FINAL QUALITY ASSURANCE PROJECT PLAN (QAPP)

for

Passive Sampling for Persistent Organochlorine Pollutants (POPs) in the Water Column of the Palos Verdes Shelf (2013)

Submitted to

United States Environmental Protection Agency
Region 9
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and

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1.0 PROJECT DESCRIPTION AND OBJECTIVES

1.1 Project Quality Objectives

This quality assurance project plan (QAPP) has been developed for sampling the marine water column at Palos Verdes Shelf (PV Shelf), Los Angeles County, California, using passive water samplers. PV Shelf is Operable Unit (OU 5) of the Montrose Chemical Corporation Superfund Site located near Torrance,, California. In accordance with Section 2.6, *Project Quality Objectives and Measurement Performance Criteria*, of the *Uniform Federal Policy for Quality Assurance Project Plans, Evaluating, Assessing, and Documenting Environmental Data Collection and Use Programs, Part 1: UFP-QAPP* Manual (United States Environmental Protection Agency [EPA] and Department of Defense [DOD], 2005), project quality objectives (PQOs) have been developed and are presented in the following paragraphs.

Sediment on PV Shelf in the vicinity of the diffuser portions of the marine outfalls at White Point, San Pedro, California, are contaminated with persistent organochlorine pollutants (POPs). The outfalls discharge treated wastewater from the Joint Water Pollution Control Plant (JWPCP), Carson, California (Figure 1). JWPCP and the White Point outfalls are operated and maintained by the Sanitation Districts of Los Angeles County (Sanitation Districts).

Dichlorodiphenyltrichloroethane (DDT) and its breakdown products (DDE, DDD, DDMU, and DDNU; to be collectively referred to as DDX), and polychlorinated biphenyls (PCBs) are the primary POPs of concern for PV Shelf. Although POP input via the White Point outfalls was largely eliminated in the early 1980s, fish and other forms of marine life in the vicinity of the outfalls continue to exhibit elevated concentrations of DDX, the magnitude of which has resulted in fish consumption advisories for certain species. As a result, EPA has issued an Interim Record of Decision (IROD) for PV Shelf stipulating a remedial action (RA) to reduce the impact of DDX- and PCB-contaminated marine sediment on ecological and human health (EPA, 2009a). Two components of the selected interim remedy are: placing a chemical isolation cap (e.g., clean sand) over highly contaminated PV Shelf sediment near the Sanitation Districts' benthic monitoring stations BA8C and BA7C at the White Point outfall diffusers (see Figure 1); and monitored natural recovery (MNR) of sediment. At this time, EPA is re-evaluating the value of the interim cap.

As part of the RA at PV Shelf, EPA is conducting sampling of the environmental media, including the water column. Conventional methods that quantify ultra-low water column concentrations of POPs are traditionally unwieldy, time consuming, and expensive. Recently, the *in situ* application of passive sampling devices (PSDs) for measuring dissolved-phase POPs has shown great promise. Zeng used cartridge-type devices based on solid-phase microextraction (SPMEs) in determining sub-nanograms-per-liter (ng/L) concentrations of DDTs in seawater of the Southern California Bight, including several stations in the vicinity of the White Point outfalls (Zeng *et al.,* 2004, 2005). More recently, Fernandez used two types of PSDs – SPMEs and polyethylene devices (PEDs) – in side-by-side deployments at PV Shelf and demonstrated a favorable comparison (Fernandez *et al.*,2012).

In addition to the six relatively common isomers of DDT (i.e., the *o,p'* and *p,p'* forms of DDD, DDE, and DDT) that constitute a large portion of sediment residue concentrations in PV Shelf sediment, two additional DDT forms (*p,p'*-DDMU and *p,p'*-DDNU) have been reported (Eganhouse and Pontollilo, 2008). Although the bioaccumulation potential of these two compounds may be expected to be lower than their parent compounds (based on hydrophobicity), it is important to quantify their concentrations in both sediment and the water column to be able to account for the total mass of DDX (i.e., those being generated within the contaminated sediment horizons and subsequently released via desorption, diffusion

and advection into the water column). The Southern California Coastal Water Research Project Authority (SCCWRP) has recently calibrated PEDs and SPME devices for *p,p'*-DDMU and *p,p'*-DDNU.

1.2 Background

The PV Shelf Study Area is about 25 km in length, varies in width from about 1.5 to 4 kilometers (km), and has a slope of 1 to 4 degrees. Kelp beds and rocky patches are found near shore while most of the shelf has a soft sediment composition. A shelf break (e.g., transition from the relatively flat to steeper continental slope) occurs at an ocean depth of approximately 120 meters (m). The continental slope drops seaward from the shelf, an average of 13 degrees, to a depth of approximately 800 m (Lee, 1994). The PV Shelf Study Area is defined as the area of the shelf and continental slope between Point Fermin and Redondo Canyon from the shore to the 200-m isobath
(Figure 1).

Since 1937, the Sanitation Districts have discharged treated sewage effluent (domestic and industrial) generated at JWPCP onto PV Shelf from the White Point outfalls. Marine sediment on PV Shelf became contaminated with DDT, PCBs, metals, and other contaminants through industrial effluent. It has been estimated that PV Shelf received over 800 tons of DDT pesticide between the late 1950s and the early 1970s (CH2M Hill, 2007). Though the Sanitation Districts disconnected Montrose from its sewer system in 1971 and concentrations of PCBs have not been detected in JWPCP effluent since 1986, these chemicals continue to be detected in PV Shelf sediment; the highest concentrations remain near the diffuser portions of the White Point outfalls along the 50-to-70-m isobaths (Sanitation Districts, 2008).

In August 2000, EPA initiated a pilot capping project that placed clean sediment over a small area (about one percent) of the affected area. The capping project provided an opportunity to evaluate sand placement methods and construction related impacts. In 2002, EPA concluded that cap construction was technically feasible. Subsequently, several data gap studies were initiated to better understand the fate and transport of DDTs and PCBs in PV Shelf sediment.

In 2010, SPME and PEDs were co-deployed in the water column along PV Shelf. Observed concentrations of DDTs and PCBs increased with depth, and indicated maximum concentrations occur down-current of the most highly contaminated sediment (Fernandez *et al.*, 2012). However, the two types of samplers produced results that were well correlated (R^2=0.95), but offset by a factor of three on average. One possible reason for the offset between sampler results could be that the PEDs used performance reference compounds (PRCs) for calibration of disequilibrium, while SPMEs were deployed without PRCs and were assumed to be fully equilibrated. Computer modeling of mass transfer of POPs between SPMEs and water suggested that the equilibrium assumption may not have been correct.

The study described herein looks at the feasibility of monitoring the water column with newly developed PSDs to establish background (i.e., pre- remediation) water-column concentrations before a large-scale capping program begins, to investigate the change in these concentrations over a 3-year period (i.e., since last sampled in 2010), and to compare disequilibrium calibrations by incorporating PRCs into both types of samplers.

1.3 Objectives

Given the need to establish a baseline and characterize the spatial variability in water column concentrations at PV Shelf, the objectives of this work are as follows:

(1) To assess whether using PRCs in both PEDs and SPMEs addresses the problem of offset in the 2010 results from PED and SPME samplers;

(2) To measure the dissolved concentrations of DDX and PCBs in different horizons of the water column and along a spatial gradient away from the highly contaminated zone and at stations up-current of the most highly contaminated sediment; and

(3) To compare dissolved DDX and PCB concentrations to those measured using the same (*i.e.* PED), and similar (*i.e.* SPME), methods in September 2010.

2.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

Robert Burgess will serve as the ORD lead.

Keith Maruya of SCCWRP, 3535 Harbor Boulevard, Suite 110, Costa Mesa, California 92626, will be the task leader responsible for preparation of SPMEs and laboratory analyses of PEDs and SPMEs.

Loretta Fernandez of Fluen Point Environmental (FPE), 6 Mooring Road, Marblehead, Massachusetts 01945, will be the task leader responsible for design, preparation, and deployment of PEDs, and analysis of analytical data generated by SCCWRP for both PEDs and SPMEs.

Fred Stern of the Sanitation Districts will be task leader responsible for sampler deployment and recovery.

Judy Huang is the Remedial Project Manager (RPM) for the PV Shelf Superfund site and will serve as the overall project lead for EPA.

Robert Lindfors of ITSI Gilbane Company, 2730 Shadelands Drive, Walnut Creek, California 94598, is the contract manager for this effort.

3.0 EXPERIMENTAL APPROACH

3.1 General Approach

Passive samplers (PEDs and SPMEs) will be co-deployed at five stations along PV Shelf (BA4C, BA7C, BA8C, BA9C, W3) and at one reference station (T11; Figure 1). PEDs will be deployed at eleven additional stations within and surrounding the PV Shelf Superfund site. A seawater sample will be collected at selected stations and depths where PEDs and SPMEs are co-deployed for determination of dissolved organic carbon (DOC). Critical parameters to be measured are analyte mass in the passive samplers, temperature, and salinity. Based on these data, dissolved concentrations in the water column will be calculated. Contaminants to be measured include congeners of DDT and their breakdown products (including *p,p*'-DDMU and -DDNU) and up to twenty-eight of the PCB congeners measured in previous sampling events at PV Shelf (Table 1).

