PORTLAND HARBOR RI/FS

ROUND 2 GROUNDWATER PATHWAY ASSESSMENT SAMPLING AND ANALYSIS PLAN

ATTACHMENT 2
FIELD SAMPLING PLAN
TRANSITION ZONE WATER SAMPLING

~~DRAFT~~

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~~July 8~~~~February 24~~March 27, 200~~5~~6

Prepared for

The Lower Willamette Group

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ASTM	American Society for Testing and Materials
BTEX	benzene, toluene, ethylbenzene, xylenes
CAS	Columbia Analytical Services
CAS	Colombia Analytical Services, Inc.
CH	clean hands
COC	chain-of-custody
COI	chemical of interest
DDD	dichloro-diphenyl-dichloroethane
DDE	dichloro-diphenyl-dichloroethene
DDT	dichloro-diphenyl-trichloroethane
DGPS	digital geographical positiong system
DH	dirty hands
DI	deionized
DQO	data quality objective
EPA	U.S. Environmental Protection Agency
FSP	field sampling plan
GC/ECD	gas chromatography/electron capture detector
GC/FPD	gas chromatography/flame photometric detection
GPS	geographical position system
HSP	health and safety plan
LDPE	low-density polyethylene
LNAPL	light non-aqueous phase liquid
MSS	Marine Samplin Systems
MTBE	methyl-tert-butyl ether
MW	monitoring well
NAPL	non-aqueous phase liquid
PAH	polycyclic aromatic hydrocarbon
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
RI/FS	remedial investigation and feasibility study
SAP	sampling analysis plan
SOP	standard operating procedure
SVOC	semivolatile organic compound
TDS	total dissolved solids
TPAH	total polycyclic aromatic hydrocarbons
TPH	total petroleum hydrocarbons
TPH-D	diesel-range total petroleum hydrocarbons
TPH-G	gas-range total petroleum hydrocarbons
TPH-R	residual-range total petroleum hydrocarbons
TZW	transition zone water
USGS	U.S. Geological Survey

VOC	volatile organic compound

FOREWORD

This document is Attachment 2 to the Round 2 Groundwater Pathway Assessment Sampling and Analysis Plan (Integral et al. 2005). This attachment presents the analysis of the transition zone water sampling results from the pilot study (Integral 2004a) as well as the field sampling plan for collection of transition zone water samples and sediments at nine sites along the Willamette River. Detailed sampling plans for the nine sites are presented in Addendum 1 and Addendum 2 (Integral 2005a,b). This final draft of Attachment 2 has been prepared following completion of the subject field work (completed December 2, 2005) to provide a complete and final document, which responds to comments and reflects the modifications to the sampling effort agreed upon for conditional approval by EPA and its agency partners.

1. INTRODUCTION

This field sampling plan (FSP), which is Attachment 2 to the Round 2 Groundwater Pathway Assessment Sampling and Analysis Plan (SAP), presents the approach and procedures for transition zone water sampling to support the Round 2 Groundwater Pathway Assessment for the Portland Harbor Remedial Investigation and Feasibility Study (RI/FS).

Transition zone water sampling is the second phase of the Round 2 Groundwater Pathway Assessment and ~~will~~ follows mapping of potential areas of groundwater discharge to the Willamette River from upland sites. Attachment 1 to the SAP details the discharge mapping program. The ~~objective of the~~ field work described in this FSP ~~is to collect and analyze samples of transition zone water~~is intended ~~-~~to quantify concentrations of groundwater-related chemicals of interest (COIs) in areas of plume discharge identified during the groundwater discharge mapping field effort.

As described in the SAP, ~~data needs~~this FSP addresses ~~related to~~ transition zone water sampling ~~are considered in this FSP for~~offshore of the following nine sites:

- Kinder Morgan Linnton Terminal
- ARCO Terminal 22T
- ExxonMobil Oil Terminal
- Gasco
- Siltronic
- Rhone Poulenc (Bayer)
- Arkema
- Willbridge Bulk Fuels Terminal
- Gunderson.

Groundwater discharge mapping and transition zone water sampling may also be performed at the Oregon Steel Mills and Premier Edible Oils sites under Round 3 of the RI/FS, depending on the findings from shoreline groundwater investigations planned for 2005 at these two sites. The need, if any, for groundwater discharge mapping and transition zone water sampling at these sites will be determined in consultation with EPA during Round 3 scoping.~~Specifically, if the planned upland investigations at these sites either 1) show evidence supporting the existence of a complete pathway to the river or 2) are not finished before the completion of Round 3 scoping, groundwater discharge mapping and transition zone water sampling at one or both of these sites may be identified as a Round 3 data gap.~~

Project and site-specific background information are presented in detail in Appendix A of the SAP.

The remaining sections of this report include the following information:

- **Section 2** presents an overview of the transition zone water sampling results from the Round 2 Groundwater Pathway Assessment Pilot Study, which was performed in late 2004 and early 2005. This discussion includes intra-method and inter-method comparisons of the transition zone water sampling results to evaluate the reproducibility and comparability of the transition zone sampling methods—forming the basis for the selection of sampling methods that will be implemented during the Round 2 Groundwater Pathway Assessment. Complete pilot study data sets are presented in the Pilot Study Data Report (Appendix B of the SAP).
- **Section 3** presents a discussion of the transition zone water sampling results in relation to upland groundwater conditions and pilot study discharge mapping results at the three study areas considered in the pilot study.
- **Section 4** presents the planned approach for developing the transition zone water sampling programs for each site based on the groundwater discharge mapping results.
- **Section 5** presents the schedule for the transition zone water sampling program.
- **Section 6** presents standard operating procedures (SOPs) for the field investigation.
- **Section 7** provides the references cited in this FSP.

Detailed site-specific sampling plans were~~were~~ prepared and submitted to U.S. Environmental Protection Agency (EPA) as addenda to this FSP following completion and evaluation of groundwater discharge mapping at each site. The FSP addenda ~~will ~~include, for each site, a summary of the results of the discharge mapping findings, relevant site background information including maps and cross sections showing the nature and extent of COIs in groundwater, a map of the proposed transition zone water sample locations, planned sampling methods for each location, and a table summarizing sample counts, target depth intervals, and COIs to be analyzed. In addition, the addenda ~~will include~~provide a brief summary of the rationale supporting the selection of the proposed sampling locations for each site.

2. ANALYSIS OF PILOT STUDY TRANSITION ZONE WATER SAMPLING METHODS

A pilot study was performed in late 2004 and early 2005 to evaluate selected groundwater discharge mapping tools and transition zone water sampling methods under realistic field conditions to support scoping of the Round 2 Groundwater Pathway Assessment. The scope of the pilot study is described in detail in the Groundwater Pathway Assessment Pilot Study Field Sampling Plan (Integral 2004a). Detailed results of the pilot study are presented in the Groundwater Pathway Assessment Pilot Study Data Report (Appendix B of the SAP).

~~The following~~This section presents an evaluation of the pilot study findings to assess the effectiveness of the tested transition zone water sampling methods. The various transition zone water sampling methods are evaluated in terms of the method implementability, reproducibility of results in sample replicates, and inter-method comparability. This evaluation forms the basis for transition zone water sampling method selection for the Round 2 Groundwater Pathway Assessment.

2.1. OVERVIEW OF PILOT STUDY TRANSITION ~~ZONE~~ ZONE WATER SAMPLING

The transition zone water sampling portion of the pilot study was performed from November 2004 to January 2005 at two sites within the Portland Harbor Superfund Site Study Area – ARCO Bulk Terminal (ARCO) and Arkema Inc. (Arkema; formerly ATOFINA Chemicals, Inc.). These two sites included three study areas: 1) the ARCO dock area, 2) the area offshore of the former Arkema Acid Plant, and 3) the area offshore of the former Arkema Chlorate Plant. The specific transition zone water sampling techniques evaluated and activities performed are summarized in this section.

~~The following~~Six transition zone water sampling techniques were evaluated in the pilot study: the Trident Probe, the UltraSeep System, small- and large-volume peepers, vapor diffusion samplers, and bulk sediment sampling and centrifuge separation. These tools were selected based on an analysis of available methods for transition zone water sampling, considering the advantages and disadvantages of the methods relative to the predominant conditions in the lower Willamette River and the objectives of the Round 2 Groundwater Pathway Assessment. This analysis and the specific transition zone sampling methods selected for the pilot study are described in detail in the Pilot Study FSP (Integral 2004a). Most aspects of the discharge mapping phase of the pilot study were implemented as planned in the FSP; however, some deviations occurred, largely due to unanticipated field conditions and/or response to observations made in the field. These deviations are detailed in the Groundwater Pathway Assessment Pilot Study Data Report (Appendix B of the SAP).

Analyte groups sampled during the pilot study are presented for each site and sampling method in Table 2-1. This table also explains why select analyte groups were not sampled by certain methods and why certain methods were not used. Reasons cited include site access issues, volume limitations, anticipated method limitations, and field observation of excessive sediment in sample containers.

Transition zone water samples were collected during the pilot study at three locations ~~from~~ in each of the three study areas using each of the sampling methods,[1] ~~,~~ with the exception of the UltraSeep. The UltraSeep seepage meter and sampling system was deployed three times during the pilot study, and samples were collected during two of the deployments[2] offshore of the Arkema site. The locations for the transition zone water samples were selected based on the results of the groundwater discharge mapping component of the pilot study (Figures 2-1 through 2-3). The Trident and UltraSeep sampling efforts were completed from November 19-24, 2004. The diffusion-based sampling devices (small- and large-volume peepers, vapor diffusion samplers) were deployed from December 20-22, 2004 and retrieved January 10-12, 2005. The bulk sediment samples were collected from January 18-21, 2005. Bulk sediment samples were couriered to the analytical laboratory (Columbia Analytical Services in Kelso, WA) following completion of the sampling effort, where they were centrifuged to separate the transition zone water from the sediments within 1-2 days upon receipt at the laboratory.

In conjunction with the transition zone water sampling effort at the ARCO site, a barge-mounted, direct-push drill rig was used to collect lithologic data and shallow groundwater samples from two depths beneath each of the transition zone water sampling locations. This sampling was completed February 7 and 8, 2004.

The following sections describe each of the transition zone water sampling methods evaluated in the pilot study.

2.1.1. Trident Probe

The Trident Probe is a simple, direct-push system equipped with temperature, conductivity, and water sampling probes (Figure 2-4). Transition zone water is collected through a small-diameter, Teflon®-coated, stainless-steel probe. Near the tip of the probe there is a sample port covered by a small mesh (241-µm), stainless-steel screen. The Trident Probe is driven to the desired depth in the sediment, and water is drawn through tubing connected to the sampling probe using a peristaltic pump. A sand pack is often placed over the sampling probe to prevent/delay clogging

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[1] A fourth location was sampled with the Trident Probe at the Chlorate Plant area to provide additional insight into conditions observed while mapping temperature and conductivity.

[2] During the deployment at station AP04D at the Arkema Acid Plant, no discharge was observed by the Ultrasonic flow meter; therefore, the sampler was not triggered.

of the intake by silt and clay. ~~During the pilot study, t~~Transition zone water was ~~primarily~~ collected from a depth of 30 cm below ~~the~~ mud~~-~~line. ~~, although at~~ At one location (CP-07-B), a second sample was also collected at 60 cm, for comparison with COI concentrations at 30 cm and testing of the equipment's capabilities.~~.~~

2.1.2. UltraSeep System

The UltraSeep system is a seepage meter that is capable of time-series flow-rate measurement and automated sample collection (Figure 2-5). The meter relies on a Teflon®-coated, stainless-steel, open-bottomed chamber measuring 48 × 46 cm to funnel the seepage water to a flow sensor. The flow sensor is connected to the high point of the funnel via 12-mm Teflon® tubing, allowing free flow of water between the funnel and the outside environment. Based on the measured flow conditions, the water sampling system is activated during periods of active groundwater discharge[3] to pump water to up to six sequential Teflon® sampling bags mounted around the perimeter of the meter. Additional details and system specifications are presented in SSC et al. (2003). During the pilot study, the UltraSeep was deployed for a 24-hour period at three locations—all of which were offshore of the Arkema site[4]—~~—~~AP04B and AP04D offshore of the former Acid Plant area and CP07B offshore of the former Chlorate Plant area.

2.1.3. Small-Volume Peepers

The small-volume peepers used during the pilot study are commercially available, 6-~~inch~~ × 18-~~-~~inch plate peepers (Figure 2-6). The plate peeper is equipped with 28 rows of sample ports ranging in volume between 3.5 mL and 9 mL. The sampler is capable of collecting approximately 250 mL of water over a 38-cm sediment depth. The peepers were fitted with a ~5-µm Teflon® membrane. Prior to deployment, the small-volume peepers were filled with anoxic DI water. The entire peeper assembly was maintained in an anoxic (argon-sparged) water bath~~atmosphere~~ until immediately prior to deployment.

The small-volume peepers were deployed by a diver, who drove or pushed the peepers directly into the sediments until the uppermost sampling port was just below the sediment mudline (i.e., the ports were spaced from 0 – 38 cm below the sediment surface). Multiple peepers were deployed at each sampling location, as necessary, to achieve sufficient sample volume by compositing. All of the peepers were left in place to equilibrate for a 3-week period, after which they were retrieved and brought to the surface. Water was then extracted from each of the sample ports by inserting a needle through the membrane and extracting the water with a syringe. Each sample

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[3] Sampling is only activated when there is a measured positive flux of groundwater discharge to the river. Sampling is de-activated during periods when surface water is ~~discharging~~ recharging to the sediments (defined as a negative flux).

[4] Access to the ARCO site was ~~limited~~ prevented during the UltraSeep deployment phase of the pilot study due to conflicts with the facility's barge schedule.

bottle was filled with water from sample ports distributed across the entire peeper to ensure that the sample was a vertical composite, representative of the entire 38-cm depth of sediment.

2.1.4. Large-Volume Peepers

The large-volume peepers were ~~specially~~ constructed using a perforated 1,000-mL polyethylene bottle and a 41-µm macrofilter mesh. A series of ~1-inch-diameter holes were drilled into each of the bottles and the mesh wrapped around the bottle to cover the holes. The mesh was placed over the holes in the bottles and affixed using Teflon® tape overlain by stainless-steel hose clamps (see Figure 2-~~.~~6). Prior to deployment, the peepers were filled with anoxic deionized (DI) water. The entire peeper assembly was maintained in an anoxic (argon-sparged) water bath~~atmosphere~~ until immediately prior to deployment.

The large-volume peepers were deployed by a diver. In soft bottom sediments, the diver was able to gently loosen the sediments with one hand such that the peeper could be gently pushed into the sediment with his other hand to a depth of typically 7 to 10 inches below the sediment surface. This approach minimized the sediment disturbance and loss of fine-grained materials to the overlying water column. This approach was not feasible in coarser-grained sediments. At such locations, the large-volume peepers were installed by placing the peeper in a hole excavated in the sediment using a stainless-steel trowel and backfilling the hole with sediment. This ~~approach~~ often resulted in a loss of considerable amount of fine-grained material to the flowing river water, and it was ~~difficult~~ not always possible to maintain the integrity of the excavated hole in areas with steeply sloping river bottom. In some cases, these conditions limited the depth of burial that could be achieved for the large-volume peepers.

Multiple peepers were deployed at each sampling location, as necessary, to achieve sufficient total sample volume by compositing. All of the peepers were left in place to equilibrate for a 3-week period. After this equilibration period, the peepers were retrieved and brought to the surface. At the surface, each large-volume peeper was immediately transferred to a 1-gallon Ziploc® bag, which was in turn placed in a container filled with water. This equalized the pressure on the bottle, allowing for the cap of the peeper to be removed without causing the water to flow out of the peeper through the mesh-covered holes. Water from within the peeper was then removed using a peristaltic pump and dedicated tubing, and directed to the appropriate sample bottles.

2.1.5. Vapor Diffusion Samplers

The vapor diffusion samplers consisted of an uncapped, glass vial enclosed in two sealed polyethylene membranes (two sealable sandwich bags; Figure 2-7). A diver deployed three samplers at each sampling location (6 at replicate stations) by pushing the samplers to a sediment depth of approximately 6 inches. In locations where the sediments consisted of coarse-grained materials, the samplers were installed by placing the sampler in a 7- to 8-inch deep hole excavated in the sediment using a stainless-steel trowel and backfilling the hole with sediment. This approach often resulted in the loss of a considerable amount of fine-grained material from the sediments to the flowing river water. Further, it was ~~difficult~~ not always possible to maintain the integrity of the excavated hole in these locations, particularly when located in areas where the river bottom slope was relatively steep.

The samplers were left in the sediment for a 3-week period to allow volatile chemicals in the transition zone water to equilibrate with the air in the sampler by vapor diffusion across the polyethylene membranes. After equilibration, the samplers were retrieved, the outer bag removed, and the ~~bottle~~ septum cap was~~-~~ ~~sealed~~ replaced with the inner bag still in place. The samplers were visually inspected for rips in the inner polyethylene bag ~~that may have compromised the sample~~ or for the presence of water in the sampler, which would indicate that the sampler was compromised. Any samplers with torn membranes and/or with water present were discarded.

