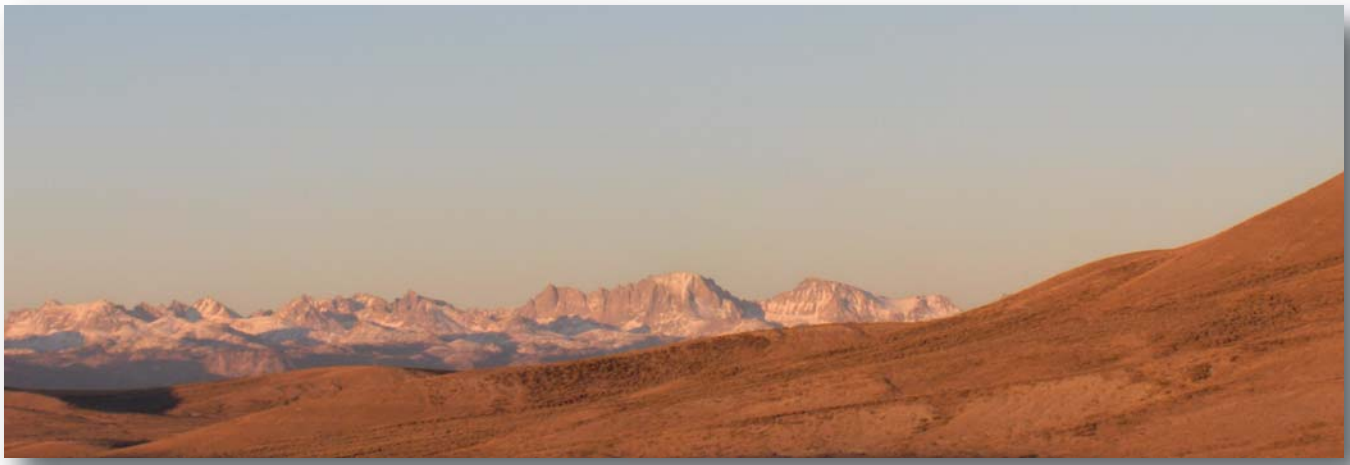
F I N A L

TECHNICAL REPORT
EVALUATION OF POTENTIAL SOURCES OF LOW-LEVEL PETROLEUM HYDROCARBON COMPOUNDS DETECTED IN GROUNDWATER
INTERIM PLAN

Pinedale Anticline Project Area ROD
Sublette County, Wyoming



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2013

NewFields amec QEP Resources, Inc. Ultra Resources, Inc.

FINAL

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EVALUATION OF POTENTIAL SOURCES OF LOW-LEVEL PETROLEUM HYDROCARBON COMPOUNDS DETECTED IN GROUNDWATER

INTERIM PLAN
Pinedale Anticline Project Area ROD
Sublette County, Wyoming

Prepared for:

U.S. Department of Interior, Bureau of Land Management, Pinedale Field Office
Wyoming Department of Environmental Quality, Water Quality Division
U.S. Environmental Protection Agency, Region 8
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GLOSSARY OF ACRONYMS AND SYMBOLS

Term	Definition
‰	per mil or parts per thousand
δ	delta
µg/L	micrograms per liter (equivalent to parts per billion)
AAPG	American Association of Petroleum Geologists
AMEC	AMEC Environment & Infrastructure, Inc. (previously AMEC Geomatrix, Inc., or Geomatrix Consultants, Inc.)
AMEC Geomatrix	AMEC Geomatrix, Inc.
AN	Antelope (production area)
APD	application for permit to drill
API	American Petroleum Institute
bbl	barrel
BDE	BLM/DEQ/EPA
BLM	U.S. Department of the Interior, Bureau of Land Management
BO	Boulder (production area)
BTEX	benzene, toluene, ethylbenzene, and xylenes
$C_1/(C_2+C_3)$	ratio of methane to ethane + propane
cc/L	cubic centimeters per liter
CFR	Code of Federal Regulations
CGF	central gathering facility
CGI	combustible gas indicator
C_n	organic compound containing *n* number of carbon atoms
CRDS	cavity ring-down spectroscopy
D	deuterium
DA	development area
DIC	dissolved inorganic carbon
EB	equipment blank
EDTA	ethylenediaminetetraacetic acid
E&P	exploration and production
EPA	U.S. Environmental Protection Agency
FB	field blank
FID	flame ionization detector
GC	gas chromatography
Geomatrix	Geomatrix Consultants, Inc.

GLOSSARY OF ACRONYMS AND SYMBOLS

Term	Definition
GPA	Gas Processors Association
H	hydrogen
HDG investigation	hydrogeological data gaps investigation (AMEC 2012)
HDPE	high-density polyethylene
HEM	n-hexane extractable material
HWY	Highway (production area)
ID	sample identification code
Interim Plan	Interim Groundwater/Aquifer Pollution Prevention, Mitigation, and Monitoring Plan (AMEC Geomatrix, 2008)
Intertek	Intertek Westport Technology Center in Houston, Texas
IRMS	isotope ratio mass spectrometry
$isoC_4$	isobutane
$isoC_4/nC_4$	ratio of isobutane to n-butane
$isoC_5$	isopentane
$isoC_5/nC_5$	ratio of isopentane to n-pentane
Isotech	Isotech Laboratories of Champaign, Illinois
LCS	laboratory control sample
LEL	lower explosive limit
LGS	liquid-gathering system
LLPHC	low-level petroleum hydrocarbon compounds
LMWL	local meteoric water line
LNAPL	light nonaqueous-phase liquid
MCFD	thousand cubic feet per day
MCL	Maximum Contaminant Level
MDL	method detection limit
meq/L	milliequivalents per liter
mg/kg	milligrams per kilogram (equivalent to parts per million)
mg/L	milligrams per liter (equivalent to parts per million)
mol %	mole percent
MS	Mesa (production area)
nC_4	n-butane
nC_5	n-pentane

GLOSSARY OF ACRONYMS AND SYMBOLS

Term	Definition
ND	not detected
NM	North Mesa
NP	North Pinedale
NPM	non-polar materials
O	oxygen
Operators	Ultra, Shell, and QEP
P&A	plugging and abandonment
PAH	polycyclic aromatic hydrocarbon
PAPA	Pinedale Anticline Project Area
PARCC	precision, accuracy, representativeness, completeness, comparability
PCS	petroleum-contaminated soil
PG	Petrogulf (production area)
PHC	petroleum hydrocarbon compound
ppm	parts per million
POS	plan of study
PQL	practical quantitation limit
Precision	Precision Analysis of Riverton, Wyoming
psi	pounds per square inch
QA	quality assurance
QC	quality control
QEP	QEP Energy
Questar	Questar Applied Technologies of Rock Springs, Wyoming
RB	Rainbow (production area)
RCRA	Resource Conservation and Recovery Act
ROD	Record of Decision
RPD	relative percent difference
RS	Riverside (production area)
SAP	Sampling and Analysis Plan
SAR	sodium adsorption ratio
SCADA	supervisory control and data acquisition
SCCD	Sublette County Conservation District
SEIS	Supplemental Environmental Impact Statement

GLOSSARY OF ACRONYMS AND SYMBOLS

Term	Definition
SGT	silica gel treatment
Shell	SWEPI LP
SN	Sundry Notice
SOP	standard operating procedure
SP	Stewart Point (production area)
SVOCs	semivolatile organic compounds
TAI	thermal alteration index
TDS	total dissolved solids
TEH	total extractable hydrocarbons
TIC	tentatively identified compound
TPgH	total purgeable hydrocarbons
TPH	total petroleum hydrocarbons
TPH-DRO	total petroleum hydrocarbons – diesel-range organics
TPH-GRO	total petroleum hydrocarbons – gasoline-range organics
UCM	unresolved complex mixture
Ultra	Ultra Resources, Inc.
VOCs	volatile organic compounds
VPDB	Vienna PeeDee Belemnite
VRP	Voluntary Remediation Program (Wyoming)
VSMOW	Vienna Standard Mean Ocean Water
WB	Warbonnet (production area)
WOGCC	Wyoming Oil and Gas Conservation Commission
Wyoming DEQ	Wyoming Department of Environmental Quality

EXECUTIVE SUMMARY

This report documents the evaluation of low levels of organic chemicals, or *constituents*, detected in groundwater samples collected from water wells in the Pinedale Anticline Oil and Gas Exploration and Production Area (also known as the Pinedale Anticline Project Area, or PAPA). *Low levels* refer to concentrations of organic constituents less than regulatory standards for groundwater. The PAPA covers approximately 309 square miles of federal, state, and private land in Sublette County, Wyoming. AMEC Environment & Infrastructure, Inc. (AMEC), in association with NewFields Companies LLC (since September 2012), conducted this independent investigation under contract to three oil and gas companies. This report is required under terms of a Record of Decision (ROD) issued by the U.S. Department of Interior, Bureau of Land Management (BLM).

The investigation identified no evidence of widespread impacts to groundwater in the PAPA as a result of natural gas exploration and production. Evaluation of the potential sources of organic chemicals considered in this study identified the following known or likely sources of low levels of organic constituents in water wells:

- Upward seepage by natural processes of natural gas from deep, underlying gas reservoirs over time into overlying geologic layers where groundwater occurs;
- Organic constituents introduced into water wells during drilling, installation, and operation of the well; and
- Naturally occurring organic matter in groundwater or associated with particles suspended in well water during sample collection.

Organic constituents introduced during drilling, installation, or operation of a water well, as well as particles of organic matter suspended in well water during sample collection, would not reflect groundwater conditions beyond the immediate vicinity of the well. Upward seepage of natural gas into groundwater and naturally occurring organic matter in groundwater reflect natural conditions. The sources of low-level organic constituents detected in some wells may be a combination of both organic material introduced into the wells and other organic material that occurs naturally. In many cases, it is impossible to differentiate between natural and man-made sources.

BACKGROUND

Water supply wells have been installed throughout the PAPA to provide water needed for natural gas exploration and production activities, which began in the PAPA in 1939. Groundwater samples have been collected from water wells in the PAPA annually since 2004. Low levels of organic constituents, which have been previously reported as *petroleum hydrocarbons*, have been detected in groundwater samples collected from a number of these water supply wells. This study was conducted to identify and evaluate the sources of these low-level organic constituents.

DEFINITION OF PETROLEUM HYDROCARBONS

Hydrocarbons are organic chemical compounds that contain varying numbers of carbon and hydrogen atoms. Refined petroleum products and unrefined petroleum extracted from the ground (crude petroleum) contain mixtures of many individual hydrocarbon compounds, which are referred to as *petroleum hydrocarbons*. Mixtures of hydrocarbons and other organic compounds also occur naturally in organic matter associated with groundwater or sediments. Laboratory methods have been developed by state and federal agencies to analyze for the presence of and determine the composition of mixtures of hydrocarbons. The methods used in this study were originally developed primarily to identify the types of hydrocarbons found in crude petroleum and refined petroleum products. However, these methods detect a broad range of organic constituents that include both hydrocarbon and non-hydrocarbon compounds and that can originate from both petroleum-based and non-petroleum sources.

Additional laboratory tests can be used to identify other specific chemicals present in the mixture. The specific types and amounts of chemicals present in the mixture produce what is called a *chemical signature*. The chemical signatures of mixtures of organic compounds can be used to help identify the potential source of these compounds. Likewise, the chemical signatures of different samples can be compared to assess whether they originate from the same source.

HIGH-LEVEL VERSUS LOW-LEVEL DETECTIONS

This study seeks to identify sources of low levels of organic constituents identified in samples from water wells. *Low level* means that detected concentrations are less than regulatory standards (applicable groundwater standards), and in most cases more than 10 times or even 100 or more times lower.

A few water wells in the PAPA sampled for this study contained high levels of organic constituents. *High level* means that concentrations are above the applicable groundwater standards. The State of Wyoming Department of Environmental Quality, Voluntary Remediation Program, is overseeing cleanup and/or further investigation of the few cases where high levels of organic constituents have been identified in water wells. The nature of the high-level detections, as well as the potential sources of the high-level detections, are not the focus of this report.

RESULTS OF SAMPLING AND ANALYSIS

AMEC collected samples of materials that could be potential sources of low-level organic constituents in water wells as part of a sampling and analysis plan that was developed for this study and accepted by BLM in consultation with the U.S. Environmental Protection Agency (EPA) and Wyoming Department of Environmental Quality (Wyoming DEQ). The potential source materials represent a variety of materials used in, or by-products of, natural gas exploration and production activities, including the natural gas produced from the gas wells. Samples of groundwater and gas

were collected from water wells selected for sampling in the PAPA. All samples were analyzed for a broad suite of organic constituents and other chemicals. The chemical signatures of groundwater samples collected from water wells were then compared to those of the material samples to identify if any of these materials could be contributing to low-level detections of organic constituents in the water wells. Sampling and analysis followed the sampling and analysis plan accepted by the BLM in consultation with the U.S. EPA and Wyoming DEQ.

The sampling results identified two main chemical signatures for organic constituents detected in these samples:

- Low-level detections of *volatile organic constituents*; and
- Low-level detections of *semivolatile organic constituents*.

Volatile and *semivolatile organic constituents* are general categories of organic constituents that are based on the *volatility* of the constituent (i.e., how easily the chemical evaporates). Volatile organic constituents are generally made up of smaller, volatile molecules, such as methane, which is generally the most abundant component of natural gas. Semivolatile organic constituents are generally made up of larger, less volatile molecules, such as naphthalene. These types of organic constituents may originate from a different source or sources. They occur in petroleum-containing substances, but also commonly occur naturally under a variety of conditions.

POTENTIAL SOURCES OF EXISTING LOW-LEVEL ORGANIC CONSTITUENTS

The following potential sources of organic constituents found in water samples were identified in accordance with the sampling and analysis plan:

- Natural gas wells
- Natural gas facilities, such as pits, pipelines, and storage tanks
- Injection wells for wastewater disposal
- Known waste facilities or contaminated sites unrelated to natural gas exploration and production activities
- Products and practices associated with water supply wells
- Sampling and laboratory procedures
- Upward seepage of natural gas by natural processes
- Naturally occurring organic matter

LOW-LEVEL DETECTIONS OF VOLATILE ORGANIC CONSTITUENTS

The low-level detections of volatile organic constituents in water wells consist primarily of hydrocarbon gases, based on chemical testing of the groundwater samples. The chemical signatures of gas in samples from water wells do not match the chemical signature of natural gas produced from natural gas production wells. Therefore, the low-level detections of volatile organic constituents in water wells are not directly linked to leaking natural gas wells or activities related to natural gas development. Something has caused the chemical signature of gas present in groundwater to change relative to the natural gas produced in the PAPA. Changes to the chemical signatures of gas can occur by natural processes when natural gas moves from one place to another.

Figure ES-1 presents a conceptual model for the movement of natural gas into groundwater in the PAPA.

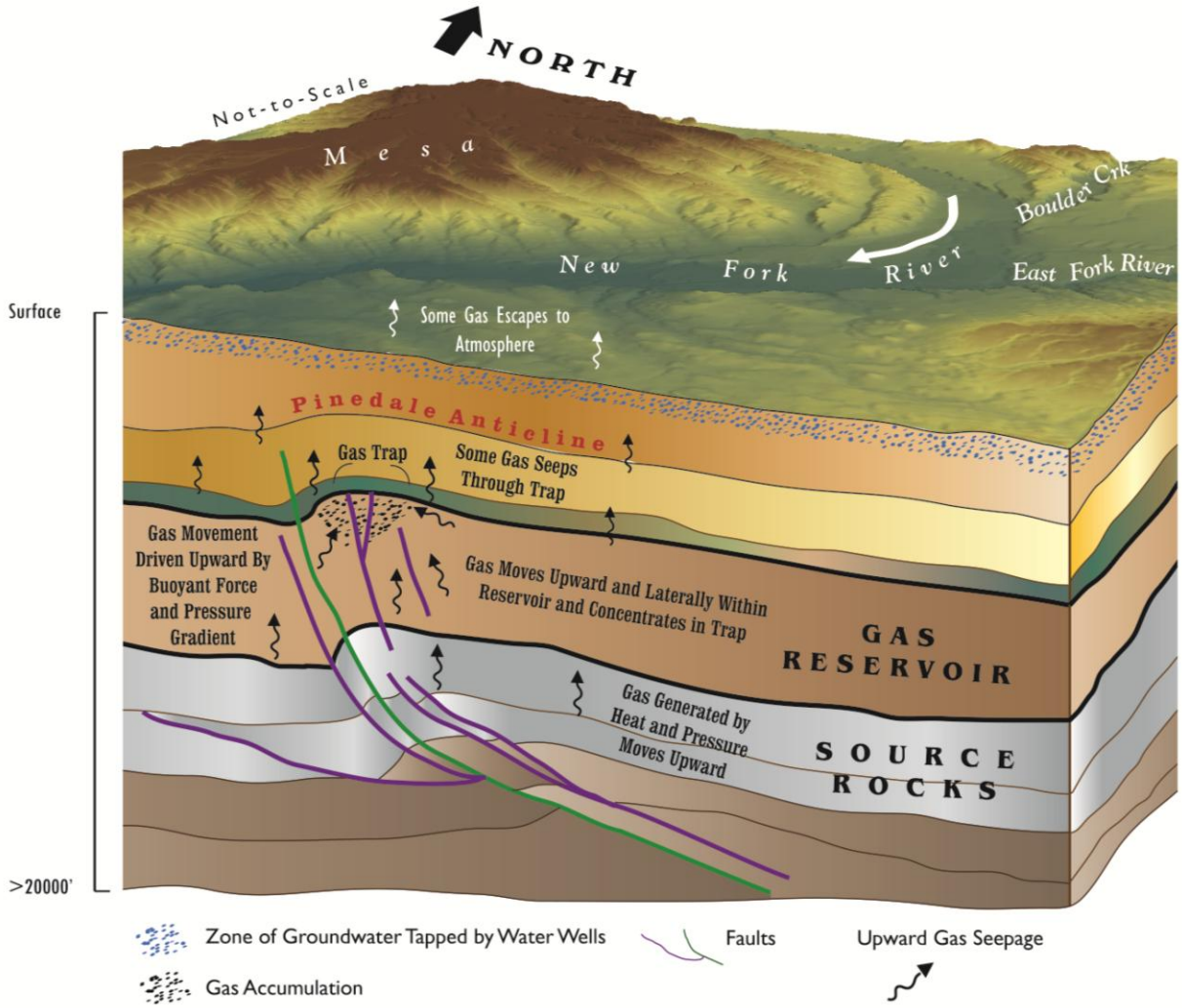


Figure ES-1. Conceptual Model for Natural Gas Generation and Seepage in the PAPA

Natural gas is generated in source rocks at great depth in the PAPA. This natural gas has moved upward until reaching relatively impermeable rock that traps the gas in an underground reservoir. Some natural gas seeps through the trap into the overlying geologic formations where groundwater occurs. The chemical signature of natural gas likely changes as the gas moves up through the thick layers of rock over geologic time. Where the gas comes in contact with groundwater, a portion of the natural gas becomes dissolved in groundwater. Gas can also move upward from groundwater in a water well into the air space below the well cap. Studies conducted at other gas fields have shown that natural gas tends to move upward to the ground surface over time. Moreover, the presence of gas in groundwater has been noted in water wells in the PAPA before natural gas wells had been drilled in those areas. Therefore, based on geologic conditions, the presence of natural gas in near-surface groundwater is expected as a natural condition in the PAPA.

LOW-LEVEL DETECTIONS OF SEMIVOLATILE ORGANIC CONSTITUENTS

Semivolatile organic constituents were also detected at low levels in water wells sampled for this study. The semivolatile organic constituents present in water wells do not appear to be related to the volatile organic constituents present in water wells. The locations of water wells where low levels of semivolatile organic constituents were detected are shown on **Figure ES-2**.

It is difficult to pinpoint the exact source of most of the low-level semivolatile organic constituents due to the absence of a distinctive chemical signature at most wells; however, these chemical signatures clearly do not match the chemical signatures of most potential source materials sampled for this study. Low levels of semivolatile organic constituents detected in water well samples appear to be related to one or more of the following materials, most of which are associated with drilling, construction, or use of the water well itself:

- Substances that are used or handled while drilling, installing, and operating water wells; and/or
- Naturally occurring organic matter present in groundwater or associated with particles of sediment suspended in well water during sample collection.

Organic constituent detections resulting from water well drilling, installation, and operating practices would primarily affect the quality of water inside the well with minimal or no impact to groundwater quality beyond the immediate vicinity of the well.

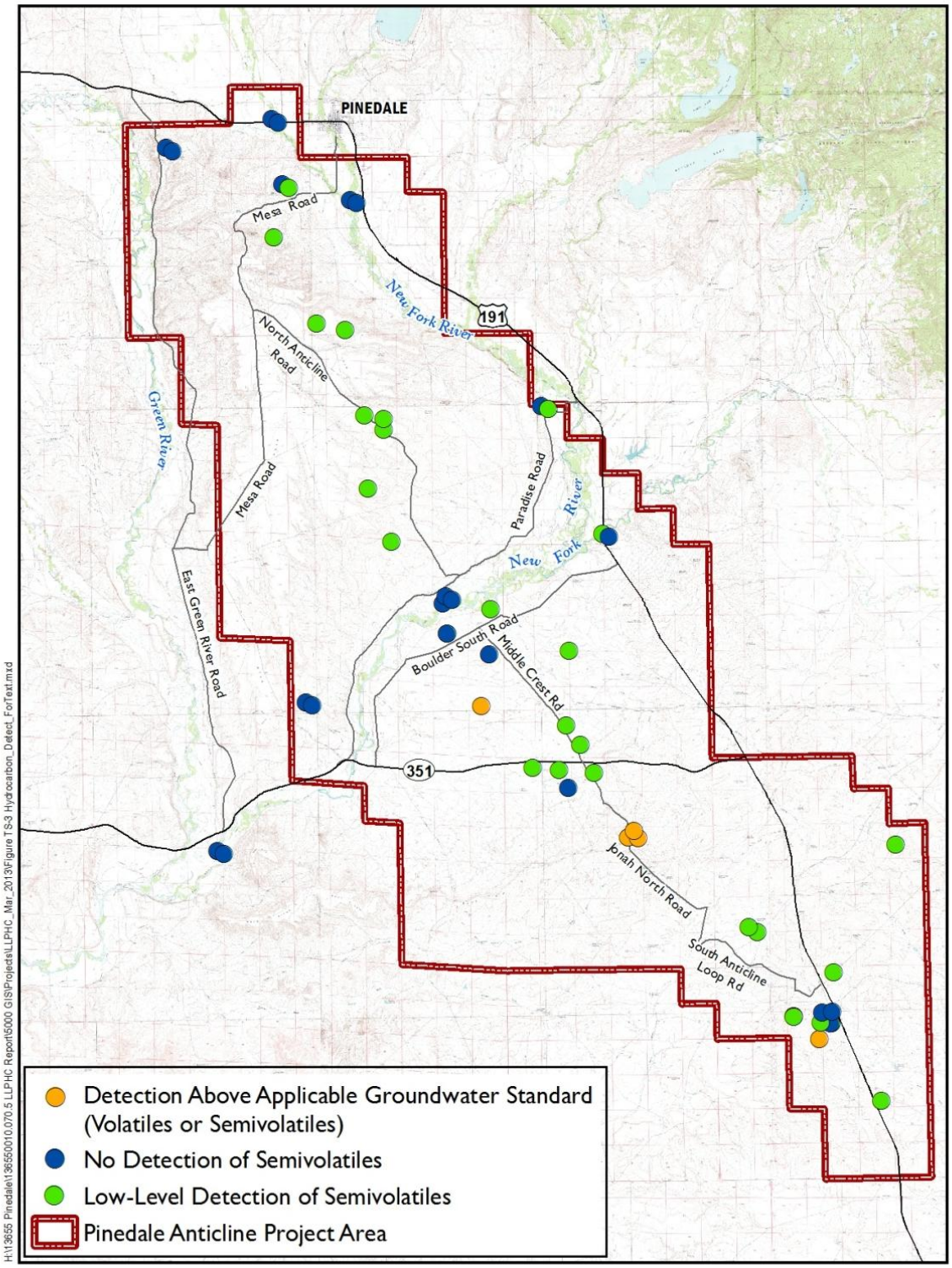


Figure ES-2. Detection of Semivolatile Organic Constituents in Water Wells

NO WIDESPREAD IMPACT TO GROUNDWATER IN THE PAPA

This study produced no evidence of widespread impact to groundwater in the PAPA caused by sources associated with natural gas exploration and development. Both the chemical signatures of groundwater from water wells and various other evidence support this conclusion. Some potential sources related to natural gas development had not yet been constructed or were not fully operational in the PAPA by the time the low levels of organic constituents were first detected in water wells. Some potential sources are not likely related to the low levels of organic constituents because they are located too far away from water wells or are located on the uphill side based on the direction of groundwater flow (*upgradient*) relative to water wells in the PAPA. Many low-level detections occur only sporadically in time and appear to be localized to the immediate vicinity of the water well. The distance between the ground surface and groundwater is large in most areas of the PAPA, and groundwater movement is relatively slow. This distance and slow rate of groundwater flow reduce the risk of widespread impact to groundwater due to spills at the ground surface. The few wells with high-level detections do not appear to be related to or contributing to the low levels of organic constituents detected in water wells. The use of environmentally responsible best practices during natural gas development and rigorous oversight by regulatory agencies minimize the risk of widespread impact to groundwater.

SUMMARY OF FINDINGS

Analysis of the evidence and data gathered in this study produced four main conclusions.

1. Low-level volatile organic constituents detected in groundwater are largely attributable to natural gas that seeps upward from deep geologic layers and into groundwater by natural processes over time.
2. The source or sources of semivolatile organic constituents detected at low levels in groundwater samples is not readily apparent. These constituents likely originate from the products and practices used to drill, install, or operate water wells and/or from naturally occurring organic matter present in groundwater or associated with particles of sediment suspended in water wells during sample collection.
3. No widespread impact to groundwater in the PAPA is evident as a result of spills or leaks of materials used in, or by-products of, natural gas development.
4. Based on this study, no additional measures are necessary to mitigate either the low-level volatile or semivolatile organic constituents detected in water wells in the PAPA.

These conclusions do not mean that releases from natural gas exploration and production activities could not affect groundwater in the future. Continued application of environmentally responsible best practices during these activities will help protect groundwater resources. Ongoing groundwater monitoring will help identify potential changes to groundwater conditions in the future.

TECHNICAL SUMMARY

This report documents an evaluation of organic constituents detected in groundwater samples and reported as low-level petroleum hydrocarbons (LLPHC). For purposes of this study, *low levels* are defined as concentrations in groundwater samples that are below applicable groundwater quality standards, specifically with respect to organic compounds or organic constituents. The groundwater samples were collected from water wells in the Pinedale Anticline Oil and Gas Exploration and Production Area (also known as the Pinedale Anticline Project Area, or PAPA). The PAPA covers approximately 309 square miles in Sublette County, Wyoming. The U.S. Department of the Interior, Bureau of Land Management (BLM), manages 80 percent of the land within the PAPA.

AMEC Environment & Infrastructure, Inc. (AMEC), in association with NewFields Companies LLC (since September 2012) conducted this study under contract to Ultra Resources, Inc. (Ultra), Shell SWEPI LP (Shell), and QEP Energy (QEP) (known collectively as Operators). This study was performed to fulfill requirements specified in a BLM Record of Decision (ROD) issued in 2008. A groundwater characterization called for in the ROD included a study to evaluate potential sources for low-levels of organic constituents detected in water wells. A consortium of federal and state agencies and the Operators prepared an *Interim Groundwater/Aquifer Pollution Prevention, Mitigation and Monitoring Plan* (Interim Plan) (AMEC Geomatrix, 2008) that required a Plan of Study (POS) be developed outlining the technical approach to perform this evaluation (AMEC Geomatrix, 2009a). This report presents the results of executing that POS.

This study is supported by the findings of two companion studies:

- A hydrogeological data gaps (HDG) investigation as reported in the *Technical Report – Hydrogeologic Data Gaps Investigation* (HDG investigation) (AMEC, 2012); and
- A groundwater flow and solute fate and transport modeling study as documented in the *Final Numerical Groundwater Modeling Report* (AMEC, 2013).

The direction and velocity of groundwater flow were determined as part of the HDG investigation, and this information was used in concert with the chemical data from this study to evaluate the occurrence of the observed low-level detections of organic constituents in groundwater in the PAPA. Inorganic water quality data from the HDG investigation were used in concert with inorganic water quality data from this study to evaluate the influence of hydrogeologic factors on inorganic geochemistry. Results of the fate and transport modeling study were used in combination with observed organic constituent detections in water wells to evaluate the fate and transport of these constituents if they were to be released.

The results of these three studies as prescribed by the 2008 ROD will be consulted when preparing the *Final Groundwater/Aquifer Pollution Prevention, Mitigation, and Monitoring Plan* for the PAPA.

Further information regarding the regulatory framework for this project, federal and state agencies involved, and other related documents are provided in **Section 1.0** of this report.

REPORT ORGANIZATION

An **Executive Summary** presented at the beginning of this report is geared toward the general public and provides a succinct summary of the findings of the study. This **Technical Summary** provides a more in-depth overview of the findings of the study geared to a more technical reader. The main text of the report presents a detailed description of the background, methodology, findings, and conclusions of this study.

BACKGROUND

Numerous industrial water supply wells are located throughout the PAPA to provide water to support natural gas exploration and production (E&P) activities. The BLM's initial ROD for natural gas development in the PAPA (BLM, 2000) outlined requirements for water resources inventories and water quality monitoring, which included annual groundwater sampling of domestic, stock, and miscellaneous (industrial) water supply wells located within 1 mile of proposed or existing oil and gas wells in the PAPA. In 2006, the Wyoming Department of Environmental Quality (Wyoming DEQ) became aware of organic constituents that were discovered in water samples collected from four industrial water supply wells. It was suspected that these wells were impacted due to siphoning, or backflow, of contaminated water into the wells. As a result of this discovery, BLM's 2008 ROD for expanded natural gas development in the PAPA required a study to evaluate potential sources of the organic constituents detected in water wells.

As part of this study, AMEC compiled and reviewed available information regarding potential sources of low-level detections in water wells in the PAPA and performed spatial and temporal analyses of existing groundwater quality data with respect to potential sources of organic constituents. Based on the data gaps discovered during that evaluation, AMEC developed the *Sampling and Analysis Plan for Evaluating Potential Sources of Low-Level Petroleum Hydrocarbon Compound Detections* (the SAP; AMEC Geomatrix, 2010). The SAP, which was accepted by BLM in consultation with the Wyoming DEQ and U.S. Environmental Protection Agency (EPA), describes the methodology and rationale for additional sampling and analysis needed to further evaluate the source(s) of low-level organic constituents detected in water wells.

HIGH-LEVEL VERSUS LOW-LEVEL DETECTIONS

Most of the organic constituent detections in water wells in the PAPA are considered low level, which means that detected concentrations are less than applicable regulatory standards for groundwater. This study seeks to identify sources of these low levels of organic constituents identified in water wells.

A few water wells in the PAPA exhibit high-level detections of organic constituents. *High-level detections* means that concentrations are above the applicable groundwater standards. These high-level detections appear to have originated from materials used or generated during natural gas E&P activities, and the Wyoming DEQ Voluntary Remediation Program (VRP) is overseeing cleanup and/or further investigation of the few cases of high-level detections in industrial water supply wells in the PAPA. The nature of the high-level detections, as well as the potential sources of the high level detections, are not the focus of this report, but are described briefly in **Section 8.5** in order to provide context and assess if these high-level detections are related to the low-level detections observed in water wells in the PAPA.

COMPOSITION OF PETROLEUM

The low-level concentrations of selected organic compounds and mixtures of compounds that have been detected historically in wells throughout the PAPA have largely been reported as *petroleum hydrocarbons* due to the colloquial name applied to the laboratory methods most commonly used for preparation and analysis of samples.

Petroleum consists of mixtures of up to hundreds or even thousands of individual hydrocarbon compounds. Mixtures of petroleum hydrocarbon compounds (PHCs) are often defined in terms of the number of carbon atoms, or the range in the number of carbon atoms, present in the individual compounds that make up the mixture (see **Figure 2-3**). The proportions of the different types of hydrocarbons, as well as the carbon-number ranges of the hydrocarbon compounds present in a sample, provide clues to the origin of the PHCs, whether from a refined petroleum product, unrefined petroleum, or other naturally occurring organic matter.

Unrefined petroleum products, such as crude oil or condensate, tend to have a broader range in the number of carbon atoms in the individual constituents compared to refined products, since refining processes specifically produce petroleum products containing hydrocarbons with a narrower carbon-number range for a variety of specific uses. Crude oil may contain some fractions of non-hydrocarbon organic compounds, but refined petroleum products typically contain smaller amounts of non-hydrocarbon compounds. Naturally occurring organic matter can contain an abundance of non-hydrocarbon compounds. Detailed information regarding hydrocarbons and the composition of petroleum is presented in **Sections 2.1.1** and **2.1.2**, respectively.

ANALYTICAL TECHNIQUES FOR TOTAL PETROLEUM HYDROCARBONS

Total petroleum hydrocarbons (TPH) is a measurement of the sum total of all organic compounds present in an environmental sample captured and quantified by sample preparation and analytical methods defined by the laboratory. TPH was analyzed for this study using U.S. EPA Method 8015, which measures sums of all of the volatile and semivolatile (less volatile) organic compounds present in a sample based on gas chromatography (GC) with a flame-ionization detector (FID). TPH

methods are non-specific laboratory methods and detect all organic compounds, both hydrocarbons and non-hydrocarbons, within that specified carbon number range. Detailed information regarding sample preparation and other methods of TPH analysis, silica gel treatment of semivolatile extracts, the evaluation of gas chromatograms, and other testing methods for organic compounds are presented in **Sections 2.1.3** and **2.1.4**, respectively.