3.2 Deployment Strategy

3.2.1 Passive Sampler Deployment

PEDs or SPMEs or both will be deployed at each of the seventeen stations as described in Section 3.1. PEDs will be threaded on to stainless steel wire loops in two pieces (one 95 cm x 10 cm piece with no PRCs, and one 5 cm x 10 cm piece containing PRCs; Adams *et al.* 2007). SPME fibers will be encased in drilled, thin-walled copper tubing with end caps (Zeng *et al*., 2004, Maruya *et al*., 2009). At each site, triplicate PEDs and triplicate SPMEs will be set at each of three depths as follows: 5 m above the bottom, mid-depth, and 5 m below the surface. Samplers will be deployed in the field for a minimum of 30 days before recovery. All recovered samplers will be labeled noting station ID, depth, and replicate number. Upon recovery, samplers with be transported and transferred following proper chain-of-custody (COC) protocol. Field blank samples of each type will accompany recovered samplers.

3.2.2 Seawater Collection

Seawater will be collected with a Niskin bottle at each depth for the six stations where PEDs and SPMEs are co-deployed (i.e. BA4C, BA7C, BA8C, BA9C, W3 and T11). An aliquot of seawater (250 ml) will be transferred into a pre-cleaned glass jar and shipped to the laboratory in an ice chest. Samples will be maintained at 4°C prior to DOC analysis.

3.3 Analysis Strategy

Passive samplers will be analyzed for DDX and PCB congeners (Table 1) by gas chromatography/mass selective detection (GC/MSD) in the selected-ion monitoring (SIM) mode. PED sample data will be quantified by the method of internal standards, while SPME sample data will be quantified by the method of external standards.

3.4 Approach to Evaluating Project Objectives

The overall goal of the sampling and analysis activities to be conducted as part of this project is to provide a baseline for monitoring the effectiveness of the remedial action in reducing water column concentrations of DDTs and PCBs on PV Shelf. Estimated dissolved concentrations obtained using passive sampling techniques will be used to provide baseline water column concentrations. Values obtained during this work will be compared to those measured using the same and similar methods in September 2010 to determine if water column concentrations have changed over a 3-year time period.

4.0 SAMPLING PROCEDURES

The field practices for this study were selected to ensure that sampling procedures meet the requirements for the intended use of the data. Deployment of samplers will be performed under the supervision of SCCWRP and EPA representatives. General field information including field location, type of vessel, type of equipment, and weather, will be recorded and maintained in a laboratory notebook. Deployment locations are shown in Figure 1.

4.1 Sample Archival

Sample extracts will be held by SCCWRP for 1 year. Disposal records for unextracted samples, extracted samples, sample containers, and sample extracts will be sufficient to provide tracking from collection, through laboratory receipt, to sample disposal. The project leads will maintain, as part of the study records, copies of all disposal/destruction records of samples.

5.0 TESTING AND MEASUREMENT PROTOCOLS

5.1 Analytical (Measurement) Methods

The target analytes with corresponding method detection and reporting limits are listed in Table 1. PRCs to be used in determining the fractional equilibration of PEDs with the water column are listed in Table 2. Table 3 provides a summary of base method, sample preparation description and analysis description for the methods to be used. The laboratory methods are summarized below. Supporting Standard Operating Procedures (SOPs) are in Table 4.

5.1.1 DOC

Water samples will be analyzed for DOC per SOPs listed in Table 4.

5.1.2 Temperature and Salinity

Temperature and conductivity (to be reported in terms of salinity) will be recorded using a SeaBird 9/11+ at each depth, for each station, at the time of deployment and again upon retrieval.

5.1.3 Chemical Analysis of Passive Samplers

SPME fibers will be analyzed using an Agilent 7890 digital gas chromatograph (GC) coupled to a 5975C quadrupole mass selective detector (MSD). Fibers will be manually injected using a split/splitless injector operated isothermally at 280ºC. A 30 m × 0.25 mm I.D. DB-XLB fused silica column (J&W Scientific, Folsom, California) will be used. The carrier gas will be ultrahigh purity (>99.999%) helium with a constant flow rate of ~1 ml/min. The quadrupole, source and transfer line temperatures will be maintained at temperatures optimized for the target compounds. The MSD will be operated in electron ionization (EI) mode (70 eV). A single quantitation ion per target compound will be acquired using the selected-ion monitoring (SIM) mode. A five-point external standard calibration curve will be generated to quantify target compounds. These will include eight DDT forms (the six standard DDT forms plus *p,p'*-DDMU and *p,p'*-DDNU), and 28 PCB congeners (Table 1).

Field-exposed PEDs will be rinsed with deionized water and wiped clean of visible surface residue (as needed) with a clean Kimwipe, cut into small pieces with solvent-rinsed stainless steel scissors and placed in a solvent rinsed 300 mL glass bottle. The PEDs will then be spiked with recovery surrogates and extracted three times by sonicating in dichloromethane (DCM) for 15 minutes. The PED extracts will then be filtered through pre-combusted (at 500^{o}C) Na_2SO_4.

The combined extract will be concentrated and solvent exchanged to hexane. The volume of the extract will be reduced to final volumes appropriate for the expected ambient seawater concentrations and PED mass using a gentle stream of high purity N_2.

After addition of internal standards, extracts will be analyzed by GC-MSD in EI and negative chemical ionization (NCI) modes for the target analytes (Table 1) and a suite of performance reference compounds (PRCs) pre-spiked into the PEDs (Table 2). Calibration standards will include all internal standards, PRC compounds, eight DDT forms and breakdown products, and 28 PCB congeners (Table 1).

5.2 Calculation of POP Concentrations in Seawater

The concentration of each target analyte in seawater, C_W, will be calculated both for PEDs and SPMEs. For SPMEs, compound-specific water partition coefficients (K_f) have been measured (Zeng *et al*., 2004) and will be used to calculate C_Ws as follows:

$$C_W = N^{\infty}_f / (K_f V_f) \quad (1)$$

where N_f is mass of analyte sorbed to the fiber and V_f is the sorptive coating volume. The units for $K_f V_f$ are μL_W.

A similar calculation is used to convert concentration in the PED, C_{PE}, to C_W.

$$C_W = C^{\infty}_{PE} / K_{PEW} \quad (2)$$

where K_{PEW} is the compound-specific polyethylene-water partition coefficient (Table 1).

Because full equilibration between the samplers and the water column following deployment is not assumed, each C_W will be calculated from the concentration of analyte taken up by the sampler and the fraction of PRC released as follows (Adams *et al*., 2007; Fernandez *et al*., 2009; Fernandez *et al*., 2012):

$$N^{\infty}_f = N_f / f_{eq} \quad (3)$$

$$C^{\infty}_{PE} = C_{PE} / f_{eq} \quad (4)$$

where N^{∞}_f and C^{∞}_{PE} are the equilibrium analyte mass or concentration in the PED or SPME, respectively, N_f and C_{PE} are the mass or concentration in the PED and SPME following deployment, f_{eq} is the fractional equilibration of the sampler determined from PRC mass or concentrations as described by Fernandez *et al*. (2012). For PEDs, C_W will be calculated using both the K_{PEW} listed in Table 1 and a K_{PEW} adjusted for the temperature and salinity of the specific sampling location (Adams *et al*., 2007; Lohmann, 2012).

5.3 Equipment and Instrument Calibration

Table 5 provides calibration information for routine laboratory equipment and Table 6 provides calibration information for instrument calibration. All instruments will be calibrated according to the manufacturer's recommended procedures.

Certified calibration standards used for instrument calibration will be obtained from commercial vendors (e.g., Ultra Scientific, North Kingstown, Rhode Island). PRCs will be obtained from Cambridge Isotope Laboratories, Inc., 50 Frontage Road, Andover, Massachusetts. Where possible, standards will be traceable to National Institute of Standards and Technology (NIST), 100 Bureau Drive, Gaithersburg, Maryland). Calibration standards must contain each compound that will be quantified in the analysis.

Stock solutions containing target analytes, surrogate compounds and other inorganic compound mixtures will be made from reagent-grade chemicals. These solutions may be used to make intermediate standards from which calibration standards are prepared. All analytical stock solutions will be prepared using Class A volumetric glassware. Documentation relating to the receipt, mixing, and use of standards will be recorded in the laboratory notebooks or on data sheets.

6.0 QA/QC CHECKS

6.1 Measurement Quality Objectives

Quantitative and qualitative measurement quality objectives (MQOs) have been established for this project to define required data quality for measurement data. The sampling design and analytical methods for this project were selected based on their ability to achieve project MQOs. The working definitions for the project MQOs are established below.

Accuracy is defined as the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations. Accuracy will be expressed as percent recovery.

Precision is defined as the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves. Precision will be expressed as relative percent difference or percent difference.

Comparability is a measure of the confidence with which one data set can be compared to another. This is a qualitative assessment that has been addressed primarily in sampling design through use of comparable analytical procedures.

Representativeness is the degree to which data accurately and precisely represent a characteristic of a population. This is a qualitative assessment and has been addressed primarily in the sampling design, through the selection of sampling sites, and procedures that reflect the project goals and environment being sampled. It will be ensured during the field and laboratory phase through proper sampling and sample handling procedures.

Sensitivity is the capability of a test method or instrument to discriminate between measurement responses representing different levels (e.g., concentrations) of a variable of interest. Sensitivity has been addressed primarily through the selection of appropriate analytical methods, equipment, and instrumentation. It will be monitored through the achievement of the established method detection limits, instrument calibration, and procedural blanks.

