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MEMORANDUM

To:	Gary Miller U.S. Environmental Protection Agency	**Date:**	February 12, 2016
From:	Jennifer Sampson, Integral Consulting Inc. David Keith, Anchor QEA, LLC		
Cc:	Dave Moreira, McGinnes Industrial Maintenance Corporation Philip Slowiak, International Paper Company		
Re:	Addendum 1 to the *Sampling and Analysis Plan (SAP): TCRA Cap Porewater Assessment* for additional assessment of porewater within the TCRA armored cap, San Jacinto River Waste Pits Superfund Site		

INTRODUCTION

This memorandum is an addendum to the Sampling and Analysis Plan (SAP) for the Time-Critical Removal Action (TCRA) cap porewater assessment at the San Jacinto River Waste Pits (SJRWP) Superfund site (Site) (Integral and Anchor QEA 2012). This addendum is submitted on behalf of International Paper Company (IPC) and McGinnes Industrial Maintenance Corporation (MIMC) (collectively referred to as Respondents), pursuant to the requirements of Unilateral Administrative Order (UAO), Docket No. 06-03-10, which was issued on November 20, 2009 (USEPA 2009). The UAO requires Respondents to conduct a Remedial Investigation and Feasibility Study (RI/FS) for the Site.

This addendum to the TCRA cap porewater assessment SAP (Integral and Anchor QEA 2012) was prepared following identification of data gaps by the U.S. Environmental Protection Agency (USEPA). These data gaps are described in an email to David Keith on August 6, 2015 (USEPA 2015). Respondents and USEPA engaged in additional discussions of the data gaps for porewater chemistry on September 2, September 17, and September 29, 2015. Results of USEPA's initial communication, the September 2015 meetings, and USEPA comments on the draft of this memorandum form the basis of this SAP addendum, and are synthesized below.

In addition to addressing the Data Quality Objectives (DQOs) for porewater sampling, this addendum provides for all quality assurance and quality control (QA/QC) procedures that will be applied during the porewater sampler deployment, analysis, data validation, and reporting. Sampling and information management described in this addendum will be conducted in full compliance with the approved TCRA cap porewater assessment SAP (Integral and Anchor QEA 2012) and related appendices (including the Field Sampling Plan, which is Appendix A to the SAP). Only those aspects unique to the cap porewater sampling to be conducted in 2016 are addressed by this document.

DATA QUALITY OBJECTIVES

The RI/FS is being undertaken to address contamination of environmental media in the San Jacinto River in the vicinity of the impoundments within USEPA's preliminary site perimeter, and to prepare for remedial action if appropriate. Information on the mechanisms and pathways of release and transport of Site-related contaminants under post-TCRA conditions is necessary for a complete and accurate conceptual site model (CSM), which is used to inform the evaluation of remedial alternatives.

These DQOs address porewater sampling requested by USEPA in an e-mail to David Keith on August 6, 2015, and discussed in subsequent meetings. The DQOs and methods to achieve them are the same as for the study conducted in 2012, with the exception of the list of analytes and some minor methodological changes. Results will provide one line of evidence to address and evaluate potential pathways of contaminant transport from paper mill waste to the environment outside of the TCRA cap. Other lines of evidence include new information on sediment, surface water, and groundwater, discussed in separate documents.

Problem Statement

Verification that the armored cap is preventing transport of dioxins and furans from the paper mill waste into surface water is necessary to support selection of a final remedy for the waste impoundments north of I-10. Sampling is needed to determine whether dissolved dioxins and furans are present in porewater of the TCRA armored cap, whether vertical gradients in concentrations of dioxins and furans in the porewater of the cap are present, and whether porewater concentrations in the cap differ from concentrations in surface water above the cap.

Information Inputs

Activities and findings that inform the development of these DQOs include the implementation of the TCRA and construction of the armored cap, the 2012 study on the TCRA cap porewater quality, and the dioxin and furan congeners accounting for the majority percentage of pre-TCRA risk associated with sediments from within the perimeter of the impoundments north of I-10. This information is summarized below. Additional information inputs include partitioning characteristics of the chemicals to be evaluated.

Performance of the TCRA

Concurrent with the RI/FS, the TCRA was implemented by IPC and MIMC under an Administrative Order on Consent (AOC) with USEPA (Docket No. 06-12-10, April 2010; USEPA 2010). The TCRA program involved capping and isolation of the wastes in the impoundments north of I-10, with related construction completed in July 2011. The purpose of the TCRA was to stabilize the entire area within the original 1966 perimeter of the impoundments north of I-10 (the TCRA Site) (Figure 1), until a final remedy is implemented (USEPA 2010).

As required by the AOC, the Respondents prepared a TCRA alternatives analysis (Anchor QEA 2010) of potential design options for the TCRA. Upon review of the TCRA alternative analysis, USEPA selected a granular cover designed to withstand a storm event with a return period of 100 years. The major construction elements of the selected design were as follows:

- Construction of a security fence on the uplands to prevent unauthorized access to the TCRA Site; this initial work was completed as of April 29, 2010, with additional fencing installed in December 2010
- Placement of “Danger” signs indicating that this location is a Superfund site, and providing a phone number to contact authorities with more information
- Preparation of the TCRA Site (including clearing vegetation), preparation of a staging area, and construction of an access road
- Installation of a stabilizing geotextile barrier over the eastern cell
- Installation of a low-permeability geomembrane and geotextile barrier in the western cell
- Installation of granular (e.g., rock) cover

- Use of appropriate health and safety and environmental control measures during construction
- Design and implementation of an operations and maintenance plan for the TCRA.

TCRA construction has been completed, and operations, monitoring, and maintenance are ongoing.

TCRA Cap Porewater Assessment in 2012

An assessment of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF) in porewater of the TCRA armored cap was performed during May, June, and July 2012. The assessment was performed to evaluate the effectiveness of the TCRA armored cap, and to address uncertainties identified by USEPA, as described in the TCRA cap porewater assessment SAP (Integral and Anchor QEA 2012).

The objective of the TCRA armored cap porewater assessment was to generate new information relevant to two study elements described in the RI/FS Work Plan (Anchor QEA and Integral 2010):

- Study Element 3—Physical CSM and Fate and Transport Evaluation
- Study Element 4—Engineering Construction Evaluation.

For Study Element 3, the sampling objective was to determine whether vertical concentration gradients are present within the TCRA armored cap, and whether porewater concentrations within the cap differ from those in surface water immediately above it. The absence of vertical gradients in porewater concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF was interpreted to indicate that there are no ongoing releases of these congeners from the wastes into the surface water.

Data generated from this sampling event for Study Element 4 also support evaluation of remedial alternatives that incorporate the TCRA armored cap into the final remedy. The data support decisions about whether, and in what manner, the operations monitoring and maintenance plan should address porewater and surface water quality. Details on the methods used to collect and interpret the data from the 2012 cap porewater assessment are provided in the TCRA cap porewater assessment SAP, and in Section 5.3 of the RI Report (Integral and Anchor QEA 2013a).

Results of the 2012 TCRA cap porewater assessment indicated the absence of vertical concentration gradients of dissolved 2,3,7,8-TCDD or 2,3,7,8-TCDF in the porewater within the TCRA armored cap at the time of sampling. At Station SJCP008, the only location at which 2,3,7,8-TCDF was detectable (but estimated only), the concentration estimated using the K_{ow} for 2,3,7,8-TCDF was approximately equivalent to the Texas surface water quality standard of 0.0797 pg/L $TEQ_{DF,M}$,[1] and results at this location did not definitively indicate a concentration gradient of 2,3,7,8-TCDF. Further, an estimate of the concentration of each of the two congeners in surface water was presented in the RI Report; for all of the surface water samples, the dissolved surface water concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF estimated using the K_{ow} were below the Texas surface water quality criterion of 0.0797 pg/L $TEQ_{DF,M}$. Conclusions of the TCRA cap porewater assessment were that the TCRA armored cap is currently effective in eliminating any release of dioxins and furans associated with waste materials within the northern impoundments, and that the TCRA armored cap is also currently effective in reducing or eliminating the potential release of dissolved-phase dioxins and furans from the northern impoundments into the surface water of the river.

Risk Assessment for Sediments

The human health risk assessment (HHRA) for the San Jacinto River Waste Pits found that baseline (pre-TCRA) cancer and noncancer risks associated with hypothetical scenarios involving direct contact with sediments within the original impoundment perimeter, or "Beach Area E" were unacceptable. These risk assessment results are summarized in Tables 5-24, 5-25, and 5-26 of the RI Report, and the complete evaluation is presented in the baseline HHRA (Integral and Anchor QEA 2013b). To determine the dioxin and furan congeners to be measured in this porewater study, data for sediment samples used in these risk assessments were evaluated to determine which congeners accounted for the greatest percentage of risk. To do this, data used in calculating the exposure point concentrations for Beach Area E were identified and analyzed as follows:

[1] Toxicity equivalent concentration calculated for dioxin and furan congeners using toxicity equivalency factors for mammals.

- ProUCL was used to calculate the 95 percent upper confidence limit (UCL) on the mean for each of the seventeen 2,3,7,8-substituted congeners
- The 95 percent UCL of each congener was multiplied by its respective toxicity equivalence factor (TEF) to derive the congener-specific $TEQ_{DF,M}$, and these were summed.
- The congener-specific percent of the total $TEQ_{DF,M}$ was calculated for each congener and sorted from largest to smallest.

Results of this analysis identified the three congeners contributing the greatest to $TEQ_{DF,M}$ risks as 2,3,7,8-TCDD (63 percent), 2,3,7,8-TCDF (22 percent), and 2,3,4,7,8-PeCDF (6 percent). Together, these three congeners account for more than 90 percent of risk due to exposure to $TEQ_{DF,M}$.

Although it is possible to collect data for other dioxin and furan congeners using the method that will be applied for this study, challenges and uncertainties are associated with doing so. Because the three targeted congeners account for more than 90 percent of the risk and two of the targeted congeners (TCDD and TCDF) together constitute the majority fraction of dioxin and furan mass in samples of the paper mill waste, it is not necessary to gather data on additional dioxin and furan congeners, and the incremental value of the additional information is very small. The three targeted compounds provide the information necessary to address the objectives of this study.

Chemical Characteristics

Additional information inputs are the solid-phase microextration (SPME) fiber–water partitioning coefficients (K_{fw}) for 2,3,7,8-TCDD, 2,3,7,8-TCDF, and 2,3,4,7,8-PeCDF, or an appropriate surrogate value such as the published range of K_{ow}s for each of these chemicals (Table 1). Values for K_{fw} for each target compound have been estimated using the regression model of Hsieh et al. (2011) and are shown in Table 1. These partition coefficients were used to estimate the equivalent detection limits in water for the mass detection limits of each target compound anticipated by the analytical laboratory for the SPME fibers (Table 2). Details of how these detection limits were calculated using the Hsieh et al. (2011) regression with K_{OW} are included as a footnote to Table 2. This information is necessary to estimate porewater concentrations at locations where the analytes are detected, if any. The calculated detection limits for each of the three congeners, multiplied by their respective toxicity

equivalent factors (TEFs, van den Berg et al. 2005) and summed, is 0.04 pg/L TEQ_{DF}. Thus, estimated detection limits will provide for detection to concentrations below the Texas Surface Water Quality Standard of 0.0797 pg/L TEQ_{DF}, as required by USEPA in comments on the draft of this SAP addendum (Attachment 3).