For this study, the volatile and semivolatile fractions of TPH were determined by EPA Method 8015 (**see Figure 2-3**). The volatile fractions of TPH were reported both as *total purgeable hydrocarbons* (TPgH) and as *total petroleum hydrocarbons–gasoline-range organics* (TPH-GRO). TPgH is a measure of the sum of all volatile material (both hydrocarbon and non-hydrocarbon) that is removed from the sample using purge-and-trap sample preparation methods, captured on the GC column, and quantified based on detection by the FID. For this study, the TPH-GRO measurement contained all compounds that elute from the chromatography column between 2-methylbutane and 1,2,4-trimethylbenzene. Although they are volatile (and may be gases at room temperature), light hydrocarbon gases (approximately C_1 through C_4) are generally not quantified using TPH methods.

The semivolatile fractions of TPH were reported both as *total extractable hydrocarbons* (TEH) and as *total petroleum hydrocarbons–diesel-range organics* (TPH-DRO). TEH is a measure of all semivolatile materials that were extracted from the sample after shaking in contact with n-hexane and then captured and quantified by GC/FID. For this study, the TPH-DRO measurement represents all organic compounds that contain between 10 and 28 carbon atoms in their structure (C_{10} through C_{28}). The reported presence of TPH-GRO and TPH-DRO in a sample does not necessarily indicate that a refined product, such as gasoline or diesel fuel, is present in the sample. Moreover, the compounds eluting from the column within this time frame could be hydrocarbons or non-hydrocarbons and may or may not originate from petroleum sources.

Because reported levels of petroleum hydrocarbons are defined by the analytical method and not the source of the materials in the sample, we will not refer to *petroleum hydrocarbons* in this report unless evidence of a petroleum source exists or to *hydrocarbons* unless evidence of specific hydrocarbon constituents exists based on chemical analysis (see **Section 2.1.5**). Mixtures representing some combination of the volatile fraction of organic compounds (i.e., TPgH and TPH-GRO determined by EPA Method 8015, individual volatile organic compounds [VOCs] analyzed by EPA Method 8260, or hydrocarbon gases) may be referred to more generally as *volatile organic constituents* or simply as *volatile organics*. Mixtures representing some combination of the semivolatile fraction of organic compounds (i.e., TEH and TPH-DRO as determined by EPA Method 8015 as well as individual semivolatile organic compounds [SVOCs] analyzed by EPA Method 8270) may be referred to more generally as *semivolatile organic constituents* or simply *semivolatile organics*.

GEOLOGY AND HYDROGEOLOGY OF THE PAPA

The petroleum system currently exploited in the PAPA consists of a thick interval of low-porosity and low-permeability Cretaceous rock found within a structural trap known as the Pinedale Anticline (**Figure 2-4**). The anticline is oriented northwest/southeast, and the axis of the anticline runs parallel to the Wind River Mountains to the east.

Cretaceous-age sediments found in the PAPA were deposited in a marine environment, which eventually transitioned into an alluvial plain depositional environment. The sediments that host the gas reservoir include sandstones, siltstone, mudstones, and carbonaceous shale units of the Cretaceous-aged upper Mesaverde and Lance Formation, as well as the Tertiary Unnamed Unit (**Figure 2-5**). These gas-bearing sediments are collectively referred to as the Lance Pool, which is an over-pressurized, tight gas reservoir located 8,000 to 14,000 feet below the ground surface (**Figures 2-6** and **2-7**). Twenty natural gas wells were drilled in the PAPA between 1939 and 1982 to tap the Lance Pool (i.e., pre-1984 wells). Since 1994, the drilling of natural gas production wells has rapidly increased due in part to improvements in drilling and hydraulic fracturing technology. Most of the natural gas E&P activities are concentrated along the entire length of the crest of the anticline (**Figure 2-8**). Further information about the geology and the petroleum system exploited in the PAPA and the history of gas E&P in the PAPA is provided in **Sections 2.2** and **2.3**, respectively.

The collective sediments of the Lance Pool are overlain by approximately 8,000 feet of Tertiary-age sedimentary rocks of the Fort Union and Wasatch Formations. These sediments consist of interbedded shale, siltstone, and sandstone that were deposited in fluvial deltaic and alluvial plain environments. Groundwater in the Wasatch Formation, the uppermost water-bearing zone along the axis of the anticline, is tapped to support natural gas E&P activities, as well as domestic and stock uses. The deepest industrial water supply wells are approximately 1,000 to 1,200 feet in depth, which is approximately 7,000 feet above the top of the Lance Pool (**Figure 2-9**). Tertiary-aged formations are overlain in some discrete areas in the PAPA by unconsolidated, Quaternary- and Holocene-aged sediments.

Regionally, groundwater generally flows westward and southward from the mountains and foothills of the Wind River Range, where it is recharged, toward the Green River below the mouth of the New Fork River and into the center of the Green River Basin (AMEC, 2012). Groundwater flow is toward the south in the PAPA north of the New Fork River; groundwater flow is toward the west in the PAPA south of the New Fork River (**Figure 2-10**). Some recharge to the Wasatch Formation may occur in the area of the PAPA. Groundwater in the Wasatch Formation is typically present under semiconfined conditions due to the heterogeneous nature of the formation. Estimated average groundwater velocity in Wasatch Formation sandstone units ranges from 0.011 foot/year to 40 feet/year (see **Section 2.4.3**). The towns of Pinedale and Boulder are located hydrogeologically upgradient of natural gas E&P activities in the PAPA.

Alluvial sediments in the river corridors are in hydraulic communication with groundwater in the Wasatch Formation, and receive and transmit groundwater down valley and into the New Fork River in the central PAPA. Vertical hydraulic gradients in alluvium in the upper New Fork River valley vary seasonally, but are upward most of the year (AMEC, 2012). Numerical modeling results indicate that transport velocities in alluvial material along the New Fork and Green rivers are 100 to 700 times greater than those in the Wasatch Formation (AMEC, 2013). To put this in perspective, groundwater would travel 100 to 700 times further in one year within alluvium than it would within the Wasatch Formation. Further information about the hydrostratigraphic units and the water wells present in the PAPA, as well as details about the groundwater flow system, are provided in **Section 2.4**.

GROUNDWATER QUALITY IN THE PAPA

No comprehensive baseline groundwater monitoring was conducted prior to natural gas development in the PAPA. Annual groundwater quality monitoring has been performed by the Sublette County Conservation District (SCCD) on behalf of the Operators since 2004. Water wells that are sampled include domestic, stock, and miscellaneous (industrial) water supply wells. Analytical parameters include general water quality constituents, common ions, metals, and organic constituents. A description of general water quality characteristics in the PAPA is provided in **Section 2.5.1.** Methods of analysis for organic constituents used by SCCD are detailed in **Section 2.5.2**. As of December 31, 2011, the SCCD had collected more than 2,000 groundwater samples from over 380 water wells within 1 mile of existing or proposed oil and gas wells in the PAPA (SCCD, 2012). Results of annual monitoring by SCCD are posted on the Pinedale BLM website.[1]

A majority of wells sampled by the SCCD between 2004 and 2011 have had no detections of organic constituents (**Appendix A)**. When organic constituents have been detected in groundwater samples, most constituent concentrations have been below applicable groundwater standards, in many cases by an order of magnitude or more. The few industrial water supply wells where organic constituents have been consistently detected at concentrations greater than applicable groundwater standards have been, or are currently, under regulatory oversight (e.g., Wyoming DEQ VRP). Locations where organic constituents were detected the last time the well was sampled prior to 2012 (e.g., most recent detections as of 2011) are distributed throughout the area of the PAPA and are not clustered in any particular area (**Figures A-1** and **A-2**; **Appendix A**). A more detailed summary of organic constituent detections in water wells in the PAPA is provided in **Section 2.5.3.**

The SCCD monitors wells for the presence of combustible gases in well casings as a safety precaution prior to collection of groundwater samples. The SCCD has identified industrial water

[1] http://www.blm.gov/wy/st/en/field_offices/Pinedale/pawg/DataResults.html

supply wells in the PAPA with detectable concentrations of combustible gas in water well casings during annual groundwater monitoring. More information about gas occurrence in water wells is provided in **Section 2.5.4**.

POTENTIAL SOURCES OF ORGANIC CONSTITUENTS

Potential sources that might be contributing to the detections of organic constituents in water wells in the PAPA were identified by:

- Reviewing available aerial photographs, Operator records, and BLM files;
- Interviewing Operator representatives, water drilling contractors, and water pump installation contractors;
- Observing water well drilling and pump installation techniques;
- Reviewing public databases maintained by regulatory agencies for information on reported releases or remedial efforts; and
- Inquiring with regulatory agencies about the status of facilities that may be potential sources and applicable rules and regulations for natural gas E&P.

Additional details regarding this information gathering effort are provided in **Section 3.1**. Potential sources identified based on the information gathered are shown in **Chart TS-1**.

Natural sources are more likely to be non-point sources. For example, the upward seepage of natural gas from depth or the presence of naturally occurring organic material in groundwater may manifest itself as a more widespread or ubiquitous signature in water wells versus a discrete spill from a natural gas production facility, which would likely be reflected only in water wells near the source.

Potential sources are described in detail in **Section 4.0**. Locations of identified potential sources within and in the immediate vicinity of the PAPA are depicted on **Figure 4-1**.

Chart TS-1 Potential Sources

Potential Source	Activity
Natural Gas Production Wells	Well construction Well completions (hydraulic fracturing) Well abandonment
Natural Gas Production Facilities	Pits Tanks Production equipment In-field liquid gathering systems (LGS) or pipelines Tank batteries or central gathering facilities (CGFs)
Waste Disposal	Injection wells for produced water Landfills Permitted oil disposal facilities
Spills and Releases	From natural gas E&P activities (i.e., both on-pad and off-pad) From activities not related to natural gas E&P activities (i.e., off-pad)
Industrial Water Supply Wells	Drilling Installation Operation
Sampling and Laboratory Issues	Inconsistency in methodology (sampling and laboratory) Mis-identifications (laboratory) Cross-contamination (sampling and laboratory)
Natural Conditions	Upward seepage of natural gas from depth Naturally occurring organic matter in sediments and groundwater

SAMPLING AND ANALYSIS

Between September 2010 and February 2012, AMEC collected samples of groundwater, gas, and materials that could be potential sources of organic constituents (i.e., potential source materials) in accordance with the SAP (AMEC Geomatrix, 2010). Potential source materials sampled as part of the SAP included substances used in, or by-products of, natural gas E&P. The purpose of this sampling and analysis program was to compare the chemical signatures of the potential source material samples to the chemical signatures in groundwater samples in order to identify the source of organic constituents in low-level wells. A detailed description of sample collection and analysis methods as well as quality assurance and quality control procedures is presented in **Section 3.2**.

Groundwater samples were collected throughout the PAPA from 34 water wells:

- 25 industrial water supply wells installed in the PAPA to support natural gas E&P activities; and
- 9 study wells (i.e., SAP study wells), which were installed as part of the companion HDG investigation.

Groundwater samples were analyzed for inorganic and organic constituents by the methods outlined in **Table 2**. Inorganic constituents included general water quality parameters, total metals, and stable isotopes of water and dissolved inorganic carbon. Organic constituents included the volatile and semivolatile organic fractions of TPH (TPgH, TPH-GRO, TEH, and TPH-DRO) as well as VOCs and SVOCs. Analyses of VOCs and SVOCs included reporting tentatively identified compounds (TICs) based on probable computer matches of individual mass spectrometry chromatograms obtained from a library search. Follow-up groundwater samples were collected from selected wells to verify earlier results or to quantify reported TICs. Analytical results for groundwater samples are presented in **Section 7.0**.

Gas samples were analyzed for stable isotopes of methane and gas composition by the analytical methods and laboratories listed in **Sections 3.2.4.2** and **3.2.4.3**, respectively. Samples of dissolved gas in groundwater were collected from the 34 wells, and samples of gas found accumulating in capped water well casings were collected from 10 water wells. Samples of natural gas, which is considered a potential source material, were collected from six active natural gas production wells in the PAPA. Follow-up gas samples were collected from selected water wells to verify earlier results. The analytical results for samples of dissolved gas, casing gas, and natural gas are provided in **Section 6.0**.

Several samples of potential source materials were collected and submitted for laboratory analysis for various parameters (**Table 1**). The sampled potential source materials included oil-based drilling mud, condensate, produced water, flowback fluid, pump installation materials, light nonaqueous-phase liquid (LNAPL), and carbonaceous shale. A description of these sampled potential source materials is provided in **Section 3.2.1**; the analytical results for these potential source materials are presented in **Section 5.0**.

In **Section 9.0,** findings based on chemical testing data are coupled with findings based on spatial, temporal, physical and operational evidence to assess the potential sources of organic constituents in industrial water supply wells in the PAPA.

DATA SETS CONSIDERED IN EVALUATION

The evaluation in this study is based primarily on the data set collected as part of implementing the SAP (i.e., SAP data); however, other available chemical data sets were also used in interpreting the results of this study. A description of these data sets and how they were used in the study is presented below. Methods of data evaluation, which included graphical analysis of water quality, statistical analysis, chromatogram pattern matching, stable isotope geochemistry, and hydrocarbon gas component ratios, are described in detail in **Section 3.3**. The results of data evaluation are presented in **Sections 8.0** and **9.0**.

SCCD DATA

Annual groundwater monitoring data collected by SCCD were used in a screening capacity to identify wells for sampling and analysis and to provide context with regard to the frequency, magnitude, and spatial distribution of organic constituent detections in the PAPA.

HDG DATA

Analytical results for organic constituents in samples collected from 18 HDG study wells sampled as part of the companion HDG investigation are presented in this report (see **Section 7.0**). The HDG study wells were analyzed for a more limited suite of constituents than the SAP study wells, as described in **Section 3.3.1.2**. Details about the installation of study wells for the HDG investigation are presented in **Section 2.4.2**.

Samples from both the HDG and SAP study wells that contained detectable TEH were subjected to silica gel treatment (SGT), and re-analyzed for the semivolatile organic fraction by EPA Method 8015. SGT was applied to provide an indication of the extent of extractable organic material that could be attributed to the presence of non-hydrocarbons. Information about SGT and potential sources of the polar (non-hydrocarbon) components that are removed from the extract by SGT are discussed further in **Section 2.1.3.3**. HDG data were used to evaluate the influence of well and pump installation practices and naturally occurring organic matter on water quality in water wells.

SAP DATA

Implementation of the SAP generated a valid and comprehensive data set. SAP data consist of analytical results from groundwater, potential source material, and gas samples, which are presented in **Section 5.0** through **Section 7.0** of this report. The samples were analyzed for an extended list of parameters using various analytical methods (see **Table 2**). The results assist in identification of the potential source or sources of organic constituents in water wells in the PAPA.

Sampling and analytical methods and quality assurance/quality control (QA/QC) protocols employed for this study were selected to minimize the potential for false positive results to the extent possible (**Section 3.3.1.3**). To minimize uncertain interpretations, laboratory results less than the laboratory reporting limit or practical quantitation limit (PQL) but greater than the method detection limit (MDL) were qualified as estimated concentrations by the laboratory and were not considered in data evaluation (i.e., filtered). An evaluation was conducted to assess if filtering these estimated results would affect the interpretations presented in this report. Results of this evaluation showed that considering these estimated results would have no effect on interpreting the data in this study (**Appendix E**).

This data filtering did not apply to laboratory results qualified as estimated based on project-specific QA/QC criteria. These results are presented in data tables and used in data analysis.

POTENTIAL SOURCE MATERIAL DISTINCTION

Differentiating potential source materials sampled based on chemical signature is important in order to identify the source of chemical signatures observed in the groundwater samples. The chemical signatures of the various potential source materials sampled (except natural gas and carbonaceous shale) could be distinguished based on the relative abundance of the volatile and semivolatile fractions; the presence of certain VOCs and SVOCs; the suite of TICs reported for those samples; and characteristic profiles in chromatograms. For example, drilling mud did not contain detectable levels of benzene and showed a characteristic diesel-type signature in the chromatogram from the semivolatile organics analysis. Samples of pump installation materials were composed primarily of the semivolatile organic fraction outside of diesel-range organics (TPH-DRO) with very few, if any, VOCs and/or SVOCs detected. Produced water and condensate were characterized by having abundant benzene, toluene, ethylbenzene, and xylenes (BTEX) as well as volatile organic fractions. The composition of flowback fluid samples varied with respect to the abundance of the volatile and semivolatile organic fractions as determined using EPA Method 8015; however, the presence of TICs, such as ketones, acids, alcohols, and phenols, was characteristic. The chemical signature of the LNAPL sample did not match any other potential source materials sampled.

Certain inorganic constituents were detected in potential source materials at elevated concentrations as compared to typical groundwater in the PAPA. For example, produced water and flowback fluid contained elevated concentrations of chloride, sodium, and total dissolved solids (TDS); however, these inorganic indicators could not be used to differentiate between these two potential source materials. A detailed evaluation of distinguishing characteristics of potential source materials (excluding natural gas and carbonaceous shale) is provided in **Section 5.8** and summarized in **Table 9**.

The target of E&P activities for natural gas in the PAPA is the Lance Pool. The hydrocarbon composition and isotopic composition of methane in natural gas samples collected from production wells for this study indicate that natural gas produced in the PAPA is thermogenic in origin (**Section 8.1.4**). Stable carbon isotope of methane values in samples collected from natural gas samples ranged from -34.36 to -37.47 parts per thousand (per mil), which plot well within the thermogenic zone of a standard gas genetic classification scheme (**Figure 8-4**). C_{6+} gas components were detected in natural gas samples, and the $C_1/(C_2 + C_3)$ ratios were less than 50, which is typical of thermogenic gas (**Section 8.1.1**). Natural gas samples did not show a relative depletion of n-alkanes relative to isoalkanes (**Table 10**). Although only natural gas production wells located south of the New Fork River were sampled, it is expected that natural gas produced north of the New Fork River is similar in composition to that produced south of the New Fork River. No

other source of marketable gas is known to occur in the PAPA. Analysis of carbonaceous shale samples from the Wasatch Formation indicates that the shale is either not a good source for oil and gas generation or not thermally mature enough to generate gas (**Section 5.7**; **Appendix D**).

ORGANIC CONSTITUENT DETECTIONS IN LOW-LEVEL WELLS

For the purpose of this analysis, wells with detections of organic constituents at concentrations below applicable groundwater standards will be referred to as *low-level wells*. The constituents detected in low-level wells sampled for this study can be grouped into two general classes of organic constituents (**Table 14**):

- *Volatile organic constituents* comprise the constituents reported as TPgH and TPH-GRO by EPA Method 8015 (**Section 7.2.2.1**), hydrocarbon gases detected in the dissolved gas analysis (**Section 6.3**), and individual VOCs detected using EPA Method 8260 (**Section 7.2.2.4)**.

- *Semivolatile organic constituents* comprise the constituents reported as TEH and TPH-DRO by EPA Method 8015 (**Section 7.2.2.2**) and individual SVOCs detected by EPA Method 8270 (**Section 7.2.2.4)**.

The interpretations presented in this report are based on analytical results from groundwater, gas, and potential source material samples (**Section 5.0** through **Section 7.0)**, and the findings from research conducted for this study on potential point and non-point sources in the PAPA (**Section 4.0**). Further information and context were gleaned from the SCCD data and HDG data.

Although potential sources of volatile and semivolatile organic constituent detections are discussed separately in the sections below, the nature of the semivolatile fraction was considered when evaluating the potential sources of the volatile fraction in groundwater samples. Similarly, the volatile fraction was considered when evaluating the potential sources of the semivolatile fraction in groundwater samples. The assessment of potential sources for low-level detections of organic constituents is complicated by several factors, which are described fully in **Section 9.0**.

DETECTIONS OF VOLATILE ORGANIC CONSTITUENTS IN LOW-LEVEL WELLS

Based on assessment of the available evidence generated by this investigation, volatile organic constituents detected in water wells in the PAPA consist largely of dissolved hydrocarbon gas that has seeped upward from depth by natural processes that have occurred over geologic time. This section presents a summary of the evidence to support this finding (**Section 9.1**; **Figure 9-1**).

CHEMICAL SIGNATURE OF VOLATILE ORGANIC CONSTITUENTS IN LOW-LEVEL WELLS

The chemical signature of volatile organic constituents in low-level wells sampled for this study displayed the following general characteristics:

- All low-level wells contained dissolved methane, and approximately half of these wells also contained higher molecular weight (C_{2+}) hydrocarbon gas components along with the methane.
- Generally, no higher molecular weight gases (i.e., C_{3+} gases) were present in wells with low concentrations (<1 milligram per liter [mg/L]) of methane.
- Volatile organic fractions reported as TPgH and TPH-GRO were detected in less than half of the low-level wells at low concentrations (<600 micrograms per liter [µg/L]). Detections of TPH-GRO are associated with samples containing C_{3+} gases based on the dissolved gas analyses.
- The isotopic composition of methane generally changed moving from south to north in the PAPA. Thermogenic gas was present at the south end of the PAPA. Methane concentrations were too low in wells north of the New Fork River to perform isotope analysis.
- Individual VOCs, when detected above the reporting limit in the low-level wells sampled for this study, were limited to toluene at very low concentrations equal to or less than 5 µg/L.

Dissolved methane concentrations in groundwater generally decreased from south to north, ranging from below 0.1 mg/L in samples from wells at the northern end of the PAPA to 120 mg/L in a sample from a well at the southern end of the PAPA (**Table 11**; **Figure 8-1**). Groundwater samples with higher methane concentrations typically also contained a greater number of C_{2+} gases, whereas samples with the lowest methane concentrations generally contained no C_{2+} gases.

As discussed in detail in **Section 8.1.4.1**, the origin or chemical signature of the gas in many low-level wells at the south end of the PAPA is decidedly thermogenic, based on stable carbon isotope values of methane ranging from -35.70 to -38.02 per mil. These values plot in the thermogenic zone on a standard genetic gas classification scheme and are similar to values observed for natural

gas being produced in the PAPA (**Figure 8-4**). However, hydrogen isotope values of methane in groundwater (and casing gas) are shifted relative to those in natural gas (**Figure 8-4**). Moreover, both the dissolved gas and casing gas samples from these wells display a preferential loss of straight-chain alkanes (n-alkanes) relative to branched alkanes (isoalkanes), indicating that the thermogenic gas has been altered (**Figure 8-2**; **Figures G-1** through **G-4** in **Appendix G**). All water wells that contain gas with an altered thermogenic signature are located south of the New Fork River.

Hydrocarbon gas in wells located in the central portion of the PAPA has an intermediate signature (i.e., stable carbon isotope values of methane ranging from -53.06 to -60.96 per mil [**Figure 8-4**]). This gas exhibits influence from thermogenic gas that appears to be altered in a similar fashion as observed in low-level wells farther south, as indicated by the preferential depletion of n-alkanes relative to isoalkanes (**Section 8.1.4.2**; **Figure 8-1**). Some gas with an intermediate isotopic signature does not show preferential depletion of n-alkanes relative to isoalkanes, because the concentrations of the C_{4+} gases that would indicate alteration were too low. Therefore, the absence of C_{4+} gas components in groundwater from some low-level wells in the central PAPA does not represent an anomaly or indicate the presence of a different gas. These findings are consistent with the overall trend in the magnitude of hydrocarbon gas concentrations and with the changes observed in the chemical signatures of hydrocarbon gas in groundwater moving north in the PAPA (**Section 9.1.3.2**).

Dissolved gas with a microbial-type signature is found near the New Fork River with stable carbon isotope values of methane ranging from -72.5 to -73.63 per mil (**Section 8.1.4.3**; **Figure 8-1**). The methane isotope signature in dissolved gas from all wells located north of the New Fork River, as well as some wells located south of the New Fork River, could not be determined due to low methane concentrations in groundwater (i.e., insufficient gas volume for isotopic analysis). A general discussion of gas origin and indicators of gas origin based on stable isotopes of methane is presented in **Section 8.1.1.**

Figure TS-1 illustrates the chemical signature of dissolved gas in water wells sampled for this study based on the stable isotopic composition of methane. Dissolved gas analysis was not performed on HDG study wells sampled only for the HDG investigation.

Other volatile organic constituents detected in low-level wells included the volatile organic fractions (i.e., TPgH and TPH-GRO) and toluene at very low concentrations (on the order of micrograms per liter or parts per billion). The TPH-GRO and/or TPgH detections in several low-level wells are related to the hydrocarbon gas present in the wells, which is evident based on a series of early-eluting peaks on the GRO chromatograms and TICs commonly associated with natural gases (propane, butane, isobutane, and cyclohexanes) reported in the mass spectrometry chromatograms (see **Figures F-11** through **Figure F-13** in **Appendix F**).

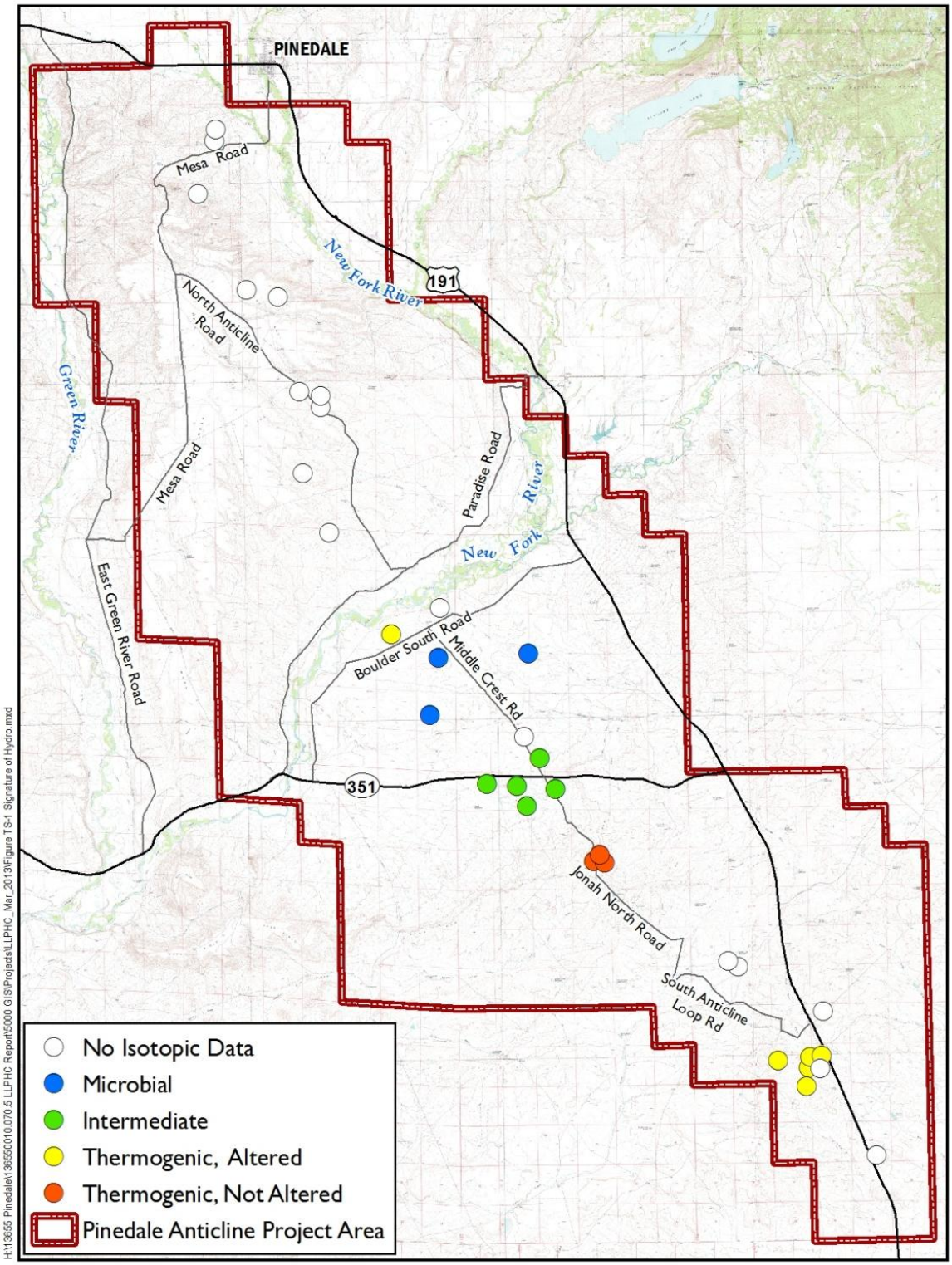


Figure TS-1. Gas Signatures in Groundwater in the PAPA

Other TPgH detections appear to be related to:

- The presence of purgeable diesel-range organics that elute beyond the laboratory-specified range for TPH-GRO (**Figure F-18** in **Appendix F**);
- One or more non-hydrocarbon TICs reported in each sample based on review of the mass spectrogram associated with the VOC analysis (**Figures F-26** and **F-31** in **Appendix F**); or
- Dissolved hydrocarbon gas plus the presence of low molecular weight compounds from the alkene/alkyne chemical groups (**Figures F-26** and **F-31** in **Appendix F**).

BTEX constituents, when detected above the laboratory reporting limit, were limited to toluene at very low concentrations (equal to or less than 5 µg/L) at several low-level wells sampled for this study (**Table 14**). BTEX constituents were detected below the laboratory reporting limit in several low-level wells sampled for this study (**Appendix E**). The detection of an individual volatile organic constituent, whether above or below the laboratory reporting limit, was not characteristic of the potential source materials sampled for this study; multiple volatile organic constituents were generally detected in the potential source material samples.

Assessment of Source of Volatile Organic Constituents in Low-Level Wells

None of the potential source materials analyzed for this study is the likely source of low levels of volatile organic constituents detected in groundwater samples. The chemical signature of the volatile organic constituents detected in groundwater samples did not match the chemical signature of any of the potential source materials sampled for this study, which included condensate (**Table 16**), produced water (**Table 17**), flowback fluid (**Table 18**), drill mud (**Table 19**), pump installation materials (**Table 20**), LNAPL (**Table 21**), and natural gas (**Table 22**). The differences between chemical signatures in condensate, produced water, flowback fluid, drill mud, pump installation materials, and LNAPL are further discussed in **Section 9.1.2**.

The chemical and isotopic signatures of natural gas produced in the PAPA differ from those of the gas observed in low-level wells (**Table 22**; **Section 9.1.2**). If the dissolved gas and casing gases originated from a leak in a natural gas production well or associated E&P infrastructure (e.g., piping) in the near surface in the PAPA, the composition of the gas would be the same as, or very similar to, the composition of the natural gas from production wells. Gas in low-level wells, at a minimum, shows slight to significant alteration based on gas composition and isotopic signatures. The exact mechanism of the alteration of gas is unknown. However, certain gas components, such as n-alkanes, may be preferentially biodegraded or lost due to adsorption on mineral substrates, phase separation, and/or diffusive effects during migration or seepage (**Section 4.8**). Changes in isotopic composition may also occur. In addition, the pronounced spatial trend in isotopic and chemical composition of gas in low-level wells across the PAPA is more characteristic of a non-

point source than a point source, such as a leaking casing of a natural gas production well or associated gas processing facility (**Figure 8-1**).

CONCEPTUAL MODEL FOR NATURAL GAS GENERATION AND SEEPAGE IN THE PAPA

Based on the chemical signatures of hydrocarbon gas in low-level wells and the regional trend in hydrocarbon gas signatures in the PAPA, another mechanism appears to be responsible for the chemical signature of hydrocarbon gas in low-level wells, which is likely migration by natural processes. All oil and gas fields are widely thought to leak to some extent, because geological seals on gas and oil accumulations are rarely perfect (**Section 4.8**). The Pinedale Anticline is not an exception. **Figure TS-2** illustrates a conceptual model for natural gas generation and seepage in the PAPA.

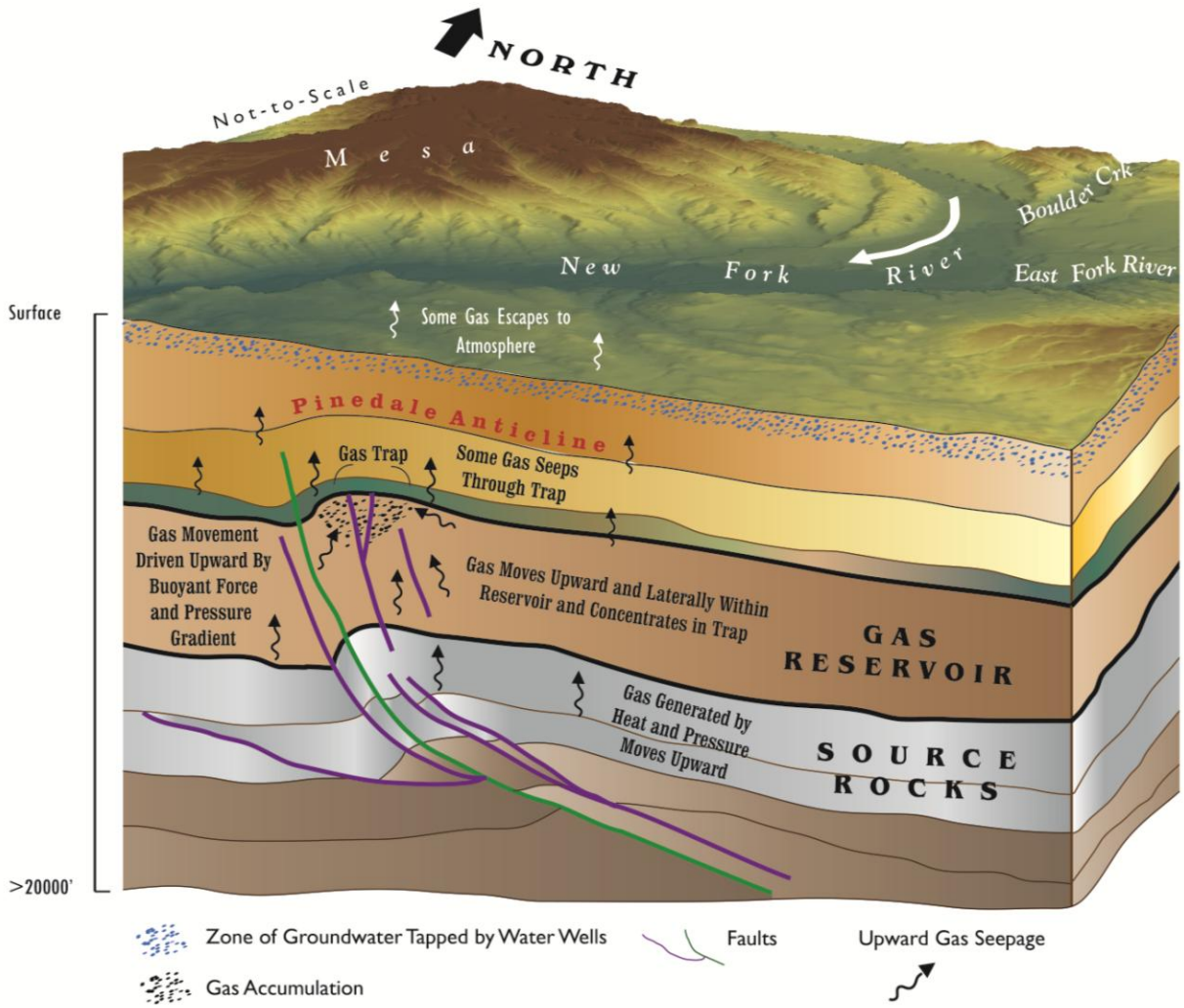


Figure TS-2. Conceptual Model for Natural Gas Generation and Seepage in the PAPA

As described in **Section 9.1.3.1**, natural gas has been generated by heat and pressure in source rocks at great depth in the PAPA. This thermogenic gas generated over geologic time in the deeper source rocks has moved upward by buoyant forces into a gas reservoir, the Lance Pool. The natural gas moves both laterally within sandstones comprising the Lance Pool and upward within the Lance Pool into a structural trap, the Pinedale Anticline.

