

Preliminary Conceptual Site Model

The CSM provides a framework for understanding the distribution and behavior of chromium in the Patapsco River adjacent to DMT based on existing data, and descriptions of relevant chemical and physical fate and transport processes and conditions that influence these processes. According to the USEPA, a preliminary CSM typically is a set of hypotheses derived from existing site data and knowledge gained from other sites (USEPA, 2005b). The preliminary CSM presented in this section focuses on the chromium sources and migration pathways at DMT, and published information about processes that influence the fate and transport of chromium in an estuarine environment. Refinements to the CSM based on the results of this sediment and surface water study are presented in Section 6.

2.1 Conceptual Chromium Sources and Migration Pathways

DMT's location in the central portion of Baltimore Harbor is such that the Patapsco River sediments are (and have been) exposed to historical and current chemical influences both related and unrelated to the Site. The Port of Baltimore is ranked 13th among the most active ports in the United States.³ It generates more than 1.4 billion dollars in annual revenue, and has approximately 126 miles of federal navigational channels. Baltimore Harbor has a long history of industrial use dating back to the late 1700s, including steel production (Sparrows Point was historically ranked the largest steel mill in the world), ship building, sugar refinement, garment manufacturing, container and shipping industry, and more recently, biotechnology.

As previously noted, DMT is located on land that was in part created by the placement of COPR fill material. A review of aerial photographs and shoreline maps indicates that active filling occurred from before 1940 to the 1970s. The COPR fill area is generally located south of East Service Road. Additional delineation of COPR was provided in the Phase I COPR Investigation Data Report (CH2M HILL, 2007), as shown in Figure 1-1. During land reclamation activities from the late 1960s to the mid-1970s, COPR fill material was stored in the southeast portion of DMT, with uncovered borrow areas and/or stockpiles located in the 1400, 1500, 1600, 1601, and 1702 areas. Surface water runoff from uncovered stockpiles and other filling operations into the Patapsco River reportedly occurred during land reclamation activities.

Potential migration pathways for the transport of chromium from DMT to the Patapsco were originally conceptualized as 1) direct discharge of groundwater to the river; 2) groundwater seepage into storm drains that discharge directly to the river via outfalls; and 3) tidal inundation of storm drains. These potential migration pathways are being evaluated in the Chromium Transport Study (CH2M HILL, 2006a). Areas of potential groundwater discharge from DMT to the Patapsco River were identified in groundwater upwelling surveys performed as part of this study (see Section 4.1.5). However, results of

³ Source: 2006, Intermodal Association of North America; Journal of Commerce PIERS—Port Import/Export Reporting Service

the Area 1501/1602 riverfront perimeter groundwater monitoring do not indicate that groundwater is a meaningful transport pathway for Cr(VI). Even when detected in groundwater samples from these wells, Cr(VI) was below the USEPA Nationally Recommended Water Quality Criteria (NRWQC) (see Section 4.1.6).

The locations of storm drains and outfalls at DMT are shown in Figure 1-1. The drains are constructed of reinforced concrete pipe and range in diameter from 12 to 96 inches. At high tide, the Patapsco River waters penetrate the storm drains associated with the whole-numbered streets from 9th to 13th Streets. The drains at the half-numbered streets are approximately 2 feet higher and therefore experience less tidal penetration. Backflow preventers were constructed at the 14th and 15th Street outfalls in the 1990s to prevent the intrusion of the Patapsco River waters at high tide (construction of similar backflow preventers is not possible at the other outfalls due to engineering and operational constraints). In 2006, a remedial system was installed at the 14th and 15th Street outfalls to collect and treat stormwater prior to discharge from a combined outfall managed under a National Pollution Discharge Elimination System (NPDES) permit. An interim remedial measure (IRM) was initiated at the 13th Street storm drain in December 2008.

The Chromium Transport Study will provide information on all the storm drains, evaluate the need to address priority storm drains, and present an approach to install collection vaults as IRMs to address dry-weather flow and facilitate cleaning and a conditions assessment. The conditions assessment and subsequent post-cleaning monitoring data will be used to determine the need for repair or rehabilitation regarding wet-weather flow.

Refinements to the preliminary CSM based on the results of this sediment and surface water study are presented in Section 6.1. Briefly, groundwater discharge does not appear to be a significant pathway for the transport of chromium from DMT to the Patapsco River. Historical surface water runoff from uncovered COPR fill stockpiles and other filling operations in the southeast part of DMT is likely to have been a former transport pathway to the river. This pathway became inactive when land reclamation activities were completed and the terminal areas were paved.

