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ENVIRONMENT

From:
 Megan E. Kellner

Date:
 June 18, 2012

Subject:
 Supplemental Investigation Work Plan
 C&O Canal/CSXT Brunswick Rail Yard, Brunswick,
 Maryland CSXT Project # 9415381

ARCADIS Project No.:
 MD843.10.05

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Comments: Enclosed is a copy of the Supplemental Investigation Work Plan with a copy on CD for the Brunswick Rail Yard, Brunswick, Maryland. Two copies of the report are also being sent to Susan Bull with one electronic copy on CD. Please contact me with questions.

Thanks, Megan Kellner

CSX Transportation, Inc.

**Supplemental Investigation Work
Plan**

C&O Canal/Brunswick Rail Yard,
Brunswick, Maryland
CSXT Project # 9415381
July 18, 2012



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Supplemental Investigation Work Plan

C&O Canal/Brunswick Rail Yard,
Brunswick, Maryland
CSXT Project # 9415381

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Our Ref.:
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1. Introduction

On behalf of CSX Transportation, Inc. (CSXT), ARCADIS has prepared this Supplemental Investigation Work Plan (SIWP) for the CSXT Brunswick Rail Yard (the Site) in Brunswick, Maryland. The objective of this SIWP is to provide detailed sampling methodology and investigation objectives for the Site and the National Park Service (NPS) property in the Chesapeake and Ohio (C&O) Canal National Historical Park located adjacent to the Site. NPS Correspondence addressed to the Maryland Department of the Environment (MDE) dated June 5, 2012 requested that CSXT conduct a comprehensive Site Evaluation on the nature, location, and extent of soil and groundwater contamination, including characterization of soil/sediment in the C&O Canal prism footprint. In response to the June 5, 2012 correspondence, CSXT proposes the supplemental investigation tasks included in this SIWP to further define the nature and extent of contamination at the Site and to fully characterize potential impacts to the C&O Canal National Historical Park property adjacent to the Site.

1.1 Site History and Investigation Activities

Sections 1.1.1 and 1.1.2 below summarize both the on-site and off-site environmental activities that have been previously completed at the Site and the adjacent NPS property. **Table 1** provides a chronology and brief description of all activities completed to date.

1.1.1 CSXT Property

The Site, which has been an active rail yard since 1892, is located adjacent to the C&O Canal in Brunswick, Maryland (**Figure 1**). The potential source areas for diesel range total petroleum hydrocarbons (TPH-DRO) in groundwater are the former aboveground storage tank (AST) System which included a 500,000-gallon diesel fuel AST and a fuel pumping house, and an active fueling area located near the former roundhouse.

Activities conducted by CSXT and their consultants since 1992 include the removal of a 16,000 gallon diesel fuel underground storage tank (UST) adjacent to the fuel pumping house along with approximately 100 cubic yards of soil petroleum impacted soil. Analysis of soil confirmation sampling from the excavation showed total petroleum hydrocarbon (TPH) concentrations below the current MDE non-residential cleanup level of 620 mg/kg (Eder, 1992). In 1994 four monitoring wells (MW-1, MW-2, MW-3, and MW-4) were installed on-Site. Liquid phase hydrocarbons (LPH), was observed at MW-2. In 1995, a second set of monitoring wells including MW-5, MW-6, MW-8, and MW-9 were installed on CSXT(MW-5) and NPS property (MW-6, MW-8, and MW-9).



Efforts to recover LPH observed at MW-2 were initiated in January 1995 and expanded in 1998 to include MW-1, MW-4, and MW-6. A Conceptual Investigation Plan (CIP), dated February 8, 1999, was developed to evaluate any potential threat to surface water and to consider scenarios for adjusting the product recovery program, if necessary. The CIP also included a remedial alternatives analysis. As part of the ongoing product delineation, eleven piezometers (TP-1 through TP-11) were installed between November 1999 and August 2000 in order to delineate the extent of LPH. A more comprehensive remedial alternatives analysis was presented in a Site Investigation Report for the C&O Canal Rewatering Project, dated December 2000.

As requested by MDE in 2002, a Corrective Action Plan (CAP) prepared by Gannett Fleming, Inc. was submitted to MDE on April 19, 2002. The CAP proposed the installation of a barrier/recovery trench (BRT) with internal collection sumps in order to provide containment of LPH. The CAP was approved by MDE in November 2002, and construction of the BRT subsequently began in October 2003 and was completed in March 2004. The BRT was installed to approximately 15 feet below ground surface (ft bgs), with 60 mil high-density polyethylene (HDPE) liner placed on the downgradient side of the trench. A geotextile liner was used to line both the trench and the HDPE liner in order to prevent damage to the HDPE. Five collector sumps (CS-1 through CS-5) were installed in the trench, constructed as 6-inch diameter polyvinyl chloride (PVC) screened wells in vault boxes. The trench was then completed with crushed stone backfill placed on the geotextile and around the collector sumps.

Beginning in July 2004, enhanced fluid recovery (EFR) activities were initiated to increase LPH recovery. These activities focused on wells that historically contained measurable LPH (MW-2, EW-3, EW-4, and EW-5) and on the collection sumps that are part of the BRT. Approximately 32,466 gallons of total fluids (LPH and water) were recovered using EFR from July 2004 through June 2009.

In September 2006, an automated product recovery pump was installed in MW-2 as requested by MDE. Recovered LPH using the pump was collected in a 55-gallon drum and was disposed of in conjunction with EFR events. A total of 54 gallons of product were recovered by the pump from September 2006 through July 2008.

Two versions of the Site Conceptual Model (SCM) were submitted on January 30, 2007 and February 8, 2008. Work conducted after the original SCM and included in the Revised SCM dated February 8, 2008 consists of the following:

- In June 2007, temporary wells TP-1, TP-3, TP-4, TP-5, TP-10, and TP-11 were abandoned, and monitoring wells MW-4R, MW-21, MW-22, MW-23, MW-24, MW-25, MW-26, and MW-27 were installed.
- In July/August 2007, a direct-push investigation was conducted, including the installation of 24 borings (GP-20, GP-26 to GP-49) at the site. All data from the June 2007 well installation event and the July/August 2007 direct-push investigation are included in the Data Package Memo dated September 10, 2007 (ARCADIS, September 2007).
- In November 2007, monitoring wells MW-20, MW-28, MW-29, MW-30, MW-31, MW-32, MW-33, MW-35, MW-37, MW-38, MW-39, MW-41, MW-43, MW-49, MW-50, MW-51, and MW-52 were installed. Data from the November 2007 well installation is included in the Revised SCM, dated February 11, 2008 (ARCADIS, February 2008b).

Additional investigation activities have been conducted as presented in the Additional Site Characterization Work Plan/Request for Corrective Action Plan Extension dated March 12, 2008 and based on comments from the May 30, 2008 letter from MDE approving the work plan. These activities include:

- Installation of direct-push borings with soil and groundwater samples in June 2008. A total of 21 borings (GP-53 to GP-73) were installed on CSXT Property (see **Figure 1** for GP locations). Soil samples were collected from each of the borings at the soil interval with the highest screening readings using a PID. Both soil and groundwater samples were collected from each boring with the exception of GP-69, where samples were collected from the fourth attempted boring at the location after three initial attempted borings hit refusal prior to the target depth (samples were collected on the fourth attempt at this location due to the refusal at the first 3 locations).
- Installation of 3 direct-push borings (GP-74 to GP-76) with soil and groundwater samples in June 2008 at the CSXT Property boundary along East Potomac Street (across from the L. S. Fuel Station located at 128 E. Potomac Street).
- Quarterly sampling of groundwater from all CSXT and NPS monitoring wells in May 2008.

A third version of the SCM was submitted on August 29, 2008, and incorporated all data collected since the February 8, 2008 SCM submittal. Several phases of

corrective measures were then completed at the Site to further define the nature and extent of contamination at the Site and enhance LPA recovery efforts. These activities include a dual-phase extraction pilot study, implementation of the CAP, additional well installations, and continued groundwater sampling activities. These activities are further described below:

- In 2008/2009, a DPE pilot study was conducted at MW-41 and EW-2 to evaluate the applicability and effectiveness of this remedial alternative at the Site. Data were collected to estimate LPH recovery rates, groundwater recovery rate, and hydraulic and pneumatic radii of influence while extracting from MW-41 and EW-2. A sample of LPH was collected at CSXT MW-49 and CSXT MW-4R in June 2008, to evaluate the physical characteristics of the LPH at the Site, which may affect LPH mobility and recoverability. Samples were analyzed for interfacial tension, viscosity, density, and specific gravity at a range of temperatures. Six new monitoring wells (MW-53 to MW-58) were installed in December 2008, as monitoring points for the DPE pilot study.
- Implementation of the CAP included installation of three LPH skimmer pumps and five passive LPH skimmers installed in July 2009 to facilitate consistent LPH recovery. Operation and maintenance (O&M) visits have been completed on a regular basis, typically bi-weekly, at the Site. All wells which contained measureable LPH within the previous six months were gauged on at least a monthly basis. LPH recovery is conducted using a peristaltic pump or absorbent sock as warranted at wells containing measureable LPH where a skimmer pump or absorbent sock was not installed.
- After the August 2008 groundwater sampling was completed, the MDE approved a reduction in the groundwater sampling monitoring well network and groundwater sampling frequency. The current groundwater sampling monitoring well network consists of CSXT MW-3, CSXT MW-6R, CSXT MW-22, CSXT MW-24, CSXT MW-25, CSXT MW-29, CSXT MW-43, CSXT MW-51, NPS MW-1, NPS MW-2, NPS MW-4, NPS MW-5, NPS MW-13, NPS MW-14, and NPS MW-16, which are sampled on a semi-annual basis.
- Three additional QED ferret skimmer pumps were installed in September 2010.
- Seven additional monitoring wells (MW-59 through MW-65) were installed in March 2012. The wells were drilled in the area around the two MARC 20,000 gallon diesel ASTs, located to the west of the roundhouse. Well locations were chosen based on the results of previous geoprobe investigations conducted at the Site.

On April 30, 2012, a fourth version of the SCM was submitted to the MDE, which incorporated all data collected at the Site since the previous submittal of the SCM.

1.1.2 NPS Property

1.1.2.1 1991 NPS C&O Canal Soil Survey

In September 1991, NPS initiated a preliminary survey of soil conditions within the prism/footprint of the canal in support of the on-going C&O Canal re-watering project. The three main objectives of the survey were to inspect the soil profile for petroleum impacts which may have migrated into the canal, document soil conditions above and below the clay liner in the re-watering zone, and to determine the thickness of the clay liner.

The survey began at Canal Lift Lock 30 and continued east to the entry of the Brunswick town camp area. The soil survey included the installation of thirty-four soil borings installed along the center of the canal to depths ranging from 0 to 5 feet below ground surface (ft bgs). Soil cores were obtained using a 4-inch bucket auger. Soil lithology was recorded and soil color was determined using the Munsell Soil Color Charts. Linear spacing between soil boring locations varied from 50 ft (western investigation area) to 200 ft (eastern investigation area). During the survey, petroleum presence was determined by odor and/or visual impacts (e.g. staining). No soil samples were submitted for laboratory analysis during this investigation. Observations from several boring locations suggested petroleum impacts. At Location 1, petroleum odor was noted at 14" - 40" bgs. At Location 13, petroleum odor was noted at 17" bgs to 34" bgs. Potential impacts were also noted in Location 14, Location 15, and Location 17 spanning a linear length of approximately 600 ft. At Location 22, impacts were noted at 12" - 35" bgs. The complete results of this canal soil survey can be found in the *Soil Investigation within C&O Canal, Mile Point 54.2 to 55.2, Brunswick, Maryland* (Eder 1994).

Petroleum impacts to soil in the canal prism/footprint appeared to occur above the clay liner. The canal survey also indicated the clay liner in the study area appears to be discontinuous. This is more evident towards the western portion of the study area where cinders and other metal fragments were observed at various depths in the soil borings.

1.1.2.2 1992 - 1993 Eder Associates Follow-up C&O Canal Soil/Sediment Investigation

In response to the NPS soil survey results, CSXT retained Eder Associates (EA) to further characterize sediments in the canal prism/footprint. A follow-up sediment

sampling event was initiated in March 1992 and sediment samples were collected from eight locations (EA-1 - EA-8) adjacent to areas where petroleum related impacts were noted during the NPS soil survey. Analytical results of the 1992 sampling event confirmed the presence of petroleum impacted sediments in samples EA-3, EA-5, and EA-7 and EA-8. As a result, three areas of concern were established for further investigation in the areas encompassing these sampling locations: Area 1 (EA-3), Area 2 (EA-5), and Area 3 (EA-7 and EA-8). The approximate locations of the three areas of concern are displayed on **Figure 2**.

In July 1993, a subsequent sediment delineation investigation was initiated to investigate the three explicit areas of concern. Thirty-three soil borings were installed and sub-surface soil samples were collected and submitted for laboratory analysis of Total Petroleum Hydrocarbons Diesel Range Organics (TPH-DRO) via U.S. Environmental Protection Agency (USEPA) Method 8015. A hollow stem auger drill rig was used to advance a 5 ft split spoon into the canal prism. Lithology of the material was logged and a photoionization detector (PID) was used to screen samples at select locations. The extent of soil contamination was defined by TPH-DRO exceedances of 400 milligrams per kilograms (mg/kg). This delineation criteria was established in the June 1, 1993 Work Plan, and agreed upon by both CSXT and NPS.

