

Investigation Scope and Approach

This section describes the scope and approach for the sediment and surface water study. Table 3-1 summarizes the study goals, inputs, spatial and temporal boundaries, data sampling and analysis plan, and data evaluation approach. The sediment and surface water study included the following elements:

- Four quarterly sampling events that included collection of pore water, surface water, and sediment samples for analysis of chromium, other COPR constituents, and geochemical parameters; and collection of vertical profiles of water column characteristics at each sampling location
- A hydrographic (bathymetric) and geophysical (sub-bottom profile) survey
- Groundwater upwelling surveys to identify areas of potential groundwater discharge from DMT to the Patapsco River.

The sediment and surface water study sampling design is described in Section 3.1, and the data evaluation approach is summarized in Section 3.2.

3.1 Overview of Sampling Design

The horizontal extent of the study area in the Patapsco River extended beyond the area of expected influence of potential groundwater discharge from DMT, and the area where surface water mixing of outfall discharges is likely to occur. Pore water, surface water, and sediment samples were collected from seven transects in the Patapsco River adjacent to DMT (Transects A-G), and two transects in Colgate Creek (Transects H-I). Each transect consisted of four stations, for a total of 36 DMT sampling locations. For the February 2008 sampling event, another transect was added in the vicinity of Area 1501/1602 (Transect J), and one station was added to the B transect. In addition, samples were collected from three reference locations in the Patapsco River (37, 37A, and 37B). A sample location map is provided in Figure 3-1.

The rationale for selecting transect and station locations is as follows:

- Transects A, B, and C are located in the vicinity of Area 1501/1602 and the 14th and 15th Street outfalls. Area 1501/1602 is the only part of the DMT shoreline that is not contained by a bulkhead. The highest concentrations of chromium previously measured in sediment near DMT were adjacent to the 14th and 15th Street outfalls (EA, 1987). The A, B, and C transects extend into relatively shallow water near the north shore of the Patapsco River.
- Transects D and E are perpendicular to the bulkhead, adjacent to the 13th and 12th Street outfalls, respectively. Four locations were sampled along each transect to (a) characterize conditions next to the bulkhead (i.e., potential effects of seepage from the bulkhead, if any, as well as potential sediment deposition from outfall discharges), (b)

characterize conditions in the deep portion of the dredged channel, and (c) characterize conditions in the shallower sediment on the far side of the dredged channel.

- Transects F and G are also located perpendicular to the bulkhead and have locations adjacent to the bulkhead, in the dredged channel, and on the far side of the dredged channel; however, there are no outfalls in the vicinity of these transects.
- Transects H and I are located in Colgate Creek, where storm drains are not within the COPR fill area. Transect H is placed along the bulkhead to characterize effects of potential groundwater seepage from the bulkhead, and Transect I is placed in a shallow portion of the creek upstream of the dredged channel.
- Transect J was added in the February 2008 sampling event to provide higher spatial resolution of chromium concentrations along the shoreline in Area 1501/1602.

The three reference locations in the Patapsco River channel (37, 37A, and 37B) were selected because the sediments in this area have similar physical characteristics as most of the sediments adjacent to DMT, and are considered beyond the influence of DMT but sufficiently close so that non-site related influences that may also affect sediments adjacent to DMT can be identified. The identification of reference locations that achieve these goals is consistent with USEPA background soil guidance (USEPA, 2002a), which states that “a background reference area should have the same physical, chemical, geological, and biological characteristics as the site being investigated, but has not been affected by activities on the site.” The guidance further states that “background reference areas are normally selected from off-site areas, but are not limited to natural areas undisturbed by human activities. It may be difficult to find a suitable background reference area in an industrial complex. In some cases, a non-impacted onsite area may be suitable as a background reference area.”

Surficial sediment and pore water samples were collected from the 0-0.5 ft depth interval at each location to represent the biologically active zone. The selection of this interval is consistent with USEPA’s 2005 EqP approach, as well as other established approaches that focus on the biologically active zone (U.S. Navy, 2003; WDE, 2005; MDE, 2004). Sediment cores were collected to a depth of 3 feet, which is well below the biologically active zone. Subsurface sediment samples were collected from a mid-depth interval (typically 1.0-1.5 feet below the sediment surface) and a deep interval (typically 2.5-3.0 feet below the sediment surface) to provide information about the vertical distribution of chromium. The depth intervals were adjusted if necessary at each sampling location so that each sample represented a single sediment type.