The bulk of the natural gas has accumulated at the highest point of the anticline to form the gas field. Although a majority of natural gas in the Lance Pool is contained beneath the structural trap (anticline), some natural gas manages to migrate through the reservoir seal and into the overlying Fort Union Formation due to poor seal development and rock quality. Once the natural gas reaches the Fort Union and Wasatch Formations, it seeps upward more quickly due to the relatively higher porosity and permeability of these formations and is present in groundwater. The chemical signature of the natural gas changes during migration, possibly due to biodegradation, adsorption, phase separation, diffusive effects, mixing, or a combination thereof.

Natural gas has likely been migrating from the Lance Pool to the surface over geologic time, thus the presence of this gas in near-surface water-bearing units is expected based on geologic conditions. In situ generation of gas in the Tertiary Fort Union and/or Wasatch Formations is not likely based on findings from other studies (**Section 9.1.3.2**) as well as the results from this study of thermal maturity analysis of carbonaceous shale in the Wasatch Formation (**Section 5.7**; **Appendix D**). While proximity to concentrated E&P activity does not appear to control the magnitude of dissolved hydrocarbon gas concentrations in water wells, subsurface geologic structures (e.g., faults) that are associated with the anticline at depth (i.e., greater than 5,000 feet) may exert a possible control on the presence of dissolved hydrocarbon gas in groundwater in the PAPA (**Figure 4-4**; **Section 9.1.3.3**).

Baseline conditions for dissolved hydrocarbon gas in groundwater were not established prior to the commencement of E&P activities in the PAPA; however, anecdotal information suggests that dissolved hydrocarbon gas was likely present in groundwater in the PAPA prior to natural gas E&P operations (see **Section 4.8; Figure 4-4**). Anecdotal evidence includes the presence of natural gas observed at the ground surface during a soil gas survey performed in the PAPA (2003-2004), shallow gas observed during the drilling of natural gas production wells early in gas field development (1960), and shallow gas encountered during the drilling of water wells at gas well pads prior to gas well installation (**Section 9.1.3.4**).

DETECTIONS OF SEMIVOLATILE ORGANIC CONSTITUENTS IN LOW-LEVEL WELLS

Most potential source materials sampled as part of this study can be unequivocally ruled out as sources of semivolatile organic constituents detected in low-level wells, but in many cases the specific source cannot be definitively identified. Pump installation materials are a potential source

of low-level semivolatile organic constituents detected in low-level wells, based on chemical indicators and chromatographic profiles that are consistent with those of groundwater samples. In addition, groundwater samples with low-level detections of semivolatile organic constituents exhibit chemical signatures and chromatographic responses that may be similar to the following materials that were not sampled for this study:

- Materials introduced to the casing or borehole during the drilling and installation of water wells; and/or
- Naturally occurring organic matter entrained in groundwater or associated with turbidity in the well during sample collection.

Presented below is a summary of findings and interpretations regarding detections of semivolatile organic constituents in low-level wells (**Section 9.2**; **Figure 9-3**).

CHEMICAL SIGNATURE OF SEMIVOLATILE ORGANIC CONSTITUENTS IN LOW-LEVEL WELLS

Semivolatile organic constituents were detected in groundwater samples in the low-level wells sampled for this study, as well as HDG study wells sampled as part of the HDG investigation, as depicted in **Figure TS-3**. No relationship is apparent between the detection of volatile organic constituents versus semivolatile organic constituents in low-level wells. It is difficult to decipher the origin or sources of the semivolatile organic constituents detected in low-level wells, as they are generally limited to low concentrations of TPH-DRO and/or TEH. Other constituents amenable to source identification were not present in many groundwater samples.

Groundwater samples from low-level wells with detections of semivolatile organic constituents are generally characterized by:

- Detections of semivolatile organics by Method 8015 reported as TEH with TPH-DRO reported in approximately one-half of the samples with TEH (**Table 14**);
- Profiles in DRO chromatograms that are mostly non-characteristic and/or characterized by an unresolved complex mixture (UCM) type signature;
- No complementary detections of SVOCs when analyzed using EPA Method 8270 (**Table 14**); and
- Few reported TICs, most of which are not characteristic of sources sampled for this study or typically associated with petroleum substances and which do not definitively implicate any specific potential source material (**Table 15**).

Further detailed information about the chemical signature of groundwater samples from these wells with respect to semivolatile organic constituents, TICs, and chromatographic profiles is provided in **Section 9.2.1.**

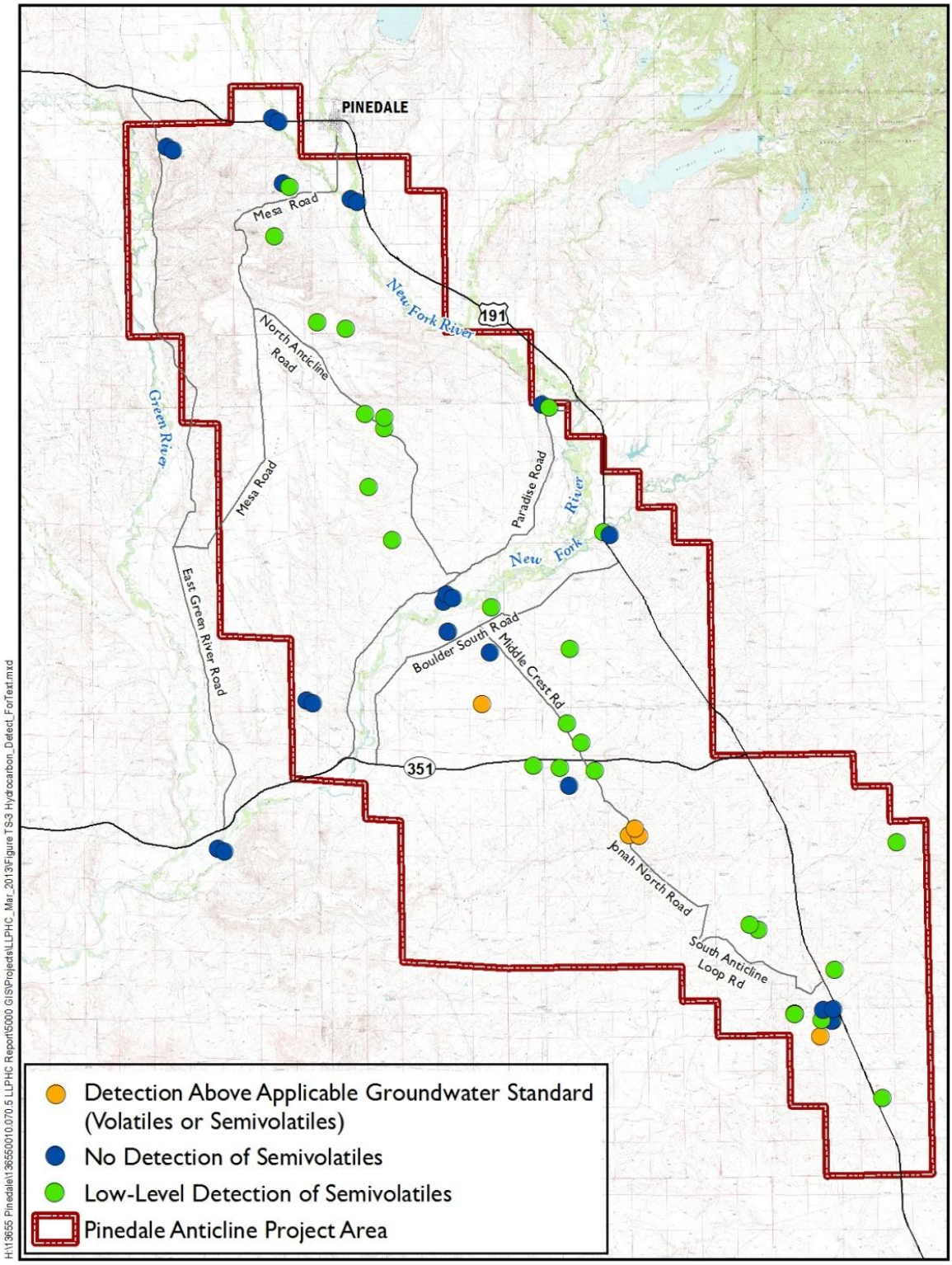


Figure TS-3. Detections of Semivolatile Organic Constituents in Water Wells

ASSESSMENT OF POTENTIAL SOURCES OF SEMIVOLATILE ORGANIC CONSTITUENTS IN LOW-LEVEL WELLS

While multiple lines of chemical and physical evidence identifies the source of the low-level volatile organic constituents observed in water wells (**Section 9.1.2**), it is more difficult to connect the low-level detections of semivolatile organic constituents to their likely source(s). The chemical indicators identified in groundwater samples that contained detectable levels of semivolatile organic constituents were compared to the chemical signatures of each potential source material sampled, as well as other potential sources that might exhibit the same chemical signature as those found in groundwater samples, to evaluate the likelihood that these sources are contributing to the semivolatile organic constituents detected in groundwater.

Materials Used or Generated during Natural Gas Exploration and Production Operations

The chemical signature of samples from low-level wells with semivolatile organic constituent detections did not match the chemical signatures of the following sampled potential source materials that are used or generated during natural gas E&P operations: condensate (**Table 16**), produced water (**Table 17**), flowback fluid (**Table 18**), LNAPL (**Table 21**), or natural gas (**Table 22**). The differences between signatures in groundwater samples as compared to the signatures for natural gas and condensate, produced water and flowback fluid, and LNAPL are described in further detail in **Sections 9.2.2.1.2**, **9.2.2.1.3**, and **9.2.2.1.4**, respectively.

Oil-based drill mud is the most likely source of organic constituents in the groundwater samples collected from well RS 15-12, based on the presence of similar potential chemical indicators (**Table 19**) and the similar chromatographic profiles (**Figure F-18** in **Appendix F)**. The DRO chromatograms for the groundwater samples collected from RS 15-12 are characteristic of a diesel-based material (predominantly C_{12} to C_{26}). TPH-DRO comprised a high percentage of the total TEH in these groundwater samples. VOCs and SVOCs were not detected in the groundwater samples collected from RS 15-12 during this study; however, this well had high-level detections of organic constituents in the past (**Appendix A**) that complement the identification of this source. Similar TIC chemical groups were reported in samples from RS 15-12 and from drill mud (**Table 19**).

The higher level detections reported historically in RS 15-12 most likely originated due to backflow of fluids from a dirty tank at the gas well pad rather than from an impact to the Wasatch Formation while drilling a nearby gas well with oil-based drill mud. The regulatory history of this well is described in **Section 9.2.2.1.1**. An abrupt decrease in the organic constituent concentrations was observed upon implementation of a well-cleaning procedure and pumping at this well (**Appendix A**), and this decrease is consistent with an isolated, intra-well source of organic constituents versus a source resulting in a widespread impact to groundwater at this location.

Materials Introduced during Operation of Water Wells

The chemical signatures of groundwater samples from most water wells with low-level detections of semivolatile organic constituents most closely resemble the chemical signature of pump installation materials among the potential source materials sampled for this study (**Table 20**). Pump installation materials sampled for this study are characterized predominantly by the presence of semivolatile organic fractions (i.e., TPH-DRO and/or TEH) and the almost complete absence of organics in the volatile fractions, including TICs. This chemical signature is most similar to the chemical signatures found in groundwater samples. Most chromatographic profiles in wells with low-level detections of semivolatile organic constituents are characterized by a broad hump eluting between retention times of about 8 to 10 minutes and 18 to 20 minutes (or longer) (**Figures F-14** through **F-15**; **Figures F-18** through **F-29**; and **Figure F-31** in **Appendix F**). This profile is typical of a UCM signature and characteristic of the chromatographic profiles observed for pump installation materials sampled for this study (see **Figures F-8** and **F-9** in **Appendix F**).

AMEC field personnel have observed grease and/or pipe dope on wellheads and pipe fittings, and greasy films were observed on some pump housings when pumps were removed from industrial water supply wells in order to collect samples for this study (**Section 9.2.2.2**). These substances are confined mainly to pump housings or what has been squeezed out between the joints of the discharge piping for the pump (i.e., drop pipe); minor amounts of these substances are exposed to the groundwater (**Figure 4-3**). The use of "environmentally friendly" pipe dope has been required of pump contractors by Operators in recent years. The environmentally friendly pipe dope sampled for this study (PD-Baseline) contains abundant higher molecular weight compounds that are reported in the semivolatile fraction (**Table 3**).

Operators have identified the backflow of fluids containing petroleum hydrocarbons directly into industrial water supply wells as the source of some historical detections of organic constituents in wells (AMEC Geomatrix, 2010), including industrial water supply wells WB 8-6 and RS 15-12, which were sampled for this study. In these instances, organic constituents typically have since been removed from these wells by over-pumping and/or implementing procedures to clean the interior of the well casing and remove impacted water above the perforated intervals (**Appendix A**). Operators are required by BLM's 2008 ROD (BLM, 2008b) to implement backflow prevention measures when filling any tanks or pits from an industrial water supply well. These measures should minimize or eliminate the occurrence of these types of impacts to water wells in the PAPA.

Materials Introduced during Drilling and Installation of Water Wells

The chemical signatures of the well drilling and construction materials used to install water wells were not determined for this study and thus are not available for comparison to the chemical signatures observed in groundwater samples. However, the nature of the low-level detections of semivolatile organic constituents observed in the PAPA is consistent with the types of petroleum-based substances that may be introduced while drilling or constructing a well (i.e., heavier oils or greases) (**Section 4-3**). For example, DRO chromatograms from four of the SAP and HDG study

wells (T-5-RW, T-9-RW, X-3-SW, and T-8-A) (**Figures F-14** and **F-15** in **Appendix F**) resemble the reference chromatogram for a mineral oil standard (**Figure F-30** in **Appendix F**) (William Brown, personal communication, 2011). Because these study wells share a common history of well drilling, installation, and operational practices, this pattern may indicate the presence of a refined petroleum substance introduced during these activities. Natural gas E&P activities cannot be the source of semivolatile organic constituents detected in these four study wells, as these wells are located off-pad and east of the anticline (**Figure 3-2**) in an upgradient groundwater flow direction from E&P activities (**Figure 2-10**).

Naturally Occurring Organic Matter in Water Samples

In parallel with the possible presence of microbially generated gas in the Wasatch Formation, organic matter inherent to Wasatch Formation sediments may be contributing to the semivolatile organic signature detected in water samples. The low concentrations of semivolatile organic constituents and minimal response in chromatograms can be attributed to naturally occurring organic material (William Brown, personal communication, 2011). Organic constituent detections attributable to naturally occurring organic matter have been observed in groundwater and surface water samples in studies published in the literature, as described in **Section 9.2.2.4**.

Semivolatile organic constituents detected in low-level wells cannot be definitively attributed to naturally occurring organic matter in the Wasatch Formation, because carbonaceous shale and other organic sediments from the Wasatch Formation were not analyzed for semivolatile organic constituents as were the other potential source material samples. However, the removal of semivolatile organic constituents upon SGT in many study wells is a strong indicator of the presence of organic matter. Although semivolatile extracts of samples from industrial water supply wells were not treated with silica gel, this finding can likely be extrapolated to industrial water supply wells in the PAPA, particularly those wells in which low levels of semivolatile organic constituents were detected (**Section 9.2.2.4**).

NO EVIDENCE OF WIDESPREAD IMPACT FROM E&P ACTIVITIES IN THE PAPA

This study did not produce any evidence of widespread impact to groundwater in the PAPA as a result of natural gas E&P operations through releases of condensate, produced water, drill mud, flowback fluid, natural gas, or other materials used or generated during these operations. The chemical signatures of organic constituents in low-level wells indicate that widespread releases of sampled potential source materials from natural gas production wells and other E&P facilities (pipelines, produced water injection wells, pits, tanks, CGFs, and LGS) have not occurred (**Table 23**; **Figure 9-4**). Volatile organic constituents detected in low-level wells are largely sourced from the upward seepage of natural gas from depth by natural processes that have likely occurred over geologic time (**Section 9.1**; **Figure 9-1**). Low levels of semivolatile organic constituents detected in water wells are likely sourced from substances used in the drilling, installation, and operation of

water wells (**Section 9.2**; **Figure 9-3**; **Table 23**) or from naturally occurring organic matter present in the Wasatch Formation sediments (**Section 9.2.2.4**; **Figure 9-3**; **Table 23**).

In addition to the chemical evidence, evidence from temporal, spatial, physical, and operational factors support the finding that no widespread impact to groundwater has occurred from E&P activities.

TEMPORAL AND SPATIAL EVIDENCE

Source identification, source pathways, and assessment of impacts to groundwater in the PAPA from natural gas E&P operations are informed by several temporal and spatial factors (**Figure 9-4**):

- Low-level detections were reported before the development and establishment of CGFs, LGS, and injection wells for disposal of produced water. Because low levels of organic constituents had already been detected before these facilities were fully developed, the potential sources are not likely the sources of existing low-level detections (**Section 9.3.2.1**)
- Many low-level organic constituent detections are not consistently reported between annual sampling events performed by SCCD, which could be attributed to several factors (**Section 9.3.2.2**); however, this finding is not consistent with a continuous and widespread source of organic constituents.
- The distribution of the low-level detections of semivolatile organic constituents in the PAPA is not characteristic of a large, continuous plume of contaminants, or multiple plumes of contaminants originating from E&P activities (**Section 9.3.2.3**). High-level detections of organic constituents observed at some gas well pads are isolated (see **Section 8.4**) and do not appear to be contributing to these low-level semivolatile (or volatile) organic constituent detections in water wells, based on the chemical evidence gathered during this study and the historical groundwater sampling record (**Appendix A**).
- Several potential off-pad sources (e.g., landfills, listed underground storage tank sites, or hazardous waste sites) are not considered likely sources of organic constituents in water wells because of their location away from the main gas field development areas, the degree of regulatory oversight or regulatory closure achieved (e.g., permitted oil-disposal facilities, landfills), or their location hydraulically downgradient of most water wells in the PAPA (most produced water injection wells) (**Section 9.3.2.4**).

HYDROGEOLOGICAL AND FATE AND TRANSPORT CONSIDERATIONS

The hydrogeology of the PAPA, as well as the fate and transport properties of solutes in the unsaturated and saturated zones, control the likelihood that a release from any of these potential point sources would impact groundwater. The results of the hydrogeological data gaps investigation (AMEC, 2012) and the groundwater flow and solute fate and transport modeling study (AMEC, 2013) support the findings of this study with respect to the observed distribution of organic constituent detections in groundwater in the PAPA.

Assuming no preferential pathways exist in the Wasatch Formation, the volume of any spill or release would need to be substantial in order to reach groundwater in the Wasatch Formation in areas along the crest of the anticline where concentrated E&P activities occur. A hypothetical release would typically have to migrate vertically over 200 feet (and up to 500 feet in some places) through the unsaturated (vadose) zone to reach the regional groundwater system in the Wasatch Formation (**Section 9.3.3.1**). A spill or release large enough to reach groundwater, or occurring directly in the Wasatch Formation, would migrate slowly in groundwater within the Wasatch Formation due to the relatively low velocity of groundwater in this unit. This velocity ranges from 0.011 to 40 feet per year, based on the observed range of hydraulic gradients and the range of hydraulic conductivity values determined from aquifer testing during the HDG investigation. (**Section 2.4.3**). Based on these velocity estimates, it would take at least 5 years for groundwater to travel the width of a typical gas well pad (**Section 9.3.3**).

When release scenarios were modeled using the fate and transport model, widespread plumes of organic constituents did not develop in groundwater (**Section 9.3.3.2**), which is consistent with the hydrogeological data collected during the HDG investigation, the chemical data collected annually by the SCCD (**Appendix A**), as well as the results of this study. Results of hypothetical release scenarios simulated within the area most susceptible to groundwater quality impacts (e.g., New Fork River corridor in the center of the PAPA) indicate that predicted concentrations of benzene and toluene in groundwater do not exceed applicable groundwater standards at distances greater than 150 feet from simulated sources (AMEC, 2013).

Based on what is known about the hydrogeology in the PAPA, as well as the fate and transport of organic constituents, low levels of organic constituents detected in water wells are not the result of large releases from E&P activities. Not enough time has elapsed since the beginning of E&P operations in the PAPA (~1939) to the timing of this study (i.e., 2010) for a widespread plume of organic constituents to develop in groundwater and result in the low-level organic constituent detections observed in the PAPA. In addition, based on chemical data collected for this study and by the SCCD, widespread plumes of organic constituents are not evident, and high-level organic constituent detections appear to be isolated in nature.

BEST PRACTICES

Chemical evidence produced by this study indicates that past and current E&P activities have not caused widespread groundwater impacts in the PAPA. Although the exact composition of all fluids used and generated during historic operations is unknown, the fluids used on-record were petroleum-based and refined or unrefined. If widespread releases of these fluids had occurred from historical practices, SCCD's annual groundwater monitoring results would show more high-level detections in the PAPA than are currently observed, and these high-level detections would exhibit chemical signatures that could likely be traced to a particular fluid type.

Based on the overview of current E&P operations presented in **Section 4.0,** the potential for impacts to groundwater are further minimized by the following current E&P best practices:

- Secondary containments and closed-loop systems are increasingly used.
- Modern well casing and cementing programs (**Section 4.1**) are employed in the construction of natural gas production wells.
- Well integrity testing of natural gas wells and pressure monitoring are employed during hydraulic fracturing operations.

State and federal agencies provide regulatory oversight of natural gas E&P activities in the PAPA. Permitting and reporting requirements as prescribed by the state and federal agencies are followed by Operators, and E&P activities are subject to compliance inspections during the drilling and production phases.

CONCLUSIONS

This report documents the results of groundwater, gas, and potential source material sampling and evaluates potential point and non-point sources of low-level organic constituents detected in water wells in the PAPA. Low-level detections are considered those that are below applicable groundwater standards. This study, which was designed and implemented in accordance with a SAP accepted by the BLM in consultation with the U.S. EPA and Wyoming DEQ (AMEC Geomatrix, 2010), resulted in four primary conclusions (**Figures 9-1**, **9-3**, and **9-4**).

Conclusion 1: The low-level detections of volatile organic constituents in water wells are largely attributable to the upward seepage of natural gas from the Lance Pool over geologic time by natural processes (see **Figure 9-1**).

This conclusion is based on the following findings and supporting evidence:

- Hydrocarbon gases in low-level wells are not the same as natural gas produced in the PAPA, as evidenced by:

  - The hydrocarbon gas in low-level wells exhibits chemical and isotopic signatures that indicate the gas is altered thermogenic or microbial, and these signatures change moving from south to north in the PAPA (**Table 22**; **Figure 8-1**). In contrast, the chemical and isotopic signature of natural gas produced in the PAPA indicates the gas is unaltered thermogenic (**Table 22**).
  - The chemical and isotopic signatures of natural gas may be altered during migration by microbial activity, diffusion, phase separation, and adsorption. Gas that has been altered by biodegradation may show a preferential depletion of n-alkanes relative to isoalkanes, which was observed in low-level wells sampled for this study that displayed an altered thermogenic signature or intermediate signature (**Figures G-1** through **G-5** of **Appendix G**).

- Natural gas likely migrates to the ground surface over geologic time in the PAPA, which is illustrated in the conceptual model for gas generation and seepage on **Figure TS-1.** This finding is supported by the following evidence:
  - Natural gas was observed at the ground surface during a soil gas survey performed in the northern portion of the PAPA (**Section 4.8**).
  - Hydrocarbon gas was observed at shallow depths during the drilling of natural gas production wells early in development of the gas field in the PAPA (**Figure 4-4**; **Section 9.1.3.4**).
  - Hydrocarbon gas has been encountered during the drilling of water wells at gas well pads prior to gas well installation (**Figure 4-4**; **Section 9.1.3.4**).
  - The gradual change in hydrocarbon gas signatures across the PAPA is more consistent with a non-point source (upward seepage) versus a point source (leaking natural gas production well).
  - According to published literature, natural gas that has accumulated beneath other geological traps similar to the Pinedale Anticline is known to migrate to the ground surface over time (**Sections 4.8** and **9.1.3**).

In addition, the detection of individual, dissolved-phase VOCs (e.g., toluene) is not consistent with the chemical signatures of potential source materials sampled for this study (e.g., condensate, produced water, drill mud, flowback fluid, LNAPL) (**Tables 16-21**; **Section 9.1.2**). Thus, these potential source materials are not sources of the volatile organic constituents detected in low-level wells in the PAPA (**Table 23**).

Conclusion 2. The source of low-level detections of semivolatile organic constituents in water wells is not readily apparent, but likely originates from substances introduced during the drilling, installation, and operation of the wells and/or from naturally occurring organic matter (see **Figure 9-3).**

This conclusion is based on the following findings and supporting evidence:

- The chemical signatures of groundwater samples from most of the low-level wells with detections of semivolatile organic constituents above laboratory reporting limits most closely resembled the signature of pump installation materials. This finding is supported by the following evidence:
  - No complementary VOCs or SVOCs were detected above the reporting limit in these wells (**Table 14**).
  - Few to no TICs were reported and, when reported, most TICs were not characteristic of sources sampled for this study or typically associated with petroleum substances.
  - TEH was always detected and TPH-DRO was detected along with TEH in some wells.
  - Chromatographic profiles were mostly non-characteristic and/or characterized by UCMs (**Section 9.2.1.3**).
  - Grease and/or pipe dope has been observed on pumps and/or pipe fittings during pump removal and well sampling.
  - One exception is RS 15-12. This well exhibited a chemical signature resembling drill mud, which is suspected to have resulted from the backflow of fluid via improper well/pump operation.
- Low-level detections of semivolatile organics in some low-level wells may be attributed to naturally occurring organic matter. This finding is based on the following evidence:
  - TEH was removed from the extract of samples collected from several study wells following treatment by silica gel.
  - Sediments containing organic matter (carbonaceous shale) are present in the Wasatch Formation.
  - Particulates of organic matter may be introduced to water wells during well drilling and installation and become entrained in groundwater samples. Suspended sediment was observed in several study wells prior to sampling in June 2011 (AMEC 2012).
  - Laboratory analysts have identified naturally occurring organic matter as a potential source of semivolatile detections based on the observed chromatographic response.

- The chemical signature in four study wells resembled the chemical signature of a refined petroleum-based substance, which may be attributable to well installation materials. This finding is based on the following evidence for these four wells:
  - TPH-DRO was detected and not removed upon silica gel treatment.
  - The chromatographic profiles exhibited a narrow, symmetrical response in the diesel-range organics, which most closely resembled the reference chromatogram for a mineral oil standard.
  - The use of petroleum-based substances during water well drilling and installation may introduce semivolatile organic materials into the well.
  - These study wells share a common history of well drilling and installation and are located upgradient of E&P activities.

Conclusion 3. This study did not produce any evidence of widespread impact to groundwater in the PAPA as a result of E&P operations through releases of condensate, produced water, drill mud, flowback fluid, natural gas, or other materials used or generated during these operations (see **Figure 9-4).**

This conclusion is based on the following findings and supporting evidence:

- The chemical signatures of most potential source materials sampled for this study, including produced water, condensate, drill mud, natural gas, and flowback fluid, are not present in low-level wells (**Table 23**; **Figure 9-4**). This finding is based on the following evidence:
  - Multiple individual VOCs and SVOCs characteristic of petroleum substances were consistently detected above the reporting limit in most potential source material samples, but not in low-level wells (**Tables 16–21**).
  - Both volatile and semivolatile organic fractions (e.g., TPH-GRO and TPH-DRO) were detected above the reporting limit in most potential source material samples, but not in low-level wells (**Tables 16–21**).
  - Many TICs typically associated with petroleum substances were reported in potential source material samples, but not generally in low-level wells (**Tables 16–21**).
  - Diagnostic chromatographic profiles present in most potential source material samples did not match those from low-level wells (**Tables 16–21**).
  - Elevated concentrations of inorganic constituents were present in some of these potential source material samples (where analyzed), but not in low-level wells (**Tables 16-21**).

  - An unaltered thermogenic signature is present in samples of natural gas, but not in dissolved hydrocarbon gas in groundwater from low-level wells (**Table 22**).

- Several potential sources evaluated in this study are not likely the source of low-level detections observed in the PAPA (**Figure 9-4**), as suggested by the following spatial and temporal factors:
  - Low-level organic constituent detections were observed in the PAPA before produced water injection wells, liquid gathering systems, and central gathering facilities were constructed or fully operational (**Section 9.3.2.1**).
  - Several potential off-pad sources, such as landfills, underground storage tanks, and hazardous waste sites, are located outside of the PAPA or away from the main gas field development area (**Section 9.3.2.4**).
  - Most produced water injection wells are located hydraulically downgradient of water wells in the PAPA (**Section 4.4**).

- Migration of organic constituents, if released, would be of limited extent in the subsurface due to the hydrogeology of the PAPA, as well as the fate and transport properties of organic and inorganic constituents in the unsaturated and saturated zones (**Section 9.3.3**; **Figure 9-4**). This finding is based on the following evidence:
  - Organic compounds, if released, would not migrate appreciable distances (>150 feet) due to retardation and biodegradation in groundwater.
  - Groundwater movement is relatively slow in the Wasatch Formation due to the interbedded nature and relatively low permeability of sediments.
  - A thick unsaturated (vadose) zone in most areas of the PAPA impedes the migration of a release to groundwater.
  - No chemical evidence was found to indicate that flowback fluid or produced water is migrating upward over thousands of feet of geologic strata.

- High-level wells are not the source of low-level detections in the PAPA (**Figure 9-4**). This finding is based on the following evidence:
  - The chemical signatures in high-level wells do not resemble the signatures in low-level wells (**Sections 8.5**, **9.1**, **9.2**, and **9.3.2.3**).
  - Not enough time has elapsed for impacts from high-level wells to reach nearby water wells based on the relatively low groundwater velocities in the PAPA.

  - Low-level detections of semivolatile organic constituents typically would not reflect groundwater conditions beyond the immediate vicinity of the well, based on potential sources identified (**Sections 9.2** and **9.3.2.3**).
  - High-level detections are isolated geographically in the PAPA based on the results of annual groundwater sampling by SCCD.
  - Many low-level organic constituent detections are not consistently reported between annual groundwater sampling events performed by SCCD, indicating the absence of a high-level, continuous source (**Section 9.3.2.2**).

- Current E&P best practices minimize the potential for impacts to groundwater in the PAPA (**Sections 4.1**, **4.2**, and **9.3.4**; **Figure 9-4**). This finding is based on the following evidence:
  - Secondary containments and closed-loop systems are increasingly used.
  - Modern well casing and cementing programs (**Section 4.1**) are employed in the construction of natural gas production wells.
  - Well integrity testing of natural gas wells and pressure monitoring are used during hydraulic fracturing operations.
  - State and federal agencies provide regulatory oversight of E&P operations, and permitting and reporting requirements are followed consistently.

Although the exact composition of all fluids used and generated during historic operations is unknown, the fluids used on-record were petroleum-based and refined or unrefined. If widespread releases of these fluids had occurred from historical practices, SCCD's annual groundwater monitoring results would show more high-level detections in the PAPA than are currently observed, and these high-level detections would exhibit chemical signatures that could likely be traced to a particular fluid type.

Conclusion 4. The Interim Plan (AMEC Geomatrix, 2008) and the Plan of Study (AMEC Geomatrix, 2009a) stipulated that potential sources for the low-level detections be identified so that additional mitigation measures (beyond those in the 2008 ROD) may be developed and implemented, if necessary. Based on the findings of this study, no additional measures are necessary to mitigate the existing low-level volatile or semivolatile organic constituents detected in water wells in the PAPA.

This conclusion is based on the following findings:

- The source of the low-level detections of volatile organic constituents in groundwater is attributed to the upward seepage of natural gas by natural processes over geologic time.

The presence of the gas in near-surface groundwater in the PAPA can be expected based on geologic conditions and cannot be mitigated.