Method Detection Limits (MDLs) are the minimum concentrations of a substance detected at signal to noise ratio of ≥ 3. The MDLs reported in Table 1 were calculated based on the instrument detection limits and conservative estimates of extract and injection volumes (for PEDs).

Reporting Limits (RLs) are the minimum concentrations of an analyte that can be reliably identified, measured, and reported with complete confidence that the analyte concentration is greater than zero. The RLs reported in Table 1 are 3 × MDLs. The sample-specific RL will be inserted into the value field for non-detected chemical parameters with the data qualifier "ND."

The MQOs established for this project are available in Tables 6 and 7.

6.2 Procedures to Assess all Identified QA Objectives

Quality assurance procedures have been incorporated into routine laboratory operations and the project design to assess the achievement of the QA objectives. These include verification that measurement equipment and instruments will be maintained and calibrated, and that background contamination will be minimized.

6.3 QC Checks and/or Procedures (Field and Laboratory)

The project design incorporates quality control (QC) procedures and checks in both the field and laboratory in order to assess data quality. The study design and QC samples are intended to assess the major components of total study error, thereby facilitating the final evaluation of whether environmental data are of sufficient quality to support project related conclusions. The QC sample requirements are designed to provide measurement error information that can be used to initiate corrective actions with the goal of limiting the total measurement error.

6.3.1 Field Sampling

This section describes the collection of field QC samples. Table 8 defines each QC sample type and defines the collection frequency. Field QC samples will be collected in the same type of sample containers and in all other ways handled in the same manner as other field samples.

6.3.1.1 Field Blanks

Unexposed PSDs (PEDs and SPMEs) will be brought into the field. During each day of deployment, at one station, the field blank samplers will be removed from their jars/holders to expose them to the air. Each sampler will then be placed in a pre-cleaned glass sample jar or foil envelope. The field blanks will be stored in a freezer, in the laboratory, during the duration of the deployment. The same field blanks will then be brought back out into the field during recovery of the samplers. During recovery at each station, the field blanks will be removed from the jar and then placed back into the jar. The field blanks will be handled, processed, and analyzed in the same manner as the actual field samples.

6.3.1.2 Performance Reference Compounds (PRCs)

Before deployment, PEDs and SPMEs will be impregnated with PRCs (Table 2) to determine the extent to which samplers have come to equilibrium during the duration of exposure and will be used to adjust

measured concentrations for observed disequilibrium (Eqn. 3). PRC mass measured in unexposed samplers (PRC blanks) will be taken to be the initial PRC mass in all samplers.

6.3.2 Analytical Laboratory

Laboratory samples are processed and analyzed in analytical batches or sample delivery groups (SDGs). A suite of QC samples that monitor the accuracy and precision of the methods are incorporated for each batch. For this project, these QC samples may include method blanks, matrix spikes (MS), matrix spike duplicates (MSD), and field/laboratory duplicates. The QC samples incorporated into an analytical batch are method specific and are defined in Table 8. In addition to these QC samples, surrogate standards are spiked into each sample analyzed for organic compounds. Table 8 defines the preparation procedures for laboratory QC samples.

6.4 QC Check Frequencies, Acceptance Criteria, and Corrective Actions

The field and laboratory QC samples will be prepared at the frequency defined in Table 8. The required accuracy and precision for QC samples, along with corrective actions that must be implemented if QC criteria are not met, are specified in Table 7. All QC sample failures and associated corrective actions will be documented by the task leads.

7.0 DATA REPORTING, DATA REDUCTION, DATA VALIDATION

7.1 Reporting Requirements

The reporting requirements for this project are defined by the analytical methods and intended use of the data.

- Field measurements will be reported as follows:
  - Depth (m)
  - Salinity (PSU) and temperature (ºC)
  - Station location (using U.S. Coast Guard charts and GPS coordinates)
- Laboratory measurements will consist of the analyte mass per sampler (ng/sampler or ng/g PED). Final estimated water concentrations (ng/L) will be calculated from laboratory results in accordance with Paragraph 5.2.

7.2 Deliverables for Field and Laboratory Activities

Field data collected will be recorded in a laboratory notebook or datasheet. Analytical data generated by the laboratory will be provided in summary Microsoft Excel spreadsheets for all field and QC samples. Summary tables will list contaminant concentration data for each sample, organized by the station, depth, replicate number, and contaminant.

A final report to be prepared by the FPE Task Lead will summarize results of sample and data analyses including introduction and materials and methods sections. All relevant raw data and documentation,

including (but not limited to) logbooks, data sheets, electronic files, and final reports, will be maintained by the laboratory for at least 5 years. The laboratory data packages will contain the information shown below:

- Case narrative
- COC form or sample tracking form
- Data summary for each blank and sample
- Surrogate recovery report
- Laboratory control sample/laboratory control sample duplicate report (if applicable)
- MS/MSD report
- Instrument performance check (tuning) report – GC/MS
- Initial calibration data (summary only)
- Continuing calibration data (summary only)
- Chromatograms (if requested)

7.3 Data Reduction Procedures

All analytical chemistry data reduction will be accomplished through the use of data acquisition software that captures instrument output and calculates either sample amounts or concentrations.

7.4 Data Validation Procedures

Evaluation of laboratory performance against prescriptive requirements is assessed through the acceptability of QC sample results that are independent of sample matrix (e.g. method blanks). An assessment of the subjective requirements involves identification of potential matrix effects, and includes an evaluation of the analytical results and the results of analytical duplicates and matrix spike samples.

Laboratory data will be subjected to review by an independent party. To qualify the data, one hundred percent of the data will undergo routine verification, based on the criteria in Tables 7 and 8 and the *National Functional Guidelines for Superfund Organic Methods for Data Review* (EPA, 2008).

The items listed below are considered and evaluated in a routine verification of laboratory-generated data.

- Laboratory reports and COC form documentation (to check for errors and omissions)
- Laboratory case narratives (to check for anomalies and exceedances of QA/QC requirements)
- Laboratory reports (to check for correct reporting limits and units)
- Extraction and analysis holding times
- Method blank (to note any detected analytes and their respective concentrations)
- Surrogate compounds, their spiking levels, the reported concentrations, and the percent recoveries
- MS/MSD samples, their spiking levels, reported concentrations, percent recoveries, and relative percent differences between the MS and the MSD
- Laboratory control samples, their spiking levels, determined concentrations, and percent recoveries (if applicable)
- Laboratory duplicate samples, field duplicate samples, and relative percent differences

Routine verification will be conducted by automated data review (ADR) using the data management system provided by ITSI Gilbane. Each sample delivery group (SDG) will undergo validation as the

electronic data deliverable (EDD) is uploaded to the database directly from the laboratory. The resulting ADR report will be reviewed by the ITSI Gilbane Project Chemist for accuracy. Any necessary manual additions or changes to the qualifiers will be made at this time.

7.5 Data Storage Requirements

Storage of project data must ensure that the integrity and traceability of data are maintained. Storage locations must be appropriate for the media (paper or electronic) and limit access or availability of the data. The final location of all electronic records will be specified in the study file. After the study is complete, all project files associated with this study, including project management files and the draft data summary, will be archived by EPA for at least 10 years. Laboratory raw data and supporting equipment records will be archived by SCCWRP for at least 5 years.

7.6 Final Data Product

The final report prepared by the FPE Task Lead will include the concentrations (i.e., sampler and estimated dissolved) and distribution of POPs by station in the water column of PV Shelf based on passive samplers. The report will also include introduction and materials and methods sections.

8.0 ASSESSMENTS

The following subsections identify planned assessment and oversight activities for this project. Additional assessment activities to be performed may be identified during the course of this study, based upon findings of the planned assessment activities described below.

8.1 Quality Assurance Performance Audits

Audits will be conducted as determined by the RPM, ORD Lead, and QA Officer.

8.2 Corrective Action Procedures

An effective Quality System requires prompt and thorough correction of non-conformance conditions that can affect data quality. Rapid and effective corrective action minimizes the possibility of questionable data or documentation. Corrective action procedures for this project depend on the severity of the non-conformance condition. In cases in which immediate and complete corrective action is implemented by project personnel, the corrective action will be recorded in the appropriate log book. Non-conformance conditions which could have an impact on project data quality must be communicated to the RPM and ORD Lead within 24 hours. These types of issues require a formal corrective action and root cause analysis. The problem resolution will follow the steps listed below.

- Determine when and how the problem developed.
- Assign responsibility for problem investigation and documentation.
- Determine corrective actions to eliminate the problem.
- Define a schedule for completion of the corrective action.

- Assign responsibility for implementing the corrective action.
- Document and verify that the corrective action has eliminated the problem.

The RPM can require field or laboratory activities to be limited or discontinued until the corrective action is complete and the non-conformance issue has been eliminated.

8.2.1 Laboratory Corrective Actions

At a minimum, corrective action and/or notification of the ORD Lead will be implemented within two working days if QC requirements are not met. Corrective actions, including a data review or re-analysis will be implemented where possible. If these actions are not feasible or appropriate based on communication with the PL, then appropriate qualifiers will be added to data.

The QA Officer is responsible for verifying that corrective action is implemented according to internal laboratory policies and this QAPP. Verification may be accomplished through review of analytical data, observed improvements in procedures, and modifications to SOPs.

