SECTION 5 Quarterly Sampling Results

The DMT sediment and surface water study was performed in accordance with the USEPA technical approach for the evaluation of chromium in sediment (USEPA, 2005a), as described in the Work Plan and Section 3 of this report. The quarterly sampling program was conducted within the zone potentially impacted by chromium releases at or from DMT and at reference locations to support the following objectives:

- 1. Characterize the nature and extent of chromium in pore water, surface water, and sediment in the Patapsco River adjacent to DMT as compared to USEPA's NRWQC (as applicable) and concentrations measured at reference locations.
- 2. Evaluate the fate and transport of chromium based on the characterization of geochemical conditions that govern the presence of chromium as Cr(III) versus $Cr(VI)$.
- 3. Provide data to support the human health and ecological risk assessments for DMT, including concentrations of other COPR constituents at DMT relative to those measured at reference locations.

This section presents the results of the four quarterly sampling events, including summaries of the full data set across the seasons and quarterly data summaries that characterize seasonal influences on analytical results. This section is organized as follows:

- Section 5.1: Nature and Extent of Chromium at DMT
- Section 5.2: Delineation of Geochemical Conditions that Influence Fate and Transport of Chromium
- Section 5.3: Distribution and Extent of Other COPR Constituents
- Section 5.4: Comparison to Results from Previous Studies Conducted in Baltimore Harbor

A summary of the data validation procedures and reports are provided in Appendix D, and full analytical results are provided in Appendix E. The data validation process demonstrated and documented that analytical data were within the acceptance criteria for the associated methods, and are of sufficient quality to be used for qualitative and quantitative purposes. The only exception to this determination related to SEM mercury results for four sediment samples collected in the first quarterly sampling event^{[1](#page-0-0)}. Overall, the validation has demonstrated that the quality of the data is sufficient for achieving project objectives and can be used both in the characterization of chromium and other COPR constituents at DMT as well as the evaluation of risks, and thus is of sufficient quality for risk-management decision making. Specifically, as detailed below, the DMT data are

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¹ The SEM mercury results for these samples were determined to be unreliable (i.e., flagged as rejected [R] results) due to non-recovery of mercury in the matrix spike and matrix spike duplicate. However, the non-recovery of the spiked mercury can be attributed to the nature of the AVS extraction, and not to the sediment sample matrix.

sufficient to support the conclusion that the nature and extent of chromium in the Patapsco River and Colgate Creek are delineated, in accordance with the approach defined in the Work Plan, and as such, meet the requirements as stipulated in the Consent Decree.

5.1 Nature and Extent of Chromium

Results for chromium in all media are presented in Tables 5-1 to 5-4, which show the detection frequency, the range of detected concentrations, the average concentration, and the location-specific results for pore water, surface water, surficial sediment (0 to 6 inches) and subsurface sediment (approximately 6 inches to 3 feet below sediment surface), respectively. The maximum detected concentrations of Cr(VI) and total chromium in each medium during any sampling event is illustrated on Figure 5-1a. Pore water, surface water, and sediment results for chromium are discussed in detail below.

5.1.1 Nature and Extent of Chromium in Pore Water

Pore water results for DMT and the three reference locations for the May 2007 through February 2008 sampling efforts are presented in Tables 5-1a (DMT locations) and 5-1b (reference locations), and illustrated on Figure 5-1b. Pore water was collected from each location during each quarter of sampling, with very limited exceptions when the volume of pore water extracted from the sediment was insufficient to conduct any or all of the chemical analyses. Those sampling locations and the associated sampling event are specifically identified in Table 5-1a.

Hexavalent Chromium in Pore Water

Cr(VI) was not detected in pore water in any of the samples taken from DMT in any of the sampling events. The detection limit of $5 \mu g/L$ was well below the USEPA's saltwater acute and chronic NRWQC for Cr(VI) $(1,100 \text{ and } 50 \mu g/L)$, respectively). According to USEPA and published scientific studies, if Cr(VI) were present in sediment and biologically available, it would be detected in pore water (USEPA, 2005a; Berry et al., 2004; Besser et al., 2004). The absence of measurable Cr(VI) in pore water establishes that neither whole sediments nor pore water is contaminated with Cr(VI). The absence of Cr(VI) in pore water also demonstrates that Cr(VI) is not being transported to the Patapsco River via groundwater upwelling. The lack of measurements of Cr(VI) in pore water confirms that the nature and extent of Cr(VI) in pore water and sediment is defined.

Dissolved Total Chromium [Cr(III)] in Pore Water

As discussed in Section 3.2, USEPA NRWQCs are based on chromium as Cr(VI) and Cr(III). The absence of Cr(VI) in pore water as discussed above indicates that the dissolved total chromium that is present is in the form of Cr(III). Unfiltered total chromium concentrations (hereafter referred to as total chromium) are also shown in Table 5-1a.

Cr(III) was detected in 70 of 131 pore water samples from the four quarterly sampling events at concentrations ranging from 2.3 to 16.2 μ g/L (mean = 3.7 μ g/L), with little variation between individual sampling events. The Cr(III) concentrations detected in pore water from DMT locations were consistent with or less than those at the three reference locations (mean = 6.5 μg/L; Figure 5-1b). Most importantly, however, concentrations of Cr(III) at both DMT and reference locations were well below each of the NRWQC, the

freshwater acute and chronic criteria as well as the hardness-adjusted acute and chronic criteria as illustrated on Figure 5-2a.

Concentrations of Cr(III) in pore water were significantly lower at the shallow water Transects A, B, C and J than at the deeper water Transects D-H ($p < 0.05$; Figure 5-2b). Transects A, B, C and J are the areas with the highest total chromium concentrations in sediment (see Section 5.1.3). Cr(III) in pore water was detected in 79 percent of the samples in Transects D–H, but only 20 percent of the samples at Transects A, B, C and J. Dissolved Cr(III) is typically found associated with DOC, and Transects A, B, C and J have mostly sandy sediments that contain lower concentrations of organic carbon.

