Draft

Conceptual Groundwater-Monitoring Plan, Dundalk Marine Terminal, Baltimore, Maryland

Prepared for

Honeywell International Inc.

Maryland Port Administration

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CH2MHILL®

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Executive Summary

This Conceptual Groundwater Monitoring Plan (CGMP) describes the approach for performing groundwater monitoring at the Dundalk Marine Terminal (DMT) after corrective measures are in place. The objectives for the future groundwater-monitoring program include the following:

1. To provide a means to confirm that the remedial components remain protective of human health and the environment.
2. To provide an early warning of potential chromium migration in groundwater through the use of geochemical indicator parameters and groundwater hydraulic head measurements.

The monitoring network will be designed and maintained so that it:

- Provides monitoring wells within potential groundwater flow pathways, thereby establishing a monitoring network most likely to detect potential releases.
- Allows for continued calibration and validation of the groundwater model as remedy implementation proceeds.
- Enables potentially changing groundwater flow conditions to be monitored over time to ensure long-term effectiveness.
- Reduces opportunities for cross-contamination by limiting penetrations through the COPR fill.
- Provides representative downgradient wells to protect potential future receptors.
- Integrates with ongoing port operations at DMT.

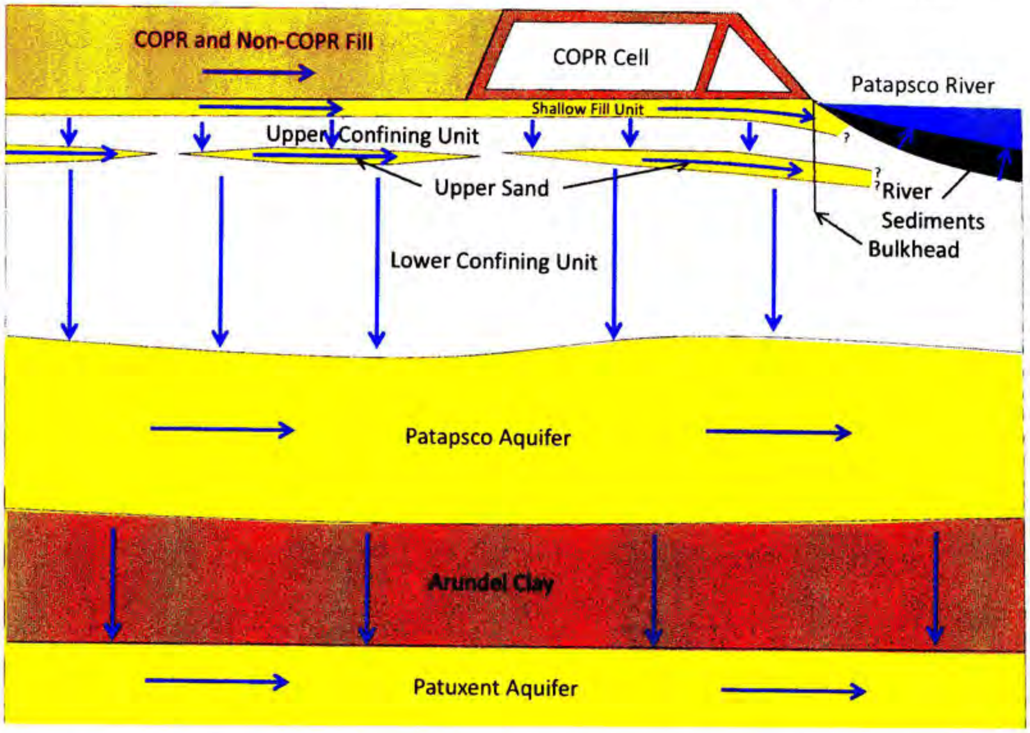
The hydrogeology at DMT is characterized by a series of interbedded permeable units, which transmit water readily, and confining units, which retard water movement, as illustrated in Figure ES-1. These conditions affect groundwater flows through the hydrogeologic system and have bearing upon the design of a long-term groundwater-monitoring plan. The high contrasts in hydraulic conductivity result in predominately vertical flow paths in confining units and horizontal flow paths in permeable units. Impacted groundwater moves laterally through the higher conductivity strata, and therefore the monitoring program will concentrate on these units to protect potential receptors.

The vertical flow of groundwater though the confining units is low. The flux (mass per unit time) of any groundwater-borne contaminants is correspondingly very low through these units. The small mass of contaminants that ultimately could move through the confining unit barrier is significantly attenuated by the high volume of groundwater flow in the underlying aquifer. The time of transport of groundwater through confining units can also be long, depending upon their hydraulic conductivities and ambient vertical hydraulic gradients. Due to these circumstances, any groundwater contamination entering an aquifer unit will migrate laterally rapidly enough to be detected in the downgradient permeable water-bearing units long before it can simultaneously migrate downward through the underlying confining unit toward the next aquifer in the hydrogeologic sequence.

FIGURE ES-1

Conceptual Hydrogeologic Cross-Section of DMT

Not to scale. COPR cell is in Areas 1501 and 1602. Bulkhead is southwest of 13.5th Street.



The implications for groundwater flow and contaminant transport in such layered systems lead to the following specific conclusions that underlie the conceptual groundwater-monitoring system proposed in this CGMP:

- Groundwater monitoring should focus on the upper water-bearing unit in the geologic sequence adjacent to or beneath the COPR fill area, the Shallow Fill Unit.
- The second water-bearing zone, separated from the COPR fill by the Upper Confining Unit, is the Upper Sand, which also warrants monitoring. Groundwater could flow vertically downward from the COPR deposit through the confining unit to the Upper Sand and then move laterally out from beneath the site. The Upper Sand should be monitored as close to the edge of the COPR boundary as practicable.
- Confining units do not need to be monitored since lateral groundwater flow and potential plume migration will almost always be confined to the aquifer units. Aquitard units are also difficult to sample due to their low hydraulic conductivity and yield.
- Each successively deeper aquifer unit (below the surficial and second shallow water-bearing zones) warrants progressively less or no monitoring attention since plume migration and detection in the monitoring network should occur in these zones long before contaminants could migrate through the intervening confining unit(s) to deeper aquifers. This is especially true as the hydraulic conductivity contrast between the aquifer and confining units becomes greater.

The monitoring program for DMT will be designed in accordance with the basic principles of groundwater flow within such a system and in accordance with the site-specific hydrogeologic flow regime that was extensively studied and defined during the chromium transport study (CH2M HILL, 2009a).

The hydrogeology of the DMT has been subject to considerable study and consequently is well understood. Nonetheless, it is recognized that no amount of study can fully eliminate all uncertainties relative to the hydrostratigraphy and three-dimensional groundwater flow of this or any site. Therefore, an overarching objective of the groundwater-monitoring plan will be to design a long-term groundwater-monitoring well network that is sufficiently robust to ensure that no significant migration of chromium from DMT goes undetected and that the remedy remains fully protective of human health and the environment. Moreover, the intent is that the plan will be a "living document" subject to adaptation in response to any changes in the hydrogeologic system over time, whether those changes are local to DMT or due to regional changes in groundwater supply well extraction rates.

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Acronyms and Abbreviations

µg/L	micrograms per liter
CGMP	Conceptual Groundwater Monitoring Plan
cm/sec	centimeters per second
CMAA	Corrective Measures Alternatives Analysis
COPR	chromium ore processing residue
Cr(VI)	hexavalent chromium
CSM	conceptual site model
CTS	Chromium Transport Study
DIC	dissolved inorganic carbon
DMT	Dundalk Marine Terminal
ft/day	feet per day
Honeywell	Honeywell International Inc.
LTMO	long-term optimization
MDE	Maryland Department of the Environment
MDL	method detection limit
Mgal/day	million gallons per day
MPA	Maryland Port Administration

SECTION 1
Introduction

This Conceptual Groundwater Monitoring Plan (CGMP) describes the conceptual approach for performing groundwater monitoring after corrective measures are in place at the Dundalk Marine Terminal (DMT), located in Baltimore, Maryland. The CGMP is being submitted in accordance with requirements set forth in a letter from the Maryland Department of the Environment (MDE) to Honeywell International Inc. (Honeywell) and the Maryland Port Administration (MPA) dated July 30, 2012. The letter indicated that MDE had completed its review of the Corrective Measures Alternatives Analysis (CMAA) (CH2M HILL, 2011a) for DMT, and it also provided MDE's selection of Alternative 3 as the proposed remedy for the site. The letter requires submittal of a CGMP to MDE within 90 days of receiving the letter.

Under Alternative 3, Honeywell and MPA will complete the storm drain–relining program at DMT and prepare a long-term monitoring and maintenance plan to document the performance of that program. The purpose of this CGMP is to describe how long-term groundwater monitoring will be conducted at DMT; it is intended the CGWP will:

1. Define the objectives of the future groundwater-monitoring program;
2. Present the conceptual site model (CSM) for groundwater flow beneath DMT; and
3. Conceptually describe how future groundwater monitoring will be conducted.

It is not intended that the CGMP provide a future monitoring program because it is anticipated that the storm drain relining will change the existing groundwater flow regime by significantly reducing or eliminating shallow groundwater inflow to the drains. While the drains are being relined, Honeywell and MPA will continue to perform semiannual groundwater monitoring in accordance with the *Interim Groundwater-Sampling Plan* (CH2M HILL, 2009b), which was submitted to MDE on April 20, 2009, with subsequent revisions provided to MDE in June 2009.[1] Data from the interim groundwater-sampling events will be evaluated to assess changes in the groundwater flow regime and to validate the existing groundwater model. When significant changes in groundwater flow have been identified and evaluated, the monitoring well network will be designed. A comprehensive groundwater-monitoring plan will be submitted to MDE when the storm drain relining is complete.

The remainder of this CGMP is organized as follows:

- Section 2 defines the objectives of the future groundwater-monitoring program.
- Section 3 discusses the CSM with reference to a conceptual hydrostratigraphic framework, site geology, hydrogeology, and the geochemistry of the groundwater that has been impacted by chromium ore processing residue (COPR) present beneath DMT.
- Section 4 describes how monitoring will be conducted to meet the program objectives.

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[1] Responses to MDE's comments on the April 20, 2009, *Interim Groundwater Sampling Plan* were provided to MDE on June 1 (CH2M HILL, 2009c) and June 10, 2009 (CH2M HILL, 2009d). The interim list of sampling locations was finalized in the June 10 submittal.

SECTION 2
Objectives

The objectives of the groundwater-monitoring program were developed jointly at a meeting held on September 13, 2012, between representatives of Honeywell, MPA, and MDE. The objectives for the future program include the following:

1. To provide a means to confirm that the remedial components remain protective of human health and the environment.
2. To provide an early warning of potential chromium migration in groundwater through the use of geochemical indicator parameters and groundwater hydraulic head measurements.

The first objective is to confirm that the remedial components remain protective of human health and the environment. The chromium transport study (CTS) and several rounds of interim groundwater monitoring have demonstrated that the flux of Cr(VI) in groundwater to the Patapsco River is insignificant and that there is negligible vertical migration of impacted groundwater (CH2M HILL, 2009a, 2010a, 2010b, 2011b, 2011c, 2012). This conclusion is supported by the fact that Cr(VI), which represents the most transportable chromium species in groundwater, is not typically detected in shallow wells downgradient of the COPR; nor is it detected in the deeper groundwater-bearing strata beneath DMT. Conceptually, the data showing that this objective is being met would be collected from monitoring wells that are located in water bearing units horizontally contiguous to and downgradient of the COPR fill area, or from wells that are screened immediately below the boundary of COPR fill in the anticipated downgradient flow direction for the vertically lower aquifer unit in question.

The second objective is to provide an early warning system to detect geochemical indicator parameters indicative of COPR-impacted groundwater within a network of monitoring well locations. COPR-impacted groundwater has a very different geochemical signature than that of natural groundwater, and many of the COPR indicator parameters move much faster along the path of groundwater flow than Cr(VI). Geochemical parameters can also be used to demonstrate that reducing conditions persist in groundwater that surrounds the COPR fill beneath DMT; this is important, because these conditions are a control on Cr(VI) reduction, which limits migration.

A second measure that serves as an early warning system relates to groundwater gradients. Groundwater elevation measurements can be used to show that hydraulic separation exists between water-bearing units, for example, between the Shallow Fill Unit and deeper water-bearing strata or between COPR-impacted groundwater within the COPR cell in Areas 1501 and 1602 and the Shallow Fill Unit beneath the cell. Conceptually, the data used to show that these objectives are being met may be collected from wells preferably located or screened at various distances outside the COPR fill boundary and, in limited circumstances, from within the COPR fill. The number of wells screened through the COPR fill should be minimized to reduce the potential for cross-contamination between aquifer units.

The monitoring network will be designed and maintained so that it:

- Provides monitoring wells within potential groundwater flow pathways, thereby establishing a monitoring network most likely detect potential releases.
- Allows for continued calibration and validation of the groundwater model as remedy implementation proceeds.
- Enables potentially changing groundwater flow conditions to be monitored over time to ensure long-term effectiveness.
- Reduces opportunities for cross-contamination by limiting penetrations through the COPR fill.
- Provides representative downgradient wells to protect potential future receptors.
- Integrates with ongoing port operations at DMT.

Integration with port operations is a very important criterion for protecting well heads, maintaining data integrity, facilitating the collection of samples on schedule, and keeping port operations and sampling personnel safe.

The hydrogeology of DMT has been subject to considerable study and consequently is well understood. Nonetheless, it is recognized that no amount of study can fully eliminate all uncertainties relative to the hydrostratigraphy and three-dimensional groundwater flow of this or any site. Therefore, an overarching objective of the groundwater-monitoring plan will be the design of a long-term groundwater-monitoring well network that is sufficiently robust to ensure that no significant migration of chromium from the DMT goes undetected and the remedy remains fully protective of human health and the environment. Moreover, the intent is that the plan will be a "living document" subject to adaptation in response to any changes in the hydrogeologic system over time, whether those changes are local to the DMT or due to regional changes in groundwater supply well extraction rates.