2.1.6. Bulk Sediment Sample and Centrifuge Separation

Bulk sediment samples were collected from the upper ~30 cm of sediment at each of the nine sampling locations using a power grab sampler. Once the sampler was brought to the surface, butyrate tubing was used to remove undisturbed subsamples from the sampler. A series of approximately 35-cm-long, 6-cm-diameter tubes were pushed into the sediment in the bucket of the power grab sampler. Once all of the tubes were in place, caps were placed on the ends of each tube extending out of the sediment to establish suction within the tubes. Each tube was then extracted from the sampler and the other end of the tube capped. The tubes (subsamples) were stored at 4°C and couriered to Columbia Analytical Services (CAS) in Kelso, WA. At CAS, the subsamples were transferred to an oxygen-free atmosphere (glove box), where some of the subsamples were centrifuged to separate out the transition zone water. Subsamples not centrifuged were used for analysis of bulk sediment chemical concentrations.

2.1.7. Direct Push Screen Point Sampling of Groundwater

At the three ARCO locations, a barge-mounted, direct-push drill rig equipped with a screen point sampler was used to collect shallow groundwater samples from two depths zones (3-5 ft and 6-8 ft below the mudline) below the transition zone water sampling locations.[5] Two boreholes were advanced at each location. Continuous sediment cores were collected and logged from the first borehole, and these data were used to select target intervals for groundwater sampling. Following termination of the first borehole in each pair, the Geoprobe® was moved a short distance (1-2 ft),

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[5] Geoprobe® samples were not collected offshore of the Arkema site during the pilot study because in-water Geoprobe® data are available from a previous investigation conducted by Arkema.

and the second borehole was advanced to collect the groundwater samples. Groundwater samples were collected from two discrete intervals within the second borehole of each borehole pair. Three pore volumes of the screen point sampler and tubing were purged using a peristaltic pump prior to collection of the samples.

2.2. FIELD OBSERVATIONS OF METHOD IMPLEMENTABILITY

This section presents an overview of the implementability of each of the sampling methods as influenced by conditions encountered in the field.

2.2.1. Trident Probe

The Trident Probe was ~~most~~ an efficient method~~effective~~ for sampling transition zone water in coarse-grained sediments (sands and gravels), as these materials yielded the transition zone water at a reasonable rate (>50 mL/min) during pumping. It should be noted, however, that during the discharge mapping effort the probe was unable to penetrate the sediment at three locations where the sediment was armored with large cobbles. These locations would have presented a challenge to sampling by all of the other transition zone water sampling methods as well.

The Trident Probe was less effective for sampling in fine-grained silt or clay sediments, as these materials typically yielded ~~poor~~ much lower transition zone water extraction rates (<10 mL/min). As a result, the Trident Probe is not considered to be suitable for collection of volatile organic compounds (VOCs) from these types of sediments due to the potential for volatiles loss during filling of the VOA vials. Additionally, the~~se~~ low ~~production~~ yield rates in fine-grained sediments make the Trident impractical for collection of relatively large sample volumes needed for some analyte groups (e.g., pesticides, PAHs, SVOCs)~~ from such areas~~. ~~While~~ During pumping ~~transition zone water~~ from ~~zones of~~ fine-grained sediments, the sand pack around the probe ~~was observed to clog~~clogged with particulates over time. Once the sand pack was clogged, continued sampling required that the Trident Probe be removed, the sand pack replaced, and the probe redeployed and purged.

A key consideration in ~~use of~~sampling with the Trident Probe ~~for sampling transition zone water~~ ~~is~~was to ensure that sufficient purging ~~has~~ had taken place. As expected, the water initially pumped from the probe was highly turbid in most cases—particularly in the fine-grained sediments. The water ~~was observed to~~ clarified~~clarify fairly~~ rapidly as additional water was purged from the probe.

2.2.2. UltraSeep

As ~~is~~ illustrated by the water quality data in Table 3-1b, the water samples collected by the UltraSeep system tended to be of lower concentration than samples collected from the same location using other methods. This finding is consistent with the expected influence/capture of river water in the samples collected by the system.

Although the UltraSeep does not actively collect water samples during periods of river recharge, the system, by design,[6]~~,~~ allows river water to enter the funnel at the rate of the negative groundwater flux. As a result, some river water brought into the funnel under negative groundwater discharge conditions will ultimately be captured by the UltraSeep sampler when the hydraulic system fluctuates to a positive groundwater discharge condition and the sampler is activated. At the two locations sampled by the UltraSeep during the pilot study (AP04B and CP07B), flux across the sediment interface ~~was found to cycle~~cycled from positive (active groundwater discharge) to negative (river water recharge)—generally in response to the tidal conditions. At the third location (AP04D), the flux was predominantly negative. Further, even when a positive groundwater discharge was measured, the specific discharge rates were low (maximum 15-minute reading of ~6 cm/d, measured at CP07B). As a result, the sample volumes were very low. Volume limitations allowed for collection of only unfiltered samples at the former Chlorate Plant Area, and only VOC samples from the positive flow sample at the former Acid Plant Area.

2.2.3. Small-Volume Peepers

The small-volume peepers were ~~found to be~~ most conducive to sampling transition zone water in fine-grained ("soft") sediments, into which the peepers could be most easily driven or pushed. The peepers were also fairly readily deployed at several locations containing coarse-grained, sandy sediments; however, deployment into sediments with significant cobbles and/or hard, consolidated materials was more difficult and at one location, AR03B, infeasible.

In a limited number of cases, the membrane of the small-volume peepers ~~was found to have torn~~ tore during the installation and/or ~~deployment~~ retrieval of the sampler. Tears were typically limited to only a few sample ports associated with the sampler and did not appear to have altered the integrity of the remaining sample ports. Use of the small-volume peepers for transition zone water sampling proved to be ~~fairly~~ labor and time- intensive. ~~In particular, extensive time was required for p~~Peeper assembly and ~~for~~ extraction of water from the samplers were particularly time consuming. Additionally, sample volume is limited in small-volume peepers (each peeper contains 225 mL of water); therefore, the analyte list was reduced in comparison to other methods. In accordance with the Pilot Study SAP (Integral 2004a), filtered samples, conventional analytes, metals from the former Acid Plant Area, and diesel-range total petroleum hydrocarbons (TPH-D)~~d~~ from the ARCO site were not collected.

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[6] The system is designed to measure both positive and negative groundwater flux at the sediment water interface. As such, the system is open to both directions of flow. Consequently, inclusion of river water in the samples, proportional to river water influx, is inherent to the system design.

2.2.4. Large-Volume Peepers

The large-volume peepers were ~~found to be~~ most conducive to sampling transition zone water in fine-grained "soft" sediments, into which the peepers could be most easily pushed. Deployment of the large-volume peepers in coarse-grained sediments required placing the peeper in a hole excavated in the sediment and backfilling the hole with sediment. This approach often resulted in a loss of considerable amount of fine-grained material to the flowing river water. Because of this, it is suspected that the sediment conditions were ~~significantly~~ altered in the immediate vicinity of the large-volume peepers. It was also ~~difficult~~ not always possible to maintain the integrity of the excavated hole in areas with steeply sloping river bottom. In some cases, these conditions limited the depth of burial that could be achieved for the large-volume peepers. These conditions were so pronounced at location CP07B that a large-volume peeper could not be deployed. Upon recovery, several of the peepers had considerable sediment present in the bottom of the sampler, generally as a result of visible breaches in the seal of the membrane around the sampler. At the ARCO site, in response to the observed presence of excessive sediment in the large-volume peepers upon retrieval, only filtered samples were collected (except for VOCs and gasoline-range TPH [TPH-G]).

2.2.5. Vapor Diffusion Samplers

As with the large-volume peepers, the vapor diffusion samplers were ~~found to be~~ most conducive to sampling transition zone water in fine-grained "soft" sediments, into which the samplers could be most easily pushed. A hole in the sediment had to be excavated to deploy the samplers in coarse-grained sediments, which resulted in loss of much of the fine-grained portion of the sediment and, at times, limited the depth of burial that could be achieved. More than half of the samplers were found to be compromised, with both the outer and inner membrane ripped (or the seal was broken), resulting in leakage of water into the sampler. This likely occurred during deployment/recovery operations. Compromised samplers were not submitted for analysis. Appropriate to the method and according to the pilot study field sampling plan (Integral 2004a), the analyte list was limited to VOCs.

2.2.6. Power Grab/Centrifuge Separation Samples

The power grab sampler is a versatile tool for collection of samples from a range of sediment types. At a few locations, the sampler was not able to recover sediment materials over the entire 30-cm depth targeted. The centrifuge separation process was found to be labor-~~-~~intensive and, due to logistical constraints, could not be completed until 1-2 days following the collection of the sediment sample. During planning (Integral 2004a), it was recognized that volatile chemicals could easily be lost during centrifugation; therefore, VOCs were not analyzed for samples collected using ~~analyzed for s collected~~this method.

2.3. INTRA-METHOD EVALUATION (METHOD REPRODUCIBILITY)

This section presents a~~n~~ review of analytical results to explore the reliability of the methods used in the pilot study. Reliability was assessed by examining reproducibility of replicate samples within each method. Intra-method variability and bias among sample replicates were evaluated by calculating Pearson's correlation coefficients,[7] intraclass correlation coefficients,[8] and percentage estimators of variation.

The Pearson's correlation (r) coefficient is a measure of systemic correlation between paired values from two datasets. The Pearson's correlation coefficient does not, however, provide information on systematic bias between the two datasets. Values of r approaching 1.0 indicate very good correlation. The formula to calculate r is:

$$r = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 \sum_{i=1}^{n}(y_i - \bar{y})^2}},$$

where $\bar{x}$ and $\bar{y}$ are the mean values of the two compared data sets, and n is the number of data points in the data sets.

The Intraclass correlation coefficient (ρ_i), however, is a combined measure of correlation and bias. In combination, correlation and bias are defined here as reproducibility.

The formula to calculate ρ_i is:

$$\rho_i = \frac{MS_B - MS_W}{MS_B + MS_W},$$

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[7] The Pearson product moment correlation coefficient (r) is the ratio of the covariation between the analyte concentrations in the two replicate samplers to the amount of covariation that would exist if the samplers had a perfect positive correlation. It should be noted that the Pearson correlation coefficient does not reflect system bias. Therefore, a good Pearson-type correlation does not necessarily indicate that the replicates are close to each other in value; instead it indicates that the ratio between the replicates is consistent. In other words, in interpreting results, it should be understood that a consistent bias, such as a 2:1 ratio between data sets, will give a good Pearson-type correlation.

[8] The Intraclass Correlation Coefficient (ρ_1) is a measure of the reproducibility of replicate results. Specifically, ρ_i equals the ratio of the between-analyte variance to the sum of the between- and within-analyte variance. The Intraclass Correlation Coefficient is used for pairs where designation as the dependent or independent variable is arbitrary. Specific applications include comparison of tests of the same subject by two judges or two methods and comparison of split sample laboratory results (Rosner 1995).

where MS_B refers to the mean of the squares between groups, and MS_W refers to the mean of the squares within groups.

The following ranges for ρ_i are considered standard for interpreting results (Fleiss 1986):

- $\rho_i \geq 0.8$ indicates excellent reproducibility
- $0.4 \leq \rho_i < 0.8$ indicates fair to good reproducibility
- $\rho_i < 0.4$ indicates poor reproducibility.

2.3.1. Replicate Data

The replicate samples used in this analysis were collected by placing two sets of samplers for each given sampling method at selected locations. ~~It should be noted that the r~~Replicate samples were collected at locations as close to the original samples as practicable~~; however, they are not truly collocated~~ (estimated to be typically within one to five feet). Consequently, results also include the inherent spatial variability on the scale of the distance between replicate and original samples. ~~This distance is estimated to have ranged between roughly 1 and 5 feet.~~

Three replicate pairs (one from each study area) were collected during the pilot study using the Trident, small-volume peepers, large-volume peepers, and the power grab (water and sediment). One replicate pair was collected at the Arkema Acid Plant area with the vapor diffusion samplers.[9] Additionally, filtered replicate pairs were collected at each site for the Trident, large-volume peepers, and power grab (water collected by centrifuge).

2.3.2. Data Processing

The first-level analysis of the replicate data consisted of preparing a pairwise detection/analysis summary. This analysis simply tabulated counts (for each replicate pair) of the number of analytes for which the following conditions were true:

- Both values (original and replicate) for the analyte were reported above detection limits
- Both values (original and replicate) for the analyte were reported below detection limits

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[9] No vapor diffusion samplers were deployed at the Chlorate Plant study area because VOCs were not on the analyte list. The replicate sample (all 3 VOA vials) at the ARCO study area was found to be compromised when retrieved.

- One value was reported as detected, while the other was reported ~~as~~ below detection limits
- The analyte was analyzed for in one sample, but not in the other (original or replicate).

The values are presented for each replicate pair in Table 2-~~1~~2. In general, this information showed that most replicate analyses were repeatable on the level of detect vs. nondetect (92% of analytes were either detected in both the original and the replicate or not detected in either). The pairwise detection summary was also used to provide additional insight into correlation coefficient results.

Pearson and Intraclass correlation coefficients were calculated for each replicate pair. The data set used for each pair was limited to analytes for which one or both of the samples demonstrated a detectable concentration (otherwise, the analysis would be biased to a comparison of reported detection limits) and more than two analytes were detected (otherwise, the dataset would be too small for statistical evaluation).

2.3.3. Intra-Method Evaluation Results

All calculated correlation coefficients (Pearson's and Intraclass) are presented in Table 2-~~2~~3, differentiated by study area and sampling method. With Pearson's correlation coefficients ranging from 0.97 to 0.99 and Intraclass correlation coefficients ranging from 0.91 to 0.99, replicate pairs at the ARCO site showed excellent reproducibility for the Trident samples, the small-volume peeper samples, the large-volume peeper samples, and the power grab sediment samples. In contrast, both the filtered and unfiltered centrifuged water samples from the power grab showed good correlation but poor reproducibility, with Pearson's coefficients of 0.99, but Intraclass correlation coefficients of 0.71 and 0.38, respectively.

The Arkema Chlorate Plant replicate data set showed similar findings, with excellent reproducibility for the Trident, small-volume peepers, and large-volume peepers (Pearson's correlation coefficients of 0.99 for all methods; ~~I~~intraclass correlation coefficients ranging from 0.85 to 0.99). Correlation coefficients for the power grab replicates from the Chlorate Plant could not be calculated because all the results were below detection limits.

The Arkema Acid Plant replicate data set showed generally poor reproducibility for all methods (Table 2-3). One exception was the filtered Trident samples (Pearson's and Intraclass correlation coefficients of 0.98 and 0.92, respectively); however, it should be noted that only conventional parameters and pesticides were analyzed in the filtered Trident sample (conventional parameters correlated fairly well between replicates for all methods at the Acid Plant). The poor reproducibility for methods at the Acid Plant area may reflect spatial variability at the replicate sampling site

(AP03B). Variability in concentrations observed at this location is ~~presented~~ discussed in greater detail in the inter-method evaluation ~~(~~Sections 2.4.1.2 and 2.4.2~~)~~.

In summary, the Trident, small-volume peepers, large-volume peepers, and power grab sediment replicates showed generally good reproducibility, with the exception of the Acid Plant replicate samples. The vapor diffusion sampler replicates were only available for the Acid Plant and, like other methods, showed poor reproducibility for this study area. The centrifuged power grab samples showed consistently poor reproducibility and should be considered cautiously for future application to transition zone water sampling.

2.4. INTER-METHOD COMPARISON OF CHEMICAL RESULTS

This section presents an analysis of the pilot study results focusing on the variability between sampling methods applied at the same sampling location. All data sets were considered qualitatively and, where possible, the assessments were supported by statistical analysis. The analysis compares analytical results across methods, looking for any consistent biases. Inter-method variability and bias were evaluated within classes of chemicals using Wilcoxon Rank-Sum tests (Mann-Whitney *U* tests)[10] and Kruskal-Wallis[11] tests.

The inter-method evaluation considered all pilot study water sampling results, applying the following data processing to generate workable data sets for the analyses. First, all results below the detection limit were set to zero.[12] ~~.~~ ~~–~~Next, chemicals detected by only one or by none of the methods at a given location were excluded from the rank-sum tests. Each chemical was then assigned to one of the following chemical classes: major ions, metals, VOCs, polycyclic aromatic hydrocarbons (PAHs), ~~total petroleum hydrocarbons (~~TPH~~s)~~, pesticides, or perchlorate.[13] In cases where entire chemical classes were represented by only one analyte [i.e., perchlorate at the Chlorate Plant, and metals (chromium) at the Chlorate Plant], only qualitative comparisons could be made, without the support of statistical

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[10] The Wilcoxon Rank-Sum test is the non~~-~~parametric analog to the paired t-test. It compares any two methods based on the ranks of the concentrations, rather than their actual values. The test orders results, ranks them, and scores each method by the rank. Significant difference between methods is determined both by difference in rank score and by sample size, but not magnitude of values.

[11] The Kruskal-Wallis test is a generalized form of the Wilcoxon Rank-Sum test and is able to compare multiple independent variables.

[12] Due to the wide range of detection limits reported for the various methods, it was decided that setting nondetect values to zero was the best way to limit the confounding effect of ~~this challenge in the~~variable detection limits ~~data set~~. In some cases, using a fraction of the detection limit would ~~greatly~~have confused the analysis, as ~~many~~ detection limits for some methods were sometimes ~~were~~ well above reported detected concentrations ~~at a given location by a different~~for other methods.