- **Area 1 Delineation**

Area 1 is located on the western most portion of the study area. A total of 22 soil/sediment samples were collected from 13 borings. Sampling results indicated TPH-DRO concentrations above the delineation criteria agreed to by CSXT and NPS (400 mg/kg) below the clay layer starting at the culvert (B-9) on the western portion of the study area extending to B-11. The depth of the petroleum impacted material was mainly observed between 3 and 4 ft bgs. Detections of TPH-DRO above the June 1993 delineation criteria agreed to by CSXT and NPS were observed at three locations (B-9, B-11, and B-13) with concentrations ranging from 1,400 mg/kg (B-11) to 32,000 mg/kg (B-14).

- **Area 2 Delineation**

Area 2 is located east of the Area 1 study area. A total of nine soil/sediment samples were collected from eight borings. Sampling results indicated that petroleum impacted material was only observed above the clay liner in this area (< 1 ft bgs). Detections of TPH-DRO above the June 1993 delineation criteria agreed to by CSXT and NPS were observed at two locations (B-15 and B-19) with concentrations ranging of 1,200 mg/kg and 21,000 mg/kg, respectively.

- **Area 3 Delineation**

Area 3 is located furthest east from Canal Lock Lift 30 of the three study areas. A total of 18 soil/sediment samples were collected from 12 borings. Sampling results indicated that petroleum impacted material was observed at depths between 2 and 5 ft bgs. Detections of TPH-DRO above the June 1993 delineation criteria agreed to by CSXT and NPS were observed at three locations (B-26, B-30, and B-31) with concentrations ranging from 490 mg/kg (B-26) and 1,900 mg/kg (B-30).

Complete results from the 1992-1993 canal investigation can be found in the *Soil Investigation within C&O Canal, Mile Point 54.2 to 55.2, Brunswick, Maryland* (Eder 1994).

1.1.2.3 Ecology and Environment C&O Canal Soil/Sediment and Groundwater Investigations

On behalf of the NPS, in March 1996, Ecology and Environment, Inc. (E&E) submitted the *C&O Canal – Brunswick Site, Brunswick, Maryland, Site Assessment and Characterization (Draft)* (E&E 1996) based on additional sediment and soil sampling. The results of the collection and analysis of subsurface soils (14 samples) within the canal prism indicated that there were no polycyclic aromatic hydrocarbons (PAHs) compounds exceeding the EPA Region III Risk-Based Concentrations for industrial exposure.

In July 1997 E&E submitted an Investigation Report on behalf of the NPS, *C&O Canal, Brunswick, Maryland, Site Investigation*. (E&E 1997), summarizing additional surface and subsurface soil, as well as monitoring well installation and groundwater sampling conducted in August and September 1996. Three surface soil samples (NPS SS-1 through NPS SS-3) were collected in or next to the canal. Surface soil analytical results indicated detectable PAH concentrations below screening criteria in all three samples and one TPH concentration (760 mg/kg) above the current MDE non-residential cleanup standard (620 mg/kg) at NPS-SS-1 collected in the canal (E&E, 1997). The other surface soil TPH concentrations were below MDE cleanup standards.

Results of subsurface soil sampling (ten samples collected from nine borings) indicated detectable PAH concentrations in eight of the samples (all below screening criteria) and one TPH concentration (1,000 mg/kg) above the MDE cleanup standard detected in sample NPS-SB-4 collect from 8 to 10 ft below ground surface.

In order to evaluate groundwater quality along the C&O Canal, the NPS installed five monitoring wells (NPS MW-1 through NPS MW-5) along the canal in August-September 1996. The NPS collected four rounds of groundwater samples from these



monitoring wells between 1996 and 1999 before installing additional wells (NPS MW-10 through NPS MW-17) in 2001. Only one NPS well, NPS MW-4, has previously exhibited measurable LPH, at thicknesses ranging from 0.01 to 0.65 ft. The last recordable LPH thickness at NPS MW-4 was 0.04 ft in October 2007.

From December 2002 through January 2006, the NPS collected groundwater samples from the monitoring wells on their property approximately every six months (December 2002, June 2003, January 2004, July 2004, December 2004, July 2005, and January 2006). Groundwater samples collected from the NPS wells have historically been analyzed for TPH-DRO. All NPS wells were incorporated into the CSXT monitoring program as requested by MDE in correspondence dated November 15, 2006. The current sampling program includes seven of the NPS monitoring wells, which are analyzed for TPH-DRO and full-suite VOCs including fuel oxygenates. Water-level and LPH measurements are collected at all NPS wells on a quarterly basis.

The April 30, 2012 Revised Site Conceptual Model (SCM) (ARCADIS, 2012) provides additional detail and interpretation of the previous investigations.

1.2 Local Geology

Borings on and near the Site indicate geologic conditions that are typical of a piedmont and alluvial hydrogeologic setting. The bedrock units underlying the area include a Pre-Cambrian granodiorite and biotite granite gneiss, part of the South Mountain Anticlinorium and Frederick Valley (MGS, 1958). The most common bedrock unit locally is gneissic granodiorite, commonly colored light gray to green and interlayered in places with dark hornblende diorite. This particular unit is generally of low primary porosity and therefore is not a primary source for large water supplies. None of the on-site borings penetrate the bedrock unit; however, some borings, such as NPS MW-5, indicate the presence of a thick saprolite layer at least 4 feet thick. Saprolite is generally very low permeability weathered rock and is commonly found up to thicknesses of 60 feet in this region.

Quaternary alluvium overlies the saprolite and is composed of heterogeneous layers of clay, silt, sand, and gravel. Alluvium is associated with river depositional environments; at the Site and NPS property, this material is associated with the Potomac River and its tributaries. Underlying the Site and NPS Property are two distinct overburden deposits. Directly overlying the saprolite is an orange-brown medium- to coarse-grained gravelly sand unit that has been observed in soil cores from CSXT MW-5. The gravelly sand unit thins south of the Site approaching the Potomac River (NPS MW-5). Overlying the gravelly sand is a silty clay unit, described as greenish gray or brown and up to 15 feet thick. Although the silty clay is consistently observed in borings across the site, it

appears to be thinner in locations near the former AST (GP-27, GP-30, and GP-44). This unit also thins to the south as it approaches the Potomac River. Varying types of fill materials including sand or cinders, about 2 to 4 feet thick overlie the clay unit at different locations.

1.3 Local Hydrogeology

The shallow groundwater flow system is of greatest interest to understanding the fate and transport of LPH and dissolved phase TPH-DRO at the Site and NPS property. Hydrogeologic flow regimes in the overburden water-bearing units, the shallow water-table unit and the lower gravelly sand unit that is semi-confined by the upper silty clay, are influenced primarily by surface-water flow interaction. Although groundwater flow has been observed in both units, the primary groundwater flux occurs in the gravelly sand unit. Groundwater flow directions inferred from water-level measurements in both units are perpendicular to the canal and toward the Potomac River. The saprolite and deeper bedrock units are of low permeability and therefore, do not significantly interact with shallow unconsolidated deposits.

Local perturbations in groundwater elevation and flow direction are attributed to subtle variations in the thickness of the overburden units, and the influence observed around the roundhouse foundation. March 2012 water levels in wells installed before 2009 (i.e. wells with historical water levels) ranged from 224 ft msl to 239 ft msl; since 1995, water levels in these wells have ranged from 219 ft msl to 239 ft msl. This indicates that recent results are consistent with historical data. Groundwater flow is typically below the base of the C&O Canal, which has an elevation of approximately 230 to 231 ft msl.

The BRT was installed through the silty clay unit approximately 15 feet below the water table to provide an effective barrier to migration of LPH. The BRT also behaves as a barrier to groundwater flow in the silty clay unit and therefore, produces some increase in water levels upgradient of the BRT. This slight increase in water level creates downward hydraulic gradients to allow groundwater to enter the underlying sand and gravel and flow below the BRT towards the south.

Groundwater flow directions in the eastern portion of the Site and NPS Property are more variable. Groundwater flow from the Site to the NPS property appears to be southeasterly. Large sections of concrete foundation remain in the footprint of the roundhouse, creating a slight mounding effect on groundwater flow within the footprint, and slightly redirecting flow around the roundhouse foundation. South of the C&O Canal, groundwater flow appears to transition to a southwesterly flow direction.

1.4 Supplemental Investigation Objectives

1.4.1 Off-site Objectives

There are two objectives of the off-site investigation activities described in this work plan:

- Understand how potential contamination of soil/sediment in and below the canal prism would affect future use of the canal, including re-watering the canal; and,
- Further evaluate off-site groundwater quality.

The tasks outlined in Sections 2.1 and 2.2 will be completed in support of a comprehensive evaluation of these objectives.

1.4.2 On-site Objectives

There are two objectives of the on-site investigation activities described in this work plan:

- Address data gaps related to the delineation of LPH occurrence; and,
- Further evaluate the efficacy of the current remedial strategy at the site.

The tasks outlined in Section 2.2 and 2.3 will be completed in support of a comprehensive evaluation of these objectives.

2. Supplemental Investigation Activities

2.1 Soil Characterization of the C&O Canal Prism Footprint

In order to fully characterize potential petroleum related impacts to the C&O Canal Prism/Footprint, additional soil samples will be collected from the canal prism. Soil/sediment samples will be collected along the approximate center of the canal at approximately 20 foot centers from each of the previously identified Areas of Concern (AOC) (Area 1, Area 2, and Area 3) displayed on **Figure 2**. Each soil boring will be installed to approximately 10 ft bgs or to the groundwater table if it is shallower than 10 ft bgs, using a direct-push drill rig. A core sampler with a clear acetate liner will be hydraulically driven by the direct-push rig into the ground at each sample location in order to collect soil in 4-foot intervals until the target depth is reached. Each boring will

be logged continuously to its terminal depth and soil lithology descriptions will be recorded on standard ARCADIS boring logs. A flame ionization detector (FID) will be used to continuously screen the soil cores. The thickness of the clay liner will also be recorded at each of the boring locations.

Two soil samples will be collected at each location, one from the material above the clay liner and one below the clay liner, at sample depths corresponding to the depth where the highest PID reading was recorded within each sample core above and below the clay liner. All soil/sediment samples will be shipped to TestAmerica Laboratories in Savannah, Georgia under chain-of-custody for the following analyses:

- Total Petroleum Hydrocarbon-Gasoline Range Organics (TPH-GRO) via USEPA method 8015;
- Total Petroleum Hydrocarbon-Diesel Range Organics/Oil Range Organics (TPH-DRO/ORO) with and without Silica Gel Treatment (SGT) via USEPA method 8015;
- Full-suite volatile organic compounds (VOCs) including fuel oxygenates via USEPA method 8260; and
- Semivolatile Organic Compounds (SVOCs) via USEPA method 8270.

The SGT process and the advantages of using SGT with TPH analysis are discussed in detail in *The Technical Case for Eliminated the Use of the TPH Analysis in Assessing and Regulating Dissolved Petroleum Hydrocarbons in Ground Water* (Zemo and Foote 2003) (**Appendix A**).

Each boring will be properly abandoned after sample collection by filling the boring with bentonite to the surface grade of the canal prism to eliminate a potential vertical conduit/pathway of migration. The surface of the borings will be restored to original condition. All soil/sediment cores will be properly containerized and disposed off-site.

2.2 Dissolved Phase Hydrocarbon Fate and Transport Evaluation

In order to further refine the fate and transport of dissolved phase hydrocarbons at the Site, a subset of existing monitoring wells along both the northern and southern boundaries of the canal prism will be redeveloped and sampled. Additionally, rising head testing and groundwater sampling will be conducted on a select subset of wells to support the evaluation of the vertical distribution of dissolved phase hydrocarbons. Testing and sampling methodology are presented in detail in the subsequent sections.

2.2.1 Monitoring Well Redevelopment

Thirty monitoring wells (**Table 2**) will be redeveloped to remove fines from the well and surrounding annulus using over-pumping and surging methods. The volume of water removed during well development will be at least five times the volume of the well casing. After this volume has been removed, the well will be pumped at a low-flow purge rate until the water quality parameters (pH, specific conductance, temperature, and turbidity) stabilize within 10% over three consecutive readings to ensure that water from the surrounding formation has entered the well and achieved steady state conditions.

A Well Development Log will be used to document well development activities including depth to water measurements, purge rate, volume removed, field parameters, and visual observations.

2.2.2 Groundwater Sampling

Following monitoring well redevelopment activities, groundwater samples will be collected via three volume purge methodology from eighteen supplemental monitoring wells presented on **Table 2**, concurrent with the approved semi-annual groundwater sampling event.

Groundwater samples will be collected following removal of three well volumes using disposable bailers at each of the monitoring wells being sampled. Field parameters including (pH, specific conductance, dissolved oxygen, temperature, redox potential) will be collected after each volume is purged and recorded on ARCADIS standard Groundwater Sampling Logs.

All groundwater samples will be shipped to TestAmerica Laboratories in Savannah, Georgia under routine chain-of-custody for the following analyses:

- TPH-GRO via USEPA method 8015;
- THP-DRO/ORO with and without SGT via USEPA method 8015;
- Full-suite VOCs including fuel oxygenates via USEPA method 8260; and
- SVOCs via USEPA method 8270.

2.2.3 Rising Head Testing and Groundwater Sampling

Four rising head tests will be performed as part of this SIWP in order to better understand the contribution of groundwater from both the silty clay and the gravelly sand units by measuring the rate of groundwater recharge into the well. The head tests will be conducted at four select monitoring wells, identified on **Table 2** and shown on **Figure 3**, which were selected based on proximity and screen interval. Two of the selected monitoring wells (MW-21 and MW-25) are screened only within the silty clay unit, and two monitoring wells (MW-29 and MW-35) are screened over both the silty clay and the gravelly sand units. These wells will be redeveloped using the same method described in Section 2.2.1 prior to conducting the rising head testing in order to ensure that results of the tests are representative of in situ conditions and not monitoring well annulus.