SECTION 3

Conceptual Site Model

The CSM provides a framework for understanding groundwater flow and chromium distribution in groundwater beneath DMT so that the future groundwater-monitoring program can be designed to meet the objectives presented in Section 2. Groundwater flow at DMT occurs within a layered stratigraphic regime, and some important concepts related to flow in such a setting are presented in Section 3.1. The site geology beneath DMT is discussed in Section 3.2, and the site-specific hydrogeologic units are identified and further characterized in Section 3.3. The geochemistry of COPR-impacted groundwater is described in Section 3.4, and this discussion forms a basis for understanding how an early warning system may be developed as part of the future groundwater-monitoring program.

3.1 Site Geology

The southern portion of DMT, the "DMT fill area," was constructed on lands reclaimed from prior marshlands and the Patapsco River by placement of COPR and non-COPR fill materials (Figure 3-1). The extent of COPR at DMT is defined on the basis of data collected from over 400 investigation locations and a review of historical documents, aerial photography, and drawings detailing the facility's construction (CH2M HILL, 2009b). There are approximately 2.5 million cubic yards of COPR within approximately 148 acres of the fill area (Figure 3-1). Vertically, COPR extends to a maximum depth of approximately 38.5 feet and ranges in thickness from 1 foot to 32 feet. The thickness of the non-COPR fill that overlies the COPR materials ranges typically between 2 and 22 feet. The southern and western edges of the DMT fill area end at a sheet pile wall with a pile-supported concrete platform, referred to as the "marine platform". To the southeast, the DMT fill area terminates at a riprap embankment, sloping from the terminal area to the Patapsco River along Areas 1501 and 1602.

Relatively thick deposits of alluvial sediments underlie the DMT fill area (Figure 3-2). The alluvial sediments are composed of three distinct soil lithologies: upper silt, alluvial sand, and lower silt. The alluvial sediments are believed to represent Quaternary low-land sediments that were deposited in an estuarine environment within the Patapsco River basin. The alluvial sediments were deposited within an erosional channel that was carved into the underlying Potomac Group sediments by the ancient Patapsco River. Beneath DMT, the surface of the erosional channel corresponds to the base of the alluvial sediments. The erosional channel occurs within the western two-thirds of the fill area and was filled with fine to very fine grained sediments (primarily silts) rich in organic materials. These sediments are of low permeability and highly reducing.

The Cretaceous-age Potomac Group sediments underlie the alluvial sediments. In the Baltimore City area, the Potomac Group comprises unconsolidated clay, silt, sand, and gravel beds of the Patapsco, Arundel, and Patuxent Formations (Chapelle, 1985; Bennet and Meyer, 1952). On a regional scale, the stratigraphic formations within the Potomac Group are distinguishable on the basis of lithologic, fossil, and geophysical evidence, and regional data suggest that the Patapsco, Arundel, and Patuxent Formations are continuous beneath DMT (Chapelle, 1985; Bennet and Meyer, 1952; Hansen, 1968). Investigation results from DMT suggest that the stratigraphic contacts between the formations cannot be easily distinguished on the basis of lithologic characteristics alone (CH2M HILL, 2009b). Therefore, the soil units are referred to only as the Undifferentiated Potomac Group (Potomac Group) sediments. The aquifer within the upper portion of the Potomac Group sediments at DMT is designated the Patapsco Aquifer. Clay horizons tend to thicken below a depth interval of approximately 140 to 160 feet below grade. Permeable units encountered beneath these clay horizons are designated the Patuxent Aquifer.

3.2 Conceptual Hydrogeologic Framework

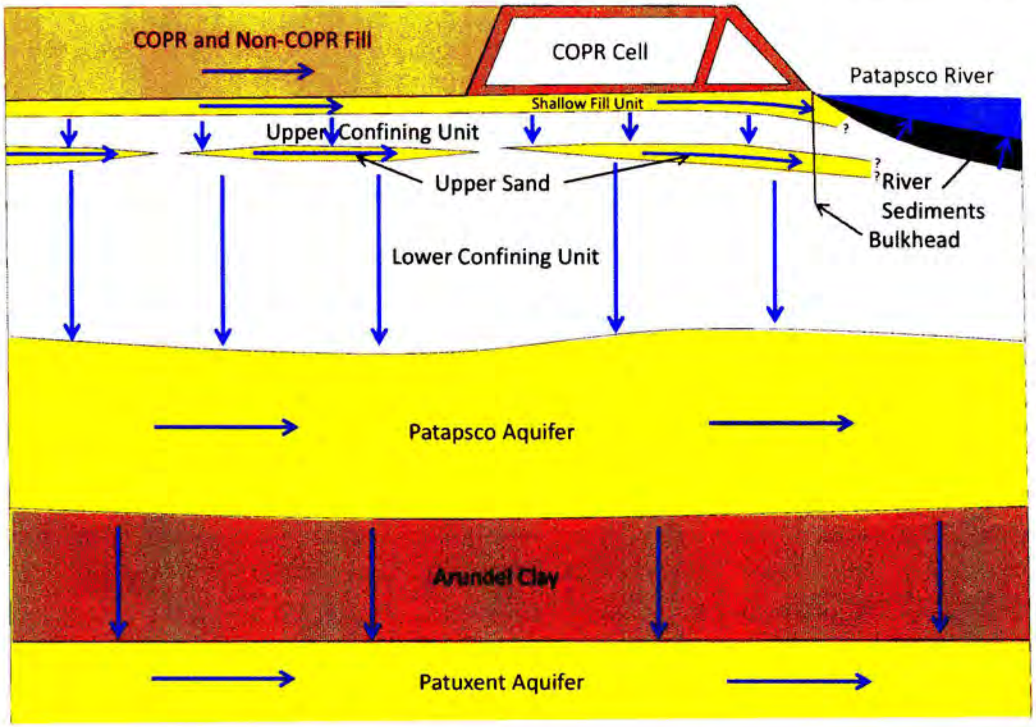
The hydrogeologic regime of the DMT is one characterized by a series of interbedded water-bearing units that transmit flow and confining units, or aquitards, that retard groundwater flow. This has bearing upon the design of a comprehensive long-term monitoring program. In interbedded aquifer/aquitard systems, the laws of groundwater hydraulics dictate that groundwater flow paths in the higher permeability strata will tend to be parallel to the bedding (horizontal in flat-lying strata) and nearly vertical in the intervening aquitards. At hydraulic conductivity contrasts of 100 or greater, which are more similar to the flow regime beneath DMT, flow paths in confining units become essentially vertical and flow paths in aquifers become essentially horizontal. A more complete discussion of this characteristic flow behavior of groundwater in interbedded aquifer/aquitard systems is given in Appendix A.

A schematic representation of the conceptual hydrogeologic framework is shown in Figure 3-3. Also shown are generalized groundwater flow lines illustrating the likely patterns of groundwater flow within this interbedded aquifer/aquitard hydrogeologic regime. As depicted in Figure 3-3, flow paths in more permeable units are generally horizontal, paralleling the stratigraphy. These more permeable units include the COPR and non-COPR fill, the Shallow Fill Unit, the Upper Sand, the Patapsco Aquifer, and the Patuxent Aquifer. In contrast, flow paths in the aquitard units are nearly vertical, or perpendicular to the stratigraphy. These units include the Upper Confining Unit, the river sediments, the Lower Confining Unit, and the Arundel Clay.

FIGURE 3-3

Conceptual Hydrogeologic Cross-Section of DMT

Not to scale. COPR cell is located in Areas 1501 and 1602. Bulkhead is southwest of 13.5th Street.



Several implications of DMT's hydrostratigraphy bear on potential contaminant transport and on the design of groundwater-monitoring systems:

1. Groundwater monitoring should be focused on the higher-permeability strata, given the propensity for lateral groundwater flow to be restricted to these aquifer units. It is typically only through these higher-conductivity strata that groundwater and any groundwater-borne contaminants can migrate laterally from beneath DMT and downgradient to receptors.
2. In contrast, groundwater in the confining units migrates typically vertically downward until higher-permeability strata are encountered. Once a higher-conductivity stratum is encountered, groundwater flow and any groundwater-borne contamination are then conveyed laterally, as described in item 1.
3. The vertical flow of groundwater though the confining units depends upon the units' vertical hydraulic conductivity and is low. Correspondingly, the flux (mass per unit time) of any groundwater-borne contaminants through the confining units is also low. As a result, even if the vertical flux of contamination in the confining unit reaches the underlying, more permeable aquifer, concentrations often decline by one or

more orders of magnitude due to mixing with the considerably higher lateral groundwater flux occurring within the aquifer.

4. Transport of groundwater through confining units can also be long, depending upon their hydraulic conductivities and ambient vertical hydraulic gradients. (Travel time through the Lower Confining Unit near the Area 1501 and Area 1602 cell is estimated at 1,850 years; see Appendix A.)
5. The combined impact of groundwater's relatively rapid lateral migration in the aquifer units (item 1) and the typically long transport time through the confining units (item 4) dictates that in most circumstances, any groundwater contamination entering an aquifer unit beneath a waste disposal site will migrate laterally rapidly enough to be detected in the downgradient groundwater-monitoring system long before it can simultaneously migrate appreciably downward through the underlying confining unit toward the next aquifer in the hydrogeologic sequence.

The implications of groundwater flow and contaminant transport in layered systems lead, in turn, to the following specific conclusions for designing a long-term monitoring program for the DMT hydrogeologic regime:

- Groundwater monitoring should focus on the upper water-bearing, or aquifer, units in the geologic sequence adjacent to or beneath the COPR fill area, the Shallow Fill Unit.
- The second water-bearing zone, separated from the COPR fill by the Upper Confining Unit, is the Upper Sand, which also warrants monitoring. Groundwater could flow vertically downward from the COPR deposit through the confining unit to the Upper Sand, the second water-bearing zone, and then move laterally out from beneath the site. The Upper Sand should be monitored as close as practicable to the edge of the COPR boundary.
- Each successively deeper aquifer unit (below the surficial water-bearing zone—Shallow Fill Unit— and the second shallow water-bearing zone—the Upper Sand) warrants progressively less or no monitoring attention since plume migration and detection in the monitoring network should occur in the surficial or second water-bearing zones long before contaminants could migrate through the intervening confining unit(s) to deeper aquifers. This is especially true as the hydraulic conductivity contrast between the aquifer and confining units becomes greater. As shown in Appendix A, groundwater travel time through the Lower Confining Unit is estimated to be approximately 1,850 years. While it is prudent to have some level of monitoring in the underlying Patapsco Aquifer the likelihood of a Cr(VI) plume ever reaching that aquifer is remote.
- Given the unlikelihood of a Cr(VI) plume ever reaching the Patapsco Aquifer and the fact that the Patapsco Aquifer is separated from the underlying Patuxent Aquifer by yet another substantial aquitard, the Arundel Clay, there is no need for water quality monitoring in the Patuxent Aquifer. The three existing wells in the Patuxent Aquifer at the DMT could remain to monitor potentiometric levels in that aquifer.
- Confining units need not to be monitored as part of the long-term monitoring program since any significant lateral groundwater flow and potential plume migration will be confined to the aquifer units. Aquitard units are also difficult to sample due to their low hydraulic conductivity and yield.

3.3 Identification of Monitoring Units

Future monitoring efforts should focus on the Shallow Fill Unit, Upper Sand, and Patapsco Aquifer. Each of these units and the Patuxent Aquifer are described below; a conceptual depiction of the hydrogeology at DMT is provided in Figure 3-4.

3.3.1 Shallow Fill Unit

3.3.1.1 Unit Outside Areas 1501 and 1602

The Shallow Fill Unit, the uppermost hydrogeologic unit beneath the site, is composed partly of the approximately 2.5 million cubic yards of COPR that underlie DMT. The remaining volume of the Shallow Fill Unit is composed almost entirely of non-COPR fill. Groundwater flow in the unit is generally to the southwest (Figure 3-5), but local variations are observed where flow is affected by the heterogeneity of the fill material or by subsurface features, including storm drains, buried historic bulkhead features, and the sheet pile bulkhead that bounds the terminal to the south and west.

Excluding Areas 1501 and 1602 (discussed below) and the immediate area between the 13.5th and 15th Streets' outfalls, the DMT fill area is bounded by vertical sheet pile bulkheads that impede the discharge of shallow groundwater to the Patapsco River. Evidence for the impeded discharge is based on groundwater levels along the immediate inboard face of the bulkhead that are approximately 2 feet above the river level and on the lack of tidal influence observed in shallow wells close to the bulkhead. While no bulkhead exists between the 13.5th and the 15th Streets' outfalls, piezometric levels and computer modeling indicate that a low-permeability zone exists along the shoreline in this area.

CTS results showed that the extent of Cr(VI) contamination in groundwater is limited to the Shallow Fill Unit (CH2M HILL, 2009a). Horizontal migration of Cr(VI) within the Shallow Fill Unit is typically limited to within 100 to 200 feet of the COPR fill. Geochemical processes appear to be reducing Cr(VI) to Cr(III) within the unit. There are also physical and chemical barriers to the vertical migration of shallow groundwater and COPR-related chemical constituents to deeper hydrogeologic units that underlie the Shallow Fill Unit. The vertical migration of shallow groundwater is also physically impeded by the presence of the Upper Silt Unit, which acts as a semiconfining layer beneath the Shallow Fill Unit. The average permeability of the Upper Silt Unit is 1.62×10^{-7} centimeters per second (cm/sec) (CM2M HILL, 2009b).

The existing network of monitoring wells within the Shallow Fill Unit is shown in Figure 3-1.

3.3.1.2 Areas 1501 and 1602

The characteristics of the Shallow Fill Unit near Areas 1501 and 1602 are discussed separately because they differ slightly owing to the way this area was constructed. The land that underlies Areas 1501 and 1602 was reclaimed by construction of an engineered containment cell where the COPR is encapsulated within a low-permeability liner and cover (CH2M HILL, 2009b). The COPR cell was constructed above the water table, and the cell is hydraulically separated from the Shallow Fill Unit, based on the substantial difference between water levels measured inside the cell and water levels measured outside (below) the cell in the Shallow Fill Unit. Below the COPR cell the Shallow Fill Unit is composed of non-COPR fill that was used to raise the grade of the river bottom to construct the cell. Groundwater flow within the Shallow Fill Unit here does appear to be affected by the presence of the 15th Street drain and pumping at the outfall structure.