[13] The data were grouped to help answer questions about the performance of each method relative to a given chemical class (e.g., How well did small-volume peepers perform for VOCs as compared to large-volume peepers?).

analysis.[14] The major ions chemical class was also excluded from the statistical analysis, deferring to the more detailed analysis of major ions signatures presented in Sections 2.7, 3.1.2, and 3.2.2.

The data processing resulted in the following data sets for statistical inter-method analysis:

- VOCs at the Acid Plant
- Pesticides at the Acid Plant
- Individual PAHs at ARCO
- LPAHs at ARCO
- HPAHs at ARCO
- TPH~~s~~ at ARCO
- Metals (zinc, copper, lead, arsenic) at ARCO.

A complete list of analytes excluded and included in the statistical inter-method analysis is presented in Table 2-4a.

Data for which the statistical inter-method analysis could not be performed were considered without statistical support and are included, as such, in the following discussion of results. These data sets include:

- Benzene, toluene, ethylbenzene, and xylenes (BTEX) at ARCO[15]
- Manganese at the Acid Plant
- Perchlorate at the Chlorate Plant
- Chromium at the Chlorate Plant.

2.4.1. Inter-Method Statistical Analysis

As mentioned above, inter-method variability and bias were evaluated within classes of chemicals using Wilcoxon Rank-Sum tests (Mann-Whitney *U* tests) and Kruskal-Wallis tests, where applicable. A threshold of $\alpha = 0.05$ was applied to define significant difference between methods (Rosner 1995). Observed inter-method variability and the Wilcoxon Rank-Sum and Kruskal-Wallis test results are discussed below for each site. A summary of the results of the statistical analyses is presented in Table 2-~~3~~4b, including α-values for each test.

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[14] The statistical significance of methodological differences between measured values of a single chemical cannot be evaluated using central tendency comparisons due to limited sample size.

[15] All BTEX concentrations measured at ARCO were less than 1.5 µg/L, which were too close to the limit of detection to allow for meaningful conclusions.

The statistical analysis presented herein assesses inter-method variability assuming sampling locations at a given site are perfectly ~~collocated~~co-located between methods. In other words, this analysis does not take into account spatial variability in concentration that may be reflected in the actual difference in sampling locations between methods (i.e., at a given sampling station, the small-volume peepers may have been deployed ~~4~~ 10 to 15 feet~~meters~~ from the corresponding sampling station for the Trident). The difference in sampling locations between methods is estimated to be up to 30 feet.

2.4.1.1. ARCO

Variability between transition zone water sampling methods was assessed for the ARCO study area by comparing results for PAHs (including LPAHs and HPAHs), metals, and TPH~~s~~. Results are presented in Figures 2-8, 2-9, and 2-10, respectively. BTEX was also analyzed in samples from ARCO; however, all results were less than 1.5 µg/L, and were considered too close to the detection limits to draw conclusions about inter-method variability.

PAH distributions show that centrifuged water samples from the power grab consistently had the highest concentrations (Figure 2-8a, b, and c). The rank-sum tests indicate that the filtered and unfiltered power grab results were not significantly different from one another. As is discussed in Section 2.6, it is hypothesized that the ~~the large forces generated during~~ centrifugation process mobilized sub-0.45µm colloids and/or residual NAPL from the sediments, which would not otherwise be mobile and therefore not observed in the transition zone samples collected by other methods. Additionally, the ~~PAH results show that the~~ small-volume peeper results were ~~s demonstrated~~ significantly higher than the Trident (filtered and unfiltered) for ~~the~~ LPAHs, but lower than the unfiltered Trident and higher than the filtered Trident for HPAHs. ~~It is not clear why f~~Filtered large volume peeper results were greater than filtered Trident results for PAHs. ~~; however, it~~~~PAH concentrations than did the Trident (filtered and unfiltered) or large-volume peeper results. The reason for this difference is unclear, but is should be noted that, w~~With the exception of AR03B, the large majority of the individual PAH results ~~are~~ were less than 1 µg/L for the small-volume peeper, Trident, and large-volume peeper. The greater variability at AR03B (concentrations of <10 µg/L) may be attributable to localized spatial variability.

For metals at ARCO, although plotting the transition zone water metals data from the ARCO site (Figure 2-9) visually suggests some variability between the sampling methods, the rank-sum tests indicated that there ~~is~~ was no significant difference across methods for the metals as a group. The rank-sum tests also indicated that AR02B has significantly lower metals concentrations than the other ARCO sampling locations.

The rank-sum statistical tests for TPH (Figure 2-10) indicated that power grab results ~~are~~ were significantly higher than the other methods (small-volume peepers and large-volume peepers). This further supports the hypothesis that the ~~large forces generated during~~ centrifugation of the samples may have mobilized sub-0.45µm colloids and/or residual NAPL from the sediments, which would not otherwise be mobile (see Section 2.6).

2.4.1.2. Acid Plant

Variability between methods was assessed for the Acid Plant study area, considering analytical results for ~~VOCs,~~ manganese, ~~and~~ pesticides, and VOCs~~, and VOCs~~. ~~At the Acid Plant, the full VOC project list was analyzed. The distribution of VOC concentrations for each sample location is presented in Figure 2-11, grouped by sampling method. The statistical rank-sum tests indicate that Trident and small-volume peeper results were not significantly different for VOCs. Large-volume peeper and UltraSeep results were both significantly lower than the Trident and small-volume peeper results, but were not statistically different from one another [(Trident = small-volume peeper) > (large-volume peeper = UltraSeep)]. Also apparent in Figure 2-11, VOCs detected at higher concentrations (chlorobenzene, chloroform, methylene chloride, and benzene) were consistent across methods for a given sampling station. VOCs were also analyzed from the vapor diffusion samplers. Results[16] compared poorly with all other sampling methods, failing to detect chloroform or methylene chloride at AP03B (observed at high concentrations by Trident and small-volume peepers), and detecting only a total of six individual VOC compounds inconsistently in four samples.~~

~~Manganese and pesticide results at the Acid Plant were also used to assess inter-method variability.~~ Sampling results are presented in Figures 2-~~12~~ 11, 2-12, and 2-13 ~~and 2-13~~12, differentiated by location and method. Manganese and pesticide results at the Acid Plant were also used to assess inter-method variability. For manganese (Figure 2-11),[17]~~,~~ Trident samples (filtered) showed the highest concentrations among all methods for which manganese samples were collected (see Table 2-1). ~~From~~ For pesticides (Figure 2-~~1312~~12), it is clear that higher concentrations of pesticides were found in the unfiltered transition zone water samples (Trident, power grab, and large-volume peeper). ~~This finding is supported by rank-sum test results (Table 2-3).~~

It should be noted that filtration removed almost all of the pesticides in the Trident and large-volume peeper samples, but not in the power grab samples. As discussed in Section 2.6, this phenomenon has been observed by Carignan et al. (1985), who

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[16] Gaseous concentrations by volume were converted to corresponding aqueous concentrations, assuming equilibrium, using Henry's constants for each detected analyte. Henry's constant values were calculated based on transition zone water temperatures measured with the Trident. Results and conversions to aqueous concentrations are presented in the Pilot Study Data Report (Appendix B to the SAP).

[17] Note: Rank-Sum tests are not applicable to inter-method comparison for single analytes.

attributed this effect to mobilization of sub-0.45 µm colloids by the centrifuge process.

At the Acid Plant, the full VOC project list was analyzed. The distribution of VOC concentrations for each sample location is presented in Figure 2-~~13~~13, grouped by sampling method. The statistical rank-sum tests indicate that Trident and small-volume peeper results were not significantly different for VOCs. Large-volume peeper and UltraSeep results were both significantly lower than the Trident and small-volume peeper results, but were not statistically different from one another [(Trident = small-volume peeper) > (large-volume peeper = UltraSeep)]. Also apparent in Figure 2-13, VOCs detected at higher concentrations (chlorobenzene, chloroform, methylene chloride, and benzene) were consistent across methods for a given sampling station. VOCs were also analyzed from the vapor diffusion samplers. Results[18] compared poorly with all other sampling methods, failing to detect chloroform or methylene chloride at AP03B (observed at high concentrations by Trident and small-volume peepers), and detecting only a total of six individual VOC compounds inconsistently in four samples. The subsections below further explore the VOC results for each of the Acid Plant area sampling locations (Figure 2-2), focusing on Trident and small-volume peeper results.

AP03B

Nearshore sampling station AP03B is characterized by sandy surface sediments. Permeability of these sediments is relatively high, as evidenced by yield rates of 100 mL/min during purging and sampling with a peristaltic pump using the Trident. Replicate samples were collected using both the Trident and small-volume peeper sampling methods. Figure 2-14a compares concentrations of selected individual VOCs detected in one or both of the replicate pairs. Two primary observations are evident: (1) The small-volume peeper sampling results consistently show much greater variability than the Trident results, and (2) the Trident results consistently lie within the range bracketed by the small-volume peeper results. These observations are consistent with the findings discussed in Section 2.3.3 that the Trident replicate samples showed better overall correlation and reproducibility than the small-volume peeper replicate samples at this location.

AP04B

Nearshore sampling station AP04B is located at the transition between the sandy nearshore sediments and mixed sand/silt farther offshore. Observed permeability of these sediments is relatively high, as evidenced by yield rates of 100 mL/min during purging and sampling with a peristaltic pump using the Trident. Transition zone water samples were collected for VOC analysis using both the Trident and small-volume

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[18] Gaseous concentrations by volume were converted to corresponding aqueous concentrations, assuming equilibrium, using Henry's constants for each detected analyte. Henry's constant values were calculated based on transition zone water temperatures measured with the Trident. Results and conversions to aqueous concentrations are presented in the Pilot Study Data Report (Appendix B to the SAP).

peeper sampling methods. Figure 2-14b compares concentrations of selected individual VOCs detected in one or both samples. These results show no systematic bias. It is notable that the results for the three chemicals detected at the highest concentrations—benzene, chlorobenzene, and toluene—were very consistent between the two sampling methods shown.

AP04D

Sampling station AP04D is located just offshore of Arkema Dock 1. The surface sediment texture at this location is characterized as silt/clay, consistent with the very low yield rate of 5 mL/min observed during purging and sampling with a peristaltic pump using the Trident. Transition zone water samples were collected for VOC analysis using both the Trident and small-volume peeper sampling methods. Figure 2-14c compares concentrations of selected individual VOCs detected in one or both samples. Although interpretation of this data set is somewhat limited by elevated detection limits in the small-volume peeper results, results for VOCs detected by both sampling methods at this location show a consistent negative bias in the Trident results. It is plausible that the low yield rates observed during purging and sampling using the Trident resulted in VOC losses due to volatilization (at the purge rate of 5 mL/min, it took roughly 8 minutes to fill a single VOA vial). This result suggests limiting Trident sampling of VOCs to locations where a much higher pumping yield rate can be maintained.

2.4.1.3. Chlorate Plant

Variability between methods was assessed for the Chlorate Plant study area by comparing results for total chromium and perchlorate, as shown in Figure 2-154. [Note: a large-volume peeper sample was not collected at station CP07B ~~this location~~ due to difficulty in deploying the sampler in the coarse-grained sediments (see Section 2.2.4).] The concentrations of total chromium and perchlorate were higher in samples from station CP07B as compared to CP08D and CP06C—a finding that is consistent with Trident discharge mapping results and UltraSeep measurements, which identified CP07B as an area of increased groundwater discharge. The large-volume peeper concentrations of chromium at CP06C and CP08D are likely due to the presence of sediment in the samples, and are not representative of the mobile chromium in the transition zone water. Sediment was observed in the large-volume peepers upon retrieval.

For station CP07B, t~~T~~he Trident samples showed higher concentrations than other methods for total chromium (both filtered and unfiltered). Perchlorate was only detected at appreciable concentrations at CP07B. At this location, the power grab sample showed the highest concentration. The Trident (original and replicate) sample concentrations were also elevated and found to be comparable to the small-volume peepers. ~~A large-volume peeper sample was not collected at this location due to difficulty in deploying the sampler in the coarse-grained sediments (see Section 2.2.4).~~

2.4.2. Additional Methodological Considerations

Some variability is expected in the chemical results for field replicates from all environmental sampling due to both heterogeneities of the natural system and the expected range of variability associated with limitations on the accuracy and precision of laboratory analytical techniques. (Considering this, the degree of replication of results at locations AR06B and CP07B by small-volume peepers and Trident is exceptional.) Some variability between results for the small-volume peepers and Trident is also expected given the significant difference in sampling physics (i.e., diffusion vs. mechanical extraction) and scale that the sampling methods test. The diffusion-based small-volume peepers sample from a very small ~~areas~~ region in the immediate vicinity of the device, whereas the Trident integrates over a larger area represented by the zone of capture during extraction of the transition zone water sample from the sediments. This may explain the observations from the pilot study of lower overall variability between replicates using the Trident. It is also noted that Trident sampling would be expected to be more comparable with samples collected using other screen-point sampling techniques, such as Geoprobe®, since the methods are fundamentally the same.

2.5. EFFECTS OF FILTRATION

The effects of filtration through a 0.45-µm filter were assessed for all methods and analytes for which filtered samples were collected in parallel with unfiltered samples. Ideally, sampling methods for transition zone water should sample only the transition zone water and the suspended and dissolved materials that are naturally mobile in the system. Avoiding entrainment of sediment particles that are not naturally mobile in the transition zone water is a major challenge in the sampling process. Filtration can be used to establish a particle-size cutoff during sampling to minimize the effects of sampling-induced mobilization of sediments. Here, filtration was performed to provide additional insight into the performance of the various sampling tools with regard to sampling-induced sediment entrainment. A summary of the percent reduction in concentration following filtration is presented in Table 2-45.

In general, results followed expectations based on analyte solubility for both Trident and large-volume peepers. As anticipated, filtration resulted in a large percent decrease in concentration of low solubility/highly sorbing COIs. For pesticides and certain metals (~~Zn, Cu, and Pb~~zinc, copper, and lead), removal upon filtration was on the order of 97 - 100%. Chromium removal by filtration was more variable, ranging from 5% (by Trident) to 100% (by large-volume peeper). Removal by filtration for PAHs also covered a large range (36 - 100%). The more soluble analytes (i.e., chloride, sulfate, perchlorate, arsenic) showed little to no reduction following filtration.

The centrifuged water samples from the power grab typically showed less of an effect of filtration. This is likely attributable to the fact that centrifugation of the sample has an effect similar to filtration, creating a sample with little or no particulate matter larger than 0.45 µm. For the power grab water samples, the mean pesticide removal by filtration was 40% (DDD) to 70% (DDT); mean TPH-~~diesel~~D removal was 70%; PAH removal varied between 7% (acenapthene) and 100% (2-methylnapthalene).

2.6. EFFECTS OF CENTRIFUGATION

The inter-method statistical analysis found that the TPH and PAH concentrations measured in the transition zone water samples collected by ~~separation~~ centrifugation of~~from the power grab~~ bulk sediment samples were biased high relative to the concentrations of these compounds measured by the other ~~transition zone water~~ sampling methods. Furthermore, as discussed in Sections 3.1.4 and 3.1.6, the TPH and PAH concentrations measured in the ~~power grab transition zone water~~ centrifuged samples are elevated relative to the concentrations expected to be associated with groundwater discharging from the ARCO site. It is suspected that the anomalously~~-~~ high TPH and PAH results may be an artifact of the centrifugation process~~ used to separate the transition zone water from the bulk sediment samples collected by the power grab. The large forces generated during centrifuging~~, which may have resulted in the release of chemicals (hydrocarbons and PAHs) to the sediment pore water.

Carignan et al. (1985) recorded evidence that colloidal (<0.2 µm) materials can be released from sediments during centrifuge separation of pore water from sediments. The authors found that transition zone water collected by centrifugation~~e separation from bulk sediment samples~~ had higher concentrations of trace metals than samples collected via diffusion-based methods. Further, the concentrations of the metals in the centrifuge porewater samples remained elevated following filtration through a 0.45-µm filter, but were similar to the levels recorded in the diffusion-based samplers when filtered to <0.2 or <0.03 µm.

The findings of Carignan et al. (1985) suggest that the anomalous PAH and TPH results for the ~~power grab~~centrifuged samples may have been the result of the release of colloids or residualized NAPL[19] to the sediment pore water during the centrifuge process. The findings that 1) the elevated levels of TPH and PAHs were only recorded in the ~~power grab transition zone water samples~~centrifuged samples and not in the Trident or diffusion-based sampling devices, and 2) the TPH and PAH levels in the ~~power grab~~ centrifuged transition zone water samples ~~are~~ were elevated relative to upgradient groundwater (see Sections 3.1.4 and 3.1.6), suggest that the TPH and PAH mass associated with the ~~power grab~~ centrifuged ~~transition zone water~~ samples is not mobile or representative of transition zone water conditions.

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[19] In the case of the ARCO pilot study data, the centrifugation process may have resulted in the release of small amounts of residualized (nonmobile) NAPL from the sediments to the power grab transition zone water samples.