Surface water samples were collected from up to three water depths (top, mid-depth, and bottom of the water column), depending on total water depth. Only two samples (top and bottom) were collected if the water depth was less than 10 feet, and only one sample (mid-depth) was collected if the water depth was less than 5 feet. Exact sample depths were determined based on temperature and salinity profiles to characterize any observed water column stratification (i.e., presence of a fresh water lens).

Pore water and surface water samples were collected in all four quarterly sampling events to characterize seasonal variations in chromium concentrations and geochemical conditions. Surficial sediment samples were collected in two of the quarterly events (May and

August 2007), and subsurface sediment samples were collected in one event only (August 2007); sediment samples were collected from Transect J stations and location B5 in February 2008 only. However, *in situ* sediment quality parameters (oxidation-reduction potential (ORP) and pH) were measured in each quarterly sampling event to assess seasonal differences in geochemical conditions. The analytical parameters for each sample type are provided in Section 4.

3.2 Data Evaluation Approach

The following section describes the data evaluation approach used to determine the nature and extent, and fate and transport of chromium in the Patapsco River and Colgate Creek adjacent to DMT pursuant to the Consent Decree and using the approaches defined in the Work Plan.

3.2.1 Nature and Extent of Chromium

The nature and extent evaluation for DMT is based primarily on a comparison of Cr(VI) and dissolved total chromium analytical results to USEPA Nationally Recommended Water Quality Criteria (NRWQC) (Figure 3-2). The extent of Cr(VI) in sediment is based on the evaluation of Cr(VI) in pore water because, according to USEPA and other published studies, Cr(VI) partitions to pore water if present and biologically available in sediment (USEPA, 2005a; Berry et al., 2004; Besser et al., 2004). In addition, there are no available sediment quality benchmarks for the evaluation of Cr(VI) in sediment (USEPA, 2005a).

In addition to NRWQC, the data evaluation approach involves the comparison of detected concentrations of chromium and other COPR constituents in pore water, surface water, and sediment at DMT to the detected concentrations in the same media from mid-channel Patapsco River reference locations (Figure 3-2). Spatial variations that occur throughout DMT are also evaluated; for instance, between shallow versus deep water sediments and chemical concentration trends with increasing distance from the DMT shoreline.

As noted above, USEPA (2006) saltwater and freshwater NRWQC are considered in the evaluation of nature and extent, as identified in Figure 3-2. As acknowledged by USEPA (2005a), Cr(VI) exhibits much greater solubility, mobility, bioavailability, and toxicity than Cr(III) in sediments and surface waters. Not only is Cr(III) relatively insoluble, which limits its bioavailability and mobility, it also is a micronutrient that exhibits very limited toxicity (Eisler, 1986). Indeed, USEPA (1986) adopted saltwater criteria to protect aquatic life only for Cr(VI) but not for Cr(III) due to its low toxicity in saltwater. Therefore, while saltwater and freshwater criteria are available for Cr(VI), only freshwater criteria are available for Cr(III).

While the mobility of Cr(III) is generally low, the presence of organic ligands can solubilize Cr(III), thereby increasing its mobility. These organo-Cr(III) complexes have been shown to remain soluble and stable over a broad pH range (Puzon et al., 2005). The ready formation of stable organo-Cr(III) complexes suggests that they are rather common and likely represent an integral part of the natural cycling of chromium.

Marine waters (i.e., saltwater) are those in which the salinity is equal to or greater than 10 practical salinity units (PSU), 95 percent of the time (USEPA, 2000). Freshwaters are defined as those in which the salinity is equal to or less than 1 PSU 95 percent of the time; however,

freshwater salinity is typically less than 0.5 PSU. According to MDE, waters in the vicinity of DMT are identified as saline and saltwater criteria are most applicable (Code of Maryland Regulations (COMAR) 26.08.02.03-1). Site-specific measures of salinity and hardness support this MDE designation. Salinity measures in the Patapsco River are discussed in greater detail in Sections 4 and 5 of this report, and generally range between 5 and 15 PSU. In addition, the presence of organisms typical of a saline environment near DMT was documented during the May 2007 sampling event (these observations are discussed further in Appendix C). Finally, the biomonitoring program performed in accordance with the MDE NPDES permit for the facility uses estuarine organisms, not freshwater organisms, for effluent testing associated with permit criteria. Therefore, saltwater criteria are most relevant for DMT. Nevertheless, freshwater criteria based on site-specific hardness values were also determined for DMT as part of the conservative assessment of nature and extent presented in Section 5.