Minor Cr(VI) impacts have been observed in wells along the south shoreline of Areas 1501 and 1602 (e.g., DMT-63S, DMT-45S, and DMT-58S), but the concentrations do not impact the river, based on the absence of Cr(VI) in pore water that was collected on four occasions as part of the sediment and surface water study (CH2M HILL and Environ, 2009). Wells installed within and through the cell are impacted by COPR expansion within the cell, and consequently, maintaining the integrity of well seals and casings is problematic and has contributed to vertical Cr(VI) cross contamination in a limited number of instances. Well seals and casings that are identified as compromised are promptly abandoned, however well penetrations through the COPR cell should be eliminated in the future to reduce opportunities for cross-contamination.

3.3.2 Upper Sand

The Upper Sand is defined as the first unit of sand encountered beneath the Upper (silt) Confining Unit, which underlies the Shallow Fill Unit. The characteristics of the Upper Sand have been defined by testing and sampling at the Upper Sand wells, most of which are west of 14th Street and are screened within thin and discontinuous lenses of fine sand interlayered within the upper silt. The Upper Sand wells east of 14th Street are screened mostly within the upper portion of the Potomac Group sediments.

Groundwater elevations measured in the Upper Sand wells in April 2012 are posted on the Shallow Fill Unit potentiometric surface map (Figure 3-5). The sands screened by the Upper Sand monitoring wells are not laterally extensive or continuous; therefore, the groundwater elevations measured in them are not contoured. Though alluvial sand units do not promote the horizontal flow of groundwater beneath DMT due to their discontinuous nature, they do represent an important monitoring interval to assess potential vertical migration of COPR-impacted groundwater, since these sands exist typically within a few feet vertically of the COPR boundary. With the exception of two samples collected from DMT-52US during the interim groundwater monitoring, Cr(VI) has not been detected in the Upper Sand.

The existing network of monitoring wells within the Upper Sand is shown in Figure 3-1.

3.3.3 Patapsco Aquifer

Regional geologic data suggest that the upper portions of the Potomac Group sediments beneath DMT are classified as the Patapsco Formation. Therefore, the medium-depth aquifer beneath the site is referred to herein as the Patapsco Aquifer, and its characteristics are defined by testing and sampling at the medium-depth (M-series) well locations.

The M-series wells (Figure 3-1) are screened in a portion of the Potomac Group sediments that is composed mainly of sand. A consistent groundwater flow has previously been observed in the Patapsco Aquifer below DMT (CH2M HILL, 2009a, 2010a, 2010b, 2011b, 2011c, 2012). The groundwater flow is directed toward the south-southwest at gradients ranging up to approximately 0.002 foot/foot (Figure 3-6). Groundwater levels in the M-series wells are consistently lower than water elevations in the Shallow Fill Unit and Upper Sand units. The difference in water elevation is further evidence that the semiconfining units serve as effective physical barriers to hydraulic communication between the Shallow Fill Unit, the Upper Sand, and the Patapsco Aquifer.

Soil and groundwater sample results collected from the M-series wells suggest that the Patapsco Aquifer below DMT is not impacted by chromium constituents (CH2M HILL, 2009a). The absence of chromium-related impacts in the aquifer is explained by the presence of the Upper and Lower Confining Units (upper and lower silt layers), which lie between the Shallow Fill Unit and the Patapsco Aquifer. Both silt units have low permeability, which allows them to function as confining units, and the presence of organic material facilitates the reduction of Cr(VI) to the relatively immobile Cr(III) species, which prevents the chromium constituents from reaching the deeper hydrogeologic units. The permeability of the lower silt, which ranges up to 50 feet thick below DMT, has been determined to be 9.77×10^{-8} cm/sec (CH2M HILL, 2009b). As shown in Appendix A, groundwater travel time through the Lower Confining Unit is estimated to be approximately 1,850 years.

The aquifer outcrops directly beneath the brackish Patapsco River and historic pumping of the aquifer caused chloride contamination within the aquifer. Use of the Patapsco Aquifer as a water resource in the vicinity of Baltimore and the Patapsco River estuary mostly ceased by 1950 due to chloride intrusion, and at present there is no major use of the aquifer in this region (Chapelle, 1985). Significant pumping of the Patapsco Aquifer does, however, occur in northern Anne Arundel County, and the nearest pumping centers are approximately 7 miles from DMT (Figure 3-7). For this reason, it is prudent to have some level of monitoring in the underlying Patapsco Aquifer, although the likelihood of a Cr(VI) plume ever reaching that aquifer is remote.

3.3.4 Patuxent Aquifer

Three deep (D-series) wells are screened in what regional geologic data suggest is the Patuxent Aquifer (CH2M HILL, 2009e). Several thick sequences of clay strata exist between the M-series and D-series wells. The clay strata are characteristically similar to the Arundel Formation, which is a regional aquitard that separates the Patapsco and Patuxent Aquifers. The function of the clay strata as an aquitard beneath the DMT is supported by the low average permeability (9.20×10^{-8} cm/sec) of the clay strata and by a substantial difference in water elevations measured in co-located D- and M-series well pairs.

The Patuxent Aquifer is unaffected by conditions at the site because the Patuxent is separated from the Patapsco by the Arundel Formation; sampling of M-series wells has indicated that the overlying Patapsco Aquifer has not been impacted. It is anticipated that monitoring of the Patuxent Aquifer in the future long-term groundwater-monitoring program will be confined to monitoring the potentiometric surface to detect any substantive changes in hydraulic gradients.

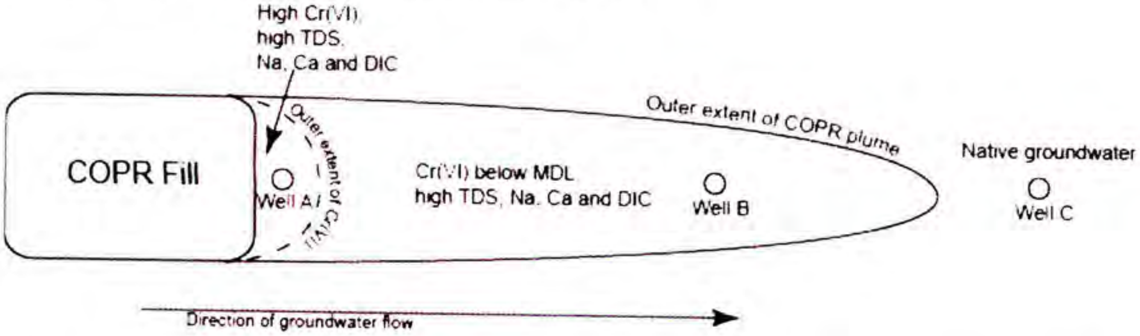
3.4 Geochemistry of Groundwater in COPR Fill

COPR at the time it was placed at DMT was composed primarily of three minerals: brownmillerite ($Ca_2(Al,Fe,Cr)_2O_5$), periclase (MgO), and portlandite ($CaOH_2$) (CH2M HILL, 2009e). These materials chemically weather in the presence of water and dissolved solutes to form various hydration products (Hiller et al., 2003; Moon et al., 2007). Five main metallic elements—calcium, iron, aluminum, magnesium, and chromium—plus oxygen constitute well over 90 percent of the inorganic mass of COPR (CH2M HILL, 2009e). As groundwater comes in contact with COPR, some of these elements will leach out.

As shown in Figure 3-8, COPR will enrich the surrounding groundwater with Cr(VI) and some major ions. A well screened in or near the COPR fill (Well A in Figure 3-8) will exhibit high concentrations of Cr(VI), total dissolved solids (TDS), Na^+, Ca^{2+}, HCO_3^-, and CO_3^{2-} (dissolved inorganic carbon, or DIC). Reductive processes have been shown to reduce Cr(VI) to Cr(III) within approximately 200 feet laterally of the COPR fill. Major ions, however, are not attenuated as rapidly and can reach downgradient wells. As shown in Figure 3-8, the outer extent of the COPR plume as defined by major ions is much farther downgradient than the outer extent of the Cr(VI) plume. Wells screened beyond the extent of Cr(VI) (Well B in Figure 3-8) will have the major ion signature of COPR-influenced water but will lack detectible Cr(VI). Wells screened outside of the COPR plume (Well C) will have a major ion signature that is representative of native groundwater.

FIGURE 3-8

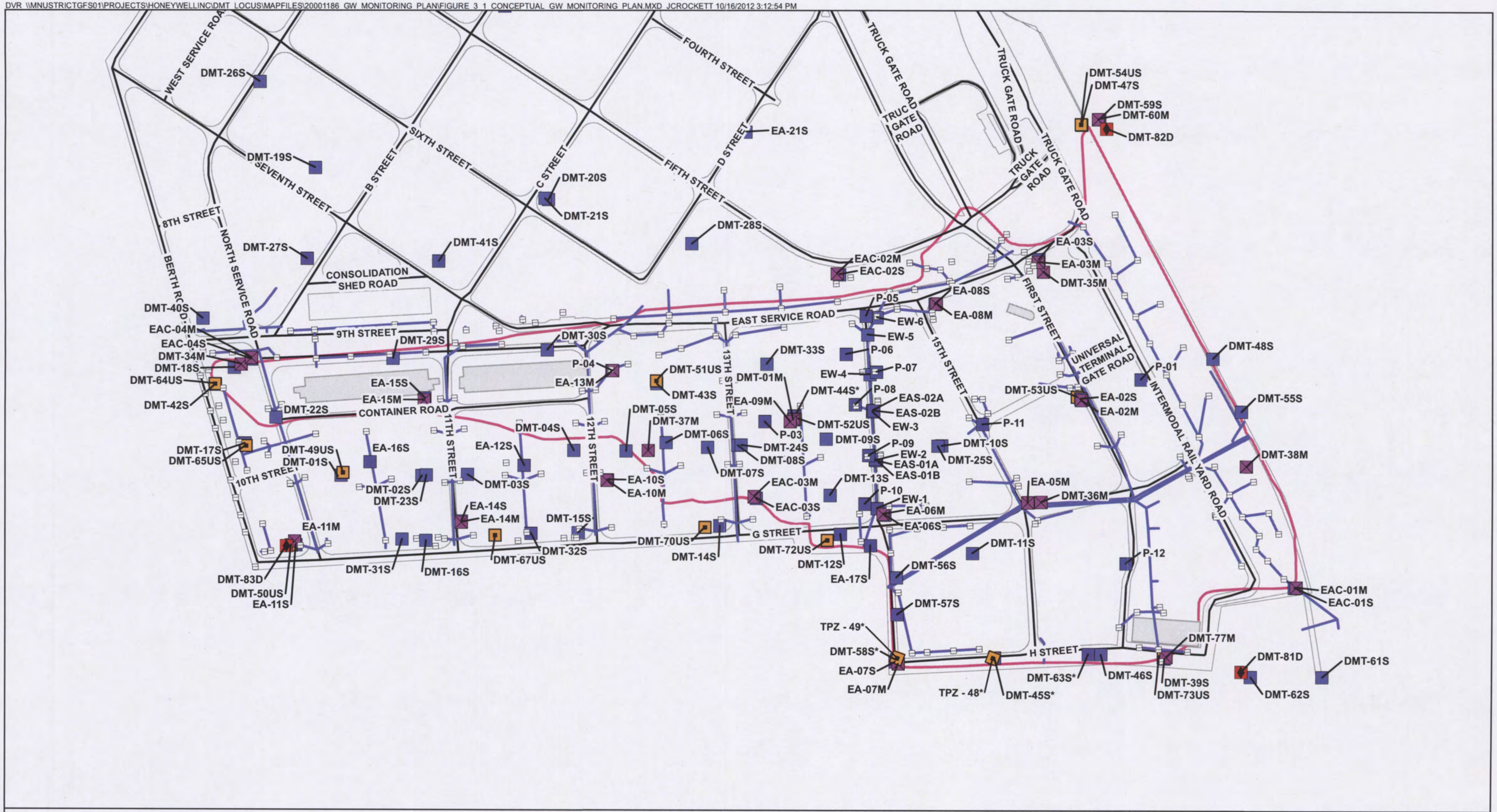
Conceptual Depiction of Groundwater in COPR Fill Behavior



Major ion data are often collected to increase understanding of water quality as it relates to the geologic character of various aquifers and to provide useful information on the source of groundwater. Most major ion data analysis methods require that a complete suite of data (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, and CO_3^{2-}) be available (Zaporozec, 1972). One of the most effective and commonly used graphical analysis methods is the so-called Piper Diagram (Figure 3-9). A Piper diagram is often used to classify waters into "hydrochemical facies" (Back, 1966). A discussion of the use of Piper Diagrams and their utility as part of an "early warning system" is discussed in Appendix B.

A well monitoring program that includes measurements of Cr(VI) and major ions will provide the necessary data to give an early warning of COPR plume migration. Chemical analysis will be performed for hexavalent and total chromium to monitor their extent of migration from the COPR fill. Major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}), anions (Cl^-, SO_4^{2-}), and total alkalinity (to obtain HCO_3^-, CO_3^{2-}) will be analyzed to prepare Piper Diagrams such as the one shown in Figure 3-10. Geochemical parameters such as pH, ORP, dissolved oxygen, ferrous iron, and dissolved manganese will be monitored to provide information on the prevalence of redox conditions, which lead to attenuation of Cr(VI).

