

Appendix H

Supplementary Evaluations of Small-Volume Chemical Water Column Monitoring Data

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ABBREVIATIONS

2,3,7,8-TCDD	2,3,7,8-tetrachlorodibenzo-p-dioxin
ANOVA	analysis of variance
cfs	cubic feet per second
COPC	contaminant of potential concern
CWCM	Chemical Water Column Monitoring
ETM	estuarine turbidity maximum
HMW PAH	high-molecular weight polycyclic aromatic hydrocarbon
LMW PAH	low-molecular weight polycyclic aromatic hydrocarbon
LPR	Lower Passaic River
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
pg/L	picograms per liter
POC	particulate organic carbon
PVSC	Passaic Valley Sewerage Commission
RI	Remedial Investigation
RM	river mile
sv	small volume
TSS	total suspended solids
USGS	Geological Survey

1 Overview

Additional analyses of the small-volume (sv)-Chemical Water Column Monitoring (CWCM) data are provided as a supplement to Section 6 (Contaminant Fate and Transport Processes) of the Remedial Investigation (RI) report. The following sections present data evaluations of tidal variability (Section 2), longitudinal trends (Section 3), and the influence of flow and tidal forcing (Section 4). Moreover, statistical evaluations of the dataset are presented to further characterize the variability in measured contaminant concentrations and their correlation to physical variables, including a regression analysis in Section 5. In the interest of brevity, the discussion focuses mainly on 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), and the more detailed data presentations are restricted to this contaminant.

To support the discussion that follows, a summary of mean sv-CWCM concentrations at the Lower Passaic River (LPR) sampling stations is provided in Figure 1-1. Mean concentrations are characterized for each of the following categorical variables: sampling depth (top panel, showing surface vs. bottom), tidal phase (second panel, showing mid-tide vs. slack tide), sampling event (third panel), and sampling station¹ (bottom panel). Within each panel, mean concentrations are reported for that categorical variable for each of the following data groupings: all data (first cluster of bars), low-flow and moderate-flow events (second and third clusters, respectively), and sampling stations (fourth through eighth clusters). Figure 1-2 shows the same information on a solids-normalized basis. Red labels are used to indicate that the mean concentrations within a given cluster are statistically different at a $p < 0.05$ significance threshold based on a one-way analysis of variance (ANOVA) on the log-transformed concentrations.² In addition, probability distributions of the underlying contaminant concentration data by station and event are provided for reference in Figures 1-3a through 1-3f, along with the corresponding salinity and suspended solids distributions in Figures 1-3g and 1-3h.

1.1 Data Treatment

This section provides information on data treatment assumptions used in this appendix as well as in Section 6 of the main RI report.

¹ The nomenclature in this and subsequent sv-CWCM figures is as follows: "T000" refers to the station at river mile (RM) 0, "T014" refers to the station at RM 1.4, and "T10.2" refers to the station at RM 10.2. "TTR1" and "TTR2" are the floating stations designed to follow the salt front. TTR1 was located at LPR RM 6.7 (when flows were greater than 1,000 cubic feet per second [cfs]) or approximately 1 mile downstream of the toe of the salt wedge (when flows were less than 1,000 cfs). TTR2 was located at LPR RM 4.2 (when flows were greater than 1,000 cfs) or halfway between the toe of the salt wedge and upstream of RM 1.4 up to RM 4.2 (when flows were less than 1,000 cfs). More generally, TTR1 can be defined as the station near the limit of the salt intrusion, and TTR2 is within the salt wedge (Appendix B). For the two "high-flow" monitoring events in February/March 2013 and June 2103, stations "T067" at RM 6.7 and "T042" at RM 4.2 were reported in place of TTR1 and TTR2, respectively.

² ANOVA significance findings reported in Figures 1-1 and 1-2 are modestly impacted by the log transformation, but the approach is favored given the distribution of the data (e.g., see Section 6, Figure 6-4).

In all sv-CWCM data evaluations presented herein, unless otherwise noted:

- The T067 data are aggregated with TTR1 data, and the T042 data are aggregated with TTR2 data; these stations were only sampled during the February/March and June 2013 sv-CWCM events (as noted above).
- Non-detect values were set to half of the method detection limit for individual contaminants (2,3,7,8-TCDD and mercury). For the contaminants of potential concern (COPCs) that are chemical sums (total polychlorinated biphenyls [PCBs], polycyclic aromatic hydrocarbons [PAHs], and DDx), if all constituents were non-detect then the sum was considered non-detect and half of the maximum method detection limit among the constituents was assigned. In the case of mixed detects and non-detects among the constituents, the sum was regarded as detect, and for the summation non-detected constituents were set to zero for PCB congeners and to half of the constituent detection limit for PAHs and DDx (due to differences in the sensitivity of the analytical methods).