The hypothesis that the ~~power grab transition zone water~~centrifuged samples are biased high for PAH compounds is supported by a comparison of the measured concentrations of individual PAH compounds to their ~~water~~ aqueous solubility limits. As shown in Figure 2-16~~5~~, the concentrations of several higher molecular weight PAH compounds approach or exceed their ~~water~~ aqueous solubilities in the two ~~power grab transition zone water~~ centrifuged samples that had the highest PAH concentrations (AR03B and AR06B). The solubility values used in this ~~presentation of information~~evaluation are idealized values for the pure phase of the compound in pure water. A number of factors can increase the apparent solubility of PAHs, including cosolvency effects and mobilization by colloids. With low VOC concentrations observed in all ARCO samples, however, it is unlikely that there are significant cosolvency effects occurring.[20] Likewise, transition water samples from other methods do not indicate colloidal mobilization that would approach the concentrations observed from the centrifuged samples. It should also be noted that a number of other factors can reduce apparent solubility of PAHs, including high salinity and the mole fraction of the PAH in the organic mixture, though these would only decrease apparent~~y~~ PAH solubility, and therefore cannot explain the results from the power grab/centrifuge samples.. Therefore, the hypothesis remains, as suggested by Carignan et al. (1985), that the anomalous PAH and TPH results for the power grab samples were released by centrifugation with the result of the release of colloids or residualized NAPL.

2.7. MAJOR ION ANALYSIS

This section presents a summary of the major ion[21] data for the transition zone water samples, ~~with respect to~~ comparing results from the various sampling methods tested during the pilot study.[22] Additional discussion of the major ion chemistry of the transition zone water is also presented in the site conceptualization discussion in Sections 3.1.2 and 3.2.2~~, as part of discussions of site conceptualizations~~.

The major ion composition measured in the transition zone water samples by the various sampling methods was evaluated relative to that of the river water and groundwater through the use of Piper and Stiff diagrams. Piper diagrams consist of three parts—two three-component ("triangle") diagrams depicting relative anion and

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[20] Cosolvency effects are primarily observed in cases where cosolvents are present in abundance (>10% by volume) and where there is insufficient water to hydrate the majority of the cosolvent molecules, allowing them to surround the solute of interest approximately in proportion to the cosolvent's volume fraction (Schwarzenbach et al. 1992).

[21] In most natural systems, water chemistry is dominated by ~~the~~ specific major cations (calcium, sodium, magnesium, and potassium),~~;~~ and specific major~~the~~ anions (chloride, sulfate, and carbonate).

[22] Due to sample volume constraints, transition zone water for major ion analysis was not collected using the small-volume peepers at the Arkema site. For the same reason, major ion analyses were not performed using the power grab/centrifuge or the UltraSeep.

cation chemistry, and one diamond-shaped diagram between the two triangles that combines the anion and cation chemistry in a single plot. The diameter of the symbol on the diamond-portion of the Piper diagram is linearly proportional to the total dissolved solids (TDS) content of the sample, and is thus a good indicator of the degree of mixing between waters of different TDS content. Stiff diagrams plot the cation and anion concentrations (as meq/L) on a single plot for each individual sample. Combined, these two diagrams are useful tools for comparing the chemistry of the water collected by each the transition zone sampling methods, relative to that of groundwater and surface water.

2.7.1. ARCO Study Area

The Piper diagram presented in Figure 2-17~~6~~ depicts the major ion chemistry for the pilot study transition zone water samples and Geoprobe® groundwater samples at the ARCO study area, relative to available major ion data for river water[23] and uplands groundwater[24] at the site (wells MW-02, MW-05, and MW-08 located at the upgradient side of the site). In general, all of the samples plot in a similar area and are predominantly calcium-carbonate waters. ~~However, the cation and anion chemistry suggests that the transition zone water samples collected by the large-volume peeper may have been influenced by river water.~~

Close inspection of the cation and anion triangle diagrams in Figure 2-17~~6~~ indicates that the river water has a slightly greater influence of sulfate/chloride (and lower relative levels of alkalinity) and sodium/potassium influence (and lower relative levels of calcium), compared to that observed in the majority of the groundwater and transition zone water samples. The cation and anion chemistry of the transition zone water collected by the large-volume peepers plots between that of the surface water and the groundwater samples on the triangle diagrams,~~—~~ suggesting that the chemistry of these samples may be reflective of a mixture of transition zone water/groundwater chemistry and river water chemistry. Conversely, the major ion chemistry and, most notably, the TDS content of the transition zone water collected by the Trident probe is consistent with the upland and Geoprobe® groundwater chemistry, suggesting that the river water did not have a significant influence on the water quality measured in the Trident samples.

The relative potential influence of surface water on the transition zone water samples is also evident in the Stiff diagrams presented in Figures 2-18 (surface water[23] and groundwater[24]) 2-19~~7~~. At all three locations, the Trident and small-volume peeper transition zone water samples show higher carbonate (alkalinity) levels than those

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[23] Major ion data for Willamette River water were taken from USGS Station 14211805, located at St. John's Bridge at approximately river mile 5.75. The USGS data set included six samples collected between February 10, 1996 and May 13, 1996. In addition, data were used for a surface water sample collected at the Arkema Plant on Feb 24, 2003.

[24] Upland groundwater data for ARCO were provided by the Oregon Department of Environmental Quality, in a memo from Tom Gainer to Integral Consulting Inc. on June 8, 2005.

measured in the large-volume peepers. This trend is consistent with a greater influence of surface water in the large-volume peepers.

The observed influence of river water on the large-volume peeper samples may reflect the shallower depth from which the samplers collect transition zone water and sediment disturbance during sampler placement. The large-volume peepers were typically buried in a hole that was excavated to a depth of 15-20 cm deep below the mudline,[25]~~,~~ while the Trident samples were collected at 30 cm (~12 inches) below the mudline. Furthermore, the deployment process resulted in the loss of fine materials in the sediment used to bury the large-volume peeper and thus may have locally increased the level of interaction of the sediments with the river water.

2.7.2. Arkema Acid Plant and Chlorate Plant Study Areas

The major ion chemistry of groundwater discharging from the Arkema site is significantly influenced by historical releases of sodium and chloride associated with salt and brine formerly stored primarily in the former Chlorate Plant area. Figure 2-~~18~~ 20 presents a Piper diagram of in-river groundwater chemistry (Integral 2003)[26] collected from offshore of the Acid Plant (immediately north of the Chlorate Plant). The groundwater samples located at the southern side of the Acid Plant (near the southern end of Dock 2, in the direction of the Chlorate Plant) are predominantly sodium chloride waters with high TDS content, while groundwater samples farther north (i.e., roughly between Dock 2 and Dock 1; Figure 2-2) tend to contain less sodium and chloride in exchange for a greater relative calcium, magnesium, and alkalinity content.

The Piper diagrams in Figures 2-~~19~~ 21 and 2-~~20~~ 22 depict the major ion chemistry measured in the transition zone water samples collected by the various pilot study methods at the Acid Plant and Chlorate Plant study areas. The general areas where the "north" and "south" in-river groundwater chemistry plotted are included for reference, along with the river water chemistry. The transition zone water samples from offshore of the Chlorate Plant are all sodium chloride waters and strongly resemble the in-river groundwater data collected from areas downgradient of the Chlorate Plant (i.e., "northern groundwater"). The transition zone water samples from offshore of the Acid Plant tend to show a weaker sodium-chloride signal and greater relative levels of calcium, magnesium, and alkalinity. These findings are similar to the trends observed in the in-river groundwater data and are consistent with the anticipated lesser influence from historical salt releases from the Chlorate Plant area.

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[25] At several locations, the large-volume peepers could only be buried to ~5 cm below the mudline due to loss of sediments during the excavation process.

[26] In-river groundwater data were collected with the Geoprobe® sampling device at shallow (1.3 ~~to~~ – 8 ft), intermediate (11 – 19 ft), and deep (19 – 35 ft) intervals below the mudline. Six shallow, five intermediate, and three deep samples were collected across eight locations in June 2002 and February and March 2003. These data were collected offshore of the Acid Plant area.

Figures 2-~~21~~ 23 and 2-~~22~~ 24 present Stiff diagrams comparing the major ion chemistry of transition zone water samples collected by various pilot study sampling methods. In general, the major ion chemistry was similar between methods. However, in all cases, the samples collected by the large-volume peepers were less concentrated than the samples collected by the Trident Probe. These data are consistent with the findings at the ARCO study area~~,~~ and suggest that the large-volume peeper samples are more influenced by river water. Several of the transition zone water samples collected by the power grab sampler also suggest the possible influence of river water.

2.8. RECOMMENDATIONS FOR METHOD SELECTION

Table 2-~~5~~ 6 summarizes the key findings of the analysis of transition zone water sampling methods. Based on all analyses, both the Trident Probe and the small-volume peepers are considered the most reliable methods for obtaining representative samples of transition zone water for analysis of the chemical classes assessed in the pilot study. Of these two methods, the Trident probe is the most applicable and efficient for sampling of transition zone water in coarse-grained sediments where purge rates can be maintained at high enough levels to allow for reasonable sample collection rates and to minimize potential for loss of VOCs during filling of VOA vials.~~, while~~ T~~t~~he small-volume peepers are an effective tool for fine-grained sediments, where they can be more easily inserted, without the need for significant disturbance of the sediment. Additional constraints on method selection may be made based on practical applicability for site-specific conditions.

3. ANALYSIS OF PILOT STUDY TRANSITION ZONE WATER SAMPLING RESULTS

This section present the analysis of the pilot study transition zone water results in the context of the site-specific conceptualizations, considering~~relative to~~ upland groundwater data, surface water data, and discharge mapping results. Discussions are presented by study area, describing how sampling locations were selected, how transition zone water results compare to groundwater and surface water data, and exploring whether the sediment-water system appears to be in equilibrium. To support these discussions, Tables 3-1a and 3-1b summarize the analytical results for selected analytes from each site. The complete data set is provided in the Pilot Study Data Report ~~(~~[Appendix B ~~of~~ to the SAP (Integral 2005c)]~~)~~.

3.1. PILOT STUDY RESULTS – ARCO STUDY AREA

The following sections discuss the transition zone water quality results from Trident and small-volume peeper sampling relative to available upland and in-river Geoprobe® groundwater data to develop an understanding of groundwater discharge from the ARCO study area.

3.1.1. Transition Zone Water Sampling Location Selection~~s~~

The three pilot study transition zone water sampling locations at the ARCO site were selected based on the available uplands hydrogeology and plume delineation, and the preliminary findings of the discharge mapping work.

As presented in the Pilot Study FSP (Integral 2004a) and Attachment 1 to the Round 2 Groundwater Pathway Assessment SAP, groundwater migration and discharge to the river at the ARCO site is believed to be strongly influenced by the presence of gravel deposits that are indicative of a buried paleochannel underlying a portion of the central area of the site. Additionally, light, nonaqueous-phase liquid (LNAPL) is present in the central area of the site, near the seawall, along with the highest nearshore results for BTEX, PAHs, arsenic, and lead in shallow upland groundwater (see Appendix A-2 of the SAP).

As discussed in Attachment 1, the results of the Trident work noted temperature signals at locations AR03B and AR06B that could be indicative of groundwater discharge. However, because seepage rate measurements could not be completed at the ARCO site,[27]~~,~~ the verification step of the discharge mapping effort was not completed. Consequently, areas of groundwater discharge offshore of the site could not be conclusively identified with the existing data set.

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[27] Planned use of the UltraSeep system to provide a direct measure of groundwater discharge at the site could not be completed during the pilot study due to conflicts with the site's barge schedule.

Locations AR03B and AR06B were selected for transition zone water sampling based on the Trident data and their position relative to the buried channel and the uplands LNAPL area. AR02B was also selected as a sampling location with the objective of collecting information at a comparable distance from the shoreline, where a more typical temperature signal was observed (Figure 3-1).

3.1.2. Major Ion Chemistry

In addition to application to the evaluation of performance of the various sampling methods in the pilot study ~~the analysis of major ions performed to assess variability between sampling methods~~ (see Section 2.7), the major ion data were analyzed to evaluate the transition zone water composition relative to river water and groundwater. As discussed in Section 2.7, the major ion chemistry of transition zone water, in-river Geoprobe® groundwater samples, and uplands groundwater at the ARCO site are all predominantly calcium-carbonate waters. River water, while predominantly of calcium-carbonate composition, has a slightly greater sulfate and chloride signal when compared to the majority of the groundwater and transition zone water samples (particularly those collected by the Trident Probe). Although uplands groundwater samples (see Figure ~~3-2~~2-18) show the same chemical signature as the Geoprobe® groundwater and the Trident transition zone water samples, the uplands groundwater tends to be less concentrated (i.e., absolute concentrations of calcium and alkalinity tend to be lower in the uplands groundwater samples),~~—~~ possibly suggesting that site factors may increase the dissolved solids content of groundwater as it migrates toward the river.

3.1.3. Metals

The concentrations of arsenic, copper, lead, and zinc measured in the Geoprobe® groundwater samples at the three ARCO pilot study sampling locations were of generally lower concentrations than those measured in upland groundwater from nearby shoreline wells. Concentrations of copper, lead, and zinc in recent (2003), unfiltered samples collected from upland groundwater wells located upgradient of the pilot study sampling locations were typically on the order of 100 – 2,000 µg/L (see Appendix A-2 of the SAP). Somewhat lower concentrations of copper, lead, and zinc were present in the unfiltered Geoprobe® groundwater samples from the three pilot study sampling locations [maximum concentrations: copper (182 µg/L), lead (166 µg/L), zinc (438 µg/L)]. The highest concentrations detected for copper, lead, and zinc were in the unfiltered sample from the 3- to 5-foot depth at AR06B. In all cases (upland and in-river groundwater samples and transition zone water samples), the concentrations of copper, lead, and zinc were greater in the unfiltered samples than in the filtered samples.

Arsenic concentrations in the Geoprobe® groundwater samples, which ranged from 0.5 to 23.3 µg/L, were also generally lower than those observed in the 2003 upland groundwater samples. Arsenic concentrations measured in 2003 in upland groundwater wells were on the order of 10 – 100 µg/L (Appendix A-2 of the SAP). Filtered and unfiltered samples did not show as much of a difference for arsenic as was observed for the other metals.

The concentrations of the metals measured in the transition zone water samples were generally lower than those measured in the Geoprobe® groundwater samples. The maximum concentrations measured for each of the metals ~~across~~ for the Trident and small-volume peeper methods~~all transition zone water samples~~ (see SAP Appendix B: Pilot Study Data Report) were as follows: arsenic (10.9 µg/L), copper (~~27.8~~8.57 µg/L), lead (26.4 µg/L), and zinc (95 µg/L). The highest concentrations of these metals were observed at AR03B and AR06B, while AR02B tended to have lower metals concentrations. As with the Geoprobe® groundwater samples, the concentrations of copper, lead, and zinc were substantially higher in the unfiltered samples than the filtered samples, but arsenic concentrations were not significantly influenced by filtration.

Because the major ion data for the Trident Probe transition zone water samples do not suggest an overwhelming ~~significant~~ influence of river water (i.e., dilution), the lower metal concentrations observed in the transition zone water relative to the underlying groundwater may suggests a potential attenuation mechanism(s) is acting on the metals. The apparent metals attenuation may be the result of changing redox conditions in the near-surface sediments (e.g., oxidation of and co-precipitation/adsorption to dissolved iron) and/or adsorption to organic matter in the surface sediments.

3.1.4. Petroleum Hydrocarbons

Petroleum hydrocarbons detected in the Geoprobe® groundwater samples favored the heavier diesel and residual fractions, with the gasoline fraction detected only at location AR02B (660~~-~~J µg/L at 3-5 feet and 400~~-~~J µg/L at 6-8 feet). Comparison of the ~~diesel-range TPH (~~TPH-D~~)~~ concentrations in the unfiltered Geoprobe® groundwater samples suggests that the shallower (3-5 ft) samples were generally of slightly higher concentration [670J – 3,600J µg/L (unfiltered)] than the deeper (6-8 ft) samples [280J – 2,800J µg/L (unfiltered)]. TPH-D concentrations were lower in the filtered samples, with the exception of the filtered samples from AR02B (from both depth zones) which had similar concentrations in both the filtered and unfiltered samples. Concentrations for residual-range TPH (TPH-R) ranged from 320 – 4,900 µg/L (unfiltered) ~~,~~and displayed similar trends as those observed for TPH-D.

TPH data are relatively limited for the ~~-~~transition zone water samples (No samples were collected with the Trident. For small-volume peepers, TPH-G ~~-G~~ was collected at all three ARCO locations, and TPH-D and TPH-R were collected at only one location).~~ particularly for unfiltered samples.~~ Considering the available data, ~~However,~~ as was the case for ~~with~~ the Geoprobe® data, the transition zone water samples favored the heavier hydrocarbon fractions, and ~~gas-range TPH (~~TPH-G~~)~~ was not detected in any of the transition zone water samples in which it was analyzed. TPH-D and TPH-R concentrations measured in the ~~large- and~~ small-volume peepers were ~~<~~190 µg/L and 82 µg/L, respectively, which is~~thus, were~~ generally lower than those measured in the underlying Geoprobe® samples. ~~The TPH-D and TPH-R levels measured in the power grab transition zone water samples from AR03B and AR06B (maximum concentrations of 19,000 and 23,000 µg/L, respectively; both in the unfiltered sample from AR06B) were significantly higher than the corresponding levels measured in transition zone water samples collected by other methods and in the underlying Geoprobe® groundwater samples. As described in Section 2.6, the anomalously high TPH results for the power grab samples are suspected to be an artifact of the centrifugation process.~~

3.1.5. BTEX and MTBE

BTEX concentrations in the Geoprobe® groundwater samples were generally below detection or, if detected, present at low concentrations (maximum of 1.2 µg/L m,p-xylene at AR02B). Similarly, the concentrations of BTEX were low in the transition zone water Trident and small-volume peeper samples (max of 1.3 µg/L toluene in the small-volume peeper from AR03B; ~~0.4~~1.0 to 1.8 µg/L total BTEX). These levels observed in the pilot study groundwater and transition zone water samples were ~~generally~~ much lower than concentrations ~~(typically 10 – 100 µg/L; Figure 2-6a of SAP Appendix A-2)~~ measured in upland wells located upgradient of the transition zone water sampling location (typically 10 – 100 µg/L; Figure 2-6a of SAP Appendix A-2).