There was no discernable relationship between Cr(III) in pore water and total chromium concentrations in sediment from DMT or reference locations as evidenced by the fact that Cr(III) in pore water was below the mean detected value at the surficial sediment sampling locations with some of the highest total chromium concentrations. Transects D and E near the 13th and 12th Street outfalls, respectively, show a trend of decreasing Cr(III) concentrations with distance from the shoreline; however, this trend was not apparent at the other transects (Figure 5-1b). There was no apparent clustering of higher Cr(III) concentrations adjacent to the shoreline or in the outfall areas. Finally, there are no significant relationship between concentrations of Cr(III) in pore water and location relative to the dredged channels.

The measurements of dissolved Cr(III) in pore water well below the NRWQC confirm that the nature and extent of Cr(III) in pore water are defined.

5.1.2 Nature and Extent of Chromium in Surface Water

Cr(VI) and total chromium surface water results for the May 2007 through February 2008 sampling events are presented in Tables 5-2a (DMT locations) and 5-2b (reference locations) and illustrated on Figure 5-1c. Note that dissolved total chromium in surface water can be Cr(III), Cr(VI), or a mixture of both. Dissolved total chromium is assumed to be Cr(III) if Cr(VI) is not present.

Surface water samples were collected from up to three discrete depths as described in Section 4.1.1 at DMT and reference locations during each of the four quarterly sampling events.

Hexavalent Chromium in Surface Water

 $Cr(VI)$ was not detected in 97 percent of the surface water samples analyzed^{[1](#page-2-0)} and in those limited locations where it was detected, concentrations were well below the USEPA's NRWQC. The majority of detected concentrations were at or near the detection limit. Detected concentrations were consistently identified in areas adjacent to stormwater outfalls, and with limited exception followed wet weather events.

In total, Cr(VI) was detected in 9 of 320 DMT surface water samples (excluding two duplicate samples). Cr(VI) was not detected in surface water at the reference locations. Cr(VI) was detected at sampling locations B3, B4, C1, D1, D3, E1 and E2 at concentrations ranging from 6 to 35 μg/L (Figure 5-1c). Cr(VI) was detected in three consecutive sampling

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¹ Sample count excludes field duplicate samples.

events at sampling location E1 but was not detected more than once at the other six sampling locations. Six of the nine Cr(VI) detections in surface water occurred during rainfall events (Table 5-5). The remaining three detections were in samples collected when rain occurred within 3 days of sampling. Typically, the detections occurred in the uppermost sampling interval (approximately 3 feet below the air-water interface). The concentrations of Cr(VI) reported in the surface water at DMT were all below the Cr(VI) saltwater acute and chronic NRWQC of 1,100 and 50 µg/L, respectively (Figure 5-3a).

There is evidence that the $Cr(VI)$ detected in surface water is rapidly reduced to $Cr(III)$ because at locations where Cr(VI) was found at concentrations above 25 μ g/L (B-4 and E-1), concentrations of dissolved total chromium were significantly higher than the site average of 2.2 μ g/L, ranging from 26 to 44 μ g/L. The reduction of Cr(VI) to Cr(III) by natural organic matter in the water column is consistent with findings from JHU studies (described further in Section 5.4).

Given the low detection frequency, no discernable pattern of Cr(VI) concentrations with increasing distance from the shoreline was evident, with Cr(VI) detections at both near and far shore sampling locations (Figure 5-1c). There was no relationship between Cr(VI) concentrations in surface water and concentrations of chromium in sediment or pore water (as total or dissolved total chromium). Finally, there was no discernable relationship between key sediment constituents that may influence chromium speciation (i.e. Fe(II), AVS, organic carbon) and the presence or absence of Cr(VI). This serves as additional evidence that the Cr(VI) detections in surface water do not originate from and are not related to concentrations of chromium in sediment.

The DMT stormwater outfalls are in the same vicinity as Transects B–E where Cr(VI) was detected (Figure 5-1c). The fact that Cr(VI) was detected during or after rainfall events suggests a potential source of Cr(VI) from these outfalls. Figure 5-3b illustrates the relationship between Cr(VI) detections in surface water and corresponding rainfall events. However, Fe(II) and DOC were detected in approximately 70 and 80 percent of surface water samples, respectively, indicating that Cr(VI) in the river is likely rapidly reduced upon interaction with key reductants in the water column and sediment.

These Cr(VI) results are consistent with the CSM showing that during the occasions when wet weather stormwater discharges are occurring, the influence of Cr(VI) on the adjacent water body is minimal even in the area where the least mixing/dilution occurs, at least in part because Cr(VI) is rapidly reduced to Cr(III). The measurements of Cr(VI) in surface water well below the NRWQC confirm that the nature and extent of Cr(VI) are defined.

Dissolved Total Chromium in Surface Water

Dissolved total chromium was detected in 19 percent of samples from the four quarters of sampling, at concentrations ranging from 2.3 to 37.6 μ g/L (mean = 2.2 μ g/L^{[1](#page-3-0)}). These concentrations are well below the acute and chronic NRWQC for Cr(III) (Figure 5-4). In samples where dissolved total chromium was detected in surface water, 94 percent of DMT samples were at or near the detection limit of $2.3 \mu g/L$. Dissolved total chromium was

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 $¹$ The mean is lower than the minimum value because the minimum value reported is the minimum detected value, whereas</sup> the mean is based on the entire data set, with a value of one-half the detection limit used for samples where chromium was not detected.

detected in 14 percent of reference samples and concentrations were not significantly different than dissolved total chromium concentrations at DMT (reference mean = $1.4 \mu g/L$; $r =$ <0.05). Moreover, there was very little variation in dissolved total chromium concentrations between sampling events.