For the analyses presented in Figures 1-1 and 1-2, as well as the regression analysis presented in Section 5, two extreme concentrations of 2,3,7,8-TCDD were excluded as high outliers to prevent undue influence on the means, ANOVA, and regressions. These high values were collected during the August 2011 and June 2012 events at the TTR1 station (1,870 and 1,830 picograms per liter [pg/L], respectively; see Figure 3-4a of this appendix or Figure 6-6a of the main RI report) and were more than an order of magnitude higher than the next highest observed concentration (111 pg/L). Likewise, two PCB results from the February/March 2013 event were excluded as low outliers with concentrations below 0.05 nanogram per liter, more than one order of magnitude lower than the next lowest sample; these low outliers were excluded mainly to avoid undue influence on the regression analysis in Section 5.

Freshwater flow rates at Dundee Dam were characterized using U.S. Geological Survey (USGS) gage #01389890. The event-mean flow rate used in Section 4 (also Section 6.2.3 of the main RI report) was calculated by averaging over the event durations shown in Table 1-1. For the regression analysis in Section 5, samples were matched to the daily average flow rate on the sample date.

Tidal range was calculated from National Oceanic and Atmospheric Administration predictions at the Point-No-Point Station³ (#8530743). The event-mean tidal range used in Section 4 was calculated by averaging individual tidal range estimates (i.e., the difference between low and high tide) over the

³ The predictions at the Point-No-Point station were used in favor of measured data at USGS gage #01392650 at the Passaic Valley Sewerage Commission (PVSC) near RM 0 because PVSC data are mostly unavailable during the two sv-CWCM "high-flow" monitoring events in 2013 (no data for February 26 to 28, March 4 to 5, and June 7 to 10, 2013). Daily tidal range estimates at Point-No-Point and PVSC locations during the sv-CWCM sampling days are well correlated ($R^2 = 0.91$). The correlation is similar for the four lower-flow events ($R^2 = 0.96$) and the moderate-flow events ($R^2 = 0.89$, but data are mainly from the August 2011 and June 2012 events). Only 2 days had differences between the stations exceeding 10% (June 5 and June 6, 2012, had differences of 15% and 13%, respectively).

event durations shown in Table 1-1. For the regression analysis in Section 5, tidal range was matched on a sample time basis.

As in Section 6 of the main RI report, contaminant concentration patterns are here evaluated on both a volumetric basis and solids-normalized basis (i.e., the total volumetric contaminant concentration divided by the suspended solids concentration). Solids-normalized concentrations are deemed relevant given the hydrophobic nature of the contaminants and the observed correlation between volumetric concentration and suspended solids concentrations (Section 6.1 of the main RI report and Section 5 of this appendix), but it is recognized that they are biased high as estimates of particulate concentration (i.e., the volumetric concentration of the particulate phase divided by the suspended solids concentration) to an extent that depends on COPC-specific contaminant behavior (the bias may be highest for the low-molecular-weight PAHs [LMW PAHs]⁴) and likely also on the concentration of suspended solids (dissolved fractions will tend to be higher at low suspended solids concentrations for reversibly sorbed contaminant).

⁴ Relative to other COPCs studied herein, LMW PAHs have a smaller variation in solids-normalized concentration (see Section 6.2 of the main RI report) and among the weaker correlations to suspended solids in the water column (Section 5 of this appendix) and organic carbon in the sediment bed (Section 4.1 of the main RI report). These factors suggest a lower solids affinity, consistent with LMW PAH physicochemical properties, which likely makes solids-normalization a poorer approximation of the sorbed particulate concentration for these compounds.

2 Supplemental Evaluations of Tidal Resuspension

Water column concentration differences between mid-tide (or max-tide) and slack tide, as well as between the surface and bottom of the water column, were discussed in the context of tidal resuspension dynamics in Section 6.2.1 of the main RI report (Figures 6-4 and 6-5). For reference, the data presentations in Figure 6-5 of the main RI report are included here as Figure 2-1, extended to distinguish individual events and to include suspended solids and salinity. Additional characterizations of tidal resuspension are provided below, including station- and event-specific considerations.

2.1 Surface vs. Bottom

On a mean basis, bottom concentrations are higher than surface concentrations when all data are aggregated, and this difference is statistically significant⁵ for all contaminants (Figure 1-1, top panel, left bar cluster; consistent with observations in Section 6.2.1 of the main RI report). The same trend occurs when data are grouped into low-flow and moderate-flow events (Figure 1-1, top panel, second and third clusters), but the statistical significance of the mean differences within each flow regime varies among the contaminants. On a station-specific basis (Figure 1-1, top panel, fourth through eighth clusters), the difference between surface and bottom is greatest for the tidal stations TTR1 and TTR2, less at river mile (RM) 10.2 and RM 1.4, and largely absent at RM 0 (with the exception of mercury). The mean differences at either TTR1 or TTR2 are statistically significant for all contaminants, whereas there are no cases of statistically different means for the RM 10.2 and RM 1.4 stations and only one for the RM 0 station (mercury). Thus, while on average, bottom volumetric concentrations are higher than surface concentrations, the degree to which this difference is significant varies by location and flow regime in a COPC-specific manner. When concentrations are solids-normalized (Figure 1-2, top panel), the differences between bottom and surface mean concentrations are substantially reduced and, in multiple cases, are reversed with statistically significant differences (e.g., PCBs, LMW PAHs, and DDx; Figures 1-2b, 1-2d, and 1-2e; perhaps reflecting differences in source influence or partitioning behavior [particularly for the LMW PAHs as noted above in Section 1]). For 2,3,7,8-TCDD (Figure 1-2a), at no station is the solids-normalized mean concentration statistically different between surface and bottom (when data are aggregated across events). Likewise, differences are not seen when events are split into low- and moderate-flow regimes and aggregated across stations (Figure 1-2a, top panel).