9.0 REFERENCES

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FIGURES

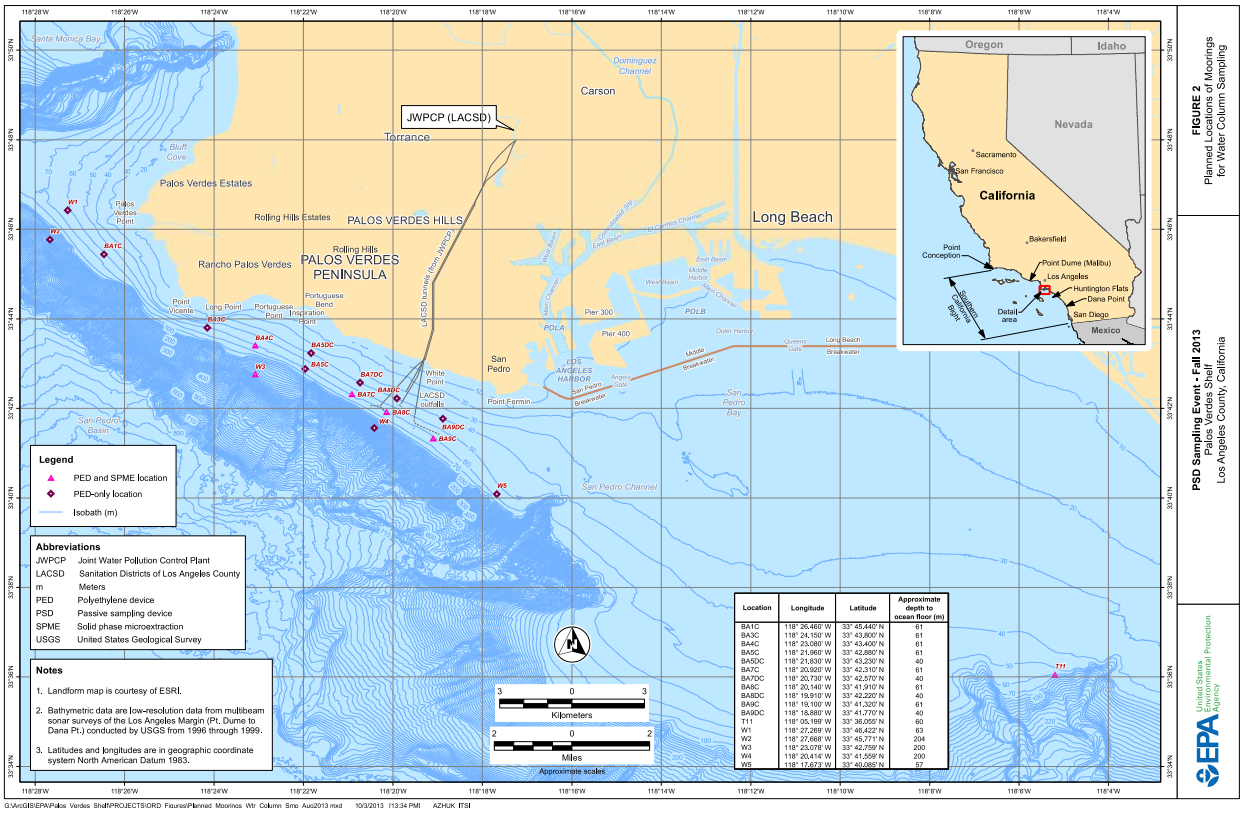

Figure 1. Passive sampling stations off Palos Verdes, California. PEDs and SPMEs will be co-deployed at six stations (BA4C, BA7C, BA8C, BA9C, W3, and T11). Only PEDs will be deployed at the remaining eleven stations.

TABLES

Table 1. Target analytes and estimated method detection limits (MDLs) and reporting limits (RLs) using solid phase microextraction (SPME) and polyethylene (PE) passive samplers

Compound	SPME MDL (ng/L)	SPME RL (ng/L)	PED MDL[1] (ng/L)	PED RL (ng/L)	SPME $K_f V_f$ (10^4 µL)	PED log K_{PEW} (L_W /kg_{PE})
PCB 8[2]	0.20	0.60	27	81	7.93	4.79
PCB 18	0.20	0.60	19	57	7.93	5.03
PCB 28	0.17	0.51	9.3	28	10.7	5.45
PCB 44	0.07	0.21	7.3	22	19.1	5.65
PCB 52	0.07	0.21	5.2	16	20.3	5.57
PCB 66	0.03	0.09	2.7	8.1	23.1	5.71
PCB 77	0.03	0.09	0.76	2.3	25.5	5.58
PCB 81	0.10	0.30	0.58	1.7	39.2	5.64
PCB 101	0.07	0.21	0.60	1.8	25.1	6.06
PCB 105	0.10	0.30	0.13	0.39	33.6	6.11
PCB 114	-	-	0.041	0.12	-	6.18
PCB 118	0.07	0.21	0.045	0.14	28.7	6.06
PCB 123	-	-	0.056	0.17	-	6.11
PCB 126	0.17	0.51	0.096	0.29	32.9	6.11
PCB 128	-	-	0.075	0.23	-	6.65
PCB 138	-	-	0.064	0.19	-	6.60
PCB 153	0.10	0.30	0.017	0.051	109	6.56
PCB 156	-	-	0.018	0.054	-	6.61
PCB 157	-	-	0.016	0.048	-	6.57
PCB 167	-	-	0.014	0.042	-	6.53
PCB 169	-	-	0.020	0.060	-	6.54
PCB 170	-	-	0.010	0.030	-	7.15
PCB 180	-	-	0.0065	0.020	-	7.11
PCB 187	-	-	0.010	0.030	-	7.07
PCB 189	-	-	0.0042	0.013	-	7.09
PCB 194	-	-	0.40[3]	1.2[3]	-	7.65
PCB 206	-	-	0.0013	0.0039	-	8.22
PCB 209[2]	-	-	0.0010	0.0030	-	8.81

Compound	SPME MDL (ng/L)	SPME RL (ng/L)	PED MDL[1] (ng/L)	PED RL (ng/L)	SPME $K_f V_f$ (10^4 µL)	PED log K_{PEW} (L_W /kg_{PE})
o,p'-DDE	0.03	0.09	0.12	0.36	58.2	6.06
p,p'-DDE	0.03	0.09	0.55	1.7	90.5	6.11
o,p'-DDD	0.07	0.21	0.85	2.6	13.9	5.34
p,p'-DDD	0.07	0.21	8.2	25	78.8	5.43
o,p'-DDT	0.03	0.09	2.2	6.6	31.3	5.88
p,p'-DDT	0.03	0.09	2.9	8.7	10.6	5.99
p,p'-DDMU	0.10	0.30	7.5	23	24.9	5.53
p,p'-DDNU	0.10	0.30	12	36	24.9	5.30

[1] PED MDLs are calculated based on instrument detection limit, 1 mL extract volumes, 1µL injection volume, and 2.3 g of polyethylene (PE) per PED. Full equilibration of sampler with water is assumed. Log K_{PEW} match those used in the 2010 passive sampling study and are not corrected for temperature or salinity effects (Fernandez et al. 2012).
[2] to be verified
[3] assuming an instrument detection limit of 25 ng per injection

Table 2. PRC compounds to be analyzed in PED extracts

PRCs

^{13}C PCB 28
^{13}C PCB 52
^{13}C PCB 118
^{13}C PCB 128*
^{13}C p,p'-DDE*
^{13}C p,p'-DDD
^{13}C p,p'-DDT

* also incorporated into SPME samplers

Table 3. Methods for Laboratory Analysis

Parameter	Sample Type	Base Method	Preparation Description	Analytical Description
PCB Congeners (including PRCs)	PED and SPME	GC/MSD	Solvent extraction or thermal desorption	GC/MSD SIM analysis
DDTs and breakdown products	PED and SPME	GC/MSD	Solvent extraction or thermal desorption	GC/MSD SIM analysis
Dissolved organic carbon (DOC)	Seawater	TOC	TOC analysis of acidified, glass-fiber filtered aliquots	High temperature oxidation analysis

Table 4. Supporting Standard Operating Procedures (SOPs)

LOP	LOP Description
SCCWRP SOP CHAPTER 24 – Determination of DOC and TN in water samples	Filtered samples are acidified and sparged to remove inorganic carbon, injected into an elemental analyzer that combusts the sample and converts all remaining carbon to CO_2 which is then analyzed by a non-dispersive infrared (NDIR) gas analyzer. The NDIR generates an analog detection signal that is proportional to the DOC concentration of the sample.
SCCWRP SOP CHAPTER 27 – Construction, deployment, retrieval and analysis of SPME samplers	SPME fibers are solvent rinsed and thermally treated prior to encasing in a pre-fabricated copper tube. Final assembly of the SPME sampler is accomplished on board. After the pre-determined field exposure period, retrieved samplers are isolated in a clean container and placed in cold storage and transported back to the lab for analysis. The field-exposed PED will be treated in a similar fashion. The SPME fiber is thermally desorbed in GC injection port and analyzed by GC-MS for the target analytes.
SCCWRP SOP CHAPTER 35 – Use of polyethylene devices (PEDs)	PE is pre-cleaned and loaded with performance reference compounds. The exposed PED is extracted with dichloromethane (DCM) by sonication. The extract is then exchanged into hexane, and reduced in volume to 0.5 mL for GC-MS analysis.