Transducers will be deployed in each well at least one half hour prior to beginning each rising head test to collect static groundwater level elevations. After the transducer has recorded static conditions, a disposable bailer will be used to purge one bailer volume from the well. The well will then be allowed to recharge to static conditions. This test will be repeated three times at each well.

Upon completion of the rising head tests, groundwater from each of the six wells will be sampled following the sampling methodology described in Section 2.2.2, and analyzed for the same parameters. A comparison of the analytical results from samples collected from these select wells (three wells screened within the silty clay unit and three wells screened across both the silty clay and the gravelly sand units) will be used to assess the contribution of groundwater contaminants from each of these units, and to evaluate the vertical distribution of dissolved phase hydrocarbons.

2.3 Further Evaluation of Liquid Phase Hydrocarbons (LPH)

2.3.1 Monitoring Well Installation on CSXT Property

Based upon review of historical LPH gauging and recovery efforts at the Site, the addition of four monitoring wells (CSXT MW-67 through CSXT MW-70) will further delineate subsurface LPH presence around the turntable and between the two existing MARC 20,000 gallon diesel aboveground storage tanks (ASTs) and the former diesel AST. **Figure 4** shows the proposed locations of the four additional monitoring wells. All four wells will be installed to twenty-five feet below ground surface. Well construction will include a 4-inch PVC riser installed to 5 ft bgs, with twenty feet of 4-inch 10-slot PVC screen. The wells will be finished as flush mounted wells. New wells containing measureable thicknesses of LPH will be evaluated for LPH recovery. Recovery

methods to be implemented at the additional wells will be evaluated based on the amount of measureable LPH observed in each well and the logistics of using the various recovery methods in certain areas of this active rail yard. Wells that do not contain measureable thicknesses of LPH will be included in the quarterly groundwater sampling program.

2.3.2 LPH Characterization

Samples of LPH and groundwater will be collected from CSXT MW-37, MW-56 and MW-62 to evaluate the physical characteristics of the LPH at the Site, which will be used to evaluate LPH mobility and recoverability. LPH samples will be submitted to PTS Laboratories in Santa Fe Springs, California under routine chain-of-custody for the following analyses at average-annual groundwater temperature:

- Viscosity;
- Density; and
- Specific gravity.

2.3.3 Short-term LPH Stress Testing

LPH recoverability can be characterized through short-term LPH stress testing, also called LPH baildown testing. LPH baildown testing will be performed at four monitoring wells, CSXT MW-37, CSXT MW-41, CSXT MW-49, CSXT MW-56 (**Table 2**). LPH recovery will be discontinued for approximately two weeks prior to completing the baildown testing. Each of the wells will be redeveloped using the same method described in Section 2.2.1 prior to baildown testing in order to ensure that results of the stress tests are representative of in situ conditions and not monitoring well annulus.

An LPH baildown test is initiated by quickly removing accumulated LPH from a well, making it analogous to a groundwater rising-head slug test. The rate of LPH flow into the well is a function of LPH saturation, permeability of the surrounding formation to LPH, physical properties of the LPH (density, viscosity, interfacial tension between LPH and water), and magnitude of the initial hydraulic gradient toward the well developed during LPH removal. Fluid levels are measured before and after an LPH baildown test and LPH recovery during the test is observed. LPH baildown tests will be performed twice at each of the four monitoring wells.

The LPH transmissivity calculated from analyzing baildown test data can be utilized to characterize the hydraulic properties of LPH on site and to quantitatively characterize LPH recoverability.

2.3.4 LPH Mobility and Recoverability Assessment

A comprehensive LPH mobility and recoverability assessment will be completed as part of this work plan. An LPH recoverability and mobility assessment uses multiple lines of evidence to determine current LPH mobility, the potential for future LPH migration, and LPH recoverability. Immobile LPH is LPH that has been functionally-locked in pore spaces. Mobile LPH is capable of moving laterally and vertically at the pore-scale. Migrating LPH has sufficient mobility at the pore-scale to cause expansion of the plume footprint. The LPH mobility and recoverability assessment will be completed using multiple lines of site-specific evidence, such as:

- LPH Distribution
 - LPH observations in monitoring wells for lateral extent
 - Historical photoionization detector and TPH results for vertical extent

- LPH Mobility
 - LPH pore velocity calculated using transmissivity resulting from baildown test data and compared to ASTM's mobility criterion

- LPH Migration Potential
 - LPH observations in monitoring wells relative to groundwater elevations
 - Dissolved-phase plume stability analysis of historical TPH-DRO concentrations

- LPH Recoverability
 - Current LPH transmissivity calculated using product skimming data and baildown test data and compared to Interstate Technology and Regulatory Council's guidance

- Decline curve analysis using product skimming data to estimate remaining timeframe of current remedial approach

The data used for the LPH mobility and recoverability assessment will be drawn from both historical data, data collected during the implementation of this work plan, and as necessary, appropriate literature-derived data. The current LPH remedial strategy will be re-evaluated based upon the results and conclusions of the LPH mobility and recoverability assessment, and recommendations will be made regarding future remedial options.

3. Reporting

All historical data and data collected from the implementation of this work plan will be comprehensively evaluated in a Supplemental Investigation Report/Revised Site Conceptual Model (SCM). The Revised SCM will include a comprehensive evaluation of both the on-site and off-site investigation objectives. The LPH Mobility and Recoverability Assessment will be included as an Appendix to the Supplemental Investigation Report/Revised SCM, and any recommendations regarding remedial strategy at the Site will be incorporated into the SCM.

4. Schedule

The activities outlined in this work plan will be completed upon MDE approval of this work plan. It is anticipated that the field activities will be completed within two months of the work plan approval, and the reporting will be completed within two months of the completion of all field activities.

5. References

ARCADIS, 2007. Data Package Memo

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ARCADIS, 2008b. Revised Site Conceptual Model.

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Supplemental Investigation Work Plan

C&O Canal/Brunswick Rail
Yard, Brunswick, Maryland

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Tables

Table 1
History of Environmental Activities Associated with the Site and the C&O Canal
C&O Canal/Brunswick Rail Yard
Brunswick, Maryland

Date/Year	Company/Agency	Action Type	Description
September 1991	NPS	Investigation	National Park Service (NPS) conducted a soil survey evaluating the presence of petroleum residuals in the C&O canal silt near CSXT property in support of a bid for a rewatering permit. Reportedly, visual identification of petroleum was made in three areas; however, no samples were submitted for analysis of petroleum constituents.
March 1992	CSXT/Eder	Remediation	CSXT/Eder Associates (Eder) provided oversight for removal of a 16,000 gallon diesel underground storage tank (UST) adjacent to the former pump house and 500,000 gallon aboveground storage tank (former AST System). The UST had been previously pumped out and taken out of service in 1974. Approximately 100 cubic yards of impacted soils related to the UST were excavated and properly treated/disposed off-site. Analysis of soil confirmation sampling from the excavation showed total petroleum hydrocarbon (TPH) concentrations below the current MDE non-residential cleanup level of 620 mg/kg.
March 1992	CSXT/Eder	Investigation	CSXT/Eder collected soil samples to characterize soils identified in the 1991 NPS report as petroleum impacted.
July 1993	CSXT/Eder	Investigation	CSXT/Eder conducted a focused sediment/soil boring investigation performed to further investigate the extent of residual petroleum compounds in the C&O Canal in the three primary areas of concern and a small area near Lock #30.
January 20, 1994	MDE	Correspondence	Maryland Department of the Environment (MDE) required that CSXT install four monitoring wells on CSXT property between the C&O Canal and four suspected source areas, including the 500,000 gallon AST, the tank car diesel fuel unloading racks, the diesel fueling pump house, and the roundhouse.
July 1994	CSXT/Eder	Investigation	CSXT/Eder installed four monitoring wells (MW-1, 2, 3, and 4) to investigate the groundwater quality between the suspected source areas and the C&O Canal. Groundwater samples collected from the four monitoring wells were analyzed for BTEX and TPH-DRO. Liquid-phase hydrocarbons (LPH) are later observed at MW-2. CSXT/Eder recommended installation of two additional monitoring wells downgradient of MWs 1, 2, and 4 on the northern canal tow path.
August 30, 1994	MDE	Correspondence	MDE approves the installation of the two additional wells and requests that CSXT install three additional monitoring wells with at least one installed on the south side of the C&O Canal.

Table 1
History of Environmental Activities Associated with the Site and the C&O Canal
C&O Canal/Brunswick Rail Yard
Brunswick, Maryland

Date/Year	Company/Agency	Action Type	Description
November 1994	CSXT/Eder	Investigation	CSXT/Eder conducts a product baildown test at MW-2. Results indicate a very slow LPH recovery rate. Based upon the slow recovery rate, a passive product recovery system was recommended by Eder.
January 1995	CSXT/Eder	Remediation	CSXT/Eder initiated passive free product recovery utilizing a Siphons Without a Pump (SWAP) 4 unit at MW-2.
August-September 1995	CSXT/Eder	Investigation	After coordination with NPS for property access, CSXT/Eder installed additional monitoring wells (MW-5, 6, 8, and 9) to further evaluate groundwater quality downgradient and in the vicinity of the former AST System. Groundwater samples were collected from MW-1, 3, 5, 6, 8, & 9 (LPH at MW-2 and MW-4). Groundwater samples were analyzed for BTEX, naphthalene, and TPH-DRO.
March 1996	NPS/E&E	Site Assessment and Characterization	On behalf of the NPS, Ecology and Environment, Inc. (E&E) prepared a Draft Site Assessment and Characterization Report based on additional sediment and soil sampling. The results of the collection of subsurface soils within the canal prism indicated that there were no PAH compounds exceeding the EPA Region III Risk-Based Concentrations for industrial exposure.
August – September 1996	NPS/E&E	Investigation	E&E installed five monitoring wells (NPS MW-1, 2, 3, 4, and 5) along the Canal on NPS property to determine if there has been any migration of residual petroleum compounds onto NPS property. Groundwater samples were collected from the five NPS wells and three CSXT wells (MW-6, 8, and 9) by NPS and analyzed for VOCs, SVOCs, and TPH. Dissolved phase total petroleum hydrocarbons (TPH) were detected in seven of the eight samples (all except NPS MW-4). PAH concentrations in groundwater were detected at two monitoring wells (NPS MW-4, and MW-6). These results were reported in the July 1997 Investigation Report (below).

Table 1
History of Environmental Activities Associated with the Site and the C&O Canal
C&O Canal/Brunswick Rail Yard
Brunswick, Maryland

Date/Year	Company/Agency	Action Type	Description
July 1997	NPS/E&E	Investigation Report	On behalf of the NPS, E&E prepared and submitted an investigation report including the results of the surface and subsurface soil sampling conducted in August and September 1996 and monitoring well installation and groundwater sampling conducted during the same timeframe. Groundwater sampling results are discussed above. Surface soil analytical results indicated detectable PAH concentrations below screening criteria in all three samples and one TPH concentration above the MDE cleanup standard at NPS-SS-1 collected in the canal. The other TPH concentrations collected from surface soils were below MDE cleanup standards. Results of subsurface soil sampling (10 samples collected from 9 borings) indicated detectable PAH concentrations in 8 of the samples (all below screening criteria) and one TPH concentration (1,000 mg/kg) above the MDE cleanup standard detected in sample NPS-SB-4 collect from 8 to 10 ft below ground surface.
February 1998	CSXT/Eder	Investigation	LPH baildown tests were conducted at two CSXT wells (MW-1 and MW-6). The results of the baildown tests indicated that free product entered both wells at an extremely low rate. The water table rose several feet in November and no product was measured in either well, suggesting a strong association between water table fluctuations and the presence of free product.
1998	CSXT/Eder/ Gannett-Fleming	Remediation	CSXT/Gannett Fleming (purchased Eder) expanded LPH recovery to include MWs 1, 2, 4, and 6.
February 8, 1999	CSXT/Gannett-Fleming	Investigation	CSXT/Gannett Fleming submitted a Conceptual Investigation Plan (CIP) to evaluate any potential threat to surface water and to consider scenarios for adjusting the product recovery program, if necessary. The CIP also included a remedial alternatives analysis.
November 1999 – August 2000	CSXT/Gannett-Fleming	Investigation	Eleven soil borings and temporary piezometers (TP-1 through TP-11) were installed near the area with LPH to delineate the extent of LPH. Two soil samples are collected for geotechnical purposes.
December 2000	CSXT/Gannett-Fleming	Feasibility Report	CSXT/Gannett-Fleming submitted a Site Investigation Report including feasibility of remedial alternatives. The conclusion of the evaluation of remedial alternatives was that a collection trench recovery system located along the CSXT/NPS property line should be considered, carefully evaluating safety and constructability due to rail operations.
2001	NPS/E&E	Investigation	E&E installed eight additional wells NPS MW-10 through NPS MW-17.