Station- and event-specific differences in the vertical distribution of contaminant are illustrated in more detail for 2,3,7,8-TCDD in Figures 2-2 and 2-3, where the data in Figure 2-1a are plotted separately for each station and event. The station-specific comparisons are in line with the

⁵ A statistical significance threshold of $p < 0.05$ is used throughout this appendix, signified by red labels in Figures 1-1 and 1-2 for the ANOVA on the log-transformed concentrations.

conclusions above, in that vertical differences are largest at the tidal stations TTR1 and TTR2 (Figures 2-2b and 2-2c, top left panels), moderate at RM 10.2 and RM 1.4 (Figures 2-2a and 2-2d, top left panels), and absent at RM 0 (Figure 2-2e, top left panel); moreover, these differences are reduced on a solids-normalized basis (top right panels), suggesting they are partly attributable to differences in suspended solids concentrations. The stronger effect at TTR1 and TTR2 is consistent with the influence of tidal resuspension and likely reflective of conditions within the estuarine turbidity maximum (ETM) that is expected near the salt front (station TTR1 was intended to target the salt front, and TTR2 is farther downstream in the estuarine portion of the LPR). In the event-specific comparisons, higher bottom concentrations are more apparent in the two moderate-flow events shown⁶ (August 2011 and June 2012; Figures 2-3a and 2-3f, top left panels) than in the four low-flow events (Figures 2-3b through 2-3e), and the bottom vs. surface concentration differences do not persist on a solids-normalized basis (consistent with the mean concentration comparisons in Figures 1-1a and 1-2a).

Figures 2-2 and 2-3 also demonstrate the higher number of non-detects for 2,3,7,8-TCDD. The downstream stations, RM 1.4 (Figure 2-2d, top left panel) and RM 0 (Figures 2-2e, top left panel) have more non-detects than the upstream stations, consistent with the generally lower concentrations (Figure 1-1a, bottom panel). Across all sv-CWCM events, about 16% and 33% of the RM 1.4 and RM 0 samples were non-detect, respectively, compared to 11%, 8%, and 6% at the RM 10.2, TTR1, and TTR2 stations, respectively. There was also some variability in the frequency of non-detects for 2,3,7,8-TCDD within events, where the March 2012 (Figure 2-3c) and February/March 2013 (not shown⁶) had 35% and 45% non-detect, respectively (compared to 15% or less for the other events). Although non-detects introduce additional uncertainty in the comparisons in Figures 1-1 and 1-2 as well as the regression analysis in Section 5, it is noted that these results were not strongly influenced by assigning non-detects the method detection limit instead of half that value.

2.2 Mid-Tide vs. Slack Tide

On a mean basis, concentrations at mid-tide are higher than at slack tide when all data are aggregated, and these differences are statistically significant for all contaminants (Figure 1-1, second panel, left bar cluster). The same trend occurs when data are grouped into low-flow and moderate-flow events (Figure 1-1, second panel, second and third clusters), but the statistical significance of the mean differences within the flow regime varies among the contaminants; mid-tide is significantly higher than slack tide for the low-flow events for all contaminants but only for the moderate-flow events in the case of 2,3,7,8-TCDD and total PCBs (note that PAHs and DDx lack data for two of four moderate-flow events). On a station-specific basis (Figure 1-1, second panel, fourth

⁶ Figures 2-1 through 2-9 exclude the February/March and June 2013 events because sampling was not conducted to capture the various tidal stages for these high-flow monitoring events.

through eighth clusters), the mean COPC concentration at mid-tide is higher than slack tide for all stations except RM 0 (where it occurs mainly for mercury), but the difference is consistently statistically significant only at TTR2. The difference is significant for four contaminants at RM 1.4 (2,3,7,8-TCDD, PCBs, high-molecular-weight [HMW] PAHs, and mercury), three contaminants at RM 10.2 (2,3,7,8-TCDD, PCBs, and HMW PAHs), and only for HMW PAHs at RM 0. TTR1 has no instances of statistical significance, although it is noted that the means filter two high outliers for 2,3,7,8-TCDD at TTR1 (Section 1.1). When concentrations are solids-normalized (Figure 1-2, second panel), the differences between mid-tide and slack tide are mostly reduced and, in some cases, reversed with slack-tide mean being higher than the mid-tide mean (most consistently for PCBs, PAHs, and DDx). The differences are significant for PCBs at TTR2 only and at no stations for 2,3,7,8-TCDD, HMW PAHs, DDx, and mercury. Conversely, the mean solids-normalized concentration of LMW PAHs is significantly higher at slack-tide than mid-tide at all five LPR stations, which may reflect the bias introduced when solids normalizing for lower partitioning chemicals and external sources (longitudinal trends suggest potential upstream and downstream influence; Section 6.2 of the main RI report) .