Table 5. Calibration Procedures for Laboratory Equipment

Equipment	Frequency of Check	Acceptance Criteria
Balance calibration check	Daily or before use with two weights that bracket target weight(s) and Annual calibration with NIST standards by certified technician	1% performance criterion to top-loading balances, and 0.1% to analytical balances. (Expanded criteria from 0.1 to 1% for top-loaders, for no standard existed for this balance type.)
Refrigerator/ freezer temperature monitoring	Daily	Refrigerators: 4 ± 2°C, Freezers: −10 to −20°C (This ASTM standard does not address freezers, but SW-846 has noted this freezer range in some methods).
Thermometer calibration check	Glass – annually Electronic - quarterly at two temperatures that bracket target temperature(s) against an NIST traceable thermometer	Appropriate correction factors applied.
Variable volume pipettes (i.e., Eppendorf)	Monthly	3% of known of true value.
Nonvolumetric glassware/lab-ware verification (applicable only when used for measuring volumes)	By lot at the time of purchase	3% of known or true value. (Standard tolerance does not exist – Class B volumetric flasks criteria vary between 0.8 to 0.05% for 5 mL to 2,000 mL, respectively – set at 3% to maintain consistency with pipette tolerance designation).
Drying ovens	Before and after use	Compliance with method-specific requirements.

Table 6. Calibration Procedures for Laboratory Instruments

Instrument Laboratory (SOP No.)	Standard Sources	Initial Calibration			Calibration Verification		
		No. Standard	Criteria	Frequency	Standards and Conc. Range	General Criteria	Frequency
GC/MSD	Ultra Scientific (North Kingstown, RI, USA) Accustandard (New Haven, CT) Cambridge Isotope (Andover, MA, USA)	5	Value for the calibration curve R^2 shall be > 0.99 for all analytes	prior to analytical run	1 varied-level calibration standard	percent difference (PD) < 25% from initial calibration value for each analyte	Every 12 hours or 12 sample injections
TOC-V$_{CPH/CPN}$	Fisher Scientific (Fair Lawn, NJ, USA)	6	0.1 SD max 2.0 CV max	Prior to analytical run	0-10 ppm calib. 1 ppm inorganic/organic control 5 ppm Carbon control 0 ppm Carbon control	percent difference (PD) < 25% from initial calibration value of controls	Every 12 samples

Table 7. Measurement Quality Criteria

QC Parameter	Acceptance Criteria	Corrective Action
Water Column Concentrations of DDTs and PCBs		
Accuracy: *Field Blanks (Equipment and Trip)(EB)*	PCB congeners and DDTs: < 5×MDL	Review data and assess results for evidence of field-related contamination. Flag all data that are > 5×MDL, unless the concentrations in the related samples are >5 times the concentrations detected in the EB. In this case no flag is required.
Method (Procedural) Blank (MB)	PCB congeners and DDTs: < 5×MDL	Perform corrective action as above and re-process (extract) sample batch. If batch cannot be re-processed; flag all field sample data that are > 5×MDL, unless the concentrations in the related samples are >5× the concentrations detected in the MB. In this case no flag is required.
Instrument Solvent Blank	PCB congeners and DDTs: < lowest calibration standard	Review data and analysis for possible sources of contamination. Reanalyze and/or document corrective action. Data must be flagged.
Matrix (PED only) Spike (Recovery)	PCB congeners and DDTs: 40 – 120% (Target spike must be > 5× the level in the background sample)	Review data to assess impact of matrix. If other QC data are acceptable and no spiking error occurred, then flag associated QC data. If QC data are not affected by matrix failure or spiking errors occurred, then re-process MS. If not possible, then flag associated QC data.
Surrogate Recovery	DBOFB and PCB208: 40 – 120%	Review data. Discuss with Task Lead. Reanalyze, re-extract, and/or document corrective action and deviations.

Table 7. Measurement Quality Criteria, continued

QC Parameter	Acceptance Criteria	Corrective Action
Precision: *Laboratory Duplicate, MS/MSD (Relative Percent Difference (RPD))*	PCB congeners and DDTs: ≤ 30% RPD (Concentration must be > 5× MDL)	Review data to assess impact of matrix. If other QC data are acceptable, then flag associated QC data. If QC data are not affected by matrix failure, then re-process duplicate. If not possible, then flag associated QC data.
Water Column In Situ Characterization		
Accuracy	Salinity , Temperature: < 5% RPD for standards, SRM, continuing calibrations	Review data. Discuss with Task Lead. Reanalyze and/or document corrective action and deviations. Flag data.
Precision: *Laboratory Duplicates (RPD)*	Salinity , Temperature: < 25% RPD	
PE Samplers		
Precision: *Method Blanks*	PRC concentrations: ≤ 30% RPD	Review data to assess impact of imprecision in the PRC initial concentrations.

Table 8. Definitions, Requirements, and Frequency for Typical QC Samples

QC Sample	Definition	Frequency
Field QC		
Equipment Blank (EB) of seawater collector	Defined as a sample of contaminant-free medium (water, PED or SPME) that has been exposed to field conditions. It is used to verify that field samples are not contaminated during collection or field processing. Samples will be processed in the lab as routine field samples.	1/field deployment and recovery
Field replicate (DU) for passive samplers	Field replicates are samples of the same matrix, which are collected, to the extent possible, at the same time, from the same area, and are handled, containerized, preserved, stored, and transported in the same manner.	a minimum of 3 replicate samples are required by the sampling design
Laboratory QC[1]		
Method or Procedural Blank (MB)	A combination of solvents, surrogates, and all reagents used during sample processing, processed concurrently with the field samples. Monitors purity of reagents and laboratory contamination. Matrices: PED and SPME	1/sample batch A processing batch MB must be analyzed with each sequence.
Matrix (PED) Spike (MS)	A PED spiked with the analytes of interest at 10 × the MDL, processed concurrently with the field samples; monitors effectiveness of method on sample matrix. For analysis of compound classes (e.g., PCBs), the spike must contain each targeted compound class.	1/sample batch
Matrix Spike Duplicate (MSD)	The duplicate is a second matrix spike sample.	1/sample batch
Surrogate Standards	All field and QC samples are spiked with a known amount of surrogate standard just prior to extraction; recoveries are calculated to quantify extraction efficiency.	Each field and QA sample

(1) A batch is defined as 20 field samples processed simultaneously and sharing the same QC samples.

SCCWRP Standard Operating Procedures

CHAPTER TWENTY-FOUR STANDARD OPERATING PROCEDURES FOR THE DETERMINATION OF DISSOLVED ORGANIC CARBON (DOC) AND TOTAL NITROGEN (TN) USING THE SHIMADZU TOC-VCPH/CPN ANALYZER*

1.0. SCOPE AND APPLICATION

This protocol describes the standard operating procedure for the determination of dissolved organic carbon (DOC) and total nitrogen (TN) in freshwater or seawater using the Shimadzu TOC-VCPH/CPN analyzer.

2.0. SUMMARY OF METHOD

Filtered samples are acidified and sparged to remove inorganic carbon. Samples are loaded into the ASI autosampler and programmed for automatic run. For the DOC analysis, the instrument injects the sample into the TC combustion tube, which is filled with an oxidation catalyst and heated to 680 °C. The sample is converted to CO_2 and analyzed by a non-dispersive infrared (NDIR) gas analyzer after passing through a dehumidifier and halogen scrubber (remove Cl). The NDIR outputs an analog detection signal that forms a peak that is proportional to the DOC concentration of the sample. For TN analysis, the instrument injects the sample into the combustion tube (furnace temp. 720 °C) where the TN is decomposed into nitrogen monoxide. The nitrogen monoxide is cooled and dehumidified and enters a chemiluminescense gas analyzer, where it is detected. A peak is generated from the signal and the total nitrogen concentration in the sample can be determined.

3.0. INTERFERENCE

3.1. All glassware should be washed with soap and water, rinsed with water and de-ionized water, and kilned at 1000 °F for one hour.

3.2. All working surfaces and equipment should be clean and free of particles and organic solvents, which will increase carbon levels in the samples. Use aluminum foil on all working surfaces.

3.3. Remove all organic solvents from area of sample preparation and limit exposure of sample to air to eliminate possibility of solvent vapors and CO_2 contamination of sample.

Updated Nov. 9, 2007

3.3.1. CO_2 in atmosphere ranges from 300 – 500 mg/L. Dissolved amounts ~0.2 mg/L depending on temperature and CO_2 in atmosphere.

3.4. If seawater is analyzed, limit sample number to <50 samples (calib. and controls included) per run to prevent overloading combustion column catalyst with salts, which will decrease analysis reproducibility. Wash or replace catalyst if sensitivity and reproducibility becomes a problem.

3.4.1. Thoroughly wash the catalyst with tap water while in the column to remove accumulated salts.
3.4.2. Neutralize alkalis with hydrochloric acid diluted to about 5:1.
3.4.3. Rinse the catalyst with tap water to remove the acid.
3.4.4. Rinse with D I water and dry at 100 °C for 8 hrs.

4.0. APPARATUS AND MATERIALS

4.1. Apparatus

4.1.1. Shimadzu TOC-VCPH/CPN w/ auto-sampler (fig 1)
4.1.2. TOC-Control V software, PC w/ Windows 95 or later.
4.1.3. 25 mm GF/F filters w/ filtering apparatus.
4.1.4. Vacuum pump.
4.1.5. 125 ml boiling flask or DO bottles.
4.1.6. Halogen scrubber (part no. 630-00992)
4.1.7. Parafilm.
4.1.8. Combustion tube (part no. 638-41323).
4.1.9. Ceramic fibers (part no. 638-60074).
4.1.10. TOC regular catalyst (part no. 638-92069-01).