Wide temperature variations can theoretically affect K_{fw} (DiFilippo and Eganhouse, 2010). However, the study used to estimate partitioning behavior of the target compounds for this study (Hsieh et al. 2011) reported results from experiments conducted at 25 °C. Water temperatures within the cap porewater are not expected to depart substantially from this value during the study, as recorded groundwater temperatures at the site were always above 14 °C, even during winter months (Integral and Anchor QEA, 2013a), and average monthly surface water temperatures range from 13 to 30 °C throughout the year (Anchor QEA, 2012). Any temperature impact on the estimated K_{fw} values will be minimal relative to analytical uncertainty, and relative to the uncertainty in the K_{fw} values themselves. We therefore do not anticipate a need to correct Hsieh et al. (2011) K_{fw} values for temperature. This will be clearly stated when reporting porewater concentrations in line with practical passive sampling guidance (Ghosh et al. 2014).

Goals of the Study

The goals of the study are to generate sufficient and robust information to provide a line of evidence for evaluating the effectiveness of the armored cap in preventing the release through the TCRA cap of dissolved dioxins and furans from the waste in the impoundments into the water column.

Study goals include collection of data to describe 2,3,7,8-TCDD, 2,3,7,8-TCDF, and 2,3,4,7,8-PeCDF in porewater within the cap and in surface water above the cap using the same sampling equipment (i.e., SPME fibers), the same methods, and the same analysis approach that was used for the related study in 2012. Locations at which the samplers will be deployed are listed in Table 3. SPME fibers will be deployed in the same locations as in the 2012 study, with one exception. Station SJCP001 (Figure 2) has been relocated to the exact location where an area of rock displacement was identified by USEPA in the December 2015 dive inspection of the TCRA cap, as required by USEPA in comments on the draft of this SAP addendum (Attachment 3). Table 3 includes a list of all sampling stations and location information, and Table 4 presents a detailed list of samples to be generated by this study is .

Analytical Approach

Data analysis will be conducted as for the TCRA cap porewater study conducted in 2012, and as described in the study results, Section 5.3 of the RI Report (Integral and Anchor QEA 2013a).

Analysis of samples: SPME fibers will be analyzed for 2,3,7,8-TCDD, 2,3,7,8-TCDF, and 2,3,4,7,8-PeCDF mass at detection limits shown in Table 2. If any of these chemicals are detected in an SPME fiber, the presence or absence of a vertical gradient in concentrations of those samplers deployed in the cap will be evaluated.

Data Analysis: For SPMEs deployed in the armored cap:

- The absence of detection of 2,3,7,8-TCDD, 2,3,7,8-TCDF, and 2,3,4,7,8-PeCDF results in no further action, and supports a conclusion that the cap is effective in containing dioxins and furans within the impoundments.
- If 2,3,7,8-TCDD, 2,3,7,8-TCDF, or 2,3,4,7,8-PeCDF is detected, then the presence or absence of a vertical gradient will be evaluated, as in the 2012 cap porewater assessment.

PROJECT ORGANIZATION, METHODS, AND QUALITY ASSURANCE PROCEDURES

The TCRA cap porewater SAP describes the means to achieve all QA/QC requirements and documentation articulated by USEPA's guidance for preparation of Quality Assurance Project Plans and Field Sampling Plans (USEPA 1998, 2001); these specifications will be applied to the collection, analysis, quality assurance review, data management, validation, and reporting of the information generated as described in this addendum.

Porewater sampling and analyses described in this addendum will be conducted in full compliance with the TCRA Cap Porewater SAP (Integral and Anchor QEA 2012) and related appendices (including Appendix A, the Field Sampling Plan), with the update to Attachment A2 to the Field Sampling Plan. The updates to Health and Safety Plan (HSP) Addendum 5 are included herein as Attachment 1. Sampling personnel will comply with the overall HSP (Anchor QEA 2009) and Addendum 1 to the overall HSP that is provided in Appendix A of the TCRA Cap Porewater SAP (Integral and Anchor QEA 2012, Appendix A, Attachment A1), as well as with the specifications of Attachment 1 to this document.

Also, a different laboratory will prepare the SPME samplers; methods used by this laboratory reflect updates to the method used in the 2012 porewater study. The entire updated method is included as Attachment 2.

Finally, the TCRA Cap Porewater Assessment SAP, Appendix B includes laboratory SOPs. The laboratory that conducts the chemical analysis has updated its SOPs for this project; the analytical SOPs for dioxins and furans are the same as those included in the Sediment SAP Addendum 3, and are not repeated here. (Refer to Attachment 2 of Sediment SAP Addendum 3.)

SCHEDULE

On September 30, 2015, the Respondents provided USEPA with a schedule for completing SAPs and conducting field work for this study and related studies, data analysis, and reporting. The USEPA approved the schedule for submittal of draft SAPs relating to the future sampling at the Site on October 8, 2015. The draft of this SAP addendum was submitted on October 23, 2015, and comments received from USEPA on January 12, 2016. As directed by USEPA, the remaining schedule for the performance of the work will be considered once this document is approved. The dates of SPME deployment and retrieval will depend on final approval of this SAP addendum. Preparation of samplers will begin no later than 1 week following approval of this sampling and analysis plan addendum, and the samplers will be deployed as soon as possible following preparation.

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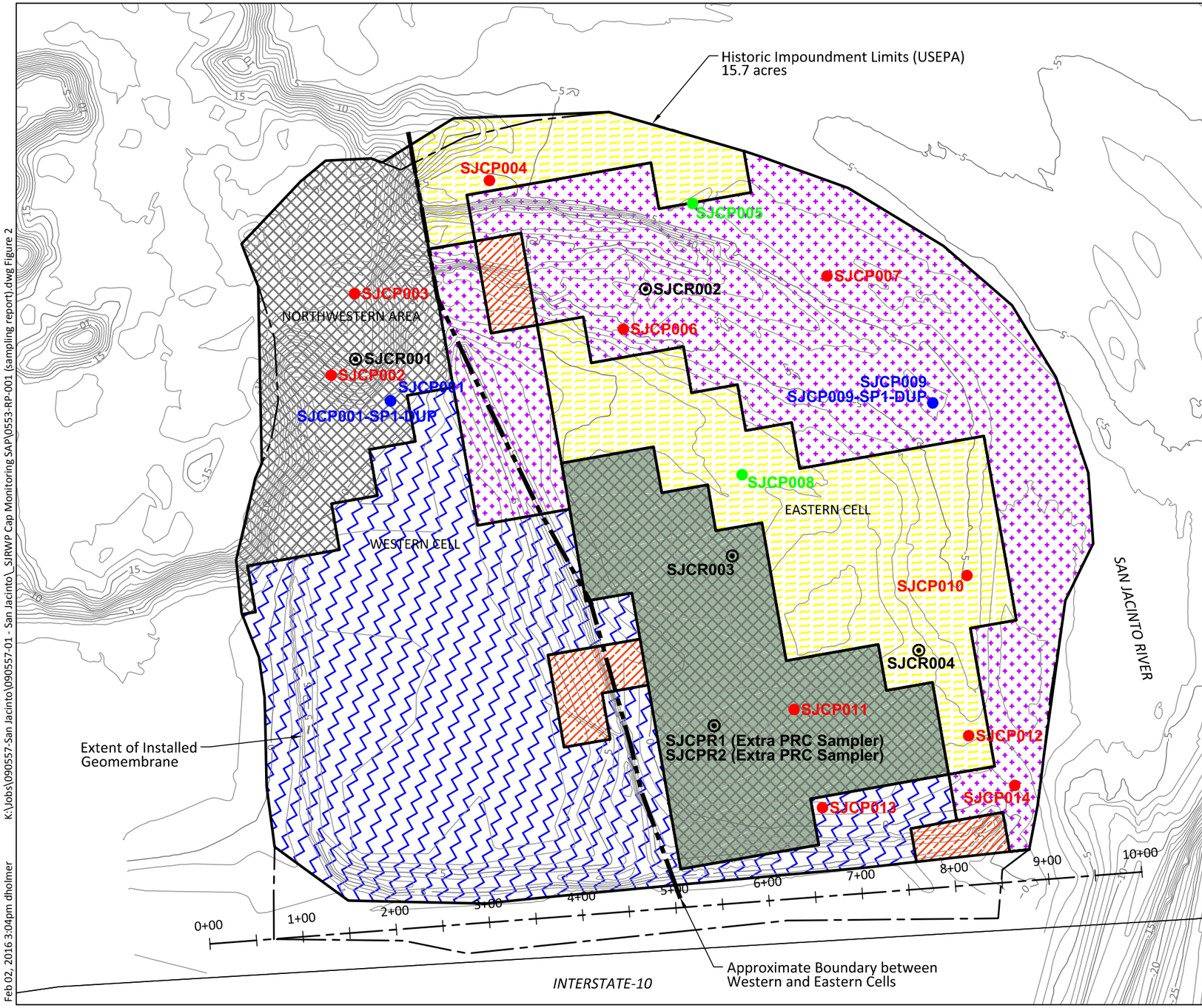
FIGURES

Figure 1
Aerial View of TCRA Project Area, Before and After TCRA Implementation, July 14, 2011
TCRA Cap Porewater Assessment SAP Addendum 1
SJRWP Superfund/MIMC and IPC



LEGEND:

- Pre-Construction Contour, 6/12/10 (1-foot interval)
- Original 1966 Perimeter of the Impoundments North of I-10
- Armored Cap $A_{(P)}$ (Recycled), 12" Design Thickness Without Geotextile
- Armored Cap $A_{(P)}$ (Recycled), 12" Design Thickness With Geotextile
- Armored Cap $B/C_{(P)}$ (Recycled), 12" Design Thickness
- Armored Cap $C_{(N)}$ (Natural), 12" Design Thickness
- Armored Cap $D_{(N)}$ (Natural), 18" Design Thickness
- Armored Cap $D_{(N)}$ (Natural), 24" Design Thickness
- Sampling Location
- Sampling Location with Sample Replicate
- Sampling Location that Included Surface Water Sample
- PRC Sampler Location

HORIZONTAL DATUM: Texas South Central, NAD83. US Survey Feet.

VERTICAL DATUM: NAVD88.

