precision.

Laboratory Replicate Samples - replicates of extracted material that measure the measurement precision.

Matrix Spike Samples (MS) - field samples to which a known amount of contaminant is added and measured to determine potential analytical interference present in the field sample.

Matrix Spike Replicate Samples (MSR or MSD) - used to assess both measurement precision and accuracy. They are especially useful when field samples may not contain many of the target compounds because measuring non-detects in replicate does not allow the data reviewer to measure the precision or the accuracy of the data in an analytical batch.

Certified Reference Materials (CRMs) - method of determining measurement accuracy, especially if a CRM contains a certified value at concentrations similar to those expected in the samples to be analyzed.

14.4 CCLEAN Laboratory Quality Control Procedures

The performance-based protocols utilized in CCLEAN for analytical chemistry laboratories consist of several elements, as follows:

14.4.1 Precision Criteria

Precision is the reproducibility of an analytical method. Each laboratory is expected to maintain control charts for use by analysts in monitoring the overall precision of the CRM or LCM. Upper and lower control chart limits (e.g., warning limits and control limits) will be continually updated; control limits based on 99% confidence intervals around the mean are recommended. The relative standard deviation (RSD) will be calculated for each analyte of

interest in the CRM based on the last seven (7) CRM analyses. Acceptable precision targets for various analyses are listed in Element 7.

14.4.2 Laboratory Replicates for Precision

A minimum of one field sample per batch of CCLEAN samples submitted to the laboratory will be processed and analyzed in duplicate or more for precision. The relative percent difference between two replicate samples or the relative standard deviation between more than two replicate samples (RPD or RSD respectively) will be less than the DQOs listed in Element 7 for each analyte of interest. Following are the calculations:

$$RPD = \frac{ABS\ (rep\ 1 - rep\ 2) \times 100}{Average\ (rep\ 1, rep\ 2)}$$

$$RSD = \frac{STDEV\ (all\ replicate\ samples) \times 100}{Average\ (all\ replicate\ samples)}$$

ABS — absolute value
STDEV — standard deviation

If results for any analytes do not meet the DQO for the RPD or RSD, calculations and instruments will be checked. A repeat analysis may be required to confirm the results. Results that repeatedly fail to meet the objectives indicate sample inhomogeneity, unusually high concentrations of analytes or poor laboratory precision. In this case, the laboratory is obligated to halt the analysis of samples and eliminate the source of the imprecision before proceeding.

14.4.3 Accuracy Criteria

The "absolute" accuracy of an analytical method can be assessed using CRMs only when certified values are provided for the analytes of interest. Nevertheless, the concentrations of many analytes of interest to CCLEAN may be provided only as non-certified values in some of the more commonly used CRMs. Therefore, control limit criteria are based on "relative accuracy", which is evaluated for each analysis of the CRM or LCM by comparison of a given laboratory's values to the "true" or "accepted" values. In the case of CRMs, this includes only certified values. The "true" values are defined as the 95% confidence intervals of the mean.

Based on typical results attained by experienced analysts in the past, accuracy control limits have been established both for individual compounds and combined groups of compounds (Element 7). There are three combined groups of compounds for the purpose of evaluating relative accuracy for organic analyses: PAHs, PCBs, and pesticides. For each group of analytes, 70% of the individual analytes must be within 35% of the certified 95% confidence interval. No individual analyte value shall exceed ±30% of the 95% confidence interval more than once in consecutive analyses without appropriate documentation and consultation with CCLEAN staff. Due to the inherent variability in analyses near the method detection limit, control limit criteria for relative accuracy only apply to analytes with true values that are >3 times the method detection limit (MDL) established by the laboratory.

14.4.4 Continuing Calibration Checks

Calibration-check solutions traceable to a recognized organization must be inserted as part of the sample stream. The source of the calibration check solution shall be independent from the standards used for the calibration. Calibration check solutions used for the continuing calibration checks will contain all the analytes of interest. The frequency of these checks is dependent on the type of instrumentation used and, therefore, requires considerable professional judgment. All organic analyses shall be bracketed by an acceptable calibration check. A calibration check standard shall be run every 12 hours at a minimum.