Dissolved total chromium concentrations in surface water appear to decrease with distance from the shoreline at Transects C, D and E. There were no notable trends in dissolved total chromium concentrations in surface water in shallow (A, B, C and J) versus deep water transects (D–H; Figure 5-1c). There were also no significant trends in concentrations of dissolved total chromium from within the dredged channels. Finally, while there appears to be a trend of higher dissolved total chromium concentrations in the uppermost water column interval versus the bottom waters, the trend is not statistically significant. The most significant relationship is between concentrations of dissolved total chromium in surface water and the few detected concentrations of Cr(VI) as discussed above.

The measurements of dissolved total chromium in surface water at concentrations well below the NRWQC and consistent with reference locations confirms that the nature and extent of chromium in surface water are defined.

5.1.3 Nature and Extent of Chromium in Sediment

Surficial (0-6 inches) and subsurface sediment samples (to a depth of 3 feet below the sediment water interface) were collected at the locations indicated in Figure 5-1b using methodologies described in Section 4.1.2. Surficial samples were collected in May and August 2007, and subsurface samples were collected in August only. An additional Transect J and one station on Transect B were added for sediment collection and analysis in February 2008 to further characterize the nature and extent of chromium at DMT. The results for the combined sediment data sets are discussed in detail below.

A total of 41 locations were sampled near DMT from three depths: 0–6 inches, and two 6– inch subsurface intervals that were selected based on sediment lithology and stratigraphy. Results are summarized in Table 5-3a and 5-3b. The primary findings associated with the sediment sample results are as follows:

- The highest concentrations of total chromium in surficial sediment were found proximate to Area 1501/1602 where concentrations were higher than the Site-wide average and reference areas. Surficial chromium concentrations were also higher than reference in Transect I.
- Overall, concentrations of total chromium in surficial sediment declined with distance from the shoreline, with total chromium concentrations at sampling locations furthest from the shoreline similar to reference concentrations at Transects A, B and D through H.
- Geochemical parameters in sediment provide compelling evidence of geochemical conditions that favor the presence of chromium as Cr(III) rather than Cr(VI), which is consistent with the CSM for DMT.

Total chromium results for surficial and subsurface sediment samples are discussed in detail below.

Total Chromium in Surficial Sediment

Results for total chromium in surficial sediment are presented in Tables 5-3a (DMT locations) and 5-3b (reference locations) and illustrated on Figure 5-1b. Chromium was detected at every location sampled at DMT and reference areas.

Concentrations of total chromium in surficial sediments near DMT ranged from 33 to 2,360 mg/kg (mean = 394 mg/kg). While chromium concentration in surficial sediments Site-wide were significantly greater than the reference locations (range = 89.2 to 166 mg/kg; mean = 127 mg/kg ; p < 0.05), chromium concentrations at Transects D-H (mean = 156 mg/kg) were consistent with concentrations seen at the reference locations.

The highest concentrations of total chromium in surficial sediments at DMT were seen closest to the shoreline at Transect J, adjacent to Area 1501/1602. Concentrations of total chromium in surficial sediments at Transect J range from 1,260 to 2,360 mg/kg (mean = 1,820 mg/kg). Concentrations of total chromium from the four transects closest to Area 1501/1602 (shallow Transects A, B, C and J) have total chromium concentrations ranging from 58 to 2,360 mg/kg (mean = 719 mg/kg), which are higher than total chromium concentrations at the deep water Transects D–H (range = 33 to 310 mg/kg ; mean = 156 mg/kg; p < 0.05). Surface sediments in Colgate Creek (Transect I) have total chromium concentrations between these two groups (mean = 410 mg/kg). There is a trend of decreasing chromium concentrations with increasing distance from the shoreline in Transects A, B and C. Total chromium concentrations at sampling locations furthest from the shoreline were similar to reference concentrations at Transects A, B, and D through H.

Total Chromium in Subsurface Sediment

Subsurface sediment samples, collected at two discrete intervals between 0.5 and 3 feet deep, were collected at DMT in August 2007 and February 2008. Results are presented in Table 5-3c and 5-3d and Figure 5-1b. Total chromium concentrations in subsurface sediment from DMT ranged from 1.2 to 8,140 mg/kg (mean = 372 mg/kg). Concentrations of total chromium in subsurface sediment from the reference locations ranged from 55 to 147 mg/kg (mean = 86 mg/kg).

The average concentration of total chromium in subsurface sediment at combined Transects A, B, C and J, which are all within close proximity to Area 1501/1602, is 674 mg/kg. These concentrations are higher than concentrations measured in subsurface samples from deep Transects D-H (mean = 111 mg/kg; $p < 0.05$), which are similar to the reference areas. Total chromium concentrations in subsurface sediment decrease with increasing distance from the shoreline in Transects A and C in Area 1501/1602. Total chromium concentrations appear to increase with distance from the bulkhead at Transect B and Transect I in Colgate Creek.

Conclusions Regarding Chromium Distribution in Surficial and Subsurface Sediment

Total chromium concentrations in surficial and subsurface sediments were highest near Area 1501/1602 and at Transect I in Colgate Creek. Concentrations in Area 1501/1602 generally decreased with increasing distance from the shoreline and with increasing depth in the sediment column. In Transect I in Colgate Creek, the highest concentrations were found at depth at the location furthest from DMT. Transects D–H have mean total chromium concentrations that are statistically similar to reference areas.