- The low-level semivolatile organic constituents detected in groundwater likely originate from substances introduced during the drilling, installation, and operation of groundwater wells and/or from naturally occurring organic materials present in groundwater. By the fall of 2008, Operators had implemented a best practice that requires contractors to clean all downhole materials and equipment used in pump installations by high pressure/hot water, and use hydrocarbon-free pipe dope compounds. Although no water wells have been drilled on BLM-administered lands since the 2008 ROD, similar best practices would be required for well drilling and installation. As organic materials are inherent to the Wasatch Formation, naturally occurring organic matter in groundwater wells in the PAPA cannot be mitigated.

These findings and conclusions do not mean that releases from potential point sources researched for this study could not become sources of organic constituents in water wells in the future. The sustained application of best practices for E&P operations in the PAPA is necessary to protect groundwater resources. Implementation of the forthcoming Final Groundwater/Aquifer Pollution Prevention, Mitigation and Monitoring Plan will provide a mechanism for evaluating groundwater conditions over the long term, determining changes over time in water quantity and quality, and detecting potential responses to anthropogenic and non-anthropogenic stressors to the groundwater system.

FINAL

TECHNICAL REPORT

EVALUATION OF POTENTIAL SOURCES OF LOW-LEVEL PETROLEUM HYDROCARBON COMPOUNDS DETECTED IN GROUNDWATER

PINEDALE ANTICLINE OIL AND GAS EXPLORATION AND DEVELOPMENT PROJECT

Sublette County, Wyoming

October 2013

1.0 INTRODUCTION

This report documents an evaluation of organic constituents detected in groundwater samples and reported as low-level petroleum hydrocarbons (LLPHC). For purposes of this study, *low levels* are defined as concentrations in groundwater samples that are below applicable groundwater quality standards, specifically with respect to organic compounds or organic constituents. The groundwater samples were collected from wells in the Pinedale Anticline Oil and Gas Exploration and Production Area (also known as the Pinedale Anticline Project Area, or PAPA), located in Sublette County, Wyoming (**Figure 1-1**). The PAPA covers approximately 309 square miles of federal, state, and private land, with an approximate maximum width of 10 miles and length of about 30 miles. The U.S. Department of Interior, Bureau of Land Management (BLM), manages 80 percent of the land within the PAPA. The PAPA is subdivided into seven exploration and production (E&P) areas, which are shown on **Figure 1-2** along with the federally managed development areas (DAs).

1.1 REGULATORY BACKGROUND

A consortium of federal and state agencies and oil and gas companies prepared an *Interim Groundwater/Aquifer Pollution Prevention, Mitigation and Monitoring Plan* (Interim Plan) (AMEC Geomatrix, 2008) that was designed to fulfill certain requirements of BLM's Record of Decision (ROD) (BLM, 2008b) for the *Final Supplemental Environmental Impact Statement (SEIS), Pinedale Anticline Oil and Gas Exploration and Development Project, Sublette County, Wyoming* (BLM, 2008a). BLM's SEIS ROD (BLM, 2008a) was prepared to address proposed changes in the long-term development plan for the PAPA and thereby supersedes an earlier ROD prepared by the BLM in 2000 (2000 ROD; BLM, 2000). AMEC Environment & Infrastructure, Inc. (AMEC; previously AMEC Geomatrix, Inc. [AMEC Geomatrix], or Geomatrix Consultants, Inc. [Geomatrix]), in association with NewFields Companies, LLC (since September 2012), was retained to perform this study between 2009 and 2012 by three oil and gas companies, Ultra Resources, Inc. (Ultra), SWEPI LP (Shell), and QEP Energy (QEP), which are cooperatively referred to as Operators, to fulfill the requirements of the PAPA SEIS ROD. The results of this study will be used to help formulate additional mitigation measures, as necessary, as specified in the Interim Plan.

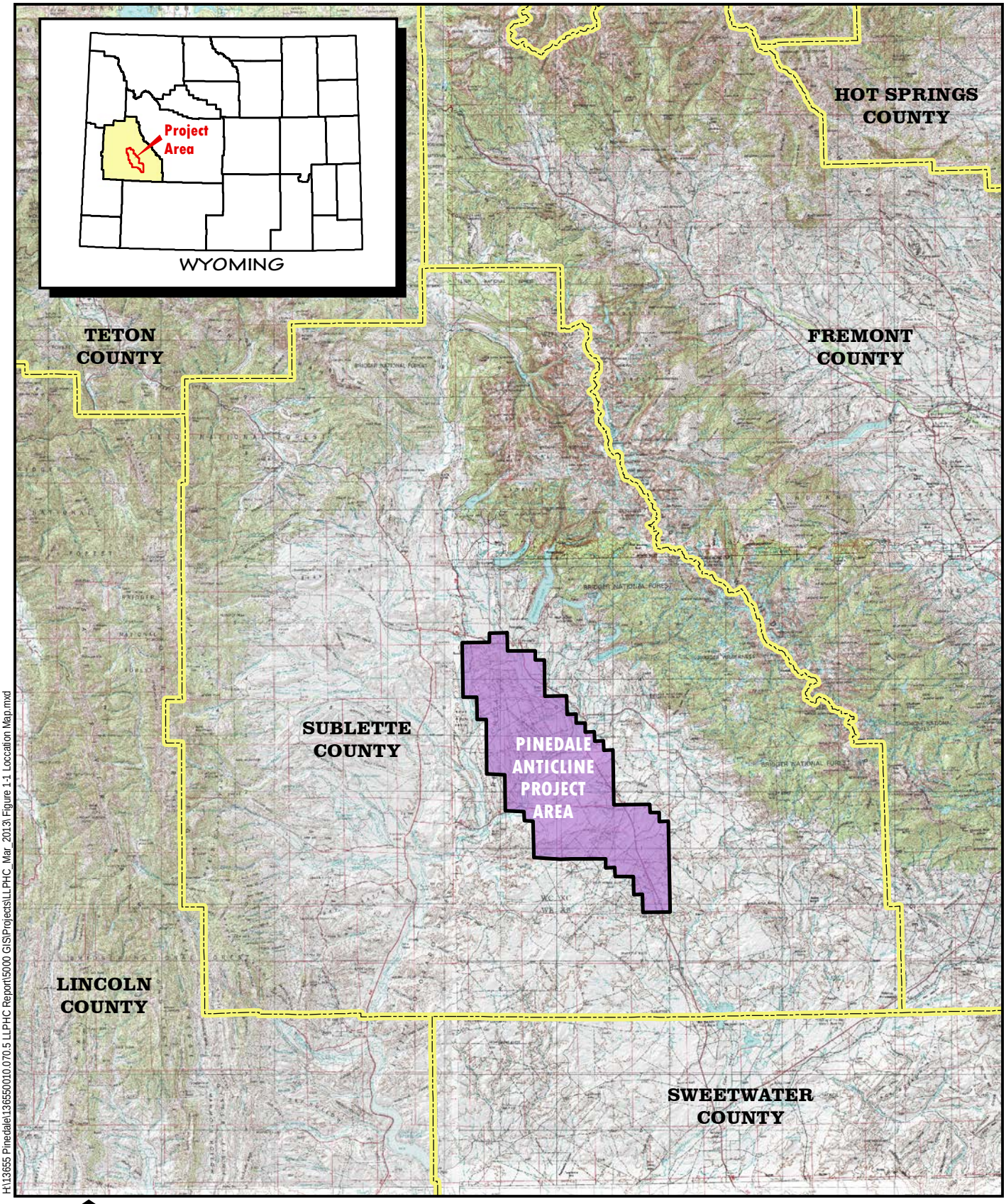
The federal and state agencies that are a part of this effort include representatives and technical specialists from the BLM, the Wyoming Department of Environmental Quality (Wyoming DEQ) Water Quality Division, and Region 8 of the U.S. Environmental Protection Agency (EPA). Collectively, the agencies are referred to herein as the BDE (**B**LM/Wyoming **D**EQ/**E**PA).

The 2000 ROD for the PAPA (BLM, 2000) outlined requirements for water resources inventories and water quality monitoring within the PAPA. To fulfill these requirements, the Operators contracted the Sublette County Conservation District (SCCD) to develop and implement a surface water and

groundwater monitoring program. In 2004, the SCCD began performing annual groundwater sampling of domestic, stock, and miscellaneous (industrial) water supply wells located within 1 mile of proposed or existing oil and gas wells in the PAPA. In 2006, the Wyoming DEQ became aware of organic constituents that were discovered in water samples collected from four industrial water supply wells (Wyoming DEQ, 2006). It was suspected that these wells were impacted due to siphoning, or backflow, of contaminated water into the wells. The Wyoming DEQ requested that the Operators obtain groundwater samples from water supply wells that are, or have been, connected to a tank, tank truck, reserve pit, or production pit and take measures to eliminate the potential for backflow into water supply wells (Wyoming DEQ, 2006). The Operators complied with the request and submitted the sampling results to the Wyoming DEQ.

BLM's SEIS ROD (2008b) states that no new BLM rights-of-way or other approvals for new industrial water supply wells will be allowed in the PAPA until the groundwater characterization is completed and the causes of hydrocarbon detections have been determined and effectively mitigated. The groundwater characterization called for in the ROD included a study to evaluate potential sources for organic constituents detected in water wells. As dictated by the Interim Plan (AMEC Geomatrix, 2008), a Plan of Study (POS) was developed that outlined the technical approach to perform this evaluation (AMEC Geomatrix, 2009a). In May 2009, the BLM in consultation with Wyoming DEQ and U.S. EPA accepted the POS, which outlined the following objectives:

1. Identify potential sources of organic constituents detected within the PAPA to the extent possible using readily available information.
2. Perform spatial and temporal analyses of existing groundwater quality data with respect to potential sources to identify the most likely sources of organic constituents at each well location where they occur.
3. Identify data gaps that impede understanding of the sources of the low-level organic constituents that have been detected and develop a Sampling and Analysis Plan (SAP) to fill these data gaps.
4. Conduct additional environmental sampling at individual locations where organic constituents have been reported in accordance with the SAP. Analyze new environmental samples for a list of analytes developed specifically based on identification of likely sources of organic constituents at that sampling location.
5. Recommend additional mitigation measures, if necessary.



H:\13655 Pinedale\136550010.070.5 LLPHC Report\5000 GIS\Projects\LLPHC_Mar_2013\ Figure 1-1 Loccation Map.mxd

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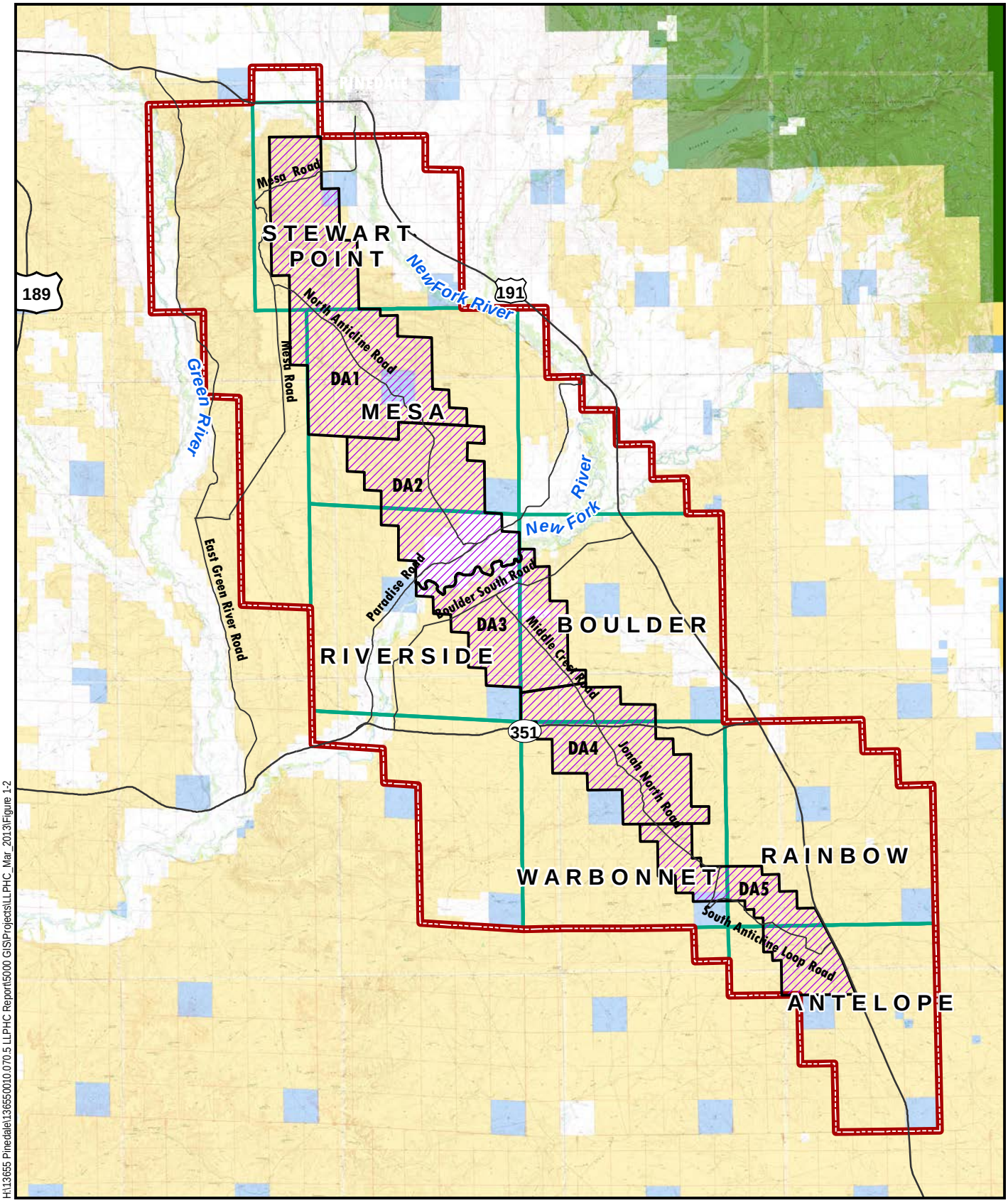
Project Location Map
Low-Level Petroleum
Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 1-1



H:\13655 Pinedale\136550010.070.5 LLPHC Report\5000 GIS\Projects\LLPHC_Mar_2013\Figure 1-2

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DA1 Development Area (DA)

MESA Production Area Boundary

Pinedale Anticline Project Area

Bureau of Land Management

State

U.S. Forest Service

Private

PAPA Exploration and Production Areas
Low-Level Petroleum
Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 1-2

This report presents the results of implementing that POS. AMEC compiled and reviewed available information regarding potential sources of low-level detections in the PAPA and performed spatial and temporal analyses of existing groundwater quality data with respect to potential sources of organic constituents. Based on the data gaps discovered during that evaluation, AMEC developed the *Sampling and Analysis Plan for Evaluating Potential Sources of Low-Level Petroleum Hydrocarbon Compound Detections* (the SAP; AMEC Geomatrix, 2010). The SAP was accepted by the BLM in consultation with Wyoming DEQ and U.S. EPA, and describes the methodology and rationale for additional sampling and analysis needed to further evaluate the source(s) of low-level detections in water wells.

Field activities to perform the work described in the SAP were conducted from September 2010 through December 2011. Additional follow-up sampling and analysis were performed at selected wells in 2012 to verify certain results of the 2010–2011 sampling.

1.2 COMPANION STUDIES

The SAP was developed specifically to obtain additional data needed to evaluate low levels of organic constituents that have been detected in selected wells and reported as petroleum hydrocarbons. In addition to the investigations conducted based on the SAP, the evaluation reported here was supported by data and findings from two companion studies:

- the hydrogeological data gaps investigation (HDG investigation; AMEC, 2012) and
- the solute fate and transport modeling study (AMEC, 2013).

The HDG investigation began in 2009, and the findings were reported in the *Hydrogeological Data Gaps Investigation Report* (AMEC, 2012). Relevant results for laboratory analyses performed as part of that companion study are presented in this report and used to assess potential sources of organic constituents detected and reported as LLPHC. The velocity and direction of groundwater flow were determined as part of the HDG investigation, and this information was used in concert with the chemical data from this study to evaluate the occurrence of the observed low-level detections of organic constituents in groundwater in the PAPA. Inorganic water quality data from the HDG investigation were used in concert with inorganic water quality data from this study to evaluate the influence of hydrogeologic factors on inorganic geochemistry.

The findings of the solute fate and transport modeling study were reported in the *Final Numerical Groundwater Modeling Report* (AMEC, 2013). Results of the fate and transport modeling study were used in combination with results from this study to evaluate the fate and transport of organic constituents if released.

The collective outcome of these studies as prescribed by the 2008 ROD and defined by the Interim Plan will be a *Final Groundwater/Aquifer Pollution Prevention, Mitigation, and Monitoring Plan* for the PAPA.

1.3 REPORT PURPOSE AND ORGANIZATION

This report presents the results of the sampling and analysis described in the SAP, presents relevant analytical results for laboratory analyses from the HDG investigation, summarizes previously existing information regarding groundwater quality in the PAPA, and presents a summary evaluation of the likely sources of low-level organic constituents in water wells in the PAPA.

In brief, this report addresses the following objectives:

1. Report the findings of research into potential point and non-point sources of organic constituents.

2. Present the results from sampling and analysis of potential source materials, gases, and groundwater obtained as part of implementing the SAP.

3. Identify the most likely, potential sources for the low-level organic constituents detected in water wells in the PAPA.

This report consists of the following sections:

- **Section 1.0** describes the regulatory background and the purposes of this report.
- **Section 2.0** provides a brief introduction into the composition and methods of analysis for mixtures of organic compounds in environmental media and presents a brief background of the PAPA, including the geologic framework, an overview of gas field development, a hydrogeologic conceptual model, the occurrence and distribution of organic compounds detected in groundwater samples collected during annual monitoring by the SCCD, and the presence of gas observed in industrial water supply wells.
- **Section 3.0** describes the technical approach for field work and data analysis to implement the SAP and thereby evaluate potential point and non-point sources of organic compounds detected in groundwater samples collected in the PAPA.
- **Section 4.0** presents a summary of the characteristics of potential point and non-point sources of organic constituents.
- **Section 5.0** presents the results of analytical testing on samples of potential source materials.
- **Section 6.0** provides the results of gas sampling and analytical testing.

- **Section 7.0** presents the results of groundwater sampling and analytical testing.
- **Section 8.0** presents an overview of the results of sampling and analysis and a summary evaluation of the data collected during implementation of the SAP.
- **Section 9.0** summarizes the available data and presents an evaluation of potential sources of organic constituents detected in water wells in the PAPA.
- **Section 10.0** summarizes the conclusions of this study.
- **Section 11.0** presents a list of references cited in the report.

An **Executive Summary** presented at the beginning of the report is geared toward the general public and provides a succinct summary of the findings of the study. A **Technical Summary** follows the **Executive Summary** and provides a more in-depth, technical overview of the findings of the study geared to the technical reader.

Supporting data are presented in tables and charts. Comprehensive compilations of data are presented as numbered tables at the end of this report. Tables are numbered sequentially and listed with table number and title in the table of contents. Brief summaries of key data are presented as charts within the body of the text to support or amplify the discussion in text. The charts are numbered sequentially by section (e.g., **Chart 2-2**) and referenced in the table of contents by both title and page number. Figures are presented within the text of the report in the order of presentation. Figures are also numbered sequentially by section (e.g., **Figure 1-1**) and are likewise listed in the table of contents along with both title and page number.

Additional supporting data and information are provided in **Appendices A–H**.

2.0 BACKGROUND

Natural gas development in the PAPA began in 1939, and expanded rapidly after about 1994. SCCD began periodic water quality monitoring in selected wells in the PAPA in 2004. No comprehensive baseline groundwater monitoring was conducted in the PAPA prior to gas field development.

This section presents a summary of background information about the PAPA needed to interpret the data presented in this report. **Section 2.1** presents background information on the composition and analysis of organic compounds that are commonly referred to as *petroleum hydrocarbons*. **Section 2.2** describes the general geologic framework of the PAPA, including the geologic structures bearing the main petroleum system of consequence. **Section 2.3** presents a brief history of gas field development activities in the PAPA from 1939 to the present. A summary of the hydrogeological setting for the PAPA is provided in **Section 2.4**. **Section 2.5** presents an overview of general groundwater quality characteristics in the PAPA, summarizes previously existing information regarding organic constituents detected in samples from water wells in the PAPA, and describes the occurrence of combustible gas in well casings of water supply wells in the PAPA.

2.1 COMPOSITION AND ANALYSIS OF PETROLEUM HYDROCARBONS

Low-level concentrations (i.e., concentrations less than applicable groundwater quality standards) of selected organic compounds and mixtures of compounds have been detected historically in wells throughout the PAPA. The detected constituents have largely been reported as *petroleum hydrocarbons* due to the colloquial name applied to the laboratory methods most commonly used for preparation and analysis of samples. This section presents a brief definition of *hydrocarbons* and the composition of petroleum, and describes laboratory methods used to test for organic compounds in environmental samples. This information is critical in interpreting the laboratory data presented in this report and previous reports and evaluating potential sources of the organic constituents detected in groundwater samples in the PAPA.

2.1.1 Definition of Hydrocarbons

Hydrocarbons are organic compounds that contain varying numbers of carbon and hydrogen atoms in varying structural configurations. Hydrocarbons, strictly defined, contain only carbon and hydrogen atoms. Other organic compounds that contain oxygen, nitrogen, and/or other atoms will be referred to in this report as *non-hydrocarbon compounds*, which include ketones, alcohols, aldehydes, and acids. All hydrocarbons are organic compounds, since they contain carbon; however, not all organic compounds are hydrocarbons.

Hydrocarbon compounds that contain carbon molecules linked by one or more single bonds between adjacent carbon atoms are referred to as *paraffins* or *alkanes*. Alkanes are arranged in three basic configurations: straight-chains (i.e., normal alkanes or n-alkanes), branched chains (i.e., isoalkanes), and cyclic rings (i.e., cycloalkanes) (**Figure 2-1**).

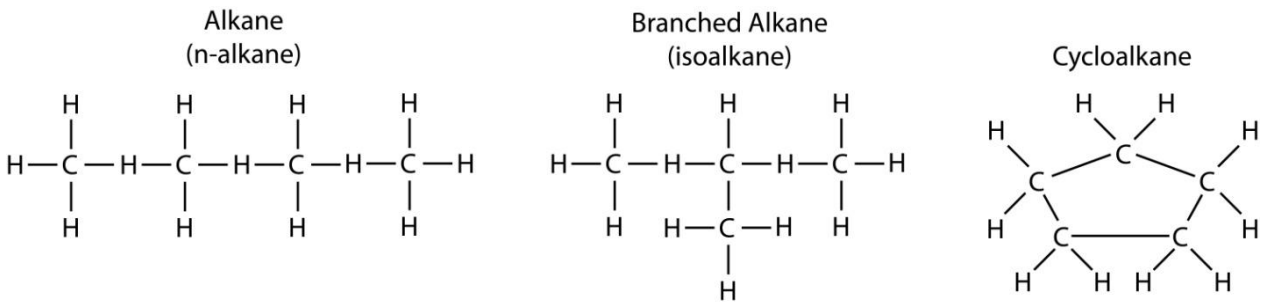


Figure 2-1 Typical Alkane Compounds

Hydrocarbons that contain double bonds between carbon atoms are divided into two subclasses: alkenes (also referred to as olefins) and aromatics. Alkenes consist of a chain with at least one double bond between carbon atoms. Aromatic hydrocarbons consist of one or more cyclic structures or rings with alternating single and double bonds, in which electrons are delocalized and the bonds are hybrids of single and double bonds (**Figure 2-2**).

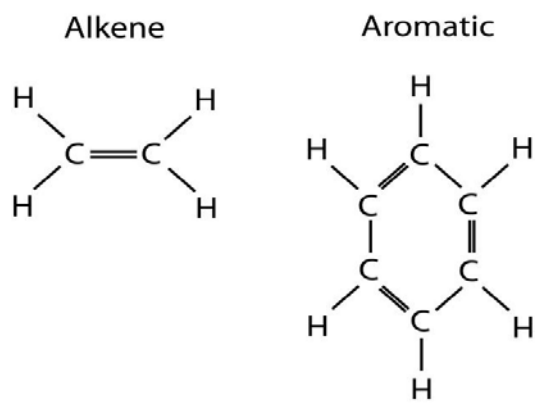
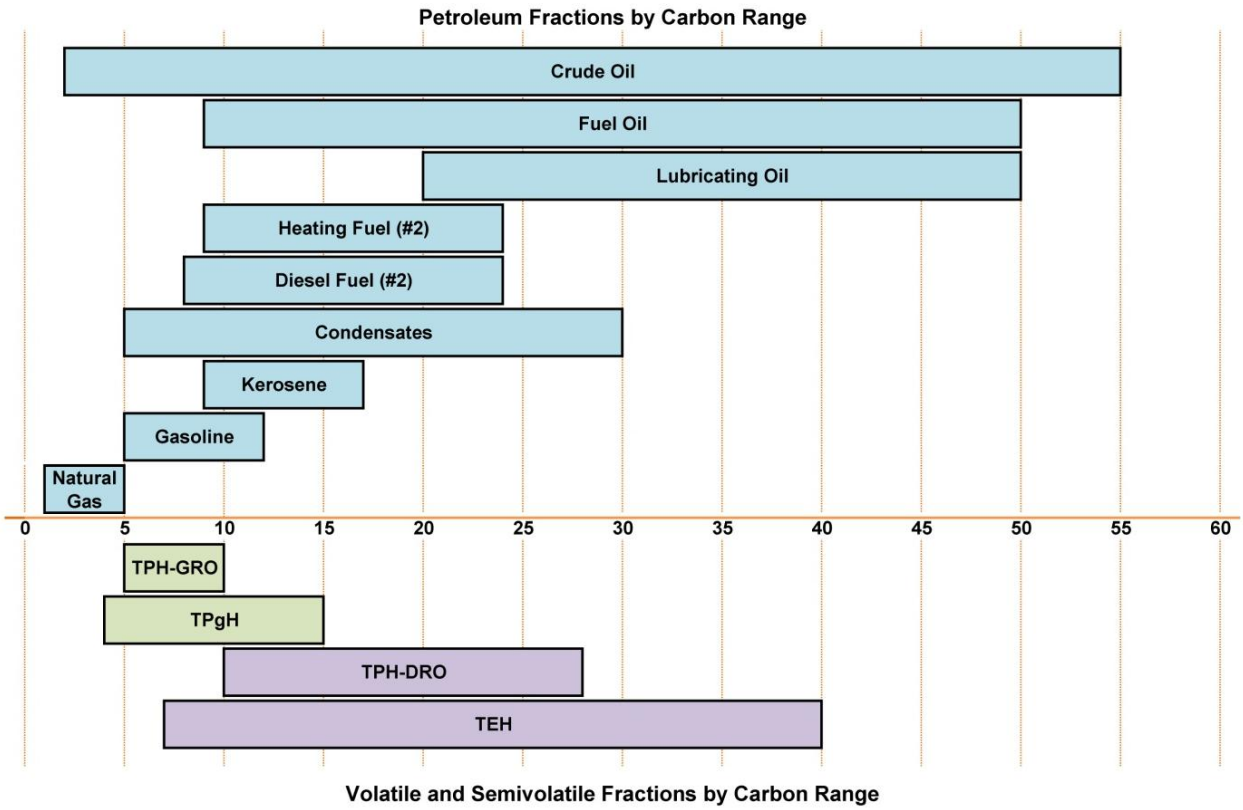


Figure 2-2 Typical Alkene Compounds

Monocyclic aromatic hydrocarbons contain one ring (e.g., benzene), whereas polycyclic aromatic hydrocarbons (PAHs) contain two or more rings (e.g., naphthalene). Alkenes are formed during the process of petroleum refining and are present in most refined products (McMillen et al., 2001).

2.1.2 Composition of Petroleum

Petroleum consists of mixtures of up to hundreds or even thousands of individual hydrocarbon compounds. Mixtures of petroleum hydrocarbon compounds (PHCs) are often defined in terms of the number of carbon atoms, or the range in the number of carbon atoms, present in the individual compounds that make up the mixture (see **Figure 2-3**). For example, gasoline consists of mixtures of hydrocarbons that have mainly from 4 to 12 carbon atoms (i.e., C_4 or C_6 to C_{12}) in their chemical structure, while diesel generally consists of hydrocarbons that contain from 10 to 28 carbon atoms (i.e., C_{10} to C_{28}). Natural gas contains an abundance of hydrocarbons with smaller carbon numbers (i.e., C_1 to C_{4+}).



Source: Petroleum fractions by carbon range adapted from http://www.caslab.com/Petroleum-Hydrocarbon-Ranges; volatile and semivolatile fractions by carbon range for EPA Method 8015 from Energy Laboratories of Billings, Montana.

Figure 2-3 Typical Ranges in the Numbers of Carbon Atoms for Petroleum Fractions and Volatile and Semivolatile Organic Fractions Identified by Method 8015

The proportions of the different types of hydrocarbons (e.g., alkanes versus alkenes) as well as the carbon-number ranges of the hydrocarbon compounds present in a PHC mixture provide clues to the origin of the PHCs. Refined petroleum products (crude petroleum that has been chemically refined upon extraction), unrefined petroleum (i.e., PHCs extracted from sedimentary formations but not yet refined), or other naturally occurring organic matter contain different proportions of these various hydrocarbon and non-hydrocarbon constituents.

Unrefined petroleum products, such as crude oil or condensate, tend to have a broader range in the number of carbon atoms in the individual constituents compared to refined products, since refining processes specifically produce petroleum products containing hydrocarbons with a narrower carbon-number range for a variety of specific uses. Crude oil may contain some fractions of non-hydrocarbon organic compounds, but refined petroleum products typically contain smaller amounts of non-hydrocarbon compounds. Naturally occurring organic matter can contain an abundance of non-hydrocarbon compounds.

2.1.3 Analytical Techniques for Total Petroleum Hydrocarbons

Low-level concentrations of organic compounds and mixtures of compounds detected in wells throughout the PAPA have historically been reported as "petroleum hydrocarbons" (SCCD 2009, 2010, 2011, 2012, 2013). However, the presence of these *petroleum hydrocarbons* refers to the laboratory methods used to test the groundwater samples, and not to the specific compounds present nor to the origin of those compounds. This section summarizes some of the analytical approaches used to identify and quantify mixtures of organic constituents in environmental samples.

Total petroleum hydrocarbons (TPH) is a measurement of the sum total of all organic compounds present in an environmental sample captured and quantified by sample preparation and analytical methods defined by the laboratory. Commonly, the results are reported based on compounds that fall within a specific range in the number of carbon atoms (i.e., carbon number range). TPH methods are not intended to identify or quantify individual compounds, only the sum of all compounds identified as defined by the specific method used.

TPH can be measured using gas chromatography (GC), which is an analytical technique used to separate and generally identify individual organic compounds in a sample. EPA Method 8015 is a GC-based method commonly used to quantify TPH. TPH analysis using EPA Method 8015 measures sums of all of the volatile and semivolatile (less volatile) organic compounds present in a sample based on GC with a flame-ionization detector (FID).

TPH methods are non-specific laboratory methods and detect all organic compounds, both hydrocarbons and non-hydrocarbons, within that specified carbon number range. Non-hydrocarbons can originate from refined petroleum products and unrefined petroleum, as well as from substances or compounds that are not considered petroleum (e.g., silicone grease, naturally occurring organo-sulfur compounds, organic acids, humic materials). Thus, although the result is reported as *total petroleum hydrocarbons*, this measured value provides no conclusive information on the source or specific chemical composition of the constituents. The constituents detected may be hydrocarbons or non-hydrocarbons, and may or may not originate from petroleum sources.

2.1.3.1 *Sample Preparation*

The volatile and semivolatile fractions are defined based on the sample preparation method used prior to separation by GC and detection with the FID. Volatile organic fractions are typically prepared by purge-and-trap sample preparation methods prior to GC analysis. For this method, the water sample is purged with an inert gas, and the volatilized compounds are trapped on a sorbent prior to quantification using GC/FID. Results may be reported as *total purgeable hydrocarbons*. Semivolatile fractions are typically prepared for analysis by extracting the target compounds by shaking the water sample in the presence of a non-water-soluble solvent (typically n-hexane). The

extracted fraction is then captured and quantified by GC/FID. Results may be reported as *total extractable hydrocarbons*.

2.1.3.2 *Organic Fractions*

Specific fractions of hydrocarbon compounds can be reported using TPH methods. Specific fractions, as defined by the method or laboratory, are used to bracket the range of compounds or materials reported from the analysis. These fractions are often selected to represent the range of compounds typically encountered in petroleum-based products, as shown in **Figure 2-3**.

For this study, the volatile fraction was analyzed by EPA Method 8015 and reported both as *total purgeable hydrocarbons* (TPgH) and as *total petroleum hydrocarbons–gasoline-range organics* (TPH-GRO). TPgH is a measure of the sum of all volatile material (both hydrocarbon and non-hydrocarbon) that is removed from the sample using purge-and-trap sample preparation methods, captured on the GC column, and quantified based on detection by the FID. TPH-GRO is a more limited measurement of the volatile organic constituents present. Typically, TPH-GRO is a measurement of all volatile organic compounds that contain between 6 and 10 carbon atoms in their structure. For this study, TPH-GRO was defined as a summation of all organic compounds that elute from the chromatography column between 2-methylbutane and 1,2,4-trimethylbenzene. Although they are volatile (and may be gases at room temperature), light hydrocarbon gases (approximately C_1 through C_4) are generally not quantified using TPH methods.

For this study, mixtures of semivolatile organic compounds were analyzed by EPA Method 8015 and reported both as *total extractable hydrocarbons* (TEH) and as *total petroleum hydrocarbons–diesel-range organics* (TPH-DRO). TEH as determined by Method 8015 is a measure of all semivolatile materials that were extracted from the sample after shaking in contact with n-hexane and then captured and quantified by GC/FID. For this study, TPH-DRO is defined as a measurement of all semivolatile organic compounds that contain between 10 and 28 carbon atoms in their structure (C_{10} through C_{28}).