If the control limits for analysis of the calibration check solution (set by the laboratories) are not met, the initial calibration must be repeated. The calibration check for 90% of the analytes shall not deviate more than ±25% from the known value for PAHs and ±20% for PCBs and pesticides. If possible, the samples analyzed before the calibration check solution that failed the DQOs will be reanalyzed following recalibration. The laboratory will begin by reanalyzing the last sample analyzed before the calibration check solution that failed. If the RPD between the results of this reanalysis and the original analysis exceeds precision DQOs (Element 7) the instrument is assumed to have been out of control during the original analysis. If possible, reanalysis of samples will progress in reverse order until it is determined that the RPD between initial and reanalysis results are within DQOs (Element 7). Only the re-

analysis results will be reported by the laboratory. If it is not possible or feasible to perform reanalysis of samples, all earlier data (i.e., since the last successful calibration control check) are suspect. In this case, the laboratory will prepare a narrative explanation to accompany the submitted data.

14.4.5 Laboratory Reagent Blank

For POP analyses, one laboratory reagent blank will be run in every sample batch. The reagent blank will be processed through the entire analytical procedure in a manner identical to the samples. Reagent blanks should be less than the MDL or not exceed a concentration greater than 10% of the lowest reported sample concentration. A reagent blank concentration > 2x the MDL or > 10% of the lowest reported sample concentration for one or more of the analytes of interest will require corrective action to identify and eliminate the source(s) of contamination before proceeding with sample analysis. If eliminating the blank contamination is not possible, all impacted analytes in the analytical batch shall be flagged. In addition, a detailed description of the contamination source and the steps taken to eliminate or minimize the contamination shall be included in the transmittal letter. Subtracting method blank results from sample results is not permitted.

14.4.6 Injection Internal Standards

The usage of the terms injection internal standard, surrogate, and internal standard varies considerably among laboratories. Surrogates are compounds chosen to simulate the analytes of interest in POP analyses. These are used to estimate analyte losses during the extraction and clean-up process and must be added to each sample, including QA/QC samples, prior to extraction. The reported concentration of each analyte is adjusted to correct for the recovery of the surrogate compound, as done in the NOAA NS&T Program. The surrogate recovery data will be carefully monitored; each laboratory must report the percent recovery of the surrogate(s) along with the target analyte data for each sample. If possible, isotopically-labeled analogs of the analytes will be used as surrogates.

Each laboratory will set its own warning limit criteria based on the experience and best professional judgment of the analyst. It is the responsibility of the analyst to demonstrate that the analytical process is always "in control" (i.e., highly variable surrogate recoveries are not acceptable for repeat analyses of the same certified reference material and for the matrix spike/matrix spike duplicate). The warning limit criteria used by the laboratory will be provided in the standard operating procedures submitted to CCLEAN.

14.4.7 Dual-Column Confirmation

Dual-column chromatography is required for analyses using GC-ECD due to the high probability of false positives arising from single-column analyses.

14.4.8 Matrix Spikes and Matrix Spike Duplicates

A laboratory-fortified sample matrix (a matrix spike, or MS) and a laboratory fortified sample matrix duplicate (a matrix spike duplicate, or MSD) will be used both to evaluate the effect of the sample matrix on the recovery of the compounds of interest and to provide an estimate of analytical precision. A minimum of 5% of the total number of samples submitted to the laboratory in a given year will be selected at random for analysis as matrix spikes and matrix spike duplicates. A field sample is first homogenized and then split into three subsamples. Two of these subsamples are fortified with the matrix spike solution and the third subsample is analyzed to provide a background concentration for each analyte of interest. The matrix spike solution should contain as many representative analytes from the CCLEAN POP analyte list as feasible. The final spiked concentration of each analyte in the sample will be at least 10 times the MDL for that analyte, as previously calculated by the laboratory. Additionally, the total number of spikes should cover the range of expected concentrations. Recovery is the accuracy of an analytical test measured against a known analyte addition to a sample. Recovery is calculated as follows:

$$\text{Recovery} = \frac{\text{Matrix plus spike result - Matrix result) X 100}}{\text{spike}}$$