DVR \\MNUSTRICTGFS01\PROJECTS\HONEYWELLINC\DMT_LOCUS\MAPFILES\20001186_GW_MONITORING_PLAN\FIGURE_3_1_CONCEPTUAL_GW_MONITORING_PLAN.MXD JCROCKETT 10/16/2012 3:12:54 PM



Legend

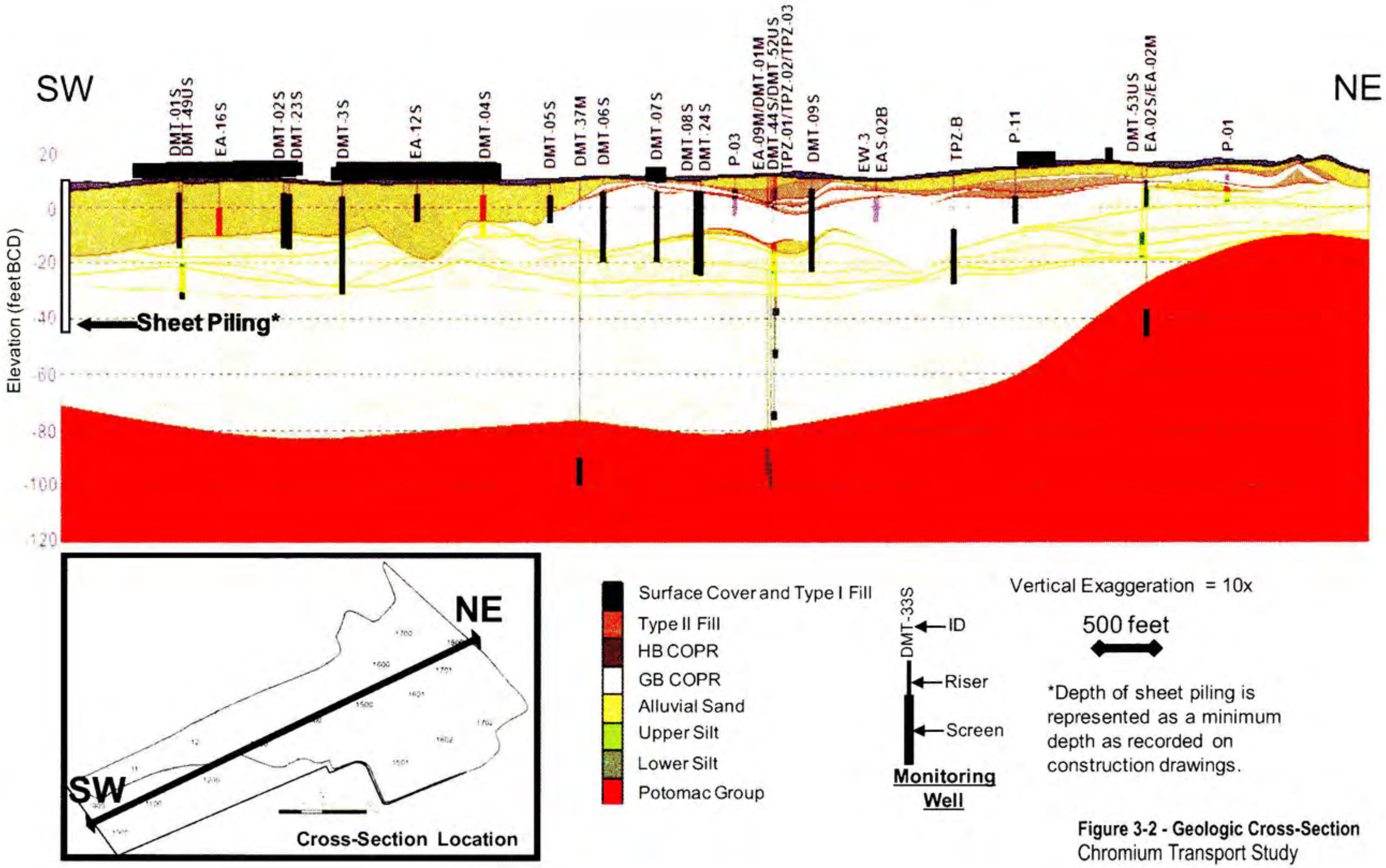
Monitoring Wells

- ■ Shallow Well
- ▣ Upper Sand Well
- ☒ M-Series Well
- ◆ D-Series Well
- ⊟ Inlet
- — Storm Drain System
- ☐ Shoreline/Bulkhead
- ▭ Buildings
- ☐ COPR Extent (CH2M Hill, 2012)

*Asterisk indicates that the monitoring well has been abandoned since initiation of the interim monitoring program

Figure 3-1 – Site Map
Conceptual Groundwater Monitoring Plan
Dundalk Marine Terminal
Baltimore, Maryland

CH2MHILL.



Vertical Exaggeration = 10x

*Depth of sheet piling is represented as a minimum depth as recorded on construction drawings.

Figure 3-2 - Geologic Cross-Section
Chromium Transport Study
Dundalk Marine Terminal
Baltimore, Maryland

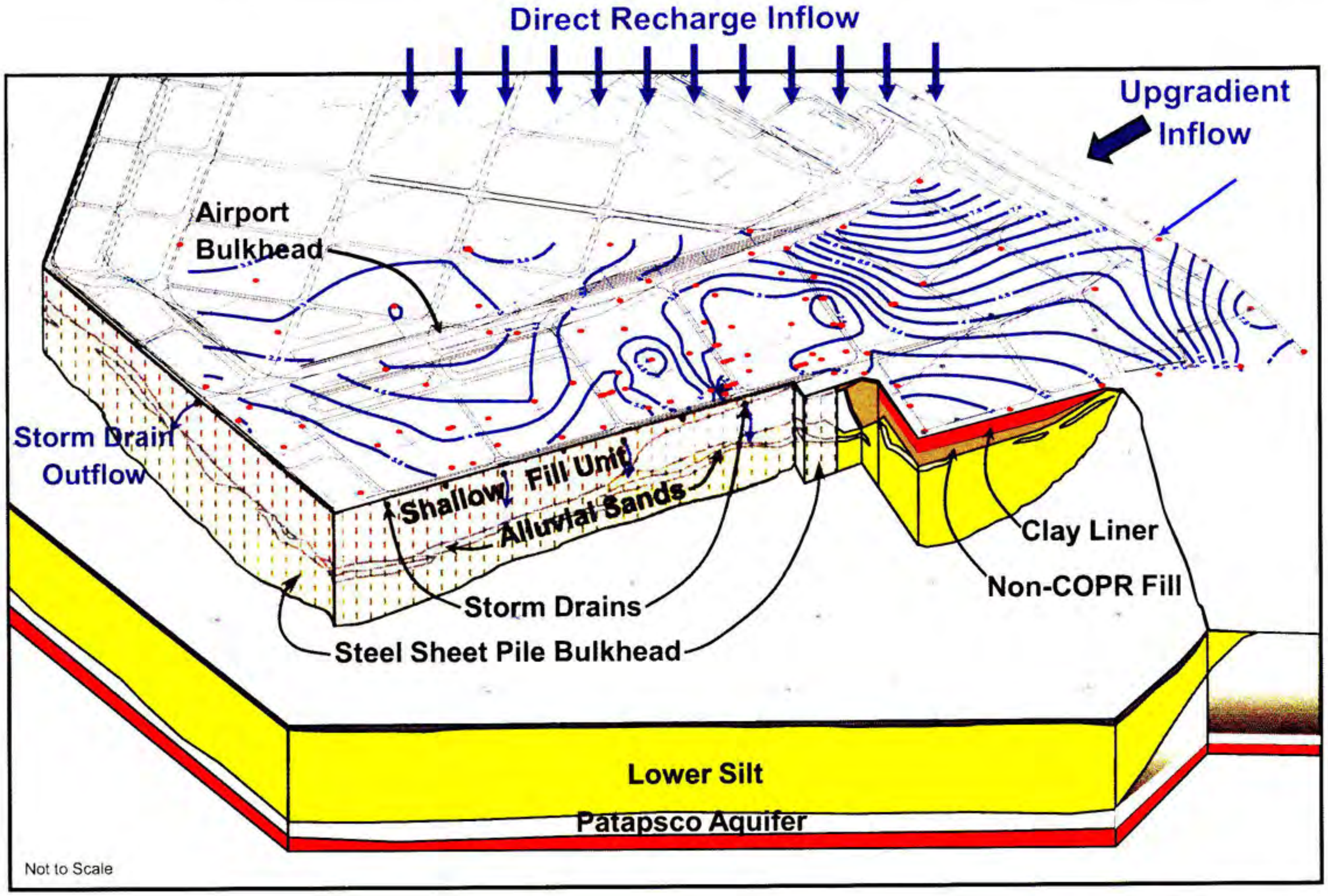
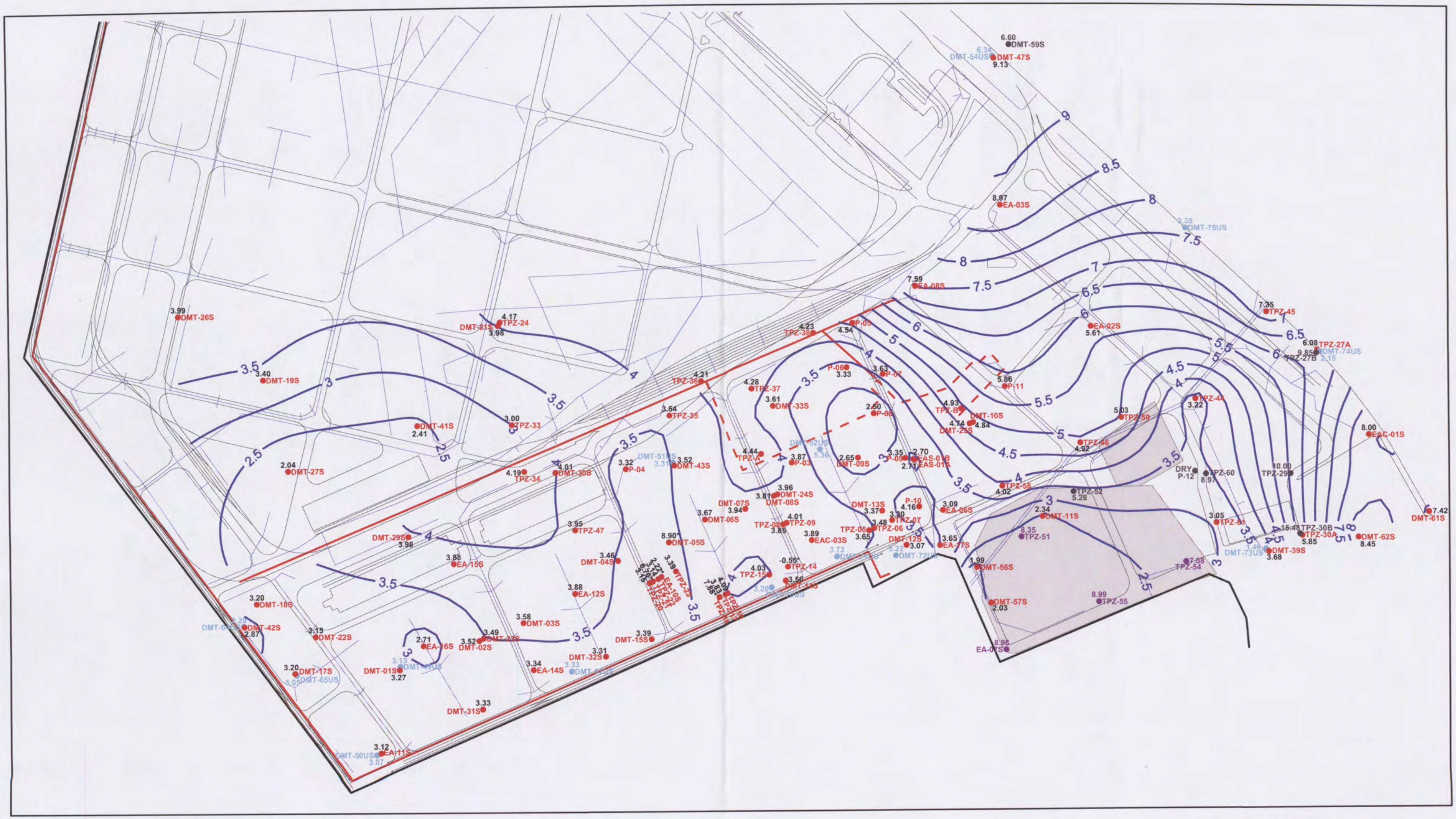


Figure 3-4 – Hydrogeologic Conceptual Model
Conceptual Groundwater Monitoring Plan
Dundalk Marine Terminal
Baltimore, Maryland

CH2MHILL



Legend

3.36 ● EA-17S	Shallow Well and Water Level
6.58 ● TPZ-41	Non-Aquifer Well and Water Level
3.49 ● DMT-51US	Upper Sand Well and Water Level
6.58 ● TPZ-51	COPR Cell Well and Water Level
2.38*	Measurement Not Used for Contouring
	(All Elevations in ft BCD)

—4—	Shallow Aquifer Potentiometric Contour
—4—	COPR Cell Groundwater Potentiometric Contour
—	Bulkhead
- - -	Historic Bulkhead
▨	COPR Cell

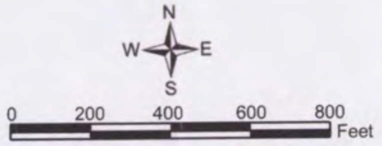


Figure 3-5– Water Levels Measured in Shallow Fill Unit, COPR Cell, and the Upper Sand Wells on April 16, 2012
Conceptual Groundwater Monitoring Plan
Dundalk Marine Terminal
Baltimore, Maryland