TPH can also be reported by other analytical techniques, such as infrared spectroscopy (e.g., EPA Method 418.1), gravimetric methods (e.g., EPA Method 1664), or immunoassay (e.g., EPA Method 4030) (Weisman, 1998). Different analytical methods for TPH used on the same sample can produce different results due mainly to differences in solvent type, extraction method, detection method, and quantification standards (McMillen et al., 2001). Thus, the TPH result is defined by the analytical method that is used to measure it.

The reported presence of TPH-GRO and TPH-DRO in a sample does not necessarily indicate that a refined product, such as gasoline or diesel fuel, is present in the medium sampled; "gasoline" or "diesel" in the name of the analytical method implies only a mixture of compounds in the sample that elute from a chromatographic column in the same time range defined by the elution of n-alkanes within the method-specified range in the number of carbon atoms. The compounds eluting

from the column within this time frame could be hydrocarbons or non-hydrocarbons and may or may not originate from petroleum sources (Weisman, 1998).

2.1.3.3 *Silica Gel Treatment*

Many substances that are not considered "petroleum hydrocarbons," such as plant waxes, soil humic material, and animal fats, may also be measured as TPH. TPH has been reported in many items found in nature, including peat moss, pine needles, and cow manure (McMillen et al., 2001). TPH measurements may also include the presence of non-hydrocarbon compounds, such as carbon-containing compounds that also contain nitrogen, sulfur, or oxygen atoms, which are polar constituents and more soluble in water than hydrocarbons are.

Silica gel treatment (SGT) of environmental samples prior to TPH analysis removes polar constituents and can provide a more representative measure of hydrocarbon content. Silica gel is a chemical adsorbent used to pretreat organic samples, often for the purpose of removing interferences from naturally occurring organic matter (Lundegard and Sweeney, 2004). The silica gel adsorbs polar (non-hydrocarbon) components of the extract, leaving the nonpolar (hydrocarbon) components in the extract. These nonpolar constituents are then quantified upon analysis. The non-hydrocarbon, polar material could be derived from one or more of the following sources:

- Naturally occurring organic matter unrelated to petroleum-based substances;
- Biodegradation of a petroleum-based substance, such as an unrefined (e.g., condensate or crude oil) or a refined (e.g., diesel fuel or motor oil) petroleum substance; or
- The non-hydrocarbon component of an unrefined or refined petroleum substance.

These polar, non-hydrocarbon components are most commonly associated with the breakdown of organic matter. Refined petroleum products, such as diesel and motor oil, predominantly consist of nonpolar, hydrocarbon components, because polar components have been removed during processing (API, 2001).

2.1.3.4 *Evaluation of Gas Chromatograms*

In order to evaluate the source of constituents reported as TPH (petroleum-based source or other sources), the chromatogram generated from the GC analysis (i.e., the chromatographic profile) is compared to the chromatographic profiles of a set of known reference substances or standards (typically petroleum products) procured by the laboratory. Gas chromatogram pattern matching is a forensics tool commonly used to identify sources or types of petroleum hydrocarbons in sampled media (Zemo, 2007; Stout and Wang, 2007). Gas chromatograms give an indication of the carbon number range and hydrocarbon type for the total petroleum hydrocarbons within a mixture (McMillen et al., 2001). Chromatograms can also be compared to chromatographic profiles of potential source materials to assess whether they could originate from the same materials. This

approach is not routinely done with TPH analysis in general at most commercial environmental laboratories and is mostly done in forensic applications.

Many substances produce similar chromatographic patterns, and it may not be possible to positively match the chromatogram of the sample to the correct reference standard or sampled material, especially if weathering or biodegradation has occurred in the sampled media. Interpretation of the degree to which a sample chromatogram matches that of a previously known reference substance or sampled source material therefore requires a laboratory analyst with extensive skill and experience, as well as an adequate response in the chromatogram with respect to amplitude and/or pattern.

Despite these limitations, a consistent appearance of certain compounds in the chromatograms provides evidence of potential sources of TPH detections.

2.1.4 Other Testing Methods for Organic Compounds

TPH methods are not intended to identify or quantify individual compounds. Individual volatile organic compounds (VOCs) are sometimes quantified using GC with photoionization and electrolytic conductivity detectors (e.g., EPA Method 8021) or FID (e.g., Method 8015); however, these methods use only retention time within the GC column to identify constituents, and can result in false-positive results due to the presence of interfering organic compounds in complex mixtures. Individual VOCs and semivolatile organic compounds (SVOCs) can be quantified and often identified by combining GC with mass spectrometry (i.e., EPA Methods 8260 and 8270, respectively). Mass spectrometry provides structural information about the compounds detected in a sample, which yields more definitive identification of the organic compounds, especially for interfering compounds with similar retention times. For this study, individual VOCs and SVOCs were analyzed using EPA Methods 8260 and 8270, respectively.

Tentatively identified compounds (TICs) can be reported as part of VOC and SVOC analyses based on probable computer matches of the individual mass spectrometry chromatograms from a library search. While the identification of individual TICs is by definition tentative, and quantitation results for TICs are rough estimates based on internal standards that are often chemically different from the actual compound represented by the chromatogram, the results may be useful because the TICs present in a sample can be compared to TICs in sampled source materials to assess whether they could have originated from the same source. Identification is tentative because mass spectrometry cannot differentiate among chemical isomers (compounds with the same molecular formula but different structures). Definitive identification requires analyzing the actual individual compound expected, which should match in retention time to the respective compound identified as such in the sample.

Light hydrocarbon gases (approximately C_1 through C_4) that are dissolved in groundwater are generally not quantified using TPH methods (e.g., EPA Method 8015), nor during analysis of volatile

or semivolatile organic compounds (e.g., EPA Methods 8260 or 8270). Methods of dissolved gas analysis use different sample preparation and analytical techniques that are more amenable to the capture and quantification of these lighter hydrocarbon gases.

In addition to dissolved gas analysis, analytical techniques used in determining the isotopic composition of gas and thermal maturity assessments of organic matter can provide clues to the origin or potential source of hydrocarbon gas.

2.1.5 Terminology in This Report

Because reported levels of petroleum hydrocarbons are defined by the analytical method and not the source of the materials in the sample, we will not refer to *petroleum hydrocarbons* in this report unless evidence of a petroleum source exists or to *hydrocarbons* unless evidence of specific hydrocarbon constituents exists based on chemical analysis. Constituents identified by the above-listed methods will instead be referred to more accurately as *organic constituents* or *organic compounds*. Organic compounds and constituents will be further defined based on the laboratory methods used for sample preparation and analysis.

Mixtures representing some combination of the volatile fraction of organic compounds (i.e., TPgH and TPH-GRO determined by EPA Method 8015, individual VOCs analyzed by EPA Method 8260, or hydrocarbon gases) may be referred to more generally as *volatile organic constituents* or simply as *volatile organics*. Individual VOCs as determined by Method 8260 will be referenced by specific compound, or generically using the acronym *VOCs*. The acronym *VOCs* will be reserved specifically for those compounds analyzed by and reported using EPA Method 8260.

Mixtures representing some combination of the semivolatile fraction of organic compounds (i.e., TEH and TPH-DRO as determined by EPA Method 8015 as well as individual SVOCs analyzed by EPA Method 8270) may be referred to more generally as *semivolatile organic constituents* or simply *semivolatile organics*. Individual SVOCs as determined by Method 8270 will be referenced by specific compound, or generically using the acronym *SVOCs*. The acronym *SVOCs* will be reserved specifically for those compounds analyzed by and reported using EPA Method 8270.

References to specific laboratory values reported as one of these fractions (TEH, TPgH, TPH-GRO, TPH-DRO, etc.) does not imply that the presence of hydrocarbons or any particular source has been confirmed. The constituents detected may be hydrocarbons or non-hydrocarbons, and may or may not originate from petroleum sources.

Light hydrocarbon gases in groundwater will also be referred to as *dissolved hydrocarbon gases* or *dissolved gas* in this report. Mixtures of volatile and semivolatile organic constituents that cannot be readily identified based on chemical fingerprinting may be referred to as *volatile materials* or *semivolatile materials*, respectively.

When discussing data presented in earlier reports, results may be referred to as "reports of low-level petroleum hydrocarbon detections" because that is how these analyses have historically been reported, or simply as "low-level detections." The use of this terminology reflects historic nomenclature and does not imply that the presence of hydrocarbons or a petroleum source has been confirmed for these samples.

2.2 GEOLOGIC FRAMEWORK

Natural gas E&P activities in the PAPA are centered on the Pinedale Anticline, a geologic structure that is oriented northwest/southeast and is approximately 35 miles long and 6 miles wide. The anticline has approximately 2,000 feet of structural relief in Cretaceous-age rocks (Law and Johnson, 1989), and the axis of the anticline runs parallel to the Wind River Mountains to the east. The anticline is located within the Green River Basin, a structural geologic basin that formed during the Laramide Orogeny, approximately 70 to 80 million years ago during the late Cretaceous geologic period. Industrial water supply wells have been completed in the uppermost water-bearing zone along the axis of the anticline to support natural gas drilling and completion activities.

This section describes the general geologic setting of the PAPA, including the structural geology, stratigraphy, and characteristics of the petroleum-bearing geologic system. Descriptions of structural geology in this report are from Law and Johnson (1989), and stratigraphic nomenclature follows the nomenclature presented by Montgomery and Robinson (1997), except as otherwise referenced.

2.2.1 Structural Geology

The Pinedale Anticline is an asymmetrical, double-plunging anticline with a steeper plunging limb to the west. The anticline is a thrust-rooted detachment structure that probably formed due to the southwest direction of the Wind River Mountains compressional orogeny (Law, 1984; Law and Johnson, 1989; Shuster, 1986; Shuster and Steidtmann, 1988) (**Figure 2-4**). The uplift of the Wind River Mountains was likely an episodic event that may have started as early as 90 million years ago (Law and Johnson, 1989), prior to the development of the rest of the northern Green River Basin.

Both sides of the anticline are bounded by thrust faults (Law and Johnson, 1989). The anticline is bounded to the west by the Pinedale Thrust Fault, a high-angle, east-dipping, reverse or thrust fault that flattens with depth. This fault has up to 1,000 feet of vertical displacement and apparently terminates in the overlying Tertiary-age formations. The anticline is bounded to the east by the Wind River Thrust Fault. According to Govert (2011), normal faults exist at depth along the crest of the anticline but do not appear to be expressed through the thousands of feet of Tertiary-age rock overlying the anticline. These faults are mostly very small, and their vertical displacement is unknown. East/west-trending strike-slip faults appear to exist at depth along the anticline at the south end and at the mid-point. According to Law and Johnson (1989), expression of the Pinedale

Anticline is subtle in geologic units near the surface (i.e., the Wasatch Formation; see **Section 2.2.2**), with observed dips of only 1 degree to 2 degrees on flanks of the structure.

2.2.2 Stratigraphy

The Pinedale Anticline comprises Cretaceous-age sediments thousands of feet thick (**Figure 2-4**). These sediment layers are listed below in order from oldest to youngest:

- Hilliard Shale: siltstone, shale;
- Rock Springs Formation/Lower Mesaverde: fine- to medium-grained sandstone, siltstone, shale, and carbonaceous mudstone;
- Ericson Sandstone: sandstone, minor siltstone/shale; and
- Lance Formation/Upper Mesaverde: fine- to medium-grained sandstone, siltstone, and carbonaceous mudstone.

This sequence of strata indicates a transition in depositional environments from marine to alluvial plain. The Hilliard Shale was deposited over 100 million years ago in a marine environment. The Rock Springs Formation is often referred to as lower Mesaverde (Montgomery and Robinson, 1997). The upper (undifferentiated) Mesaverde Group sediments (referred to as upper Mesaverde; Montgomery and Robinson, 1997) and Lance Formation were deposited in a fluvial environment and are described as having medium- to very fine-grained cemented sandstone channels interbedded with overbank mudstone-siltstones and splay sandstones (Chapin et al., 2009; Govert, 2011).

The Cretaceous-age formations are overlain by up to 8,000 feet of Tertiary-age sedimentary rock formations (**Figure 2-5**). The lithology of these Tertiary-age formations is indicative of fluvial deltaic and alluvial plain depositional environments.

These formations are in order from oldest to youngest:

- Unnamed Unit: conglomerate, sandstone, siltstone, and mudstone;
- Fort Union Formation: sandstone, siltstone, mudstone, and carbonaceous mudstone; and
- Wasatch Formation: sandstone, siltstone, mudstone, and carbonaceous mudstone.

The Unnamed Unit has a lithologic description similar to the upper Mesaverde and Lance Formation, but also contains coarse feldspathic channel deposits (Chapin et al., 2009), the source of which is the Wind River Mountains. The Fort Union Formation is approximately 3,500 feet thick in the PAPA. Coals that are generally associated with the Fort Union Formation in other parts of the Green River Basin are not present at Pinedale (Law and Johnson, 1989). However, some thin coals are present in the Fort Union Formation in the Jonah field located immediately to the south of the anticline (DuBois et al., 2004).

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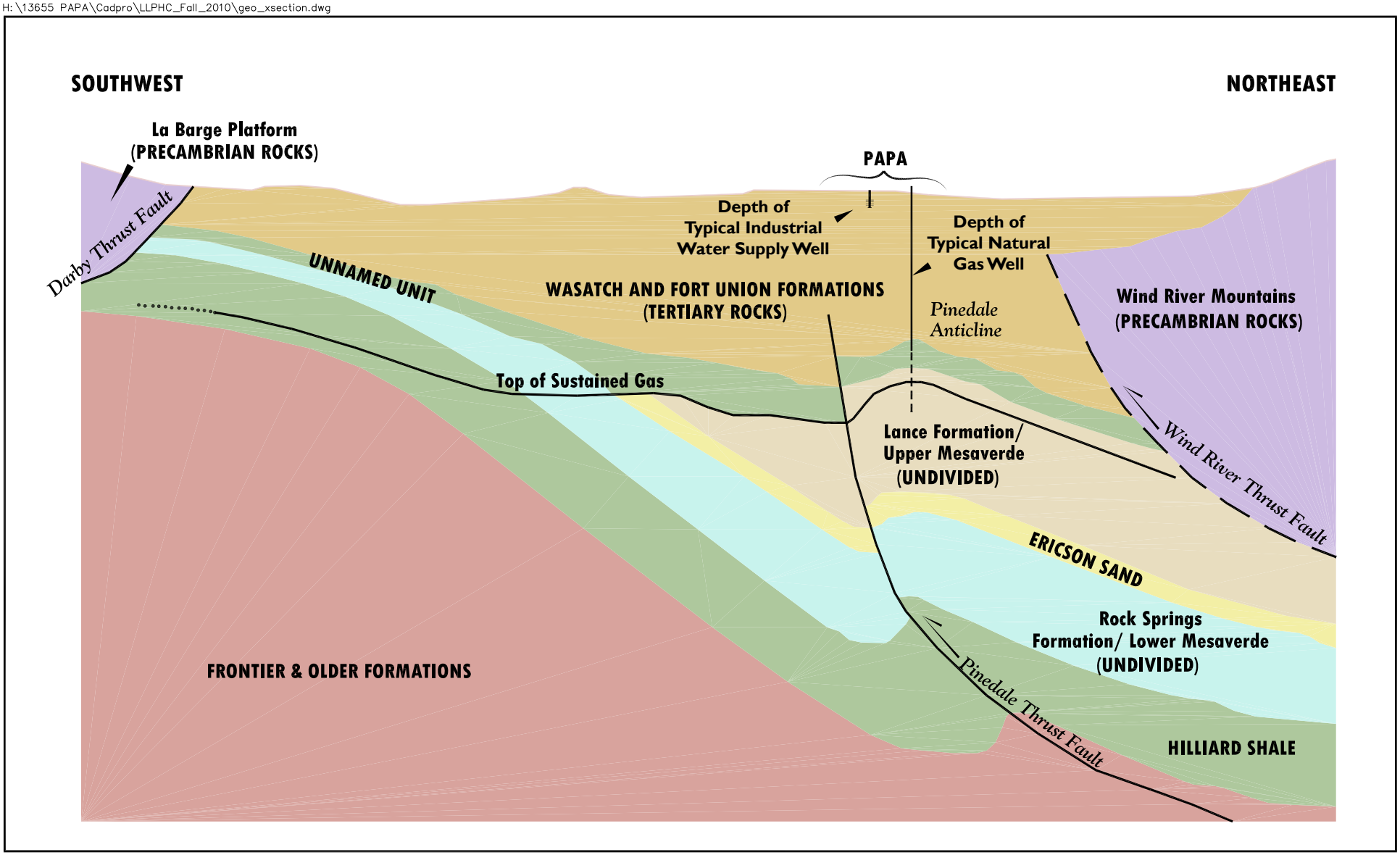

NOTES:
Adapted from Law and Johnson, 1989
Stratigraphy from Montgomery & Robinson, 1997
PAPA - Pinedale Anticline Project Area

Not to Scale

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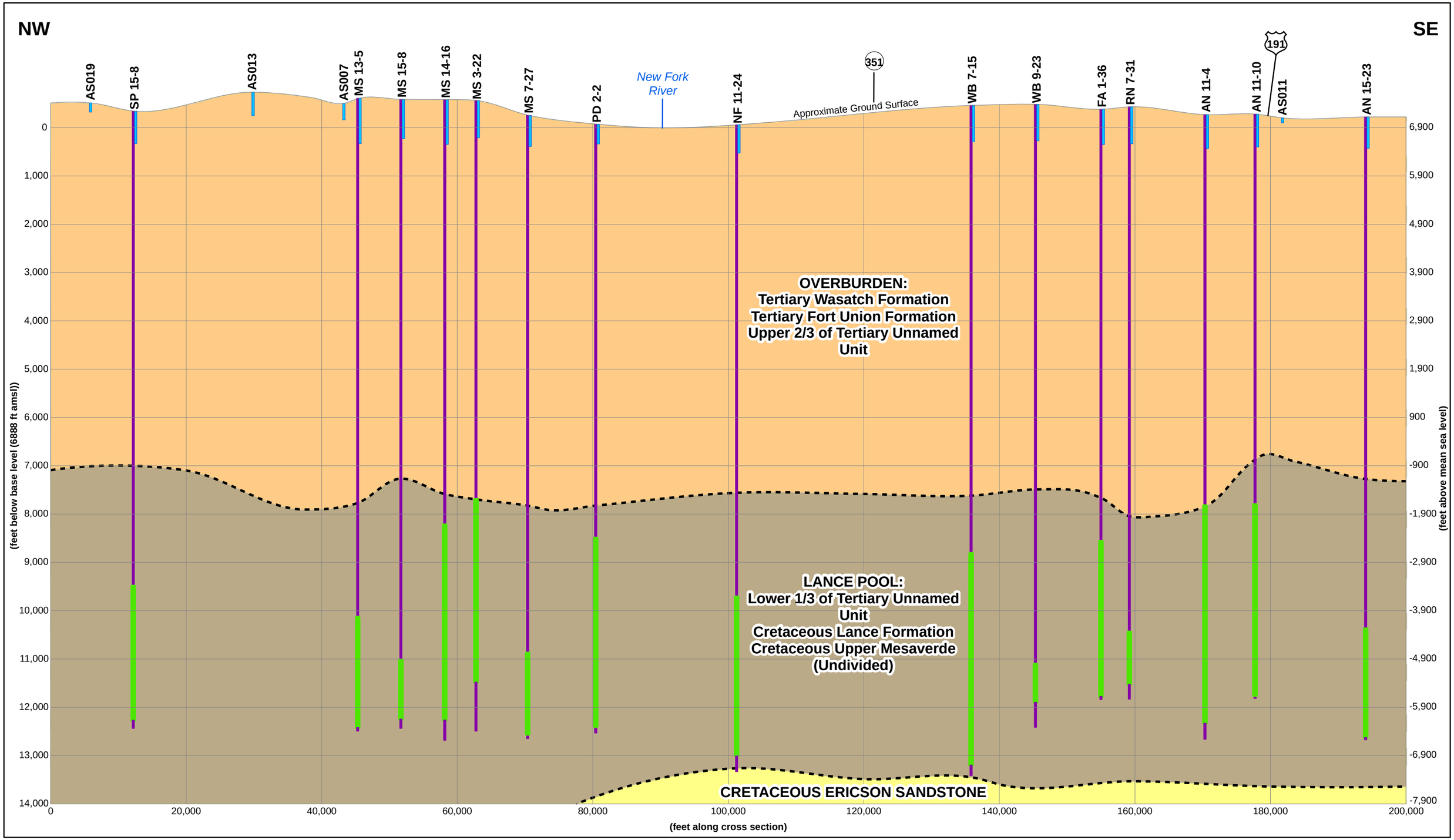
Generalized Structural Cross Section
Green River Basin and Pinedale Anticline Area
Low-Level Petroleum Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 2-4



Notes:
Scale and Locations are Approximate
Approximately 7x Vertical Exaggeration
Gas Well Data from WOGCC: geologic data from Operators
Gas wells depicted as vertical for simplicity but are likely directionally drilled

Natural Gas Production Well
- Casing
- Perforated Interval

Water Supply Well
- Stock or Industrial
- Estimated Contact

amec

Geologic Cross Section of the PAPA
Low-Level Petroleum Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 2-5

The Wasatch Formation consists primarily of fluvially deposited sandstone, representing channel deposits, and shale/siltstone, representing overbank deposits. It is approximately 3,500 feet thick in the PAPA. Deposition of the Wasatch Formation ended approximately 37 million years ago. In the PAPA, approximately one-third of the Wasatch Formation consists of sandstone, and the remaining two-thirds consists of siltstone/shale (AMEC, 2012). Sandstone and siltstone/shale are interbedded and laterally discontinuous on a scale of 1,000 feet, and vertical discontinuity can be on the order of 5 feet. Average thickness is about 18 feet for sandstone interbeds and 33 feet for siltstone/shale interbeds.

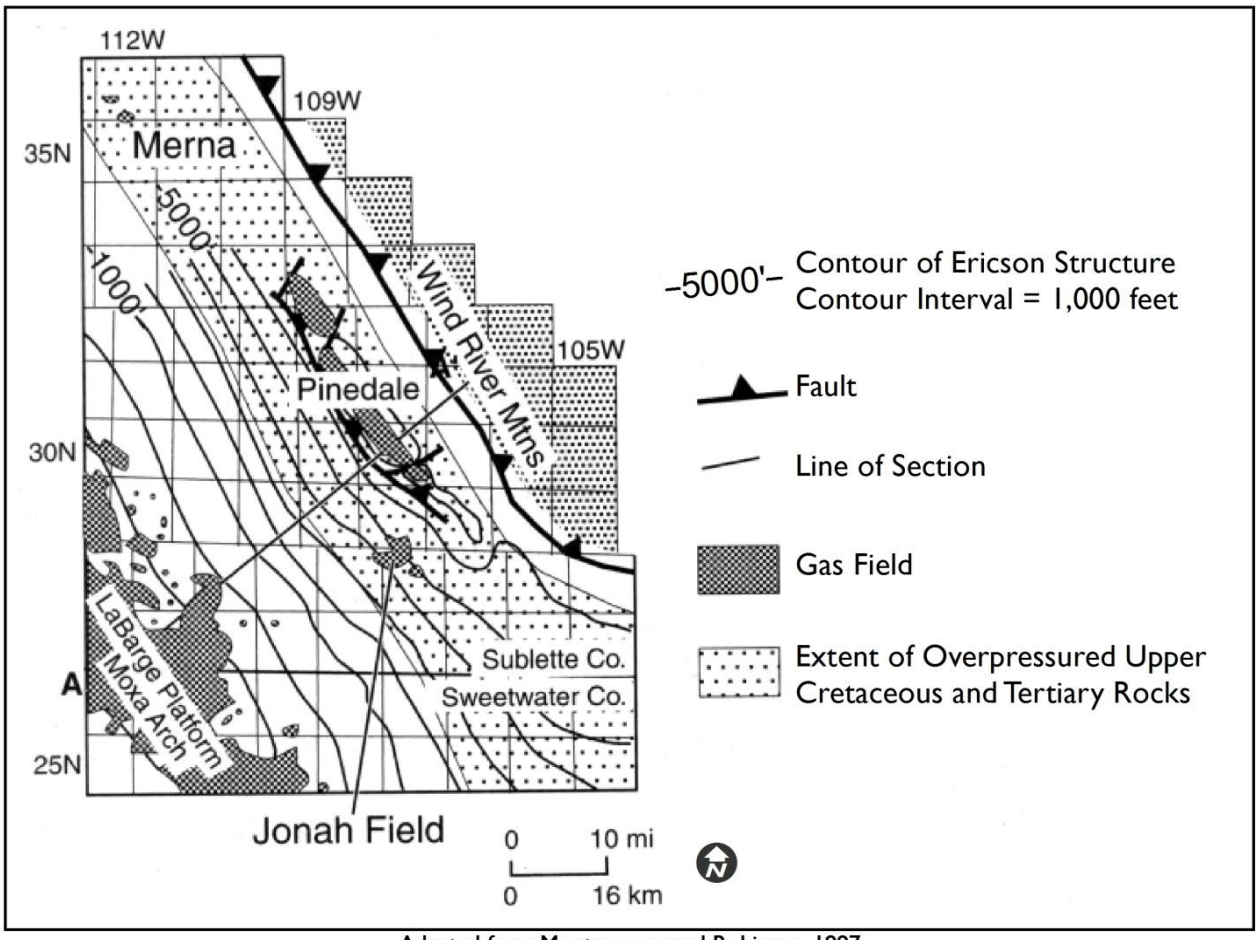
Tertiary-aged formations are overlain in some discrete areas by unconsolidated, Quaternary- and Holocene-aged sediments. These sediments consist predominantly of alluvial deposits of sand and gravel in stream/river valleys, with depths typically less than 100 feet (AMEC, 2013) and a veneer of terrace gravel (i.e., Mesa gravel) overlying the north-central portion of the PAPA, which is known locally as the Mesa.

2.2.3 Petroleum System

The petroleum system currently exploited in the Pinedale Anticline consists of a thick interval of low-porosity and low-permeability rock found within a structural trap (Shanley et al., 2004). The anticline lies adjacent to and north of the Jonah Field, another natural gas field in an area in the northern portion of the Green River Basin. The sediments that host the present gas accumulations, or reservoir, include the upper Mesaverde, the Lance Formation, and the Unnamed Unit. With regard to natural gas E&P, these gas-bearing sediments are collectively referred to as the Lance Pool (**Figure 2-5**).

The Lance Pool is an over-pressurized, tight gas reservoir. Prior to focused development of the Pinedale Anticline pursuant to BLM's 2000 ROD, Spencer (1989) reported abnormally high pressures in Cretaceous-aged rocks located in the northwest part of the greater Green River Basin. **Figure 2-6** shows the extent of over-pressurized Upper Cretaceous and Tertiary rocks in the vicinity of the Pinedale Anticline. The reservoir is over-pressurized as a result of natural gas accumulating at a rate greater than the rate of depletion.

Figure 2-7 shows a representative plot of pressure versus depth measured in natural gas wells in the PAPA based on data collected by PAPA Operators (2012). Up to depths of almost 8,000 feet, the pressure gradient follows the hydrostatic pressure gradient for fresh water of approximately 0.43 pounds per square inch per foot (psi/foot). Below depths of approximately 8,000 feet, the pressure gradient increases, indicating an over-pressurized condition. The over-pressurized condition of the Lance Pool is favorable for natural, pressure-driven, upward migration of gas and fluids.



Adapted from Montgomery and Robinson, 1997

Figure 2-6 Extent of Over-Pressurization—Pinedale Anticline Project Area

The Lance Pool sediments were deposited as sandstone lenses interbedded with less permeable rocks (siltstone and mudstone), resulting in a heterogeneous package of sediments. These types of sediments in a structural trap can contain imperfect seals and may be fractured. This would result in a trap with a *leaky seal,* allowing natural gas to migrate upward from the target formations. Given the likelihood of a leaky seal, upward seepage of natural gas from the target formations in the PAPA through overlying strata to the ground surface is expected over long periods of time. Porosity of the upper Mesaverde and Lance Formation generally ranges from 0 to 12 percent, and permeability is in the microdarcy range (Chapin et al., 2009; Govert, 2011).

Natural gas in the Lance Pool originates from a mixed source. Some natural gas and condensates are sourced in situ from Mesaverde Group sediments. However the primary source is the deeper cracked hydrocarbons (hydrocarbon cracking is the process of breaking long-chain hydrocarbons into short ones) originating from the Hilliard Shale, which were generated under high temperatures

and pressures, and subsequently migrated into the Lance Pool. Govert (2011) suggested that approximately 4,000 feet separate the top of the Hilliard Shale and the base of the Upper Mesaverde (e.g., base of Lance Pool). Natural gas migrates upward from the source rocks due to both buoyant forces and because of the upward pressure gradient shown in **Figure 2-7**. The anticline serves to focus the accumulation of natural gas in the Lance Pool.

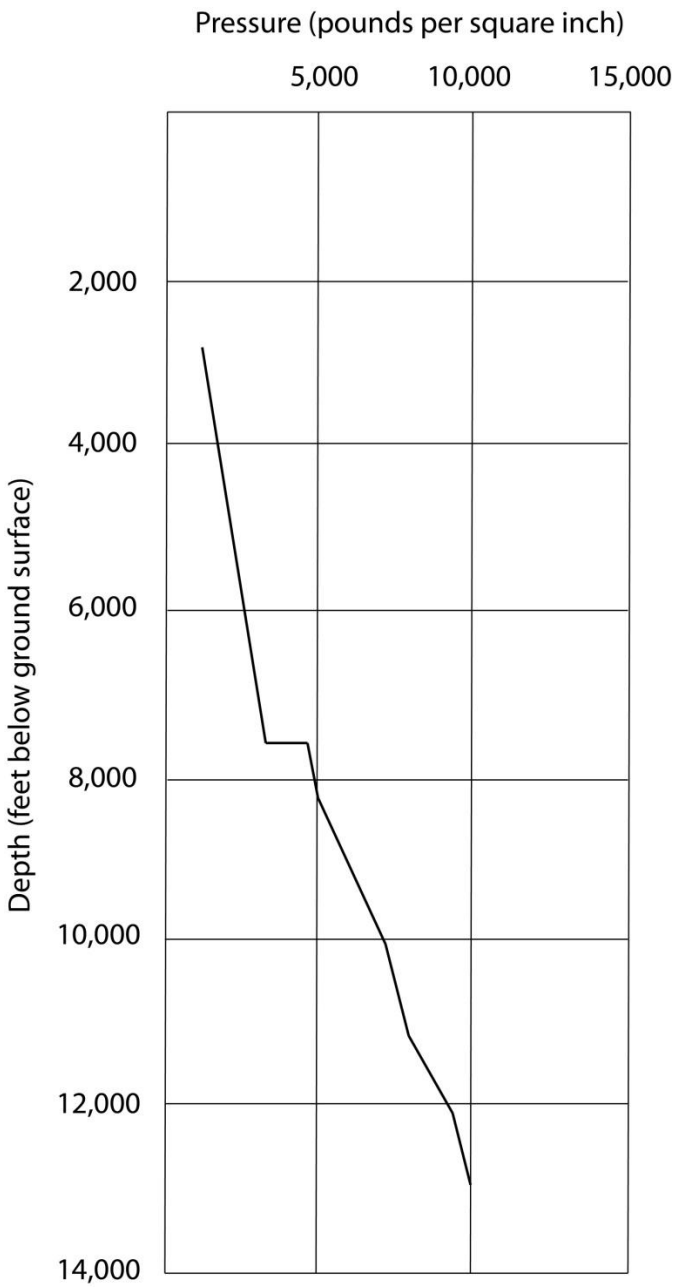


Figure 2-7 Representative Plot of Natural Gas Well Pressure versus Depth

2.3 History of Gas Exploration and Production Activities in the PAPA

The history of natural gas E&P activities in the Pinedale Anticline began in 1939 with drilling of the Government 1 well by the California Company. Gas production was initially low, and the nearest pipeline was too far away to warrant further development. Eleven natural gas production wells were drilled in the PAPA from 1949 to 1963, and an additional eight natural gas production wells were installed from 1980 to 1982; however, the low flow of gas rendered further gas development economically infeasible. The locations of these 20 early natural gas production wells, or pre-1984 wells, are illustrated on **Figure 2-8**.