Table 1
History of Environmental Activities Associated with the Site and the C&O Canal
C&O Canal/Brunswick Rail Yard
Brunswick, Maryland

Date/Year	Company/Agency	Action Type	Description
June 2003	NPS/E&E	Investigation	E&E conducted groundwater sampling of the NPS wells for analysis of TPH-DRO, LPH is observed at NPS-MW-4.
October 2003 – March 2004	CSXT/Gannett-Fleming	Remediation	CSXT/Gannett-Fleming constructs a barrier/recovery trench to stop migration of petroleum to NPS property. The initial design was to approximately 525 ft long and 12-15 feet deep. However, the design was revised after it could not be constructed solely on CSXT property. The design was revised a second time when the trench, running from west to east, could not be extended to a point south of TP-4 because construction would subvert a utility pole. The trench as constructed includes five collector sumps, accumulated LPH is removed via a vacuum truck. CSXT/Gannett Fleming installed barrier/recovery trench (BRT) with 5 internal collection sumps (CS-1 through CS-5).
July 2004	CSXT/Gannett-Fleming	Remediation	CSXT/Gannett-Fleming initiated monthly enhanced fluid recovery (EFR) events at monitoring wells/collector sumps with LPH. CSXT/Gannett Fleming began enhanced fluid recovery (EFR) activities to reduce measurable liquid phase hydrocarbons (LPH) at MW-2, EW-3, EW-4, and EW-5 and BRT collections sumps. EFR activities expanded to include all wells with measurable LPH.
January 2005	CSXT/ARCADIS	Remediation	CSXT/ARCADIS continued with monthly EFR events, Approximately 32,466 gallons of total fluids (LPH and water) were removed from July 2004 through June 2009.
September 2006	CSXT/ARCADIS	Remediation	CSXT/ARCADIS installed an automated LPH recovery pump in MW-2. A total of 54 gallons of LPH were recovered from September 2006 through July 2008.
January 30, 2007	CSXT/ARCADIS	SCM and Work Plan Submittal	CSXT/ARCADIS submitted the <i>Site Conceptual Model and Supplemental Work Plan</i> including installation of additional monitoring wells and abandonment of temporary wells.
April 16, 2007	MDE	Correspondence	MDE approved the <i>Site Conceptual Model and Supplemental Work Plan</i> dated January 30, 2007.
June 2007	CSXT/ARCADIS	Investigation	CSXT/ARCADIS abandoned 6 temporary wells (TP-1, TP-3, TP-4, TP-5, TP-10, and TP-11) and installed 8 permanent groundwater monitoring wells (MW-4R and MW-21 through MW-27).
July 18, 2007	CSXT/MDE	Consent Order	MDE and CSXT signed the Consent Order.

Table 1
History of Environmental Activities Associated with the Site and the C&O Canal
C&O Canal/Brunswick Rail Yard
Brunswick, Maryland

Date/Year	Company/Agency	Action Type	Description
July/August 2007	CSXT/ARCADIS	Investigation	CSXT/ARCADIS installed 24 direct-push borings (GP-20 and GP-26 through GP-49) with soil and groundwater sampling.
October 3, 2007	CSXT/ARCADIS	Work Plan Submittal	CSXT/ARCADIS submitted the <i>Work Plan for Monitoring Well Installation and Groundwater Sampling</i> .
November 9, 2007	MDE	Correspondence	MDE approved the <i>Work Plan for Monitoring Well Installation and Groundwater Sampling</i> dated October 3, 2007.
November 2007	CSXT/ARCADIS	Investigation	CSXT/ARCADIS installed 17 permanent groundwater monitoring wells (MW-20, MW-28 through MW-33, MW-35, MW-37, MW-38, MW-39, MW-41, MW-43, and MW-49 through MW-52).
February 8, 2008	CSXT/ARCADIS	SCM Submittal	CSXT/ARCADIS submitted the <i>Revised Site Conceptual Model (SCM)</i> (second version of the SCM).
March 12, 2008	CSXT/ARCADIS	Work Plan Submittal	CSXT/ARCADIS submitted the <i>Additional Site Characterization Work Plan</i> .
May 30, 2008	MDE	Correspondence	MDE approved the <i>Additional Site Characterization Work Plan</i> dated March 12, 2008.
June 2008	CSXT/ARCADIS	Investigation	CSXT/ARCADIS installed 24 direct-push borings (GP-53 through GP-76) with soil and groundwater sampling.
August 29, 2008	CSXT/ARCADIS	SCM and CAP Submittal	CSXT/ARCADIS submitted the <i>Revised SCM</i> (third version of the SCM) and the <i>Corrective Action Plan</i> , including the Dual-Phase Extraction (DPE) pilot test.
October 28, 2008	MDE	Correspondence	MDE approved the DPE pilot test portion of the <i>Corrective Action Plan</i> , with modifications.
December 16-18, 2008	CSXT/ARCADIS	Investigation	CSXT/ARCADIS installed 6 permanent groundwater monitoring wells (MW-53 to MW-58) as monitoring points for the DPE pilot test.
January 7 - 13, 2009	CSXT/ARCADIS	Investigation	CSXT/ARCADIS conducted DPE Pilot Test at MW-41 and EW-2.
March 2, 2009	CSXT/ARCADIS	CAP Addendum Submittal	CSXT/ARCADIS submitted the <i>Corrective Action Plan Addendum</i> which included the <i>Dual-Phase Extraction Pilot Test Results</i> .

Table 1
History of Environmental Activities Associated with the Site and the C&O Canal
C&O Canal/Brunswick Rail Yard
Brunswick, Maryland

Date/Year	Company/Agency	Action Type	Description
May 27, 2009	MDE	Consent Order Milestone	MDE approved the <i>Corrective Action Plan Addendum</i> dated March 2, 2009, start of three year remedial goal specified in Consent Order.
July 14, 2009	CSXT/ARCADIS	Remediation	CSXT/ARCADIS implemented LPH removal activities in accordance with the <i>Corrective Action Plan Addendum</i> dated March 2, 2009. Activities included the installation of 3 LPH skimmer pumps and 5 passive LPH skimmers.
May 2010	CSXT/ARCADIS	Remediation	Approximately 267 gallons of LPH recovered since implementation of LPH removal activities in accordance with the <i>Corrective Action Plan Addendum</i> in July 2009.
June 4, 2010	CSXT/ARCADIS	Remediation	CSXT/ARCADIS submitted <i>Proposed LPH Recovery System Enhancements</i> .
July 8, 2010	MDE	Correspondence	MDE approved <i>Proposed LPH Recovery System Enhancements</i> , dated June 4, 2010.
September 2, 2010	CSXT/ARCADIS	Remediation	CSXT/ARCADIS installed 3 additional LPH skimmer pumps per the <i>Proposed LPH Recovery System Enhancements</i> , dated June 4, 2010.
December 15, 2011	CSXT/ARCADIS	Investigation	CSXT/ARCADIS submitted a Proposed Additional Well Installation Letter Work Plan which included the installation of 8 additional monitoring wells (MW-59 through MW-66).
January 25, 2012	MDE	Correspondence	MDE approved the Proposed Additional Well Installation Letter Work Plan and requested the submittal of a Well Installation Summary Report by March 31, 2012 and an Updated SCM by April 30, 2012. CSXT/ARCADIS requested that the documents be combined into one for submittal on April 30, 2012.
March 2012	CSXT/ARCADIS	Investigation	Seven of the 8 proposed monitoring wells (MW-59 through MW-65) were installed and developed. MW-66 could not be installed due to subsurface infrastructure obstructions (i.e. the former roundhouse foundation).
April 30, 2012	CSXT/ARCADIS	Remediation	Approximately 600 gallons of LPH have been recovered since implementation of LPH removal activities in accordance with the <i>Corrective Action Plan Addendum</i> in July 2009. A Revised Site Conceptual Model was submitted to MDE.

Table 2
Field Data Collection Program Summary
C and O Canal/Brunswick Rail Yard, Brunswick, Maryland

Well Identification	Property Owner	Current Semi-Annual Sampling Program ¹	Proposed Supplemental Groundwater Sampling ²	Existing Wells For Proposed Redevelopment	Rising Head Testing / Groundwater Sampling	LPH Stress Testing	LPH Physical Characteristics Analysis ⁴
CSXT MW-03	CSXT	X		X			
CSXT MW-06R	CSXT	X		X			
CSXT MW-08	CSXT		X	X			
CSXT MW-09	CSXT		X	X			
CSXT MW-20	CSXT		X	X			
CSXT MW-21	CSXT		X	X	X		
CSXT MW-22	CSXT	X		X			
CSXT MW-24	CSXT	X		X			
CSXT MW-25	CSXT	X		X	X		
CSXT MW-29	CSXT	X		X	X		
CSXT MW-35	CSXT			X	X		
CSXT MW-37	CSXT			X		X ⁵	X
CSXT MW-41	CSXT			X		X ⁶	
CSXT MW-43	CSXT	X	X	X			
CSXT MW-49	CSXT			X		X ⁵	
CSXT MW-51	CSXT	X		X			
CSXT MW-56	CSXT			X		X ⁶	X
CSXT MW-59	CSXT	X		³			
CSXT MW-60	CSXT	X		³			
CSXT MW-61	CSXT	X		³			
CSXT MW-62	CSXT	X		³			X
CSXT MW-63	CSXT	X		³			
CSXT MW-64	CSXT	X		³			
CSXT MW-65	CSXT	X		³			
CSXT MW-67	CSXT	PMW					
CSXT MW-68	CSXT	PMW					
CSXT MW-69	CSXT	PMW					
CSXT MW-70	CSXT	PMW					
NPS MW-01	NPS	X	X	X			
NPS MW-02	NPS	X	X	X			
NPS MW-03	NPS		X	X			
NPS MW-04	NPS	X	X	X			
NPS MW-05	NPS	X	X	X			
NPS MW-10	NPS		X	X			
NPS MW-11	NPS		X	X			
NPS MW-12	NPS		X	X			
NPS MW-13	NPS	X	X	X			
NPS MW-14	NPS	X	X	X			
NPS MW-15	NPS		X	X			
NPS MW-16	NPS	X	X	X			
NPS MW-17	NPS		X	X			

Notes:

¹ - Current Semi-annual sampling program includes analysis of TPH-DRO and full suite VOCs including fuel oxygenates

² - Proposed Supplemental Groundwater Sampling includes analysis of TPH-GRO, TPH-DRO/ORO with and without silica gel treatment, full suite VOCs including fuel oxygenates, and SVOCs

³ - Well were installed and developed in March 2012, do not require redevelopment.

⁴ - LPH Physical Characteristic Analysis includes interfacial tension, viscosity, density, and specific gravity at a range of temperatures

⁵ - LPH is currently recovered from the well using a passive skimmer.

⁶ - LPH is currently recovered from the well using a skimmer pump.

NPS - National Park Service

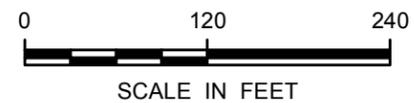
PMW - Proposed monitoring well which has not yet been installed. Well will be included in the semi-annual sampling program upon installation completion.

Figures



LEGEND

-  WELL LOCATIONS
-  EXISTING CANAL
-  AREA OF CONCERN



COORDINATE SYSTEM: NAD 1983 StatePlane Maryland FIPS 1900 Feet
 DATE SOURCE:
 -IMAGERY PROVIDED BY BING MAPS, ACCESSED ON 7/13/2012
 THROUGH ARCGIS ONLINE USING ARCMAP 10.