4.2. Glassware.

4.2.1. 40 ml I-Chem glass vials w/ caps.
4.2.2. 1000 ml volumetric flask.
4.2.3. 100 ml volumetric flask.

4.3. Gas Supply

4.3.1. Compressed air ultra-zero.
4.3.2. Compressed Nitrogen ultra-high purity.

4.4. Reagents

4.4.1. Concentrated HCl.
4.4.2. Milli-Q water
4.4.3. Potassium hydrogen phthalate (KHP) reagent grade.
4.4.4. Sodium bicarbonate reagent grade.
4.4.5. Sodium carbonate reagent grade.
4.4.6. Potassium nitrate reagent grade.
4.4.7. Ammonium chloride reagent grade.

5.0. SAMPLE HANDLING AND PRESERVATION

5.1. Sample Handling.

5.1.1. A chain of custody should be maintained. As samples are received they are checked for damage and logged into the laboratory logbook.

5.2. Sample Storage.

5.2.1. Store aqueous samples in clean kilned glass jars.

5.2.2. Store samples in a refrigerator at 4 °C until analyzed or freeze and store at -20 °C for longer holding periods.

5.2.3. Holding time of 28 days after acidification/filtration should be observed.

5.2.4. High conc. standard stock solution (1000 ppm) can be stored for about 2 months in an air tight glass flask at 4 °C while diluted standard solutions can be stored for only 1 week.

6.0. PROCEDURE

6.1. Sample Processing.

6.1.1. Filter water samples through GF/F filter before analysis to remove organic particulates. (Do not filter if organic particulates is needed to be included in analysis)

6.1.2. Collect enough filtrate to fill a 125 ml boiling flask and cap leaving no head space.

6.1.3. Acidify sample with concentrated HCl to pH-2. At this point samples can be stored for a short period of time 1-2 days.

6.1.4. Pour acidified sample into a 40 ml sampling vial (minimize headspace) and cover with parafilm.

6.1.5. Load samples on instrument carousel. (Samples with particulates will have to be homogenized by pipet stirring just before sample pickup)

6.2. Prepare TC Standard Stock Solution

6.2.1. Accurately weigh 2.125 g of reagent grade potassium hydrogen phthalate (KHP) that was previously dried at 105-120 °C for 1 hr and cooled in a desiccator.

6.2.2. Transfer KHP to a 1 L volumetric flask and add Milli-Q water to the 1 L mark. Mix the solution. Carbon conc. of the solution is 1000 mg C/L (1000 ppm C)

6.2.3. Prepare 5 calibration concentrations from TC standard stock solution. Calibration point concentrations will change depending on sample range but for most seawater samples the calibration concentrations will be as follows.

Calibration pt. 1 – 0 ppm C
Calibration pt. 2 – 0.5 ppm C
Calibration pt. 3 – 1.0 ppm C
Calibration pt. 4 – 2.5 ppm C
Calibration pt. 5 – 5.0 ppm C
Calibration pt. 6 – 10.0 ppm C

Calibration preparation:

1000 ppm stock C.

100 ml vol.

0.5 ppm C – 50 µl 1000 ppm C
1.0 ppm C – 100 µl 1000 ppm C
2.5 ppm C – 250 µl 1000 ppm C

5.0 ppm C – 500 µl 1000 ppm C
10.0 ppm C – 1000 µl 1000 ppm C

dilute to 100 ml with milli-Q water.

6.2.4. Prepare QA/QC controls.

0 ppm C (milli-Q water)
1.0 ppm IC/OC
5.0 ppm C

6.2.4.1. Prepare a sparge control solution of 1.0 ppm organic C / 1.0 ppm inorganic C and treat as an unknown sample (acidify and sparge).

1.0 ppm IC/OC – 100 µl 1000 ppm C and 100 µl 1000 ppm IC
diluted to 100 ml with milli-Q water. Add conc. HCl to pH 2.

6.3. Prepare TN Standard Stock Solution

6.3.1. Accurately weigh 7.219 g of reagent grade potassium nitrate that was previously dried at 105-110 °C for 3 hr and cooled in a desiccator.

6.3.2. Transfer potassium nitrate to a 1 L volumetric flask and add zero water to the 1 L mark. Mix the solution. Nitrogen conc. of the solution is 1000 mg N/L (1000 ppm N)

6.3.3. Prepare 5 calibration concentrations from TN standard stock solution. Calibration point concentrations will change depending on sample range but for most seawater samples the calibration concentrations will be as follows.

Calibration pt. 1 – 0 ppm N
Calibration pt. 2 – 0.25 ppm N
Calibration pt. 3 – 0.5 ppm N
Calibration pt. 4 – 1.0 ppm N
Calibration pt. 5 – 2.5 ppm N

6.3.4. Prepare QA/QC controls.

0 ppm N
0.5 ppm N

1.0 ppm N

6.3.5. Prepare a sparge control solution of 1.0 ppm organic C / 1.0 ppm inorganic C / 0.3 ppm N and treat as an unknown sample (acidify and sparge).

6.4. Prepare IC Standard Stock Solution.

6.4.1. Accurately weigh 3.50 g of reagent grade sodium hydrogen carbonate that was previously dried for 2 hrs in a silica gel desiccator, and 4.41 g of sodium carbonate previously dried for 1 hr at 280-290 °C and cooled in a desiccator.

6.4.2. Transfer the weighed materials to a 1L volumetric flask and add zero water to the 1L mark. Mix the solution. Conc. of this solution is 1000 mg C/L (1000 ppm C) inorganic carbon.

6.4.3. Use this stock solution for the inorganic carbon fraction of the sparge control solution.

6.5. Load calibration, controls and sample vials on ASI-V turntable.

6.6. Turn power on main instrument.

6.7. If TN analysis is performed, turn power on the TN unit and ozone generator.

6.8. Adjust instrument carrier gas pressure to 200 kpa.

6.8.1. Adjust the flow rate to 150 ml/min.

6.9. Adjust ozone source airflow knob on the TN unit to 500 ml/min.

6.10. Start TOC Control V software and select sample table editor and enter user name (System) and password (TOC6001).

6.10.1. If sample table have already been created, open it from the file menu.

6.10.2. Establish communication between software and the instrument by selecting [connect] from the instrument menu.

6.11. If sample table has not been created, continue with sample table setup and establish communication between the software and the instrument when table is completed.

6.12. Create a calibration file.

6.12.1. Select [New] [Calibration curve] in file menu. Currently using npoccal06.

6.12.2. Select the following in the calibration curve options.

6.12.2.1. System – TC/TN for DOC or TN analysis.
6.12.2.2. Calibration curve type – Edit calibration points manually.
6.12.2.3. Analysis information – TC (enter sample name and sample ID)
6.12.2.4. File name - Enter calibration file name.
6.12.2.5. Zero shift - option if linear regression is to pass through origin.
6.12.2.6. Units – ppm.
6.12.2.7. No. washes – 2
6.12.2.8. Enter calibration points info.
6.12.2.9. Repeat with TN calibration.

6.12.3. Enter the calibration standard runs in the sample table.

6.12.4. Place cursor in the first row of the sample table.

6.12.5. Select [calibration curve] in the insert menu.

6.12.6. Specify calibration file used for the analysis and click open.

6.12.7. Enter vial positions in the sparge/acid addition window.

6.13. Create a method file for unknown samples.

6.13.1. Select [New] [Method] in file menu.

6.13.2. Select the following in the method options. Currently using NPOCmethod07.

6.13.2.1. Analysis information – TC/TN (enter sample name and sample ID)
6.13.2.2. File name - Enter method file name.
6.13.2.3. Calibration curve 1 – Enter calibration file used.

6.14. Enter the unknown samples in the sample table.

6.14.1. Place cursor in the row following the calibration curve entry in the sample table.

6.14.2. Select [sample], in the insert menu

6.14.3. Specify calibration file and method file used for the analysis.

6.14.4. Enter sampling parameters. Always include 5 minutes of sparging.

6.14.5. Enter vial positions in the sparge/acid addition window.

6.14.6. Save sample table by selecting [save] from the file menu.

6.15. Check status of the instrument detectors before starting analysis. Temperature should read 680 °C (720 °C if TN analysed) in background monitor.

6.15.1 Fill ASI auto-sampler rinse bottle (see 1, fig 1) with zero water.

6.15.2 Check humidifier (see 1, fig 2) water level and fill if needed.

6.15.3 Flush lines to TC furnace and auto-sampler by performing line wash in maintenance.

6.15.4 Perform auto regeneration of IC solution in maintenance if level is low or nearly empty.

6.15.5 Check Halogen scrubber (see 3, fig 2) for discoloration of absorbent inside casing as it absorbs chlorine. Replace if discoloration band reaches ~2 cm from end of scrubber.

6.16. Start run.

6.16.1. In the instrument menu select [start]

6.16.2. Verify the vial positions when the sparge/acid addition window appears and click OK.

6.16.3. Start ASI measurement.

6.16.4. Check status of measurements by selecting [sample window] in the view menu. A graph display will appear for the current injection.

6.16.5. If analysis locks up (occurs with insufficient memory on computer) select, stop halt analysis, highlight the last sample analyzed and select [delete data] in the edit menu. Restart the analysis by

selecting [start (continue)] in the instrument menu. Be sure to type in the vial location of the sample (deleted data) in the vial position window that appears before analysis begins. The program will begin analysis from the next sample after the last successful analysis.