CH2MHILL

ES092812202919WDC Figure 3-10 bp/dk

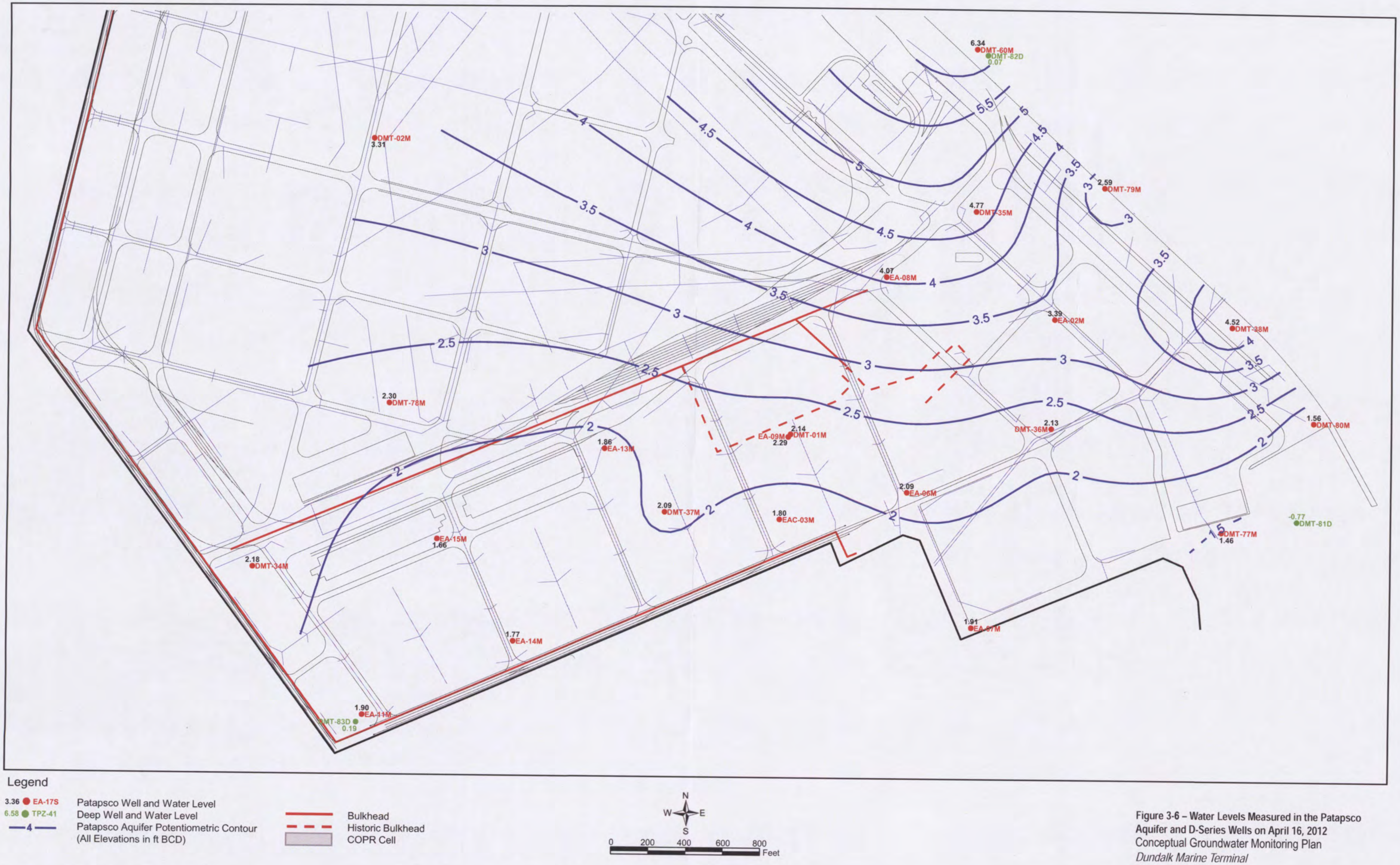


Figure 3-6 – Water Levels Measured in the Patapsco Aquifer and D-Series Wells on April 16, 2012
Conceptual Groundwater Monitoring Plan
Dundalk Marine Terminal
Baltimore, Maryland

DVR \\MNUSTRICTGFS01\PROJECTS\HONEYWELLINC\DMT LOCUS\MAPFILES\20001186 GW MONITORING PLAN\FIGURE 3 13 GW PUMPING CENTERS NEAR DMT.MXD JCROCKETT 10/16/2012 7:50:28 AM

Legend

- ● Location of production wells or well fields in the Upper Patapsco aquifer supplying water to users pumping greater than 10,000 gallons per day
- ● Location of production wells or well fields in the Lower Patapsco aquifer supplying water to users pumping greater than 10,000 gallons per day
- ▭ DMT Boundary
- ▭ County Boundaries

Note:
Well locations plotted after Andreasen, 2007.

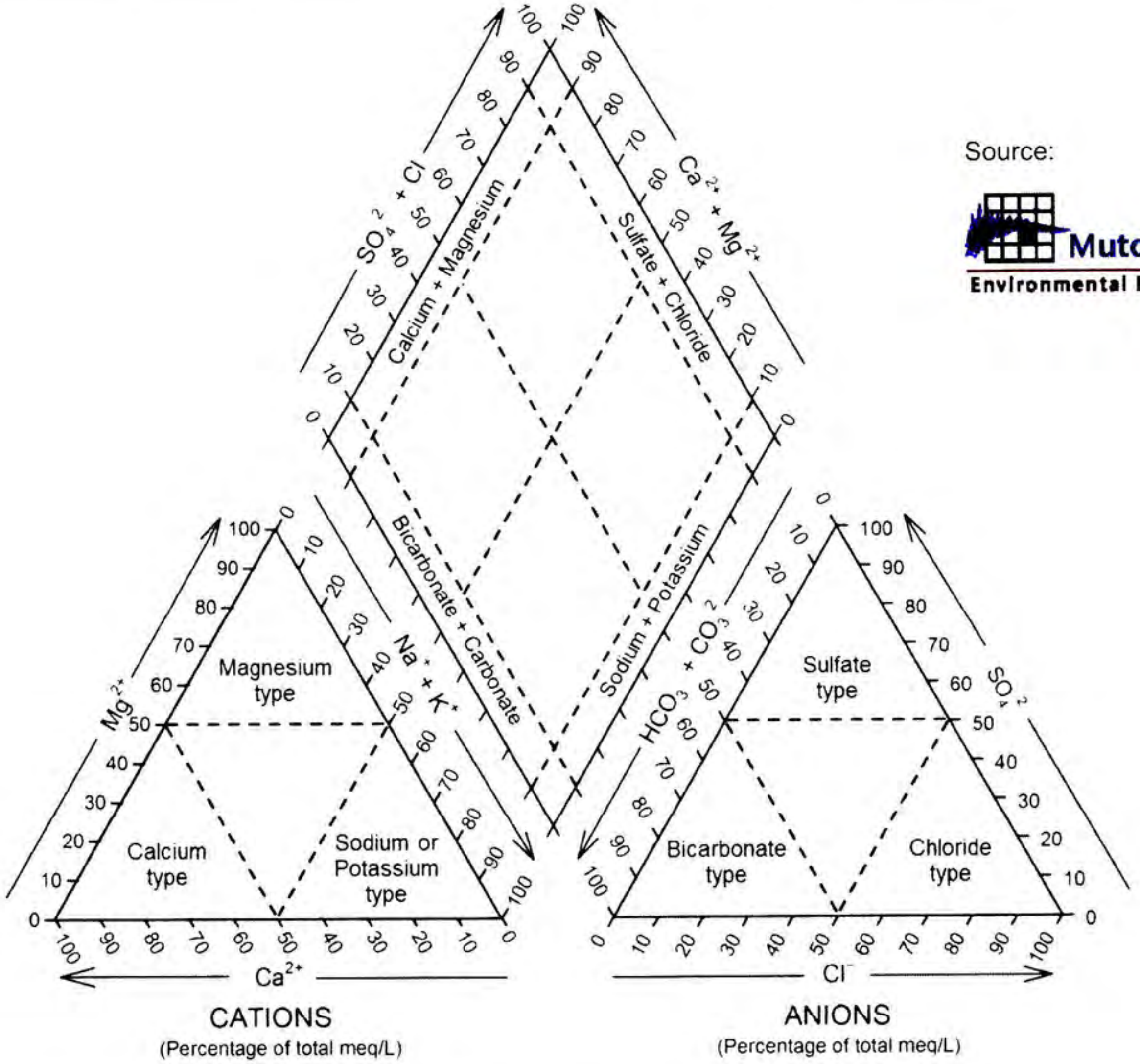
N W E S

0 3 6 Miles

1 in = 3 miles

Figure 3-7
Groundwater Pumping Centers Near DMT
Conceptual Groundwater Monitoring Plan
Dundalk Marine Terminal
Baltimore, Maryland

CH2MHILL.



Source:

Mutch Associates, LLC
Environmental Engineers and Scientists

Figure 3-9 – Piper Diagram Showing the Various Geochemical Facies
Conceptual Groundwater Monitoring Plan
Dundalk Marine Terminal
Baltimore, Maryland

CH2MHILL

Source:

Mutch Associates, LLC
Environmental Engineers and Scientists

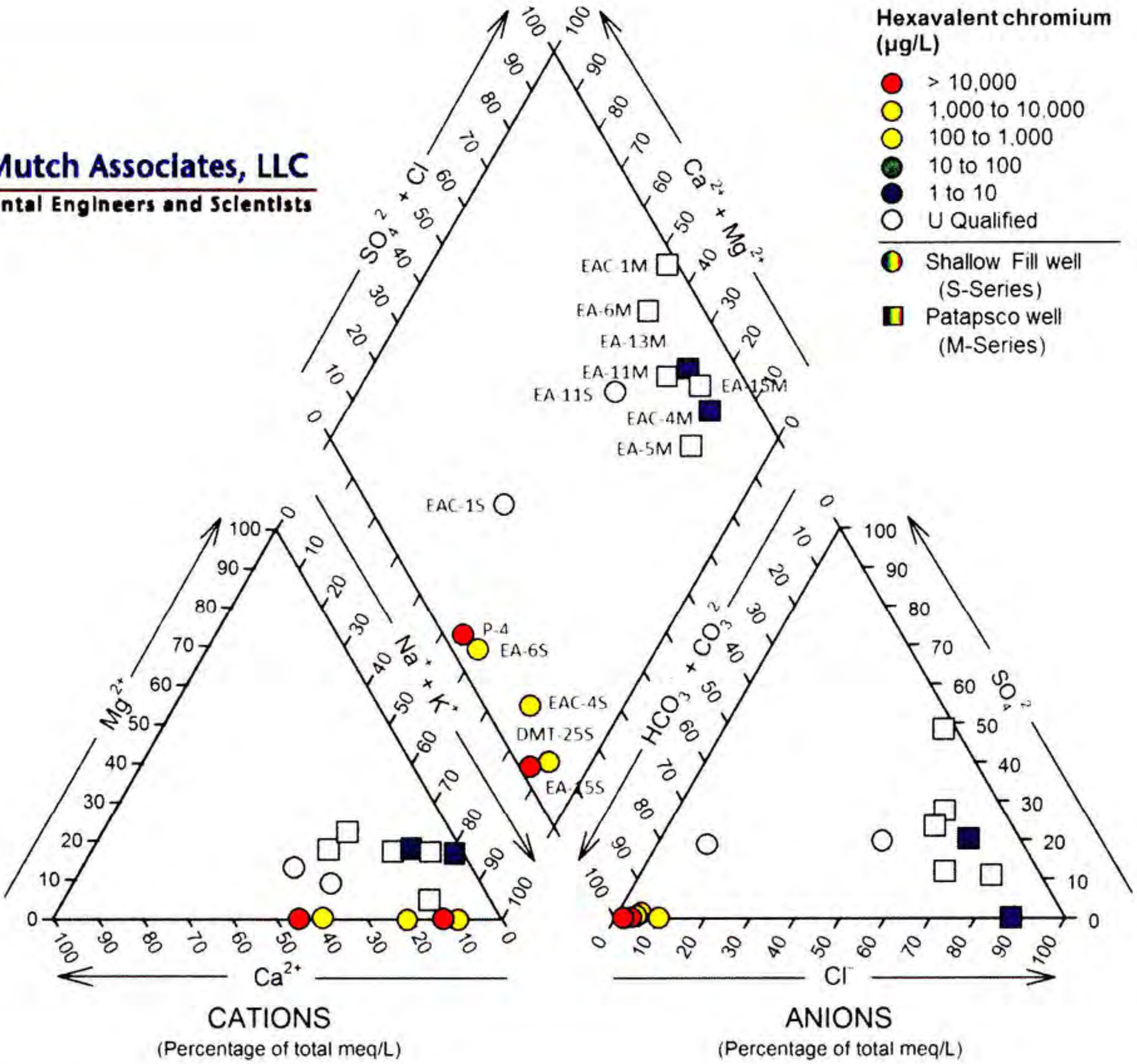


Figure 3-10 – Piper Diagram Showing Major Ion Distribution of Shallow Fill and Patapsco Wells
Conceptual Groundwater Monitoring Plan
Dundalk Marine Terminal
Baltimore, Maryland

CH2MHILL

SECTION 4

Conceptual Groundwater-Monitoring System Design

The conceptual approach to future monitoring of groundwater at DMT is explained below with reference to each monitoring unit. This conceptual approach will be regularly evaluated as the storm drain relining progresses using data collected during the interim semiannual groundwater-sampling events. The interim data will be evaluated against the predictive capabilities of the existing groundwater flow model, and the groundwater flow model will be amended as necessary to help identify any changed condition. Once the effects of the storm drain relining on groundwater flow have been identified and evaluated, Honeywell and MPA will design a groundwater-monitoring well network that will meet the objectives defined in Section 2.

A comprehensive groundwater-monitoring plan will be submitted to MDE when the storm drain relining has been completed. The plan will present an updated conceptual model for the site based on the results of the drain-lining evaluation and will detail the monitoring network and the sampling, analysis, data evaluation, and reporting procedures. It is anticipated that the program will use a long-term optimization (LTMO) strategy such as that described by AFCEE (2006). Such a strategy will allow Honeywell, MPA, and MDE to periodically review the program to see that the objectives of the program remain current and are being met efficiently and cost-effectively. An LTMO strategy will also allow for review of the decision rules for the program and the defined sampling frequency to make sure that the methods for well sampling, sample analysis, data validation, data management, and reporting remain up to date through the life of the program. Periodic LTMO reviews also mean that innovative technologies can be incorporated into the program as they are developed and become available for use.