0 120
Scale in Feet

ANCHOR QEA

integral consulting inc

Figure 2
Locations of SPME Sampling Stations
TCRA Cap Porewater Assessment SAP Addendum 1
SJRWP Superfund/MIMC and IPC

TABLES

Table 1
Summary of Literature and Data-based Partition Coefficients for Selected Dioxin and Furan Congeners

Compound	log K_{ow} Literature Range[a]	log K_{ow} Govers and Krop (1998)	log K_{fw} [b]
2,3,7,8-TCDD	5.4–8.9	6.96	6.68
2,3,7,8-TCDF	5.8–7.7	6.46	6.16
2,3,4,7,8-PeCDF	6.9–7.8	7.11	6.83

Notes

PeCDF = pentachlorinated dibenzofuran
TCDD = tetrachlorodibenzo-*p* -dioxin
TCDF = tetrachlorodibenzofuran

[a] As presented in Mackay et al. (1992)

[b] A correlation of log K_{fw} with log K_{ow} based on PCBs, log K_{fw} = 1.03 × log K_{ow} - 0.49 (Hsieh et al. 2011)

Table 2
Analytes, Analytical Concentration Goals , Method Reporting Limits, and Estimated Detection Limits

Analyte	CAS Number	Analytical Concentration Goal (pg/L)	PDMS Method Reporting Limit (pg) [a]	Equipment Detection Limit (pg) [b]	Calculated Detection Limit in Porewater (pg/L) [c]
Dioxins/furans					
2,3,7,8-Tetrachlorodibenzo-*p* -dioxin	1746-01-6	NA	10	0.68	0.03
2,3,7,8-Tetrachlorodibenzofuran	51207-31-9	NA	10	0.70	0.08
2,3,4,7,8-Pentachlorodibenzofuran	57117-41-6	NA	50	0.80	0.02
TEQ_{DF} Mammals[d]	57117-41-6	NA	NA	NA	0.04
$^{13}C_{12}$ -PRCs[e]					
$^{13}C_{12}$-2,3,7,8-TCDD	76523-40-5	NA	TBD	TBD	TBD
$^{13}C_{12}$-2,3,7,8-TCDF	89059-46-1	NA	TBD	TBD	TBD
$^{13}C_{12}$-2,3,4,7,8-PeCDF	116843-02-8	NA	TBD	TBD	TBD

Notes

CAS = Chemical Abstracts Service
HRGC = high-resolution gas chromatography
HRMS = high-resolution mass spectrometry
NA = not applicable
PDMS = polydimethylsiloxane
PeCDF = pentachlorinated dibenzofuran
PRC = performance reference compound
TBD = to be determined
TCDD = tetrachlorodibenzo-*p* -dioxin
TCDF = tetrachlorodibenzofuran
TEF = toxicity equivalence factor
TEQ = toxic equivalent

[a] The required minimum mass of the target compound to be detected by HRGC/HRMS (in picograms).

[b] The minimum mass of the target compound can be detected by HRGC/HRMS reported by the analytical laboratory (in picograms).

[c] The detection limit of the target compound in pore water, estimated using PDMS fiber-water partition coefficient, PDMS fiber length, PDMS fiber unit volume, and a correction factor based on the fraction of equilibrium achieved as below:

$$C_w = \frac{M_{det}}{K_{fw} L_f V f_e}$$

Where:

C_w = Concentration of the target compound in pore water (pg/L)
M_{det} = Equipment detection limit (pg)
K_{fw} = Fiber/water partition coefficient (L/L); provided in Table 1 and based on Hsieh et al. (2011)
L_f = Length of fiber (m); 0.05 m for the PDMS used in the study
V = PDMS fiber unit volume (L/m); 113.8 uL/m for the PDMS used in the study
f_e = Fraction of equilibrium achieved (-); assumed equilibrium (f_e = 1.0)

[d] TEQs are calculated using World Health Organization 2005 TEFs for the three congeners (Van den Berg et al. 2006)

[e] Detection limits for PRCs are expected to be about the same as for the target compounds.

Table 3
Sampling Location Coordinates

Name	X	Y
SJCP001	3216959.00000	13857783.00000
SJCP002	3216916.37960	13857840.67460
SJCP003	3216973.61159	13857909.98880
SJCP004	3217164.77768	13857931.61640
SJCP005	3217332.47733	13857805.89160
SJCP006	3217211.38503	13857726.25620
SJCP007	3217425.07137	13857647.29020
SJCP008	3217239.50460	13857519.90670
SJCP009	3217458.48268	13857475.25310
SJCP010	3217400.93060	13857311.45100
SJCP011	3217169.70136	13857282.32860
SJCP012	3217313.67886	13857162.87290
SJCP013	3217132.77283	13857168.72360
SJCP014	3217333.41519	13857090.65000
SJCR001	3216959.39662	13857851.02180
SJCR002	3217257.08001	13857759.18880
SJCR003	3217189.46253	13857455.35280
SJCR004	3217318.03255	13857269.81470

Notes

Datum: NAD83; State Plane Texas S. Central FIPS 4204 (feet)

Table 4
TCRA Cap Porewater Sampling

Sampling Location	Sample Code	Sampler Type	Depth Interval (inches)
SJCP001	SJCP-001-SP-1-A-DUP	SPME with duplicate	1-3
SJCP001	SJCP-001-SP-1-B-DUP	SPME with duplicate	4-6
SJCP001	SJCP-001-SP-1-C-DUP	SPME with duplicate	7-9
SJCP001	SJCP-001-SP-1-A	SPME	1-3
SJCP001	SJCP-001-SP-1-B	SPME	4-6
SJCP001	SJCP-001-SP-1-C	SPME	7-9
SJCP002	SJCP-002-SP-1-A	SPME	1-3
SJCP002	SJCP-002-SP-1-B	SPME	4-6
SJCP002	SJCP-002-SP-1-C	SPME	7-9
SJCP003	SJCP-003-SP-1-A	SPME	1-3
SJCP003	SJCP-003-SP-1-B	SPME	4-6
SJCP003	SJCP-003-SP-1-C	SPME	7-9
SJCP004	SJCP-004-SP-1-A	SPME	1-3
SJCP004	SJCP-004-SP-1-B	SPME	4-6
SJCP004	SJCP-004-SP-1-C	SPME	7-9
SJCP005	SJCP-005-SP-1-A-W	SPME with surface water	5-7
SJCP005	SJCP-005-SP-1-A	SPME	1-3
SJCP005	SJCP-005-SP-1-B	SPME	9-11
SJCP005	SJCP-005-SP-1-C	SPME	17-19
SJCP006	SJCP-006-SP-1-A	SPME	1-3
SJCP006	SJCP-006-SP-1-B	SPME	5.3-7.3
SJCP006	SJCP-006-SP-1-C	SPME	9.5-11.5
SJCP007	SJCP-007-SP-1-A	SPME	1-3
SJCP007	SJCP-007-SP-1-B	SPME	10-12
SJCP007	SJCP-007-SP-1-C	SPME	19-21
SJCP008	SJCP-008-SP-1-A-W	SPME with surface water	5-7
SJCP008	SJCP-008-SP-1-A	SPME	1-3
SJCP008	SJCP-008-SP-1-B	SPME	10-12
SJCP008	SJCP-008-SP-1-C	SPME	19-21
SJCP009	SJCP-009-SP-1-A	SPME	1-3
SJCP009	SJCP-009-SP-1-B	SPME	10-12
SJCP009	SJCP-009-SP-1-C	SPME	19-21
SJCP009	SJCP-009-SP-1-A-DUP	SPME with duplicate	1-3
SJCP009	SJCP-009-SP-1-B-DUP	SPME with duplicate	10-12
SJCP009	SJCP-009-SP-1-C-DUP	SPME with duplicate	19-21
SJCP010	SJCP-010-SP-1-A	SPME	1-3
SJCP010	SJCP-010-SP-1-B	SPME	10-12
SJCP010	SJCP-010-SP-1-C	SPME	19-21
SJCP011	SJCP-0011-SP-1-A	SPME	1-3
SJCP011	SJCP-0011-SP-1-B	SPME	4.5-6.5
SJCP011	SJCP-0011-SP-1-C	SPME	8-10
SJCP012	SJCP-012-SP-1-A	SPME	1-3

Table 4
TCRA Cap Porewater Sampling

Sampling Location	Sample Code	Sampler Type	Depth Interval (inches)
SJCP012	SJCP-012-SP-1-B	SPME	7-9
SJCP012	SJCP-012-SP-1-C	SPME	13-15
SJCP013	SJCP-013-SP-1-A	SPME	1-3
SJCP013	SJCP-013-SP-1-B	SPME	10-12
SJCP013	SJCP-013-SP-1-C	SPME	19-21
SJCP014	SJCP-014-SP-1-A	SPME	1-3
SJCP014	SJCP-014-SP-1-B	SPME	8.5-10.5
SJCP014	SJCP-014-SP-1-C	SPME	16-18
SJCR001	SJCR-001-SP-2-A	PRC with surface water	5-7
SJCR001	SJCR-001-SP-2-A	PRC	1-3
SJCR001	SJCR-001-SP-2-B	PRC	4-6
SJCR001	SJCR-001-SP-2-C	PRC	7-9
SJCR002	SJCR-002-SP-2-A	PRC	1-3
SJCR002	SJCR-002-SP-2-B	PRC	8-10
SJCR002	SJCR-002-SP-2-C	PRC	15-17
SJCR003	SJCR-003-SP-2-A	PRC	1-3
SJCR003	SJCR-003-SP-2-B	PRC	5.5-7.5
SJCR003	SJCR-003-SP-2-C	PRC	10-12
SJCR004	SJCR-004-SP-2-A	PRC	1-3
SJCR004	SJCR-004-SP-2-B	PRC	7.2-9.2
SJCR004	SJCR-004-SP-2-C	PRC	13.5-15.5

Notes

PRC = performance reference compound
SPME = solid-phase microextraction
TCRA = time critical removal action

ATTACHMENT 1
UPDATE TO ADDENDUM 5 TO THE OVERALL HEALTH AND SAFETY PLAN

ATTACHMENT 1
UPDATE TO ADDENDUM 5 TO THE OVERALL HEALTH AND SAFETY PLAN

Prepared for

McGinnes Industrial Maintenance Corporation

International Paper Company

Prepared by

Anchor QEA LLC

614 Magnolia Avenue

Ocean Springs, Mississippi 39564

October 2015

CERTIFICATION PAGE

This update to Addendum 5 to the overall health and safety plan (HASP; Anchor QEA 2009) for the San Jacinto River Waste Pits Superfund site (the Site) has been reviewed and approved by Anchor QEA for the 2015–2016 TCRA cap porewater assessment study at the Site in support of the Remedial Investigation and Feasibility Study (RI/FS) for the Site.

David Keith	Christopher Torell
Project Manager	Field Lead
Anchor QEA LLC.	Anchor QEA LLC.
Date: _____	Date: _____

HEALTH AND SAFETY PLAN ACKNOWLEDGEMENT FORM

Project Name: San Jacinto River Waste Pits Superfund Site

This update to Addendum 5 to the overall HASP (Anchor QEA 2009) is approved by Anchor QEA for use at the San Jacinto River Waste Pits Superfund Site (the Site). The overall HASP and the updated Addendum 5 are the minimum health and safety standard for the Site and will be strictly enforced for all sampling and other consulting personnel including subcontractors where applicable.

I have reviewed this update to Addendum 5, dated October 23, 2015 to the overall HASP for the project. I have had an opportunity to ask any questions I may have and have been provided with satisfactory responses. I understand the purpose of the plan, and I consent to adhere to its policies, procedures, and guidelines while an employee of Anchor QEA LLC, or its subcontractors.