6.17. End measurement.

6.17.1. Select standby in the instrument menu [shut down instrument]. A 30 min countdown to instrument shutdown begins.

7.0. Quality Assurance/ Quality Control

7.1. Sample blank

7.1.1. A zero C/N water blank is processed for every batch of 12 samples. Currently using template control06_0C.

7.2. Control samples.

7.2.1. One set of 0.5 ppm N and 1.0 ppm N, 5.0 ppm C is processed for every 12 samples. Currently using template control06_5C for carbon.

7.3. Sparge control.

7.3.1. One set of an acidified and sparged mixture of 1.0 ppm KHP, 1.0 ppm inorganic carbon and 0.3 ppm N solution is processed for every 12 samples. Currently using template cont06_1ppm for carbon.

7.4. Sample replicate.

7.4.1. One or more replicate samples is processed for each batch of 12 samples.

8.0. Safety

8.1. Analyst should wear safety glasses and gloves during all procedures to prevent sample and chemical contact with the skin and eyes.

8.2. Analyst should be careful not to touch hot connections near combustion columns.

8.3. Analyst should read MSDS for all the chemicals and reagents used and follow all safety recommendations in the MSDS.

Fig. 1

Fig. 2

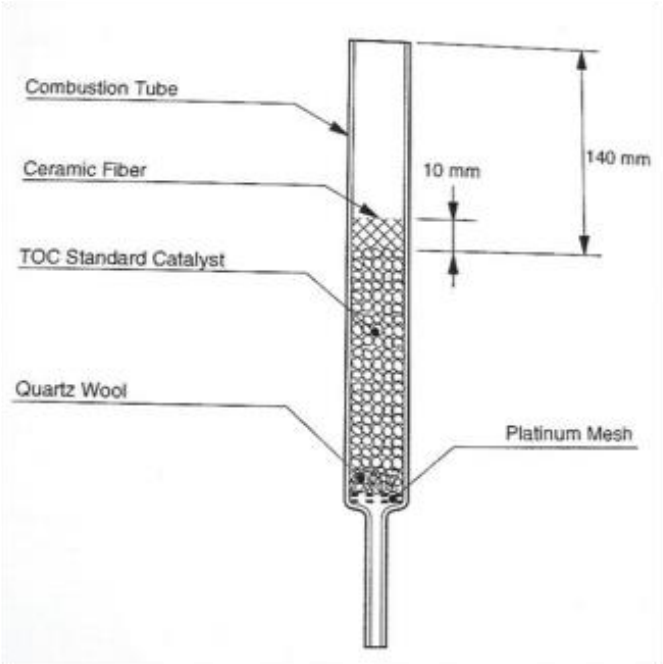
Combustion Tube
Ceramic Fiber
TOC Standard Catalyst
Quartz Wool
10 mm
140 mm
Platinum Mesh

Fig. 3

CHAPTER TWENTY-SEVEN STANDARD OPERATING PROCEDURES FOR CONSTRUCTING, DEPLOYING RETRIEVING AND ANALYZING SPME SAMPLERS.

1.0. Scope and Application

The purpose of this SOP is to describe a standard method for the construction, deployment and retrieval of SPME samplers at sea.

2.0. Summary of the Method

SPME fiber is cleaned in solvent and conditioned in GC injection port. SPME sampler casings are constructed using copper piping, cleaned and loaded with a activated fiber in the lab, transported onboard ship and deployed on site. Allowing 2-3 weeks to reach equilibrium, samplers are retrieved, water samples are taken for each SPME sampler and transported back to the lab for analysis. The SPME fiber is thermally desorbed in GC injection port for 6 min.

3.0. Interference

3.1. All SPME copper casings and hose clamps should be cleaned by washing and scrubbing with soap and water to remove corrosion and marine growth. It may be necessary to sonicate in soapy water for 30 min to thoroughly remove all problems with casing. Rinse with DI water and sonicate for 30 min with 50/50 methylene chloride and methanol followed by 30 min sonication with hexane.

3.1. Baked activated SPME fibers should be dipped or rinsed in Hexane before deployment.

3.2. All water bottles should be washed with soap and water, rinsed with distilled water and kilned at 1,050°F (566°C) for 4 h.

3.3. SPME fibers are activated by baking in a GC column at temperatures depending on fiber composition and thickness.

100 µm PDMS – 30 minutes @ 250 °C.
7µm PDMS – 1 hour @ 320 °C.

4.0. Apparatus and Materials

4.1. Apparatus

4.1.1. SPME 100 µm (red hub) or 7 µm (green hub) Polydimethylsiloxane (PDMS) coating fiber.
4.1.2. Copper casing ½" OD (fig. 1)
4.1.3. Copper end caps ½"
4.1.4. Copper screen 16 mesh .011 wire diameter.
4.1.5. Rubber septa (11.5 mm diameter).
4.1.6. Teflon tape.
4.1.7. Sharpie (permanent marker)
4.1.8. Hose clamps (no. 8)
4.1.9. Pre-cleaned 60 ml vials with Teflon caps.
4.1.10. Aluminum foil
4.1.11. Amber 1L bottles.
4.1.12. Niskin water sampling bottle (5L)

4.2. Reagents

4.2.1. Methylene chloride - HR-GC
4.2.2. n-Hexane – Ultra Resi-analysed
4.2.3. Methanol - Optima
4.2.4. Wet or dry ice.

5.0. Sample Handling and Preservation

5.1. Precautions should be made not to contaminate SPME fiber tip especially upon retrieval. Do not handle fiber except for hub and outer protective sleeve. Do not expose fiber tip to the atmosphere longer than necessary.

5.2. Store SPME fibers at –20 °C or use dry ice in the field and transport using pre-cleaned 60 ml vials with Teflon lined caps.

5.3. Water samples should be stored and transported at 4 °C.

6.0. Procedures

6.1. SPME fiber solvent cleaning up and conditioning.

6.1.1. New or used PDMS coating SPME fiber is sonicated in solvent (methanol/ acetone, 1:1, v/v) for 15-30 min.

6.1.2. Insert the SPME fiber at half of the needle depth into the GC injection port at 250 °C for conditioning 30 min.

6.1.3. Store SPME fiber in clean glass jar with Teflon-lined screw cap and put in freezer.

6.2. Construction of SPME water column sampling unit.

6.2.1. Cut 1/2" copper piping into 6" segments.

6.2.2. Drill 4 rows of holes with 19/64" drill 0.5 cm apart.

6.2.3. Sand ends of copper piping to insure proper fitting of 1/2" copper caps.
Use pliers to shape ends if necessary to hold caps in place snug but not too lose.

6.2.4. Drill a hole using a 11/64" drill on one cap and thread with a 10-32 threader. This cap will hold the SPME fiber in place in the assembly.

6.2.5. Cut a section of copper screen ~1 cm less than the length of the casing and ~1 layer in thickness when rolled and inserted in the casing.

6.2.6. Roll copper screen and insert into the casing and spread out to line interior of tubing.

6.3. Load clean copper casing with SPME fiber.

6.3.1. Screw threaded hub into casing cap (use Teflon tape for proper fit).

6.3.2. Slip septa on protective sleeve to keep fiber tip from making contact with copper casing. Be sure fiber tip is completely withdrawn into protective sleeve before sliding septa on sleeve.

6.3.3. Insert cap/fiber assembly into casing. Teflon tape may be necessary to secure cap to casing if cap is too loose.

6.3.4. Label SPME fiber number on cap with a permanent marker.

6.3.5. Wrap loaded casings in foil, store in pre-cleaned glass jar and seal. Store in freezer at –20 °C until transported to ship.

6.4. Transport loaded casings on wet or dry ice.

6.5. Prepare casing and fibers for deployment upon reaching station.

6.5.1. Record casing/fiber number in the field record worksheet (fig. 3).

6.5.2. Remove cap/fiber assembly from copper casing and pull protective fiber sleeve back exposing fiber.

6.5.3. Dip fiber tip in Hexane for 15 seconds to remove any trace contaminants.

6.5.4. Pull the septa mounted on the protective sleeve forward till it is ~2 cm away from the exposed fiber tip.

6.5.5. Insert the cap/fiber assembly back into the casing being careful not to make contact with the casing.

6.5.6. Samplers can be preloaded with exposed SPME fibers up to a day ahead of time if field conditions makes it difficult to expose fibers.

6.6. Secure casing to line (fig. 2) with 1 hose clamp. Repeat with each depth needed.

6.6.1 When line is being lowered take precautions not to bump casing on the sides of the boat or cause any severe jolt or snapping action on the line.

6.7. Retrieve SPME casing.

6.7.1. Take precautions not to bump casing on the sides of the boat or cause any severe jolt or snapping action on the line.

6.7.2. Remove hose clamp securing casing to line. Any unusual growth or problems should be noted on field record worksheet (fig. 3).

6.7.3. Remove cap/fiber assembly carefully without having tip touch sides of casing. Note condition of fiber tip. Rinse entire shaft including fiber tip with DI water. Slide the protective sleeve over the exposed fiber tip causing the sleeve to shave off any unwanted deposit or growth on the fiber. Once the fiber tip is protected slide the septa off the sleeve. Pull back the protective sleeve again and rinse the fiber tip for a second time with DI water. Slide the sleeve back covering the fiber tip and store in pre-clean 60 ml glass vials and transport on ice. At this stage use caution sliding the protective sleeve over the fiber tip. The mechanism or adhesive

that holds the SPME fiber in place can be weakened in extended seawater use causing the fiber to slide out of its holder.