Methyl tertiary-butyl ether (MTBE) was observed in both Geoprobe® groundwater samples and transition zone water samples. The Geoprobe® results varied from 3.5 µg/L in the 3-5 ft below mudline interval at AR06B to 29 µg/L in the same depth interval at AR02B. In contrast, the highest Trident and small-volume peeper transition zone water results were observed at AR06B (15 µg/L MTBE), while the AR02B transition zone water MTBE was below detection. Both in-water Geoprobe® groundwater and transition zone water sampling results were generally lower than upgradient, upland groundwater concentrations (typically 10 – 100 µg/L; Table 1a of SAP Appendix A-2).

3.1.6. Polycyclic Aromatic Hydrocarbons

PAH results are ~~presented~~ discussed in the following sections. The first section summarizes the observations from Geoprobe®, Trident, and small-volume peeper samples, and the second section presents an analysis of the result relative to published ~~partitioning~~ equilibrium partitioning values.

3.1.6.1. Summary of PAH Results

Concentrations of total polycyclic aromatic hydrocarbons (TPAH) in the Geoprobe® groundwater samples ranged from 0.16 µg/L (filtered sample from 6-8 ft at AR06B) to 14.2 µg/L (unfiltered sample from 3-5 ft at AR02B). In general, the TPAH concentrations were significantly higher in the unfiltered samples vs. the filtered samples, indicating that a significant portion of the PAH mass measured in the unfiltered samples was associated with particulates or colloids greater than 0.45-µm in size. The TPAH levels measured in the Geoprobe® groundwater samples are not substantially different from those measured in nearshore, uplands groundwater samples. Table 3-2 summarizes the TPAH concentrations measured in transition zone water at the ARCO site by Trident and small-volume peepers~~the various methods~~ and identifies the PAH compound detected at the highest concentration by the method. The TPAH concentrations in the Trident and ~~diffusion-based samplers~~small-volume peepers ranged from 0.007 to 24.2~~were typically on the order of 1-20~~ µg/L~~-~~, with acenaphthene most frequently present at the highest relative concentration. These~~, and~~ are consistent with ~~levels~~ concentrations measured in offshore and upland groundwater (see SAP Appendix A-2).

~~The TPAH concentrations in the transition zone water samples collected by the power grab from AR03B and AR06B ranged from 60 to 368 µg/L, and were found to be biased high relative to the levels measured by the other methods (see Section 2.4.1.1). Unlike the other transition zone water samples, the predominant PAH compound in these samples was phenanthrene. The higher TPAH levels measured in the power grab transition zone water samples are consistent with the anomalous TPH concentrations recorded in these samples, and are likely an artifact of the centrifugation process used to separate the transition zone water from the bulk sediment samples collected by the power grab (see Section 2.6).~~

3.1.6.2. PAH Equilibrium Partitioning Analysis

The following analysis compares the measured concentrations of PAHs in co-l~~l~~ocated sediment and transition zone water samples to published equilibrium partitioning coefficients. ~~Under certain idealized conditions, it anticipated that sediment transition zone water will be in equilibrium with the surrounding sediment. When such conditions exist, the equilibrium partitioning calculations can be used to estimate the concentrations of chemicals in transition zone water based on the concentrations measured in sediments.~~ Equilibrium partitioning theory assumes that the mass of a chemical in the sediment (C_s; mg/kg) is directly proportional to the solute concentration in the associated pore water (C_{aq}), and that this relationship can be described by a distribution coefficient (K_d), as shown in the equation below:

$$K_d = \frac{C_s}{C_{aq}}$$

In sediment environments, equilibrium partitioning calculations are particularly relevant to highly hydrophobic compounds (e.g., PAHs, pesticides), which have a strong tendency to partition to organic matter in the sediments. The tendency for these chemicals to partition to organic matter associated with the sediment is described by the soil- or sediment-organic carbon partition coefficient, K_{oc}. A substantial amount of research has been done to estimate K_{oc} values for organic contaminants; however, the site-specific partitioning coefficient depends on such factors as sediment surface area, sediment surface material, organic material composition, salinity of the aqueous solution etc. A sediment-specific K_d value can be estimated for a given chemical based on the chemical's K_{oc} value and the fraction of organic carbon (f_{oc}) in the sediment according to the equation below:

$$K_d = f_{oc} \times K_{oc}$$

~~, and~~ EPA has compiled recommended values for use in partitioning calculations in the Soil Screening Guidance (EPA 1996a). Additionally, EPA (2003) recommends calculating K_{oc} values from K_{ow} values (octanol-water partitioning coefficients) using the relationship published by Di Toro et al. (1991). ~~A sediment-specific K_d value can be estimated for a given chemical based on the chemical's K_{oc} value and the fraction of organic carbon (f_{oc}) in the sediment according to the equation below:~~

~~$K_d = f_{oc} \times K_{oc}$~~

Observed partitioning to sediment organic carbon can be calculated from the sediment and transition zone water data, using the observe f_{oc} values[28], applying the following equation:~~The co-located sediment and transition zone water chemistry results for PAH compounds were used to explore whether partitioning is occurring at equilibrium for these compounds in the sediment system at the ARCO site. Specifically, the transition zone water (from various methods) and bulk sediment data at each sample location were used to calculate location-/method-specific K_{oc} values per the equation below:~~

$$\text{Observed Partitioning} = \left(\frac{C_s}{C_{aq}}\right) \Big/ f_{oc}$$

Comparison of t~~T~~hese ~~location-/method-specific K_{oc}~~observed organic carbon partitioning values to~~were then compared to the~~ literature K_{oc} values can provide insight into the nature of the system and possibly into whether the ~~to evaluate whether~~ system conditions approach equilibrium~~ conditions~~. ~~This analysis was completed using data for transition zone water samples collected by the small-volume peepers and Trident (filtered) sampling methods[29], and was limited to detected results.~~

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[28] The measured f_{oc} values for the pilot study at the ARCO site are as follows: AR02B = 0.0169; AR03B = 0.0279; and AR06B = 0.0235.

[29] It should be noted that, while the transition zone water samples collected by the Trident and small-volume peepers were collected from the same area, they were technically not co-located with the power grab sediment samples. As such, the K_{oc} values estimated from these data are approximate.

Figure 3-~~3~~ 2 summarizes the results of the ~~equilibrium~~ partitioning analysis, which shows the calculated method-specific ~~K_{oc}~~ observed partitioning values for 15 PAH compounds for each of the three ARCO study area sampling locations. ~~for the three transition zone water sampling methods.~~ This analysis was completed using data for transition zone water samples collected by the small-volume peepers and Trident (filtered) sampling methods,[30] and was limited to detected results. The chart is oriented such that the PAHs are ordered from highest to lowest molecular weight.

~~The K_{oc} values calculated based for indeno(1,2,3-cd)pyrene and dibenz(a,h)anthracene (molecular weights ~260 g/mole), which were detected in the small-volume peeper samples, reasonably approach the literature K_{oc} values. However, the K_{oc} values calculated for the lower molecular weight PAHs (<230 g/mole) detected in the small-volume peeper and filtered Trident samples tended to overestimate the literature K_{oc} values. This suggests that equilibrium conditions may not be established in the sediment system at the ARCO sampling locations and that the system favors partitioning of the low molecular weight PAH compounds to sediment. In other words, these data suggest that use of equilibrium partitioning calculations to estimate transition zone water concentrations from bulk sediment data at these locations would overestimate actual transition zone water concentrations.~~ At all locations, the observed partitioning coefficient generally decreases with molecular weight of the PAH compound—a trend that echoes the published K_{oc} values. The filtered Trident aqueous concentrations are consistently lower than those observed in the small-volume peeper samples, resulting in consistently higher observed partitioning values for the filtered Trident samples. (Note: filtered Trident concentrations for the higher molecular weight PAHs are all below detection, and are therefore not shown.) This trend could suggest that the 0.45 µm filter mesh used for the Trident samples removed a greater fraction of solids to which PAHs were sorbed. than the 5-µm mesh used with the small-volume peepers. From this analysis, it is not clear whether this fraction would be mobile in the transition zone water.

Based on this analysis, observed concentrations of higher molecular weight PAHs at the ARCO site are lower than would be predicted by applying published equilibrium K_{oc} values to measured bulk sediment concentrations and f_{oc} values.

3.1.7. Summary of Pilot Study Findings – ARCO Study Area

The key findings of the pilot study transition zone water sampling at the ARCO site are highlighted below:

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[30] ~~It should be noted that, w~~While the transition zone water samples collected by the Trident and small-volume peepers were collected from the same area, they were ~~technically~~ not precisely ~~collocated~~co-located with the power grab sediment samples. As such, the K_{oc} values estimated from these data are approximate.

- The pilot study groundwater discharge mapping data, discussed in Attachment 1 to the SAP, indicate that higher rates of groundwater discharge may be occurring at locations AR03B and AR06B, relative to AR02B.
- The major ion data suggest that the transition zone water samples collected by the Trident and small-volume peepers are chemically similar to uplands groundwater at the ARCO site. ~~Furthermore, as discussed in Section 2.7.1, these data indicate that the large-volume peeper samples may have been diluted by river water.~~
- The concentrations of trace metals in the transition zone water were generally lower than those recorded in uplands and in-river groundwater samples, suggesting that metals attenuation may be taking place in the surficial sediments.
- TPH measured in the transition zone water samples favored the heavy TPH-D and TPH-R fractions, with little volatile hydrocarbons (TPH-G, BTEX, MTBE) detected in the samples. ~~The TPH-D and TPH-R results for the transition zone water samples collected with the power grab sampler are anomalously high relative to levels in site groundwater and in transition zone water samples collected by other methods.~~
- The PAH concentrations measured in transition zone water by the ~~diffusion~~small-volume peepers~~-based sampling devices~~ and the Trident Probe are generally similar to concentrations in upland and in-river groundwater samples from the site. ~~Two of the power grab transition zone water samples displayed anomalously high PAH levels, with several of the higher molecular weight PAHs at concentrations near or above water solubility limits.~~
- ~~As discussed in Section 2.6, the anomalously high TPH and PAH results observed in the power grab transition zone water samples are thought to be the result of the release of chemical mass associated with colloids and/or residual NAPL from the bulk sediment sample during the centrifuging. Therefore, the power grab transition zone water samples are not considered representative of actual *in situ* transition zone water chemistry.~~
- Evaluation of site transition zone water and bulk sediment data from the three pilot study sampling locations at the ARCO site suggests that the sediments and transition zone water ~~are not in~~vary from published K_{oc} values, and that observed concentrations of higher molecular weight PAHs at the ARCO site are lower than would be predicted by applying published equilibrium K_{oc} values to measured bulk sediment concentrations and f_{oc} values.

3.2. PILOT STUDY RESULTS – ARKEMA ACID PLANT AND CHLORATE PLANT STUDY AREAS

The following section provides a summary of the Trident and small-volume peeper sampling results of the pilot study water quality sampling at the Arkema Acid Plant and Chlorate Plant study areas.

3.2.1. Transition Zone Water Sampling Location Selection~~s~~

A Trident temperature and conductivity survey was completed at the Arkema site as part of the pilot study. Based on the results of this survey, a total of six locations were selected for transition zone water sampling: three~~—3~~ offshore of the Acid Plant (AP03B, AP04B, and AP04D; Figure 3-~~4~~3) and ~~3~~ three offshore of the Chlorate Plant (CP06C, CP07B, and CP08D); Figure 3-~~5~~4). Locations AP03B and CP07B are both sandy sediments that showed a high temperature gradient relative to similarly situated locations evaluated during Trident discharge mapping, ~~—~~potentially suggesting focused discharge areas at these locations. This hypothesis was verified by seepage rate measurements recorded at CP07B, which demonstrated that groundwater discharge in this area was greater than that recorded at the other two locations evaluated with the UltraSeep meter (AP04B and AP04D). Silty surface sediments were present at sampling locations AP04B, AP04D, CP06C, and CP08D. UltraSeep measurements at AP04B showed a very low net positive discharge of groundwater, while AP04D UltraSeep measurements showed no net positive discharge of groundwater over the 24-hr deployment period. These results suggest that the low permeability of the sediments inhibits groundwater discharge at these locations.

3.2.2. Major Ion Chemistry

As discussed in Section 2.7, the major ion chemistry of groundwater discharging from the Arkema site is significantly influenced by historical releases of sodium and chloride associated with salt and brine formerly stored primarily in the former Chlorate Plant area. These influences are most evident in the in-river groundwater samples collected from locations offshore of the Chlorate Plant, where the groundwater has a very strong sodium-chloride signature (see Figure 2-20~~18~~). The sodium-chloride influences are also evident in the in-river groundwater samples collected offshore of the southern end of the Acid Plant, but groundwater ~~further~~ farther north tends to contain less sodium and chloride in exchange for a greater relative calcium, magnesium, and carbonate levels. These spatial trends in major ion composition were also observed in the transition zone water chemistry (see Figure 2-~~19~~21). All salt and brine source materials were removed from the site in 2001 after plant shutdown. Upland groundwater data collected since the removal action demonstrates that salt concentrations are steadily decreasing in upland groundwater. It is anticipated that, as groundwater migrates through the system, salt concentrations in in-river groundwater and sediment transition zone water will also decrease.

3.2.3. Acid Plant Study Area Chemicals of Interest

The primary chemicals of interest associated with groundwater discharge from the Acid Plant are VOCs (primarily chlorobenzene) and DDT/DDD/DDE. The concentrations of the chemicals measured in the transition zone water samples are summarized in Table 3-1b. The following sections discuss the transition zone water quality results for Trident and small-volume peepers relative to available groundwater data to develop an understanding of groundwater discharge from the Acid Plant ~~Study~~ study area.

3.2.3.1. VOCs

Consistent with the groundwater discharge mapping results, the highest concentrations of VOCs were measured at location AP03B. The dominant VOCs detected at this location were chloroform and methylene chloride. Concentrations of chloroform and methylene chloride in the transition zone water samples from AP03B were widely variable~~ within and across methods~~, ranging from 1.7 – 770,000 µg/L for chloroform and ~~0.21~~25 – 520,000 µg/L for methylene chloride. The maximum concentrations of these compounds detected in transition zone water samples from the other two sampling locations were 5.5 µg/L (chloroform) and ~~<~~6.8 µg/L (methylene chloride).

Chloroform was sporadically detected in the in-river groundwater samples collected by Integral (2003), but at significantly lower concentration (maximum 610 µg/L) than the maximum concentrations detected in transition zone water at AP03B. Methylene chloride was only detected in two of the in-river groundwater samples (Integral 2003) at a maximum concentration of 2.6 µg/L [although the detection limit was elevated (100-200 µg/L) for several of the samples].

Concentrations of chlorobenzene in the Acid Plant ~~study~~ area transition zone water samples ranged from ~~0.1J~~4.6 µg/L (measured in the ~~UltraSeep~~ Trident sample from ~~AP04B~~AP03B) to 12,000 µg/L (measured in the small-volume peeper sample from AP04D). ~~The highest chlorobenzene concentration measured by the large-volume peepers (930 µg/L) and vapor diffusion samplers (199 µg/L)[31] were also from location AP04D.~~ The Trident sample from AP04D was 41 µg/L, which~~—~~ likely reflected~~ing~~ the loss of volatiles as the sample bottles were filled due to the low pumping rates that could be achieved at this location (<6 mL/min), discussed further in Section 2.4.1.2. ~~Concentrations of chlorobenzene measured in transition zone water samples (across all methods) from locations AP03B and AP04B ranged from 2.6 – 110 µg/L and 0.1J – 200 µg/L, respectively.~~

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[31] Gaseous concentrations by volume were converted to corresponding aqueous concentrations, assuming equilibrium, using Henry's constants for each detected analyte. Henry's constant values were calculated based on transition zone water temperatures measured with the Trident. Results and conversions to aqueous concentrations are presented in the Pilot Study Data Report (Appendix B to the SAP).

Although data are limited, transition zone water concentrations appear to agree with near-surface in-river groundwater results. In-river groundwater data collected from offshore of the Acid Plant area suggest that elevated chlorobenzene concentrations are present in groundwater in the immediate vicinity of location AP04D (Integral 2003). A groundwater sample collected from 11 feet below the mudline at a location adjacent to AP04D (location WB-11 on Supplemental Figure 11~~,~~ in Integral 2003) contained 32,000 µg/L chlorobenzene. The groundwater sample collected from 5 feet below the mudline at location WB-13, which is near AR03B, contained only 23 µg/L chlorobenzene. No near-surface groundwater samples were collected near AP04B, although deeper samples suggest that chlorobenzene is present in groundwater at depths well below the mudline.

3.2.3.2. DDT, DDD, and DDE

~~The highest~~Unfiltered Trident samples contained significantly higher concentrations of DDD, DDE, and DDT (referred to collectively hereafter as “DDX”) than~~were measured in the unfiltered Trident, power grab, and large-volume peeper transition zone water samples, while~~ the small-volume peeper and ~~samples and the filtered large-volume peeper samples and the~~ filtered Trident samples.~~ generally contained significantly lower DDX concentrations.~~ Total DDX concentrations in the unfiltered ~~transition~~ Trident~~zone water~~ samples ranged from 0.001~~below detection~~ to 2.42 µg/L, while the concentrations in the small-volume peeper and filtered ~~large-volume peeper and~~ Trident samples ranged from below detection to 0.0135 µg/L.