Recovery data for the fortified compounds ultimately will provide a basis for determining the prevalence of matrix effects in the samples analyzed during the project. If the percent recovery for any analyte in the MS or MSD is less than the recommended warning limit of 50 percent, the chromatograms and raw data quantitation reports will be reviewed. If an explanation for a low percent-recovery value is not discovered, the instrument response may be checked using a calibration standard. Low recoveries of matrix spikes may result from matrix interferences and further instrument response checks may not be warranted. This is especially true if the low recovery occurs in both

the MS and MSD, and the other QC samples in the batch indicate that the analysis was "in control". An explanation for low percent-recovery values for MS/MSD results will be discussed in a cover letter accompanying the data package. Corrective actions taken and verification of acceptable instrument response will be included. Analysis of the MS/MSD is also useful for assessing laboratory precision. The RPD between the MS and MSD results should be less than the target criterion listed in element 7 for each analyte of interest.

14.4.9 Field Replicates and Field Split Samples

As part of the quality assurance program of CCLEAN, duplicate or split samples will be collected for sediment and mussels samples for subsequent chemical analysis. Field duplicates or splits will be submitted as blind samples to the analytical laboratory. Field splits also will be collected and sent blind to additional laboratories selected to participate in the split sample analysis. One field duplicate or field split will be collected for interlaboratory analysis from each sample matrix each year. The analysis of field replicates and field splits can provide an assessment of both inter-and intra-laboratory precision and variance in the sample matrix at the field site. Splits also may be made of laboratory extracts for analysis of POPs. Analysis of these splits can be used to determine variation within and between laboratories in the actual measurement of POPs.

15. INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

15.1 Field Equipment

Field measurement equipment will be checked for operation in accordance with the manufacturer's specifications. This includes battery checks, routine replacement of disposable parts, and cleaning as required. All equipment will be inspected for damage at a minimum when first installed / used and when returned from use. Contractors performing sampling operations will be responsible for ensuring that all equipment in their use is maintained properly. Spares parts for all field equipment are stored at the respective field sampling contractor facilities. Any equipment deficiencies that occur during sampling will be corrected immediately by trained field personnel. Impairments of samples due to equipment problems will be reported to the Program Director as soon as possible and solutions agreed upon. All such sampling problems will be reported in the Sampling Report.

15.2 Laboratory Equipment

All laboratories providing analytical support for chemical or biological analyses will have the appropriate facilities to store, prepare, and process samples. Moreover, appropriate instrumentation and staff are necessary to provide data of the required quality within the schedule required by the program. Laboratory operations must include the following procedures:

- A program of scheduled maintenance of analytical balances, microscopes, laboratory equipment, and instrumentation.
- Routine checking of analytical balances using a set of standard reference weights (American Society of Testing and Materials (ASTM) Class 3, NIST Class S-1, or equivalents).
- Checking and recording the composition of fresh calibration standards against the previous lot, wherever possible. Acceptable comparisons are < 2% of the previous value.
- Recording all analytical data in bound (where possible) logbooks, with all entries in ink, or electronic format.
- Monitoring and documenting the temperatures of cold storage areas and freezer units once per week.
- Verifying the efficiency of fume hoods.
- Having a source of reagent water meeting ASTM Type I specifications (ASTM, 1984) available in sufficient quantity to support analytical operations. The conductivity of the reagent water will not exceed 18 megaohms at 25°C. Alternately, the resistivity of the reagent water will exceed 10 mmhos/cm.
- Labeling all containers used in the laboratory with date prepared, contents, initials of the individual who prepared the contents, and other information, as appropriate.
- Dating and safely storing all chemicals upon receipt. Proper disposal of chemicals when the expiration date has passed.
- Having QAPP, SOPs, analytical methods manuals, and safety plans readily available to staff.
- Having raw analytical data, such as chromatograms, accessible so that they are available upon request.