Date	Name (print)	Signature	Company

Date	Name (print)	Signature	Company

SITE EMERGENCY PROCEDURES

Emergency Contact Information

Table A

Site Emergency Form and Emergency Phone Numbers

Category	Information	
Chemicals of Potential Concern	Dioxins/Furans, PCBs, mercury	
Minimum Level of Protection	Level D	
Site(s) Location Address	(No formal address, see Figure A) Channelview, TX 77530 Coordinates [29° 47' 38.49"N, 95° 3' 49.55"W]	
Emergency Phone Numbers		
Ambulance	911	
Fire	911	
Police	911	
Poison Control	911 and then 1-800-222-1212 if appropriate	
Project-Specific Health and Safety Officers' Phone Numbers		
Integral Field Lead and Integral Site Safety Officer (SSO)	Ian Stupakoff	Office: (360) 705-3534 ext.420 Cell: (360) 259-2518
Integral Corporate Health and Safety Manager (CHSM)	Matthew Behum	Office: (410) 573-1982 ext.512 Cell: (443) 454-1615
Integral Project Manager	Jennifer Sampson	Office: (206) 957-0351 Cell: (360) 286-7552
Anchor QEA Project Manager	David Keith	Office: (228) 818-9626 Cell: (228) 224-2983
Anchor QEA Field Lead and SSO	Christopher Torell	Office: (315) 414-2017 Cell: (315) 254-4954
Anchor QEA CHSM	David Templeton	Office: (206) 287-9130 Cell: (206) 910-4279
Client Contact – McGinnes Industrial Maintenance Corporation (MIMC)	Dave Moreira	Office: (603) 929-5446 Cell: (781) 910-6085
Client Contact – International Paper Company (IPC)	Phil Slowiak	Office: (901) 419-3845 Cell: (901) 214-9550
Reporting Oil and Chemical Spills		
National Response Center	1-800-424-8802	
State Emergency Response System	(512) 424-2138	
EPA Environmental Response Team	(201) 321-6600	

Note: In the event of any emergency, contact both the Integral and Anchor QEA project managers and field leads.

Figure A

Site Location Map

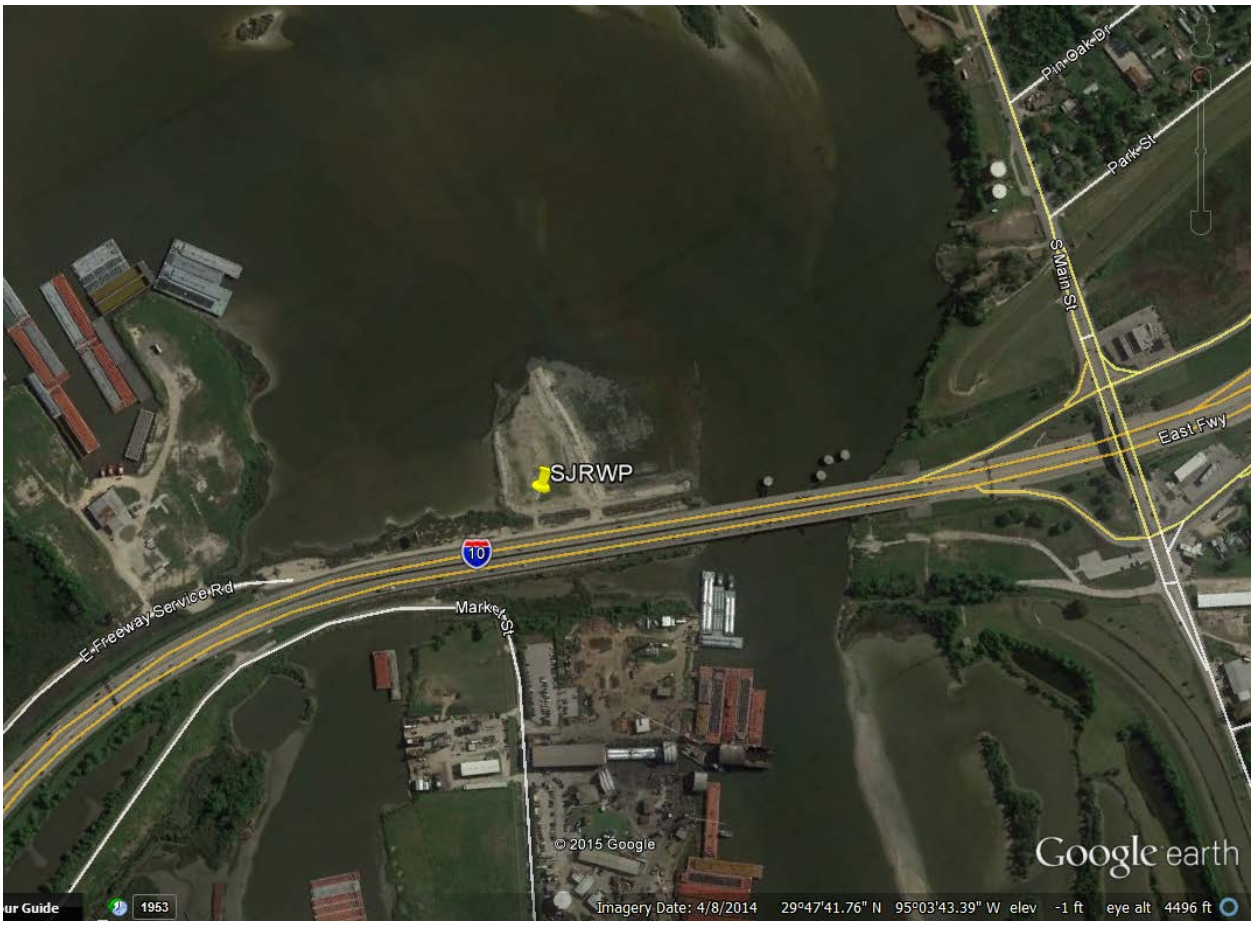


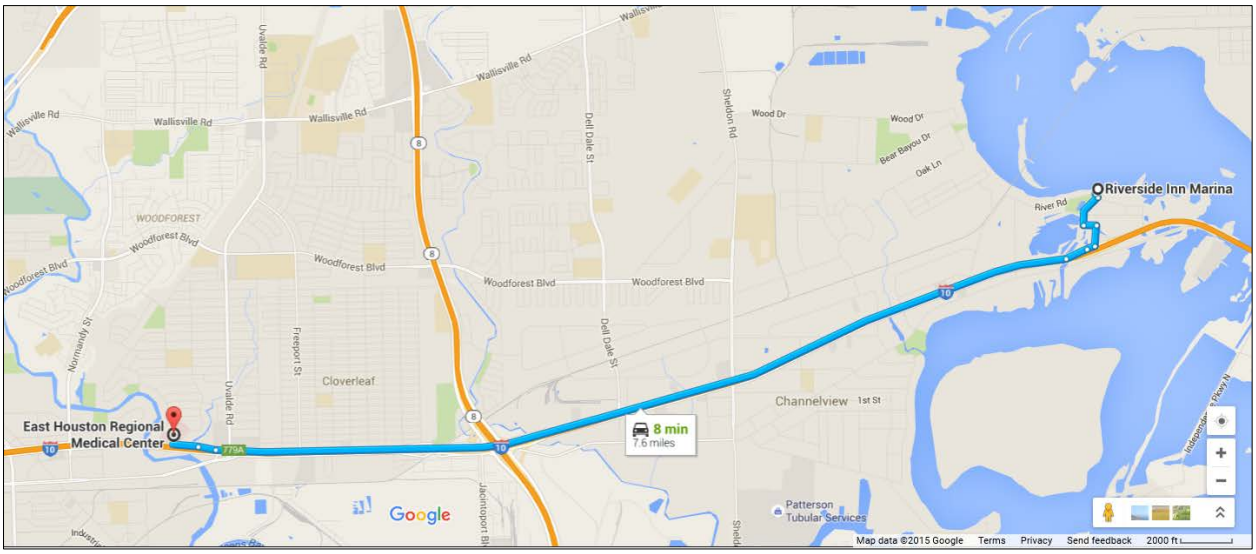
Table B

Hospital Information

Category	Information
Hospital Name	East Houston Regional Medical Center
Address	13111 East Freeway
City, State	Houston, TX 77015
Phone	(713) 393 2000 (general)
Emergency Phone	(713) 393 2118 (emergency room)

Figure B

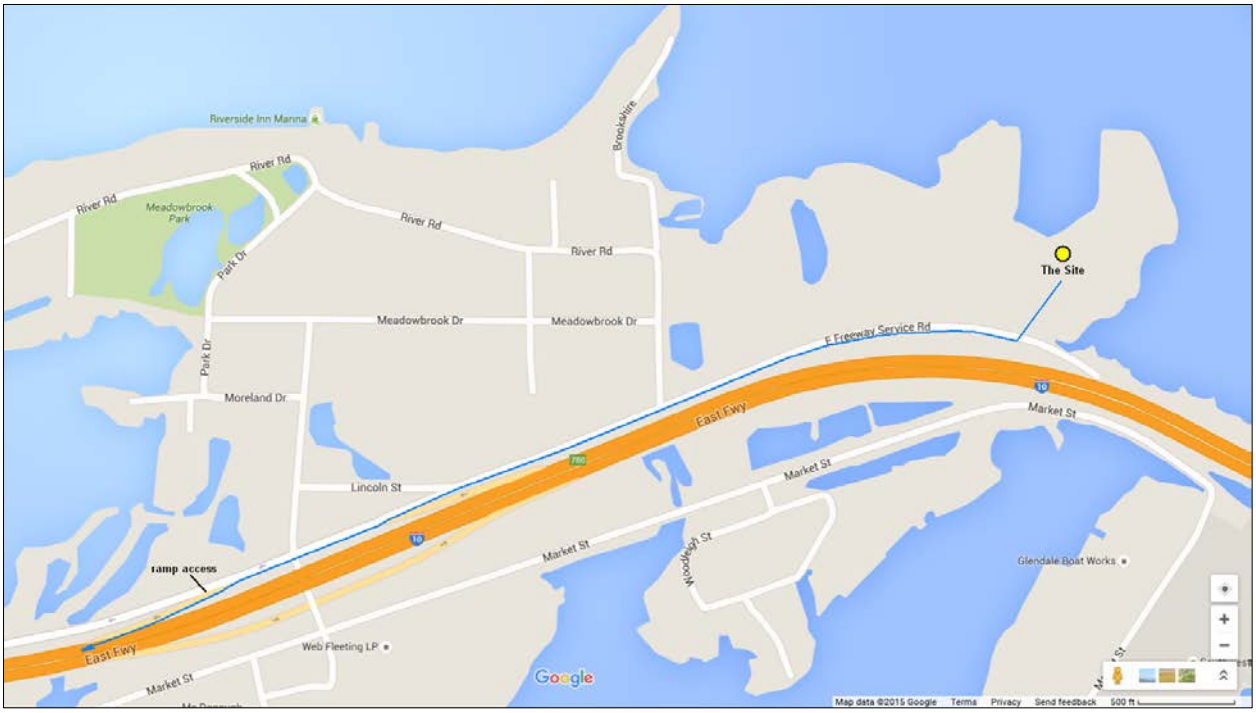
Hospital Route Map from Riverside Inn Marina boat ramp

