5.3 TCRA Cap Porewater Assessment

An assessment of TCDD and TCDF in porewater of the TCRA armored cap was performed in May through July 2012. It was performed to support assessment of the effectiveness of the TCRA armored cap, and to address uncertainties identified by USEPA in comments on the draft PSCR regarding a possible groundwater-to-surface water transport pathway for dioxins and furans originating in the wastes within the original 1966 perimeter of the impoundments north of I-10, as described in the TCRA Cap Porewater Assessment SAP (Integral and Anchor QEA 2012b). The objective of the TCRA armored cap porewater assessment was to generate new information relevant to two study elements described in the RI/FS Work Plan (Anchor QEA and Integral 2010a):

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

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

Data generated from this sampling event for Study Element 4 also support evaluation of remedial alternatives that incorporate the TCRA armored cap into the final remedy. The data can be used to support decisions about whether, and in what manner, the operations monitoring and maintenance plan should address porewater and surface water quality.

5.3.1 Methods

Information to support evaluation of the presence or absence of a vertical gradient of concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF in porewater and surface water was collected with SPME fibers during the TCRA armored cap porewater monitoring effort. These two congeners were chosen because they are known to be associated with the paper

mill waste of the kind that may have been deposited in the northern impoundments (e.g., Table 9, Integral 2011e), and they are significant contributors to total $TEQ_{DF,M}$ concentrations in sediments within the 1966 perimeter of the northern impoundments. Both are hydrophobic with similar estimated ranges of octanol-water partition coefficients (K_{OW}).

Deployment of SPME fibers into the sediment matrix is an equilibrium extraction technique used to sense dissolved concentrations of hydrophobic organic compounds in porewater, and does not require prohibitively large volumes of porewater for analysis (Mayer et al. 2000). SPME samplers were used to evaluate whether gradients in dissolved concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF (the target compounds) may be present in the porewater in TCRA armored cap material types A, B/C, C, and D (Figure 2-14). Three discrete samples from different depth intervals were collected at each sampling location (Table 5-19) to provide a vertical profile of any 2,3,7,8-TCDD and 2,3,7,8-TCDF through the TCRA armored cap at that location. The vertical samples were taken in 5-cm increments just above the geotextile fabric, midway between the fabric and the surface of the TCRA armored cap, and just below the interface of the cap material and the surface water (Figure 5-23). Because the depth of cap material within the TCRA armored cap varies, the vertical distance between fiber samples within any given sampling location varied. The use of 5-cm increments as the sample unit was selected to balance the analytical sensitivity, which is greater with greater sample mass (a function of the increment length), against the need to estimate porewater concentrations at discrete points within the vertical dimension at each sampling point.

In two locations, the SPME sampler for the location included an additional SPME fiber attached to the portion of the sampler extending above the surface of the TCRA armored cap. In these locations, a 5-cm sample from the fiber exposed to surface water was used for comparison with results in porewater (Figure 5-23). Two surface water sampling locations were deemed sufficient because the overlying surface water in the San Jacinto River was expected to be well-mixed and average concentrations for 2,3,7,8-TCDD and 2,3,7,8-TCDF in the surface water were expected to be consistent throughout the area. SPME sampling devices from which the three vertical porewater measurements were made were deployed in 14 locations within the submerged portions of the TCRA armored cap (Figure 5-23).

In addition to the SPME sampler deployed at each sampling location, four samplers were deployed containing a fiber impregnated with performance reference compounds (PRCs) to provide a method for determining the degree to which the samplers had reached equilibrium with the surrounding porewater or surface water at the time of retrieval. The PRCs for this study were carbon-13 ($^{13}C_{12}$)-labeled 2,3,7,8-TCDD and 2,3,7,8-TCDF, and the PRC samplers were impregnated with carbon-labeled 2,3,7,8-TCDD and 2,3,7,8-TCDF prior to deployment. The degree of equilibrium reached by each PRC is assessed by measuring the pre-deployment concentrations of the PRCs and comparing them to concentrations of the PRC compounds after SPME retrieval. Because the PRCs are the same as the target chemicals, except for the $^{13}C_{12}$ label, samplers with the PRC-impregnated fibers were positioned in separate sampling devices, and placed in separate, unique locations substantially separated from any regular fiber sampling location.