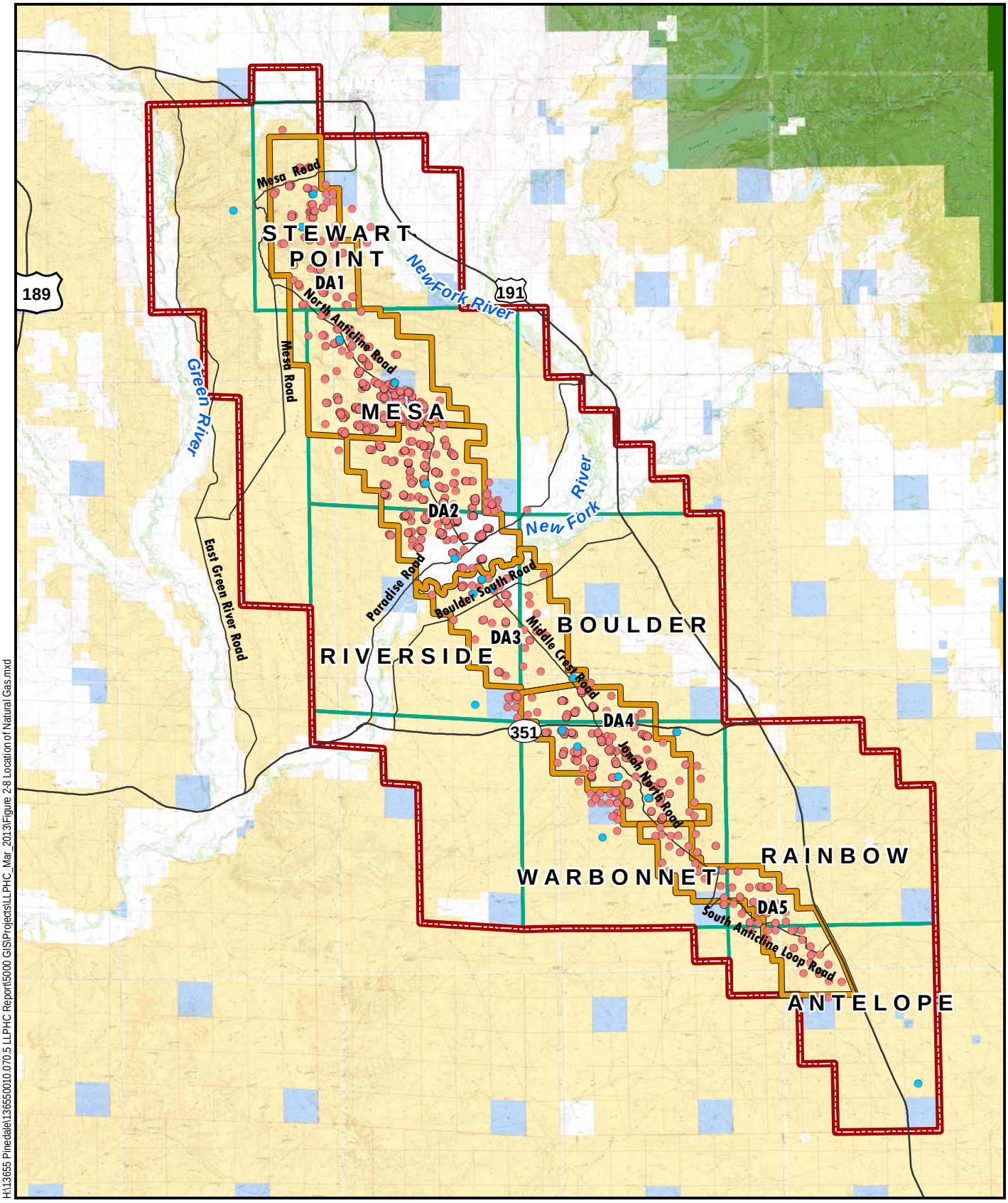
Most early gas wells were installed, tested, and either brought into production or temporarily closed (i.e., "shut-in"). Based on available records, some wells were apparently shut-in for a decade or more without further activity. The total depth of these pre-1984 gas wells ranged from 7,797 to 19,000 feet.

Some of these pre-1984 gas wells were hydraulically fractured, and in some cases, hydraulically fractured multiple times, during their history. Hydraulic fracturing involves pumping large quantities of fluids at high pressure down a well bore to produce fractures in the targeted rock formation. This technology stimulates the flow of natural gas or oil from the targeted rock formation, increasing the volume that can be recovered.

Based on available information, no new gas wells were installed between 1983 and 1993. Since 1994, however, natural gas E&P activities in the PAPA have increased, and the PAPA has been subdivided into seven production areas, as illustrated on **Figure 1-2**:

- Stewart Point (SP)
- Mesa (MS)
- Riverside (RS)
- Boulder (BO)
- Warbonnet (WB)
- Rainbow (RB)
- Antelope (AN)

The rapid increase in E&P activities in the PAPA since 1994 is due in part to improvements in drilling and hydraulic fracturing technology. Newer gas wells drilled in the PAPA use directional drilling technology to recover natural gas that can be liberated from vertical completion intervals (versus horizontal completion intervals in shale gas wells) by the improved hydraulic fracturing techniques. Most of the natural gas E&P activities are concentrated along the entire length of the crest of the anticline (**Figure 2-8**). Sediments comprising the upper Mesaverde, Lance Formation, and Unnamed Unit are the targeted producing zone for post-1984, directionally drilled natural gas production wells. These producing zones range in depth from approximately 8,000 feet to 14,000 feet, depending on the precise location within the PAPA.



H:\13655 Pinedale\136550010.070.5 LLPHC Report\5000 GIS\Projects\LLPHC_Mar_2013\Figure 2-8 Location of Natural Gas.mxd

N

0 Miles 5

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DA1 Development Area (DA)

MESA Production Area Boundary

Pinedale Anticline Project Area

Bureau of Land Management

U.S. Forest Service

State

Private

Post-1984 Natural Gas Production Wells (2131 Wells Through March 17, 2012)

Pre-1984 Natural Gas Production Wells (20)

Location of Natural Gas Production Wells in the PAPA Low-Level Petroleum Hydrocarbon Evaluation Sublette County, Wyoming

FIGURE 2-8

A simplified well construction diagram of a generalized, directionally drilled natural gas production well is shown on **Figure 2-9**. Detailed information regarding ownership, locations, depths, and installation dates of the early gas wells; details of early E&P activities; and a chronology of PAPA gas field development and regulatory milestones are provided in the SAP (AMEC Geomatrix, 2010).

Many gas pads have, or have previously had, an associated industrial water supply well to provide water needed to support well drilling and completion activities. **Section 4.3** discusses general practices in construction, use, and operation of industrial water supply wells.

Additional infrastructure needed to support natural gas E&P activities has evolved over time and has included reserve pits, production equipment and associated tanks, large aboveground storage tanks, in-field fluid gathering systems (i.e., liquid gathering systems or LGS), and tank batteries and other storage/transfer facilities at centralized gathering facilities (CGFs). The use of these facilities in E&P operations has changed over time in the PAPA. Historically, recovered product awaiting delivery by tanker truck was stored at the well pad in aboveground storage tanks. More recently, networks of pipelines have been developed to deliver natural gas to CGFs for processing and delivery. These support systems and how they have changed over time are described in more detail in **Section 4.2**.

2.4 HYDROGEOLOGY

This section presents a summary of the hydrogeological setting in the PAPA.

2.4.1 Hydrostratigraphic Units

A hydrogeologic conceptual model of the PAPA, developed initially in 2008 (Geomatrix, 2008) and later refined by the results of the HDG investigation (AMEC, 2012), defined two primary hydrostratigraphic units:

- Alluvial: alluvial sediments present in the valleys of principal rivers and streams; and
- Wasatch: sediments (sandstones, siltstones, and shales) of the Wasatch Formation.

The underlying Fort Union Formation is considered a separate hydrostratigraphic unit, differentiated from the Wasatch Formation based on its greater depth and differences in groundwater quality (e.g., high concentrations of total dissolved solids [TDS]) within the PAPA. Very little information exists with regard to hydrogeology of the Fort Union Formation in the PAPA. No water supply wells within the PAPA penetrate the Fort Union Formation; the deepest industrial water supply wells are separated from the Fort Union Formation by about 3,000 vertical feet. The Fort Union Formation is used for injection of brine (e.g., produced water) generated from E&P activities.

2.4.2 Groundwater Wells in the PAPA

Over 400 water wells are located in or near the boundary of the PAPA, including wells installed for the following purposes:

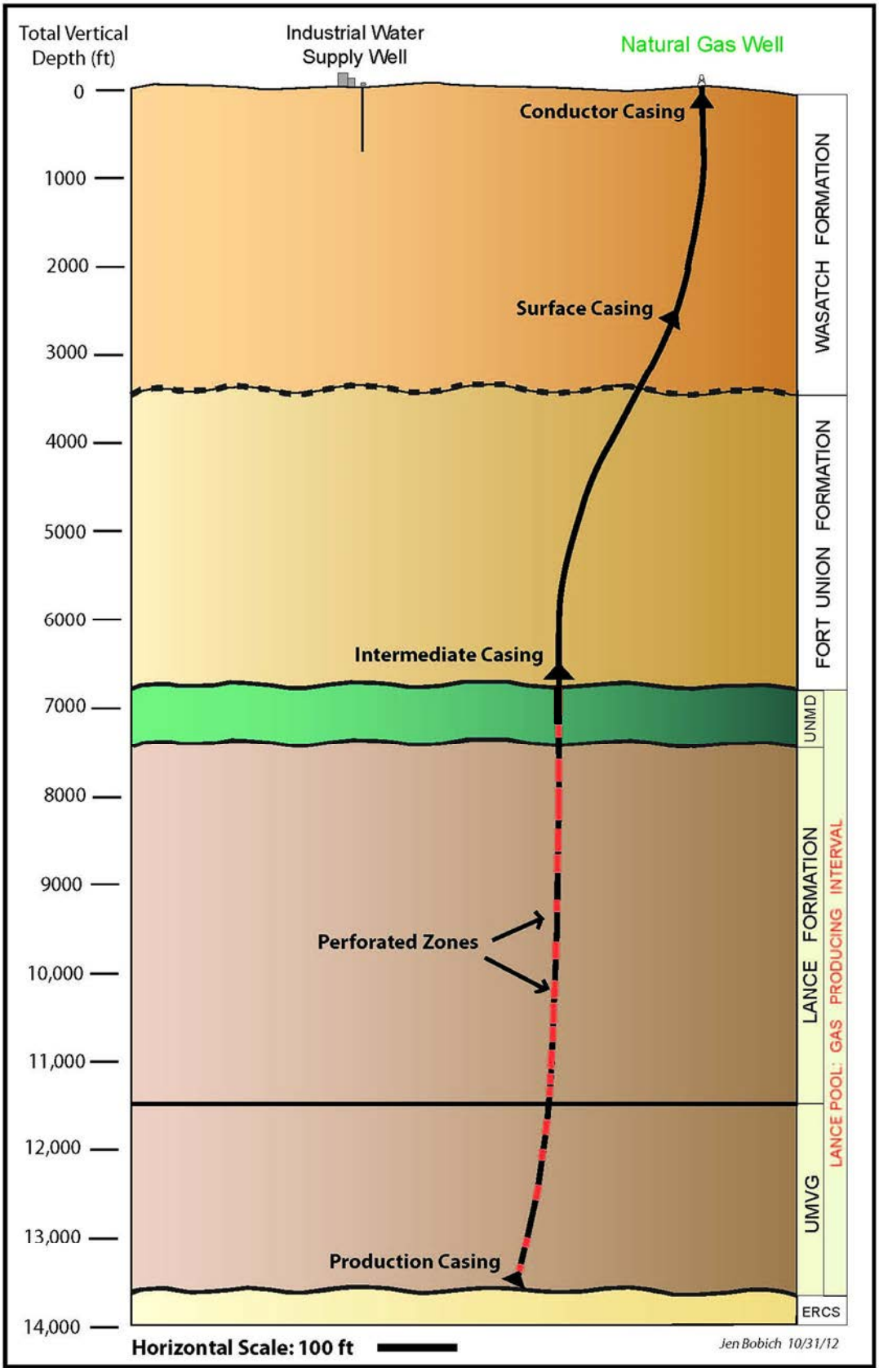
- Domestic water supply wells ("domestic wells"),
- Wells to provide water for stock ("stock wells"),
- Wells to provide water needed to support commercial or industrial activities, including natural gas well drilling and completion activities ("industrial water supply wells"), and
- Wells installed for the express purpose of collecting groundwater samples to monitor groundwater quality and collecting hydraulic data to describe groundwater flow conditions ("study wells").

In the companion HDG investigation performed by AMEC, a total of 30 new study wells were installed throughout the PAPA to characterize the hydrogeology and general water quality in the PAPA (AMEC, 2012). Two study wells were installed in the Mesa gravel, six study wells were installed in the alluvium, and 22 study wells were installed in the Wasatch Formation. The two study wells installed in the Mesa gravel have been dry, as was one study well installed in the Wasatch Formation. Ten of the 30 study wells were installed on gas well pads (i.e., on-pad study wells), which include the one dry well installed in the Wasatch Formation. Twenty of the 30 study wells were installed at various locations around the PAPA, away from E&P activities (i.e., off-pad study wells).

Owing to their intended use for industrial purposes, industrial water supply wells are not operated using the stringent sanitary procedures that would be employed for municipal or domestic water supply wells. The study wells were installed for the purpose of collecting additional hydrogeological and water quality data in the PAPA, and are being used only for monitoring purposes in general conformance with practices generally accepted by the environmental industry and in accordance with the Plan of Study accepted by the BLM in consultation with the U.S. EPA and Wyoming DEQ (see AMEC, 2012).

2.4.3 Groundwater Hydraulics

A potentiometric surface map of the Wasatch Formation developed by AMEC (2012) is presented on **Figure 2-10**. Groundwater in the PAPA generally flows west and south from the mountains and foothills of the Wind River Mountain Range toward the Green River below the mouth of the New Fork River and into the center of the Green River Basin. Some recharge to the Wasatch Formation may occur in the area of the PAPA where water migrates vertically down from the ground surface under varying degrees of saturation and at times travels laterally on top of shale/siltstone until higher conductivity sandstone is encountered. The towns of Pinedale and Boulder are upgradient of E&P activities in the PAPA.



H:\13655 Pinedale\13655001 0.070.5 LLPHC Report\5000 GIS\Projects\LLPHC Mar 2013\Figure 2-9 Conceptual Diagram.mxd

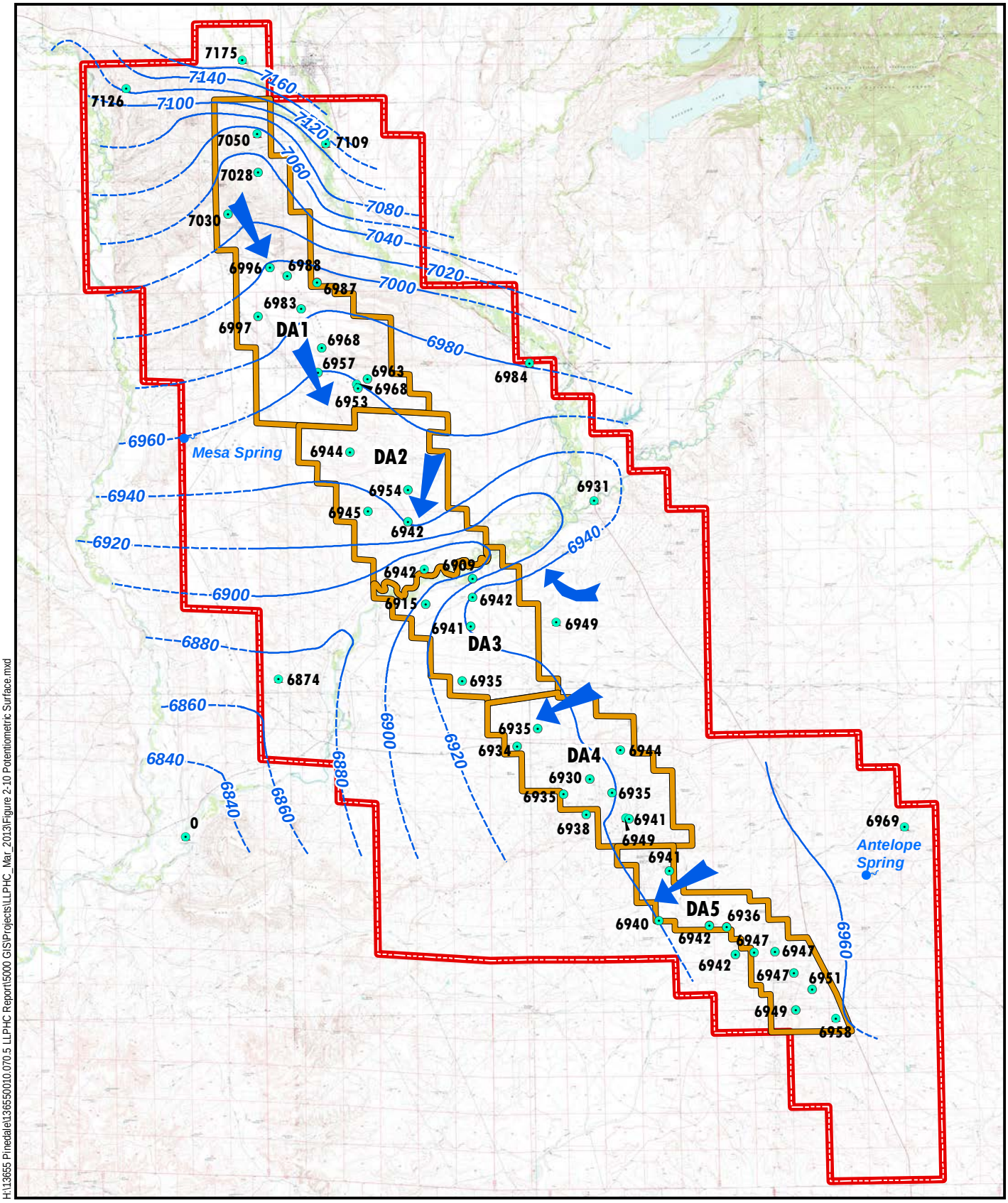
= Inferred Geologic Contact

ERCS = Ericson Sandstone
UMVG = Upper Mesaverde Group sediments (undifferentiated) or upper Mesaverde
UNMD = Unnamed Unit

= Base of Casing

amec

Conceptual Diagram of Directionally Drilled Natural Gas Production Well
Low Level Petroleum Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 2-9



H:\13655 Pinedale\136550010.070.5 LLPHC Report\5000 GIS\Projects\LLPHC_Mar_2013\Figure 2-10 Potentiometric Surface.mxd

Source: 7.5' Quads WYGISC, BLM

N

0 3
Miles

amec

DA1 Development Area (DA)

Pinedale Anticline Project Area

Groundwater Flow Direction

Well

6958 September 2010 Groundwater Elevation (AMEC, 2012a)

Potentiometric Surface (feet above mean sea level, datum NAVD88)

Inferred Potentiometric Surface

Contour Interval 20 feet

Potentiometric Surface Map
Wasatch Formation, September 2010
Low-Level Petroleum Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 2-10

Groundwater in the Wasatch Formation preferentially flows through higher permeability sandstone units, and is typically present under semiconfined conditions. The Wasatch Formation is not continuously saturated, and in some areas perched groundwater systems exist that discharge locally to springs. Groundwater in the shallow portion of the Wasatch Formation likely migrates laterally and downward, preferentially in sandstone units, and discharges to springs and rivers or migrates to the deeper saturated zone. Hydraulic gradients measured in study well clusters show downward movement of groundwater in the Wasatch Formation outside the New Fork River valley and strong upward movement of groundwater along the New Fork River below the confluence of the East Fork River.

The alluvial sediments are hydraulically connected to the Wasatch Formation, receiving and transmitting groundwater down valley and into the New Fork River in the central PAPA. Vertical hydraulic gradients in alluvium in the upper New Fork River valley vary seasonally, but are upward most of the year. Artesian groundwater conditions in bedrock in the New Fork River valley in the central portion of the PAPA cause groundwater in the Wasatch Formation to discharge into alluvium and into the New Fork River.

Most domestic, stock, and industrial water supply wells in the PAPA are completed in the Wasatch Formation. A few domestic and/or stock wells are completed in or are partially open to the alluvium. Industrial water supply wells are installed to greater depths in the Wasatch Formation compared to domestic or stock wells. Based on available information, maximum depths for domestic, stock, and industrial wells in the PAPA are approximately 320 feet, 600 feet, and 1,210 feet, respectively (AMEC, 2012), which is more than 7,000 feet above the producing zones of the natural gas production wells (**Figure 2-9**).

Based on hydraulic conductivity values estimated from aquifer testing of selected wells and hydraulic gradients calculated using water levels from study wells, AMEC estimated average groundwater velocities for alluvial deposits and Wasatch Formation sandstone units (AMEC, 2012):

- Hydraulic conductivity values for the Wasatch Formation range from 0.019 foot/day to 9.47 feet/day.
- Hydraulic gradients for the Wasatch Formation range from about 0.013 foot/foot to 0.0009 foot/foot.
- Hydraulic conductivity was estimated at 446 feet/day in alluvium, based on a single aquifer test.
- The hydraulic gradients for alluvium range from 0.0014 foot/foot to 0.0038 foot/foot.
- Estimated average groundwater velocity in alluvial deposits ranges from 1,390 feet/year to 4,270 feet/year.

- Estimated average groundwater velocity in Wasatch Formation sandstone units ranges from 0.011 foot/year to 40 feet/year.

Groundwater modeling results indicate that transport velocities in alluvial material along the New Fork and Green rivers are 100 to 700 times greater than those in the Wasatch Formation (AMEC, 2013). To put this in perspective, based on these estimates from modeling, groundwater would travel 100 to 700 times further in one year within alluvium than it would within the Wasatch Formation.

2.5 GROUNDWATER QUALITY IN THE PAPA

This section presents an overview of general groundwater quality characteristics in the PAPA, summarizes previously existing information regarding organic constituents detected in samples collected from industrial water supply wells in the PAPA, and describes the occurrence of combustible gas in well casings of water supply wells in the PAPA.

2.5.1 General Water Quality

Of the 30 study wells, the 27 wells with groundwater present were sampled during the HDG investigation. Sampling results with regard to general water quality parameters are briefly discussed below. A more detailed summary of general water quality results for study wells from the HDG investigation is provided in the hydrogeological data gaps report (AMEC, 2012).

The general quality of groundwater observed in the study wells sampled for the HDG investigation is consistent with that reported in other water quality studies conducted in the upper Green River Basin (Lowham et. al., 1985; Chafin and Kimball, 1992; Martin, 1996), and annual monitoring currently conducted by the SCCD on behalf of the Operators in the PAPA.

Calcium is the dominant cation in groundwater from five of six study wells installed in the alluvial sediments along the New Fork River; bicarbonate is the dominant anion in groundwater from all the alluvial study wells. The groundwater types in alluvial study wells are more similar to surface water of the New Fork River than to groundwater in the Wasatch Formation. Groundwater in alluvium generally contained higher concentrations of calcium and magnesium relative to groundwater in the Wasatch Formation. No state water quality standards for inorganic constituents in Class I groundwater were exceeded in alluvial study wells.

Sodium is the dominant cation in groundwater from all 21 study wells sampled in the Wasatch Formation. Bicarbonate is the dominant anion in groundwater from 13 of the 21 study wells, while groundwater in the remaining wells had sulfate or chloride as the dominant anion. A predominantly sulfate water type is generally found in study wells installed at shallower depths and in the eastern portion of the PAPA, whereas a sodium sulfate-chloride type groundwater is found in two study wells installed near the Green River in the western portion of the PAPA. Concentrations of inorganic

constituents in groundwater from study wells installed in the Wasatch Formation exceed Class I groundwater quality standards for the following parameters in at least one well: pH, TDS, chloride, sulfate, fluoride, and sodium absorption ratio (SAR).

The presence of these inorganic constituents in groundwater at levels greater than Class I groundwater standards is not limited to study wells in the area of the PAPA. Lowham et al. (1985) reported that elevated TDS and fluoride concentrations are common in groundwater in the region that includes the upper portion of the Green River Basin. The average concentration of dissolved solids in groundwater from the Wasatch Formation was 1,030 milligrams per liter (mg/L), whereas the Class I groundwater standard is 500 mg/L. A compilation of water quality data from spring and groundwater samples collected in the Green River Basin shows that about half of the samples collected in Sublette County had dissolved-solids concentrations and SAR that exceeded Class I groundwater quality standards, with several samples exceeding Class I groundwater quality standards for pH, sulfate, chloride, and/or fluoride (Zimmerman and Collier, 1985). In a detailed study of the geochemistry of the near-surface Wasatch Formation in the upper portion of the Green River Basin, seven of eight groundwater samples exceeded the Class I groundwater quality standard for pH (9.0), and two of eight samples exceeded the Class I groundwater quality standard for TDS (Chafin and Kimball, 1992).

2.5.2 Annual Groundwater Monitoring

The 2000 ROD (BLM, 2000) required that groundwater quality be monitored on an annual basis in water supply wells within 1 mile of proposed or existing oil and gas wells in the PAPA. Annual monitoring is currently conducted by the SCCD on behalf of the Operators. Water supply wells that are sampled include domestic, stock, and industrial water supply wells. Analytical parameters include general water quality constituents, common ions, metals, and organic constituents.

Sampling and analytical procedures for annual monitoring have changed over time. Upon initiation of the monitoring program in 2004, samples were analyzed for silica gel treated n-hexane extractable material (SGT-HEM; non-polar material) by EPA Method 1664. Beginning in 2008, samples were analyzed for organic compounds using a modified EPA Method 8015 (8015M), and the results were reported as TPH-GRO and TPH-DRO. These analyses measure all of the organic compounds, both hydrocarbons and non-hydrocarbons, within a specified range in the number of carbon atoms (see **Section 2.1.3**). If any TPH fraction was detected in a sample, the well was re-sampled and also analyzed for benzene, toluene, ethylbenzene, and xylenes (BTEX) by EPA Method 8021. Beginning in 2010, if the analyses produced detectable levels of any TPH fraction in a sample, the well was re-sampled and analyzed both for BTEX via EPA Method 8021 and for a suite of VOCs by EPA Method 8260.

As of December 31, 2011, the SCCD had collected over 2,000 groundwater samples from over 380 water wells located within 1 mile of existing or proposed oil and gas wells in the PAPA (SCCD,

2012). Results of annual monitoring by SCCD are posted on the Pinedale BLM website.[1] Analytical results from annual groundwater monitoring of domestic, stock, and miscellaneous (e.g., industrial) water supply wells sampled by SCCD are summarized briefly in **Section 2.5.3**.

2.5.3 Results of SCCD Sampling in the PAPA

Based on the scattered locations where detections of organic constituents have been reported and the density of wells in the PAPA (i.e., ½-mile distance between wells on average), the SCCD well sampling data indicate that no widespread plume of impacted groundwater is present in the PAPA.

Analytical results from annual monitoring of domestic, stock, and industrial water supply wells sampled by the SCCD from 2004 to 2011 are provided in **Appendix A**. A narrative summary of SCCD's 2012 monitoring results (SCCD, 2013) is included in **Appendix A**. The summary below, as well as tables and figures in **Appendix A**, do not include 2012 data; however, a review of sampling results from 2012 (SCCD, 2013) indicates no changes to the interpretations presented below based on SCCD data.

Approximately 45 percent of the water wells monitored by SCCD were used for domestic and stock purposes, while 55 percent were identified as miscellaneous wells (e.g., industrial water supply wells). Almost 95 percent of the total number of samples collected between 2004 and 2011 were analyzed for organic constituents using either EPA Method 1664 or EPA Method 8015M (see **Section 2.5.2**).

A majority of wells sampled by the SCCD between 2004 and 2011 have had no detections of organic constituents. **Chart 2-1** summarizes the frequency of detections reported in wells for volatile organic constituents and semivolatile organic constituents during this time frame.

Chart 2-1 Frequency of Detections of Volatile and Semivolatile Constituents by SCCD

Frequency of Detection (2004 – 2011)	Volatile Organic Constituents	Semivolatile Organic Constituents
Consistently not detected for 3+ years	227	245
Not detected with less than 3 years of data	82	80
Previously detected, but now not detected	22	16
Consistent or repeated detections	13	5
Insufficient data to assess frequency	42	40

[1] http://www.blm.gov/wy/st/en/field_offices/Pinedale/pawg/DataResults.html

When organic constituents have been detected in groundwater samples, most constituent concentrations have been below applicable groundwater standards, in many cases by an order of magnitude or more. Applicable groundwater standards for the organic constituents tested for by SCCD are either U.S. EPA Maximum Contaminant Levels (MCLs) or Wyoming DEQ cleanup levels for the Voluntary Remediation Program (VRP). Moreover, only a limited suite of individual constituents have typically been detected. In many cases, the detection of organic constituents has been sporadic or not repeated in subsequent sampling events. A majority of the wells with insufficient data to assess frequency or trend in detections have only been analyzed for non-polar materials (NPM); NPM was not detected in these wells.

Three of the five industrial water supply wells with consistent or repeated detections of semivolatile organic constituents have had, or currently have, concentrations above applicable groundwater standards. Only 1 of the 13 industrial water supply wells with consistent or repeated detections of volatile organic constituents has exhibited constituent concentrations above applicable groundwater standards. The few industrial water supply wells where organic constituents have been consistently detected at concentrations greater than applicable groundwater standards have been, or are currently, under regulatory oversight (e.g., Wyoming DEQ VRP[1]).

Locations where organic constituents were detected the last time the well was sampled (e.g., most recent detections as of 2011) are distributed throughout the area of the PAPA and are not clustered in any particular area (**Figures A-1** and **A-2**; **Appendix A**).

2.5.4 Gas Occurrence

The SCCD monitors wells for the presence of combustible gases in well casings as a safety precaution prior to collection of groundwater samples. The SCCD has identified 14 industrial water supply wells in the PAPA with detectable concentrations of combustible gas in water well casings during annual groundwater monitoring. AMEC also identified similar conditions at an additional five industrial water supply wells and one stock well. The 20 wells where combustible gases have been observed are listed in **Chart 2-2**.

Chart 2-2 Wells Where Combustible Gases Have Been Observed

Sherlock Federal 15-8	Warbonnet 7-4	Warbonnet 8-25
Gannet 11-16	Warbonnet 7-5	Blue Rim Well #4084 (stock well)
Mesa 14-16	Warbonnet 16-10	Rainbow 13-30
Mesa 3-27	Warbonnet 13-11	Antelope 11-10D
Mesa 5-33	Warbonnet 9-15	Antelope 1-16
Riverside 11-14	Warbonnet 1-21	Highway #7
Boulder 12A-33	Warbonnet 5-25	

[1] http://deq.state.wy.us/volremedi/index.asp

Most of the industrial water supply wells with combustible gas present in well casings are located in the southern portion of the PAPA. The presence of combustible gases in industrial water supply wells may be an indication that a pathway exists between the deeper gas-bearing zones and shallower water-bearing units. This pathway could be a man-made conduit, such as a poorly cased or improperly cemented natural gas well, or naturally occurring, such as seepage from an underlying gas field. A description of these alternative sources is presented in **Section 4.8.**

In 2009, gas samples were collected from the well casings of three industrial water supply wells where combustible gas had historically been observed in an effort to determine the origin of the gas. The samples were tested for gas composition and for isotopic ratios of methane (AMEC Geomatrix, 2009b). The hydrocarbon composition of the casing gas and the isotopic composition of methane indicated that the gas accumulating in the well casings was thermogenic in origin (i.e., produced by alteration of organic material under conditions of high temperature and pressure). It was recommended that the isotopic composition of methane in natural gas samples be determined for comparison purposes in order to aid in the identification of the source of thermogenic gas in water well casings (AMEC Geomatrix 2010). Further discussion about the origin of gas is presented in **Section 8.1**.

3.0 TECHNICAL APPROACH

This section details the technical approach used to evaluate the presence and potential sources of low levels of organic constituents found in groundwater samples within the PAPA. As noted in **Section 1.2** and **Section 1.3**, the overall approach involved three main phases:

- Review of existing data from previous investigations (**Section 3.1**),
- Implementation of the sampling and analysis plan (**Section 3.2**), and
- Data evaluation (**Section 3.3**).

The SAP was not designed to gather data on groundwater quality in a manner that could be evaluated using parametric statistical tests. Rather, the sampling plan was developed to focus on wells where low-level detections of organic constituents had been previously reported or the presence of combustible gas had been observed. Therefore, the sampling locations were not based on a statistical design.

Existing documents and records were used to refine a list of potential sources of organic constituents in wells within the PAPA. In addition, further sampling and laboratory analysis were conducted as outlined in the SAP (AMEC Geomatrix, 2010) to fill specific data gaps regarding the chemical composition of organic constituents detected in wells within the PAPA. Analytical results obtained from implementing the SAP were then evaluated in comparison with analytical results from historical monitoring conducted by the SCCD and with more recent results from the HDG investigation (AMEC, 2012). Finally, the overall results from this study were then used in **Section 9.0** to develop a discussion of the likely sources of low-levels of organic constituents detected in industrial water supply wells and study wells in the PAPA.

3.1 POTENTIAL POINT SOURCES OF LOW-LEVEL ORGANIC CONSTITUENTS

AMEC performed a review of available existing information to identify and characterize potential point sources of organic constituents in the PAPA. BDE developed a comprehensive matrix of potential point sources from which a release could result in impacts to groundwater from natural gas E&P activities in the PAPA (AMEC Geomatrix, 2008, Table 1). AMEC further identified additional potential point sources in and near the PAPA that are not directly related to E&P activities (AMEC Geomatrix, 2010).

As outlined in the POS (AMEC Geomatrix, 2009a), this research included the following activities:

- Reviewing available aerial photographs and Operator records regarding activities at gas well pads;
- Reviewing BLM files with respect to activities at historical gas well pads;

- Interviewing Operator representatives, water well drilling contractors, and water pump installation contractors with regard to standard practices related to construction, use, and operation of water supply wells in the PAPA; and
- Observing installation (e.g., drilling techniques) and sampling (e.g., pump installation) of industrial water supply wells.

In addition, AMEC reviewed information in public databases for reported releases in and near the PAPA, such as, but not limited to:

- EPA Resource Conservation and Recovery Act (RCRA) 2020 Corrective Action Universe;
- EPA Envirofacts database;
- Wyoming DEQ Storage Tank Program database;
- Wyoming DEQ and Wyoming Oil and Gas Conservation Commission (WOGCC) spill databases;
- Wyoming DEQ solid and hazardous waste site listings; and
- BLM's "Undesirable Events" database.

AMEC also reviewed available information regarding landfills and permitted oil-disposal facilities within or near the PAPA.

Complete results of the research into potential point sources are presented in **Section 4.0** of this report.

3.2 Implementation of Sampling and Analysis Plan

A field sampling and analysis program was conducted to fill gaps in data needed to determine the likely source(s) of organic constituents detected in samples collected from industrial water supply wells. Samples of both groundwater and potential source materials were collected, and the samples were analyzed for various organic and inorganic constituents as detailed in the SAP (AMEC Geomatrix, 2010). The purpose of the sampling and analysis program was to compare the overall chemical composition of the organic and inorganic constituents, or chemical signature, of potential source materials to the chemical signature of gas and groundwater samples collected from water wells. A material could be considered a potential source if the chemical signature of the groundwater sample closely matches the chemical signature of a potential source material. If the chemical signature of groundwater differs markedly from the chemical signature of the material, then that material would be considered an unlikely source.