The higher concentrations of total chromium in sediment immediately adjacent to Area 1501/1602 are likely related to historical stormwater runoff from uncovered COPR stockpiles and other filling operations prior to placement of the asphalt cover. Prior to construction of Area 1501/1602, approximately 800,000 cubic yards of COPR were stockpiled in the southeast corner of DMT. During this period, stormwater runoff containing Cr(VI) from the stockpiles entered the Patapsco River at the former shoreline that is now occupied by Area 1501/1602. The runoff was eventually contained by earthen dikes and sumps installed by MPA. Over 200,000 cubic yards of material were then placed in containment cells above the water table during construction of Area 1501/1602. During construction, clean fill material was deposited into the river to allow construction of the containment cells. This filling process likely displaced the sediments affected by previous stormwater runoff outward into the river in a progressive mud wave as the filling advanced. Therefore, it is likely that sediment samples collected near the current shoreline of Area 1501/1602 contain chromium contributions from historical runoff. Total chromium in sediment in the vicinity of Transect C may also be due to historical releases of Cr(VI) via the stormwater outfalls that reduced to Cr(III), which precipitated from the water column and accumulated in sediment.

Groundwater upwelling does not appear to contribute to chromium in sediments because Cr(VI) concentrations in groundwater samples from the perimeter of Area 1501/1602 are below the NRWQC, Cr(VI) was not detected in pore water samples, and chromium concentrations are higher in surficial sediment than in subsurface sediment, which is inconsistent with a discharging groundwater source.

The limited horizontal extent of the elevated chromium concentrations indicates that minimal sediment resuspension and transport has occurred. Results for Cr(VI) and Cr(III) in pore water samples from locations in Colgate Creek indicate that additional investigation of nature and extent of chromium in this area is not required.

Based on these findings, and given that Cr(VI) and total dissolved chromium concentrations in pore water and surface water from all DMT locations are well below the NRWQC, the nature and extent of total chromium in sediment is defined.

5.2 Delineation of Geochemical Conditions that Influence Fate and Transport of Chromium

As discussed in Section 3.2, geochemical parameters can be used to understand and predict chromium behavior in an estuarine environment. These parameters were analyzed during each of the four quarterly sampling events. Characterizing in situ geochemical conditions is critical to understanding the behavior of chromium, and provides insight into the distribution, toxicity, and long-term stability of chromium in sediments. This section describes both spatial variations in geochemical constituents at DMT as well as the influence of season on the concentration of these constituents, and evaluates whether these variations influence the behavior of chromium at DMT.

The most important constituents that reduce Cr(VI) to Cr(III) include sulfides, Fe(II), and natural organic matter (Hansel et al., 2003). While sulfides and Fe(II) are able to donate electrons for Cr(VI) reduction, organic carbon, specifically humic and fulvic acids, contain binding sites that can form complexes with chromium and reduce its bioavailability. According to USEPA (2005a), the presence of detectable AVS alone is an indication that any chromium in sediment would be present primarily as Cr(III).

Results for geochemical parameters in pore water, surface water, and sediment are provided in Tables 5-1 through 5-4. Spatial and temporal variations in geochemical conditions are described below.

5.2.1 Spatial Variations in Geochemical Constituents

To evaluate spatial variations in geochemical conditions, results for geochemical parameters at DMT locations were compared to those at the reference locations. Additionally, results for samples from the shallow, sandy transects (Transects A, B, C, and J) were compared to those from the deeper transects with finer-grained sediments (Transects D-H). While concentrations of AVS and Fe(II) were not significantly different in Site versus reference sediments, concentrations of TOC were significantly higher in the reference sediments (mean = 2.9 percent) than in Site sediments (mean = 1.8 percent; $p < 0.05$). However, concentrations of DOC were similar in surface water and pore water at the Site versus at the reference locations. Overall, concentrations of geochemical constituents in all media, including AVS/sulfides, Fe(II), and organic carbon, were substantially lower in the sandy, shallow transects (Transects A, B, C and J) than in the silty deeper Transects (Transects D– H). Despite the lower concentrations of these reducing agents in Transect A, B, C and J, there is a surplus of reducing capacity in these sediments to insure the stability of Cr(III), as evidenced by the fact that Cr(VI) was not detected in pore water at any location. Figure 5-5a clearly demonstrates that concentrations of reducing agents are found in excess in all DMT sediments.

5.2.2 Seasonal Variations in Geochemical Conditions

Seasonal variations in temperature and freshwater input may impact concentrations of key geochemical constituents. Estuarine sediments, such as those in Baltimore Harbor, tend toward anoxic or hypoxic conditions during summer months due to diminished freshwater inputs, high water temperatures, and increased biological activity; which leads to increased oxygen consumption. This results in an increase in the decay of organic matter and blooms of macroalgae throughout the estuary that consume oxygen in the sediment and water column. This decrease in oxygen concentrations is accompanied by an increase in sulfide and Fe(II) production. Reduction and subsequent immobilization of Cr(VI) results from a coupled biotic-abiotic reaction pathway in which $Fe(II)$ or hydrogen sulfide (H₂S) produced during microbial respiration catalyze the reduction of Cr(VI).

The geochemical measures of AVS and Fe(II) showed very strong evidence that there was adequate AVS and/or Fe(II) throughout the Site and during all seasons to maintain the reducing conditions that would ensure the presence of chromium as Cr(III), as illustrated on Figures 5-5a and 5-5b. Figure 5a shows that even in the limited number of areas where AVS measures were low, there were substantial amounts of excess Fe(II) indicating reducing conditions (and thus, the presence of chromium as Cr(III)). Figures 5-5a and 5-5b show seasonal fluctuations, and despite fluctuations in temperature and freshwater inputs that influence concentrations of DO, concentrations of reducing agents in sediments such as AVS and Fe(II) remain substantial. Specifically, AVS was found in concentrations that exceed concentrations of SEM in 90 percent of samples, regardless of season or DO concentration.

As discussed previously, USEPA acknowledges that geochemical factors determine both the bioavailability of chromium and its oxidation and reduction potential (USEPA, 2005a). As shown in Figure 5-5b, regardless of the variations in DO concentrations with season or depth at DMT, the concentrations of reducing agents are sufficient to ensure that chromium is stable as Cr(III). At the few locations where AVS was not found in excess, Fe(II) was available to act as the key reductant in the sediment (Table 5-4) as well as in surface and pore water. The results demonstrate that chromium remains stable as Cr(III) and is not oxidizable in even moderately oxidizing (aerobic) conditions. These results are also very consistent with findings of JHU researchers and researchers at other estuarine sites, as described in Section 5.4.