The DDX concentrations in the transition zone water samples collected from AP04D (maximum of 0.0135 µg/L) were generally less than in those the samples from the two locations where groundwater is expected to discharge at a greater rate based on the findings of the discharge mapping (AP03B - maximum of 2.42 µg/L; AP04B - maximum of ~~1.41~~0.68 µg/L). Supplemental Figure 14 (from Integral 2003) shows the DDT concentrations measured in groundwater from offshore of the Acid Plant. Elevated concentrations of DDT (contoured Geoprobe® data ranging from 10 to 1,000 µg/L) are present in groundwater in the vicinity of the three transition zone water sampling locations (AP03B, AP04B, and AP04D). Measured DDX concentrations from in-river groundwater samples in the immediate vicinity of each of the three transition zone water sampling locations were typically 10 – 100 µg/L, although a concentration of 1,900 µg/L DDT was detected in groundwater at WB-10 (approximately 75 ft shoreward of AP04D; see Supplemental Figure 14 in~~,~~ Integral 2003). In general, the concentrations of DDX detected in the in-river groundwater are greater than those measured in uplands wells during a 2003 sampling event (uplands DDX concentrations were typically <1 µg/L). It is believed that this is the result of ongoing source control measures in the uplands area of the site, including removal actions, pilot testing of *in-situ* chemical oxidation, and air sparging,[32]~~,~~ which

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[32] Chemical oxidation and air sparging target the removal of monochlorobenzene. In turn, DDT/DDE/DDD concentrations in groundwater are reduced, as the co-solvency of DDX with monochlorobenzene is reduced or eliminated.

have acted to reduce DDX concentrations in uplands groundwater. It is anticipated that, as groundwater migrates through the system, the effects of completed and on-going source control measures will result in reduced DDX concentrations in in-river groundwater and sediment transition zone water.

Figure 3-~~6~~ 5 presents a summary of the ~~calculated K_{oc}~~observed partitioning values[33] for DDD, DDE, and DDT based on the data for the transition zone water samples collected by the Trident (filtered~~), power grab (filtered),~~) and the small-volume peeper samples. This analysis was limited to detected results. As illustrated in Figure 3-~~6~~5, the limited number of ~~transition zone water data tend to produce K_{oc}~~observed partitioning values falls within the wide range of the ~~that are greater than~~ literature-based values.

~~Overall, this analysis is consistent with the findings for PAHs at the ARCO study area, and suggests that additional assessment of sediment and transition zone water should be performed following the Round 2 transition zone water sampling effort~~~~the sediments are in disequilibrium, favoring sorption to the sediments (i.e., DDX concentrations in transition zone water samples tend to be less than would be predicted based on equilibrium partitioning).~~.

3.2.4. Chlorate Plant Study Area Chemicals of Interest

The primary COIs associated with groundwater discharge from the Chlorate Plant are perchlorate and chromium. The concentrations of these chemicals measured in the transition zone water samples are summarized in Table 3-1b. The following sections discuss the transition zone water quality results for Trident and small-volume peepers relative to available groundwater data to develop an understanding of groundwater discharge from the Chlorate Plant study area.

3.2.4.1. Perchlorate

Perchlorate concentrations in the Trident and small-volume peeper transition zone water samples collected from the Chlorate Plant study area sampling locations CP06C, CP07B, and CP08D ranged from below detection to ~~201,000~~75,200J µg/L in the filtered ~~power grab~~Trident sample from CP07B. Perchlorate concentrations measured ~~in the transition zone water across all sampling methods were much greater~~ at CP07B (~~6,040~~41,600J – 75,200J~~201,000~~ µg/L) were much greater than the other two sampling locations (~~maximum perchlorate = 1.7 µg/L~~all below detection limits, <10 µg/L). This finding is consistent with the groundwater discharge mapping results, which indicated that a focused groundwater discharge is present at CP07B. The perchlorate concentrations observed in transition zone water from CP07B are consistent with the highest concentrations of perchlorate measured in 2003 in adjacent, nearshore groundwater wells ~~(~~[e.g., MWA-30 (4,700 µg/L), MWA-31i (200,000 µg/L); see Appendix A-7 of the SAP~~).~~].

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[33] The measured f_{oc} values for the pilot study at the Arkema Acid Plant site are as follows: AP03B = 0.0221; AP04B = 0.0202; and AP04D = 0.0208.

3.2.4.2. Total Chromium

Total chromium concentrations in the transition zone water samples collected from the Chlorate Plant study area sampling locations CP06C, CP07B, and CP08D ranged from below detection to a maximum of 122 µg/L in an unfiltered Trident sample from CP07B. As with perchlorate, the highest concentrations of total chromium were observed at CP07B. However, the most elevated detections were limited to the Trident samples (49.6 - 122 µg/L, CP07B), while the concentrations of total chromium in the transition zone water samples collected by ~~the power grab (max 4.6 µg/L, CP07B), UltraSeep (max 27.3 µg/L, CP07B), large-volume peepers (max 25 µg/L, CP06C), and~~ small-volume peepers (max 31.6 µg/L, CP07B) were somewhat lower. ~~With the exception of the filtered samples collected by the Trident Probe at CP07B, total chromium concentrations in the filtered samples were generally less than the concentrations measured in the corresponding unfiltered samples.~~From SAP Appendix A-7, ~~T~~the concentrations of total chromium in groundwater samples collected from upland, nearshore wells immediately upgradient of the transition zone water sampling locations ranged from 238 µg/L (MWA-32i, 6/4/2003) to 1,150 µg/L (MWA-31i, 6/4/2003), and are greater than the concentrations measured in the transition zone water from CP07B.

3.2.5. Summary of Transition Zone Water Sampling Results – Arkema Acid Plant and Chlorate Plant Study Areas

The key findings of the pilot study Trident and small-volume peeper transition zone water sampling at the Arkema site are highlighted below:

- The major ion composition of the transition zone water samples is similar to that of groundwater collected offshore of the site. The major ion chemistry of the transition zone water and groundwater is significantly influenced by releases of sodium and chloride from the site. These influences are most evident in the samples from the Chlorate Plant area and diminish to some degree in samples collected north of this area.
- The groundwater discharge mapping (described in Attachment 1 of the SAP) indicated possible areas of focused groundwater discharge at locations AP03B and CP07B. The highest concentrations of perchlorate and chromium were found at CP07B, consistent with the interpretations of the groundwater discharge mapping data. The elevated concentrations of chloroform, methylene chloride, and DDX detected at AP03B are consistent with the expected higher level of groundwater discharge at this location. However, chlorobenzene levels were not substantially elevated relative to concentrations in the center of the chlorobenzene plume.
- The occurrence and distribution of chlorobenzene and DDX compounds in the transition zone water samples from the Acid Plant study area is generally consistent with the occurrence and distribution of these chemicals in

groundwater collected offshore of the Acid Plant. The highest concentration of chlorobenzene in transition zone water, however, was detected in silty sediments at AP04D. Because no net discharge of groundwater was observed by the UltraSeep at this location, the data suggest that the chlorobenzene concentrations measured in transition zone water at this location may not be related to groundwater discharge and may be related to sediment contamination~~, possibly due to historical on-water releases around the docks during operations~~ from a different source or transport pathway.~~.~~

- Evaluation of transition zone water and bulk sediment DDT/DDD/DDE data from the three Acid Plant pilot study sampling locations suggests that ~~the sediments and transition zone water are not in equilibrium and that measured transition zone water concentrations are lower than those that would be predicted by standard equilibrium partitioning theory~~~~additional evaluation of~~the observed partitioning values, based on sediment and co-l~~l~~ocated transition zone water sample concentrations, fall within the wide range of the literature-based values.~~ following completion of Round 2 sampling, is warranted.~~~~.~~

4. GROUNDWATER PATHWAY ASSESSMENT – TRANSITION ZONE WATER SAMPLING APPROACH

This section describes the process that will be followed to develop site-specific transition zone water sampling plans for the nine sites to be considered as part of the Round 2 Groundwater Pathway Assessment.

4.1. APPROACH TO SELECTION OF TRANSITION ~~ZONE~~ ZONE WATER SAMPLING LOCATIONS

As described in the Round 2 Groundwater Pathway Assessment SAP, the locations where transition zone water samples will be collected at each of the nine study sites will be selected based on the results of the groundwater discharge mapping field effort, which is scheduled ~~for~~ to begin in August~~ and September~~ 2005[34]. The groundwater discharge mapping field effort is described in Attachment 1 to the SAP, and will include the following:

- Geoprobe® coring to fill data gaps in offshore stratigraphy
- Trident Probe temperature and conductivity profiling (and field screening, where applicable) to identify probable zones of groundwater discharge
- Field screening analysis of distinct chemical markers of upland groundwater plumes at selected sites, using transition zone water samples collected by the Trident Probe during groundwater discharge mapping
- Seepage meter measurements to verify groundwater discharge (by quantifying discharge flux rates).

The findings of the discharge mapping effort will be considered in conjunction with available site data (e.g., hydrogeology, surface sediment texture delineation, distribution of COIs in groundwater and sediments) to identify probable zones of groundwater COI discharge. Key site information relevant to the evaluation of groundwater COI discharge zones is provided for each of the sites in Appendix A to the SAP.

The transition zone water sampling locations selected for each site will focus primarily on the identified zones of possible groundwater plume discharge. Additional sampling locations will be specified to provide comparative data for transition zone water quality outside of the potential discharge zones. The exact number of sample locations for each site cannot be determined until the groundwater discharge mapping is completed. A minimum of ~~four~~ six and a maximum of 15 sampling locations will be considered for each site. At each location, transition zone

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[34] This final draft of Attachment 2 has been prepared following completion of the subject field work (completed December 2, 2005) to provide a complete and final document, which responds to comments and reflects the modifications to the sampling effort agreed upon for conditional approval by EPA and its agency partners.

water samples will be collected from a depth of 30 cm below the sediment interface. At a subset of the locations, a second, deeper sample will also be collected from a depth of at least 90 cm (up to a depth of 150 cm will be attempted at each deeper sample location). Paired 30-cm and 90- to 150-cm samples will typically be collected from at least ~~at~~ one sampling location within each identified groundwater discharge zone at each site. Overall, up to 160 samples will be collected from the nine sites. These guidelines were developed to ensure that at least the minimum necessary amount of data are collected from each site and to ensure that the transition zone water sampling program can be completed within the 8-week time frame scheduled for the transition zone water sampling program (see Section 5).

Based on the analyses of the pilot study findings presented in Sections 2 and 3 of this FSP, the Trident Probe and small-volume peepers were identified as the most reliable and effective methods for sampling of transition zone water, and have been selected for use during the Round 2 Groundwater Pathway Assessment. Transition zone water samples in coarse-grained sediments will generally be collected using the Trident Probe from a depth of 30 cm below the sediment interface. Small-volume peepers will be used in fine-grained sediments where use of the Trident Probe is impractical or would result in loss of VOC mass due to very slow water production rates (<20 mL/min). At a subset of the Trident Probe locations, a second, deeper sample will also be collected from a depth of 90 to 150 cm. (Deeper samples cannot be collected using the small-volume peeper, because excavation would be required, resulting in too much sediment disturbance.) Paired 30-cm and 90- to 150-cm samples will typically be collected at one sampling location within each identified groundwater discharge zone at each site. The paired samples will provide additional information on chemical fate and transport in the transition zone and are intended to provide additional information to assess whether groundwater COIs may be migrating to the transition zone.

Site-specific addenda to this FSP will be prepared following completion and evaluation of groundwater discharge mapping at each site. For each site, the FSP addenda will include a summary of the results of the discharge mapping findings, a map of the proposed transition zone water sample locations, and a table summarizing sample counts, planned sampling methods for each location, target depth intervals, and COIs to be analyzed. In addition, the addenda will briefly summarize the rationale supporting the selection of the proposed sampling locations for each site. This summary will include the following:

- A map of the Trident results, including temperature mapping and screening sample results
- A summary and map of the seepage meter measurements
- Updated cross-sections and a~~A~~ description of materials logged during stratigraphic coring and a revised description of offshore lithology

- Maps and ~~C~~cross-section figures ~~incorporating~~depicting groundwater COI concentrations from upland and in-water~~s~~ investigations.

This information will be discussed in the context of the current understanding of site hydrogeology and groundwater discharge for each site provided in Appendix A of the SAP.

The schedule for submitting the FSP addenda and the needed EPA review/approval period is provided in Section 5.

4.2. SAMPLING METHODS

This section presents additional discussion of the methods that will be used to sample transition zone water and the conditions under which these methods will be applied.

In general, the findings of the groundwater pilot study suggest that groundwater discharge to the river will predominantly occur through areas of coarser-grained sediments (sands, sandy silts)~~,~~ and that discharge through finer-grained sediments (silts, clays) can be inhibited by the low permeability of those materials. The Trident Probe is an effective and efficient tool for sampling transition zone water from coarse-grained sediments, and is thus anticipated to be the primary tool for transition zone water sampling during the Round 2 Groundwater Pathway Assessment. Small-volume peepers~~, on the other hand, ~~are an effective tool for characterizing transition zone water quality in fine-grained sediments and will be employed when sampling from fine-grained sediments is required.

As part of the groundwater discharge mapping effort using the Trident Probe, the surface sediment texture can and will be assessed qualitatively based on “feel~~.~~”, which will be confirmed at 10% of the mapping locations with a sediment grab sample. This information will be evaluated along with existing texture data for offshore surface sediments (provided in Appendix A) to delineate the sediment materials in the zones identified as probable groundwater discharge and to select the appropriate transition zone water sampling method.

The Trident Probe will be used to collect transition zone water samples at a depth of 30 cm below the mudline. As discussed above, the Trident will also be used at select locations to collect a sample at 90 cm to 150 cm below the mudline. At locations where sediment conditions appear likely to be conducive to Trident sampling (i.e., sediment consisting of sands, silty sands, and, potentially, sandy silts), sampling using the Trident Probe will be attempted prior to any sampling using the small-volume peepers. Sample locations characterized by very low-permeability materials (silts, clays) will be sampled using the small-volume peepers. If, at a given sampling location, purging of the Trident Probe demonstrates that the sediments have a low yield of transition zone water (<20 mL/min), the Trident Probe will be re-positioned a maximum of 2 times within 10 feet of the original target location and the purging process repeated. If low yield rates persist for a given shallow Trident sample location, the location will be sampled using small-volume peepers. In the event that low transition zone water yields persist after three attempts at any deep Trident sample location, then the deep sample will not be collected from that location.

The specific methods that will be employed for sampling transition zone water using the Trident Probe and the small-volume peepers are provided in the SOPs in Section 6.

4.3. SEDIMENT SAMPLING

Up to three surface sediment samples per site will be collected from selected transition zone water sampling locations as part of Round 2. The sediment samples will be collected from locations identified as probable groundwater discharge zones and where bulk sediment chemistry data results are not available for a similar sediment type located within 50 feet of the discharge mapping location. Bulk sediment samples will be ~~collocated~~co-located with the transition zone water samples from these locations. These data will allow for an evaluation of the ~~relationship~~ partitioning ~~between~~ of groundwater COIs ~~and~~ between the sediment matrix ~~within~~ and shallow transition zone ~~sediments~~water. The sediment sampling will be completed using the power grab sampler per the SOP presented in Section 6.

4.4. CHEMICALS OF INTEREST

Tables 4-1 and 4-2 summarize~~s~~ the site-specific analyte groups~~COIs~~ for each of the nine sites to be analyzed in transition zone water ~~and sediment~~ samples and sediment samples to be collected during the Round 2 Groundwater Pathway Assessment. These ~~COIs~~ analyte groups were selected based on a review of the history of site chemical use and on the understanding of chemicals present in uplands groundwater at the site. Chemical-specific analytical methods, sample volumes, preservation, and handling protocols are provided in the supplement to the Quality Assurance Project Plan Addendum 3 (QAPP Appendix A; ~~Appendix A~~Integral 2005d).

4.5. FIELD QUALITY CONTROL SAMPLES

The quality control (QC) samples that will be collected to support the transition zone water sampling program for the Round 2 Groundwater Pathway Assessment are described in the QAPP (Appendix A). For the Trident Probe, which is anticipated to be the primary tool for transition zone water sampling, the QC samples will be collected at a frequency of 10% (1 per 10 natural samples) per site. The QC samples for the Trident will include replicate samples and field equipment rinsate blanks. As it is anticipated that few small-volume peeper samples will be collected at each given site, the field QC samples will be collected a frequency of ~~10% for the entire~~

~~study~~one per site ~~area~~ to allow for QC for all analyte groups~~(i.e., all nine sites), and will include a minimum of two QC samples~~. Because new small-volume peepers will be used at each sampling location, one representative ~~field~~ rinsate sample ~~and decontamination blanks~~ will ~~not~~ be collected for all nine sites~~these sampling devices~~.