Hardness is measured by the concentration of calcium and magnesium in water expressed in milligrams per liter (mg/L) of calcium carbonate (CaCO_3). Water having total hardness values of 0-75 mg/L is generally classified as soft water, while values above 150 mg/L are categorized as hard water. Full strength seawater (35 PSU) has a total hardness approximating 6,600 mg/L. The Patapsco River has an average hardness, determined from four rounds of sampling at DMT, of approximately 2,250 mg/L CaCO_3 , which is consistent with salinities greater than 10 PSU. The freshwater NRWQC correspond to a freshwater hardness of 100 mg/L CaCO_3 . Criteria for use in the Patapsco River should be calculated using site-specific water hardness data using USEPA's recalculation criteria (USEPA, 2002b; 2006) because 100 mg/L does not represent a salinity of the estuarine environment. Average CaCO_3 concentrations at DMT ranged from 1,563 mg/L to 2,480 mg/L (overall mean = 2,250 mg/L). While USEPA acknowledges that increased hardness results in decreased bioavailability, a maximum value of 400 mg/L is recommended for use in the derivation formulae because the formulae are calibrated for a relatively narrow range of hardness values that are more proximate to the freshwater end of the spectrum of naturally occurring hardness values. Given that the lowest site-specific hardness values for DMT is approximately 1,500 mg/L, the use of 400 mg/L is very conservative, as a 1995 publication of the Federal Register even stated "using 400 mg/L to calculate criteria, in waters with an ambient hardness of greater than 400 mg/L, may result in overprotective..."

The freshwater criteria continuous concentration (CCC) and criteria maximum concentration (CMC) values applicable to dissolved Cr(III) are expressed as a function of water hardness, as follows:

$$\text{Chronic Criteria: CCC (dissolved)} = \exp\{0.8190 [\ln(\text{hardness})] + 0.6848\} (0.860)$$

$$\text{Acute Criteria: CMC (dissolved)} = \exp\{0.8190 [\ln(\text{hardness})] + 3.7256\} (0.316)$$

The summary in Table 3-2 uses the equations above to solve for a range of CaCO_3 concentrations yielding hardness-dependent NRWQC for (1) chromium in a typical estuarine environment with salinities between 1- 10 PSU that exist at DMT, and (2) for tidally dominated estuarine conditions with salinities between 5 and 15 PSU that also exist at DMT. An example calculation is also provided in Table 3-2.

3.2.2 Chromium Fate and Transport

The approach for evaluating the fate and transport of chromium considers the presence of geochemical conditions that influence chromium speciation and stability; as such, they were characterized during each of the four sampling events in accordance with the Work Plan. Seasonal variations in geochemical parameters were also evaluated as they may affect the reducing conditions that govern chromium speciation. According to the USEPA (2005a), geochemical factors determine both the bioavailability of chromium and its oxidation and reduction potential. Understanding *in situ* geochemical conditions and the geochemical behavior of chromium provides insight into the distribution, toxicity, and long-term stability of chromium in sediments. Because chromium exists in multiple oxidation states which exhibit widely differing geochemical properties and ecotoxicological effects, chromium speciation must be evaluated to assess potential ecological impacts in the aquatic environment (Berry et al. 2004, Besser et al. 2004, USEPA 2005a).

Numerous constituents in anaerobic or hypoxic sediments reduce Cr(VI) to Cr(III), including sulfides, ferrous iron [Fe(II)], and natural organic matter (Hansel et al., 2003). In contrast, Cr(III) is quite stable (i.e., unreactive), even under aerobic conditions. Thus, in reduced sediments, chromium will be present in its much less toxic and less soluble form as Cr(III), interstitial waters will contain little to no chromium, and the sediment will impart low toxicity as the result of chromium (Berry et al., 2004; USEPA, 2005a).