The chemical transport processes that could affect the time to reach equilibrium in each armor cap material type were assumed to be similar because the nature and thickness of those materials are similar among the cap types, and because tidal fluctuations, which would affect all areas of the TCRA armored cap in the same way, were expected to be a significant factor in the equilibration of the polydimethylsiloxane (PDMS) with the surrounding porewater. There are four primary TCRA armor cap types in the submerged portion of the TCRA armored cap (Figure 2-14); therefore, one PRC sampler was placed in each of the four submerged cap types to evaluate equilibrium conditions in those areas.

There is a fifth armor cap type, armor cap D_{24}, in areas above the normal waterline on the central and southern berm, and in a small intertidal area north of the central berm. Because most of armor cap D_{24} is thicker than the other cap types and the majority of it is not normally below the waterline, it was not specifically targeted for sampling as part of the study.

There were four sampling locations in areas within armor cap A, one within armor cap B, five sampling locations within armor cap C, and four sampling locations within armor cap D (18-inch design thickness) (Figure 2-14). Samples from TCRA armored cap types C and D included a sample interval in the surface water above the TCRA armored cap.

5.3.2 Results

Analytical results presented in this section are expressed as the mass (pg) of each congener present on each fiber at the time of extraction. The mass of each congener is considered representative of the concentration of each target compound in the PDMS coating because of uniformity of sample fiber length (5 cm) and the thickness of PDMS coating on each fiber (corresponding to 115.5 µL/m of fiber).

The pre-deployment mass of the PRC compounds in 5-cm segments of the PRC-impregnated fibers ranged from 166 to 3,140 pg for 2,3,7,8-TCDD and 144 to 4,710 pg for 2,3,7,8-TCDF. Post-retrieval PRC masses are shown in Table 5-20 and indicate the samplers were effectively at equilibrium when they were retrieved and that corrections to non-equilibrium conditions for the other samplers were not required.

The measured masses of 2,3,7,8-TCDD and 2,3,7,8-TCDF on each SPME sample are provided in Table 5-20. These results show that the masses of 2,3,7,8-TCDD in the PDMS coating of the SPME fiber samples were below the analytical detection limit for all sample intervals. The masses of 2,3,7,8-TCDF in the PDMS coating were below the analytical detection limit in 47 of 50 sample intervals. The three sample intervals that had measureable mass of 2,3,7,8-TCDF were from Station SJCP008, which is near the central part of the eastern cell. The masses of 2,3,7,8-TCDF in all three sample intervals at that location were so low they were qualified as estimated in each case, and are therefore considered to provide only an imprecise representation of the amounts of 2,3,7,8-TCDF in each of these three samples. At the coincident fiber sample exposed to surface water at Station SJCP008, the masses of 2,3,7,8-TCDD and 2,3,7,8-TCDF were below their analytical detection limits.

In regards to the sampling objective of determining whether vertical gradients in concentrations of dioxins and furans in porewater of the TCRA armored cap exist, these data indicate the absence of vertical concentration gradients of dissolved 2,3,7,8-TCDD or 2,3,7,8-TCDF in the porewater within the TCRA armored cap at the time of sampling. At Station SJCP008, results do not definitively indicate a concentration gradient of 2,3,7,8-TCDF because masses occurring in the PDMS at the end of the exposure period could only be estimated by the laboratory. These results reflect conditions at the time of sampling, consistent with the DQOs for the study.