5. SCHEDULE

Transition zone water sampling ~~during~~ for the Round 2 Groundwater Pathway Assessment is scheduled for September 23 through November 21, 2005. As discussed in Section 4, the results of the groundwater discharge mapping field effort, scheduled for July 29 through September 11, 2005, will be used to identify the locations for the transition zone sampling. Transition zone water sampling plans will be submitted for the nine sites in ~~a series~~ two ~~of~~ addenda to this FSP. To facilitate agency review and approval, ~~two rounds of~~ the addenda ~~submittals~~ will be submitted to EPA and its partners on August 25 and September 25, 2005. Additionally, a meeting will be scheduled with EPA following delivery of each addendum, to allow for efficient, in-person negotiations, informal clarifications and responses to comments, and timely conditional approval. The schedule for the discharge mapping and transition zone water sampling effort is summarized in Figure 5-1[35].

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[35] This final draft of Attachment 2 has been prepared following completion of the subject field work (completed December 2, 2005) to provide a complete and final document, which responds to comments and reflects the modifications to the sampling effort agreed upon for conditional approval by EPA and its agency partners.

6. STANDARD OPERATING PROCEDURES

This section presents the series of SOPs for the transition zone water sampling methods that will be employed during the Round 2 Groundwater Pathway Assessment 2005 field effort for the Portland Harbor RI/FS. Laboratory protocols and project-specific quality assurance (QA) objectives are presented in the QAPP addendum developed for Round 2 sampling (Appendix A).

The following SOPs present the specific procedures that will be implemented to collect transition zone water samples:

SOP A: Trident Probe Transition Zone Water Sampling

SOP B: Small-Volume Peeper Transition Zone Water Sampling

In addition, the following SOPs provide the procedures for general task elements of the 2005 transition zone water sampling effort:

SOP C: Station Positioning and Vertical Control

SOP D: Field Documentation

SOP E: Sample Labeling, Custody, and Handling

SOP F: Clean Hands/Dirty Hands Procedures

6.1. SOP A: TRIDENT PROBE TRANSITION ZONE WATER SAMPLING

The purpose of this SOP is to define and standardize the methods for collecting and processing transition zone water samples using the Trident Probe. The Trident Probe will be operated in accordance with the procedures described in *Coastal Contaminant Migration Monitoring: The Trident Probe and UltraSeep System* (SSC et al. 2003). Select portions of these procedures are incorporated here, as appropriate.

Operation of the Trident Probe will be conducted by Coastal Monitoring Associates. Integral personnel will assist in the transition zone water sample collection and will be responsible for sample handling and field documentation.

6.1.1. Summary of Method

The Trident Probe itself is a simple, direct-push system equipped with temperature, conductivity, and water sampling probes. The Trident Probe will be lowered from a vessel via a push pole for water depths up to 25 ft. For water depths greater than 25 ft, the Trident Probe will be deployed by a diver. Coupled to the mounting base that holds the temperature and water sampling probes is a submersible air hammer that can be used to assist driving the probes into the sediment.

The Trident Probe water sampling probe is used to collect *in-situ* water samples for transition zone water characterization by applying suction and drawing the transition zone water to the surface. Once at the surface, the transition zone water will be processed and transferred to the appropriate pre-preserved sample vials.

6.1.2. Sampling Vessel

A single sampling vessel will be required during the Trident transition zone water sampling. It will have a deck large enough to accommodate three crew members and the captain. Deck space will also be sufficient to hold all required supplies and equipment for sampling and appropriate safety equipment. This vessel will also be equipped with navigational lights, anchors, and basic sonar.

6.1.3. Supplies and Equipment

There are five major pieces of equipment required to operate the Trident system: 1) the Trident Probe, 2) the communications/pneumatic cable, 3) Geoprobe®'s FC4000 field computer, 4) a laptop computer with the proper system requirements, and 5) a handheld geographic positioning system (GPS) unit with an RS-232 interface. In many cases, a 12-V deep-cycle car battery and 750-watt power inverter will be required for portable power.

A full listing of the required equipment is provided in Table 6-1, including the additional equipment required for general support of the transition zone water sampling effort. Equipment and supplies include sampling equipment, utensils, sample containers, coolers, logbooks and forms, personal protection equipment, and personal gear. Protective wear (e.g., hard hats, gloves), as required for health and safety of field personnel, is as specified in the health and safety plan (HSP; Integral 2004b).

6.1.4. Procedures

6.1.4.1. Transition Zone Water Sampling Procedures

The approach to transition zone water sampling with the Trident Probe is described in Attachment 1 to the SAP. The specific procedures for use of the Trident Probe for recording sediment temperature and conductivity and for collecting transition zone water samples are described in SSC et al. (2003). The conductivity probe will be calibrated daily, prior to sampling. Calibration information will be recorded in the logbook.

Station positioning will be accomplished per SOP C. At each station, the Trident Probe will be deployed from the vessel using a push pole system if the water depth is less than or equal to 25 ft, or by diver it the water is deeper. Temperature and conductivity in the riverbed sediments will be recorded at each sampling location. The Trident Probe will employ the use of a peristaltic pump for water sampling. A volume equivalent to 3 times the pore volume of the tubing plus sampling probe will be purged at a low flow rate (<100 mL/min) from the sampler prior to sample collection. Field parameters of pH, conductivity, and turbidity will be measured following purging. The pH, conductivity, and turbidity meters/probes will be calibrated daily in accordance with the manufacturer's specifications, and the calibration will be checked daily. Calibration information will be recorded in the logbook.

After purging, the transition zone water will be pumped directly into the appropriate pre-preserved sample bottles. If filtered samples are also to be collected, the pump will then be stopped and a 0.45-µm cartridge filter attached to the pump discharge tubing. The pump will then be re-started, and the discharge will be directed to the appropriate pre-preserved sample bottles. The two-person "clean hands – dirty hands" method (EPA 1996b; SOP F) will be used, as appropriate, during this process.

There is a potential that the sample volume may be limited (e.g., due to sediment texture or clogging of the sample probe). The sample bottles for VOC analyses (if applicable) will be filled first and sealed with zero headspace. The remaining bottles will be filled in the following order, depending on site-specific analyte lists: organics, metals, and conventional parameters.

SOP E describes the sample custody, labeling, and handling procedures that will be followed. All field activities will be documented per the procedures summarized in SOP D.

6.1.4.2. Decontamination Procedures

The Trident sampling probe and associated tubing will be decontaminated prior to deployment at each sampling station. Designated tubing may also be used, negating the need for decontamination of tubing. The peristaltic pump will be used to draw the decontamination solutions through all portions of the sampling probe that comes in contact with sediment transition zone water. The decontamination process will proceed according to the following protocol:

1. Rinse with river water.
2. Wash with brush and Alconox™ or other phosphate-free detergent.
3. Double rinse with deionized water.
4. Rinse with 0.1 N nitric acid.
5. Rinse with deionized water.

To minimize sample contamination, gloves will be replaced or thoroughly washed using Alconox™ or other phosphate-free detergent and rinsed with distilled water before and after handling each sample, as appropriate. Rinse waters will be diluted with river water and discarded into the river.

6.1.5. Field Quality Control Procedures

Field QC samples will match specifications in the FSP. In addition, all volatile samples will be stored and shipped with a trip blank. Finally, an equipment rinsate blank will be collected following decontamination of the Trident sampling probe and tubing at each site.

6.2. SOP B: SMALL-VOLUME PEEPER TRANSITION ~~ZONE~~ ZONE WATER SAMPLING

The purpose of this SOP is to define and standardize the methods for collecting and processing transition zone water using small-volume peepers. This SOP utilizes and augments the procedures outlined in EPA's *Measuring and Monitoring Technologies for the 21st Century ($21M^2$): Sampling for Contaminants in Sediments and Sediment Pore Water* (EPA 2004) and the *Stormwater Effects Handbook: A Toolbox for Watershed Managers, Scientists, and Engineers* (Burton and Pitt 2002).

6.2.1. Summary of Method

Transition zone water samples for chemical analyses will be collected using small-volume peepers in areas of fine-grained sediments. These samplers will be deployed by divers at sampling stations previously determined by groundwater mapping, as described in the Round 2 Groundwater Pathway Assessment Sampling FSP (Attachment 2 to the SAP). These sampling stations will be marked and located according to the methods described in SOP C.

The samplers will be installed by divers within the upper ~30 cm of the sediment and left in place for a 3-week period to allow the fluids within the samplers to equilibrate with the transition zone water in the surrounding sediments. Divers will retrieve the samplers after equilibration and transport them to a vessel at the surface for sample processing. The transition zone water samples will be processed using the two-person, clean hands – dirty hands method (EPA 1996b; SOP F).

6.2.2. Sampling Vessels

Two sampling vessels will be required during both the deployment and retrieval phases of the *in-situ* diffusion sampling. During the deployment phase, one vessel will serve as the staging area for the divers and will be anchored near the sampling area. It will have a deck big enough to accommodate two divers and one crewmember. A second inflatable raft will provide storage space for sampling equipment, such as the coolers containing the samplers, and argon gas tanks (which will used to keep conditions inside the coolers anoxic; see below). This raft will also be used to transport supplies and personnel to and from the larger boat as needed during this phase. The dive vessel will also be equipped with navigational lights, anchors, and basic sonar.

During the sample recovery stage, two vessels will again be required. The first will act as the staging area for the divers and will be large enough to accommodate two divers, one crew member, and the captain. The second vessel will serve as a "wet-lab" for sample processing. It will have enough deck space to accommodate three crew members and the captain, sample coolers, and sampling equipment boxes containing sample bottles and other ancillary equipment. Deck space will also permit room for sample processing, which will require a bench top or table for extraction of water from the peepers and for sample aliquoting. Both of these vessels will be equipped with navigational lights, anchors, and basic sonar. A third, smaller vessel may be required during the recovery phase to shuttle supplies (e.g., sample jars, coolers, ice), samples, and replacement personnel between the larger vessels and the shore.

6.2.3. Supplies and Equipment

The general types of equipment that are required to support the small-volume peeper sampling effort are described in this section. A detailed supply and equipment list is provided in Table 6-2. Equipment and supplies include sampling equipment, utensils, sample containers, coolers, logbooks and forms, personal protection equipment, and personal gear. Protective wear (e.g., hard hats, gloves), as required for health and safety of field personnel, is as specified in the HSP (Integral 2004b).

The small-volume peepers that will be used in the Round 2 Groundwater Pathway Assessment are commercially available, 15-inch × 6-inch × 0.6-inch plate peepers. The design of this peeper is based on that described by Hesslein (1976). The sampler is made of a 0.3-cm-thick acrylic plastic cover sandwiched with a 1.3-cm-thick acrylic plastic body and held together by screws. Twenty-eight rows of horizontal, elongated sampling compartments are machined through the 0.3-cm cover and into the acrylic body. Alternate rows consist of either one 5.5-inch-long compartment spanning the width of the peeper or two 2.5-inch-short compartments separated by 0.5-inch area containing a screw.

To prepare the apparatus for sampling, the compartments of the peeper body are filled with distilled water, and a 5-µm Teflon® membrane is placed over the filled compartments. The acrylic cover, containing elongated openings spaced exactly opposite the compartments of the peeper body, is placed on top of the membrane and tightly connected to the body with stainless-steel screws. Each long compartment holds approximately 9 mL of water, and each short compartment holds approximately 3.5 mL of water. The sampler is capable of collecting an approximate total of 225 mL of sample volume over a 38-cm sediment depth (though actual volume recovered may be slightly less). The peeper will be fitted with a nylon strap, which will allow for attachment to the leader line to aid in recovery.

Once the sample chambers are filled and the peepers sealed, the peepers will be placed in a cooler filled two-thirds full with DI water. The coolers will be modified such that argon gas may be sparged through the water in the cooler while it is sealed (except for a small gas vent). This will allow the samplers to be stored under anoxic conditions during transport to the field.

6.2.4. Sampling Procedures

6.2.4.1. Station Positioning

The correct position of the sampling station will be located using the methods prescribed by SOP C. The captains will anchor the vessels near the sampling station and switch off the engines. To guide the deployment and recovery of the small-volume peepers, a diver will tie a “leader line” to the base of a nearby fixed structure (e.g., dock, piling) that can be easily re-located during the recovery phase. The line will be placed along the river bottom such that it extends from the fixed structure to approximately 10 feet beyond the sampling station location. Plastic-coated anchors will be attached to the rope such that they will rest on either side of the sampling station and prevent the line from moving. A loop will be tied in the ropes marking the location where the peepers will be located. Each peeper that is deployed at the location will be attached to the loop in a radial pattern and spaced at approximately 2-ft intervals. A diver will deploy the leader line by tying the lines to the fixed structure and extending the rope across the sampling location—taking care to ensure that the rope is taut between the two anchors that span the sampling station. Appropriate precautions will be taken to ensure that the leader rope is situated such that it will not be tampered with or inadvertently disturbed (e.g., by boat traffic).

6.2.4.2. Sampler Deployment

The following steps will be taken in order to install the small-volume peepers:

1. The peepers will be removed from the storage cooler and handed to the diver for deployment. The diver will carry as many samplers as practical and safe, and will make repeated dives as necessary to deploy all of the samplers. The diver will also carry a small sledge hammer and a small trowel to assist in the sampler deployment.
2. The diver will descend to the base of the fixed structure, locate the appropriate lead line, and then move along the lead line to the first loop indicating the first location for sampler deployment at the sampling station.
3. The diver will push the first small-volume peeper into the sediment such that the uppermost sampling chambers are just below the mudline. The sledge hammer will be used, as necessary, to drive the sampler into the sediment. In the event that the sampler cannot be completely driven into the sediments, the number of sample compartments present above the mudline will be recorded so that these sampling compartments are not included in sample composite during the sampler recovery and processing phase. Each peeper will be equipped with a

nylon strap with a carabiner at its end. This will allow the peeper to be connected to the loop in the leader line marking the sampler location. Care will be taken to ensure there is plenty of slack in the strap above the sediment surface. At sampling stations requiring multiple small-volume peepers, the diver will move to the next loop in the rope and repeat the peeper placement process.

6.2.4.3. Sampler Recovery

The following steps will be taken in order to recover the small-volume peepers:

1. The correct position of the sampling station will be located using the methods prescribed by SOP C. The captain will anchor the vessel near the sample site and switch off the engines.
2. The diver will descend along the lead line to the sampling station. The diver will be equipped with a recovery line that will extend from the sampling station to the vessel.
3. The diver will carefully extract the peeper sampler and attach it to the recovery line using a carabineer. The diver will then signal the crew member to reel in the lead recovery line and bring the sampler to the surface.
4. Once the samplers are brought to the surface, they will be transferred to the sample processing vessel, and the sampler recovery process will be repeated for the next sampling station.

6.2.4.4. Sampler Processing

Three crew members will be responsible for processing the small-volume peeper samples. Clean hands - dirty hands methods, per the general protocols outlined in SOP F, will be employed, as appropriate, during the sample processing.

SOP E describes the sample custody, labeling, and handling procedures that will be followed. All field activities will be documented per the procedures summarized in SOP D.

The sample processing of the small-volume peepers will be completed according the following protocol:

1. City water will be used to wash any loose sediments from the front of the small-volume peeper where the membrane covering the sample chambers is exposed.
2. The clean hands (CH) person will use a syringe to extract transition zone water from the chambers of the small-volume peeper. The sample will be extracted from each chamber of the peeper by piercing the membrane with the syringe needle and pulling back on the syringe plunger. The transition zone water sample water will be extracted from pre-selected sample chambers such that each aliquot will be representative of the upper 30-cm vertical profile of the

sediment column. After extraction, the syringe needle will be replaced with clean, flexible LDPE tubing to minimize aeration during filling of the sample containers. The water will be extracted to fill sample bottles in the following order: VOCs, TPH-G, other organic parameters, metals, perchlorate, and conventional parameters. Multiple small-volume peepers will likely be required at each sampling station to obtain the required sample volume.

3. After the target sample volume is transferred to the sample bottle, the CH person will close the bottle and will fill out the label (per SOP E).
4. Once all of the sample bottles are filled and labeled, the dirty hands (DH) person will then wrap the sample bottles in packing materials and place them in the coolers (per SOP E).

6.2.4.5. Equipment Decontamination

Because new equipment will be used at each sample station and no equipment will be reused, equipment decontamination is not required.

6.2.4.6. Field Quality Control Procedures

Field QC samples will match specifications in the FSP. In addition, all volatile samples will be stored and shipped with a trip blank. Because all equipment will be new and designated to each sampling station, one ~~E~~equipment rinsate blank~~s~~ will ~~not~~ be collected, and considered representative for all sites~~, as~~. ~~all equipment will be new and designated to each sampling station.~~

6.3. SOP C: STATION POSITIONING AND VERTICAL CONTROL

The purpose of this SOP is to define and standardize the methods by which sample station positioning and vertical control will be established during the 2005 transition zone water sampling effort.

Latitude and longitude coordinates for the sampling stations will be obtained using a digital GPS (DGPS). The standard projection method to be used during field activities is Horizontal Datum: North American Datum of 1983, State Plan Coordinate System, Oregon North Zone. The positioning objective is to accurately determine and record the positions of all sampling stations to within ±2 meters.

The DGPS consists of a GPS receiver on the vessel and a differential receiver located at a horizontal control point. At the control point, the GPS-derived position is compared with the known horizontal location, offsets or biases are calculated, and the correction factors are telemetered to the GPS receiver located on the boat. Positioning accuracies on the order of ±2 meters can be achieved by avoiding the few minutes per day when the satellites are not providing the same level of signal. The GPS system provides the operator with a listing of the time intervals during the day when accuracies are decreased. Avoidance of these time intervals permits the operator to maintain better positioning accuracy. The GPS receiver routes latitude and longitude to an integrated navigation system, which displays the vessel's position in plan view. Navigation data, such as range and bearing from the target buoy location, are provided at a user-defined scale to guide the vessel's pilot to the desired location.