Prior to this study, potential source materials related to historic and current E&P activities in the PAPA had not been systematically sampled for purposes other than waste characterization. Further

investigation into impacts in individual industrial water supply wells had not been fully assessed using advanced laboratory methods to identify the potential source(s) of detected organic constituents. Gas discovered in the casings of industrial water supply wells had not been fully characterized with respect to gas composition and origin.

Based on these remaining data gaps, the sampling and analysis plan (AMEC Geomatrix, 2010) specified collection and analysis of the following samples:

- Potential source material samples; and
- Groundwater and gas samples from selected industrial water supply wells and study wells.

Table 1 and **Table 2** present a summary of the sample collection and analysis program as specified in the SAP. Samples were submitted to the laboratory for the following categories of analyses:

- General water quality parameters, total metals, volatile and semivolatile organic fractions, VOCs, and SVOCs to develop a broad characterization of the chemical signature for both potential source materials and for groundwater samples collected from wells where detections of organic constituents had been reported;
- Stable isotope ratios to compare the isotopic signatures of groundwater samples versus potential source material samples to assess the likelihood that they share a common source (**Section 3.3.5**);
- Hydrocarbon gas composition to compare the "wetness" of gas and provide an indication of the degree of alteration of gas in groundwater and gas samples (**Section 3.3.6**); and
- Thermal maturity analyses to evaluate whether the organic material present in the carbonaceous shale of the Wasatch Formation has been exposed to conditions needed to generate natural gas in situ (**Section 3.2.4.4**).

Additional details regarding site name, sample date, sample ID, and the location where each sample was collected are provided in **Tables B-1**, **B-2,** and **B-3** of **Appendix B**.

This section presents a brief summary of the data collection activities and procedures employed during the sampling and analysis program. Complete details on the sampling and analysis program are presented in the SAP (AMEC Geomatrix, 2010). Results of the sampling and analysis program, as well as additional analytical data from the companion HDG investigation, are presented in **Sections 5.0** through **7.0** of this report.

3.2.1 Potential Source Material Sampling

A total of 34 samples of potential source materials were collected and analyzed from September 2010 through March 2011 as listed in **Chart 3-1**.

Chart 3-1 Numbers of Source Material Samples

Source Sampled	Number of Samples
Drill Mud	3
Natural Gas Condensate	1
Produced Water	6
Flowback Fluid	4
Pump Installation Materials (e.g., pipe dope)	17
Light Nonaqueous-Phase Liquid (LNAPL)	1
Carbonaceous Shale	2

Media that were considered potential sources included materials used in support of E&P activities, materials generated by the production of natural gas in the PAPA, and free-phase substances that were encountered in water wells (i.e., light nonaqueous-phase liquid [LNAPL]). The drill mud, natural gas condensate, produced water, LNAPL, pump installation materials, and flowback fluid samples collected are representative of materials currently used or generated during E&P operations and considered representative for the purposes of general source identification. Materials potentially used or generated in past E&P operations were not sampled. Carbonaceous shale is considered a potential natural (non-point) source. The potential source material samples were analyzed for the list of parameters and test methods presented in **Table 2**. The locations where potential source material samples were collected are shown on **Figure 3-1**.

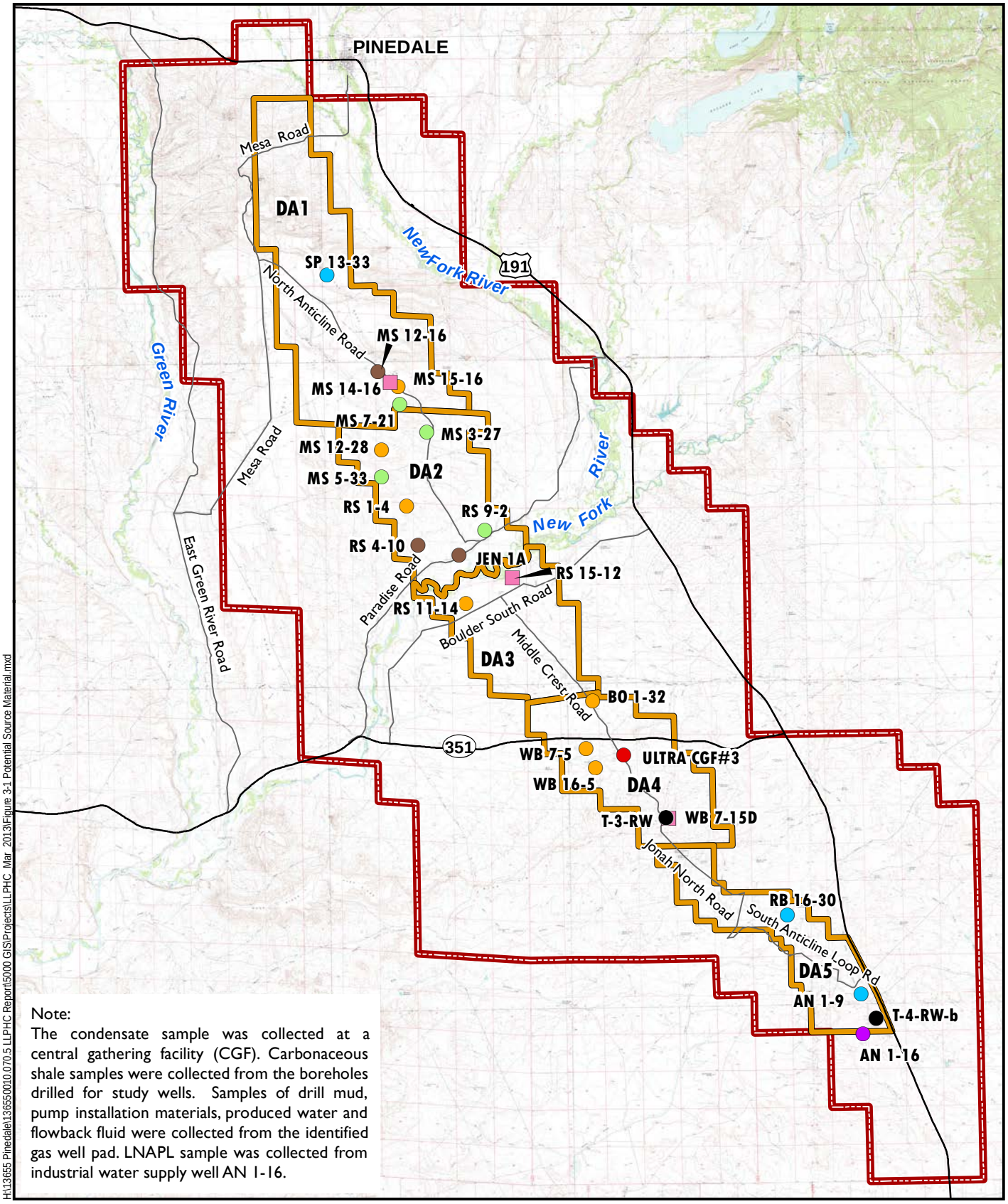
Additional details regarding site name, sample date, sample ID, and the location where each potential source material sample was collected are provided in **Table B-1** of **Appendix B**.

3.2.1.1 *Drill Mud*

Three samples of oil-based drilling mud were collected with Operator assistance from the active system of a drill rig during the drilling of a natural gas production well. One sample was collected from each Operator at the three natural gas well pads shown on **Figure 3-1.**

3.2.1.2 *Natural Gas Condensate*

One sample of natural gas condensate (light oil) was collected from an aboveground storage tank at Ultra's Central Gathering Facility #3 (Ultra CGF #3), located along the Jonah North Road south of Highway 351 (**Figure 3-1**).



Note:
The condensate sample was collected at a central gathering facility (CGF). Carbonaceous shale samples were collected from the boreholes drilled for study wells. Samples of drill mud, pump installation materials, produced water and flowback fluid were collected from the identified gas well pad. LNAPL sample was collected from industrial water supply well AN 1-16.

H:\13655 Pinedale\136550010.070.5 LLPHC Report\5000 GIS\Projects\LLPHC Mar 2013\Figure 3-1 Potential Source Material.mxd

N

0 Miles 4

amec

DA1 Development Area (DA)

Pinedale Anticline Project Area

Carbonaceous Shale

Flowback Fluid

Pump Installation Materials

Drill Mud

Condensate

Produced Water

LNAPL

Produced Water & Pump Installation Materials

Potential Source Material Sample Locations
Low-Level Petroleum Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 3-1

3.2.1.3 *Produced Water*

One sample of produced water was collected from each of the following six E&P areas in the PAPA: Stewart Point (SP), Mesa (MS), Riverside (RS), Rainbow (RB), Warbonnet (WB), and Antelope (AN) (**Table 1; Figure 3-1**). Samples of produced water were collected immediately downstream from the oil-water separator for each targeted natural gas well at the pad or from the discharge pipe exiting the separator and entering the liquid gathering system, as identified in **Table B-1** of **Appendix B**. An attempt was made to collect a well-separated sample (i.e., to minimize as much as possible the amount of free-phase material intermingled in the water sample), although samples likely contained some condensate.

3.2.1.4 *Flowback Fluid*

Flowback fluid consists of fluid that flows back from natural gas production wells at the conclusion of well completion activities, or hydraulic fracturing. Flowback fluid represents a mixture of hydraulic fracturing fluid and fluids from the gas reservoir that are released upon "flowing back" the natural gas production well after hydraulic fracturing operations are completed.

Four samples of flowback fluid were collected, at least one from each Operator, to represent the varying hydraulic fracturing processes used in the PAPA. The flowback fluid sampling locations are shown on **Figure 3-1.** Three samples were collected relatively early (less than 15 hours after flowback began) in the process of flowing back a natural gas well. One sample was taken later in the flowback process (36 hours). The percentage of hydraulic fracturing fluid in flowback fluid decreases and the percentage of formation fluid (e.g., condensate and produced water) increases as the flowback process progresses at the natural gas production well.

Details regarding sample collection with respect to sample identification, sample collection date, timing of sample collection with respect to start of flowback, and types of hydraulic fracturing fluids used at the wells are provided in **Table B-1** of **Appendix B**. A photograph of flowback fluid sample collection is provided in **Photo C-16** in **Appendix C**.

3.2.1.5 *Pump Installation Materials*

Seventeen samples of pipe- and/or pump-related substances (**Table 1**) were collected from September through November 2010 during the removal of pumps and associated piping in industrial water supply wells at locations shown on **Figure 3-1** (**Photos C-1** and **C-2, Appendix C**). The pumps were being removed by Operator-approved pump installation contractors in anticipation of groundwater sampling (**Section 3.2.3**). Samples consisted primarily of pipe dope, which is a general term used to describe anti-seize compounds used by water well contractors on threaded pipe joints during the installation of well equipment to facilitate breaking the joint at a later time. Pipe dope samples were collected from the threads of drop pipe or from threads at the point of connection between the drop pipe and pump housing (see **Photo C-3** in **Appendix C**).

Two of the samples designated "black film" (BO 1-32-2 and RS 11-14-Pump) consisted of a black substance on the outside of the drop pipe (**Photo C-4**, **Appendix C**). One sample (PD Baseline) was collected directly from a tube of "environmentally safe" pipe dope (Best-o-Life), which has been recommended for use by Operators in the PAPA. One sample (MS 14-16-2) consisted of Teflon tape used on some pipe threads. Descriptions of the sample substance and sample collection locations are provided in **Table B-1** of **Appendix B**.

3.2.1.6 *Light Nonaqueous-Phase Liquid*

Industrial water supply wells and study wells were checked for the presence of LNAPL (free-phase substance) using a disposable bailer (i.e., bailer check) prior to collection of groundwater samples (see **Section 3.2.3**). The disposable bailer was deployed to the top of the water column in the well and then retrieved. The outside and inside of the retrieved bailer were checked for the presence of LNAPL. LNAPL was observed in only one well, AN 1-16, sampled for this study (**Figure 3-1**). LNAPL or product samples (AN 1-16 PHC) were collected from AN 1-16 on two different dates, because the laboratory holding time for volatile organics analyses was exceeded prior to analysis for the first sample collected (**Table B-1** of **Appendix B**).

3.2.1.7 *Carbonaceous Shale*

Two samples of carbonaceous shale were collected from drill cuttings while drilling boreholes for the installation of study wells for the companion HDG investigation (AMEC, 2012). The shale samples were collected at the depth in the boring where combustible gas was first encountered. One sample was collected from a depth of 445 to 455 feet in study well borehole T-3-SW, and one sample was collected from a depth of 434 to 455 feet at study well T-4-RW-b (**Figure 3-1**). The samples were submitted to a laboratory to assess the thermal maturity of the carbonaceous shale (**Table 2**).

The purpose of the thermal maturity analysis is to evaluate whether the organic material present in the carbonaceous shale of the Wasatch Formation has been exposed to conditions conducive to generation of natural gas in situ.

3.2.2 Gas Sampling

Three types of gas samples were collected for this study:

- Samples of dissolved gas in groundwater (i.e., dissolved gas samples),
- Samples of combustible gas that accumulates in capped water well casings (i.e., casing gas samples), and
- Samples of natural gas from natural gas production wells (i.e., natural gas samples or produced gas samples).

The purpose of collecting these gas samples was to characterize, as well as contrast, the composition and isotopic ratios of dissolved gas in groundwater and gas in water well casings to the composition and isotopic ratios of natural gas produced from gas production wells in the PAPA. Gas samples with similar composition and isotopic ratios may potentially originate from the same source, whereas if gas composition varies greatly between different sample types, then it is less likely that these gases share a common source.

The collection of casing gas and natural gas samples is described below. Further details about casing gas and natural gas sample collection are included in **Table B-2** of **Appendix B**. The collection of groundwater samples for analysis of dissolved gas in groundwater is described in **Section 3.2.3**.

3.2.2.1 *Casing Gas Samples*

Samples of casing gas were collected from the well casings of the following 10 water wells from October to December 2010 (**Table 1** and **Figure 3-2**):

- Seven industrial water supply wells where elevated levels of combustible gas had previously been detected (AN 1-16, AN 11-10D, Highway [HWY] 7, WB 7-4, WB 7-5, BO 12A-33, and RS 11-14) ; and
- Three study wells (T-4-RW-a, T-4-RWb, and T-3-SW) where combustible gas was present in the well casing prior to groundwater sampling.

Additional casing gas samples were collected from T-3-SW in February 2011, and from BO 12A-33 in February 2012, as a follow-up to the results obtained from sampling for the SAP implementation in 2010 and 2011 (**Table 1**). Collection of a follow-up sample of casing gas was also planned at WB 7-4 in 2012; however, an insufficient quantity of gas had accumulated in the well casing to allow for sampling. Gas sample collection was performed in accordance with the SAP (AMEC Geomatrix, 2010), unless otherwise indicated below.

Only water wells located south of the New Fork River had sufficient amounts of combustible gas when capped for the collection of casing gas samples (**Figure 3-2**). Industrial water supply well MS 14-16, which is located north of the New Fork River, had been previously identified by the SCCD as a well with combustible gas (**Chart 2-2; Section 2.5.4**), and this well was included in the SAP for gas sampling. However, combustible gases were not detected in the capped well casing after repeated testing using a combustible gas indicator (CGI) (see example of testing capped well casing with CGI, **Photo C-7, Appendix C**). Thus, a casing gas sample was not collected from this well, and this industrial water supply well is no longer considered a well with combustible gas for the purposes of this report.

Casing gas samples were collected from the top of the capped well casings and directly analyzed for gas composition using mobile gas chromatography, as indicated in **Table 2 (Photo C-13**,

Appendix C). Samples for isotope analysis were collected in a Cali-5-Bond® gas bag after the conclusion of the on-site gas composition analysis (**Photo C-14**, **Appendix C**). The isotopic analyses were performed by an off-site laboratory. Although the SAP specified sampling only after measurable air (gas) flow was recorded at the capped well, air flow movement was not measureable in some wells, and the decision was made in the field to proceed with gas sampling (**Table B-2** of **Appendix B**).

3.2.2.2 *Natural Gas Samples*

Samples of natural gas were collected from six natural gas production wells, which were either located on the same gas well pads where casing gas samples were collected, or on a nearby drill pad in the case of the casing gas samples collected in the Antelope area (**Table 1**). Thus, because casing gas samples could not be collected from wells north of the New Fork River, all samples of natural gas were collected from natural gas production wells located south of the New Fork River (**Figure 3-2**). Samples for gas composition analysis were collected directly from the natural gas wellhead and analyzed using mobile gas chromatography (**Photo C-15**, **Appendix C**). Samples for isotopic analysis by an off-site laboratory were collected in a pressurized, stainless steel cylinder after completion of the mobile gas analysis.

Because of access issues at the wellhead for natural gas well BO 12A-33, the natural gas samples for both gas composition and isotopic composition of methane were collected from the meter run at this well pad. Because of safety considerations with the use of pressurized cylinders in sampling the natural gas production wells at the AN 1-9 and WB 7-5 gas well pads, the gas samples for isotopic analysis were collected from the meter run at these pads.

3.2.3 Groundwater Sampling

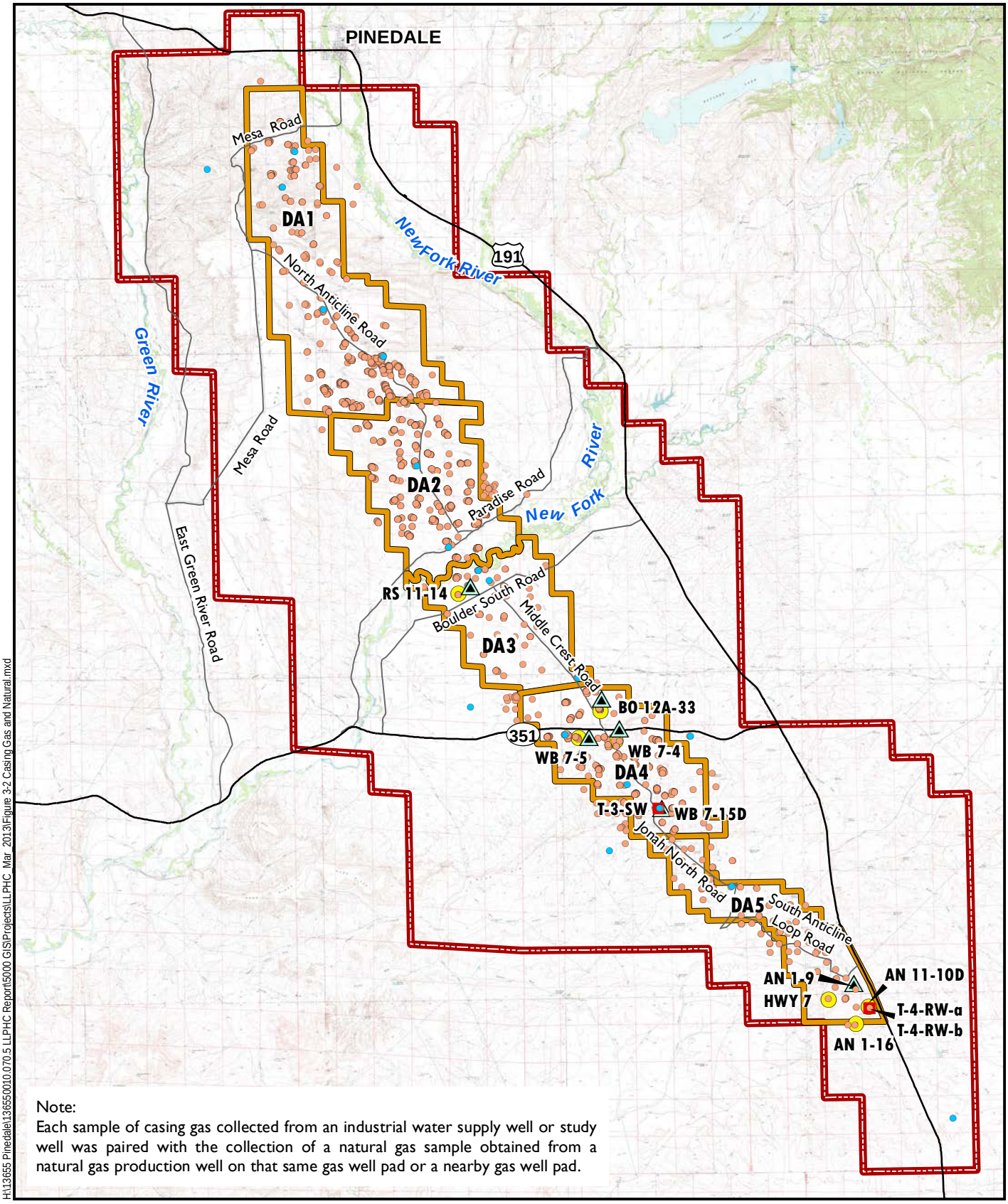
The SAP designated a total of 37 proposed wells for sampling. Wells proposed for sampling consisted of two types of wells:

- Industrial water supply wells (27 proposed wells), and
- Study wells (10 proposed wells).

The industrial water supply wells proposed for sampling in the SAP were selected based on one of the following criteria:

- Wells with previous detections of organic constituents in water samples during annual monitoring by SCCD, and
- Wells with documented presence of combustible gas in well casings.

One or both of these criteria was met for 21 of the 27 industrial water supply wells proposed for sampling. The remaining six wells were selected as control wells with no previous reported detections of organic constituents and no reports of combustible gas.



Note:
Each sample of casing gas collected from an industrial water supply well or study well was paired with the collection of a natural gas sample obtained from a natural gas production well on that same gas well pad or a nearby gas well pad.

H:\13655 Pinedale\136550010.070.5 LLPHC Report\5000 GIS\Projects\LLPHC_Mar_2013\Figure 3-2 Casing Gas and Natural.mxd

N

0 Miles 4

amec

DA1 Development Area (DA)

Pinedale Anticline Project Area

Natural Gas Well

Casing Gas in Water Supply Well

Casing Gas in Study Well

Post-1984 Natural Gas Production Wells (Through March 17, 2012)

Pre-1984 Natural Gas Production Wells

Casing Gas and Natural Gas Sample Locations
Low-Level Petroleum Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 3-2

The 10 study wells included in the SAP were a subset of the 30 wells that had been previously installed as part of the companion HDG investigation (see AMEC, 2012), pursuant to the 2008 ROD (BLM, 2008a). These 10 study wells were selected in part to evaluate the influence on groundwater quality of typical practices associated with installation of industrial water supply wells (drilling, construction, and use) and well pumps.

Samples from the 10 study wells included in the SAP were to be tested for a more comprehensive set of analytes than had been tested for during the HDG investigation (**Section 3.2.4**). The 10 study wells included in the SAP will be referred to in this report as *SAP study wells*. The remaining study wells installed for the HDG investigation but not designated for sampling as part of the SAP will be referred to as *HDG study wells*. When differentiating between the two groups of wells is not meaningful, the SAP and HDG study wells will be referred to collectively as *study wells*. The locations of the SAP study wells sampled for this study and the remaining HDG study wells are illustrated on **Figure 3-3**. Eight of the SAP study wells were located on four natural gas well pads (**Figure 3-3**).

The wells designated for sampling in the SAP thus fall into four general categories, based on the rationale for their inclusion in the SAP (see **Table 1**):

- *PHC wells* comprise industrial water supply wells where analyses for TPH fractions had historically produced detections during annual monitoring by SCCD.
- *LEL wells* comprise industrial water supply wells that have exhibited the presence of combustible gas when screened for lower explosive limit (LEL) using a CGI during annual monitoring by SCCD.
- *Control wells* are wells where no detections of organic constituents had previously been reported by SCCD during the period of record and no combustible gases had been observed.
- *SAP study wells* comprise selected wells installed as part of the HDG investigation.

Samples collected as part implementing the SAP were analyzed for the parameter groups indicated in **Table 1**. The samples were analyzed for selected analytes, which are further described in **Section 3.2.4**. Further details about groundwater sample collection and results of field parameter tests are included in **Table B-3** of **Appendix B**.

3.2.3.1 *Sampling for SAP Implementation in 2010 and 2011*

Groundwater samples were successfully collected from 25 industrial water supply wells from October through December 2010 and from nine SAP study wells in June 2011 as part of the implementation of the SAP (**Photo C-5** and **Photo C-6**, **Appendix C**). Follow-up sampling on selected wells was conducted in February 2012.

The numbers of wells proposed and sampled for the SAP investigation are summarized in **Chart 3-2** for each of the four categories of wells sampled for this study (see **Table 1**).

Chart 3-2 Numbers of Wells Proposed and Sampled for This Study.

Well Category	Number of Wells Sampled for SAP (sampled / proposed)
PHC	12 / 13
LEL	7 / 8
Control	6 / 6
SAP Study	9 / 10

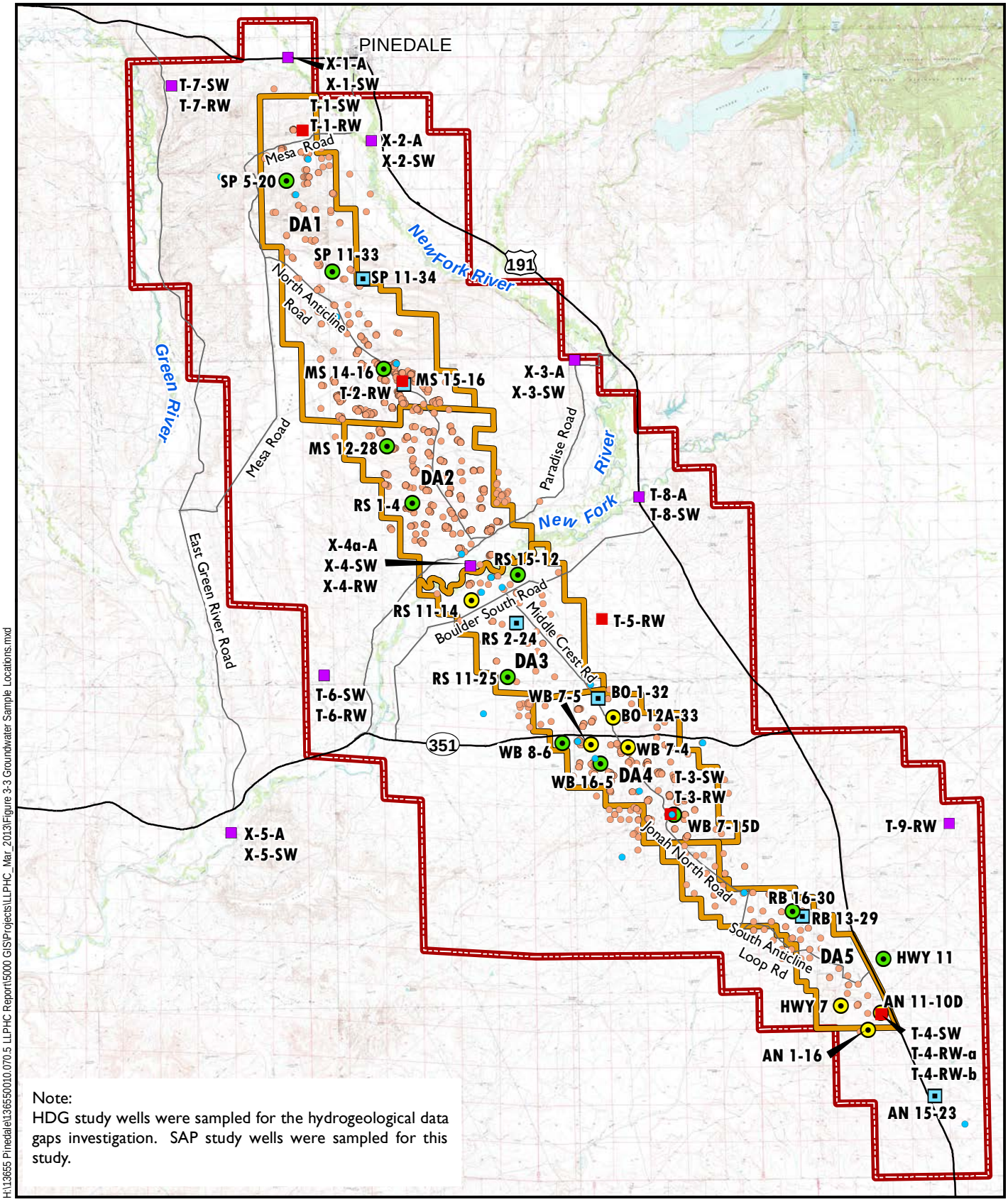
Of the 37 wells proposed for sampling in the SAP, two PHC wells, industrial water supply wells Petrogulf (PG) 36-9 and AN 15-4, were not sampled as specified in the SAP. Access was not granted to collect a groundwater sample from PG 36-9, and AN 15-4 was plugged and abandoned prior to the sampling event. One SAP study well, T-2-SW, could not be sampled as planned because it was dry. As noted in **Section 3.2.2.1**, one industrial water supply well that was designated an LEL well in the SAP, MS 14-16, is now considered a PHC well due to the absence of combustible gas in the well casing during sampling for this study.

All sampled wells are completed in the Wasatch Formation to depths ranging from 190 to 1,020 feet below ground surface (see **Table B-3** in **Appendix B**). Approximately 85 percent of the wells are more than 400 feet deep. Of the 34 wells sampled based on implementing the SAP, 24 are located south of the New Fork River, whereas 10 wells are located north of the New Fork River (**Figure 3-3**). A list of groundwater samples collected and the associated parameter groups analyzed are provided in **Table 1**.

3.2.3.2 *Follow-Up Sampling in 2012*

As a follow-up to the sampling completed in 2010 and 2011, groundwater samples were collected in February 2012 from the following locations (**Table 1**):

- Eight industrial water supply wells (BO 12A-33, WB 7-4, WB 7-5, MS 12-28, MS 14-16, RS 1-4, SP 5-20, and WB 8-6); and
- Two SAP study wells (T-4-RW-a and T-4-RW-b).



Note:
HDG study wells were sampled for the hydrogeological data gaps investigation. SAP study wells were sampled for this study.

H:\13655 Pinedale\136550010.070.5 LLPHC Report\5000 GIS\Projects\LLPHC_Mar_2013\Figure 3-3 Groundwater Sample Locations.mxd

N

0 Miles 4

amec

DA1 Development Area (DA)

Pinedale Anticline Project Area

Pre-1984 Natural Gas Production Wells

Post-1984 Natural Gas Production Wells (Through March 17, 2012)

T-9-RW HDG Study Well

T-5-RW SAP Study Well

AN 15-23 Control Well

WB 16-5 PHC Well

HWY 7 LEL Well

Groundwater Sample Locations
Low-Level Petroleum Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 3-3

These follow-up samples were collected for analyses to quantify concentrations of selected tentatively identified compounds that were reported by the laboratory for groundwater samples collected from those wells in 2010-2011 during the SAP implementation. Dissolved gas samples were also collected from WB 7-4 and BO 12A-33. Follow-up samples were also collected from WB 8-6 and MS 14-16 to assess if quantified detections of inorganic and organic constituents, respectively, would be duplicated. Groundwater sample collection was performed in accordance with methods specified in the SAP, which are summarized in **Section 3.2.3.3**. The TICs selected for quantification at each well, and the rationale for the selected analytes, are provided in **Section 3.2.4.6**.

3.2.3.3 *Groundwater Sample Collection Methods*

Groundwater sampling was performed following methods in accordance with the SAP, which are described briefly below. Detailed descriptions of all groundwater sampling procedures are provided in the SAP (AMEC Geomatrix, 2010), which includes standard operating procedures (SOPs) for all data collection activities, manuals for the sampling device employed, and standard field forms.

A variety of groundwater sampling techniques were considered for this study. Evaluation of sampling methods was based on multiple factors, including well types, well depths and diameters, depths to groundwater, depths to well screens/perforations, the rural setting of the study area, aquifer types, sample volume requirements, sampling equipment decontamination requirements, and distances between sampling locations. A comparative evaluation of several possible well sampling methods for this study was presented to agencies and Operators during development of the SAP in 2010. As a result of the evaluation and discussions, HydraSleeve™ sampling devices manufactured by GeoInsight were specified in the SAP, as accepted by BLM in consultation with Wyoming DEQ and U.S. EPA, to obtain groundwater samples for the study. A HydraSleeve™ is a no-purge (passive), single-use, grab sampling device that is used to collect a representative sample from a water well. The sampling device allows the collection of a whole water sample from a user-defined interval with no drawdown and minimal agitation.

The premise behind using the single-use, no-purge sampling devices is that water in the well adjacent to the well screen/perforations and water in the formation is in dynamic equilibrium. As such, samples collected by HydraSleeves™ represent formation-quality water. GeoInsight reports in their SOP that HydraSleeve™ samples generally produce more conservative analytical sampling results than well-volume purging and low-flow purging sampling techniques. Because the groundwater sampling method for this study was consistent across all sampled wells, results should not show bias that could be introduced by employing different sampling techniques at different sampling locations.

All sampling methods and procedures were performed in general accordance with the manufacturer's SOP (Appendix C of the SAP; AMEC Geomatrix, 2010). After installing

HydraSleeves™ in water wells, the water column was allowed to re-stabilize for 12 to 24 hours prior to sample collection for most groundwater samples. Given that most wells had a casing diameter of 6 inches and the HydraSleeve™ displaces very little water (<100 milliliters), it is likely that only a slight disturbance occurred in the water column at the time of HydraSleeve™ installation.

HydraSleeves™ are manufactured from medical-grade polyethylene, which allows diffusion across the polyethylene membrane given adequate time. According to the HydraSleeve™ developer (Kent Cordry, personal communication, 2012), any diffusion of constituents in the water column into the HydraSleeve™ and sorption onto the inside of the HydraSleeve™ would be minimal during the deployment period of up to 24 hours used for this study. The time elapsed between filling the HydraSleeve™ and emptying the HydraSleeve™ into sampling containers was between 5 and 10 minutes. According to Mr. Cordry (personal communication, 2012), this is insufficient time for any constituent to adsorb or desorb from the HydraSleeve™.