Chromium is stable as Cr(III) at DMT because reduction processes out-compete oxidation processes, despite fluctuations in concentrations of various geochemical constituents. Concentrations of reducing agents available to reduce Cr(VI) to Cr(III) far exceed the concentrations of the few oxidizing agents known to oxidize Cr(III) to Cr(VI) even in moderately aerobic sediments (Eary and Rai, 1987; Stanin, 2005). Furthermore, while oxidation of Cr(III) is extremely slow in environmentally relevant geochemical and thermodynamic conditions, reduction of Cr(VI) is very rapid under reducing or even mildly oxidizing conditions, making reduction the favored reaction under environmentally relevant pH/redox conditions (Schroeder and Lee, 1975).

5.3 Distribution and Extent of Other COPR Related Constituents

Although the Work Plan focused on the characterization of chromium in sediment and surface water adjacent to DMT, other COPR constituents (aluminum, calcium, iron, magnesium, manganese, and vanadium) were also analyzed to provide data for the human health and ecological risk assessments. Sample results for pore water, surface water, and sediment are provided in Tables 5-1 through 5-3.

The analytical results for the other COPR constituents in surficial sediments are shown in Figure 5-6. The spatial distributions vary for each parameter, indicating that these constituents do not co-occur. Aluminum and iron concentrations tend to be lower in the sandy sediments near Transects A-C relative to the finer-grained sediments in Transects D-H and the reference locations. Calcium and magnesium concentrations tend to be highest along the shoreline of Area 1501/1602. Manganese concentrations are highest along the D and E transects, and vanadium concentrations are generally uniform throughout DMT and in the reference locations. Concentrations of other COPR constituents in surficial sediment have been delineated relative to reference concentrations.

5.4 Comparison to Results from Previous Studies Conducted in Baltimore Harbor

This section includes a discussion of studies conducted by JHU and other researchers at estuarine sites where chromium is a primary constituent of interest. The results from the DMT study are consistent with the findings of these other research efforts regarding the behavior, predictability and stability of chromium in sediments. Each of the studies

presented below used approaches consistent with the USEPA approach for evaluating chromium toxicity in different media which includes the direct measurement of chromium species (Cr(VI) and Cr(III)) and geochemical parameters such as AVS and Fe(II) (Berry et al., 2004; USEPA, 2005a). These studies are discussed briefly below and are discussed in significant detail in a chromium literature review (ENVIRON, 2008).

This section concludes with a discussion of the relationship of DMT findings to historical studies at DMT, as well as the similarities of DMT findings from other chromium-related sites (i.e., the JHU and peer reviewed studies described in this section).

5.4.1 Johns Hopkins University Center for Contaminant Transport, Fate, and Remediation

JHU's CTFR performed a series of comprehensive multi-year experiments to evaluate the relationship between the presence of chromium species and toxicity in Baltimore Harbor sediments, pore water, and the water column. The initial investigations by JHU researchers characterized chromium speciation in Baltimore Harbor sediments and pore water (Graham et al., 2009). The characterization study was followed by a series of experimental studies using Baltimore Harbor sediments to evaluate chromium stability (Graham and Wadhawan, 2007a,b). The characterization and experimental studies are summarized below.

Baltimore Harbor Sediment and Pore Water Characterization (Graham et al., 2009)

The JHU researchers evaluated the geochemistry and speciation of chromium in sediment and pore water from 22 Baltimore Harbor locations using a reverse-phase ion-pair high performance liquid chromatography/inductively coupled plasma-mass spectrometry (HPLC/ICP-MS) method. The sample locations in the study included one location from DMT and two locations in Colgate Creek. The study included consideration of geochemical parameters that indicate reducing conditions and thus contribute to the understanding of chromium speciation (e.g. AVS, Fe(II), Mn(II), TOC). The researchers concluded that their findings were consistent with the USEPA EqP model for chromium which indicates that Cr(VI) is unlikely to be present in sediments with measurable AVS concentrations. Their findings further showed that Harbor sediments have considerable capacity to reduce Cr(VI) to Cr(III) based on spiking studies that were performed as part of method validation.

JHU CTFR Experimental Studies on Chromium Stability

The CTFR studies included multiple experimental studies that focused on two key questions related to chromium stability:

- 1. What geophysical conditions in sediment promote the reduction of $Cr(VI)$ to $Cr(III)$, and how fast are these reduction processes?
- 2. Once Cr(VI) is reduced to Cr(III), will the chromium remain as Cr(III) or can it be reoxidized to Cr(VI)?

JHU Experiment 1: Determination of Conditions Conducive to the Reduction of Cr(VI) to Cr(III) in Aquatic Environments and Sediment (Graham and Wadhawan, 2007a)

Graham and Wadhawan (2007a) conducted a study to better understand the fate and rates of reduction of Cr(VI) entering Baltimore Harbor. The study results showed that Cr(VI) was reduced to Cr(III) in a matter of seconds when spiked into harbor and creek sediments. The

amount of Cr(VI) used in several of the experiments was 10 times the Cr(VI) NRWQC for marine ecosystems. Study results also showed that the reduction of Cr(VI) was highly correlated to AVS concentrations. The rate of reduction was in fact proportional to the sediment AVS concentration and, therefore, consistent with USEPA guidance (2005a). The researchers concluded that AVS was a good predictor of Cr(VI) reduction kinetics in Baltimore Harbor sediments and that in sediments containing AVS, Cr(VI) is very quickly reduced to Cr(III).