2.2 Chromium Fate and Transport

The chemical and physical processes that influence the fate, transport, and stability of chromium in the estuarine environment are described below. These fate and transport characteristics were used to guide the development of the sediment and surface water sampling approach for DMT.

2.2.1 Chromium Geochemistry

Chromium concentrations in excess of naturally occurring background levels are widespread in sediments in urbanized and industrialized estuaries, due to runoff from road surfaces, combined sewer overflows, and municipal and industrial discharges (Meador et al., 1994; Paul et al., 2002; USEPA, 2004a). Although early efforts to evaluate sediment quality and the significance of chromium in sediment focused on analyses of total chromium (Long et al., 1995), recent studies suggest that chromium speciation in sediment must be understood to support more accurate evaluations of potential ecological impacts (USEPA, 2005a; Berry et al., 2004; Besser et al., 2004; Martello et al., 2007; and Sorensen et al.,

2007). USEPA's efforts related to understanding chromium in aquatic environments culminated with the publication of the 2005 Equilibrium Partitioning (EqP) Guidance for Metals Mixtures (USEPA, 2005a). This information is relevant to DMT because the sampling design utilized for the sediment and surface water study is consistent with the USEPA EqP approach.

USEPA states that geochemical processes govern the reduction of Cr(VI) to Cr(III) in aquatic environments, and geochemical processes are critical to the attenuation of chromium in sediments. The presence of Cr(III) is strongly favored in natural waters and sediments because the concentrations of sediment constituents known to reduce Cr(VI) to Cr(III) generally far outweigh the concentrations of the few constituents known to oxidize Cr(III) to Cr(VI). Furthermore, once reduced, Cr(III) is very stable in aquatic environments and highly unlikely to oxidize to Cr(VI). Thus, chromium in sediments is more likely to be in its Cr(III) form than its Cr(VI) form (James and Bartlett, 1983; Fendorf and Zasoski, 1992; Milacic and Stupar, 1995; Weaver and Hochella, 2003).

The USEPA (2005a) approach can be summarized as follows with regard to Cr(VI) partitioning in sediments and the role of acid volatile sulfides (AVS), one of the key geochemical indicators of chromium speciation:

- The extent of Cr(VI) in sediment is based on evaluation of Cr(VI) in pore water because Cr(VI) will only partition to pore water if present and biologically available in sediments.
- USEPA recognizes the geochemical relationship between chromium and reducing agents, including AVS.
- AVS is formed only in reducing environments.
- Cr(VI) is thermodynamically unstable in reducing environments (i.e., anaerobic sediments).
- Therefore, in the presence of AVS, Cr(VI) is readily transformed to Cr(III), making Cr(III) the dominant species in sediments where total chromium has been measured.
- Cr(VI) reduction is not necessarily limited to areas with high AVS and can be catalyzed by other reductants. The advantage of AVS is that it is easily, reliably, and inexpensively measured.
- Aquatic toxicity data show that Cr(VI) is much more toxic than Cr(III). Cr(III) is very poorly soluble in water and exhibits very low aquatic toxicity.
- Therefore, when AVS is present in sediment, chromium-related toxicity is unlikely, especially in estuarine environments.

Chromium speciation is important because Cr(III) and Cr(VI) exhibit widely differing chemical properties and ecotoxicological effects. Cr(VI) exhibits much greater solubility, mobility, bioavailability, and toxicity than Cr(III) in sediments and surface waters (Richard and Bourg, 1991; James, 2002; USEPA, 1986 and 2005a). Cr(III) is relatively insoluble at environmentally relevant pH levels, even in geochemically simple aqueous solutions, due to the formation of insoluble hydroxide and oxide compounds. In sediment, Cr(III) solubility is

further limited by strong complexation with sediment minerals and organic ligands (Sass and Rai, 1987; Fendorf and Zamoski, 1992; James, 2002). For example, binding of iron and Cr(III)-containing compounds lowers solubility considerably, similar to the inert, highly stable crystalline chromite ore ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) (James, 2002). The insolubility of Cr(III) generally limits its bioavailability and mobility in saline environments (Eisler, 1986). Indeed, due to a lack of Cr(III) toxicity in saltwater exposures, the USEPA has adopted saltwater criteria to protect aquatic life only for Cr(VI) (USEPA, 1986).