Station- and event-specific variations in the differences between mid-tide vs. slack-tide are illustrated in more detail for 2,3,7,8-TCDD in Figures 2-2 and 2-3, separating near-surface samples (middle panels) from near-bottom samples (bottom panels). The mid-tide vs. slack-tide cross plots at RM 10.2 and TTR2 (Figures 2-2a and 2-2c, left panels) are consistent with the comparisons of means in Figure 1-1a (2nd panel, discussed above) in that mid-tide concentrations tend to be notably higher than slack-tide. Cross plots also indicate that mid-tide concentrations tend to be higher than slack-tide concentrations at TTR1 (Figure 2-2b, left panels) and RM 1.4 (Figure 2-2d, particularly the near-bottom samples [bottom left panel]), which was less apparent in the mean comparisons in Figure 1-1a. Only at RM 0 (Figure 2-2e) is a difference between mid-tide and slack-tide not indicated, partly because the large fraction of non-detects clouds the interpretation. Looking at similar cross plots by sampling event (Figure 2-3a through 2-3f), the elevation of mid-tide over slack-tide is most apparent in the August 2011, August 2012, December 2012, and June 2012 events, whereas it is weaker in February 2012 and March 2012 events. The lack of tidal resuspension signal in the latter case seems consistent with the March 2012 event having the smallest tidal range of all the events and fairly low concentrations with 35% non-detects; likewise, the February 2012 event also had fairly low concentrations (Figure 1-1a, third panel).

Consistent with the discussion in Section 6.2.1 of the RI report, the mid-tide vs. slack-tide comparisons indicate overall a strong influence of tidal resuspension on water column contaminant concentrations; however, they also indicate that the influence varies by location and event, as would be expected given the time-variable tidal dynamics.

2.3 Flood Tide vs. Ebb Tide

The portion of the data in Figure 2-1 that was sampled at mid-tide (i.e., flood tide and ebb tide samples but not slack-tide samples) is plotted in a similar fashion in Figure 2-4 to compare flood and ebb concentrations at mid-tide for all contaminants (Figures 2-4a through 2-4f) and for salinity and suspended solids (Figures 2-4g and 2-4h). These data are shown on a station- and event-specific basis for 2,3,7,8-TCDD only in Figures 2-5 and 2-6, respectively (i.e., these figures are analogous to Figures 2-2 and 2-3, with the data restricted to mid-tide samples only). In each case, the data for all depths are plotted together in the top panels, and the surface-only and bottom-only subsets of the data are shown in the middle and bottom panels, respectively.

As discussed in Sections 3 and 6 of the main RI report, near-bottom suspended solids concentrations within the salt front of the LPR are typically higher during flood than ebb (as a consequence of asymmetries in tidal currents and vertical mixing), which gives rise to a net upstream transport of solids during low-flow conditions. Flood-dominant total suspended solids (TSS) concentrations were observed in bottom samples collected during the sv-CWCM program (Figure 2-4g, bottom panel) (i.e., concentrations are, on average, higher on flood than on ebb, consistent with the flood-dominant currents that are observed within the estuarine portion of the LPR). A corresponding flood-dominant asymmetry in contaminant concentration is, on average, indicated for each contaminant to varying degrees in bottom samples (Figures 2-4a through 2-4f, bottom left panels), which suggests that tidal resuspension has the potential to induce a net upstream transport of contaminant within the LPR (consistent with the interpretation of longitudinal patterns in the sediment bed concentrations discussed in Section 6 of the main RI report). Note that the asymmetry in contaminant concentrations is reversed in the near-surface samples for most COPCs (Figures 2-4a through 2-4f, middle left panels), except perhaps mercury, and the suspended solids concentration follows suit. Although the data are insufficient to calculate the net vertically integrated contaminant flux during the sv-CWCM program, the fact that concentrations tend to be higher near the bottom (Figure 2-1, top left panels) indicates the potential for a net upstream transport of contaminant.⁷ On a solids-normalized basis (Figure 2-4, right panels), the asymmetry in contaminant concentrations appears COPC-specific, with indications of ebb dominance for PCBs, PAHs, and DDx; flood dominance for mercury; and no apparent difference for 2,3,7,8-TCDD.

Station- and event-specific differences in flood tide vs. ebb tide are evaluated for 2,3,7,8-TCDD in Figures 2-5 and 2-6. The station-specific comparisons indicate that the flood-dominant near-bottom contaminant concentrations were primarily observed at the downstream stations: TTR2, RM 1.4, and RM 0 (Figures 2-5c through 2-5e; bottom left panels). This is consistent with the influence of the

⁷ See Section 7 of the main RI report for model evaluations sediment and contaminant transport, which predict net upstream transport under low-flow conditions that can occur in the estuarine portion of the LPR.

aforementioned estuarine processes, in that the salt front was not observed to clearly reach the RM 10.2 station during any of the events (it came closest during the August 2012 event; see Figure 6-8a in the main RI report and discussion in Section 4 below), and the TTR1 station was not fixed in space but rather floated in an effort to sample the salt front and ETM. The event-specific comparisons (Figure 2-6, bottom left panels) suggest flood dominance in near-bottom COPC concentrations to varying degrees for four of the six events with tidal phase data (the exceptions being February 2012 where no asymmetry is apparent [Figure 2-6b] and March 2012 where non-detects cloud the interpretation [Figure 2-6c]).