JHU Experiment 2: Study to Determine the Likelihood that the Reduction of Cr(VI) to Cr(III) will be a Permanent Process—Cr(III) Oxidation (Graham and Wadhawan, 2007b)

An extension of JHU's initial study was to evaluate whether the reduction of Cr(VI) to Cr(III) is a permanent process. The primary objective of this study was to determine the significance of oxidants (e.g., manganese oxides and oxygen) in transforming Cr(III) to Cr(VI) in pore water, sediments and the water column. The researchers found that oxidants introduced into an experimental vessel containing Baltimore Harbor sediments were quickly reduced by organic matter, which is found in abundance in harbor sediments as well as DMT. The researchers found that while it was possible to catalyze the reaction of Cr(III) to Cr(VI), the specific conditions necessary to catalyze the reaction are not consistent with conditions occurring in the natural environment. This study demonstrated that Cr(III) is very stable in sediments unless under extreme laboratory conditions that are not characteristic of conditions likely to be encountered in Baltimore Harbor. Therefore, the authors concluded that the reduction of Cr(VI) to Cr(III) can be considered a permanent process. These results are consistent with the findings at DMT in that regardless of seasonal variations in temperature and concentrations of DO, chromium in sediments does not oxidize to $Cr(VI)$. If oxidation were occurring in sediments, then $Cr(VI)$ would have been detected in the pore water.

These findings by Graham and Wadhawan (2007b) are in agreement with the peer reviewed literature that indicates that once reduced, Cr(III) is geochemically stable and unlikely to transform to Cr(VI), even in the presence of oxidizing agents such as DO and manganese oxides (Magar et al., 2008; Saleh et al., 1989; Eary and Rai, 1987). According to the results of numerous peer reviewed articles, the oxidation of aqueous Cr(III) solely by DO is too slow to be considered a significant factor in the formation of Cr(VI) (Rai et al., 1986, Schroeder and Lee, 1975, Eary and Rai, 1987, Nakayama et al., 1981). The slow oxidation kinetics enable Cr(III) to be involved in other reactions (sorption or precipitation) that are much faster (Stanin, 2005) and maintain chromium in its reduced form as Cr(III). Thus, in the event that the water quality conditions in Baltimore Harbor improve in the future, it would still be highly improbable for the redox capacity of the sediments to be altered to the extent necessary for the spontaneous formation of Cr(VI).

While several studies other than JHU have reported the manganese oxide catalyzed oxidation of Cr(III) in the laboratory, the conditions necessary to drive the reaction are artificial and are inconsistent with the in situ conditions at DMT. Cr(III) must be soluble and/or manganese oxides must be fresh and amorphous in order for Cr(III) to adsorb onto manganese oxides surface sites (a necessary step for Cr(III) oxidation by manganese oxides; Wu et al., 2005; Kim et al., 2002). According to Wu et al. (2005) aged and well-crystallized MnO₂ (i.e., pyrolusite), which is what would typically be found in sediments, is weak and slow to oxidize Cr(III). Also, Cr(III) has very low solubility at environmentally relevant pH

due to the formation of insoluble hydroxide and oxide compounds and because Cr(III) forms strong complexes with sediment minerals and organic ligands (Fendorf, 1995). Therefore, manganese oxides and $Cr(VI)$ should not exist under the Eh-pH conditions present at DMT.

Overall, the CTFR studies determined that nontoxic Cr(III) is favored in Baltimore Harbor waters because the concentrations of reducing agents available to reduce Cr(VI) to Cr(III) far exceed the concentrations of the few oxidizing agents known to oxidize Cr(III) to Cr(VI). In addition, the kinetics of $Cr(VI)$ reduction to $Cr(III)$ is very fast, thereby outcompeting reactions involving Cr(III) oxidation.

The JHU studies also determined that oxidizing agents, even in the unlikely event that they might be present in environmentally relevant concentrations at DMT, are reduced by constituents readily available in the sediments, namely, organic matter. Moreover, Cr(III) is highly stable in sediments in Baltimore Harbor and only rigorous laboratory conditions will catalyze the formation of $Cr(VI)$ from $Cr(III)$. These studies showed that $Cr(VI)$ cannot persist in the natural environment and that the reduction of Cr(VI) to Cr(III) is likely a permanent process.

5.4.2 Hackensack River Chromium Investigations

The following section summarizes the results of studies conducted at chromium contaminated sites in the lower Hackensack River, New Jersey. The lower Hackensack River is a tidally influenced stretch of river with many characteristics that are similar to the Patapsco River and the DMT site.

The study areas described below have been used for industrial and commercial purposes for more than 100 years, including sodium dichromium manufacturing. It was common practice in the mid-1900s to use COPR generated during chromate production as fill material.

Geochemical Stability of Chromium in Sediments from the Lower Hackensack River, New Jersey (Magar et al., 2008)

Magar et al. (2008) conducted sediment resuspension and oxidation experiments to investigate the potential for release of Cr(III) or Cr(VI) and other chemicals of concern in sediment to the water column in response to a sediment disturbance event at a chromium contaminated site in the lower Hackensack River, NJ. The intertidal sediment exposure experiment was designed to investigate potential aqueous release of Cr(III) or Cr(VI) from intertidal surface sediments during low tide, the conditions under which sediments experience the greatest level of oxygen exposure.

Results revealed no detectable concentrations of Cr(VI) and thus no measurable potential for Cr(III) oxidation to Cr(VI) despite the fact that the experiments were designed to maximize the oxidation potential in surface and suspended sediment samples due to exposure to oxygen. The results of this study demonstrated that Cr(III) is stable and is expected to remain geochemically stable in the study area sediments under ambient conditions, severe weather conditions, and anthropogenic scouring events.