4.1 Monitoring the Shallow Fill Unit

Monitoring the Shallow Fill Unit is the most important element of the program, to ensure that the remedial components remain protective of human health and the environment. For most of DMT, the samples would be collected from shallow monitoring wells outside the COPR fill as an early warning system for Cr(VI) migration. Previous investigation data suggest that the non-COPR fill in the Shallow Fill Unit is fairly homogeneous and that there are no preferential pathways. Therefore, the shallow wells would be spaced along the site boundary with adequate density to spatially represent conditions within the unit.

Hydraulic monitoring in the Shallow Fill Unit, in the form of groundwater elevation measurements, will be an important component of the future long-term groundwater-monitoring program. Hydraulic monitoring in the shallow wells would be performed both inside and outside the COPR fill. Within the COPR fill, the hydraulic monitoring will be used to verify that groundwater is not infiltrating the storm drains after their relining, to compare vertical hydraulic gradients with those of deeper units, and to confirm that impacted groundwater within the COPR cell in Areas 1501 and 1602 remains hydraulically isolated from the Shallow Fill Unit below the cell. Hydraulic measurements outside the COPR fill would be used to confirm that the sheet pile bulkhead remains an impediment to the direct discharge of shallow groundwater to the Patapsco River.

Monitoring of the Shallow Fill Unit downgradient of Areas 1501 and 1602 will be especially important because shallow groundwater does discharge to the Patapsco River along the boundary of this area, as evidenced by an upwelling study performed during the sediment and surface water study (CH2M HILL and Environ, 2009). Shallow groundwater flow in this area occurs though the granular fill that lies beneath the COPR cell and that was used to reclaim this area prior to the cell's construction. Well penetrations through the COPR cell should be limited to reduce opportunities for cross-contamination.

The conceptual plan for monitoring this area includes a series of sentinel monitoring wells immediately offshore of the area and outside the boundary of the COPR cell. Monitoring within the inland portion of the COPR cell is not desirable due to the COPR heave that has been observed in this area, which has compromised previous monitoring wells. The exact location of the offshore monitoring wells depends on how far the toe of the granular fill below the COPR cell extends into the Patapsco River. Honeywell and MPA may initiate an additional near-shore investigation to verify subsurface conditions in this area before determining monitoring well locations and screen interval. Any additional investigations would be conducted while the storm drain relining is taking place and prior to submittal of the final groundwater monitoring plan.

4.2 Upper Sand

Monitoring the Upper Sand is a second important component for verifying remedy protectiveness. Within the COPR boundary, the Upper Sand wells will be used for early warning of vertical chromium migration because the Upper Sand is the first hydraulic unit that is encountered below the COPR fill. In many areas, the Upper Sand lies within 5 feet of the bottom of the COPR fill.

Outside the COPR boundary, the Upper Sand may be used to monitor for horizontal and vertical chromium migration through wells placed along the downgradient edge of the COPR boundary, where ongoing monitoring of the shallow fill unit suggests vertical migration may soon occur, based upon the geochemical principles discussed in Section 3.4. Upper sand wells will also be considered along the shoreline of Areas 1501 and 1602 depending on the findings of additional assessment and potential investigation to be conducted in this area. The most important unit to monitor along the shoreline of Areas 1501 and 1602 shoreline is the granular fill that lies below the COPR cell (as discussed in Section 4.1), but Upper Sand wells may be necessary to monitor for chromium-impacted groundwater if the granular fill is not identified laterally outside the boundary of the COPR cell.

4.3 Patapsco Aquifer

Data collected during the CTS and ongoing groundwater-sampling events show that the Patapsco Aquifer has not been impacted by chromium constituents. While the potential for hexavalent chromium contamination of the Patapsco is remote, monitoring of the unit is prudent given the significant pumping of the Patapsco Aquifer that occurs in northern Anne Arundel County beginning approximately 7 miles from DMT (Figure 3-7). DMT represents a very small fraction of the total aquifer area from which the pumping wells will draw water; nonetheless, monitoring of the Patapsco at DMT is important to protect potential future receptors. Therefore, early warning monitoring using geochemical parameters will be a primary component of the Patapsco monitoring program to identify any COPR-related impacts or changes in water quality before chromium impacts are observed in the aquifer.

With the possible exception of Area 1501/1602, existing data suggest that the present configuration of M-series wells contiguous to and downgradient of the edge of the COPR fill is adequate for representative monitoring of the Patapsco. The location of any additional Patapsco monitoring wells will be determined through an evaluation of existing data and results obtained during the interim monitoring program as storm drain lining proceeds.

The conceptual plan for monitoring of the Patapsco Formation downgradient of Areas 1501 and 1602 depends upon evaluating the impact of further storm drain relining on the groundwater hydraulics, continued calibration of the groundwater model, and the results of any further investigation of the area offshore Areas 1501 and 1602. A detailed rationale for placement of any additional Patapsco monitoring wells will be provided in the comprehensive groundwater-monitoring plan.

4.4 Patuxent Aquifer

As discussed in Section 3.3.4 the Patuxent Aquifer is unaffected by conditions at the site based on sampling results from this formation and the overlying Patapsco Aquifer that show no detections for Cr(VI) in groundwater. Additionally, the low-permeability Arundel Formation exists between the Patapsco and Patuxent Aquifers. The Arundel creates hydraulic separation between the two units and severely limits the vertical transport of groundwater. It is anticipated that future monitoring of the Patuxent will include piezometric measurements within the existing D-Series wells to monitor for any changes in water levels over time.

4.5 Validation of the Conceptual Framework

The hydrogeology of the DMT has been subject to considerable study and consequently is well understood. Nonetheless, it is recognized that no amount of study can fully eliminate all uncertainties relative to the hydrostratigraphy and three-dimensional groundwater flow of this or any site. The overarching objective of the comprehensive groundwater-monitoring plan will be to design a long-term groundwater-monitoring well network that is sufficiently robust to ensure that no significant migration of chromium from DMT goes undetected and that the remedy remains fully protective of human health and the environment. The conceptual approach discussed herein will be periodically reevaluated as remedy implementation progresses using data collected during the interim semiannual groundwater-sampling events. The intent is that the plan will be a "living document" subject to adaptation in response to any changes in the hydrogeologic system over time, whether those changes are local to DMT or due to regional changes in groundwater supply well extraction rates. Once the effects of the storm drain relining on groundwater flow have been identified and evaluated, Honeywell and MPA will submit a comprehensive groundwater-monitoring plan. That plan, which will be submitted for MDE review and approval, will provide a detailed design and rationale for the monitoring network and describe the sampling, analysis, data evaluation, and reporting procedures to be included in the program.

SECTION 5

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Appendix A
Groundwater Flow in Interbedded Aquifer/Aquitard Systems

Mutch Associates, LLC
Environmental Engineers and Scientists

Memorandum

Project Number: HWEL.004

To: Chris French
From: Robert D. Mutch, Jr., P.Hg., P.E.
Subject: Groundwater Flow in Interbedded Aquifer/Aquitard Systems
Date: 10/13/12

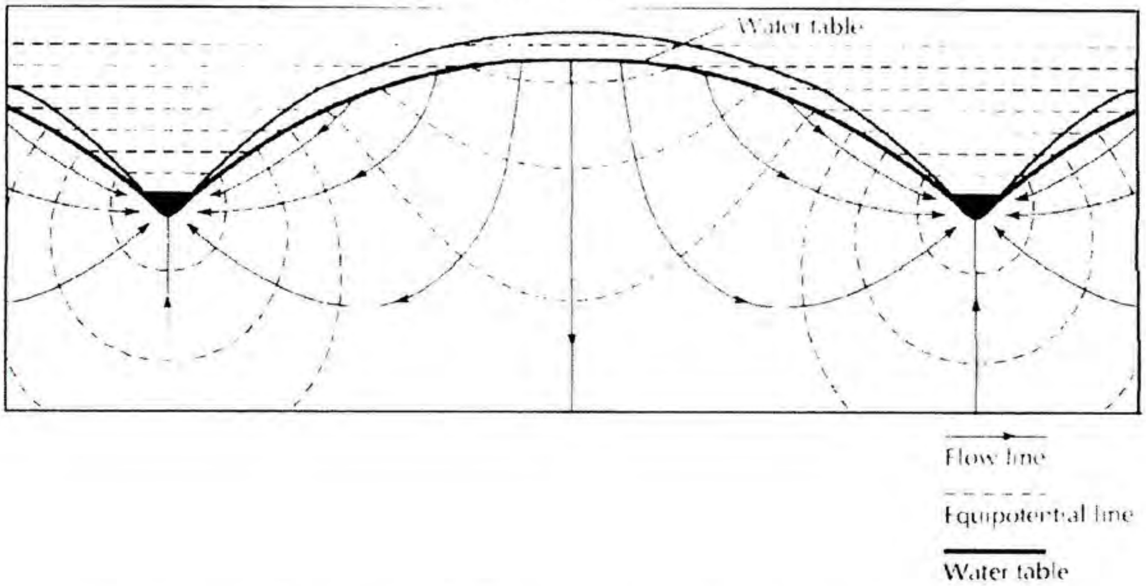
The hydrogeologic regime of the DMT is one characterized by a series of interbedded water-bearing units and confining units, also termed aquitards.[1] The site-specific sequence of water-bearing units and confining units present at DMT are described in Section 3.1 of the CGMP. DMT's hydrogeologic system, being characterized by interbedded, higher-permeability water-bearing zones and lower-permeability confining units, affects groundwater flow through the hydrogeologic system and has bearing upon the design of a comprehensive long-term monitoring program.

In a homogeneous hydrogeologic system (unlike that which is present at DMT), groundwater flow paths tend to be curvilinear. In these systems, groundwater flows from groundwater recharge areas to groundwater discharge areas along streams, rivers, and other water bodies. A simple depiction of such a flow system in a homogeneous and isotropic geologic medium is illustrated in Figure 1.

FIGURE 1

Cross-Sectional Flow Net in an Isotropic, Homogeneous Aquifer

Source: C.W. Fetter, Applied Hydrogeology, *Third Edition, 1994.*



In contrast, groundwater flow beneath DMT is controlled by a layered hydrogeologic regime.

The primary differences between the homogeneous regime and layered flow regime are illustrated in Figures 2a, 2b, and 2c. Figure 2a depicts a cross-section through a simple, homogeneous geologic medium with groundwater divides at either side and a no-flow boundary at the base. Recharge of precipitation produces a steady-state water table, which forms the upper boundary of the cross-section.

---

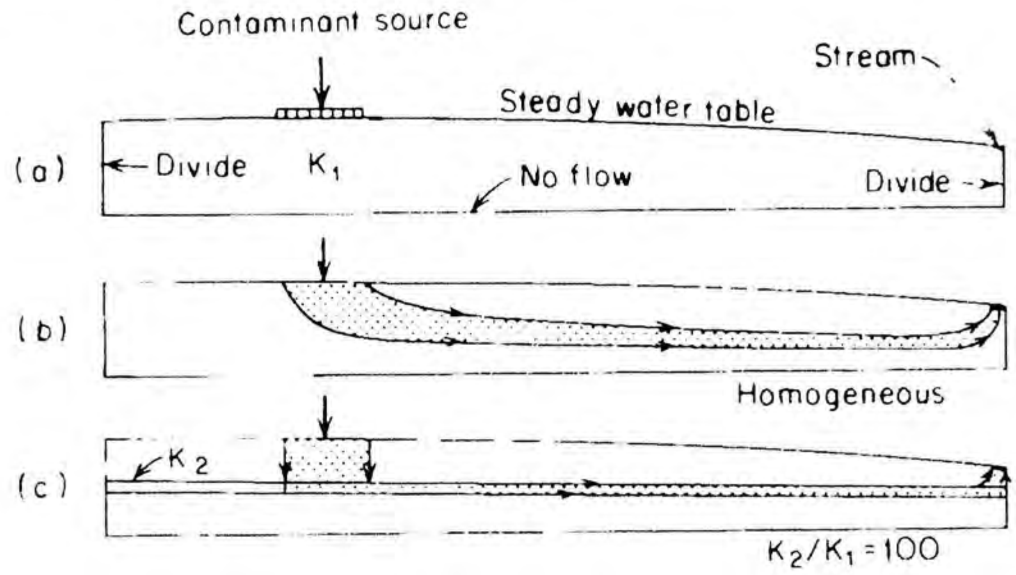
[1] Aquitards are geologic units that retard groundwater flow.

A contaminant source is also depicted in the upland portion of the recharge area. In Figure 2b, flow lines are illustrated that define the boundaries of a plume of groundwater contamination emanating from the source area. The flow lines defining the plume derived are curvilinear, reflecting the homogeneous nature of the geologic medium. In contrast, Figure 2c illustrates how the plume-defining flow lines would travel if the geologic medium was interbedded with confining units and contained a single stratum having a hydraulic conductivity 100 times greater than that of the surrounding geologic material. As illustrated in Figure 2c, flow lines emanating from the contaminant source area migrate vertically downward through the lower-permeability stratum; they then move horizontally through the high-permeability stratum until the discharge area is reached. At that point, flow becomes nearly vertically upward through the lower permeability stratum to the point of discharge in the stream.