2.4 High Slack vs. Low Slack

The portion of the data in Figure 2-1 that was sampled at slack tide (i.e., high-slack and low-slack samples but not mid-tide samples) is plotted in a similar fashion in Figure 2-7 to compare concentrations at high slack and low slack for all contaminants (Figures 2-7a through 2-7f) and for salinity and suspended solids (Figure 2-7g and 2-7h). These data are shown on a station- and event-specific basis for 2,3,7,8-TCDD only in Figures 2-8 and 2-9, respectively (i.e., these figures are analogous to Figures 2-5 and 2-6, with the data restricted to slack-tide samples instead of mid-tide samples). In each case, the data for all depths are plotted together in the top panel, and the surface-only and bottom-only subsets of the data are shown in the middle and bottom panels, respectively.

Aggregating all LPR data, concentrations tend to be higher on low slack than on high slack for all contaminants in both surface and bottom samples (Figures 2-7a through 2-7f, left panels), consistent with the suspended solids concentrations (Figure 2-7g). This asymmetry in contaminant concentration is reduced on a solids-normalized basis (right panels), though it appears to persist somewhat in a contaminant-specific fashion for all but the LMW PAHs (Figure 2-7d). The contaminant-specific behavior may reflect differences in boundary loadings, bed concentration patterns, and partitioning effects (particularly in the case of LMW PAHs, given the trends noted in Section 2.2 regarding Figure 1-2d). The dynamics that give rise to the higher TSS measurements at low slack are not clear; while TSS may be expected to be lower on ebb tide than flood tide below the salt front due to lower shear stresses and lower vertical mixing (due to greater stratification), resuspension above the salt front may be enhanced during ebb and a shorter slack period may allow for less settling at low slack relative to high slack (e.g., Geyer 1993).

Station- and event-specific differences in low slack vs. high slack are evaluated for 2,3,7,8-TCDD in Figures 2-8 and 2-9, respectively. Similar to the evaluations of flood vs. ebb tide, the station-specific comparisons indicate that the higher low-slack concentrations were primarily observed at the three downstream stations: TTR2, RM 1.4, and RM 0 (Figures 2-8c through 2-8e; left panels), consistent with the interpretation that estuarine processes give rise to the noted asymmetry; thus, they are not expected at the RM 10.2 and TTR1 stations (Figures 2-8a through 2-8b; left panels) for the reasons

noted in the preceding section. The event-specific comparisons (Figure 2-9) suggest the higher concentrations at low slack were observed for four of the six events with tidal phase data; the exceptions are the February 2012 and March 2012 low-flow events (Figures 2-9b and 2-9c, left panels; again, the higher number of non-detects influences the latter event interpretation), which also showed lower mid-tide vs. slack-tide differences as noted in Section 2.2.

3 Supplemental Evaluations of Longitudinal Transport Trends

Section 6.2.2 of the main RI report presented longitudinal spatial plots of COPC concentrations measured during each sv-CWCM event to illustrate the large-scale trends of contaminant concentrations moving across the LPR and into Newark Bay. Spatial concentration trends were shown on a volumetric basis (Figure 6.2-6) and a solids-normalized basis (Figure 6.2-7), and salinity and suspended solids trends were also provided for reference (Figure 6.2-8). These data presentations grouped the data by station and grouped the floating tidal stations into the nearest fixed station (i.e., into bins centered on RM 0, RM 1.4, RM 4.2, RM 6.7, and RM 10.2). Data were also pooled in the vertical, combining near-surface and near-bottom measurements in each bin. Non-detects were set to half of the detection limit.

Alternate versions of these longitudinal plots are provided here for reference, which unravel the data binning in the Section 6 figures as follows:

- Figures 3-1 and 3-2 show the volumetric and solids-normalized COPC concentrations, respectively, using the same longitudinal binning but with near-surface and near-bottom samples plotted separately (top and bottom panels, respectively). Samples from the T175 station at Dundee Dam were collected at mid-depth and are here shown together with the near-surface samples. The events are still grouped by flow (low-flow events are followed by moderate-flow events). Figure 3-3 shows salinity and suspended solids in a similar fashion. Note that all COPCs were not sampled for all events, but the panel positioning is maintained for ease of comparison.
- Figures 3-4 and 3-5 show the volumetric and solids-normalized COPC concentrations, respectively, using no data binning and with near-surface and near-bottom samples distinguished. Figure 3-6 shows salinity and suspended solids in a similar fashion.

The large-scale longitudinal trends discussed in Section 6.2 apply to these data presentations as well, although they reveal additional detail about the location and depth of individual samples. For example, Figure 3-4a shows that two extreme 2,3,7,8-TCDD measurements occurred in the surface sample during the August 2011 event and in the bottom sample in the June 2012 event, both at TTR1—the station targeting the salt front. Figure 3-6 also provides more perspective on the approximate correspondence of the salt front estimates with the individual salinity measurements.