Uptake of each congener into the polymer is described by a PDMS-water partitioning coefficient, or $K_{P\text{-}W}$. Using the congener-specific $K_{P\text{-}W}$, the dissolved water concentrations can be derived as (Mayer et al. 2000):

$$C_{PW} = C_{PDMS}/K_{P\text{-}W} \qquad \text{(Eq. 5-1)}$$

where:

C_{PW}	=	concentration in porewater (pg/L)
C_{PDMS}	=	concentration in the PDMS coating on the fiber (pg/L)
$K_{P\text{-}W}$	=	PDMS-water partitioning coefficient (L/L)

Unless congener-specific $K_{P\text{-}W}$ values are available from other publications or are measured using a site-specific bench-scale study, then the $K_{P\text{-}W}$ value in the equation above is substituted with the published, congener-specific K_{OW}. The K_{OW} is then used to estimate the concentration of each congener in porewater from the C_{PDMS}. Because the K_{OW} is not equal to the $K_{P\text{-}W}$ (e.g., Lu et al. 2011; Mayer et al. 2000), the resulting C_{PW} cannot be interpreted as an estimate of the actual porewater concentration. For this analysis, two different studies were used to estimate the parameters needed to extrapolate from measured concentrations in SPME fibers to estimate the maximum surface water concentration of dissolved 2,3,7,8-TCDD and 2,3,7,8-TCDF. In these cases, the estimate is based on the detection limit concentration for that SPME sample. As shown in Table 5-21, two estimated $K_{P\text{-}W}$ values were used.

In all cases, using the range of $K_{P\text{-}W}$ shown in Table 5-21 and the analytical detection limits in the surface water at sample location SJCP008 in Equation 5-1, the dissolved surface water concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF are below 0.01 pg/L $TEQ_{DF,M}$. As discussed in detail in Section 5.6.4, the observed concentrations of $TEQ_{DF,M}$ in water at TMDL Station 11193 near the northern impoundments during surface water evaluations conducted prior to implementation of the TCRA are between 0.02 pg/L and 0.26 pg/L. These results indicate the TCRA armored cap is currently effective in eliminating any release of dioxins and furans associated with waste materials within the northern impoundments, and the TCRA armored cap is also currently effective in reducing or eliminating the potential release of dissolved-

phase dioxins and furans from the northern impoundments into the surface water of the river.

In regards to the question of whether porewater concentrations in the TCRA armored cap differ from concentrations in surface water above the cap, the results indicate that, with the exception of Station SJCP008, there were no detectable concentrations of 2,3,7,8-TCDD or 2,3,7,8-TCDF in the SPME fibers exposed to porewater or surface water. In the samples from Station SJCP008, where there were detectable concentrations of 2,3,7,8-TCDF, the estimated $TEQ_{DF,M}$ concentration is below 0.01 pg/L $TEQ_{DF,M}$.

5.4 Source Evaluation

USEPA guidance for conducting an RI/FS under CERCLA (USEPA 1988) indicates that identification of sources of contamination is a primary and central component of the RI. The source evaluation informs the FS because effective remediation depends upon control of contaminant sources. Sources of COCs to the northern impoundment area and the aquatic environment resulting from disposal of paper mill wastes are discussed in Sections 1.1 and 5.1 of this RI Report. In addition to those sources, the CSM for the northern impoundments and the aquatic environment acknowledges regional sources of dioxins and furans, including atmospheric inputs, industrial effluents, publicly owned treatment works, and stormwater runoff. These regional sources may also contribute substantial amounts of the other COCs within USEPA's Preliminary Site Perimeter.

As described in Section 5.2, spatial patterns of the COCs other than dioxins and furans in sediments and tissue within USEPA's Preliminary Site Perimeter are not fully explained by proximity to the northern impoundments, suggesting that the wastes may not be a source of all the COCs, or that significant sources of COCs other than the impoundments north of I-10 occur within or near USEPA's Preliminary Site Perimeter. Sources of COCs to tissue may be even more complex and broadly distributed than sources to sediments, and sources to tissue of the more mobile blue crab and hardhead catfish likely include specific and non-specific municipal sources in the broader Houston environment.