TABLE 3-1
 Data Quality Objectives for the Sediment and Surface Water Study
 Dundalk Marine Terminal, Baltimore, Maryland

Problem Statement: Sediments, pore water, and surface water in the Patapsco River and Colgate Creek adjacent to the Dundalk Marine Terminal (DMT) may be impacted by releases of chromium from the DMT site.			
Study Goals: (1) characterize the nature and extent of chromium in surface water, pore water, and sediments within the zone potentially impacted by chromium releases from the DMT site; (2) characterize the fate and transport of chromium in surface water, pore water, and sediment; (3) provide analytical chemistry, geochemical, and other data to support screening-level ecological and human health risk assessments.			
Study Inputs	Study Boundaries	Sampling and Analysis Plan	Data Evaluation Approach
1. Conceptual site model 2. Scientific literature regarding the fate and transport of chromium in the environment 3. Measured concentrations of chromium in stormwater, groundwater, surface water, pore water, and sediment 4. Measurements of geochemical parameters that influence chromium speciation and bioavailability 5. Delineation of groundwater upwelling areas 6. Delineation of surface water column stratification 7. Geophysical survey results (bathymetry and sub-bottom profiling)	1. Horizontal: a. Study area extends from the DMT shoreline outward to the far side of the berthing channels to the west and south of DMT, beyond the expected influence of groundwater discharge and the surface water mixing zone. b. Study area includes Colgate Creek between the Broening Highway bridge and the confluence with the Patapsco River. 2. Vertical: a. Surface water: the thickness of the water column b. Pore water: the biologically active layer (0-0.5 ft) c. Sediment: to a depth of 3 ft to provide initial assessment of the vertical extent of contamination 3. Temporal: a. Quarterly sampling of pore water and surface water for one year to characterize seasonal changes in hydrodynamic and geochemical conditions b. Biannual sampling for surface sediment; single sampling event for subsurface sediment c. Sampling will occur at slack low tide during a neap tide if possible. d. Sampling will occur when the 14 th St. diffuser is not operating. e. Sampling will target low flow conditions 4. The area of investigation for the groundwater upwelling study is from the DMT shoreline to the lateral limit of identifiable groundwater upwelling 5. Water column properties will be characterized at every surface water, sediment, and pore water sampling station 6. The investigation area for the geophysical surveys extends from the DMT shoreline outward 2000 feet in all directions.	1. Sampling locations for surface water, pore water, and sediment (see Figure 3-1): a. 7 transects perpendicular to DMT shoreline; 4 stations per transect: 1 nearshore station, 2 stations within the berthing channel, and 1 station on the far side of the berthing channel. b. 2 transects in Colgate Creek; 1 parallel and 1 perpendicular to the channel with 4 equally-spaced stations per transect. c. Three mid-channel reference stations d. If the water column is stratified, then surface water samples will be collected from 3 ft below the surface, at mid-depth, and 1.5 ft from bottom e. Pore water samples will be extracted from a 0-0.5 ft sediment sample f. Bulk sediment samples will be collected from 0-0.5 ft, 0.5-1.5 ft., and 1.5-3 ft intervals 2. Sampling in groundwater upwelling areas: 2 pore water samples will be collected in identified upwelling areas; bulk sediment samples will be collected at one location. 3. Samples will be analyzed for the following parameters: a. Surface water and pore water: total chromium, Cr(VI), geochemical parameters b. Sediment: total chromium and geochemical parameters 4. Groundwater upwelling study): sampling transects along the periphery of the DMT site; measurements will be taken at 100 ft intervals along each transect until upwelling areas are delineated. 5. Vertical profiles of water column temperature, conductivity, dissolved oxygen, and turbidity will be measured at each sampling station. 6. The geophysical surveys will be performed along 50-foot spaced tracks parallel to the DMT terminal facades, from the shoreline outward 2000 feet in all directions.	1. Nature and extent of chromium: a. Concentrations of chromium in surface water and pore water will be compared with USEPA's Nationally Recommended Water Quality Criteria (NRWQC). If the extent of surface water and pore water with chromium concentrations exceeding NRWQC is delineated, then the extent of contamination will be defined. b. Chromium concentrations in sediments, surface water and pore water from the study area will be compared with results from mid-channel reference stations. c. If the extent of contamination is not delineated, then additional study may be required. 2. Fate and Transport: a. Chromium results for stormwater and surface water samples will be used to evaluate the stormwater discharge pathway, and results for groundwater and pore water samples will be used to evaluate the groundwater discharge pathway. b. Results for chromium and geochemical parameters will be used to characterize chromium speciation and bioavailability 3. Groundwater upwelling areas will be identified by delineating areas with different pore water conductivity and temperature than overlying surface water. Groundwater upwelling data will be integrated with groundwater modeling results from a separate investigation to characterize groundwater-surface water interactions. 4. Any water column stratification will be identified based on measurement of water column properties. 5. Results of the geophysical surveys will be used to refine sample locations for surface water, pore water and sediment sampling.