Regarding the discussion in Section 6 of the main RI report on longitudinal trends in the mean contaminant concentrations and the likely importance of tidal processes on longitudinal transport within the LPR, Figure 1-1 provides additional perspective. Aggregated over all events, differences in station-specific contaminant means are statistically significant for all contaminants (Figure 1-1, bottom panels, first cluster). The significance of differences between stations persists when split into

low-flow and moderate-flow events, with the exception of mercury during low-flow events (Figure 1-1f). Mean 2,3,7,8-TCDD concentrations are highest at the two tidal stations⁸ (TTR1 and TTR2) relative to the upstream RM 10.2 station and the downstream RM 1.4 and RM 0 stations (Figure 1-1a, bottom panels), which suggests the influence of estuarine processes and the ETM in longitudinal contaminant patterns. A similar pattern is observed for PCBs and mercury (Figures 1-1b and 1-1f), whereas for DDX and the PAHs (Figures 1-1c through 1-1e), the RM 10.2 station has a similar mean as TTR1 and TTR2, perhaps reflecting their stronger upstream boundary loadings. The RM 1.4 and RM 0 stations have lower means than the tidal stations for all contaminants, which may in part reflect dilution and greater settling associated with the rapidly expanding cross section as the LPR mouth is approached. These patterns have some event-specific variations, as discussed in the next section. Solids normalization tends to flatten out the longitudinal pattern (Figure 1-2, bottom panel), though statistically significant differences persist for all contaminants except LMW PAHs (Figure 1-2d)—again, suggesting a somewhat different behavior for LMW PAHs, which may be tied to external source influence and/or partitioning behavior.

⁸ The mean 2,3,7,8-TCDD concentration at TTR1 in Figures 1-1a and 1-2a exclude two extreme concentrations from the August 2011 and June 2012 moderate-flow events. Including these data points causes the mean at TTR1 to be substantially higher than all others (see Figure 6-6a of the main RI report and Figure 3-1b of this appendix).

4 Supplemental Evaluation of Flow and Tidal Forcing Influence

The relationship between aggregate LPR contaminant concentrations and event-mean flow and tidal forcing was discussed in Section 6 of the main RI report with reference to Figure 6-9 therein. In general, these comparisons indicated no clear relationship between contaminant concentration and aggregate flow/tide statistics when data are aggregated across all LPR stations. The differences among events and variations with the mean flow and tidal conditions are considered further below.

On a mean concentration basis, variations across all sv-CWCM events are statistically significant for 2,3,7,8-TCDD, PCBs, and mercury (Figures 1-1a, 1-1b, and 1-1f, third panel, first cluster of bars). They also exhibited statistically different means when events are split into moderate- and low-flow events (Figures 1-1a, 1-1b, and 1-1f, third panel, second cluster of bars). The differences among these means are reduced when solids normalized but remain significant for 2,3,7,8-TCDD, PCBs, and mercury when all data are aggregated (Figures 1-2a, 1-2b, and 1-2f, third panel, first cluster of bars) and within the moderate-flow grouping (second cluster of bars). Mean concentrations were not statistically different between events for PAHs or total DDx on an overall or flow-regime-specific basis or on a volumetric (Figures 1-1c through 1-1e) or solids-normalized basis (Figures 1-2c through 1-2e).

The station-specific mean concentrations indicate statistically significant differences among events for all stations for 2,3,7,8-TCDD and PCBs (Figures 1-1a and 1-1b, third panel) and at the three upstream stations for mercury (Figures 1-1f, third panel; T102, TTR1, and TTR2).

To further explore the nature of the concentration responses among events and, specifically, the influence of flow and tidal forcing, a station-specific version of Figure 6-9 in the main RI report is provided in Figure 4-1, focusing on 2,3,7,8-TCDD for brevity. This comparison suggests an influence of flow and tidal forcing on RM 10.2 concentrations, consistent with Figure 1-1a. The flow dependence is illustrated for 2,3,7,8-TCDD in Figure 4-1a in that the highest concentrations at RM 10.2 occurred during two of the lowest-flow events (August and December 2012; see also Figure 1-3a). The dependence on tidal forcing is suggested by the March 2012 event, which was an equally low-flow event with a smaller tidal forcing that experienced substantially lower concentrations. Both effects are consistent with salt front influence; salinity levels (Figure 1-3g) were highest at RM 10.2 during the August and December 2012 events, reaching above 0.5 parts per thousand, whereas salinity levels were lower during the March 2012 event (and other events). The relatively high concentrations are also seen for PCBs and mercury during the August 2012 event but not during the December 2012 event (Figures 1-1b and 1-1f and Figures 1-3b and 1-3f, respectively). Differences in response among contaminants is expected, given differences in bed concentration gradients and boundary loadings, both of which interact with the flow and tidal forcing.