Chromium Geochemistry and Bioaccumulation in Sediments from the Lower Hackensack River, New Jersey, U.S.A. (Martello et al., 2007)

Martello et al. (2007) measured total chromium and Cr(VI) in sediment and sediment pore water in the lower Hackensack River, NJ to assess the relationship between sediment geochemistry and chromium speciation, which in turn controls the mobility, bioavailability and toxicity of chromium. Between 2003 and 2005, more than 100 surface sediment samples (0 to 6 inches) were tested for total Cr, Cr(VI), AVS, Fe(II), Mn(II), ammonia, and organic carbon. Sediment pore water samples were collected by centrifugation or *in situ* samplers co-located with the collection of sediments. Concentrations of AVS and other geochemical measurements indicated reducing conditions in the majority of sediment samples.

Chromium concentrations in whole tissues of polychaetes and clams exposed in the field or in the laboratory showed no relationship with total chromium or Cr(VI) concentrations in the sediment or pore water and no statistical differences in concentrations of chromium in tissues of animals exposed to sediments from site versus reference locations. The results of this study are consistent with the USEPA (2005a) EqP approach as well as sediment studies conducted elsewhere indicating low chromium bioavailability in sediment under reducing and even moderately oxidizing conditions.

Despite the occurrence of elevated concentrations of total chromium in sediments of the lower Hackensack River, the results of this study indicate that little, if any of the chromium is present as Cr(VI), and, therefore, risks associated with exposure to chromium are particularly low. Further, Cr(VI) was not detected in any of the pore water samples. These results are consistent with multiple geochemical indicators showing reducing conditions in pore water and sediment. The low bioaccumulation of chromium to benthic invertebrates is also consistent with these conclusions.

5.4.3 Similarities between Current DMT Study and Recent Chromium-Related Studies

Each of the studies described above were conducted either in the Baltimore Harbor or in river systems with similar characteristics. The findings from these chromium-related studies reported in the peer reviewed literature have substantial similarities to DMT. Specifically,

- Even at sites like DMT that contain high concentrations of chromium in sediment, the chromium exists overwhelmingly in the trivalent form.
- Regardless of high concentrations of total chromium in sediment, Cr(VI) was consistently not detected in the pore water.
- Like DMT, each of these studies has reported measurable concentrations of geochemical constituents, such as AVS and Fe(II), that have been shown to reduce $Cr(VI)$ to $Cr(III)$.
- Cr(III) was shown to be highly stable in each of the studies where Cr(III) oxidation potential was tested.

(a) For detection frequency, where duplicate samples were present, they were counted as one sample.

(b) Where duplicate samples were present, the greatest value for each analyte was used to calculate range, average, and standard deviation.

(c) Average concentration and standard deviation calculated by using one-half of the detection limit for non-detects.

max = Maximum

mg/L = Milligram per Liter ND = Not Detected

NA = Not Analyzed ug/L = Microgram per Liter

min= Minimum SD = Standard Deviation

mv = Millivolts SU = Standard Units

TABLE 5-1b

Summary of Reference Area Pore Water Results

TABLE 5-1b

Summary of Reference Area Pore Water Results

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TABLE 5-1b

Summary of Reference Area Pore Water Results

TABLE 5-1b

Summary of Reference Area Pore Water Results *Dundalk Marine Terminal, Baltimore, Maryland*

(a) For detection frequency, where duplicate samples were present, they were counted as one sample.

(b) Where duplicate samples were present, the greatest value for each analyte was used to calculate range, average, and standard deviation.

(c) Average concentration and standard deviation calculated by using one-half of the detection limit for non-detects.

max = Maximum

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(a) For detection frequency, where duplicate samples were present, they were counted as one sample.

(b) Where duplicate samples were present, the greatest value for each analyte was used to calculate range, average, and standard deviation.

(c) Average concentration and standard deviation calculated by using one-half of the detection limit for non-detects.

max = Maximum ND = Not Detected

 $mg/L =$ Milligram per Liter $SD =$ Standard Deviation

min= Minimum ug/L = Microgram per Liter

NA = Not Analyzed

Summary of Reference Area Surface Water Results

Summary of Reference Area Surface Water Results

Dundalk Marine Terminal, Baltimore, Maryland

(a) For detection frequency, where duplicate samples were present, they were counted as one sample.

and standard deviation.

(c) Average concentration and standard deviation calculated by using one-half of the detection limit for non-detects.

 $max = Maximum$ $ND = Not detected$

min= Minimum ug/L = Microgram per Liter

 $mg/L =$ Milligram per Liter $SD =$ Standard Deviation

NA = Not Analyzed

Dundalk Marine Terminal, Baltimore, Maryland

(a) For detection frequency, where duplicate samples were present, they were counted as one sample.

(b) Where duplicate samples were present, the greatest value for each analyte was used to calculate range, average, and standard deviation.

(c) Average concentration and standard deviation calculated by using one-half of the detection limit for non-detects.

AVS = Acid Volatile Sulfide

max = Maximum extensive max = Maximum series of SEM = Simultaneously Extracted Metals

mg/kg = Milligram/Kilogram TOC = Total Organic Carbon

min = Minimum umoles/g = Micromoles per Gram

SD = Standard Deviation

mm = Millimeter % = Percent

NA = Not Analyzed

TABLE 5-3b

Summary of Reference Area Surface Sediment Results *Dundalk Marine Terminal, Baltimore, Maryland*

TABLE 5-3b Summary of Reference Area Surface Sediment Results *Dundalk Marine Terminal, Baltimore, Maryland*

TABLE 5-3b Summary of Reference Area Surface Sediment Results *Dundalk Marine Terminal, Baltimore, Maryland*

(a) For detection frequency, where duplicate samples were present, they were counted as one sample.

standard deviation.

(c) Average concentration and standard deviation calculated by using one-half of the detection limit for non-detects.