CSX TRANSPORTATION, INC.
 BRUNSWICK, MARYLAND

REPORT

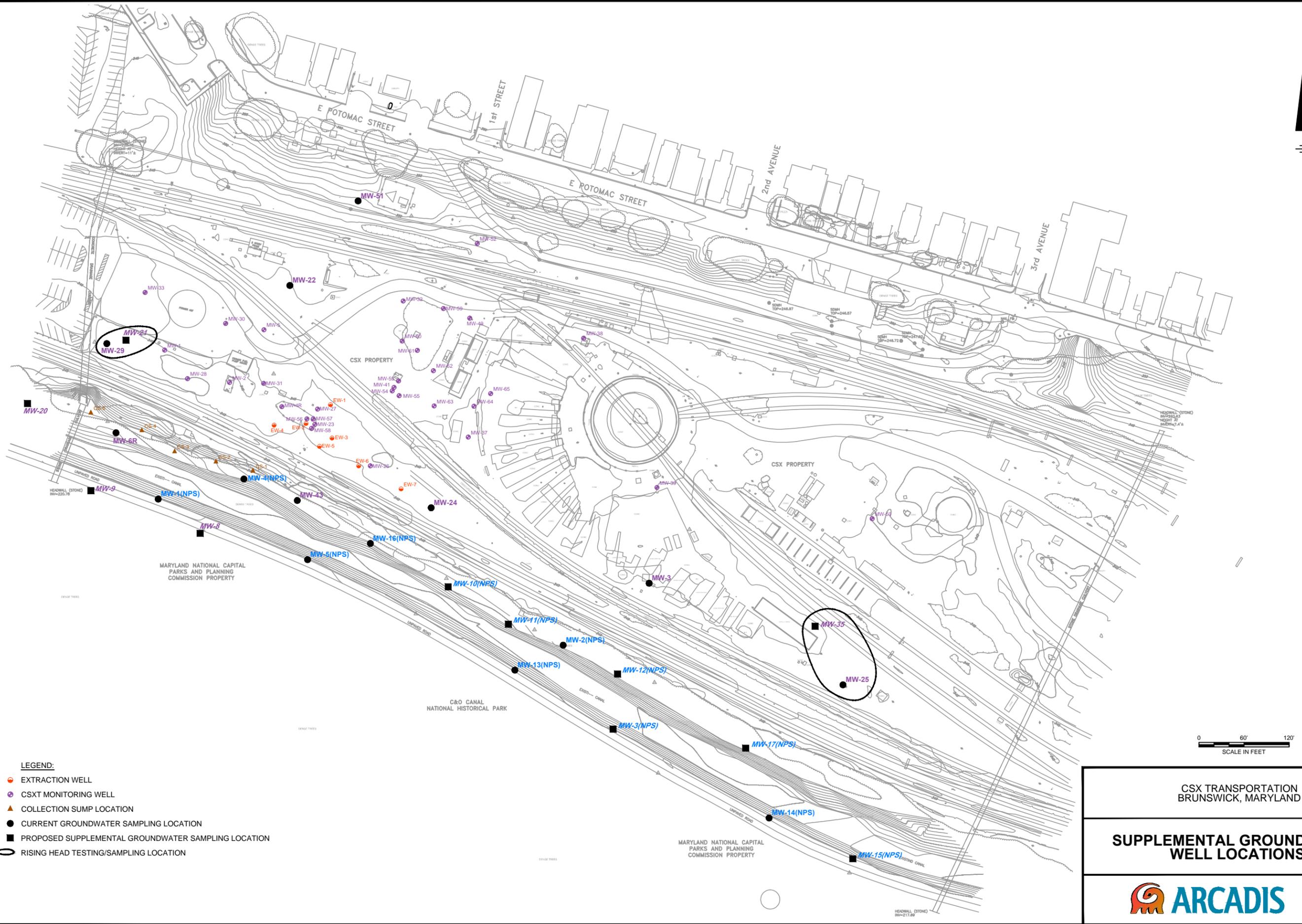
**C&O CANAL
 AREAS OF CONCERN**



FIGURE

2

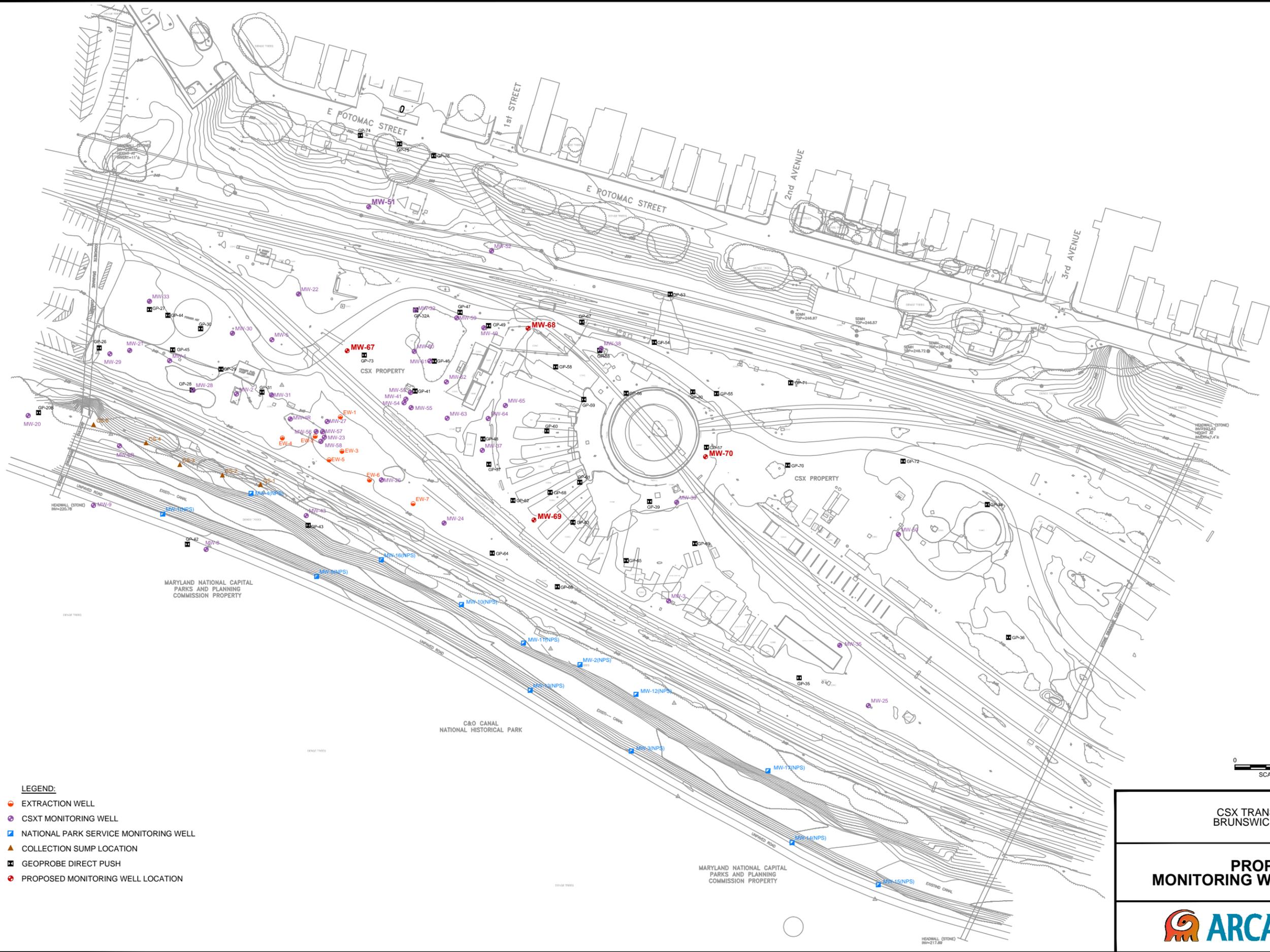
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- LEGEND:**
- EXTRACTION WELL
 - CSXT MONITORING WELL
 - ▲ COLLECTION SUMP LOCATION
 - CURRENT GROUNDWATER SAMPLING LOCATION
 - PROPOSED SUPPLEMENTAL GROUNDWATER SAMPLING LOCATION
 - RISING HEAD TESTING/SAMPLING LOCATION

0 60' 120'
SCALE IN FEET

CSX TRANSPORTATION BRUNSWICK, MARYLAND	
SUPPLEMENTAL GROUNDWATER WELL LOCATIONS	
	FIGURE 3



- LEGEND:**
- EXTRACTION WELL
 - CSXT MONITORING WELL
 - NATIONAL PARK SERVICE MONITORING WELL
 - ▲ COLLECTION SUMP LOCATION
 - GEOPROBE DIRECT PUSH
 - PROPOSED MONITORING WELL LOCATION

CSX TRANSPORTATION BRUNSWICK, MARYLAND	
PROPOSED MONITORING WELL LOCATIONS	
	FIGURE 4



Appendix A

The Technical Case for Eliminated
the Use of the TPH Analysis in
Assessing and Regulating Dissolved
Petroleum Hydrocarbons in Ground
Water (Zemo and Foote 2003)

The Technical Case for Eliminating the Use of the TPH Analysis in Assessing and Regulating Dissolved Petroleum Hydrocarbons in Ground Water

by Dawn A. Zemo and Gary R. Foote

Abstract

In many states, the total petroleum hydrocarbons (TPH) analysis based on gas chromatography-flame ionization detection (GC-FID) is still being used to assess and regulate ground water quality at petroleum release sites. The soluble fraction of fresh crude oil or fresh products that could potentially be dissolved into the ground water is limited to relatively few petroleum hydrocarbon constituents (primarily the C₆ to C₁₄ aromatics). Research by numerous investigators has shown that the reported TPH concentrations of ground water samples frequently do not represent dissolved petroleum hydrocarbons but rather represent nondissolved petroleum or polar nonhydrocarbon compounds. Nondissolved petroleum is frequently entrained within a sample when sampling ground water within affected soil, and polar nonhydrocarbons are present in ground water as a result of petroleum biodegradation or other factors. These constituents are being measured because the TPH analysis does not include steps to remove nondissolved petroleum or a silica gel cleanup to remove polars.

Many states have regulatory action levels for TPH in ground water that are in the 0.1 to 2 mg/L range. The technical basis for these action levels appears to be toxicity and/or organoleptic (taste and odor) properties of the dissolved petroleum hydrocarbons associated with fresh oil or fresh products. The presence of compounds measured as TPH that are not dissolved petroleum hydrocarbons has proven problematic for regulatory decision-making because the comparison of concentration data to the regulatory criteria may not be correct. Because the TPH analysis does not reliably distinguish between dissolved petroleum hydrocarbons and other compounds, it should not be used to assess or regulate dissolved petroleum hydrocarbons in ground water. We recommend that constituent-specific analyses be used to assess and regulate ground water quality at petroleum hydrocarbon release sites. If TPH must be used due to regulatory requirements, samples should be cleaned up with silica gel to remove polars (and turbidity should be removed, if present) prior to analysis so that comparison to regulatory action levels that are based on properties of dissolved petroleum hydrocarbon constituents is technically appropriate.

Introduction

Based on a recent summary of states' soil and ground water cleanup standards (Nascarella et al. 2002), many states use a total petroleum hydrocarbon (TPH) analysis that is based on gas chromatography with flame ionization detection (GC-FID) to regulate ground water quality at petroleum release sites. In these states, many sites have not achieved regulatory closure solely because of TPH detections in ground water, even though the soluble petroleum hydrocarbon constituents benzene, toluene, ethylbenzene, or xylenes (BTEX), alkylated benzenes, or small polynuclear aromatic compounds (PNAs) are not present. Elevated concentrations of "dissolved-phase" TPH in the absence of soluble petroleum hydrocarbon constituents are inconsistent with petroleum hydrocarbon chemistry, and indicate that the TPH analysis is measuring compounds other than dissolved petroleum hydrocarbons.

The first purpose of this paper is to summarize the technical findings from our investigations regarding the source of TPH concentrations in ground water samples, and to discuss

results from other investigators' TPH studies. This specific topic has been an area of active applied research among several investigators since about 1993, notably Girard and Edelman (1994), Zemo et al. (1995), Zemo and Synowiec (1995), Zemo (1997a, 1997b), Foote et al. (1997), Army and Wright (1997), Lundegard and Sweeney (1999), and Lundegard and Knott (2001).

The second purpose of this paper is to place the implications of these technical findings about the TPH analysis within the national regulatory context regarding TPH regulatory criteria for ground water.

To provide adequate technical background for the conclusions presented herein, this paper is organized into sections that review fundamental technical issues including: (1) the generalized chemistry of crude oil and refined products, (2) the components and concentrations of the water-soluble fraction (WSF) of fresh crude oil and products, (3) the mechanics of the TPH analytical method, (4) potential sources of analytical interference, (5) research findings about the magnitude of TPH interference problems in ground water

samples, and (6) our understanding of the use of and scientific basis for existing TPH regulatory criteria.

Chemistry of Crude Oil and Refined Petroleum Products

To evaluate what portion of crude oil or refined products might partition or dissolve into water and thereby affect ground water quality, we must first review the generalized chemistry of the whole mixtures. Crude oils and refined petroleum products are complex mixtures of hundreds to thousands of individual petroleum constituents, which include hydrocarbons and nonhydrocarbons. Hydrocarbons are composed exclusively of carbon and hydrogen atoms that make up nonpolar molecules classified structurally as alkanes (or paraffins), aromatics, or alkenes (or olefins) (Hart 1991). Alkanes have carbon-carbon single bonds with structures that are normal, branched, or cyclic. Aromatics have conjugated carbon-carbon double bonds in single ring (mono-) or multiple ring (polynuclear-) structures. Alkenes, which occur only in refined products (Leffler 2000), have carbon-carbon double bonds with structures that are normal or branched. Crude oils also contain various amounts of polar constituents with nitrogen, sulfur, or oxygen in their molecular structure, which are not hydrocarbons and are known as hetero-atoms (NSOs; average of ~5% to 14% by weight [Tissot and Welte 1978; Metcalf and Eddy 1993]). Refined low- to mid-boiling products typically contain few NSOs associated with the crude feedstock (Leffler 2000; Kaplan and Galperin 1996).

Crude oils, which contain a large range of constituent boiling points, are refined into products that have smaller ranges of boiling points. The refining specifications for various products are primarily performance-based rather than constituent-based. Accordingly, the exact composition of a given product type varies but generally falls within certain ranges as follows (Bruya 2001; Zemo et al. 1995; Kaplan and Galperin 1996; Cline et al. 1991; Coleman et al. 1984; Lee et al. 1992; Chen et al. 1994; Uhler et al. 2001):

- Gasolines commonly contain C_4 to C_{12} alkanes, alkenes, C_6 to C_{11} monoaromatics (BTEX, alkylated benzenes), C_{10} to C_{11} PNAs, blending agents and performance additives. The weight percent of each petroleum structural class in gasolines is typically 35% to 70% total alkanes, 25% to 55% total aromatics, and 5% to 10% alkenes.
- Mid-boiling products such as kerosene, jet fuel, diesel, and fuel oil commonly contain C_{10} to C_{24} alkanes, C_6 to C_{11} monoaromatics, C_{10} to C_{20} PNAs (dominated by naphthalenes), minor NSOs, and performance additives. The weight percent of each petroleum structural class in jet fuels/kerosene is typically 70% to 85% total C_8 to C_{18} alkanes, 10% to 20% total aromatics, and 1% to 4% alkenes; and for diesels and fuel oil #2 is typically 50% to 80% total C_{10} to C_{24} alkanes, 20% to 35% total aromatics, 2% to 5% alkenes, and 1% to 5% NSOs.
- High-boiling products such as fuel oil #4 and #6 (Bunker C) and lubricating oils commonly contain C_{20} and larger alkanes, C_{14} and larger PNAs, NSOs, and metals such as nickel and vanadium. The fuels in this cate-

gory have a wide variety of constituent classes due to their residual nature; the lubricating oils are more highly refined to meet specialty performance specifications. The weight percent of each petroleum structural class in Bunker C fuel is typically 20% to 60% total C_{20} to C_{40+} alkanes, 20% to 40% total aromatics, unknown amounts of alkenes, and 30% to 50% NSOs/residuals; and for lubricating (motor) oil is typically 70% to 90% total C_{20} to C_{30} alkanes (mostly branched and cyclic) and 10% to 30% total aromatics.