An influence of flow and tidal forcing on TTR2 concentrations has also been noted. Here, the highest 2,3,7,8-TCDD concentrations are associated with three of the four moderate-flow events (August 2011, June 2012, and June 2013; see Figures 4-1c and 1-1a, third panel). A similar response is seen for mercury (Figure 1-1f, third panel) and, to a lesser extent, PCBs (Figure 1-1b, third panel). Presumably, the higher concentrations reflect increasing shear stresses associated with the high flow, although the nature of that increase is complex within the salt front (e.g., it is not apparent in the February/March 2013 moderate-flow event) and may be muted by the dilution that would occur during higher flows. A relationship to event-mean tidal forcing is not apparent at this station for 2,3,7,8-TCDD (Figure 4-1c). Flow and tidal forcing influences on 2,3,7,8-TCDD are not apparent for the other stations due to the more variable response of concentrations (Figures 4-1b, 4-1d, and 4-1e).

It is noted that the comparisons in Figure 4-1 may be influenced by differences in the sample collection for the February/March 2013 and June 2013 events. Unlike the preceding six events in 2011 and 2012, which were designed to capture concentration variations through a tidal cycle, the 2013 events were designed to capture the rising limb, peak, and falling limb of the hydrograph during a freshwater discharge event. As discussed in Section 6.2.3 of the main RI report, removing falling limb samples from the concentration distributions has nominal impact to the comparison in Figure 6-9 of that section, partly because most samples were collected during the rising limb and peak of the hydrograph. The trends in Figure 4-1 in this appendix are likewise not materially impacted by excluding the falling limb data. Nevertheless, the highest 2,3,7,8-TCDD concentrations for these events were observed during the rising limb/peak sampling subperiod, and in aggregate the data suggest higher volumetric concentrations on the rising limb and peak of the hydrograph relative to the falling limb⁹ (Figure 4-2a, top left panel), particularly in the surface samples (middle panel). Thus, they do suggest a concentration response within the LPR to freshwater discharge events, although the magnitude and timing of this response is presumably influenced by factors such as the time history of conditions leading up to the event (e.g., the February/March 2013 and June 2013 events were preceded by similar moderate-flow [Regime 2] conditions) and the shape of the hydrograph during the event (e.g., the June 2013 event hydrograph had a second higher-flow peak that was not sampled). Rising limb and peak concentrations during these events also appear to be higher than falling limb concentrations for the other COPCs (Figures 4-2b through 4-2f, top left panels), perhaps to a lesser extent for DDx and mercury. An evaluation of the tidal phases during these two sampling events was performed to assess whether the comparison of rising and falling limb concentrations in Figure 4-2 may be biased due to the tidal phases sampled, given that mid-tide samples tend to have higher concentrations than slack-tide samples (due to tidal

⁹ The mean flow rates for the rising limb/peak and falling limb sampling sub-periods were approximately 2,300 and 2,000 cfs, respectively, for the February/March 2013 event and 3,200 and 3,200 cfs for the June 2013 event. In the latter event, there was a higher peak flow of about 6,000 cfs on June 15 between the two sampling sub-periods (June 7 to 11 and June 20 to 22); thus, the data for the June 2013 event do not capture the true hydrograph peak flow during this period.

resuspension; see Section 6.2 of the main RI report and Section 2 of this appendix) and the sampling design, which did not target the full tidal cycle like the other six sv-CWCM events. Using tidal phases assigned based on model-predicted water surface elevations at each station, the evaluation indicates that the rising and falling limb samples in these events covered a mix of tidal phases; approximately 40% and 60% of the rising limb and peak samples (combined) were collected during mid-tide and slack-tide, respectively, versus 75% and 25% for the falling limb samples. Because the somewhat higher proportion of mid-tide samples in the falling limb dataset would tend to bias the falling limb samples high if at all, the observation from Figure 4-2 that rising limb concentrations tend to be higher for several COPCs is not likely to be an artifact of biased sampling of the tidal cycle. Moreover, the analysis also indicated that the proportions of mid-tide and slack-tide samples across both events were approximately equal (estimated to be 50% and 50%, respectively), meaning that tidal phase sampling bias is not likely to have impacted the event mean concentrations examined in Figure 4-1 (also in RI Section 6, Figure 6-9). Further evaluation of the influence of flow and tidal forcing is incorporated into the regression analysis summarized in Section 5, which also considers other physical parameters.

5 Regression Analysis of the sv-CWCM Dataset

As a supplement to the preceding discussions and Section 6 of the main RI report, a regression analysis of the sv-CWCM data across all LPR stations and events was performed to quantify the strength of the relationships between water-column concentrations¹⁰ and physical variables, including river mile, flow¹¹ (Dundee Dam), tidal range (Point-No-Point), salinity, TSS, and particulate organic carbon (POC). The analysis consisted of both single-variable and multiple-variable regressions. In addition, the analysis was repeated on a station-specific basis (across all events), and on a flow-regime-specific basis considering the four low-flow events and the four moderate-flow events separately (across all LPR stations). In all regressions, contaminant concentration, TSS, and POC were log-transformed, as this improved the goodness of fit. Cross plots of the regressed variables across the full dataset are provided in Figure 5-1, and the correlation coefficients are provided in Table 5-1. The regression results (as R^2 , coefficient of determination¹²) are summarized for each contaminant in Tables 5-2a through 5-2f, for both the single- and multiple-variable¹³ regressions.