Laboratories will maintain appropriate equipment per the requirements of individual laboratory SOPs and will be able to provide information documenting their ability to conduct the analyses with the required level of data quality. Such information might include results from interlaboratory comparison studies, control charts and summary data of internal QA/QC checks, and results from certified reference material analyses. Spares parts for all laboratory equipment are stored at the respective analytical laboratories. Any equipment deficiencies that occur during analyses will be corrected immediately by trained personnel. Impairments of analytical results due to equipment problems will be reported to the Program Director as soon as possible and solutions agreed upon. All such equipmentproblems will be reported in the narrative data report.

16. Instrument/Equipment Calibration and Frequency

Although no field measurements are currently made by CCLEAN, immediately before any such measurements, pH measurement devices will be calibrated against standards.

Conductivity devices cannot be calibrated, however a calibration curve has been established by plotting known conductivity standards against device readings. Correction factors are derived from the chart. The devices are checked by analyzing a conductivity standard and determining if, after correction, the reading agrees within the relevant accuracy criteria.

Thermometers used for the project will be checked against NIST certified thermometers a minimum of once annually.

All project laboratories maintain calibration practices as part of the method SOPs. Individual laboratory QA officers are responsible for ensuring that calibration practices are performed as required by SOPs. Records of all calibration measurements will be maintained by each individual laboratory. Any equipment deficiencies that occur will be corrected immediately by trained personnel. Impairments of samples due to equipment problems will be reported to the Program Director as soon as possible and solutions agreed upon. All such sampling problems will be reported in the Sampling Report.

17. INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

Field sampling contractors and analytical laboratories are responsible for inspection / acceptance of all project-related materials. Contractors and laboratories will perform inspections per the acceptance criteria within their respective SOPs.

18. NON-DIRECT MEASUREMENTS (EXISTING DATA)

Two types of non-direct data are used in the CCLEAN program, as follows

- Flow data are obtained for wastewater treatment plants from treatment plant flow meters, which also provide electronic signals to the automated sampling equipment. Flow data are used to estimate the loads of water constituents using the concentration data measured directly by the program (i.e., load = concentration x flow volume). It is assumed that functional flow meters and access points for sampling effluent are necessary for this program.
- Data on concentrations of ocean chlorophyll are obtained from satellite images provided by NASA for assessment of the effects of nutrient discharges to Monterey Bay. CCLEAN does not apply any measures of data quality to the satellite imagery and associated chlorophyll concentrations. Use of satellite data requires internet access to the appropriate NASA data portals.
- National Status and Trends (NS&T) Mussel Watch data on concentrations of POPs in mussels are an important part of CCLEAN, as they cover areas of Monterey Bay not sampled by CCLEAN. NS&T QA procedures are very stringent and have been the basis for procedures used to collect and analyze shellfish for POPs nationwide. Access to NS&T data require functional internet access for downloading from the NS&T website.

19. DATA MANAGEMENT

CCLEAN monitoring data will be maintained as established in Element 9 above. Hard copies of all field logs, COCs, and other data sheets will be maintained by contractors conducting field sampling operations. Hard copies of lab reports will be stored at the Program Director's office as well as with the responsible laboratories. Supporting documentation for laboratory reports will be maintained by individual laboratories per their respective SOPs.

Data from lab reports will be transferred into an electronic spreadsheet(s) that will be maintained at the Program Director's office as a password-protected file. A data delivery template has been developed for all analytical laboratories to submit data. This template includes the necessary fields to streamline delivery of data to the SWAMP database. After delivery to the Program Director, all data will undergo checks to verify that QC results fall within required DQOs. Checked data will be delivered to the Central Coast Regional Water Quality Control Board via the online web-checking tool by January 31 each year for the program year ending the previous June 30.