TABLE 3-2

Nationally Recommended Water Quality Criteria for Chromium as a Function of Hardness
Dundalk Marine Terminal, Baltimore, Maryland

Environment	Salinity (ppt)	CaCO ₃ Concentration (mg/L)	CMC (Acute FW NRWQC; mg/L)	CCC (Chronic FW NRWQC; mg/L)
Current USEPA Freshwater NRWQC	—	100	0.57	0.074
USEPA Upper Limit Hardness Value ^a	—	400	1.77	0.231
DMT May 2007 (Estuarine)	5–15	1,563 ^b	5.4	0.704
DMT August 2007 (Estuarine)	11–16	2,412 ^b	7.2	1.0
DMT December 2007 (Estuarine)	7-16	2,480 ^b	7.9	1.03
DMT February 2008 (Estuarine)	5–12	2,090 ^b	6.9	0.893

^a USEPA's upper limit for the use of hardness values in the equations provided below.

^b Based on mean measured CaCO₃ concentration in surface water collected at DMT during specified event.

ppt = parts per thousand

CMC = criteria maximum concentration

FW = freshwater

NRWQC = Nationally Recommended Water Quality Criteria

CCC = criteria continuous concentration

Example calculation:

Parameters for Calculating Freshwater Dissolved Metals Criteria That Are Hardness-Dependent:

Chemical	m _A	b _A	m _C	b _C	Freshwater Conversion Factors (CF)	
					CMC	CCC
Chromium III	0.8190	3.7256	0.8190	0.6848	0.316	0.860

Current Water Quality Standards based on 400 mg/L CaCO₃

$$\text{CMC (dissolved)} = \exp\{m_A [\ln(\text{hardness})] + b_A\} \text{ (CF)}$$

$$\text{CMC (dissolved)} = \exp\{0.819 [\ln(400)] + 3.7256\} \text{ (0.316)}$$

$$\text{CMC (dissolved)} = \exp\{0.819 [5.99] + 3.7256\} \text{ (0.316)}$$

$$\text{CMC (dissolved)} = \exp\{4.91 + 3.7256\} \text{ (0.316)}$$

$$\text{CMC (dissolved)} = \exp\{8.63\} \text{ (0.316)}$$

$$\text{CMC (dissolved)} = 5597 \times 0.316$$

$$\text{CMC (dissolved)} = 1,769 \text{ ug/L} = 1.77 \text{ mg/L}$$

$$\text{CCC (dissolved)} = \exp\{m_C [\ln(\text{hardness})] + b_C\} \text{ (CF)}$$