For all the evaluated contaminants, variability in water column concentrations across all LPR stations and events is best explained by variations in TSS and POC, as indicated by the correlation coefficients in Table 5-1 (0.66 to 0.83 for TSS; 0.62 to 0.83 for POC) and discussed in Section 6.2 of the main RI report. The relationship between volumetric concentrations and TSS and POC can also be seen on the bottom left and bottom right panels of Figures 5-1; higher COPC concentrations are associated with higher TSS and POC levels (these variables are also highly correlated with each other; not shown). After TSS and POC, salinity has the next highest correlation with contaminant concentration, for all contaminants (Table 5-1 and Figure 5-1, bottom middle panel) followed by river mile¹⁴ (top left panel). Flow and tidal range (Figure 5-1, top right panels) are typically the least correlated variables globally, though their correlation is somewhat higher for the PAHs, and for DDx, the correlation with tidal range is similar to that of salinity and river mile. These relationships are borne out in the regression results (Table 5-2).

¹⁰ The concentration dataset was restricted to those where each of the other physical variables was available so that a multivariate regression could be performed. Nineteen samples were excluded due to missing salinity values (13 samples from August 2011, two samples from August 2012, and four samples from February/March 2013). Also, two high 2,3,7,8-TCDD outliers and two low total PCB outliers were excluded from the regression analysis, as noted in Section 1.1.

¹¹ As discussed in Section 1.1, flow was matched to samples on a daily average basis and tidal range was calculated based on the elevation difference between the low/high tides bracketing the sampling time. The time history of these forcings (e.g., rising vs. falling limb of the hydrograph) is not considered in this analysis.

¹² R^2 values noted in red indicate statistically significant regression slopes with p-values of <0.05.

¹³ The multi-variable regression excluded POC due to its collinearity with TSS. Using POC in place of TSS results in a statistically significant p-value for POC and higher p-values for the other variables.

¹⁴ As expected, river mile is correlated to salinity; see Figure 6-8a of the main RI report.

For 2,3,7,8-TCDD, the single variable R^2 values for the combined dataset are highest for TSS and POC (0.42 and 0.39, respectively), followed by salinity (0.19). The remaining variables have R^2 of <0.08 . The goodness of fit of the multiple-variable regression ($R^2 = 0.54$) is slightly higher than that of TSS, reflecting a contribution of salinity. The strong influence of TSS in this analysis supports the discussion in Section 6.2 of the main RI report regarding the importance of resuspension/deposition and the particulate phase on contaminant transport.

Stratifying the data into low- and moderate-flow regimes shifts the relative importance of the variables somewhat for 2,3,7,8-TCDD (Table 5-2a). For low flows, salinity takes on a greater relative importance as an explanatory variable (0.18) but remains less correlated than TSS and POC (0.29 and 0.31, respectively). At moderate flows, TSS and POC take on a greater importance (0.55 and 0.43, respectively, vs. 0.15 for salinity) and dominate the multiple regression R^2 .

Stratifying the data by station reveals that TSS and POC are the dominant explanatory variables for 2,3,7,8-TCDD concentrations at all stations except RM 0 (T000), and salinity is only a statistically significant regression variable at the RM 1.4 (T014) and RM 0 stations (Table 5-2a). At RM 1.4, salinity contributes strongly to the multiple variable regression, and it dominates as the main explanatory variable at RM 0. The influence of salinity is consistent with the longitudinal gradient in concentration moving from the LPR to Newark Bay, reflecting dilution of the LPR sediment source with lower concentrations (water and solids). Flow becomes a stronger explanatory variable at the lower stations (TTR2, T014, and T000) and at RM 0 has an influence on par with TSS and POC; however, it is not dominant in any cases and the highest R^2 for flow is 0.12 (at TTR2).

The regression results for the other contaminants (Tables 5-2b through 5-2f and Figures 5-1b through 5-1f) indicate that the highest R^2 values are found for TSS and POC in each case, but the relative contribution of salinity and the other variables shows some contaminant-specific behaviors. Total PCB regression results are most similar to 2,3,7,8-TCDD in that salinity is statistically significant only at the downstream stations (T014 and T000) and dominant at RM 0, while the other variables are fairly small contributors throughout. For HMW PAHs, salinity is also significant at T014 and T000, but it is not dominant at RM 0. Salinity is only statistically significant at TTR2 for LMW PAHs and at RM 1.4 for DDx and mercury (weaker for mercury). Total DDx and, to a lesser degree, LMW PAHs show the highest influence of tidal range, and it is a significant explanatory variable at all stations except TTR2—unlike the other contaminants where it is significant at two or less stations. LMW PAH shows the largest flow influence, where it is a significant variable at all stations except RM 10.2 (T102) and the largest explanatory variable at RM 0 along with POC. For all contaminants, the highest-flow influence occurs at TTR2 (consistent with observations in Section 4) and it is a significant variable there for all contaminants. The variation in explanatory variables among the contaminants is

presumably due to the influence of boundary loadings, spatial patterns in bed concentrations, and partitioning behavior.

6 Reference

Geyer, W.R., 1993. "The Importance of Suppression of Turbulence by Stratification on the Estuarine Turbidity Maximum." *Estuaries* 16(1):113–125.