GROUP C: ASSESSMENT AND OVERSIGHT

20. ASSESSMENTS & RESPONSE ACTIONS

The Project Director and project managers for each contractor will ensure that qualified personnel are employed in all phases of project implementation and that all personnel receive appropriate training to complete assigned tasks consistent with the CCLEAN workplan.

20.1 Field Audits
Annual audits will be conducted of field sampling procedures to ensure adherence to the CCLEAN QAPP. However, before any field sampling is conducted, the Project Manager for each subcontractor will verify that proper equipment is available for all field personnel. This includes sampling equipment, safety equipment, and field measurement equipment (if appropriate). It will also be verified that all personnel involved in field activities have received sufficient training and are able to properly use the equipment and follow procedures. The Project Manager or Field Program Manager may also verify the application of procedures and equipment periodically. If the Project Manager or Field Program Manager finds any deficiencies, corrective actions will be put in place and reported, and follow-on inspections will be performed to ensure the deficiencies have been addressed. Information from field audits will be included in the annual QA Audit report submitted to the CCLEAN Steering Committee and the Regional Board by November 31 each year.

20.2 Laboratory Performance Audits
Initially, a QA performance audit may be performed by CCLEAN Program Director to determine if each laboratory is in compliance with the procedures outlined in the QAPP and to assist the laboratory where needed. Reviews will be conducted at least once every five years during the duration of the program. Results will be reviewed with laboratory staff and corrective action recommended and implemented where necessary. Moreover, laboratory performance will be assessed on a continuous basis through the use of laboratory intercomparison studies, such as EPA and NIST round-robins, and analysis of split samples by contract and SWAMP laboratories. An annual QA Audit report will be submitted by the Program Director to the CCLEAN Steering Committee and the Regional Board by November 31 each year.

20.3 Corrective Actions
If an audit of any field sampling or laboratory operation discovers any discrepancy, the Program Director will discuss the observed discrepancy with the appropriate person responsible for the activity (see organization chart). The discussion will begin with whether the information collected is accurate, what were the cause(s) leading to the deviation, how the deviation might impact data quality, and what corrective actions might be considered. The Program Director and QA Officer have the power to halt all sampling and analytical work if the deviation(s) noted are considered detrimental to data quality.

21. REPORTS TO MANAGEMENT

21.1 CCLEAN Reports

CCLEAN requires an Annual Report (Table 22) to be submitted to the Central Coast Regional Water Quality Control Board by January 31 each year. The report includes the following items:

- a description of the study design,
- locations of sampling sites,
- a summary of sampling methods,
- highlights of temporal trends and spatial variation in data,
- comparison to water quality objectives and other applicable standards or alert levels, as described in Section 5.3
- synthesis of results relating data from different measurements to each other, and
- any recommended program changes.

Data are submitted to the Water Board electronically and are available to interested parties on DVD.

The goal of the report is to provide a summary of results that addresses each program question and is understandable to informed lay people. Core management and scientific questions are stated first, followed by a concise summary of the major findings and the degree of confidence associated with these. Figures and maps are the main mode of presenting findings and a single tabular summary of sampling effort is included. Statements about patterns in the monitoring results are accompanied by interpretations that discuss the implications of the results. More detailed data summaries, information on sampling and analysis methods, and discussion of QA/QC issues are presented in appendices.

As the CCLEAN program is revised, the QAPP will be updated accordingly. Draft and final QAPP documents are submitted on the schedule shown in Table 19.

Table 19. Project reports.