Water-Soluble Fraction of Crude Oil and Refined Petroleum Products

The preceding section demonstrates that crude oils and refined products are extremely complex mixtures of hundreds to thousands of constituents. The portion of a fresh crude oil or product that is soluble and will dissolve into water, also called the water-soluble fraction (WSF), is less complex and consists of significantly fewer constituents because it is a function of several parameters.

Pure-Compound Solubilities

Within a given molecular class, lower molecular weight petroleum constituents usually have higher pure-compound solubilities. Alkanes and alkenes have low pure-compound water solubilities of <10 mg/L at molecular weights exceeding six carbon atoms (C_6) (Mackay and Shiu 1992; Yaws et al. 1990). The monoaromatics (BTEX and alkylated benzenes) have higher pure-compound water solubilities (>100 mg/L), with the lowest molecular weight (C_6) benzene having the highest relative pure-compound solubility (1780 mg/L). The lower molecular weight PNAs (e.g., naphthalene [C_{10}]) have low to very low pure-compound water solubilities (30 to <1 mg/L), with the higher molecular weight PNAs (e.g., benzo(a)pyrene [C_{20}]) being virtually insoluble in water (<0.01 mg/L).

Partitioning of Petroleum Hydrocarbons into Water from a Mixture (Effective Solubility)

The composition of the WSF of a mixture is controlled by the effective solubility of each constituent in the mixture. Effective solubility of each constituent is a function of its pure-compound solubility, its mole fraction within the mixture, and its partitioning coefficient between water and the other organics in the mixture. This mixture effect has been shown to follow Raoult's law for ideal mixtures and has been discussed often and documented in the literature (Cline et al. 1991; Lee et al. 1992; Shiu et al. 1990; Mackay and Shiu 1992; Chen et al. 1994). A recent study confirmed that Raoult's law gives a conservative estimate of the effective solubility of petroleum hydrocarbons in water (O'Reilly et al. 2001).

On the basis of effective solubility, the measureable WSF should be limited to a few petroleum constituents out of the thousands that make up the petroleum product or crude oil, and the equilibrium concentrations of each constituent within the WSF should be significantly less than its pure-compound solubility. For example, the theoretical maximum concentration of dissolved benzene in ground water in equilibrium with

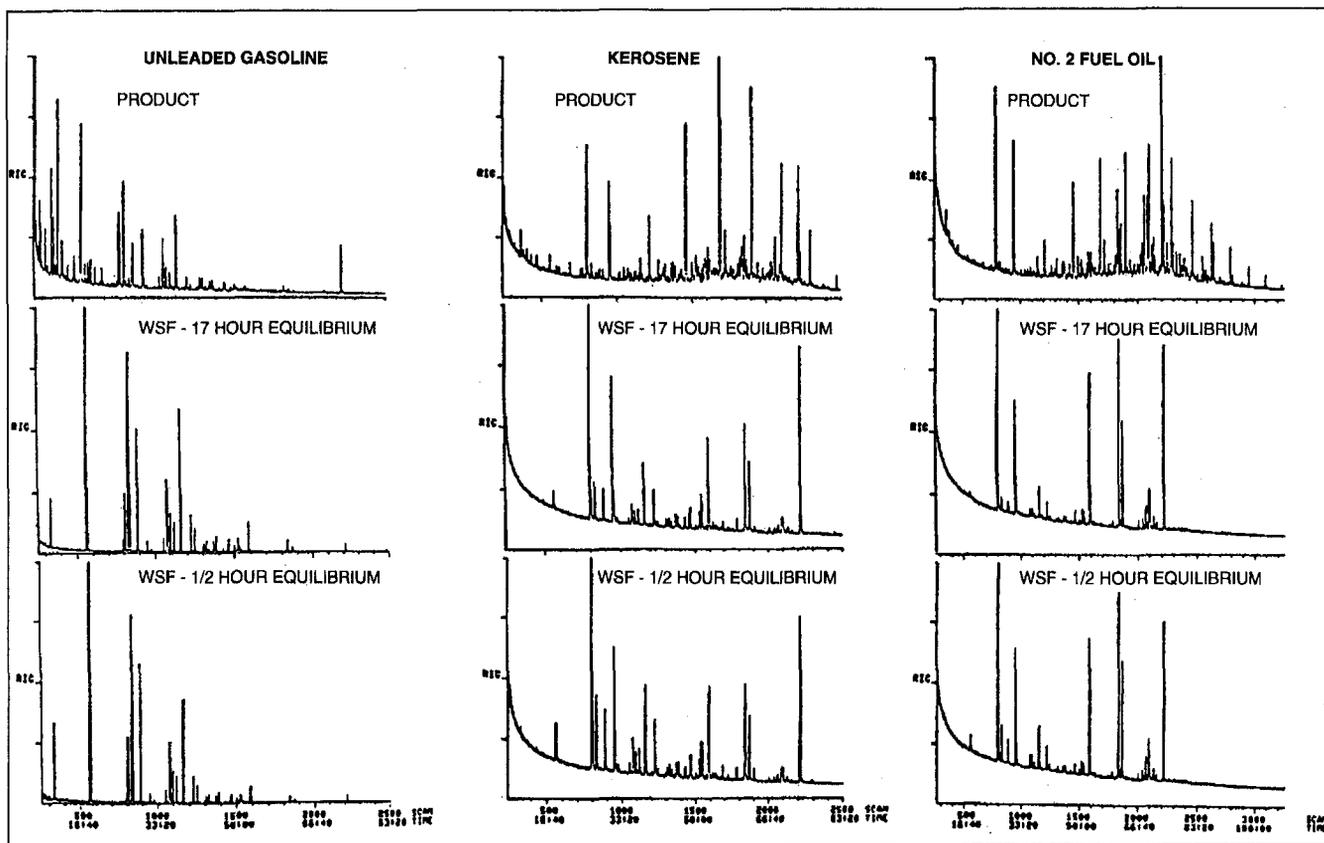


Figure 1. Reconstructed ion chromatograms showing the half-hour and 17-hour equilibrium water-soluble fractions (WSF) of gasoline, kerosene, and fuel oil no. 2; adapted with permission from Figures 1, 3, and 5 of Coleman et al. (1984).

fresh gasoline would be ~18 mg/L, assuming that benzene is 1% of the gasoline (1780 mg/L \times 0.01) and ignoring partitioning effects. Using the theory of effective solubility and data on the aromatic content of 69 different crude oils, O'Reilly et al. (2001) presented multiple calculations that demonstrated theoretically that only the C₆ to C₁₄ aromatics had the potential to be dissolved in ground water at concentrations of 0.005 mg/L or greater. The validity of these theoretical estimates and the effective solubility approach is demonstrated by the laboratory research described as follows.

Composition of WSFs from Laboratory Studies

The composition of the WSF of fresh petroleum products (including gasolines, kerosenes, jet fuels, diesels, Bunker C fuel, and motor oils) and fresh crude oils has been investigated under laboratory conditions by several researchers using various analytical methods (Coleman et al. 1984; Shiu et al. 1990; Bruya and Friedman 1992; Thomas and Delfino 1991; Chen et al. 1994; Potter 1996). Details of these studies are provided in Zemo (1997b).

The results from all of these studies are consistent and provide clear evidence that the petroleum hydrocarbon constituents within the measurable WSF of fresh crude oil and fresh products are limited primarily to the C₆ to C₁₁ monoaromatics (BTEX and the alkylated benzenes), the C₁₀ to C₁₄ PNAs (naphthalene, alkylated naphthalenes, acenaphthene, fluorene, phenanthrene, and anthracene), and smaller amounts of the alkanes with six carbons or fewer. Thomas and Delfino (1991) and Potter (1996) also reported phenol and methylated phenols in the WSF of the products they

tested. The contrast between a mixture and the limited and discrete nature of its WSF was clearly illustrated in the Coleman et al. (1984), Bruya and Friedman (1992), Shiu et al. (1990), and Thomas and Delfino (1991) studies, which compared chromatograms from fresh product to those of the corresponding WSF. The chromatograms of the WSF for each product was composed of discrete peaks, did not have a large unresolved complex mixture (UCM) or "hump," and did not resemble the original product. Figures 1 and 2 show results from Coleman et al. (1984) and Bruya and Friedman (1992), respectively.

The discrete constituents in the WSF can be reliably identified and quantified by routine GC-MS methods. The recognition of the petroleum hydrocarbon constituents within and the chromatographic character of the WSF of various fresh products has great significance for interpretation of TPH analytical results from ground water samples.

It is important to note that these studies and our work have focused on the petroleum hydrocarbon constituents comprising the WSF of fresh crude oil and products. Polar blending agents or additives, such as oxygenates, have both relatively high pure-compound solubilities and large mole-fractions within the product mixture, and therefore can be a large part of the WSF of a given product. As previously mentioned, polar NSOs may be present in fresh crude oils or fresh products, therefore these polar compounds could be part of the WSF of a fresh crude or fresh product, depending on the pure-compound solubility, its mole-fraction within the mixture, and its oil/water partitioning coefficient (e.g., phenols found by Thomas and Delfino [1991] and Potter [1996]).

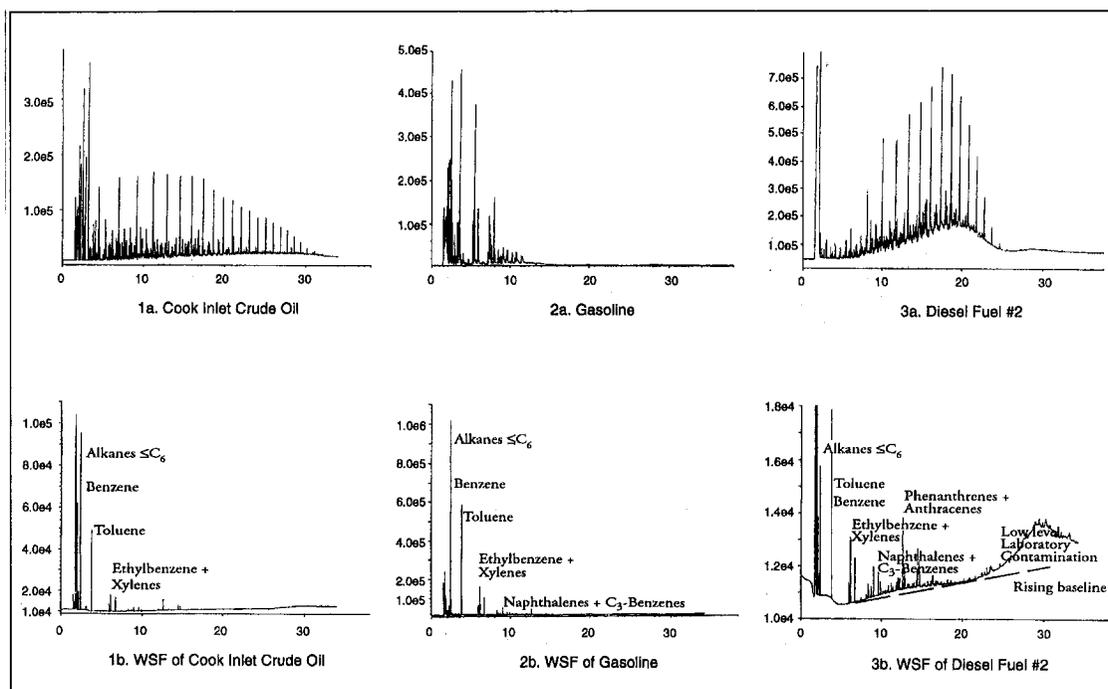


Figure 2. GC-FID chromatograms for various fresh petroleum products and their water-soluble fractions (WSF); adapted from Bruya and Friedman (1992). Figure reprinted with permission from Zemo (1997a); copyright Amherst Scientific Publishers.

These nonhydrocarbon compounds can be identified and quantified using GC-MS methods.

Aggregate Concentration of WSFs from Laboratory Studies

In addition to evaluating the composition of the WSFs, the Shiu et al. (1990) and Potter (1996) studies investigated the maximum aggregate concentration of the WSF of fresh crude oils or fresh products. Excluding additives such as ethers, the maximum aggregate concentration of the WSF of fresh products tested varied from ~100 mg/L for gasolines (Potter 1996; Shiu et al. 1990), 3 to 40 mg/L for diesels and fuel oils (Shiu et al. 1990; Potter 1996), 15 to 65 mg/L for jet fuels (Potter 1996), and ~6 mg/L for Bunker C (Shiu et al. 1990). Shiu et al. (1990) found that the aggregate concentration of the WSF of several fresh crude oils varied from ~10 to 58 mg/L, and the WSF of a natural gas condensate was ~75 mg/L.