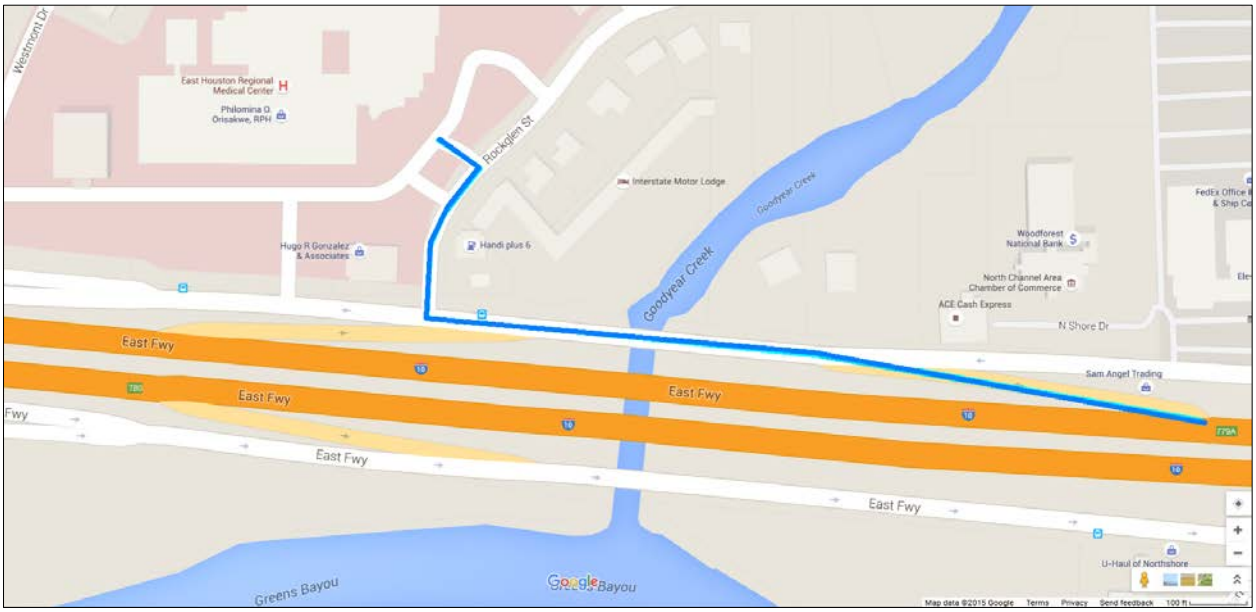


From Riverside Inn Marina boat ramp to East Houston Regional Medical Center.

Figure C

Access from Site to I-10 West





Path to hospital when exiting from Exit 779A on I-10.

Turn right on Rockglen St. after exiting I-10.

East Houston Regional Medical Center emergency entrance.

Driving Directions from Riverside Inn Marina to Hospital

Riverside Inn Marina
17433 River Road, Channelview, TX 77530

Get on I-10 W from Park Dr and Monmouth St

2 min (0.8 mi)

1. Head southeast on River Rd toward Park Dr

167 ft

2. Turn right onto Park Dr

0.2 mi

3. Turn left onto Moreland Dr

0.1 mi

4. Turn right onto Monmouth St

0.2 mi

5. Turn right onto E Freeway Service Rd

331 ft

6. Use the left lane to take the ramp onto I-10 W

0.2 mi

Follow I-10 W to East Fwy/E Freeway Service Rd/N Shore Dr. Take exit 779A from I-10 W

6 min (6.7 mi)

7. Merge onto I-10 W

6.5 mi

8. Take exit 779A toward Westmont St

0.1 mi

Merge onto East Fwy/E Freeway Service Rd/N Shore Dr
Destination will be on the right

20 s (0.2 mi)

9. **Turn right on Rockglen St.**

East Houston Regional Medical Center
13111 East Freeway, Houston, TX 77015

EMERGENCY RESPONSE PROCEDURES

In the event of an emergency, refer to the procedures in the San Jacinto River Waste Pits Superfund Site Overall HASP (Anchor QEA 2009).

A copy of this update to Addendum 5 must be included with the overall HASP, and both copies must be available in the field at all times during field work.

ATTACHMENT 2
SEDIMENT POREWATER SAMPLING WITH SPME USING PDMS-COATED GLASS FIBER—METHOD DESCRIPTION

SEDIMENT POREWATER SAMPLING WITH SPME USING PDMS-COATED GLASS FIBER—METHOD DESCRIPTION

SCOPE AND APPLICATION

This document describes the method for collecting *in situ* sediment porewater samples and surface water samples using solid-phase microextraction (SPME). Porewater is defined as interstitial water within the sediment matrix, or water occupying the spaces between sediment particles (USEPA 2001). The equipment and methods described herein were developed for sampling porewater of the engineered cap at the San Jacinto River Waste Pits (SJRWP) for dioxins and furans, by Dr. Danny Reible at the University of Texas at Austin and others (Mayer et al. 2000; Gschwend et al. 2011; Lu et al. 2011), Integral Consulting Inc., and Anchor QEA LLC.

This method description was specifically developed for use in collecting information on concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in porewater of the armor cap at the SJRWP site. Methods for preparation of the SPME fibers and their deployment, retrieval, and processing are described.

SUMMARY OF METHOD

Sediment porewater concentrations can be measured *in situ* using SPME sampling devices (Mayer et al. 2000; Fernandez et al. 2009; Lu et al. 2011). The technology discussed herein uses SPME sampling devices that consist of a glass fiber core coated with polydimethylsiloxane (PDMS; a polymer sorbent) placed in a modified piezometer casing. The casing allows for deployment directly into the sediment while avoiding physically damaging the fibers.

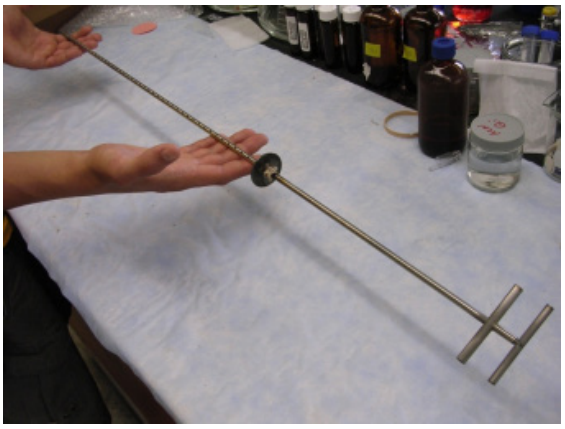
The SPME sampling device is placed into the sediment or cap material or exposed to surface water and left in place for approximately 60 days to allow target chemicals in the sediment matrix to achieve a high degree of equilibrium with the PDMS coating on the fiber. After the exposure period, the SPME sampling devices are retrieved and the PDMS-coated glass fibers are analyzed for concentrations of hydrophobic organic chemicals. The contaminant concentration that accumulates in the polymer sorbent at equilibrium is directly proportional to the dissolved contaminant concentration in the porewater. A proportionality constant, such as an octanol–water partitioning coefficient (K_{OW}), or a polymer–water partition coefficient, in conjunction with an estimate of the fraction of equilibrium achieved, if necessary, can be used to estimate the concentration of each chemical in the porewater sampled from the concentration in the PDMS coating. The accuracy of the porewater concentration estimate depends on the type

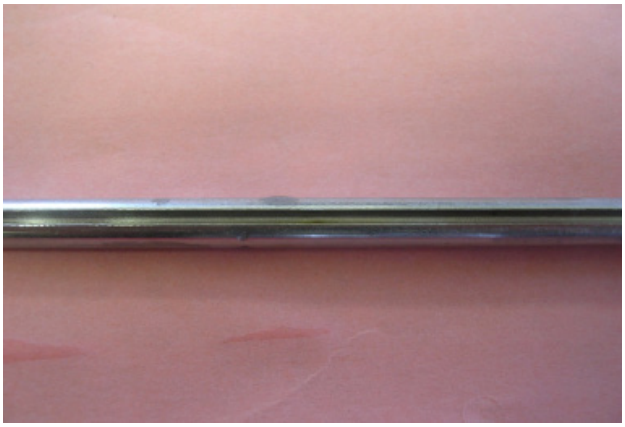
of proportionality constant used; refer to the TCRA Cap Porewater Assessment SAP (Integral and Anchor QEA 2012), Section 1.6.1 for a detailed discussion.

To measure or estimate concentration profiles of hydrophobic organic compounds in the porewater of the cap using PDMS-coated glass fibers, a field-deployable porewater profiling apparatus will be used to deploy the SPME sampling devices directly into the coarse cap materials within a protective casing.

PDMS-coated fibers are the central element to this sampling method. These fibers are commonly used in optical applications. The fibers that will be used in this study will be 1,000-µm-diameter fibers with a 35-µm coating of PDMS, which corresponds to about 113.8 µL of PDMS per meter of fiber.[1] The fiber used is manufactured by Polymicro Technologies of Phoenix, Arizona, which produces the glass fibers with the PDMS coating. In production, they maintain quality control by regular measurement of the fiber coating.

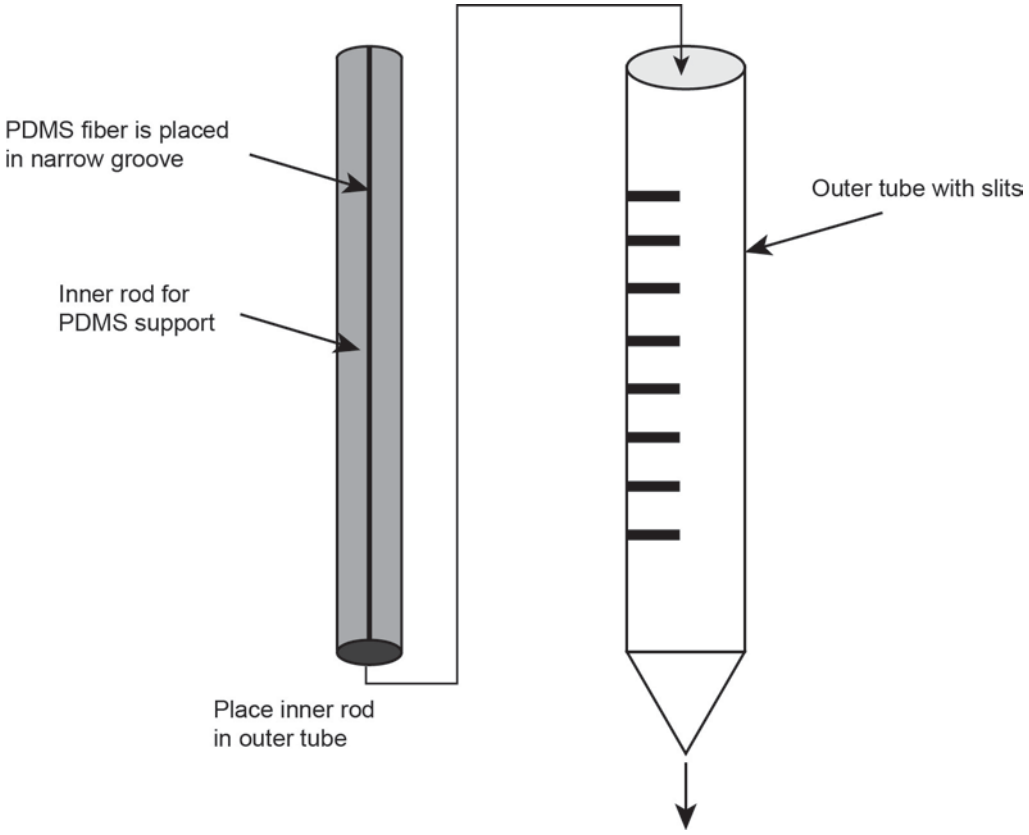
Prior to deployment, individual PDMS-coated glass fibers are placed into the inner rod of the sampler, in an approximately 2-mm-wide rectangular groove in the inner rod. This inner rod is placed into a protective case consisting of a piezometer with approximately 0.5-mm-thick slits cut at a spacing interval of 6 mm. These openings in the casing allow sediment porewater to flow to the PDMS-coated glass fiber surface throughout the study. The bottom and top of each rod will be sealed with silicone caulk to prevent an inflow of sediment through the system during deployment.