AVS = Acid Volatile Sulfide

mm = Millimeter % = Percent

NA = Not Analyzed

max = Maximum extracted Metals SEM = Simultaneously Extracted Metals mg/kg = Milligram/Kilogram TOC = Total Organic Carbon min = Minimum distribution of the matrix of the modes with the umoles/g = Micromoles per Gram

SD = Standard Deviation

TABLE 5-3c Summary of DMT Subsurface Sediment Results *Dundalk Marine Terminal, Baltimore, Maryland*

TABLE 5-3c

Summary of DMT Subsurface Sediment Results

TABLE 5-3c Summary of DMT Subsurface Sediment Results *Dundalk Marine Terminal, Baltimore, Maryland*

(a) For detection frequency, where duplicate samples were present, they were counted as one sample.

(b) Where duplicate samples were present, the greatest value for each analyte was used to calculate range, average, and standard deviation.

(c) Average concentration and standard deviation calculated by using one-half of the detection limit for non-detects.

AVS = Acid Volatile Sulfide

mg/kg = Milligram/Kilogram TOC = Total Organic Carbon

mm = Millimeter % = Percent

NA = Not Analyzed

SD = Standard Deviation

max = Maximum contracted Metals contracted Metals SEM = Simultaneously Extracted Metals

min = Minimum umoles/g = Micromoles per Gram

TABLE 5-3d

Summary of Reference Area Subsurface Sediment Results

Dundalk Marine Terminal, Baltimore, Maryland

(a) For detection frequency, where duplicate samples were present, they were counted as one sample.

standard deviation.

(c) Average concentration and standard deviation calculated by using one-half of the detection limit for non-detects.

AVS = Acid Volatile Sulfide

max = Maximum extension of the Simultaneously Extracted Metals

mm = Millimeter $\%$ = Percent

mg/kg = Milligram/Kilogram TOC = Total Organic Carbon

SD = Standard Deviation

min = Minimum umoles/g = Micromoles per Gram

NA = Not Analyzed

TABLE 5-4

Summary of AVS-SEM Results

Dundalk Marine Terminal, Baltimore, Maryland

(b) Analytes that were not detected are presented here as present at 1/2 of the detection limit.

AVS Acid Volatile Sulfides

TABLE 5-5 Cr(VI) Detections at DMT and Cumulative Rainfall Totals *Dundalk Marine Terminal, Baltimore, Maryland*

(a) Refers to cumulative rainfall totals in inches.

Cr(VI) was not detected in surface water in May 2007 (Q1)

P A T A P S C O

P $\frac{1}{2}$

Legend

Sample Location Sample Location - February 2008 only

Sample Location - not sampled in December 2007 or February 2008

Storm Sewer Line COPR Extent

+++ Railroad Centerline Areas

L = analyte present; reported value may be biased low. Actual value may be higher. UL = Not Detected, quantitation limit is probably higher K = Analyte present. Reported value may be biased high. Actual value may be lower.

U = not detected

J = estimated value UJ = not detected; the associated detection limit is an estimate and may be inaccurate or imprecise

B = Not detected substantially above the level reported in laboratory or field blank

\\Perseus\projects\HoneywellInc\327494DMT\Projects\SW_SD_Sampling_Plan\Q4\Final_Report\Figure 5-1c - Total Chromium and Cr(VI) Results for Surface Water.mxd

Legend

Sample Location Sample Location - February 2008 only

Sample Location - not sampled in December 2007 or February 2008

Storm Sewer Line COPR Extent

THE Railroad Centerline **Areas**

ENVIRON **CH2MHILL**

National hronic Dissolved

Water Depth in Feet (NAVD88) -4 feet

-50 feet

Figure 5-2a. This figure shows that even the maximum concentration of dissolved Cr(III) in pore water at DMT is not only below the current chronic NRWQC but is far below the hardness adjusted value recommended by USEPA for sites that are estuarine or marine and even further below the acute criterion. **Figure 5-2b.** This figure demonstrates the higher concentrations of dissolved Cr(III) in pore water at the deeper water Transects D – H than in the shallow Transects A, B, C and J. Only Transect D and E show a declining trend in dissolved Cr(III) concentrations with distance from the shoreline.

¹ Cr(III) as dissolved total chromium

FIGURE 5-2a-b Dissolved Chromium in Pore Water Dundalk Marine Terminal, Baltimore, Maryland

Figure 5-3a. This figure shows that even the maximum concentrations of Cr(VI) at DMT are below both the acute and chronic NRWQC. Cr(VI) was detected at Transects B, C, D and E only. **Figure 5-3b**. This figure demonstrates the relationship between Cr(VI) detections in surface water and corresponding 3-day rainfall totals.

> **FIGURE 5-3a-b Cr(VI) in Surface Water Dundalk Marine Terminal, Baltimore, Maryland**

Figure 5-4. This figure shows that even the maximum concentration of dissolved chromium in surface water at DMT is not only below the current NRWQC but is far below the hardness adjusted value recommended by USEPA for sites that are estuarine or marine and even further below the Freshwater Acute Criterion of 570 ug/L. Organisms that inhabit the water column would only be acutely exposed to dissolved chromium in surface water.

Figure 5-5a. This figure shows that in the few areas where SEM metals exceed AVS or AVS only slightly exceeds SEM, there is abundant Fe(II) so that divalent metals are not biologically available for uptake by biota and there is sufficient reducing power in the sediments to insure the existence of Cr(III) vs. Cr(VI). **Figure 5-5b.** This figure shows how changes in the water temperatures that occurs with season influences salinity and dissolved oxygen concentrations which in turn influences concentrations of the key reductants AVS and Fe(II). Note that AVS and Fe(II) are highest in the warmest months due to increases in microbial activity that deplete oxygen in the water column. Despite seasonal fluctuations there is ample reducing power in DMT sediments to insure the stability of Cr(III).

> **FIGURE 5-5a-b Geochemical Constituents in Sediment Dundalk Marine Terminal, Baltimore, Maryland**

9.1 - 18.2