FIGURE 2

Impact of Higher-Conductivity Layer on Flow Paths in Shallow Flow System

Adapted from Freeze and Cherry, Groundwater, *1979.*



Groundwater flow in interbedded systems is dictated by the "tangent law," which describes the refraction of flow lines across geological boundaries, as illustrated in Figure 3 (Freeze and Cherry, 1979; Hiscock, 2005). The tangent law is defined as:

$$\frac{K_1}{K_2} = \frac{\tan\theta_1}{\tan\theta_2}$$

Where: K_1 = Hydraulic conductivity of the upper layer through which the flow lines travel before reaching the boundary

K_2 = Hydraulic conductivity of the lower layer through which the flow lines travel after crossing the boundary

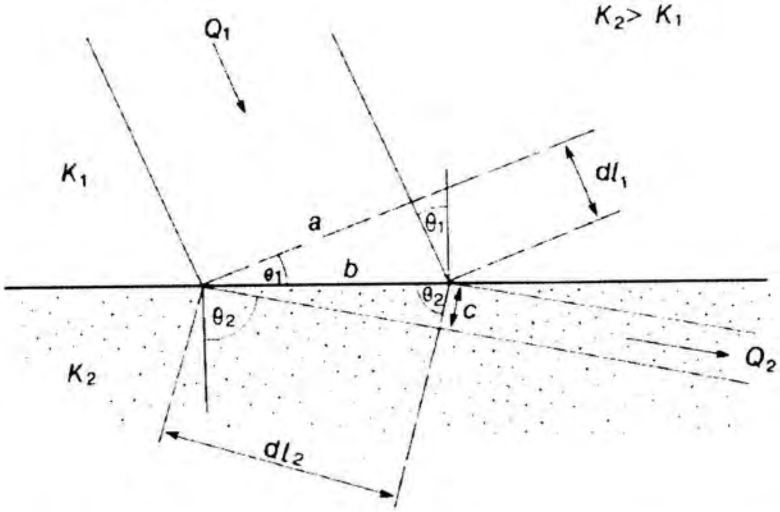
θ_1 = Angle of flow lines from the vertical in Layer 1

θ_2 = Angle of flow lines from the vertical in Layer 2

FIGURE 3

Refraction of Flow Lines at a Geological Boundary

Source: Hiscock, Hydrogeology: Principles and Practice, *2005.*

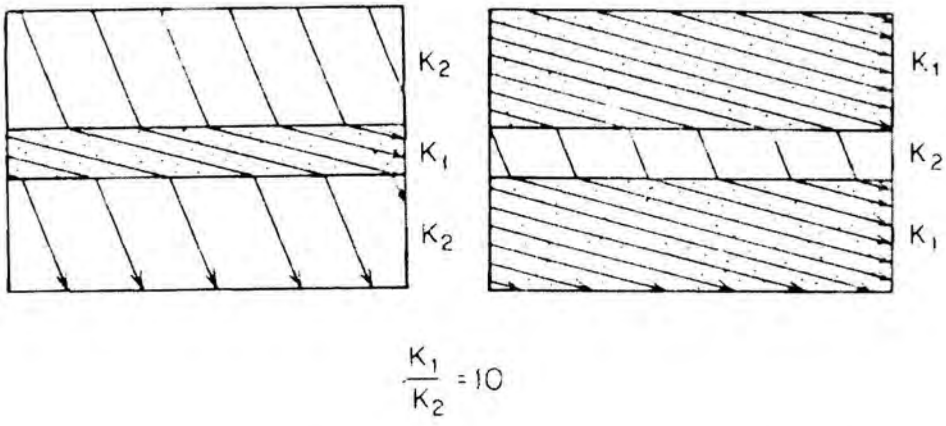


The result of the tangent law is that flow lines have longer, horizontal components of flow in transmissive aquifer layers and shorter, vertical components of flow in low-permeability confining layers. Figure 4 illustrates this behavior in a layered geologic sequence where the ratio of aquifer to confining unit hydraulic conductivity is only 10. Note that hydraulic conductivity contrasts within the DMT system are far higher than 10:1. As the hydraulic conductivity contrast between the aquifer and confining unit increases, flow paths in the confining unit become increasingly vertical (either upward or downward), and flow paths in the aquifer become increasingly horizontal. At hydraulic conductivity contrasts of 100 or greater (which are more similar to the flow regime beneath DMT) flow paths in confining units become essentially vertical and flow paths in aquifers become essentially horizontal.

FIGURE 4

Refraction of Flow Lines in an Aquifer/Aquitard System where $K_1/K_2=10$

Source: Freeze and Cherry, Groundwater, *1979.*

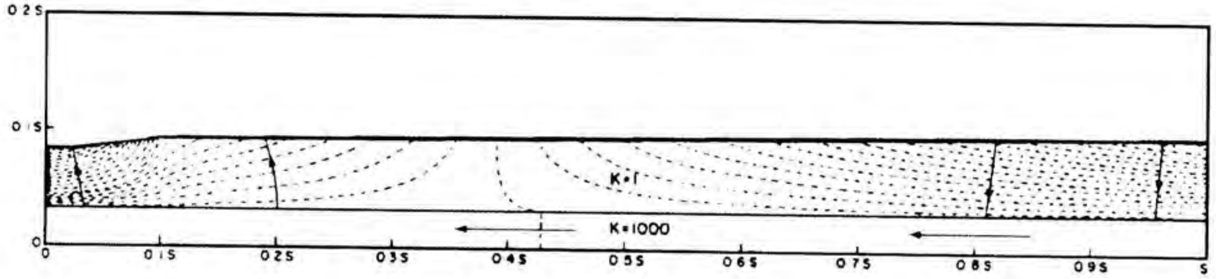


This principal is further illustrated in Figure 5, which shows a cross-section through a hydrogeologic regime with two horizontal strata. The upper stratum has a hydraulic conductivity of 1 and the lower stratum has a hydraulic conductivity of 1,000 (units are relative). The groundwater table is sloped from right to left. The right side of the figure represents a recharge area where flow in the upper stratum is essentially vertical. The left side of the diagram is a discharge area where flow in the upper, lower-conductivity stratum is also nearly vertical; however, in this case, flow is vertically upward toward the surface water discharge point. Flow throughout the deeper, higher-conductivity stratum is essentially horizontal, from right to left.

FIGURE 5

Regional Flow in a Layered Hydrogeologic System with a Deep, More Conductive Stratum

Adapted from Freeze and Witherspoon, Theoretical Analysis of Regional Groundwater Flow, 2: Effect of Water-Table Configuration and Subsurface Permeability Variation, 1967.



The vertical flow in aquitard units is often quite low with correspondingly long travel times. As an example, we can readily estimate the approximate travel time for groundwater to penetrate the Lower Confining Unit (LCU) in the vicinity of the 1501/1602 cells. The low hydraulic conductivity and substantial thickness of the LCU beneath the DMT, together with the relatively low vertical hydraulic gradient across the LCU, mean that it would require centuries for groundwater to pass through the unit and into the Patapsco Aquifer. The average linear groundwater velocity ($\bar{v}$) through the LCU can be calculated with the following variation of Darcy's Law (Freeze and Cherry, 1979):

$$\bar{v} = \frac{Ki}{n_e} \tag{1}$$

Where:

$\bar{v} =$ Average linear groundwater velocity, L/T

$K =$ Hydraulic conductivity, L/T

$i =$ Hydraulic gradient, dimensionless

$n_e =$ Effective porosity, dimensionless

Vertical Hydraulic Conductivity of the Lower Confining Unit (K)

The vertical hydraulic conductivity of the LCU has been determined by three independent means to be less than 1.0×10^{-3} feet per day (ft/day): laboratory permeability testing of representative samples; a Neuman and Witherspoon "ratio method" analysis of the propagation of drawdown through the aquitard during an aquifer test of the Patapsco Aquifer; and calibration of the groundwater flow model.

Laboratory hydraulic conductivity testing of samples from the LCU indicated an average hydraulic conductivity of 2.77×10^{-4} ft/day (CH2M HILL, 2009a). The Neuman and Witherspoon "ratio method" analysis of the aquifer test of DMT-01M showed that the vertical hydraulic conductivity of the LCU was less than 6×10^{-4} ft/day (CH2M HILL, 2009a). The calibrated groundwater flow model uses a value of 2.8×10^{-4} ft/day. The model sensitivity analysis indicated that the calibration of the model deteriorated if the hydraulic conductivity of the LCU was raised above 1×10^{-3} ft/day. In this illustrative example, we will use the model-calibrated hydraulic conductivity of 2.8×10^{-4} ft/day.

Hydraulic Gradient (i)

The hydraulic gradient across the LCU can be calculated by dividing the typical hydraulic head difference across the LCU by the thickness of the unit. A review of the groundwater model development report in Appendix B of the CTS (CH2M HILL, 2009a) indicates that the head difference across the LCU, between the Upper Sand and the Patapsco Aquifer, in the area of the 1501/1602 cells, varies from about 1 to 2 feet. We will use 2 feet in this calculation. The thickness of the LCU beneath the 1501/1602 cells varies from 37 to 48 feet. We will use 37 feet to be conservative. The vertical hydraulic gradient through the LCU can then be calculated as follows:

$$i=\frac{\Delta h}{l} \tag{2}$$

Where: i = Hydraulic gradient, dimensionless

Δh = Hydraulic head difference, in feet

l = Thickness of LCU, in feet

$$i=\frac{2\text{ feet}}{37\text{ feet}}=0.054$$

Effective Porosity (n_e)

The effective porosity is estimated to be 0.30. This value is also conservative as the total porosity of the LCU is approximately 0.54 (CH2M HILL, 2009b).

Estimated Travel Time through the LCU

Using the above-described parameters and Equation 1, the average linear groundwater velocity through the LCU can be calculated as follows:

$$\begin{aligned}\overline{v}&=\frac{2.8\times10^{-4}\text{ ft/day}\times0.054}{0.3}\\ \overline{v}&=5.04\times10^{-5}\text{ ft/day}\end{aligned} \tag{3}$$

The travel time through the LCU can then be calculated by dividing the thickness of the LCU by the calculated average linear groundwater velocity as follows:

$$\begin{aligned}\text{Travel time}&=\frac{\text{Thickness of the LCU (l)}}{\text{Average linear groundwater velocity}}\\ \text{Travel time}&=\frac{37\text{ feet}}{0.02\text{ ft/day}}=1850\text{ years}\end{aligned} \tag{4}$$

Several implications of the above-described flow mechanics of layered systems bear on contaminant transport in such systems and on the design of groundwater-monitoring systems. These implications include the following:

1. The propensity for lateral groundwater flow to be restricted to the higher permeability strata, particularly in layered systems with high hydraulic conductivity contrasts, is why groundwater-monitoring wells are almost exclusively screened in the higher-permeability strata in a geologic sequence. It is typically only through these higher conductivity strata that groundwater and any

groundwater-borne contaminants can migrate laterally out from beneath a waste disposal site and then potentially downgradient to receptors. In contrast, in confining units, groundwater flow or groundwater-borne contaminants typically migrate vertically downward until higher-permeability strata are encountered. Once a higher-conductivity stratum is encountered, groundwater flow and any groundwater-borne contamination are then conveyed laterally, as described above.

2. The vertical flow of groundwater though the confining units can be quite low depending upon their vertical hydraulic conductivity. Correspondingly, the flux (mass per unit time) of any groundwater-borne contaminants also tends to be quite low through the confining units. As a result, even if the vertical flux of contamination in the confining unit ultimately reaches the underlying, more permeable aquifer, concentrations often decline by one or more orders of magnitude due to mixing with the considerably higher lateral groundwater flow occurring within the aquifer.
3. The time of transport of groundwater through confining units can also be quite long depending upon their hydraulic conductivities and ambient vertical hydraulic gradients. As described above, the estimated groundwater travel time through the LCU in the Area 1501 and 1602 COPR cells is approximately 1,850 years.
4. The combined impact of relatively rapid lateral migration in the aquifer units (item 1) and the typically long time of transport of groundwater through the confining units (item 3) dictates that, in most circumstances, any groundwater contamination entering an aquifer unit beneath a waste disposal site will migrate laterally rapidly enough to be detected in the downgradient groundwater-monitoring system—long before it can simultaneously migrate appreciably downward through the underlying confining unit toward the next aquifer in the hydrogeologic sequence.

All of the above-described implications of groundwater flow and contaminant transport in layered systems lead, in turn, to the following specific conclusions, relative to conceptual design of groundwater-monitoring systems in such hydrogeologic regimes:

- The principal focus of groundwater monitoring should be on the upper water-bearing or aquifer units in the geologic sequence beneath the waste disposal site. If there is a surficial, water-bearing unit through which contaminants could flow laterally from the waste disposal site, it should be monitored. If there is a second, deeper, water-bearing zone, separated from the waste disposal site by a confining unit, it also warrants monitoring; groundwater could flow vertically downward from the waste disposal site through the confining unit to that second water-bearing zone and then move laterally out from beneath the waste disposal site. Monitoring of the second water-bearing zone should be conducted as close as practicable to the edge of the waste boundary.
- Confining units rarely need to be monitored since lateral groundwater flow and potential plume migration will almost always be confined to the aquifer units. Aquitard units are also difficult to sample due to their low hydraulic conductivity and yield.
- Each successively deeper aquifer unit (below the surficial and second water-bearing zones) warrants progressively less or no monitoring attention since plume migration and detection in the monitoring network should occur in the surficial or second water-bearing zones long before it could migrate through the intervening confining unit(s) to deeper aquifers. This is especially true as the hydraulic conductivity contrast between the aquifer and confining units becomes greater.

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Appendix B
COPR Plume Geochemistry

Mutch Associates, LLC
Environmental Engineers and Scientists

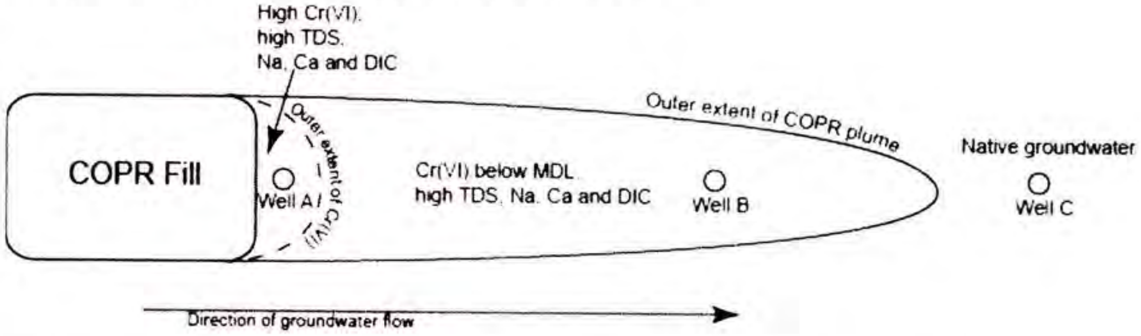
Memorandum

Project Number: HWEL.004

To: Chris French
From: Robert D. Mutch, Jr., P.Hg., P.E.
Subject: COPR Plume Geochemistry
Date: 10/16/12

COPR at the time it was placed at DMT was composed primarily of three minerals: brownmillerite ($Ca_2(Al,Fe,Cr)_2O_5$), periclase (MgO), and portlandite ($CaOH_2$) (CH2M HILL, 2009a). These materials chemically weather in the presence of water and dissolved solutes to form various hydration products (Hiller et al., 2003; Moon et al., 2007). Five main metallic elements—calcium, iron, aluminum, magnesium, and chromium—plus oxygen constitute well over 90 percent of the inorganic mass of COPR (CH2M HILL, 2009a). As groundwater comes in contact with COPR, some of these elements will leach out. As shown in Figure 1, COPR will enrich the surrounding groundwater with Cr(VI) and some major ions. A well screened in or near the COPR fill (Well A in Figure 1) will exhibit high concentrations of Cr(VI), total dissolved solids (TDS), Na^+, Ca^{2+}, HCO_3^-, and CO_3^{2-} (dissolved inorganic carbon, or DIC).