6.7.4. Store SPME sampler/fiber in clean glass jar with Teflon-lined screw cap.

6.8. If the SPME fiber was successfully retrieved a 1 L water sample should be taken for that depth to determine DOC. Take a large sample (4L) of water if TSS is needed.

6.9. Transport samples to lab and store SPME fibers at –20 °C and water samples at 4 °C.

6.10. Analysis

6.10.1 Set GC into manual injection mode, and splitless injection purge time at 6 min.

6.10.2. Take SPME fiber out of the storage vial from the freezer.

6.10.3. Attach the fiber assembly to the SPME holder.

6.10.4. Waiting for 1-2 min to let the temperature of fiber reach to room temperature. Extrude the fiber out of its protective sleeve and gently wipe out the water on the fiber with KimWipes.

6.10.5. Insert the SPME fiber into the GC injection port at half of the needle depth, and press START button of GC. After thermal desorption for 6 min, withdraw the fiber into the sleeve and pull out the needle out of the injection port.

7.0. Quality Assurance/Quality Control

7.1. Sample replicate.

7.1.1. Replicates is deployed for each 10 stations.

8.0. Safety

8.1. The analyst should wear approved clothing, safety glasses and gloves during all procedures to prevent sample and chemical contact with skins and eyes.

8.2. The analyst should read MSDS for all the chemicals and reagents used and follow all safety recommendations outlined in the MSDS.

8.3. Exercise caution as extremely heavy weights are handled when deploying or recovering equipment at sea. Follow all boat safety regulations on board ship.

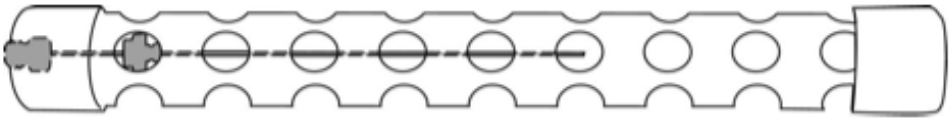

Fig. 1

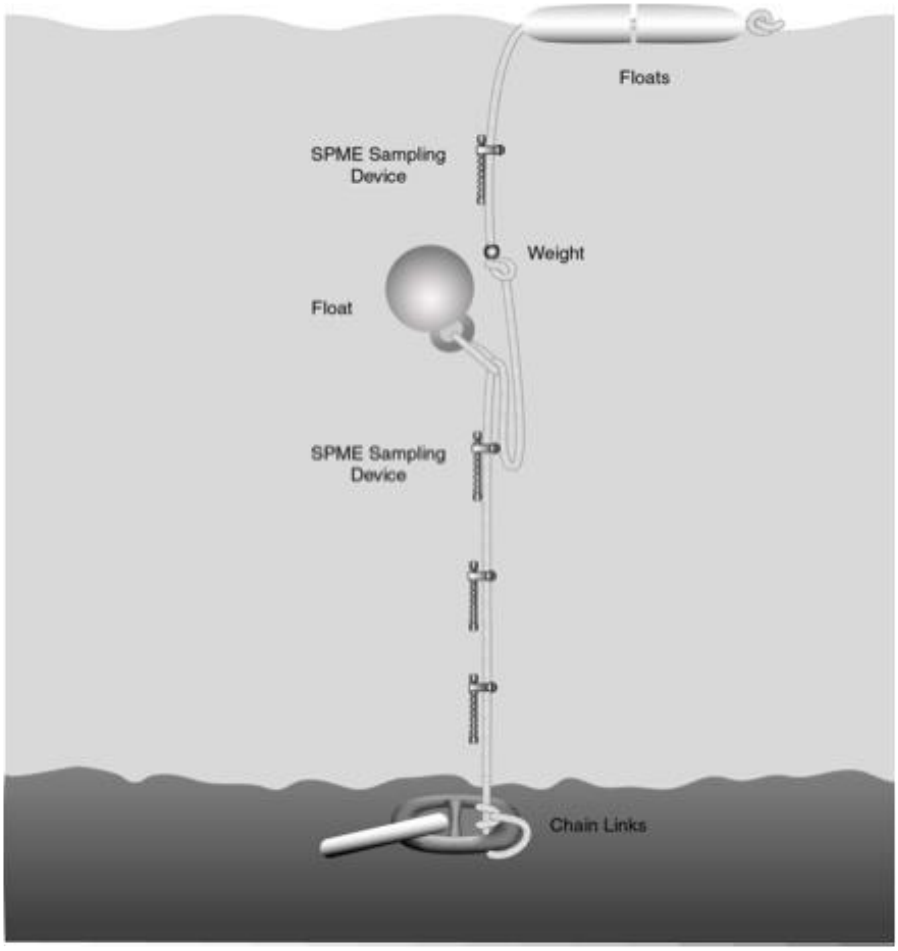
Floats
SPME Sampling Device
Weight
Float
SPME Sampling Device
Chain Links

Fig. 2

No.	Station	Date of Deployme	Date of Retriev	Fiber #	Fiber # Depth 2	Fiber #	Fiber #	Fiber # Depth	Remarks
1									
2									
3									
4									
5									
6									
7									
8									
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Fig. 3

edited from SCCWRP CHAPTER THIRTY-FIVE

STANDARD OPERATING PROCEDURES FOR THE USE OF PEDS (POLYETHYLENE DEVICES).

1.0. Scope and Application

The purpose of this SOP is to describe a standard method for the use of PEDs in the field and laboratory.

2.0. Summary of the Method

PEDs are cut to size and are cleaned in the lab by soaking in solvents before being equilibrated with performance reference compounds. Following deployment in the field or use in lab experiments, PEDs are extracted by sonication with methylene chloride.

3.0. Interference

3.1 All glassware should be washed with soap and water, rinsed with distilled water and rinsed with methanol followed by methylene chloride. Glassware used in extractions should be baked at 450° C for 24 hr and rinsed with methylene chloride.

4.0. Apparatus and Materials

4.1. Equipment

4.1.1. 4L and 1L wide-mouth glass jars
4.1.2. 300 mL glass bottles
4.1.3. Sonicator
4.1.4. Aluminum foil
4.1.5. Low density polyethylene (LDPE) film (ACE Hardware Corp., Oak Brook, IL, USA) or similar, 1 mil thickness (25.4 μm)
4.1.6. Forceps
4.1.7. Gloves

4.2. Reagents

4.2.1. Methylene chloride – Baker Ultraresi-analyzed (Philipsburg, NJ, USA) or similar
4.2.2. Methanol – Baker Ultraresi-analyzed (Philipsburg, NJ, USA) or similar

4.2.3. Deionized water

5.0. Sample Handling and Preservation

5.1. Store PEDs samples in clean glass jars with foil-lined screw caps.

5.2. Handle PEDs only with forceps and gloves. Expose to air as little as possible.

6.0. Procedures

6.1. Cut PED's into strips (10 cm x 100 cm) using rotary cutter, mat, and straight-edge.

6.2. Pre-clean PED

6.2.1. In a 4L wide mouth jar immerse up to 25 PED in methylene chloride overnight. Transfer PEDs to a second 4L jar of methylene chloride and soak overnight, again.

6.2.2. Transfer PEDs to 4L wide mouth jar containing methanol and soak overnight two times as for methylene chloride.

6.2.3. Rinse PEDs several times in DI water and repeat soaking procedure used for methylene chloride and methanol for water.

6.3. Load PED with performance reference compounds (PRCs)

6.3.1. Fill 1L wide-mouth jar with about half of 940 mL DI water and add PRC compounds (mass to be determined for each application) in ~100 μL of methanol or acetone.

6.3.2. Add one PED to jar and fill with remainder of the 940 mL of DI water (just to lip of jar).

6.3.3. Seal jars with foil lined caps and tip to mix.

6.3.4. Jars should be stored in the dark, at room temperature, long enough for the PRCs to evenly diffuse through PED thickness (order of months for high molecular weight compounds such as DDTs)

6.4. Before deployment PED should be removed from the PRC solution, threaded onto copper wire loops, wrapped in foil, and stored in a freezer or on ice.

6.5. Upon retrieval PED is removed from the copper wire, wiped clean of any solids adhering to PE using a laboratory tissue, and rinsed with DI water. The PED is stored in a clean bottle and shipped on ice back to the lab.

6.6. Extraction.

6.2.1. Remove any sediment, animals, algae or diatom growth before extraction.

6.2.2. Insert the PED in a 300 ml glass bottle. Spike surrogate standards directly onto the PED.

6.2.3. Add methylene chloride, seal the flask with aluminum foil and sonicate for 15 minutes.

6.2.4. Remove the methylene chloride and repeat for a total of 3 times.

6.2.5. Combine the extracts, concentrate and exchange solvent to hexane.

6.2.6. Blow down the final extract volume to ~ 0.5 ml.

6.2.7. Add injection standards just before analysis.

7.0. Quality Assurance/Quality Control

7.1. Sample replicate.

7.1.1. Replicates is deployed as needed.

8.0. Safety

8.1. The analyst should wear approved clothing, safety glasses and gloves during all procedures to prevent sample and chemical contact with skins and eyes.

8.2. The analyst should read MSDS for all the chemicals and reagents used and follow all safety recommendations outlined in the MSDS.