[1] A fiber unit volume of 115.5 µL of PDMS per meter of fiber was reported in the 2012 RI report. This has been recalculated to be 113.8 µL assuming a total outer diameter of 1,070 µm in the PDMS coated glass fiber and a glass fiber diameter of 1,000 µm as per factory specifications.

The SPME sampling device containing the PDMS-coated glass fiber is inserted into the modified piezometer rod, as shown below, to protect the fiber from potential mechanical degradation during installation into the armor rock cap.



Laboratory and Field Quality Control Samples

Quality assurance and quality control (QA/QC) samples will be collected in all major steps of this study. These samples will include the following:

- Samples collected during the preparation of the samplers to ensure that chemicals detected in samples after exposure in the field did not come from the original fibers themselves or from elements of the sampling apparatus such as caulk
- Samples collected during sampler deployment to ensure that contamination is not introduced during the transportation to and installation of the SPME sampling devices in the field

- Samples collected during sampler retrieval to ensure that contamination is not introduced during the procedures of collecting the samplers in the field
- Replicate samples to assess the variability of the results of samples in the field
- Preparation of materials to support laboratory internal quality control samples, including blank spikes, blank spike duplicates, and blank samples.

A summary of these quality control samples is presented in Table 1. The details of quality control sample preparation and collection are described in the relevant section below.

Study Stage	QA/QC Sample Types	Purpose	Frequency
Sampler Preparation	Caulk blank	Ensure caulk used in samplers does not contribute 2,3,7,8-TCDD, 2,3,7,8-TCDF, or 2,3,4,7,8-PeCDF to final sample	1
	SPME blank	Ensure fibers do not contain 2,3,7,8-TCDD, 2,3,7,8-TCDF, or 2,3,4,7,8-PeCDF prior to deployment	1
	Solvent rinse blank	Ensure that decontamination of samplers prior to deployment is effective	2
	Fibers for laboratory quality control	Provide materials for laboratory internal matrix-specific quality control	Three 5-cm long fibers
Sampler Deployment	Field replicate samples	Assess field variability	2
	Environmental blank	Assess if air-deposited SPME contamination occurs during sampler deployment	1
Sampler Retrieval	Environmental blank	Assess if air-deposited SPME contamination occurs during sampler retrieval	1
	Temperature blanks	Ensure that samples maintain proper temperature	One per shipping cooler

Notes:
2,3,4,7,8-PeCDF = 2,3,4,7,8-pentachlorodibenzo-*p*-dioxin
2,3,7,8-TCDD = 2,3,7,8-tetrachlorodibenzo-*p*-dioxin
2,3,78-TCDF = 2,3,7,8-tetrachlorodibenzofuran

SUPPLIES AND EQUIPMENT

The equipment required is as follows:

- Preparation
  - Glass fiber coated with PDMS
  - Sampling device, including the modified piezometer to serve as an external sheath
  - Sampler tags
  - Alconox®, Liquinox®, or equivalent industrial detergent
  - Performance reference compound (PRC) stock solution. PRCs for this study are $^{13}C_{12}$-labeled 2,3,7,8-TCDD, 2,3,7,8-TCDF, and 2,3,4,7,8-PeCDF
  - Hexane, pesticide grade or equivalent
  - Distilled water
  - Properly labeled squirt bottles
  - Polyethylene or polypropylene tub (to collect solvent rinsate)
  - Container tubes with caps on both ends, constructed from polyvinyl chloride (PVC) or equivalent and large enough to carry assembled samplers before deployment and after retrieval
  - Drying oven
  - Kimwipes®
  - Waterproof caulk (hydrocarbon-free silicone)
  - Waterproof marker
  - Heavy-duty aluminum foil
  - Personal protective equipment as specified in the health and safety plan (e.g., nitrile gloves)
- Deployment
  - Dive boat (sampling vessel)
  - Diving gear (as stipulated by the dive company)
  - Prepared SPME sampling devices (modified piezometer)and auxiliary fiber holders for surface water samples, wrapped in foil and stored in appropriate containers
  - Differential global positioning system (DGPS)
  - Watch

  - Waterproof sample tags, waterproof marker, and cable ties
  - Hose clamps or zip ties to be used to attach the auxiliary surface water sampler to the primary SPME sampler at three locations
  - Sufficient line to extend from SPME to shore
  - Stakes and flagging tape to affix and mark SPME line on the shore
  - Buoys and tags (if unable to affix SPME line on the shore)
  - Personal protective equipment for field team (e.g., rain gear, steel-toed boots, nitrile gloves)
  - Health and safety plan
  - First aid kit
  - Cell phone
  - Rebar or equivalent (probe)
  - Logbooks, indelible blank-ink pens, and field forms
- Retrieval
  - Dive boat (sampling vessel)
  - Diving gear (as stipulated by the dive company)
  - Sample coolers and ice
  - Container tubes with caps on both ends, constructed from PVC or equivalent and large enough to carry assembled samplers before deployment and after retrieval
  - DGPS
  - Watch
  - Sample tags, waterproof marker, and cable ties
  - Heavy-duty aluminum foil
  - Personal protective equipment for field team (e.g., rain gear, steel-toed boots, nitrile gloves)
  - Health and safety plan
  - First aid kit
  - Cell phone
  - Logbooks, indelible blank-ink pens, waterproof markers, and field forms

- Processing
  - Kimwipes®
  - Deionized water (analyte-free; received from testing laboratory or other reliable source)
  - Heavy-duty aluminum foil
  - Ceramic column cutter
  - Ruler
  - Hexane, pesticide grade or equivalent
  - Auto-pipette, syringe, or other devices capable of delivering volumes of 1 mL and 2 mL
  - 2-mL screw cap auto-sampler vials, amber glass
  - Waterproof marker
  - Personal protective equipment as specified in the Health and Safety Plan.

PROCEDURES

General Procedures

During all procedures discussed herein, the following general guidelines will be followed:

- Fiber samples will be handled with nitrile-gloved hands. At no point should skin contact fibers.
- Sampling and sample processing staff will endeavor to minimize the amount of time fiber samples are exposed to air to minimize the chance of cross contamination.
- The time, place, staff involved, and any deviations from this sampling plan will be rigorously documented in appropriate laboratory and/or field notebooks.

Preparation of Fibers and SPME Sampling Devices

Preparation of the SPME devices will take place in a laboratory prior to deployment in the field. As with all handing of fibers, clean nitrile gloves will be worn for all steps of the preparation process. The sampling devices (modified piezometers) will be disassembled and all surfaces of the individual pieces will be washed with Alconox® (or Liquinox®) and hot water. This wash will be followed by a sequential series of rinses of the pieces of the metal casing with hexane, acetone and distilled water, followed by drying in an oven overnight.

Using one sampler, after the apparatus has been dried, the metal rod that holds the PDMS-coated glass fibers inside the casing and the casing will be rinsed with hexane and the rinsate collected. In addition, prior to assembly of any samplers, all fibers will be rinsed with hexane, and the rinsate collected. This combined rinsate sample will be analyzed immediately and results obtained prior to deployment of samplers.[2] This rinsate will be analyzed as a solvent rinse blank for 2,3,7,8-TCDD, 2,3,7,8-TCDF, and 2,3,4,7,8-PeCDF. Staff preparing fibers will use sufficient volume of solvent to thoroughly rinse the sampling device, but not generate excess solvent.

Two types of fibers will be prepared: sampling fibers and PRC-impregnated fibers. Because the PRC is the same as the target chemical but is $^{13}C_{12}$-labeled, sample fibers will be deployed in separate deployment devices, in separate locations. Spatial segregation of the porewater samplers from samplers containing the PRC-impregnated fibers is necessary to prevent $^{13}C_{12}$-labeled compounds diffusing out of the PRC-impregnated fiber and being absorbed by a sample fiber directly adjacent to it. In this case, spacing between porewater samplers and the sampling device with the PRC should be at least 20 feet.

With 14 stations to be sampled and 5 PRC stations, the following fibers will be prepared:

- Sixteen sampling fibers and fiber deployment equipment for field samples at 14 stations with two replicates.
- Six PRC fibers and deployment equipment for field samples at 5 stations with one replicate.
- The fiber length (both sampling and PRC fibers) will be equal to the design depth of the cap at that location (30 cm for the 12-inch design depth and 45 cm for the 18 inch design depth) to optimize analytical resolution. These fibers will be placed in the bottom of the 2-foot (30 cm-) samplers, so that they sample the design depth immediately above the geotextile fabric.
- Two 5-cm sampling and two PRC fibers for the backup samplers.
- Two 5-cm sampling fibers and one PRC-impregnated fiber in casings appropriate for sampling surface water concentrations (i.e., above the sediments). This sampler will be attached to the end of a 2-foot long sampler that extends above the sediment–water interface. A total of three surface water extensions will be deployed.
- One 5-cm fiber for an SPME blank.
- One 5-cm fiber for a deployment environmental blank sample.

[2] If it is not possible to collect and analyze a single rinsate blank for all fibers associated with the study, and to obtain results prior to deployment of samplers, rinsate blanks for individual fibers may be needed to ensure that each individual fiber is uncontaminated upon deployment. Individual rinsate blanks will allow investigators to address contamination of samplers on an individual sampler basis.

- One 5-cm fiber for a retrieval environmental blank sample.
- Five 5-cm PRC fibers to assess initial PRC concentrations.
- Three 5-cm sample fibers for laboratory quality control samples.

Each sampling device will include one fiber, so the number of fibers that will be cleaned will equal the number of samplers to be assembled, plus the additional fibers prepared for quality control samples.

The sample fibers are used to collect the porewater sample, while the PRC-impregnated fiber is used to indicate the fractional extent of equilibrium of the fiber with the sediment. The initial preparation of the fibers is the same. The PRC-impregnated fibers undergo the additional step of impregnation with PRC.

Prior to assembly, the PDMS-coated glass fibers will be cleaned by soaking in solvent overnight, with hexane as the solvent for the sampling fibers. As is standard throughout this procedure, the fibers will be handled using nitrile-gloved hands. After the PDMS-coated glass fibers have soaked overnight, the fibers will be rinsed with distilled water, and blotted dry with Kimwipes®. After cleaning, the fibers will be wrapped in aluminum foil and placed in a decontaminated container such as a modified PVC tube with caps on each end until the SPME sampling devices are assembled.