Vertical positioning is required to establish the elevation of the riverbed at the sampling stations. Depth to mudline will be measured using a lead line or fathometer immediately prior to buoy placement. Vertical measurements will be recorded to the nearest 0.1 foot. Water depths will be converted to elevations (feet Columbia River Datum) based on the river stage at the time of sampling as recorded at the Morrison Street Bridge.

A vessel-mounted DGPS will be used to locate the vessels and sampling equipment at the coordinates of the transition zone water sampling stations.

6.4. SOP D: BULK SEDIMENT AND EX-SITU TRANSITION ~~ZONE~~ ZONE WATER EXTRACTION

The purpose of this SOP is to define and standardize the methods for collecting bulk sediment samples using a power grab sampler for collection of bulk sediment samples. Samples will be collected in a consistent, repeatable manner with a hydraulic power-grab sampler provided by Marine Sampling Systems (MSS), Burley, WA. The sampler will be attached to the vessel via a winch cable with a ball-bearing swivel to prevent twisting movements during deployment. The device will be raised and lowered through the water column by the vessel's winch at a rate of no more than 20 meters per minute. This will ensure that the sampler does not flip over on descent and will prevent disturbance of the sediment surface upon retrieval.

The maximum penetration of the power-grab sampler is 30 cm, and a minimum penetration of 20 cm will constitute an acceptable grab. Materials remaining in the power-grab sampler following collection of materials for sample analyses will be logged by an experienced geologist per the methods prescribed in SOP H.

6.4.1. Sampling Vessels

One sampling vessel will be required during bulk sediment sample collection. This vessel will be the *Peter R*, which will be provided by MSS. The *Peter R* is 29-ft-long and 10-ft wide, and draws about 2 feet. This vessel provides deck space sufficient to accommodate three crew members, a navigator, and the captain, as well as coolers and sampling equipment boxes. It is also large enough for the footprint of the power-grab sampler and provides sufficient workspace for sample processing. The vessel is equipped with navigational lights, anchors, and basic sonar. A smaller vessel may be required to shuttle supplies (e.g., sample tubes, coolers, ice), samples, and replacement personnel between the larger vessel and the shore.

6.4.2. Supplies and Equipment

The general types of equipment that are required are described in this section. A detailed supply and equipment list is provided in Table 6-3. Equipment and supplies include sampling equipment, utensils, sample containers, coolers, logbooks and forms, personal protection equipment, and personal gear. Protective wear (e.g., hard hats, gloves), as required for health and safety of field personnel, is as specified in the HSP (Integral 2004b).

The power-grab sampler that will be used in the pilot study is commercially available and constructed of stainless steel. The sampler weighs 200 lbs, though additional weights can be added to the base to allow for deeper penetration in sandy sediments, resulting in a total weight of 450 lbs. The sampler collects sediment from a 0.3-m^2 riverbed area to a depth of up to 30 cm.

6.4.3. Sampling Procedures

Bulk sediment collection will employ a stainless-steel hydraulic power grab sampler, provided by MSS. Sediment sample collection will follow the procedures described in the Portland Harbor RI/FS Round 2 Field Sampling Plan for Sediment Sampling and Benthic Toxicity Testing, Appendix F (Integral et al. 2004).

6.4.4. Equipment Decontamination

The entire power grab assembly will be decontaminated after each sample is collected. The apparatus will first be rinsed with river water and then will be thoroughly washed with Alconox® or other phosphate-free detergent using a bristle brush before use at a new station. If residual creosote or petroleum sheen remains on the corer or is difficult to remove using the decontamination procedures above, a hexane rinse may be added. Following these steps, the corer will be rinsed with deionized water, rinsed with 0.1 N nitric acid, and given a final rinse with deionized water. To minimize sample contamination, gloves will be replaced or thoroughly washed using Alconox™ or other phosphate-free detergent and rinsed with distilled water before and after handling each sample, as appropriate.

Prior to use, the butyrate tubes will be decontaminated according to the following protocol:

1. Rinse with river water.
2. Wash with brush and Alconox™ or other phosphate-free detergent.
3. Double rinse with deionized water.
4. Rinse with 0.1 N nitric acid.
5. Rinse with deionized water.

6.4.5. Field Quality Control Procedures

Field QC samples will consist of a field replicate at two select locations. An equipment rinsate blank will not be required for the box corer because sediment that comes into contact with the walls of the power grab sampler will not be collected for analysis. This blank will be collected by rinsing a decontaminated tube with DI water and collecting the water for chemical analysis.

6.5. SOP E: FIELD DOCUMENTATION

This SOP describes the general protocols that will be followed to document the field activities.

All the field activities and observations will be noted in a field logbook during fieldwork. The field logbook will be a bound document containing individual field and sample log forms. Information will include personnel, date, time, buoy designation, sampler device, types of samples collected, and general observations. Any changes that occur at the site (e.g., personnel, responsibilities, deviations from the FSP and SOPs) and the reasons for these changes will be documented in the field logbook.

Logbook entries will be clearly written with enough detail so that participants can reconstruct events later, if necessary. Requirements for logbook entries will follow the guidelines specified in the QAPP (Appendix A).

When the field activity is complete, the logbook will be entered into the Portland Harbor project file. A sample collection checklist will be provided prior to sampling and competed following sampling operations at each station. The checklist will include station designations, types of samples to be collected (e.g., one bottle for metals), and the field QC samples to be collected.

6.6. SOP F: SAMPLE LABELING, ~~HANDLING~~HANDLING, AND ~~CUSTODY~~CUSTODY

The purpose of this SOP is to define and standardize the methods for sample labeling, handling, and custody during the 2005 transition zone water sampling effort.

6.6.1. Sample Labeling

A unique code is assigned to each sample as part of the data record. This code indicates the project phase, sampling location, sampling method, and level of replication. Sample identifiers consist of three components separated by dashes. The first component, LWG2, identifies the data as belonging to the Lower Willamette River Round 2 sampling effort. The second component indicates whether the sample was collected by the Trident Probe (T) or by small-volume peepers. The station number is the next component, followed by “unf” or “fil” to designate whether the sample was filtered in the field. A single digit number is used to indicate field replicates or splits in the third component of the sample identifiers.

Note that in cases where samples consist of multiple bottles from the same station, each bottle will be assigned the same sample number. Replicates from the same station, however, will be assigned a different sample number, as will filtered vs. unfiltered samples.

The sample number, tag number, and ID will be recorded on the sample label, the chain-of-custody (COC) form, and the logbook. The sample labels and log book will include the project name, sampler's initials, analysis to be performed, date, and time.

6.6.2. Sample Custody

6.6.2.1. Field

The field leader or other designated field sample custodian is responsible for all sample tracking and chain-of-custody (COC) procedures until sample custody is transferred to the laboratory. Custody procedures in the field are as follows:

1. Record all field and sample collection activities (including sample number, sample tag, sample ID, collection time and date) in the field logbook. While being used in the field, the logbook remains with the field team at all times. Upon completion of the sampling effort, the logbook is reproduced and then kept in a secure area.
2. Complete a COC form whenever samples are being transferred or removed from the custody of field sampling personnel. Record each individual sample on the form. Include additional information to assist in sample tracking such as collection date and time, number of containers, and sample matrix. The COC may also serve as the sample analysis request form, with the required analysis indicated for each individual sample.
3. Sign the form and ensure that the samples are not left unattended unless secured.
4. Store, pack, or ship samples as described in the following section. Place the original completed COC form in a sealed plastic bag inside the shipping container. A copy is retained by the shipping party.
5. Complete a separate custody form for each individual shipping container or a single form for all samples in multiple shipping containers in a single shipment, with the number of containers noted on the custody form.
6. Attach completed custody seals to any shipping container that will be sent to the laboratory by delivery service or courier. Delivery personnel are not required to sign the custody form if custody seals are used. Custody seals are used to detect unauthorized tampering with the samples. Gummed paper or tape should be used so that the seal must be broken when the container is opened. The

laboratory sample custodian (or other sample recipient) will establish the integrity of the seals.

7. The laboratory custodian (or other sample recipient) acknowledges receipt of the samples by signing, dating, and noting the time of transfer on the COC form. The condition of the samples and any problems or irregularities (e.g., cracked or broken jars, loose lids, evidence of tampering) should also be recorded. Return a copy of the completed custody form to the project manger or designated sample coordinator.

6.6.2.2. Laboratory

The laboratory designates a sample custodian who is responsible for receiving samples and documenting their progress through the laboratory analytical process. Each custodian ensures that the COC and sample tracking forms are properly completed, signed, and initialed on transfer of the samples. Specific laboratory COC procedures should be in writing, included in the laboratory QA plan, and approved prior to beginning sampling and analysis. Laboratory custody procedures include the following:

- A designated laboratory person initiates and maintains a sample tracking log that will follow each sample through all stages of laboratory processing and analysis.
- The laboratory tracking log includes, at a minimum, the sample number, location, and type of storage; date and time of each removal; and signature of the person removing or returning the sample.

The final disposition of the sample is recorded.

6.6.2.3. Chain-of-Custody Quality Control

Complete and correct COC is essential to ensure and demonstrate sample integrity. Errors in entering information or transferring custody can result in analytical or data reporting errors. Inaccuracies or errors in sample tracking and custody records can compromise data usability, particularly as legal evidence.

QC procedures include the following:

- Allow adequate time to take accurate and complete field records and to carefully complete COC forms.
- When possible, work in pairs or more to complete the COC form and check for accurate information entry.
- Complete all custody records in ink; errors should be neatly crossed out and corrected and initialed by the person making the change.
- Immediately notify the project manager of any deviation from required custody procedures.

6.6.3. Sample Processing

The samples collected during the 2005 transition zone water sampling effort will be processed according to the protocols proscribed by the specific sampling method (and associated SOP). This section describes the general sample processing protocols that are common to all or most of the methods.

The analytical laboratory will supply sample containers and preservatives, as well as coolers and packing material. Commercially available pre-cleaned bottles will be used, and the laboratory will maintain a record of certification from the suppliers. The bottle shipment documentation will record batch numbers for the bottles. With this documentation, bottles can be traced to the supplier, and bottle wash analysis results can be reviewed. The bottle wash certificate documentation is archived in the Integral project file. Field personnel will not obstruct these stickers with sample labels. Sample containers will be clearly labeled at the time of sampling.

Environmental samples will be packed in a manner to reduce the chance of sample breakage, ensure sample integrity, and prevent material leakage and potential exposure to hazardous materials in the event of breakage. Samples will be placed in sealed plastic bags and packed in a sturdy container with adequate packing material to prevent breakage. Ice or dry ice may be included to maintain sample storage conditions. Samples will be transported by field personnel or shipped via courier or common carrier. Shipping procedures are in accordance with U.S. Department of Transportation regulations (49 CFR 173.6 and 49 CFR 173.24).

Upon completion of final sample inventory by the field sample custodian and completion of COC, samples will be packed as follows:

1. Line a cooler bottom with bubble wrap and place a large, 30-gallon bag inside another bag of same size and place it inside the cooler. The cooler should have the drain sealed with duct tape.
2. Wearing disposable powderless nitrile gloves, wrap each double-bagged glass sample container in bubble wrap or place it in a bubble wrap plastic bag. [*Note*: When samples are being transported by field personnel directly from the field site to the laboratory (thereby ensuring careful handling), this step is recommended but may be omitted. However, this step is required when a courier or delivery service is transporting the samples.]
3. Place the samples tightly inside the double bag in the shipping container:
    - Use dividers or bubble wrap to separate all glass containers.
    - Seal large plastic bags with rubber bands or plastic tie.
    - Fill any empty space in the shipping cooler or box with packing material so that the jars are held securely.

4. Place the original completed COC form in a sealed plastic bag and place it inside the shipping container. If using a cooler or ice chest, the form should be securely taped to the inside of lid.
5. If required to meet sample storage requirements, fill the ice chest with crushed or block ice, blue ice (refrigerated samples, 4°C) or dry ice (frozen samples). A temperature blank (provided by the laboratory) should be packed in each cooler.
6. Seal shipping container securely with packing or duct tape.
7. If the shipping container will be transported by anyone other than the person who completed and signed the COC form, attach completed custody seals so that the shipping container cannot be opened without breaking the seal.
8. Attach a *This End Up* label to each side of the shipping container to ensure that jars are transported in an upright position. A *Fragile* label may also be attached to reduce rough handling of the samples.
9. Label the shipping container with all appropriate information (name of project, time and date, responsible person and company name, address and phone) to enable positive identification.

All preserved samples will be shipped as soon as possible after completion of sampling. This minimizes the number of people handling samples and protects sample quality and security.

Packed containers may be delivered to the laboratory or storage facility by field personnel, courier, or common carrier (FedEx, UPS). However, any outside carrier or courier service must provide a delivery receipt. The carrier or courier must also ensure delivery time if holding time and storage conditions are critical. Unless arranged in advance, shipping charges should be prepaid by sender to avoid confusion and possible rejection of the package by the laboratory.

The adequacy of handling and shipping procedures is reflected in the condition of the samples upon receipt by the laboratory:

- No jars are cracked or broken.
- There is no evidence of sample leakage.
- Measuring the temperature of the temperature black indicates that correct storage conditions have been maintained.

The sample custodian or other designated person is responsible for confirming that copies of all shipping documents, completed in full and correctly, are on file at Integral.

6.7. SOP G: CLEAN HANDS - DIRTY HANDS TECHNIQUE

This SOP describes the general protocols for use of the clean hands – dirty hands technique for sample processing was developed based on the methods presented in EPA (1996b).

The clean hands - dirty hands technique requires two or more people working together. At the field site, one person is designated as CH and a second person as DH. Although specific tasks are assigned at the start to CH or DH, some tasks overlap and can be handled by either as long as contamination is not introduced into the samples. Both CH and DH wear appropriate non-contaminating, disposable, powderless nitrile gloves during the entire sampling operation and change gloves frequently, usually with each change in task (wearing multiple layers of gloves allows rapid glove changes).

CH takes care of all operations that involve equipment that comes into contact with the sample, including the following responsibilities:

- Handles the small- and large-volume peepers and the vapor diffusion samplers
- Prepares a clean workspace (inside boat)
- Sets up the processing
- Sets the equipment (i.e., the syringes and sample bottles)
- Works exclusively on aliquoting samples into sample bottles.

DH takes care of all operations that involve contact with potential sources of contamination, including the following responsibilities:

- Works exclusively exterior to the sample processing area
- Handles the tools, such as hammers, wrenches, keys, locks, and argon tank regulators
- Measures and records the water depths.

6.8. SOP H: SEDIMENT MATERIALS AND LITHOLOGIC LOGGING

Surface sediments collected during the bulk sediment sampling and cores collected during the Geoprobe® investigation will be systematically logged by an experienced geologist. The following information will be recorded for each core:

- Physical sediment description (i.e., sediment type, density/consistency, color)
- Odor (e.g., hydrogen sulfide, petroleum)
- Visual stratification and lenses

- Vegetation
- Debris
- Evidence of biological activity (e.g., detritus, shells, tubes, bioturbation, live or dead organisms)
- Presence of oil sheen
- Other distinguishing characteristics or features.

The visual description of sediment lithology (dominant grain sizes) will be the primary criteria for determining sample intervals (i.e., lithologic units) in the cores.

For consistency, core descriptions and terms used will follow the criteria below, which are modified from methods presented in ASTM D 2488-00 (ASTM 2000).

1. Visual estimates of the grain-size percentages of sediment units within each core will be recorded on the core logs so that the total sum will add up to 100%. Estimates of gravel, sand, and fines (silt and clay) content will generally be made to the nearest quartiles:

    - 0% to 25%
    - >25% to 50%
    - >50% to 75%
    - >75% to 100%.

    The sediment may also be described narratively on the log based on the estimated grain-size percentages. The dominant constituent grain size will be the primary unit descriptor, with the abundance of other grain sizes present described using the following terms:

    - The grain-size adjective (e.g., *gravelly, sandy, silty, or clayey*), if estimated to constitute more than 25% of the sediment
    - *With*, for example, sand with silt, silt with sand, etc., if estimated to constitute less than 25% of the sediment
    - *Trace*, if estimated less than 5% of the sediment (and not included in the total 100%).

2. For other features observed, such as organics or debris, additional descriptive terms may include:

    - *Mostly*, if estimated to comprise 50% or more of the unit
    - *Some*, if estimated to comprise more than 25% to 50% of the unit

- *Little*, if estimated to be 25% of the unit or less
- *Trace*, if estimated less than 5% (and not included in the total 100%).

3. Consistency will be described using the following terms:

    - Density: *loose*, if easily penetrated with a sampling spoon, or *dense*, if penetration is more difficult.
    - Consistency: *very soft*, if present as an ooze that holds no shape
      soft, if saggy
      stiff, if it holds a shape
      very stiff, if penetration with a spoon is low
      hard, if no penetration with a spoon is possible.

4. Other observations (e.g., obvious anthropogenic material, dramatic color changes) may also be used to define or help define sample intervals.

The boundaries of lithologic units will be determined primarily by changes in the top two dominant grain sizes estimated visually (e.g., a change from a silty sand to a gravelly sand or to a sandy silt).

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