As a crude oil or product weathers in the subsurface, both the constituents and the concentration of the dissolved petroleum hydrocarbons potentially associated with the weathered petroleum will change. As the original soluble constituents are leached out or are biodegraded, their mole-fraction decreases within the remaining mixture, which further decreases their effective solubility. Ultimately the residual crude oil or product is depleted in the original soluble constituents to the point where they will no longer partition to the dissolved phase. This was well illustrated by Shiu et al. (1990), where dramatic decreases in the measured aggregate WSF concentration were evidenced after laboratory evaporative "weathering" of the crude oils and products; most aggregate WSF concentrations of the weathered crude oil or product were reduced to ~1 mg/L or less, regardless of the original WSF concentration associated with the fresh oil or product. Accordingly, aggregate concentrations of dissolved petroleum hydrocarbons in ground water at sites affected by

weathered crude oil or products would not be expected to exceed ~1 mg/L in most cases.

Discussion of GC-FID TPH Analytical Methods

In the 1980s, samples were commonly analyzed for petroleum hydrocarbons using U.S. Environmental Protection Agency (EPA) Method 418.1 ("total recoverable petroleum hydrocarbons"; TRPH). Method 418.1 was an improvement over the previously existing "total oil and grease" analyses and it included a silica gel cleanup step that removed or reduced polar nonhydrocarbons in the sample extract prior to analysis. However, it was still a relatively coarse analysis and was not useful for volatile components.

TPH analytical methods based on GC-FID were introduced in the late 1980s and early 1990s as an improvement over Method 418.1. EPA Method 8015M and its GC-FID equivalents (combined hereafter as TPH analyses) measure the amount of volatile (purgeable) or semivolatile (extractable) organics that elute within selected boiling ranges; these data are compared to petroleum product standards such as gasoline, diesel, and motor oil for quantitation as TPH. Boiling ranges and response integration protocol for quantitation are often not specified by the method and can vary significantly among laboratories. The FID is not selective, and there is no attempt to identify individual peaks based on retention time. The TPH analysis is fundamentally an aggregate rather than a constituent-specific analysis and transmits no direct information about which constituents are present in the sample.

Information about boiling point of the aggregate mass present and the ability to separately analyze purgeable and extractable components was a distinct improvement over Method 418.1; however, the GC-FID TPH methods did not include the silica gel cleanup step present in Method 418.1

that removed polars. This omission allowed for the measurement of polar nonhydrocarbons present in the sample, and effectively made the TPH analysis a total organics measurement rather than a total petroleum hydrocarbons measurement. The reason for the cleanup omission is unclear, but likely stems from the fact that the original EPA Method 8015 was designed to measure discrete nonhalogenated organics, including polar compounds such as alcohols, ketones, and aldehydes (EPA 1996) and therefore had no cleanup step to remove such compounds. It is important to note that the original EPA Method 8015 cautioned that there was "potential for many nontarget compounds present in samples to interfere with this analysis" due to the nonselectivity of the FID, and "if this method is used for the analysis of petroleum hydrocarbons, it is limited to analysts experienced in the interpretation of hydrocarbon data" (EPA 1996).

The mechanics of using GC-FID for the TPH analysis and its general shortcomings, including interference problems, quantitation range inconsistencies, product identification problems, and poor inter-laboratory repeatability, have been discussed by multiple authors (Bruya 2001; Girard and Edelman 1994; Zemo et al. 1995; Potter 1991; Morrison 1999; and Uhler et al. 1998).

This paper focuses on the TPH analyses that are not "fractionated." Several fractionated TPH analyses were developed in the late 1990s (e.g., Massachusetts volatile petroleum hydrocarbons/extractable petroleum hydrocarbons [MA VPH/EPH], Alaska 101AA/102AA; TPH Criteria Working Group Method) and are being used by several states. In summary, a fractionated TPH analysis essentially breaks the measurement down into pieces that are categorized by both constituent molecular class (alkanes and aromatics) and multiple narrow boiling-point ranges. The mechanics of these analyses will not be discussed here. For the purpose of this paper, the most important difference between the TPH and fractionated TPH analyses are that the TPH analysis does not use a silica gel or alumina column for cleanup and separation of the sample extract into aliphatic (alkanes) and aromatic fractions. The use of the silica gel or alumina column in the fractionated analyses removes the polars.

Sources of Interferences to TPH Analysis of Ground Water

As a practical matter, analyses of ground water samples are intended to characterize the dissolved, and therefore mobile, constituents. Based on representative regulatory guidance (e.g., CA LUFT Manual 1989; EPA 1996), the TPH analysis appears to be intended to measure the petroleum hydrocarbon constituents within a sample. Therefore, the fundamental purpose in analyzing a ground water sample using the TPH analysis is to estimate the aggregate concentration of dissolved petroleum hydrocarbon constituents. For the purpose of this paper, and based on EPA's cautions about modifying and using Method 8015 for analysis of petroleum hydrocarbons, "interferences" are defined as factors that produce a TPH concentration in a ground water sample that are not dissolved petroleum hydrocarbon constituents.

As discussed earlier, the constituent composition, chromatographic character, and aggregate concentration range of

dissolved petroleum hydrocarbons associated with crude oils and products has been scientifically investigated. Based on this research, the predominant petroleum hydrocarbon constituents that should be measurable in the dissolved phase of fresh petroleum products or fresh crude oil are the C₆ to C₁₄ aromatics and the alkanes with six or fewer carbons. The TPH chromatogram should be composed of discrete peaks lower boiling than C₁₄ and have no UCM or "hump." Furthermore, the TPH concentration should not exceed the range of aggregate WSF concentrations given for each type of product discussed earlier, especially if the mixture is weathered. Therefore, it follows that TPH measurements that reflect (1) a significant mass of alkanes larger than C₆, (2) material higher boiling than C₁₄, (3) a chromatogram with a hump instead of discrete peaks, or (4) concentrations that exceed the range of ~100 mg/L for a fresh gasoline release to ~1 mg/L for a weathered high-boiling product release are not representative of dissolved petroleum hydrocarbons.

Zemo and Synowiec (1995), Zemo (1997a, 1997b), Foote et al. (1997), Army and Wright (1997), Girard and Edelman (1994), and Lundegard and Sweeney (1999) have shown that the TPH concentration of ground water samples resulting from constituents other than the alkanes with six or fewer carbons or aromatics with 14 or fewer carbons were a direct result of one or both of the following interferences: (1) the samples contained nondissolved petroleum, or (2) the samples contained soluble nonhydrocarbons (such as polar compounds including biodegradation products). Samples affected by either or both of these sources of interference do not provide an accurate assessment of concentrations of dissolved-phase petroleum hydrocarbon constituents in ground water.

Nondissolved petroleum may be incorporated into water samples by passing a bailer or other sampling device through a sheen on top of the water column or by entraining petroleum that is sorbed onto sediment (turbidity) suspended in the water column inside a well or sampling device. This is a prevalent problem when "grab ground water sampling" within affected soil areas or smear zones, or when sampling monitoring wells that are screened directly across affected soil in the smear zone. Nondissolved petroleum included in the sample will be extracted along with the water at the laboratory when using standard analytical procedures. Consequently, the TPH result for the ground water sample will include these nondissolved constituents. The TPH chromatogram for this type of interference looks like the product that is in the sheen or sorbed to the soil.

Soluble nonhydrocarbons such as polar compounds (including NSOs within fresh petroleum, biodegradation products, and natural organic compounds) may be incorporated into water samples when wells or grab samples are screened within or downgradient from petroleum-affected soil. As discussed earlier, NSOs may be a portion of the WSF of fresh crude oil or certain products, and constituents of potential concern can be evaluated with GC-MS methods.

As the petroleum biodegrades, many new compounds are created that have oxygen in their molecular structure. During biodegradation, petroleum hydrocarbons are oxidized to initially form alcohols, which undergo further oxidation to organic acids and then to carbon dioxide and water; interme-

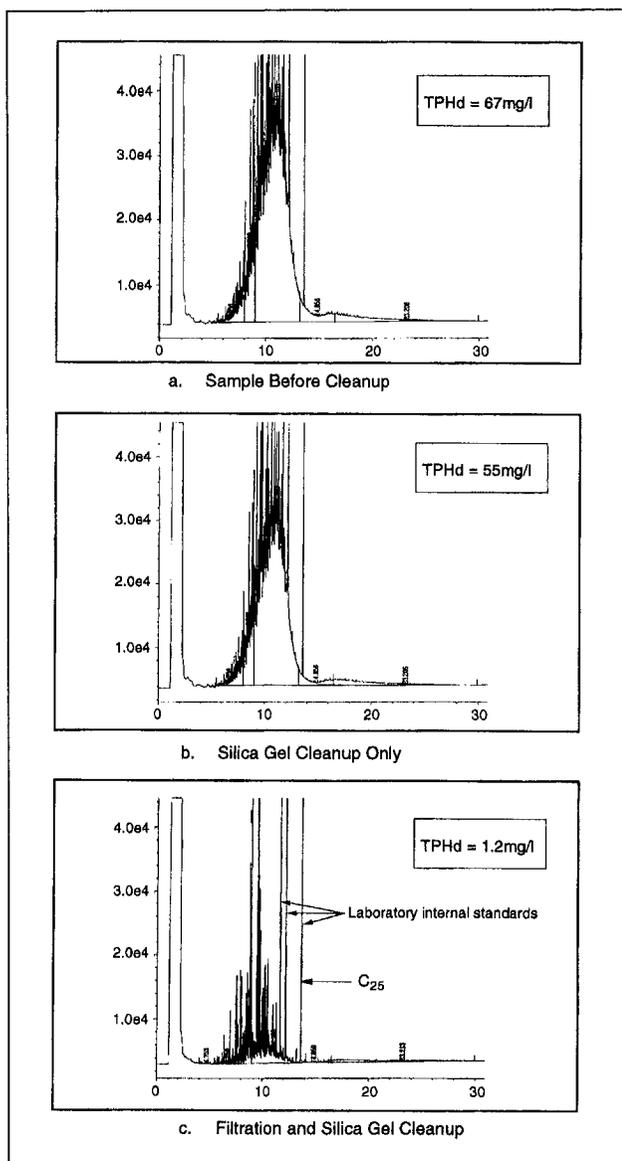


Figure 3. GC-FID TPH chromatograms for blind duplicate ground water samples demonstrating removal of nondissolved petroleum sorbed to particulates via filtration prior to extraction and analysis by Method 8015M. Cleanup was incomplete. Figure reprinted with permission from Zemo (1997a); copyright Amherst Scientific Publishers.

diolate metabolites primarily include aldehydes, phenols and ketones (Cozzarelli et al. 1994; Barcelona et al. 1995; Barcelona et al. 1996; Dragun 1998; Cookson 1995; Beller et al. 1995). Collection of these polar nonhydrocarbons within the ground water sample is unavoidable because of their relatively high solubility and their presence will be measured as TPH. In addition to interference by polar nonhydrocarbons resulting from intrinsic biodegradation of petroleum, Girard and Edelman (1994) demonstrated interference to TPH analysis of ground water samples caused by polar nonhydrocarbons derived from decomposition of wood waste (e.g., degradation byproducts of tannin/ lignins), and Zemo et al. (1995) showed interference to TPH analysis of ground water samples caused by paint propellant ethers. The TPH chromatogram reflecting interference by polar nonhydrocarbons resulting from natural organics or biodegradation products typically has a significant UCM or hump. Interference by

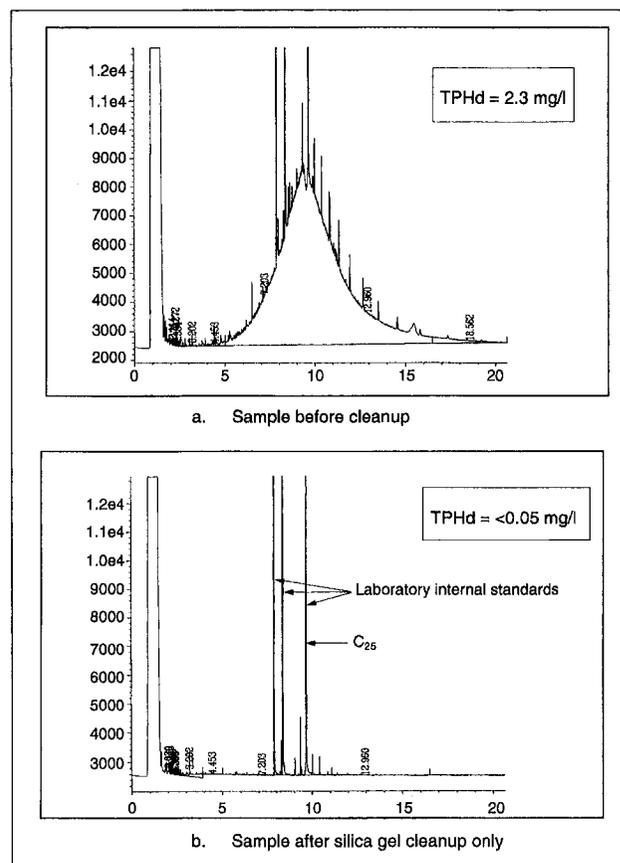


Figure 4. GC-FID TPH chromatograms for blind duplicate ground water samples demonstrating removal of polar nonhydrocarbons via silica gel cleanup of extract prior to analysis by Method 8015M.

polar nonhydrocarbons that are synthesized compounds (e.g., phthalates and chlorinated hydrocarbons) may be evidenced by individual peaks that are not the C_6 and smaller alkanes or the C_6 to C_{14} aromatics.

Magnitude of Interferences to Ground Water Data

A variety of studies have shown that TPH concentrations frequently do not represent dissolved petroleum hydrocarbons in ground water. This section provides summaries of results from quantitative investigations performed by the authors and by others. These studies demonstrate the magnitude of the interferences from nondissolved petroleum and polar nonhydrocarbons in terms of concentration.