The PRC-impregnated fibers are prepared by spiking a known volume of the PRC reference stock solution (which will be mixed with a carrier such as methanol first) into a known volume of deionized water in a volumetric flask and mixing well (at least 10 full inversions), to produce a soaking solution with a specific concentration. The PDMS-coated glass fibers to be impregnated with PRC will be placed into a 5 cm by 1 m glass tube with screw cap ends with Teflon-sealed caps, and tumbled for a minimum of 21 days. After tumbling, five 5-cm segments of the PRC-impregnated fibers will be analyzed to determine the PRC concentrations in the PDMS of the impregnated fibers.

The sampling devices themselves will be prepared after all the fibers are prepared. A cleaned sampling fiber, or fiber impregnated with the PRC, will be placed into the groove on the side of the inner rod of the sampler. To make sure the fiber is securely in place, a clean, nitrile-gloved finger should be run along the groove. Then, the entire inner rod will be inserted into the sampling device casing, and the casing will be affixed with approximately 1 cm of waterproof, hydrocarbon-free, silicone caulk at both ends. The caulk will serve to hold the fiber in place, and fill any gaps in the insertion tool, eliminating any vertical water movement. Silicone caulk shall not be placed anywhere on the screened length (i.e., the active measurement portion) of the insertion tool. The device preparer will also avoid placing excessive caulk that could hinder the insertion tool separation during sample retrieval and processing. One complete sampler will be rinsed with hexane and the rinsate collected as a second rinsate blank, to ensure that samplers are not contaminated prior to deployment.

Each of the samplers will be labeled with a unique sampler number with a waterproof marker on a waterproof tag attached to the SPME sampling device handle. The length of fiber loaded onto each sampling device will be documented to the nearest millimeter, and the length entered in the laboratory notebook for that sampler. Samplers containing a PRC fiber will be given a unique sampler number and will be clearly noted as such with a waterproof marker and tag on the deployment device. Once each sampling device has been loaded with the inner rod containing a sampling fiber or a PRC-impregnated fiber, the caulk will be allowed to dry for 1 hour. After assembly, each sampling device will be wrapped individually in aluminum foil and stored in a sealed container (e.g., modified PVC tube with caps) in a secure location prior to deployment.

Sample Custody and Shipping

Sample custody will be maintained in accordance with procedures outlined in Section 3.2 of the Field Sampling Plan (FSP) and detailed in SOP AP-03, *Sample Custody*. Samplers prepared and stored in the SPME laboratory will be documented on chain-of-custody (COC) forms, and maintained in a secure cooler at the laboratory prior to deployment. Upon deployment, COCs will be signed by the SPME laboratory into the custody of the Anchor QEA field lead. At the time of retrieval, a second set of COCs will be completed in the field, and used to document custody of samplers through analysis at the analytical laboratory.

Summary of Analytical and Quality Control Samples Developed during Sampler Preparation

The following analytical samples will be collected during sampler preparation:

- A caulk blank sample, consisting of a 1-g aliquot of the caulk used to attach the fibers to the sampling device in a glass jar.
- An SPME fiber blank sample. This sample consists of an SPME sampling device that is identical to the SPME sampling devices that are deployed in the field. Following preparation, the SPME blank will be stored in foil, placed in a sealed container and shipped to the analytical laboratory just prior to the field event. The SPME field blank will be stored by the analytical laboratory at 4±2°C. The SPME field blank will be analyzed at the same time as those that were deployed in the field.
- A solvent rinse blank sample of all sample fibers and a single cleaned apparatus prior to assembly.
- A solvent rinse blank of a fully assembled sampler collected prior to deployment.
- Five PRC-impregnated fibers for analysis of the initial PRC concentration in the fibers.

In addition to the samples sent to the laboratory, the following materials will be prepared for subsequent quality control analysis:

- One fiber for a deployment environmental blank sample
- One fiber for a retrieval environmental blank sample
- Three 5-cm sample fibers for laboratory quality control samples.

Deployment

In waters greater than ~1 m depth, deployment of SPME sampling devices will be done by trained, appropriately certified scuba divers or sampling personnel wading. The divers will deploy the devices as described below.

When the diver reaches a station, the diver, assisted by sampling crew on the surface boat, will insert rebar or a similar metal rod of known length into the cap to determine the thickness of the cap at that location (taking care not to penetrate the geotextile underlying the cap). Depending on the design depth of the cap at that location (either 12 or 18 inches), different lengths of the SPME sampling device will be used (30 or 45 cm).[3] Samplers must be pushed down to the geotextile, taking care that the device does not penetrate the geotextile material. In the area without geotextile (the Armor Cap Material A in the northwestern portion of the armored cap), the sampling device should be installed to the design depth of the armored cap in that area (12 inches), or until a significant textural change is felt at the base of the armor cap if that change is apparent before penetrating 12 inches.

The diver and surface crew will then measure the amount of "stick up" of the probe above the cap surface to determine the depth of penetration by subtraction. The field lead, or designee, at the surface will record the thickness of the cap in the field log. The penetration depth of the SPME sampling device placed at this sampling location will be approximately equal to the depth of the armored cap at that station, as measured by the probing device.

Before the deployment of any SPME devices, the field team will shut off all petroleum-driven motors, and don fresh nitrile gloves before handling the foil-wrapped, prepared SPME sampling devices. The prepared SPME sampling device will be removed from the airtight transportation container and the aluminum foil protective wrap will be removed. A second tag, in addition to the sampler number tag, will be affixed to the handle of the SPME sampling device with a cable tie. The tag must contain the following information:

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[3] In this document, in references to the cap, English units are used to be consistent with other project documents. In references to the SPME fiber lengths, metric units are used to facilitate calculations.

The SPME sampling device will be inserted along the surface of the cap probing device and perpendicular to the sediment surface by the diver, to a depth just above the geotextile membrane on top of the cap in locations where the geotextile base is present (see Figure A-3 of the FSP), taking care that the device does not penetrate the geotextile material. After the SPME sampling device is in place, the probing device will be gently removed and armor cap materials will naturally fill in any void space around the SPME device that may be left by the removal of the probe. Armored Cap Material A in the northwestern portion of the armored cap does not have a geotextile underlayment. In this area, the sampling device should be installed to the design depth of the armored cap in that area (12 inches), or until a significant textural change is felt at the base of the armor cap if that change is apparent before penetrating 12 inches. All sampling devices will be connected via nylon cording to stakes marked with flagging tape or to buoys that will serve as markers for their retrieval after the exposure period.

At all locations, the 2-foot SPME sampling device should be sufficiently long to extend above the cap surface–water interface. In two sampling locations and one PRC location, these will be deployed such that an auxiliary casing with a length of fiber for the water sample can be attached to the portion of the device that extends at least 6 inches above the cap surface. This auxiliary device will be attached to the sampler with decontaminated hose clamps, zip ties, or similar. This length of fiber will provide a sample that can be used to estimate the concentration of 2,3,7,8-TCDD, 2,3,7,8-TCDF, and 2,3,4,7,8-PeCDF in the surface water, with all the fiber in the auxiliary device above the sediment–water interface. The following information will be recorded in the field logbook at the time of deployment for each deployment location:

- Date and time that the SPME sampling device was inserted into the cap
- Station number
- The sampler number assigned to the SPME sampling device in the preparation step
- The length of the SPME sampling device that was inserted into the cap at a given location
- Water depth
- Depth of sediment or cap material into which the sample is deployed
- Notation of any petroleum-driven motor watercraft being used in the area of the sampling vessel
- DGPS station location coordinates
- Photograph numbers for a specific station
- Information from the diver on the description of the area near the station (e.g., vegetation, debris, evidence of surface disturbance, organisms).

After deployment, the SPME sampling devices will be left *in situ* for approximately 60 days (see project-specific FSP).

Deployment Quality Control Samples

The following field quality control samples will be collected in the field during SPME sampling device deployment and analyzed by the analytical laboratory:

- Field replicate samples are co-located with SPME sampling devices at two locations, and collected in an identical manner over the same exposure period to provide a measure of the field and laboratory variance, including variance resulting from sample heterogeneity. Field replicate samples will be prepared by deploying and collecting two completely separate SPME sampling devices from the same station and submitting them for analysis as separate samples. Samplers will be assigned unique sample numbers in the field and will not be identified as field splits to the laboratory.
- The environmental blank is prepared in the field to evaluate potential background concentrations present in the air during deployment.

  To prepare an environmental blank in the field, the foil is removed from a prepared SPME sampling device while at a sample collection site, the SPME is exposed to the ambient air during the time that the diver is underwater for the period of deployment of one sampler, and then resealed in the foil. The environmental blank is assigned a unique sample number on a tag affixed to the handle of the SPME sampling device according to the sample numbering scheme. The environmental blank will then be placed in a sealed container and taken or shipped to the analytical laboratory. The SPME environmental blank will be stored by the analytical laboratory at 4±2°C, and analyzed at the same time as those that were deployed in the field.

Field Measurements

A water depth measurement will be collected at every sampling location. The depth of penetration of the cap will also be recorded. There are no field measurements of the *in situ* environment required for this study.

Station Location Coordinates

Station locations for all field sampling will be determined using a DGPS. The accuracy to which the latitude and longitude of a station location is determined is specified in the FSP. The DGPS consists of two satellite receivers linked to each other by a VHF telemetry radio system. The receiver will be on the sampling vessel. Details on collection of accurate station coordinates can be found in SOP AP-06, *Navigation.*

Retrieval

After completion of the exposure period of approximately 60 days, the field team and the dive crew will return to each sampling location to retrieve the SPME sampling devices.

Once on station, all petroleum-driven motors will be turned off.

Once a sampler is located, it will not be disturbed until the location on the SPME casing of the sediment-water interface is marked by affixing a zip tie on the sampler at the sediment surface. The zip tie must be sufficiently firmly placed to remain in place until samplers are processed in the laboratory. The SPME sampling device will then be removed from the sediment surface by the diver and immediately transported up to the sampling vessel. SPME sampling devices from only one station will be collected before returning to the sampling vessel. Only one SPME will be collected and handled by the divers at a time.

Before taking the retrieved SPME sampling device from the diver, sampling personnel will don a new, clean pair of nitrile gloves at each station. The tag affixed to the handle of the SPME sampling device will be checked to confirm the station number. If the tag is missing or illegible, a replacement tag with the sample ID will be attached to the sampler. The SPME will be immediately wrapped in aluminum foil and placed into a sealed container, and stored in coolers on ice at 4±2°C.

The following information will be recorded in the field logbook:

- Date and time that the SPME sampling device was retrieved
- Length of the sampler below the zip tie used to indicate the position of the cap surface upon retrieval by the diver
- Station number
- Sampler number
- Water depth
- Notation of any petroleum-driven motors watercraft being used in the area of the sampling vessel
- DGPS station location coordinates
- Photograph number for a specific station
- Information from the diver on the description of the area near the station (e.g., vegetation, debris, evidence of surface disturbance, organisms).