The presence of Cr(III) is strongly favored in natural waters and sediments because the concentrations of sediment constituents known to reduce Cr(VI) to Cr(III) generally far outweigh the concentrations of the few constituents known to oxidize Cr(III) to Cr(VI). Thus, chromium in sediments is more likely to be in its Cr(III) form than its Cr(VI) form. Several organic and inorganic constituents in anaerobic sediments facilitate rapid reduction of Cr(VI) to Cr(III), including sulfides, ferrous iron, and organic matter (Hansel et al., 2003); bacterially mediated reduction of Cr(VI) is also known (Schmieman et al., 1998). Reduction of Cr(VI) to Cr(III) is rapid under reducing or even mildly oxidizing conditions, occurring within minutes to days depending on the reducing agent (Berry et al., 2004; Lin, 2002; Richard and Bourg, 1991; Schroeder and Lee, 1975; Stollenwerk and Grove, 1985).

The extent to which Cr(III) oxidizes to Cr(VI) in a laboratory environment depends on the presence and mineralogy of manganese (hydr)oxides, pH, and the form and solubility of Cr(III); however, once reduced in a natural aquatic environment, Cr(III) is very stable and highly unlikely to oxidize to Cr(VI) (James and Bartlett, 1983; Fendorf and Zamoski, 1992; Milacic and Stupar, 1995; Weaver and Hochella, 2003). Cr(III) oxidation is less likely to occur in the environment than under laboratory conditions because aged waste materials containing Cr(III) are typically less soluble and more inert to oxidation, especially because $\text{Cr}(\text{OH})_3$ precipitates may form on manganese (hydr)oxide surfaces (James and Bartlett, 1983; Fendorf and Zamoski, 1992; Fendorf, 1995; Martello et al., 2007). This finding was confirmed in research conducted in 2007 by Johns Hopkins University Center for Contaminant Transport, Fate, and Remediation (CTFR) that found that Cr(III) is highly stable in Baltimore Harbor sediments. Baltimore Harbor sediments were oxidized for 10 days, and Cr(VI) was not detected in any of the daily time series measures of Cr(VI) taken from the water in which the sediment was being aerated (Graham and Wadhawan 2007a,b).

2.2.2 Physical Fate and Transport Processes

Once released into the aquatic environment, chromium can be transported in dissolved phase in the water column, or adsorbed to sediment particles and transported in the solid phase. The hydrodynamic and sediment transport processes that may influence the transport of chromium are described below.

The Baltimore Harbor portion of the Patapsco River is a tidally-influenced tributary of Chesapeake Bay. The tidal range was approximately 3 feet in the vicinity of DMT during this study. The tidal Patapsco River receives very little freshwater inflow from the upper reaches of the river, and is primarily influenced by flow from the Bay (USACE, 2006). Circulation patterns are influenced by wind conditions, and by the interaction between denser tidal waters moving into the Harbor from Chesapeake Bay and converging with less dense freshwater from rivers and other sources (USACE, 1997).

Multiple dye studies were conducted in April 1987 on the 15th Street (96-inch) drain at DMT (EA, 1987). Dye concentrations were measured with fluorometers at the bulkhead and onboard a vessel in the mixing zone. Three separate surveys were performed: two at high tide and one at low tide. The results of the dye study suggested that a “conservative” parameter would undergo a dilution between 1:200 and 1:400 within 2,000 feet of the outfall. Dilutions of 1:1,000 to 1:3,000 would apply within 5,000 feet of the discharge point.

No flow or current measurements are available in the immediate vicinity of the DMT. Current velocities in the Patapsco River tend to be weak and variable, with maximum velocities of less than 30 cm/sec (USACE, 2006). Modeling conducted for the Masonville Dredged Material Containment Facility (Masonville) in Baltimore Harbor indicates that low velocities (less than 5 cm/sec and even close to zero) can be expected in areas around DMT.

Baltimore Harbor is a net depositional environment for sediment. The primary source of sediment to the Harbor is suspended sediment from Chesapeake Bay. Shoaling rates in channels and anchorages adjacent to DMT are about 3 inches per year (USACE, 1997). Once deposited, sediments could potentially be resuspended by currents, tides, waves, dredging, ship traffic, or other human activities. A study of sediment resuspension in Baltimore Harbor indicated that a loosely consolidated surface “fluff” layer is commonly present on top of a well-consolidated sediment bed (Maa et al., 1998). Under normal flow conditions, bottom shear stresses due to wave and current activity are insufficient to erode the consolidated sediment bed, but can readily resuspend and transport fluff. Based on existing information regarding flow velocities and sediment transport in Baltimore Harbor, consolidated sediments in the vicinity of DMT are expected to be relatively stable under typical hydrodynamic conditions.