$$\text{CCC (dissolved)} = \exp\{0.819 [\ln(400)] + 0.6848\} \text{ (0.860)}$$

$$\text{CCC (dissolved)} = \exp\{0.819 [5.99] + 0.6848\} \text{ (0.860)}$$

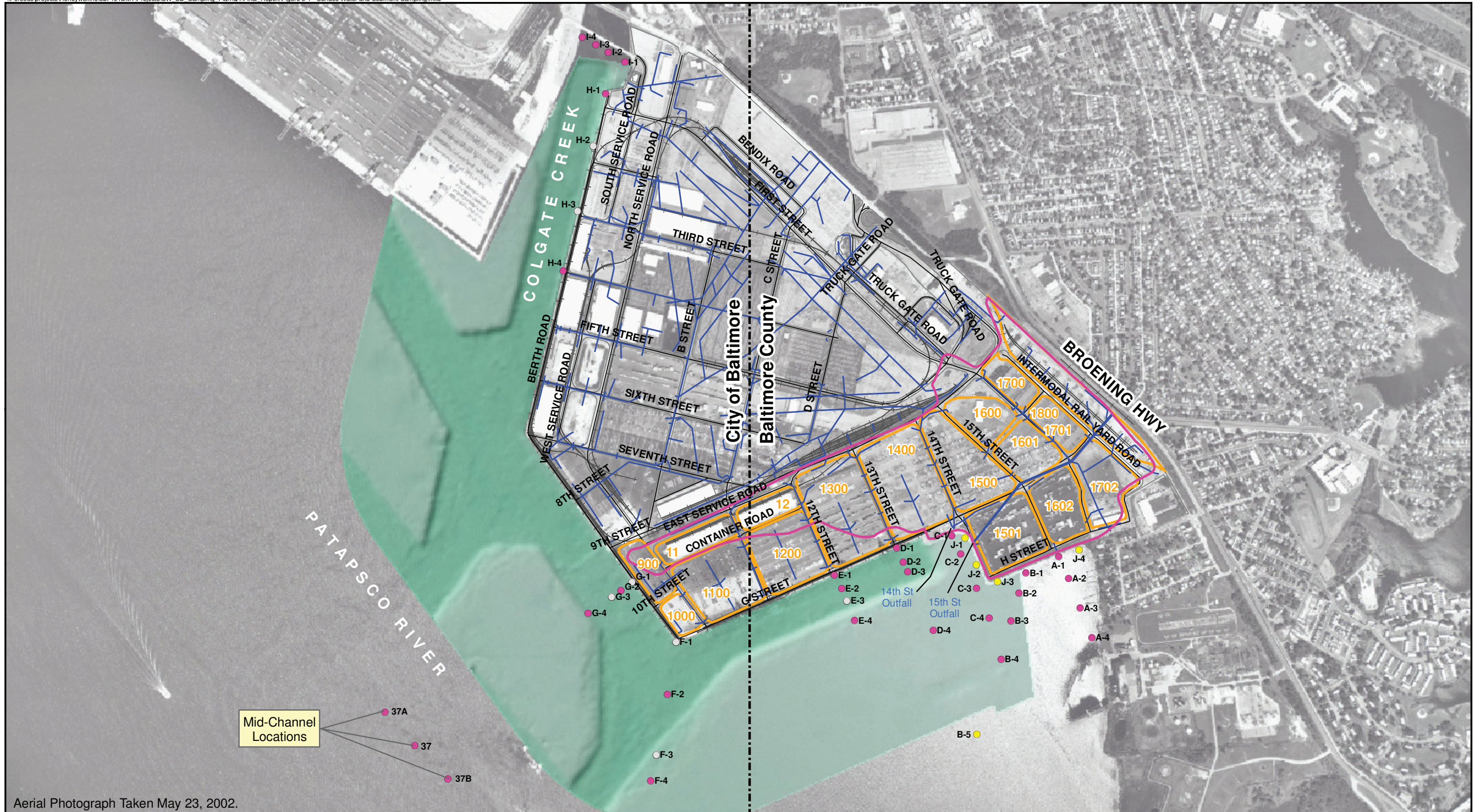
$$\text{CCC (dissolved)} = \exp\{4.91 + 0.6848\} \text{ (0.860)}$$

$$\text{CCC (dissolved)} = \exp\{5.59\} \text{ (0.860)}$$

$$\text{CCC (dissolved)} = 268 \times 0.860$$

$$\text{CCC (dissolved)} = 231 \text{ ug/L} = 0.231 \text{ mg/L}$$

Source: <http://www.epa.gov/waterscience/criteria/wqcriteria.html>



Aerial Photograph Taken May 23, 2002.

Legend

- Sample Location
- Sample Location - February 2008 only
- Sample Location - not sampled in December 2007 or February 2008
- COPR Extent
- Storm Sewer Line
- Railroad Centerline

Areas

Water Depth in Feet (NAVD88)