Type of Report	Frequency (daily, weekly, monthly, quarterly, annually, etc.)	Projected Delivery Dates(s)	Person(s) Responsible for Report Preparation	Report Recipients
Draft CCLEAN Annual Report	Annually	Dec 31	Program Director	CCLEAN Steering Committee and Water Board
CCLEAN Annual Report	Annually	Jan 31	Program Director	Water Board
CCLEAN electronic data	Annually	Jan 31	Program Director	Water Board
CCLEAN QA Audit	Annually	Nov 31	Program Director	CCLEAN Steering Committee
Revisions to CCLEAN QAPP	Annually, as necessary	June 1	Program Director	CCLEAN Steering Committee and Water Board
Revisions to CCLEAN QAPP	Annually, as necessary	July 1	Program Director	Water Board

GROUP D: DATA VALIDATION AND USABILITY

22. DATA REVIEW, VERIFICATION, AND VALIDATION REQUIREMENTS

Data generated by project activities will be reviewed against the data quality objectives cited in Element 7 and the quality assurance/quality control practices cited in Elements 14, 15, 16, and 17. Data will be separated into three categories: data meeting all data quality objectives, data failing precision or recovery criteria, and data failing to meet accuracy criteria. Data meeting all data quality objectives, but with failures of quality assurance/quality control practices will be set aside until the impact of the failure on data quality is determined. Once determined, the data will be moved into either the first category or the last category.

Data falling in the first category is considered usable by the project. Data falling in the last category is considered not usable. Data falling in the second category will have all aspects assessed. If sufficient evidence is found supporting data quality for use in this project, the data will be moved to the first category, but will be flagged consistent with lookup tables provided by the SWAMP web-based data checker.

23. VERIFICATION AND VALIDATION METHODS

Each laboratory's QA Officer will be responsible for performing checks for all data per laboratory quality assurance procedures prior to submission to the Program Director. Once received by the Program Director, all data records will be checked visually and recorded as checked by initials and dates.

Issues will be noted. Reconciliation and correction will be done by a committee composed of the CCLEAN Program Director, and the respective laboratory's Manager, or QA Officer.

24. RECONCILIATION WITH USER REQUIREMENTS

As CCLEAN's studies include designs to estimate sources, loads, trends and effects of pollutants, any appropriate data that achieve the data quality objectives will contribute to the program's ability to answer its core questions. Such data may include those from other programs, such as the CCAMP and National Status and Trends Mussel Watch programs. The project needs sufficient numbers of data points, as represented by the completeness data quality objective in order to do trend analyses and determine the trends and effects of POPs on the prioritized beneficial uses. The ability of the project to determine trends will increase with each subsequent year of data. Trend analysis is performed with linear regression analysis or Seasonal Kendall Test to determine the relationship between data values and times or with analysis of variance for differences among years or locations. The CCLEAN Steering Committee annually reviews project results and this review helps ensure that the project is satisfying the program objectives. Moreover, program findings are regularly presented to regulatory agencies and the scientific community for peer review. Any limitations affecting the ability of the data to be used to meet original project objectives will be noted in annual reports.

The users of CCLEAN data have various requirements for data and information. The current program participants need data and information to inform decisions about achievement of NPDES permit effluent limits, control of contaminant sources, wastewater plant performance, the effects of their discharges on beneficial uses and ways of reducing those effects. In order to support regulatory stakeholders, CCLEAN data will be delivered to SWAMP/CEDEN and to Region 3 to be included in 303(d) /305(b) assessments. Other stakeholders, such as the Monterey Bay National Marine Sanctuary and California Department of Fish and Game, use the data to assess the condition of marine water quality and establish priorities for management or remedial actions to improve the quality of marine habitats, especially for threatened species. Consequently, CCLEAN must adapt to the changing interests and priorities of program participants.

Regardless of the questions or priorities of participants, CCLEAN should provide the data necessary for testing hypotheses associated with program questions as efficiently as possible as well as to inform management actions. In order to base management actions on program results, it is necessary to know the sources and relative amounts of error in program data and variables derived from the data. Data for each of the program questions is discussed in this context below.

What are the status and long-term trends in the quality of nearshore waters, sediments, and associated beneficial uses?