Field Quality Control Samples

Details on collection of field quality control samples (e.g., field replicate SPME sampling devices) are specified in the project-specific FSP and above. At a minimum, the following field quality control samples will be collected in the field during SPME sampling device retrieval and analyzed by the analytical laboratory:

- An environmental blank will be collected during sample retrieval. The environmental blank will be prepared in the field by removing the foil from prepared SPME sampling device while at a sample collection site, exposing the SPME during the time that the diver is underwater, and then resealing it in the foil. The environmental blank will be assigned a unique sample number on a tag affixed to the handle of the SPME sampling device. The foil-wrapped environmental blank will then be placed in an appropriate closed container and taken or shipped to the analytical laboratory. The SPME environmental blank will be stored by the analytical laboratory at 4±2°C. The SPME environmental blank will be analyzed at the same time as those that were deployed in the field.
- Temperature blanks will be used by the laboratory to verify the temperature of the samples upon receipt at the testing laboratory. Temperature blanks will be prepared at the testing laboratory by pouring distilled/deionized water into a vial and tightly closing the lid. The blanks will be transported unopened to and from the field in the cooler with the sample containers. A temperature blank shall be included with each sample cooler shipped to the testing laboratory.

Field Measurements

A water depth measurement must be collected at every sampling location during sample retrieval.

Station Location Coordinates

Station locations for all field sampling will be confirmed during sample retrieval using a DGPS. Details on collection of accurate station coordinates can be found in SOP AP-06, *Navigation.*

Sample Custody and Shipping

Sample custody will be maintained in accordance with procedures outlined in SOP AP-03, *Sample Custody*. Upon retrieval, a second set of COCs will be prepared by the Anchor QEA field team, and will accompany the samplers the transfer to the analytical laboratory. All samples will be packaged and shipped (or may be delivered by courier) in accordance with procedures outlined in SOP AP-01, *Sample Packaging and Shipping*.

Processing

SPME processing will take place at the analytical laboratory. The SPME sampling device will be dismantled and the fiber carefully removed from the inner rod using nitrile-gloved hands. Each fiber will then be rinsed with deionized water and placed on a foil-covered surface. During this process, laboratory staff will take care to keep track of the position of the sediment–water interface on the sampler casing. If the fibers are broken at the time of removal, the sample handler will maintain the relative vertical position of the pieces. The overall length of the fiber recovered will be documented to the nearest millimeter in the laboratory bench sheet or log book, including notation of any missing pieces or broken fibers. Each fiber will be rinsed thoroughly with deionized water.

For each depth interval to be sampled, one 2-mL auto-sampler vial will be prefilled with 2 mL of hexane. These vials will be labeled with a waterproof marker noting the solvent and volume used. If the samples are prepared at the analytical laboratory, the laboratory blank will be prepared using the same solvent as is placed into the vials.

A ceramic column cutter will then be used to section the fiber from each location into 5-cm lengths at the depth intervals specified in the FSP, and the lengths will be recorded. The 5-cm lengths will then subsequently be cut into to 1–2 cm segments and placed into prefilled 2-mL amber auto-sampler vials. Between each cut of fiber required for a unique sample (within a given sampling device), the ceramic column cutter will be decontaminated.

The cap on the vial will be sealed and, using a waterproof marker, labeled with the sample ID, whether the fiber is a PRC-impregnated or sample fiber, total length of segments in the vial, date and time the sample was processed, and the analysis to be conducted; this information will also be noted on the laboratory bench sheet or logbook. The meniscus of the solvent will be marked on the vial with a waterproof marker.

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ATTACHMENT 3
AGENCY COMMENTS ON DRAFT TCRA CAP POREWATER ASSESSMENT ADDENDUM 1 AND RESPONSES

Table 1. EPA Comments on SJRWP Draft *Sampling and Analysis Plan: TCRA Cap Porewater Assessment Addendum 1*, and Responses

Comment No.	Section	Page	Line	Comment	Response to Comment—Proposed Revision
EPA1				Depending on the limitations of the available SPME (solid-phase micro extraction) technology, the PRPs shall ensure that the proposed approach is capable of detecting porewater concentrations at or below the human health Texas surface water quality standard (i.e., 7.97 x 10^{-8} ug/L (or 0.0797 pg/L) 2,3,7,8 –tetra-chloro-dibenzo-p-dioxin (TCDD) equivalents.	Detection limits are estimated from information available prior to conducting the study. The information used to estimate detection limits includes regression models and octanol-water partition coefficients (K_{ow}). The draft *Sampling and Analysis Plan: TCRA Cap Porewater Assessment Addendum 1* (Porewater SAP Addendum 1) presents three methods (in Table 1) for estimating the porewater concentration from the resulting mass of a target compound in the sampling fiber. Using two of these (the log K_{ow} of Govers and Krop [1998] and the published regression model of Hsieh et al. [2011]), we estimate that the study design and equipment will produce results that, when converted to estimated porewater concentrations, will have a value of 0.04 pg/L toxicity equivalent, dioxins and furans (TEQ_{DF}). The study design and equipment are therefore consistent with the U.S. Environmental Protection Agency's (EPA's) requirement for analytical sensitivity sufficient to report 0.0797 pg/L TEQ_{DF}. Details have been added to the text to explain how this calculation is performed and how this conclusion is substantiated. To clarify the estimation of detection limits using the SPME equipment that will be used in this study, the information presented in the draft Porewater SAP Addendum 1 has been revised to be consistent with past presentations (i.e., in the remedial investigation report and in the time-critical removal action [TCRA] cap porewater assessment SAP). For consistency with data generation and presentation in 2012 and 2013, the regression model developed by Anchor QEA has been removed from the document, including its use in Table 2 and its presentation in Attachment 3. The Anchor QEA model has not undergone peer review; therefore, Hsieh et al (2011), which is also the model presented in prior documentation, is preferred. A correction to calculations made in the preparation of the draft Porewater SAP Addendum 1 was also required. An error in the calculation of detection limits was such that the poly-di-methyl-siloxane (PDMS) volume on each fiber was incorrectly assumed to be 58.8 µL/m when it was actually 113.8 µL/m. As a result of this error, the "Calculated Detection Limit in Pore Water (pg/L)" values were inflated in Table 2 of the draft Porewater SAP Addendum 1. The error has been corrected for each congener by applying the correct assumptions to the estimates using the regression model by Hsieh et al. 2011. Please also note a correction to the text of the subject document on p. 5 that describes the results of the 2012 study. Results of that study confirmed that estimated porewater and surface water concentrations were at or below the Texas surface water quality standard, not below 0.01 pg/L, as stated previously.
EPA2				It is not clear if Figure 2 provides the number and locations of proposed pore water samples, or sampling performed in the past. In any case, the Addendum shall provide information on the number and types of samples to be collected, and provide a table of these samples, as was provided in Addendum 3 to the sediment sampling plan.	Figure 2 is intended to convey the number and locations of samplers to be deployed. Text has been added to clarify this, and the requested table has been provided.
EPA3				The Addendum shall include one additional porewater sampling location in the northwest portion of the cap where an area of rock displacement was identified.	Sampling station SJCP001 and its associated duplicate SJCP001-SP1-DUP, already located in close proximity to this area, have been relocated to sample the exact location where rock displacement was identified.

EPA4				The 2012 assessment targeted 2,3,7,8-TCDD and 2,3,7,8-TCDF in porewater. For the winter 2015/2016 monitoring, 2,3,4,7,8-PeCDF will be added to the analytes. The Kfw (fiber-water partition coefficients) are different than those used in 2012. Additionally, it is unclear if the fiber unit volumes are the same. The Addendum shall discuss the reason for this difference and how it may impact comparisons with the 2012 porewater results.	This change was implemented at the request of EPA. We have revised the document to improve consistency with the 2012 study. The K_{fw} values presented for TCDD and TCDF have been revised using the approach described in our response to comment EPA1. This approach relies on Hsieh et al. (2011); we will no longer consider the unpublished regression model presented in Attachment 3 of the draft Porewater SAP Addendum 1; the second column of log K_{fw} values (footnote c) has been removed from Table 1, and Attachment 3 has been removed. The K_{fw} value for 2,3,4,7,8-PeCDF calculated using the regression model of Hsieh et al. (2011) will remain as shown in Table 1 of the draft SAP. Further, the values for the partition coefficients shown in Table 1 that were rounded to two significant figures will be restored to three significant figures, to be consistent with the K_{ow} values estimated from Govers and Krop (1998). Attachment 2 to the subject document describes the SPME method. Page 2 of the attachment specifies the diameter of the fibers and thickness of the PDMS to be used. These specifications are the same as for the 2012 porewater assessment. However, the fiber unit volume described in the 2012 TCRA cap porewater assessment SAP was found to be incorrect; it has been corrected in the text of Attachment 2 (fiber unit volume is 113.8 µL/m, not 115.5 µL/m). This will have no impact on comparisons with 2012 porewater results.
EPA5				The Addendum estimated Kfw values for dioxins based on a regression equation correlating Kfw with octanol-water partition coefficients for PCBs, pesticides, and PAHs. There was a brief discussion on this derivation (i.e., Attachment 3). The Addendum shall evaluate the discussion in DiFilippo and Eganhouse (DiFilippo, E.L., and R.P. Eganhouse. 2010. Assessment of PDMS-Water Partition Coefficients: Implications of Passive Environmental Sampling of Hydrophobic Organic Compounds. Environmental Science and Technology. 44(18): 6917-6925), and determine if the conditions in the selected studies are similar to the expected site temperature and fiber coating thickness of the selected SPME fibers. The Addendum shall adjust the regression equation if this analysis indicates a need to re-evaluate the studies used in the Kfw and logKow correlation proposed for this study.	Please see response to comments EPA1 and EPA4. The document has been revised for consistency with the 2012 study, including the use of Hsieh et al (2011) to estimate K_{fw} values, and the use of K_{ow} values from Govers and Krop (1998). Hsieh et al. (2011) conducted all experiments at 25°C. Water temperatures within the cap porewater are not expected to depart substantially from this value, so any temperature impact on the estimated K_{fw} values will be minimal relative to analytical uncertainty and relative to the uncertainty in the K_{fw} values themselves. We therefore do not anticipate a need to correct Hsieh et al. (2011) K_{fw} values for temperature. The Porewater SAP Addendum 1 has been revised to clearly state that no temperature corrections were made when reporting porewater concentrations, consistent with practical passive sampling guidance (Ghosh et al. 2014). As described by DiFilippo and Eganhouse (2010), the coating thickness should not impact K_{fw} values.
EPA6				While the deployment of sampling devices is described in some detail, the procedures and Quality Assurance information for chemical analysis of the poly-di-methyl-siloxane (PDMS) fibers are not provided. The Addendum shall provide more detail on the analytical and quality assurance procedures, so that the quality of the results can be evaluated. The Addendum shall also discuss why it is necessary to limit analysis to only three of the seventeen dioxin/furan congeners that are typically quantified.	As noted on page 8 of the subject document, "…the analytical SOPs for dioxins and furans are the same as those included in the Sediment SAP Addendum 3 and are not repeated…." Thus the standard operating procedures are available in Sediment SAP Addendum 3 and are incorporated by reference. Text on pages 5 and 6 explains that the three selected congeners account for more than 90 percent of the risk attributable to dioxins and furans associated with exposure to sediments in the hypothetical exposure scenarios addressed by the human health risk assessment. Although it is not necessary to limit the evaluation to these three congeners, by doing so, respondents obtain sufficient information to address the data quality objectives and avoid the logistical challenges of addressing another 14 compounds that will have very little informational value. Text has been added to the discussion of data quality objectives to clarify this.

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