- 4 feet
- 50 feet

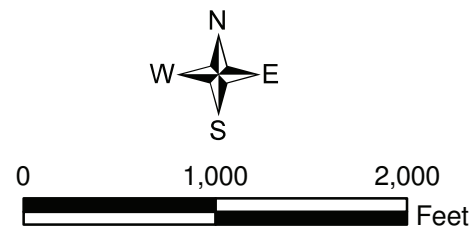
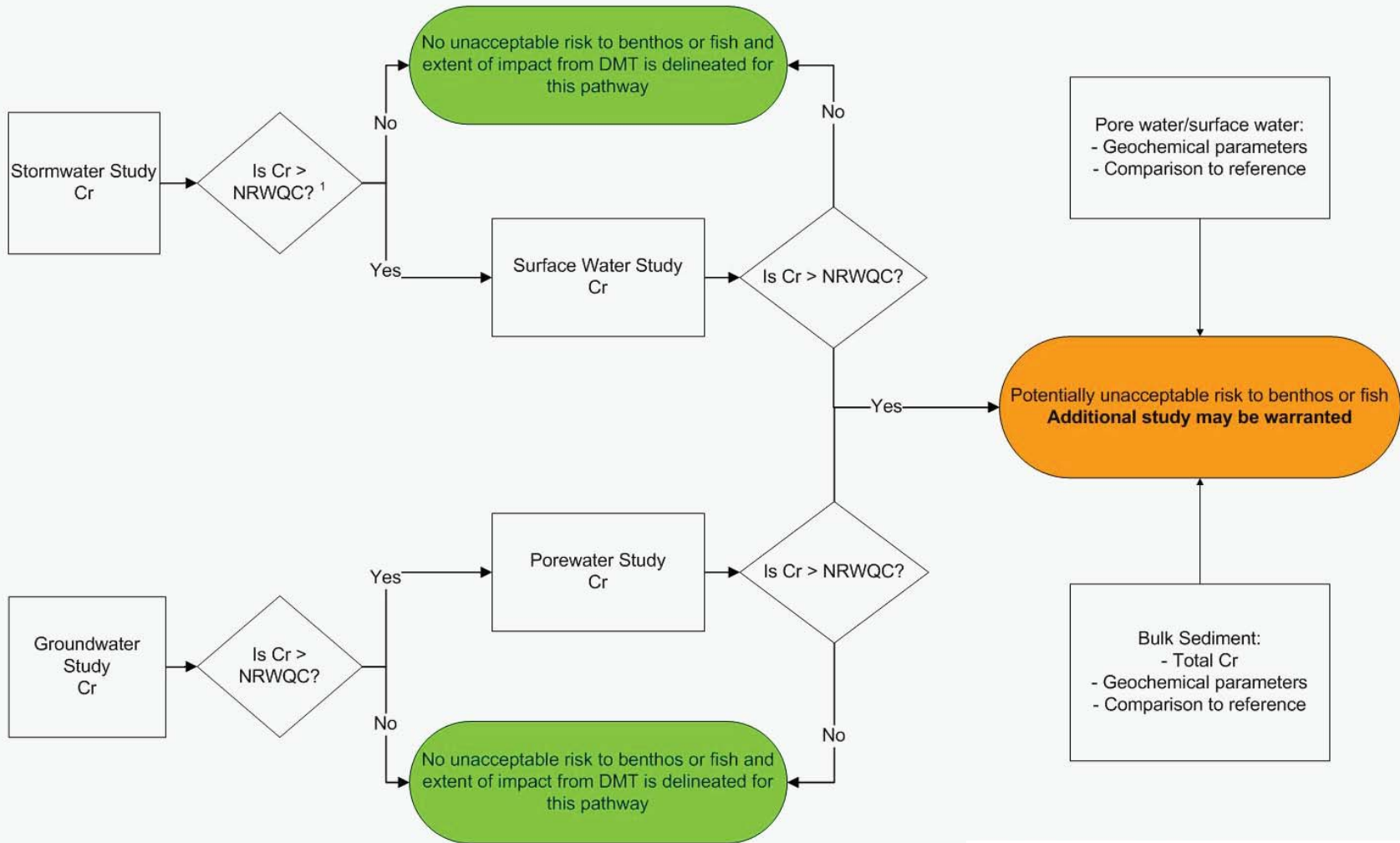


Figure 3-1
Surface Water and Sediment Sampling Locations
Dundalk Marine Terminal
Baltimore, Maryland

Flow Chart for Evaluating Nature and Extent of Chromium in the Patapsco River and Colgate Creek Adjacent to Dundalk Marine Terminal



¹ USEPA National Recommended Water Quality Criteria

Figure 3-2
Flow Chart for Evaluating Nature and Extent of Chromium
Dundalk Marine Terminal
Baltimore, Maryland