This question is answered by analyzing samples of water, tissue and sediment, comparing the results to regulatory and other criteria and testing them for trends. The main sources of error in these data are natural differences associated with small-scale variation in field samples and laboratory analytical error. Analysis of field duplicates of mussel samples provides an estimate of error that incorporates both sampling and analytical error. Analysis of field duplicates for dieldrin over the life of the CCLEAN program has yielded an average difference between field duplicates of 23.4%. We can get a more accurate estimate of analytical error from the analysis of Certified Reference Materials (CRMs). The average difference between certified concentrations of dieldrin in the CRM NIST 1588a) analyzed by the laboratory (Axys) has been 20.6%. By taking a conservative approach and propagating the error through both sources (square root of ($23.4\%^2 + 20.6\%^2$) we estimate the true value to be the reported value ±31.2%. We do not have data for field duplicates of sediment samples, but analysis of CRM (NIST 1944) in the CCLEAN program indicates an average difference between the reported value and the certified value for 4,4-DDT is 19.3%, which is very similar to the 20.6% error for dieldrin in mussels.

There are not applicable CRMs for water, but experiments performed by Axys, in which known amounts of contaminants were added to a large volume of water that was sampled with the Axys XAD-2 resin, provided data for estimating sampling efficiency (i.e., percent retention x percent recovery) for this method. Percent retention was calculated by passing a known amount of a pollutant through a column and determining the amount retained by analysis of the input and the output:

$$\text{Retention Efficiency} = \frac{\text{Input} - \text{Output}}{\text{Input}}$$

Recovery efficiency was calculated by eluting a retained pollutant from a column and analyzing the eluate:

$$\text{Recovery Efficiency} = \frac{\text{Amount recovered}}{\text{Amount on column prior to elution}}$$

The sampling efficiency for dieldrin was 81.8%±6.6 (retention = 100±1; recovery = 81.8±6.6). This equates to a sampling error of 19.2%. Sampling efficiencies for other compounds are presented in the Axys Infiltrex 300 User's Manual, included in Appendix B.

Sampling error and natural variation also affect our ability to detect trends. This error consists of the natural and sampling-related variation in the measured variable at each point in time, as well as the variation between times. A consideration of such variation can inform the redesign of CCLEAN where trend detection might be the primary objective of sampling and high inherent variability allows a lower sampling frequency without substantially reducing the time required to detect a significant trend.

Do nearshore waters and sediments comply with California Ocean Plan and associated NPDES permits?
This question is answered by comparing measured concentrations of contaminants to the California Ocean Plan NPDES permit effluent limits and other sediment criteria. The same sources of error apply as for the question above.

What are the major sources of contaminants to nearshore waters?
The same errors associated with sampling water, as described above, apply to this question. Moreover, there is error associated with the estimates of flow. Loads estimates previously made for rivers were based upon the average of the daily loads calculated for each sampling period, which were multiplied by 365. The average flow rates during the sampling periods varied from the overall daily average flow by an average of 130%. Consequently, when the sampling and analytical error are combined with the error in flow estimates, the error in load estimates for rivers could be as high as 133%. Because flows of wastewater effluent vary much less than rivers throughout the year, averages from the 30-day sampling periods are more similar to the annual average and associated errors in load estimates are much smaller. Calculations for wastewater reveal an average error in the flow estimate of 6.6%, resulting in an error of 20.3% in load estimates.

What are the effects of wastewater discharges in nearshore waters?
Hypothesis testing associated with this question involves both measures of association between load estimates and ambient ecological variables, as well as the screening of effluent for reproductive endocrine disruption in the fish assays. We are not aware of methods for estimating the error of these methods.

Other user requirements could lead to future changes in the CCLEAN program. For example, changes from the current method of high-volume water sampling could be made in response to changes in the contaminants of concern. Increased interest in the environmental effects of pharmaceuticals and personal care products could result in broader application of POCIS to sample these polar compounds.

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