Studies Performed by the Authors

Table 1 presents TPH concentration data from 22 sites in which filtering (to reduce or remove nondissolved petroleum sorbed to particulates) and/or silica gel cleanup (to reduce or remove polars) was performed on blind duplicate pairs of ground water samples prior to the extractable TPH analysis. Twenty-one of the sites were impacted by weathered middle- to high-boiling products or crude oil; one site (Site 22) was affected by a relatively fresh gasoline-jet fuel mixture. The ground water analytical results from Sites 1 through 21 were typical in that they had elevated concentrations (0.2 mg/L to

Table 1

TPH (EPA Method 8015M) Analytical Results for Ground Water Samples Before and After Cleanup

Site	Conventional TPH (mg/L) ¹	Cleaned-up TPH (mg/L) ²			Interference ³
		F only	SG only	F+SG	
1	20		<1		PNH
2	110	15	55	1.2	grab sample w/NDP; IC
3	0.100		<0.05	<0.05	PNH
4	0.200		<0.05	<0.05	PNH
5	0.390		<0.05	<0.05	PNH
6	6.6		0.14	0.14	PNH; IC
7	0.630			<0.05	PNH
8	120			0.69	grab sample w/NDP; IC
9	4.5			0.75	PNH; IC
10	1.1	0.390	<0.05		PNH; minor NDP
11	0.790		<0.05	<0.05	PNH
12	1.5		<0.05	<0.05	PNH
13	2.23		<0.05		PNH
14	2.0		<0.05		PNH
15	3.9		1.9		NDP w/minor PNH; IC
16	2.6		0.27		PNH; IC
17	2.3		<0.05		PNH
18	1.8		0.100		PNH; IC
19	1.4	1.3	<0.05		PNH
20	1.7		<0.05		PNP
21	0.810	0.840	<0.05		PNH
22	3.0		2.5		(Relatively fresh dissolved-phase gasoline/jet fuel plume)

¹Analysis for extractable TPH by EPA Method 8015M using a diesel standard; quantitation range varied among laboratories, typically C8 to C30. Data originally reported in µg/L.

²Blind duplicate(s) filtered (F) by laboratory using glass fiber TCLP filter (0.7 micron) and/or silica gel cleanup (SG) by either 418.1 or Method 3630B equivalents (see text) prior to analysis.

³Major component of interference based on review of chromatograms: PNH = polar nonhydrocarbons, NDP = nondissolved petroleum hydrocarbons, IC = incomplete cleanup assessed by comparing duplicate chromatograms.

>100 mg/L) of extractable TPH (C₁₀ to C₃₆ measured using EPA Method 8015M) with no or very low detections of BTEX or PNAs (measured using EPA Methods 8021 or 8260B, and 8270 SIM or 8310). Most TPH concentrations were well above the expected solubility limit for weathered products. In addition, the chromatograms for ground water samples collected at these sites had a characteristic hump pattern and not the discrete peak pattern typical of the WSF of products or crude oils found by Coleman et al. (1984), Shiu et al. (1990), Bruya and Friedman (1992), and Thomas and Delfino (1991). Figures 3 and 4 show example TPH chromatograms of duplicate ground water samples with and without filtration and/or silica gel cleanup.

Filtering, when used, was accomplished by the laboratory prior to extraction using a glass fiber (0.7 micron) filter that is used in the toxic characteristic leaching procedure (TCLP). Several other filter materials, including the material sometimes used for the 0.45-micron filter typically used in inor-

ganic analysis, were found to be unacceptable because of potential for adsorption of the dissolved petroleum constituents (Foote et al. 1997). It is important to note that some particulates and colloidal material will pass the 0.7-micron filter mesh and a smaller filter mesh (e.g., 0.45 micron) would be desirable to better assess dissolved constituents as defined by EPA.

After extracting the sample in methylene chloride, the laboratory performed a silica gel cleanup to remove polars based on EPA Method 3630B (with no solvent exchange). Our experience shows that use of a glass column packed with silica gel typically results in an adequate cleanup; a cleanup based on EPA Method 418.1 (adding 3 grams of silica gel to the extract and shaking the mixture) frequently did not result in adequate removal of polar nonhydrocarbons. Completeness of a silica gel cleanup can be assessed only by reviewing the chromatograms; a cleanup may be incomplete due either to the polarity or the mass of polar compounds in the extract.

For the data shown in Table 1, laboratory QA/QC was assessed by standard methods (e.g., acceptable blind duplicate relative percent differences and acceptable spike and surrogate recoveries in both the conventional and cleaned-up samples) to ensure that silica gel cleanup was not causing negative bias by removing dissolved petroleum hydrocarbons from the sample. In a separate study, Foote et al. (1997) assessed potential negative bias due to filtration and demonstrated a 96% recovery of dissolved naphthalene from an aqueous mixture passed through the glass fiber TCLP filter. The 1997 results are corroborated here, where in three of the four sites where only filtering was performed (Sites 1, 19, and 21), the filtering had no significant impact on the results indicating that filtering did not introduce negative bias.

Comparisons of chromatograms (e.g., Figures 3 and 4) and quantitative results from Sites 1 through 21 (Table 1) show that the conventional TPH analysis did not represent dissolved petroleum hydrocarbons in ground water and was significantly affected by nondissolved petroleum and polar nonhydrocarbon interferences. Prior to filtration and/or silica gel cleanup, TPH concentrations ranged from 0.1 to 120 mg/L, with the typical site in the 0.5 to 2.5 mg/L range. As shown in the table, significant decreases of about two orders of magnitude were observed in TPH concentration after filtration and/or silica gel cleanup; in 14 of the 21 cases TPH was no longer detected. Please note that filtration and/or cleanup was incomplete for the remaining seven of the 21 samples as evidenced from review of the chromatograms. Polar nonhydrocarbons, likely resulting from in situ biodegradation, were the major source of interference at 18 of the 21 sites.

Based on the technical data provided earlier, it follows that sample filtration and/or silica gel cleanup should make virtually no difference in TPH concentrations in cases where ground water is in fact affected only by dissolved petroleum hydrocarbons. As a point of comparison with the 21 sites affected by weathered petroleum, in which TPH concentrations in ground water were elevated but BTEX and PNAs were absent, Table 1 also includes TPH ground water data from a site affected by a relatively fresh gasoline/jet fuel mixture (Site 22). Ground water samples collected within this plume contain elevated concentrations of BTEX and the

small PNAs, in addition to TPH. The data show that in the presence of a true dissolved-phase petroleum plume such as this, the conventional and cleaned-up TPH concentrations are similar (3 and 2.5 mg/L, respectively).

Please note that similar interferences to the purgeable TPH analysis are expected and have been observed (e.g., Zemo et al. 1995). However, the conventional sample preparation has not been modified because of the potential for loss of volatiles, and therefore the magnitude of the impact to the purgeable TPH analysis cannot be quantified. Modification of the TPH analysis to address these sources of interference in the purgeable range is an area requiring future work.

Studies Performed by Other Investigators

Girard and Edelman (1994) performed one of the early studies in which nonhydrocarbon sources of TPH concentrations in ground water were identified and quantified using several analytical methods. The authors showed that virtually all of the 0.27 mg/L TPH concentration in a ground water sample collected downgradient from a wood-waste disposal site consisted of tannin, lignin, and their degradation byproducts from decomposition of the wood (0.22 mg/L by Standard Method 5550B). No PNAs or NSOs expected from a petroleum source were detected using GC-MS.

Army and Wright (1997) studied the impact of petroleum-affected particulates on TPH concentrations of ground water samples at several sites. At a site affected by degraded diesel fuel, they observed significant decreases in TPH concentrations when wells were carefully purged and sampled using a low-flow pump versus other types of pumps/bailers (13 to 73 mg/L before using low-flow method and 0.8 to 1.6 mg/L after using low-flow method). Army and Wright pointed out that the original concentrations of their samples and of the majority of samples in the Massachusetts statewide database exceeded the expected solubility for weathered diesel by a large margin and indicated interferences to the TPH measurement on a pervasive scale.

Lundegard and Sweeney (1999) built upon earlier work by Zemo (1997a, 1997b) and Foote et al. (1997) and performed a detailed investigation into the source of TPH concentrations in ground water samples at a site affected by degraded crude oil. Lundegard and Sweeney observed significant decreases in TPH concentrations in ground water samples of one to two orders of magnitude after either filtration and/or silica gel cleanup. The authors documented their QA/QC testing of both their filtration and silica gel cleanup procedures using prepared standard mixtures and found that neither procedure produced negative bias on the concentration of petroleum constituents, except for loss of n-decane (C_{10}) during filtration that they attributed to volatilization. Twenty-one samples with TPH concentrations ranging from 0.142 to 42.6 mg/L were filtered and/or cleaned up with silica gel; after filtration and/or cleanup, 13 samples were non-detect (<0.1 mg/L), seven samples were 0.1 to 0.5 mg/L, and one sample was reduced to 2.8 mg/L. Lundegard and Sweeney concluded that TPH concentrations in ground water at their site resulted from a combination of nondissolved oil, polar nonhydrocarbons unrelated to the presence of the oil, polar NSOs originally within the oil, and polar nonhydrocarbons resulting from biodegradation of the oil.

In summary, all of these studies demonstrate that the TPH analysis is imprecise and unreliable for the measurement of dissolved petroleum hydrocarbons in ground water. In many cases, the entire reported TPH concentration represents nondissolved petroleum or polar nonhydrocarbons.

Regulatory Context for the Use of TPH Analysis

The preceding sections show that reported TPH concentrations frequently do not represent dissolved petroleum hydrocarbons in ground water. These findings are significant because of the use of TPH in regulatory decision-making. According to Nascarella et al. (2002), approximately 19 states are still using a TPH analysis to regulate ground water quality, approximately 22 states no longer use the TPH analysis for regulatory decisions because they have adopted a constituent-specific risk-based approach to petroleum sites, and about seven states are using a "fractionated" TPH analysis in a hybrid risk-based approach (Weisman 1998). Based on the Nascarella et al. survey, the TPH action level for about half of the 19 states using TPH is site-specific (no quantitative concentration given); the remaining states have TPH action levels that range from 0.05 to 10 mg/L, with most between 0.1 and 2 mg/L.

When comparing measured TPH concentrations in ground water to TPH action levels, it is important to understand the scientific basis upon which the action level was developed. This allows an assessment of whether correct comparisons are being made. For example, several scientific research papers are often cited in regulatory guidance documents as the basis for TPH taste and odor criteria. The research indicates that the taste and odor properties studied were from stirred mixtures of fresh oil or fresh products and water at various dilutions and temperatures, measured as "parts oil/parts water" or "mg oil/L water" (Gibbons 1940; McKee and Wolfe 1963). Accordingly, the taste and odor properties that produced the thresholds, which were eventually used as the basis for regulatory criteria, resulted from the dissolved petroleum constituents associated with the fresh oil or product. This would have included dissolved petroleum hydrocarbons (and possibly NSOs) but *not* nondissolved petroleum or polar nonhydrocarbons resulting from biodegradation. Interestingly, it was shown by Gibbons (1940) that if the dissolved petroleum constituents were allowed to weather by sitting in an uncovered beaker for 11 to 16 days, the odor decreased significantly (by up to a factor of 10) and the characteristic of the odor changed. Note that these studies were not quantified as TPH because they predate the use of the GC-FID TPH analysis.

It is beyond the scope of this paper to debate the appropriateness of the concentrations that are used for TPH regulatory criteria; however, it is important to point out here that the scientific basis for many of these criteria appears to be the properties of the dissolved petroleum hydrocarbons (and possibly NSOs) associated with the fresh oil or product. Accordingly, it is critical that the TPH quantification of ground water samples reflects dissolved petroleum hydrocarbons in order to make a correct comparison to regulatory criteria. As shown in the previous section, the TPH analysis is imprecise and frequently does not represent dissolved petroleum hydro-

carbons, but rather represents nondissolved petroleum or polar nonhydrocarbons resulting from biodegradation or other sources. The concentration of these interferences measured as TPH routinely exceed the typical 0.1 to 2 mg/L TPH action levels and therefore inhibit site closure because of this incorrect comparison.

Conclusions

We conclude that the TPH analysis is imprecise and should not be used to either assess or regulate dissolved petroleum hydrocarbons in ground water. Research has clearly shown that TPH analysis of ground water samples frequently does not represent dissolved petroleum hydrocarbons but rather represents nondissolved petroleum and/or polar nonhydrocarbons; in many cases, the entire reported TPH concentration may result from these interferences. Because the TPH analysis is imprecise and can measure more than dissolved petroleum hydrocarbons, it follows logically that TPH concentrations should not be compared to existing TPH regulatory criteria that are based on dissolved petroleum hydrocarbons.

We conclude that it is better to use constituent-specific analyses rather than TPH analysis for assessing or regulating dissolved petroleum hydrocarbons in ground water. If the TPH analysis must be used due to regulatory requirements and the results are to be compared to existing TPH action levels, samples analyzed for extractable TPH should be cleaned up with silica gel to remove polars, and measures should be taken to remove turbidity, if present (e.g., filtering, low-flow purging). This will allow for a technically appropriate comparison to regulatory action levels that are based on dissolved petroleum hydrocarbons associated with fresh products. If there are circumstances when certain polar nonhydrocarbons are believed to be of concern (Lundegard and Knott 2001), we recommend that the TPH analysis *not* be used to address those constituents, but rather that the target compounds be identified based on regulatory concerns and quantified using GC-MS or other more scientifically appropriate, constituent-specific method.

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