FIGURE 1
Conceptual Depiction of Groundwater in COPR Fill Behavior



Reductive processes have been shown to reduce Cr(VI) to Cr(III) within approximately 200 feet laterally of the COPR fill. Major ions, however, are not attenuated as rapidly and can reach downgradient wells. As shown in Figure 1, the outer extent of the COPR plume as defined by major ions is much farther downgradient than the outer extent of the Cr(VI) plume. Wells screened beyond the extent of Cr(VI) (Well B in Figure 1) will have the major ion signature of COPR-influenced water but will lack detectible Cr(VI). Wells screened outside of the COPR plume (Well C) will have a major ion signature that is representative of native groundwater.

Major ion data are often collected to increase understanding of water quality as it relates to the geologic character of various aquifers and to provide useful information on the source of groundwater. The majority of major ion data analysis methods require that a complete suite of data (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, and CO_3^{2-}) be available (Zaporozec, 1972). One of the most effective and commonly used graphical analysis methods is the so-called Piper Diagram (Figure 2). Piper Diagrams utilize two trilinear plots and one diamond-shaped *x-y* scatter plot to visualize the major cation and anion distributions for multiple groundwater samples (Piper, 1944). Each vertex of the triangle represents 100 percent of a specific ion or grouping of ions on an equivalent charge basis.

A Piper Diagram is often used to classify waters into "hydrochemical facies" (Back, 1966). For example, water plotting in the upper portion of both the cation and anion triangles would be referred to as magnesium sulfate–type water. In addition, differences or similarities in groundwater origins can often be discerned on the basis of where groundwater-monitoring data plot on the diagram. Groundwaters plotting in the same location indicate a common composition and usually a common origin.

As part of the chromium transport study (CTS) (CH2M HILL, 2009b), a Piper Diagram was prepared for a subset of wells at DMT for which the complete set of major ion data was available. This diagram has been modified here as Figure 3 with color-coded data symbols to indicate concentration ranges of hexavalent chromium. Shallow fill wells are denoted by circles, while Patapsco wells are denoted by squares. Most of the shallow fill wells are sodium/potassium bicarbonate–type waters on the basis of their location on the cation and anion triangles. In contrast to the sodium/potassium *bicarbonate*–type water of the shallow fill, Patapsco groundwater is characterized as sodium/potassium *chloride*–type water. The Patapsco wells and the majority of the shallow fill wells plot in very different locations on the anion triangle and on the upper diamond as a result of their very different anion signature.

The Patapsco wells have significantly higher chloride concentrations than most of the shallow wells, and typically have Cr(VI) concentrations below the method detection limit, or MDL (U qualified). The large separation on Figure 3 between Patapsco wells and the hexavalent chromium–rich shallow wells provides further evidence that these qualified detections of Cr(VI) are not the result of plume migration from the COPR fill.

Most of the shallow fill wells shown in Figure 3 (P-4, EA-6S, EAC-4S, DMT-25S, and EA-15S) plot in the lower-left corner of the anion triangle, indicating the predominance of DIC (HCO_3^- and CO_3^{2-}). These wells are all screened in or just outside the boundary of the COPR fill, based on mappings of well locations shown in Figure 4-13 of the CTS (CH2M HILL, 2009b). Analytical results presented in the CTS indicate that COPR is clearly enriching the water with both Cr(VI) and DIC. These wells are most similar to Well A on the conceptual depiction of COPR plume behavior shown in Figure 3. The two shallow wells that do not plot with the COPR-influenced wells are EA-11S and EAC-1S. These do not possess significant amounts of Cr(VI) (U qualified; MDL = 10 µg/L).

EA-11S is approximately 600 feet from the COPR fill, at the southwestern tip of DMT. Cr(VI) was below the MDL for this well, and it shows a very different major ion signature than COPR-influenced water. EA-11S shows a large separation from the COPR-influenced wells in both the anion triangle and the upper diamond. The position of EA-11S on the Piper Diagram indicates it is not influenced by COPR. It is likely that EA-11S is composed largely of local recharge. This well is most similar to Well C on the conceptual depiction of COPR plume behavior shown in Figure 1.

EAC-1S is just outside of the COPR extent at the eastern edge of DMT. Like EA-11S, it is below the MDL for Cr(VI). EAC-1S shows only a very small separation from COPR-influenced wells, such as P-4 and EA-6S. The position of EAC-1S on the Piper Diagram indicates that it is a mixture of COPR-influenced water and native shallow groundwater. While EAC-1S shows evidence of being influenced by COPR in terms of major ions, it does not show elevated Cr(VI). This well is most similar to Well B in the conceptual depiction of COPR plume behavior shown in Figure 1. The lack of Cr(VI) along with the appearance of COPR major ions provides additional evidence for attenuation of Cr(VI).

The major ion data and associated Piper Diagram shown in Figure 3 provides an "early warning" for COPR plume migration. A shift in the major ion signature of groundwater towards sodium/potassium bicarbonate–type water is indicative of influence of the COPR plume. Major ions will appear in wells in advance of hexavalent chromium (e.g., EAC-1S) because of the attenuation mechanisms that reduce Cr(VI) to Cr(III) in the shallow fill. As a result, major ion data can be used to provide notice of COPR plume migration before the appearance of Cr(VI). While changes in major ion concentrations over time may indicate that a monitoring well is within the flow path of the COPR plume, ongoing reductive mechanisms may completely inhibit Cr(VI) transport, owing to the low source strength of COPR and the distance of the monitoring well from the COPR body.

A well monitoring program that includes measurements of Cr(VI) and major ions will provide the necessary data to give an "early warning" of COPR plume migration. Chemical analysis will be performed for hexavalent and total chromium to monitor the extent of their migration from the COPR fill. Major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}), anions (Cl^-, SO_4^{2-}), and total alkalinity (to obtain HCO_3^-, CO_3^{2-}) will be analyzed to prepare Piper Diagrams such as the one shown in Figure 3. Geochemical parameters such as pH, ORP, dissolved oxygen, ferrous iron, and dissolved manganese will be monitored to provide information on the prevalence of redox conditions, which lead to attenuation of Cr(VI).

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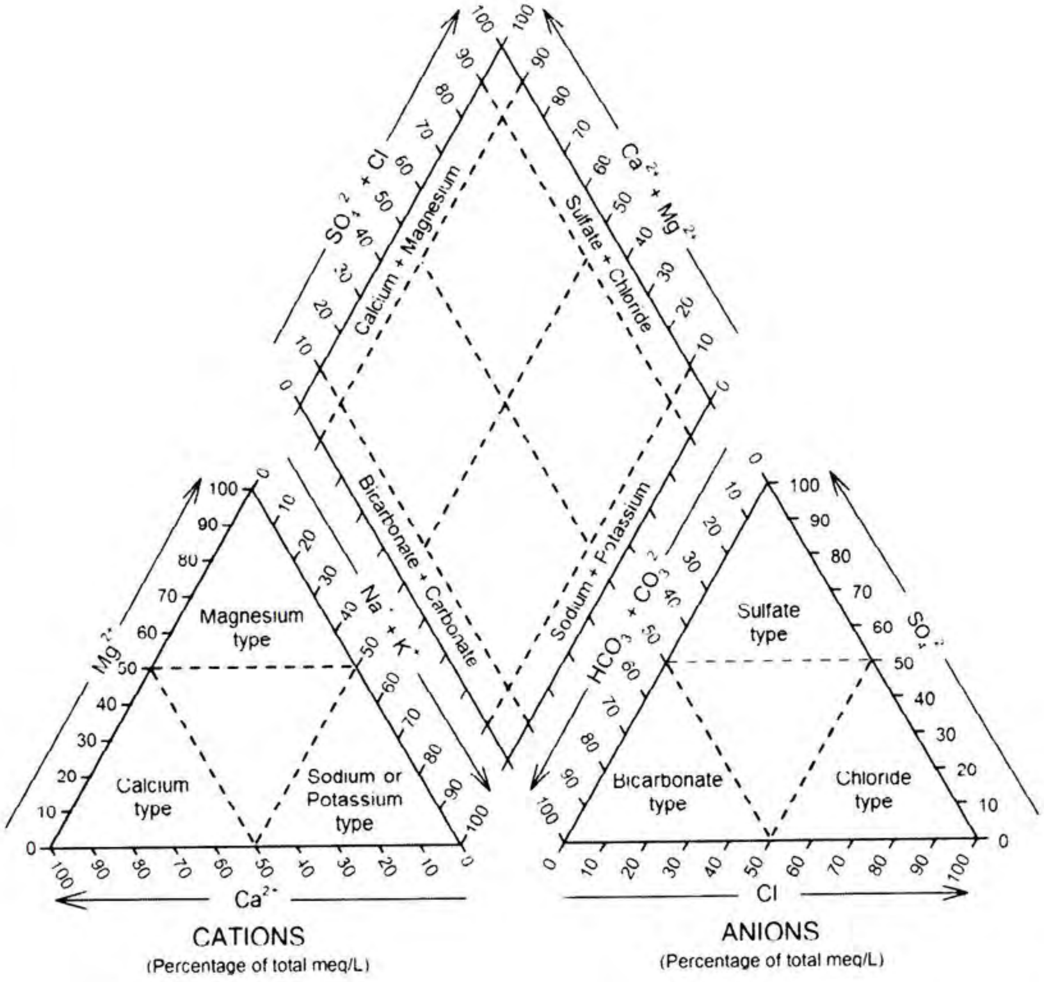

Figure 2
Piper Diagram Showing the Various Geochemical Facies.

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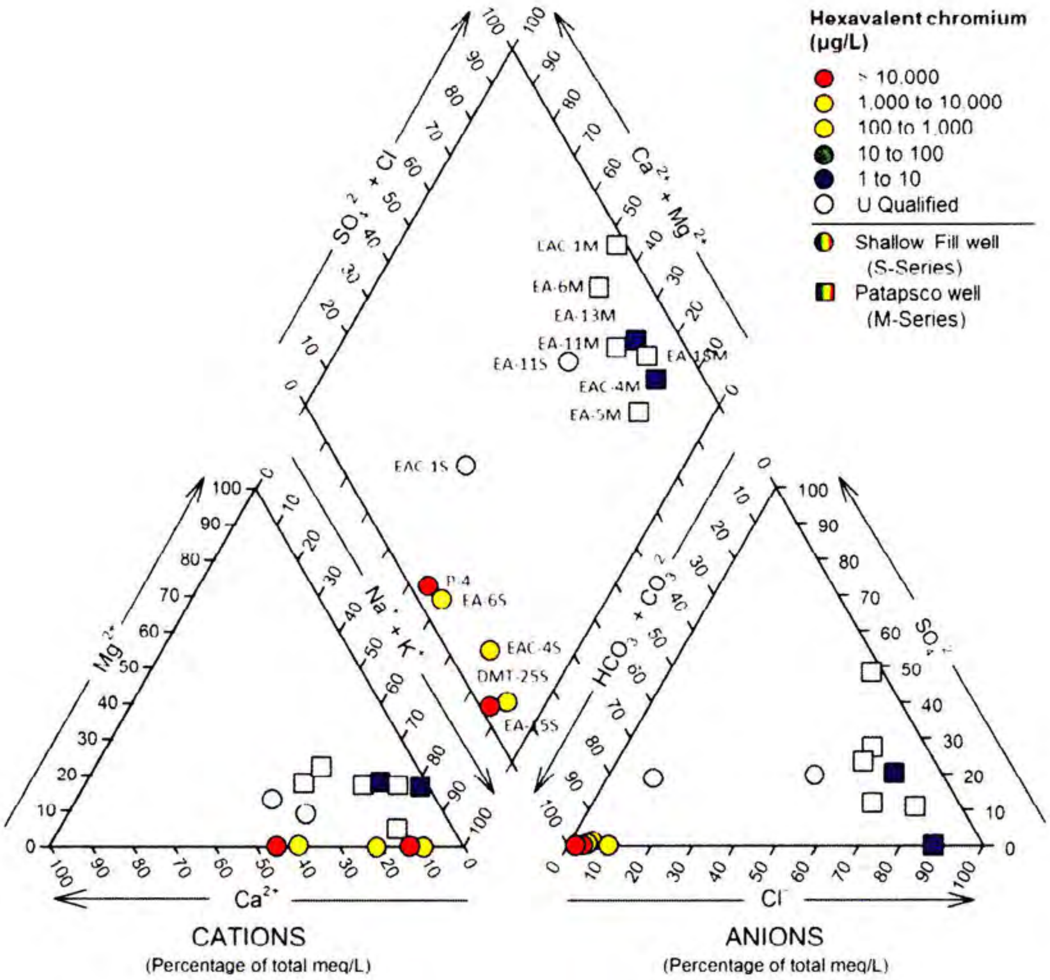

Figure 3
Piper Diagram of Shallow Fill and Patapsco Wells

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