Before the sampling devices could be deployed in the industrial water supply wells, pumps (if present) were removed from the wells by the Operators using their respective pump installation contractors.

A generalized description of key steps and notable events during groundwater sampling is presented below.

- Field personnel surveyed the atmosphere in and around the wellhead for the presence of combustible gas with a CGI upon arriving at the water well for groundwater sample collection (**Photo C-7**, **Appendix C**). If the readings were greater than 20 percent of the LEL, field personnel inerted the well using nitrogen gas in accordance with the protocol described in the SAP (AMEC Geomatrix, 2010) before proceeding with sample collection activities. The following wells were inerted with nitrogen gas during the groundwater sampling event: AN 1-16, BO 12A-33, RS 11-14, T-3-SW, T-3-RW, and T-4-RWa.
- The water level depth was measured in the well using an electronic water level indicator (e-tape) or sonic water level meter.
- A bailer was lowered to the top of the water column and retrieved to evaluate the presence of LNAPL in the well (bailer check). The presence of LNAPL (free-phase product) was observed in one industrial water supply well, AN 1-16, from which a sample was collected as described in **Section 3.2.1.6**. A bailer check at two other industrial water supply wells, RS 11-25 and RS 15-12, returned water samples with a PHC-type odor; the presence of LNAPL was not observed. Nevertheless, samples of water were collected at the top of the water column in each well (RS 11-25 PHC and RS 15-12 PHC; **Table 1**) and submitted for laboratory analysis to assess any differences in the type and/or magnitude of organic constituents at the top of the water column in the well compared to the deeper screened or perforated interval of the well.

- A series of HydraSleeve™ sampling devices were deployed to the middle of the screened or perforated interval of each well for groundwater sample collection (see **Photos C-8** through **C-11**, **Appendix C**). The HydraSleeves™ used for the groundwater sampling events typically held 1.6 to 2.5 liters of water each. Thus, a series of sampling devices were deployed in each well due to sample volume requirements. The sampling devices were deployed at the mid-point of the perforated or screened interval of most wells. The depth of sample collection in each well is provided in **Table B-3** of **Appendix B.** The perforated intervals were unknown for industrial water supply wells at pad locations AN 1-16 and RB 16-30. The sampling devices at AN 1-16 were deployed to a depth of 800 feet, which was 40 feet above the bottom of the well based on information provided by the Operator. For RB 16-30, the sampling devices were deployed to the same depth (545 feet) where previous samples had been collected by the SCCD.
- The sampling devices were retrieved from the well approximately one day after deployment. The HydraSleeve™ contains a self-sealing check value, which excludes water from the part of the water column not targeted for sample collection. Once the sampling device is full, the one-way value collapses, preventing the mixing of fluids during retrieval of the device. The transfer of a groundwater sample from a HydraSleeve™ sampling device into a sampling container is shown in **Photo C-12** of **Appendix C**.

The assembly, deployment, retrieval, and discharge of the sampling devices followed procedures described in the SAP (AMEC Geomatrix, 2010). Procedures used for decontamination, sample handling and shipping, and quality assurance/quality control are described in the SAP (AMEC Geomatrix, 2010). Sample identifiers for quality assurance/quality control samples are listed in **Table B-4** of **Appendix B.**

3.2.4 Sample Analysis

This section describes the analyses performed on samples collected during implementation of the SAP. Samples of potential source materials, casing gas, natural gas, dissolved gas, and groundwater were analyzed for the list of parameter groups shown in **Table 1**. **Table 2** specifies the analytical methods used to analyze the samples. Upon receipt of samples at off-site laboratories, the laboratories assigned laboratory-specific sample identification codes (IDs) for each sample submitted to the laboratory. **Table B-4** of **Appendix B** presents a master table matching the sample IDs assigned in the field at the time of sample collection to the laboratory identification numbers assigned by the laboratories upon receipt of samples. As noted in **Section 3.2.2**, casing gas and natural gas samples were analyzed immediately in the field for hydrocarbon gas composition by a mobile laboratory; thus, no separate laboratory identification numbers were assigned to these samples.

Additional details on sample analyses and analytical methods are presented in the following sections.

3.2.4.1 *Analysis of Inorganics, Metals, Volatile and Semivolatile Organic Fractions, VOCs, and SVOCs*

Analyses of groundwater and potential source material samples for inorganic constituents, total metals, volatile and semivolatile fractions, VOCs, and SVOCs were performed by Energy Laboratories in Billings, Montana, using methods shown in **Table 2**. Methods of analysis included standardized EPA methods, including EPA methods approved under the Safe Drinking Water Act and methods from EPA's SW 846: *Test Methods for Evaluation of Solid Waste, Physical / Chemical Methods*, as well as methods described in the most recent *Standard Methods for the Analysis of Water and Wastewater*. Laboratory reports for these analyses are provided in **Appendix D**. Laboratory reports include quantified results for the analyses performed, units reported by the laboratory for each analysis, a listing of compounds that were tentatively identified during VOC and SVOC analysis, and associated gas chromatography and mass spectrometry chromatograms.

Samples were analyzed for a wide range of organic constituents using the methods shown in **Table 2**.

Samples were analyzed for volatile and semivolatile organic fractions using EPA Method 8015. The purgeable volatile organic fraction was reported as both TPgH and TPH-GRO. TPgH concentrations comprise the total response observed during the GC analysis. In this study, TPH-GRO was defined by the laboratory as all compounds that elute from the chromatograph between 2-methylpentane and 1,2,4-trimethylbenzene. The laboratory procedures for TPgH analyses are not designed for quantitation of the lighter hydrocarbon gases, and therefore these lighter gases may be present in a sample even if the laboratory reports TPgH as not detected (**Section 2.1.4**). These lighter hydrocarbon gases were, however, captured and reported as part of the dissolved gas analysis, as discussed in **Section 3.2.4.3**.

The extractable or semivolatile organic fraction analyzed using EPA Method 8015 was reported as both TEH and TPH-DRO. TEH concentrations comprise the total response observed during the GC analysis. TPH-DRO were defined by the laboratory as all compounds eluting between the carbon number range of C_{10} to C_{28}. The responses for these fractions include the response for hydrocarbons that originate from petroleum sources, as well as responses from other organic substances that do not have a petroleum-based origin (**Section 2.1)**.

To assess the extent of the semivolatile organic fraction that could be attributed to a non-hydrocarbon source, SGT was applied to the extract in samples from study wells that contained detectable TEH, and the extract was re-analyzed.

The VOCs and SVOCs analyzed comprise a standard list of individual organic compounds analyzed in accordance with EPA Methods 8260B and 8270C, respectively. The complete list of individual VOCs and SVOCs analyzed are provided in the laboratory reports (**Appendix D**). The VOCs analyzed included BTEX. As part of VOC and SVOC analyses, a number of TICs were reported based

on probable computer matches of the individual mass spectrometry chromatograms against reference standards obtained from a library search. As discussed in **Section 2.1.4**, identification of individual TICs is tentative, and quantitation results are only rough estimates.

3.2.4.2 *Analysis of Stable Isotopes*

Stable isotopic analyses of water, dissolved inorganic carbon (DIC), and methane were performed by Isotech Laboratories (Isotech) of Champaign, Illinois (**Table 2**). Laboratory reports for the stable isotope analyses are provided in **Appendix D.** Isotopic analyses included the following tests:

- Hydrogen isotopes (^{2}H) in groundwater and produced water samples were analyzed by laser cavity ring-down spectroscopy (CRDS).
- Oxygen isotopes (^{18}O) in groundwater and produced water samples were analyzed by CRDS.
- Carbon isotopes of DIC in groundwater and produced water samples were analyzed by dual-inlet isotope ratio mass spectrometry (IRMS).
- Carbon and hydrogen isotopes of methane in samples of dissolved gas, casing gas, and natural gas were determined by mass spectrometry using conventional off-line methods after chromatographic separation, followed by combustion and analysis by dual-inlet IRMS.

Stable isotopic compositions of elements, such as oxygen, hydrogen, and carbon, are normally reported as differences in ratios (δ values) relative to a known standard (Kendall and Caldwell, 1998). Results are used to compare characteristics of a sample against a known standard or against other samples to assess the degree of similarity in different materials.

The oxygen isotope (^{18}O) and hydrogen isotope (^{2}H) values in groundwater and produced water samples are referenced to the Vienna Standard Mean Ocean Water (VSMOW) with a reproducibility of ±2 per mil (or parts per thousand [‰]) and ±0.2‰, respectively. Vacuum distillation was applied to the sample of produced water collected at the MS 14-16 well pad (MS 14-16 PDW) prior to analysis to inhibit interference from organic constituents in the sample.

The carbon isotope (^{13}C) value of DIC in groundwater and produced water samples was referenced to the Vienna PeeDee Belemnite (VPDB) with a reproducibility of roughly ±0.1‰, depending on the level of organic matter in the sample. The carbon isotope (^{13}C) value of methane was reported relative to VPDB with a reproducibility of ±0.3‰. The hydrogen isotope value of methane was reported relative to VSMOW with a reproducibility of ±5‰. The percentage reproducibility of the hydrogen isotope value of methane in gas and groundwater samples was higher than typical due to a problem with the zinc compound used in the analysis of the hydrogen isotope at the laboratory. The greater reproducibility values did not impact the overall evaluation of data. Due to

the low methane concentration in the casing gas sample collected from WB 7-4, isotopes were analyzed by on-line compound-specific analysis using IRMS.

The purpose of the isotopic analyses was to assess sources of methane in samples and to compare the isotopic signature of samples from different media to assess the likelihood that they share a similar source. Further details on interpretation of the isotopic analyses are presented in **Section 3.3.5**.

3.2.4.3 *Analysis of Gas Composition*

The composition of gas in groundwater samples (dissolved gas) was analyzed by Isotech (**Table 2**); laboratory reports for these analyses are provided in **Appendix D**. Hydrocarbon gases are purgeable hydrocarbons, but are not quantified using standard groundwater analytical methods due to methods of sample preparation and analysis. The hydrocarbon composition of dissolved gas was measured by gas chromatography using an internal laboratory method adapted from ASTM Method 1945. Concentrations of hydrocarbons (C_1 through C_{6+}) and fixed gases are reported in mole percent (mol %) with a reproducibility of ±1–2 percent.

The concentration of methane dissolved in groundwater was calculated by Isotech based on results of the compositional analysis and sample-specific parameters, including sample weight, headspace volume, pressure, and temperature. Dissolved concentrations were reported by the laboratory in milligrams per liter and cubic centimeters per liter (cc/L). Calculated dissolved methane concentrations for samples that had significant headspace (i.e., effervescent samples) are considered estimates; these results were qualified as estimated and flagged with a J qualifier for that reason. The relative proportions of gases reported in units of mole percent and milligrams per liter do not correspond exactly, since headspace volumes and sample weights varied between samples, particularly for the effervescent samples.

Most gas samples collected from well casings (i.e., casing gas) and natural gas production wells (i.e., natural gas) were analyzed on site for hydrocarbon gas composition using a mobile laboratory operated by Precision Analysis (Precision) from Riverton, Wyoming. The samples were analyzed in accordance with Gas Processors Association (GPA) Method 2261-00 *Analysis for Natural Gas and Similar Gaseous Mixtures by Gas Chromatography*. Questar Applied Technologies (Questar) of Rock Springs, Wyoming, analyzed the natural gas samples from gas production wells AN 1-9 and WB 7-5 using methods similar to Precision. The list of analytes for the extended gas composition analyses is provided in **Table 2**. Gas analyses performed by Precision and Questar were reported in mole percent, percent by weight, and percent liquid volume. Laboratory sheets for the mobile laboratory analyses are provided in **Appendix D**.

3.2.4.4 *Assessment of Thermal Maturity*

The thermal maturity of two potential source material samples (i.e., carbonaceous shale) was evaluated by vitrinite reflectance testing performed by Intertek Westport Technology Center (Intertek) in Houston, Texas. The analysis provides a crude assessment of whether the rocks were subjected to sufficient temperature and pressure to produce natural gas and/or oil, as described in the laboratory report included in **Appendix D**. Methods to quantify thermal maturity focus on identifying non-reversible, temperature-dependent, chemical or physical processes that have acted on the rock sample.

For the analysis conducted in this study, kerogen was isolated from aliquots of each sample of carbonaceous shale and then prepared into standard vitrinite and transmitted light slides by Intertek. The slides were microscopically examined for kerogen quality and vitrinite reflectance by standard techniques (see **Appendix D**). Based on the data, Intertek made a determination whether the carbonaceous shale strata in the Wasatch Formation were subjected to sufficient temperature and pressure to produce natural gas and/or oil. Additional details regarding the assessment of thermal maturity are provided in Intertek's laboratory report (**Appendix D**). This information yields insight into whether hydrocarbon gas present in the Wasatch Formation was generated in situ.

3.2.4.5 *Analytical Deviations from SAP*

Several deviations from the SAP (AMEC Geomatrix, 2010) occurred for this project with respect to laboratory analysis of groundwater and potential source material samples. Metals analysis was not performed on pipe dope samples due to lack of adequate sample volume for this analysis. A carbon scan analysis (i.e., simulated distillation) was performed on the LNAPL sampled from AN 1-16 (AN 1-16 PHC), and on selected samples of drill mud, condensate, and pipe dope, to better characterize the chemical signature of these samples. Distillation analysis is a well-established technique used to characterize organic compounds with a wide range of boiling points. This method provides additional information about the composition of the sample and also conveys the fractional amounts of different organic constituents in graphical form (Douglas et al., 2007).

3.2.4.6 *Analytes for Follow-Up Sampling*

The follow-up groundwater samples collected in 2012 were analyzed for the individual analytes listed in **Chart 3-3**.

Chart 3-3 Analytes for Follow-up Samples

Well	Analytes*
T-4-RW-a	*adamantane, 2-methyl-1-pentene, 1-heptene*
T-4-RW-b	*adamantane, 2-methyl-1-pentene*
WB 8-6	nitrate + nitrite (as nitrogen), *2-ethylhexanol*
WB 7-5	*hexanal*
BO 12A-33	*2-ethylhexanol*
RS 1-4	*2,4-dimethyl-3-pentanone, 2-ethylhexanoic acid, n-hexadecanoic acid*
MS 12-28	*2-ethylhexanol*
MS 14-16	methyl ethyl ketone, *hexanal, acetone*
SP 5-20	*hexanal, nonanal*

* Compounds that were tentatively identified in samples collected from wells during the SAP implementation are in italics.

Samples from the selected wells were analyzed to quantify concentrations of targeted TICs reported in groundwater samples collected from those wells during the SAP implementation. The targeted TICs were either a non-hydrocarbon compound (e.g., acid, alcohol, aldehyde, or ketone) or a compound with double-bonded carbon atoms (e.g., an alkene). The targeted TICs were either detected in a potential source material sample, or could possibly be associated with a potential source material based on chemical grouping.

In addition, the follow-up sample collected from WB 8-6 was analyzed for nitrate + nitrite (as nitrogen), because the concentration reported in the sample collected during the SAP implementation appeared anomalous. The follow-up sample collected from MS 14-16 was analyzed for methyl ethyl ketone, because this was the only VOC other than BTEX to be detected in groundwater during the SAP implementation. Methods of analysis followed **Table 2**; however, only the analytes of concern were reported by the laboratory.

3.2.5 Quality Assurance and Quality Control

Quality assurance (QA) and quality control (QC) procedures used for this study are specified in the SAP (AMEC Geomatrix, 2010). The QA/QC process included laboratory analysis of field and laboratory duplicate and blank samples, additional specialized analyses to test the accuracy and precision of laboratory analytical procedures, and review and validation of the field and laboratory data. The objectives of the QA/QC analyses and data review were to identify any unreliable or invalid field and laboratory measurements, and to qualify data for interpretive use. Data review procedures generally followed EPA's national functional guidelines (EPA 2008; EPA 2010). An explanation of procedures, control limits, and qualifiers used during data review, as well as detailed results of the data review and validation for this study, are presented in **Appendix E**.

The following paragraphs present a brief summary of results from the data validation relative to precision, accuracy, representativeness, completeness, and comparability (PARCC) of the data obtained during this study.

Precision

Tests of laboratory precision successfully met QC thresholds, except for several instances where the relative percent difference (RPD) for laboratory and field duplicate samples exceeded the project-specific QC control limits (20 and 35 percent, respectively). When the RPD values for laboratory duplicates were outside the control limits, or the absolute difference was less than the practical quantitation limit (PQL) or reporting limit for results less than five times the PQL, associated data were flagged with "L%" or "L," respectively, in the project database and in data tables. When the RPD values for field duplicates were outside the control limits, or the absolute difference was less than the PQL for results less than five times the PQL, associated data were flagged "F%" or "F," respectively, in the project database and in data tables. A "J" qualifier was applied to the data qualified with L, L%, F, or F%, as described above, to indicate the value is considered estimated; however, these data were deemed usable for purposes of this study.

Method-specific reproducibility goals were not met for gas samples collected at low or ambient pressures (i.e., casing gas samples) and analyzed by the mobile laboratories. These results are to be expected due to sampling conditions, and the data were not qualified. Method-specific reproducibility goals were met for pressurized-gas samples (i.e., natural gas samples).

Accuracy

Laboratory accuracy was evaluated by reviewing laboratory control sample (LCS) and matrix spike sample results. All LCS recoveries were within control limits with the exception of recoveries for trip blank samples associated with QC samples, EB Weight (equipment blank sample for Hydrasleeve™ weight), and FB (field blank). No qualification was necessary in the project database or data tables for the QC samples and associated data.

Natural samples associated with laboratory matrix spike results outside of control limits established by the laboratory were flagged "M%" in the database. A "J" qualifier was applied to the data qualified with M% to indicate the value is considered estimated; however, these data were deemed usable for purposes of this study.

A "J" qualifier was applied by the laboratory to dissolved methane concentrations at or greater than the solubility of methane at standard atmospheric pressure (approximately 28 to 32 mg/L), except for the follow-up sample collected from BO 12A-33. Calculation of dissolved methane concentration is affected by the variable headspace and sample volumes in sample containers containing

groundwater with a high dissolved gas content; thus, the laboratory qualifies these concentrations.

Mobile laboratories reported hydrocarbon gas concentrations to the fourth decimal upon request; however, the qualifier "J' was added to the project database and data tables for concentrations detected at or below the fourth decimal point. Hydrocarbon gas composition results qualified with a "J" were not used to calculate gas component ratios.

Representativeness Acceptance for representativeness is based on results of blank samples and review of the sampling design and sample collection techniques. Nitrate + nitrite as nitrogen was detected in two field blank samples at levels less than five times the concentration in the associated natural sample. According to the laboratory, detections of chloroform in trip blank samples associated with the 2010-2011 groundwater data likely resulted from laboratory contamination. Chloroform was detected in a natural sample associated with one of these trip blanks, and the result was qualified with a "B" in the project database. However, this datum was not used in this study, because the detected chloroform concentration was between the method detection limit (MDL) and PQL, or laboratory reporting limit (see **Section 3.3.1.3**).

Completeness The SAP specifies a threshold of 95 percent completeness; this threshold criterion was met. Multiple groundwater sample containers were broken upon arrival at associated laboratories; however, adequate volumes were often present in additional sample containers for the specified analyses.

Comparability Standard procedures identified in the project SAP were followed for field sampling and laboratory analyses. Standard methods, including data review procedures specified in EPA's National Functional Guidelines (EPA, 2008, 2010), were followed by the laboratory, which allows comparison to other datasets obtained by similar methods. Only minor deviations from the procedures specified in the SAP occurred, and these deviations do not affect the overall usability of the data.

Data qualified in this study based on the results of quality assurance/quality control measures are also typically assigned a "J" qualifier to indicate the result is considered an estimate. For example, if the percent recovery for a constituent in a laboratory duplicate sample exceeds acceptable limits, then the result for the associated natural samples would be qualified with "JL%" to reflect the QA/QC issue and to qualify the results as estimated. Analytical results qualified as estimated based on QA/QC criteria are presented in the data tables in this report and used in data analysis.

3.3 DATA EVALUATION

Results from the desktop study, the field and laboratory studies conducted in implementing the SAP, and historical groundwater monitoring were evaluated to develop an overall understanding of the nature, distribution, and sources of organic constituents in wells within the PAPA.

The data evaluation process for this study involved the following key steps:

- Mapping locations of potential point sources relative to water supply wells where organic constituents have been detected;
- Summarizing historic detections of organic constituents in domestic, stock, and industrial water supply wells during annual monitoring by SCCD with respect to the frequency of detections and the concentrations of detected constituents relative to water quality standards;
- Using correlation analyses to assess the relationship between the occurrence of organic constituents in groundwater and the presence of dissolved methane and selected inorganic constituents;
- Evaluating general water quality characteristics of groundwater samples by plotting the relative abundance of cations and anions using Piper and Stiff diagrams;
- Identifying potential analytical indicators of individual source media or groups of source media based on unique chemical signatures, including chromatograms;
- Using analytical results of gas composition and isotopic composition of methane to evaluate the origin of gas in water well casings and groundwater based on standard literature designations;
- Evaluating the presence of dissolved gas, the presence of organic constituents, and general water quality trends with respect to location in the PAPA;
- Identifying potential sources of organic constituents detected in wells sampled for this study based on analytical signatures characteristic of individual sources;
- Performing a literature review to aid in the interpretation of analytical results for gas composition and stable isotope composition, chromatographic profiles, and hydrocarbon gas component ratios; and
- Evaluating the likelihood of different potential point and non-point sources to be the source of organic constituents detected in wells in the PAPA.

Data evaluation activities listed above employed standard techniques commonly used for environmental investigations. This section describes the various water quality data sets used in the evaluation, and presents a summary of the approach and methods for correlation analyses,

chromatogram pattern matching, and evaluation of general water quality, gas composition, and stable isotope data.

3.3.1 Groundwater Quality Data Sets

To evaluate potential point sources of low-level detections, we used groundwater quality data from three data sets:

- **SCCD Data:** Groundwater quality data collected by the SCCD during annual monitoring events from 2004 to 2011, primarily results reported as petroleum hydrocarbons;
- **HDG Data:** Groundwater quality data collected from HDG study wells installed in the PAPA by AMEC during the companion HDG investigation (AMEC, 2012); and
- **SAP Data:** Groundwater quality data collected by AMEC from industrial water supply wells and SAP study wells in the PAPA during implementation of the SAP, as described in **Section 3.2**.

These data sets were employed in varying capacities and are described further below.

3.3.1.1 *SCCD Data*

As summarized in **Section 2.5.2** and **Section 2.5.3**, the SCCD collects groundwater samples from domestic, stock, and industrial water supply wells in the PAPA on behalf of the Operators on an annual basis. The analytical and sampling methods used in the SCCD monitoring program have changed over time, and varying levels of data validation have been performed on the data. Therefore, these annual monitoring data have been used only in a screening capacity. Specifically, these data were used to identify wells to be included for sampling as part of the SAP; to provide context with regard to the frequency, magnitude, and spatial distribution of detections of organic constituents throughout the PAPA; and to draw conclusions regarding detections in the semivolatile fraction for low-level wells.

A formal trend analysis was not performed on the data collected by SCCD at each water well due to the scarcity of data points. However, general conclusions can be drawn from the SCCD data to provide context to the low-level detections of organic constituents.

3.3.1.2 *HDG Data*

Analytical results for organic constituents in samples collected from 18 HDG study wells sampled as part of the companion HDG investigation are presented in this report. Volatile and semivolatile organic fractions were determined using EPA Method 8015, and BTEX were analyzed using EPA Method 8260. Samples from study wells (i.e., both HDG and SAP study wells) that contained detectable TEH were subjected to SGT, and the sample was re-analyzed for the semivolatile organic fraction by Method 8015. SGT was applied to provide an indication of the extent of extractable organic material that could be attributed to a non-hydrocarbon source.

Analytical results for general water quality parameters measured as part of the HDG investigation were reported previously (AMEC, 2012) and will not be repeated here. However, water types for HDG wells were re-assigned based on methods used in this study (see **Section 3.3.2**), and the resulting Stiff diagrams for HDG wells are presented in **Section 8.2**.

The data collected from the HDG and SAP study wells were used specifically to evaluate the influence of naturally occurring organic matter and water supply well and pump installation practices on water quality in the well.

3.3.1.3 *SAP Data*

Implementation of the SAP generated a valid and comprehensive data set. SAP data consist of analytical results from groundwater, potential source material, and gas samples. Samples from the SAP study wells collected for this study were analyzed for a more extensive list of chemical parameters than samples collected as part of the HDG investigation (**Section 3.2.4)**. The results will assist in identification of potential point sources and/or potential source media for low-level detections of organic constituents in water wells in the PAPA.

A high degree of certainty in the individual analytical results is needed when interpreting the chemical signature used to identify potential sources of constituents. A *false positive* analytical result occurs when the laboratory reports a detected analyte, but the analyte is not actually present in the sample, or when the detected analyte is actually present in a sample, but not representative of actual groundwater conditions. False positive results may be caused by procedural issues and conditions encountered during sample collection and handling, or during laboratory analysis (see **Section 4.7**). For example, a false positive may be caused by procedural issues and conditions encountered in the laboratory during sample analysis, such as cross-contamination by laboratory reagents or equipment or an analyte that is mis-identified by the laboratory method. A false positive may also be caused by procedural issues and conditions encountered during sample collection and handling, such as a constituent introduced to a sample by cross-contamination from sampling equipment or from other samples during sample transport. Such false positive analytical results are not representative of actual groundwater conditions.

Sampling and analytical methods and QA/QC measures employed for this study were selected to minimize the potential for false positive results to the extent possible. Nevertheless, the potential for false positive results cannot be eliminated entirely, and the possibility of false positives was considered when interpreting the analytical data generated during this study.

Interpretation of analytical data can be uncertain, particularly when few constituents are detected in a sample at very low concentrations. To minimize uncertain interpretations, the analytical data generated during implementation of the SAP were filtered based on the reported concentration relative to the PQL, which for our study was the laboratory's routine reporting limit, versus the MDL. The PQL or laboratory reporting limit is the lowest concentration of an analyte that can be reliably

measured within specified limits of precision and accuracy during routine laboratory operating conditions. In contrast, the MDL is the minimum concentration of an analyte that can be present within a sample and be detected using the specified analytical method with 99 percent confidence that the true concentration is greater than zero. Analyte concentrations that are below the reporting limit but above the MDL were reported by the laboratory as estimated concentrations and were identified with a "J" flag, or qualifier.

Since only concentrations above the PQL or laboratory reporting limit can be quantified within a specified degree of confidence by the laboratory, only these concentrations were used in data analysis. As such, estimated results based on detected concentrations below the reporting limit were retained in the project database and qualified with a "J"; however, only concentrations above the reporting limit are reported in data tables of this report and used for data analysis or evaluation. This filtering applied only to analytical results qualified as estimated specifically because the result was less than the laboratory reporting limit. Data qualified with a "J" based on QA/QC criteria, as described in **Section 3.2.5,** were retained in data tables and used for data analysis and evaluation.

An evaluation was conducted to assess if this data filtering would affect the interpretations presented in this report. Results of this evaluation showed that considering these estimated results would have no effect on interpreting the data in this study. The background, approach, and findings of this evaluation are presented in a technical memorandum in **Appendix E**. **Table 1** of **Appendix E** presents all of the results that were qualified as estimated (J-flagged) because concentrations were below the analytical laboratory's routine reporting limit.

Because the purpose of this study is to evaluate LLPHC per Subtask 3A of the Interim Plan, the evaluation emphasizes results with organic constituents detected at low concentrations, and not results with concentrations greater than regulatory standards. Water wells with constituent concentrations above regulatory standards are not considered *low-level* and are actively overseen by regulatory agencies. Water wells with these higher concentrations of organic constituents are therefore discussed briefly, primarily because they are useful with respect to potential source identification; however, these results are not the main focus of this report. Most of the data analysis and evaluation focuses on detections of organic constituents at low levels and the potential sources of these low-level detections.

3.3.2 Graphical Analysis of Water Quality

A graphical analysis of water quality was conducted to evaluate whether the presence or magnitude of inorganic constituents in groundwater was indicative of an impact from E&P activities. The ionic composition of water samples was used to classify groundwater, produced water, and flowback fluid into ionic types based on the dominant dissolved cation and anion, expressed in milliequivalents per liter (meq/L). A dissolved ion was considered the dominant

dissolved ion if it represents greater than approximately 80 to 85 percent of the total ionic composition. If no cation or anion was dominant, the water type was classified based on the cations or anions representing greater than approximately 10 to 15 percent of the total ionic composition, in decreasing order of abundance. For example, consider groundwater in which sodium is the dominant cation, no anion is dominant, and chloride and bicarbonate are the most abundant cations with only small amounts of sulfate; this groundwater would be categorized as sodium-chloride-bicarbonate water type.

The relative ionic compositions of water well samples were plotted on Piper and Stiff diagrams to compare water types between samples and by location in the PAPA. Piper and Stiff diagrams are standard methods used to interpret the chemical characteristics of water (Hem, 1985; Helsel and Hirsch, 2002).

Piper diagrams were used to compare water types between groundwater, produced water, and flowback fluid. A Piper diagram is a trilinear diagram in which cation and anion concentrations are plotted as percentages of the respective total ionic concentration in two triangles. The relative percentages of cations and anions in each triangle are projected into a diamond, where two sides represent cations and the other two sides represent anions, providing a visual depiction of water type. Piper diagrams were generated using RockWorks by Rockware.

To generate a Stiff diagram, a polygon is created from three horizontal axes that extend from both sides of a vertical axis. Cation concentrations are plotted on the left side in milliequivalents per liter; anion concentrations are plotted on the right side in milliequivalents per liter. The cation and anion concentrations are connected to form an asymmetrical polygon, where the size of the polygon is an indication of the relative concentration of total dissolved solids in the sample. Stiff diagrams were generated using AquaChem Version 2012.1 by Schlumberger.

3.3.3 Statistical Analysis

Data analyses were conducted to assess relationships among constituents in groundwater samples (i.e., samples collected from industrial water supply wells and SAP study wells) and between groundwater and potential source material samples (i.e., produced water, flowback fluid, drilling mud, pump installation materials, and condensate) collected for this study, which could provide an indication of the potential source or sources of low-level detections of organic constituents in wells.

Exploratory data analysis techniques were used to test for possible associations between low-level detections and other groundwater quality parameters. These techniques included relationship and cluster analyses. These statistical techniques were used in an exploratory fashion in an attempt to identify potential relationships that may exist. No parametric tests of significance are reported because the sampling design specified in the SAP was not random, and the numbers of observations with detected levels of organic constituents were insufficient. Therefore, the results of these analyses are intended for exploratory purposes, and not for rigorous statistical interpretation.

Relationship analyses were completed for the following constituents, which were placed in the following four analytical groups to facilitate statistical analysis:

- Inorganics: alkalinity (total, bicarbonate, carbonate), major cations (calcium, magnesium, potassium, and sodium), chloride, fluoride, sulfate, nitrogen (nitrate+nitrite and ammonia), total phosphorus, and TDS;
- Metals (total): aluminum, barium, boron, copper, iron, manganese, silicon, strontium, and titanium;
- Organics: TPH-GRO, TPH-DRO, benzene, ethylbenzene, m- and p-xylenes, o-xylene, toluene, and total xylenes; and
- Dissolved gases: methane, ethane, propane, n-butane, isobutane, n-pentane, and isopentane.

The analytical groups deviate slightly from the parameter groups listed in **Table 2** in order to facilitate the analysis. Some constituents in the parameter groups listed in **Table 2**, (e.g., bromide in the inorganics parameter group) were not included in the analyte groups because these constituents were not consistently detected in groundwater or potential source material samples. Some parameter groups were not included in the analysis because they were not detected in enough groundwater samples (e.g., SVOCs and isotopes).

Values below the laboratory reporting limit were removed from the plotted datasets to avoid false indications of correlation. Large portions of several datasets were below laboratory reporting limits, or not analyzed (e.g., antimony, barium, xylenes), thereby greatly reducing the number of data pairs and creating an insufficient dataset for calculating coefficients.

Methods for correlation analysis and cluster analysis are described below.

3.3.3.1 *Correlation Analysis*

Simple regression analysis (relating one independent variable and one dependent variable) was completed by creating a dependence matrix of every plausible constituent pair using water sample data (e.g., scatter plot of dissolved methane versus chloride). Analytes were also paired with northing coordinates to address potential geographical trends. As noted previously, the results are intended for exploratory purposes and do not imply conclusively the presence or absence of a relationship.

Scatter plots were reviewed to identify both the direction of a relationship (whether one variable is associated with an increase or a decrease in another variable) and the strength (how much a difference in the dependent variable is associated with a measured difference in the independent variable). Correlations were presented as "observed" if the scatter plot suggested a positive or negative correlation, but no significance testing is reported.

3.3.3.2 *Cluster Analysis*

Cluster analysis is a useful statistical technique that organizes a set of data into groups (clusters) so that the objects in the same cluster are more similar (in some sense or another) to each other than to those in other clusters. While the dependence matrix is a useful exercise for identifying associations between pairs of parameters, it is difficult to use these matrices to analyze multivariate dependencies, for example, methane versus a combination of sulfate, calcium, and sodium. Additionally, the presence of one analyte could be indicative of the presence of another, but the amplitude of the two data points may not coincide because other controls are implicit. Therefore, cluster analysis was used to circumvent the limitations of simple regression analyses, and to observe the data in groups with respect to methane concentration, geographical location, and source sample chemical signature.

A single algorithm is not used for cluster analysis. Instead, the data are processed using an artificial neural network framework. The neural network framework incorporates a series of nonlinear regression algorithms that relate data intervals and other statistical distributions among various parameters (Sarle, 1994). The neural network model employs an iterative process of categorizing data based on criteria emerging from the dataset itself. NeuroXL (Olsoft LLC v.3.1.2) clustering software was used in this study to categorize data. Prior to analysis, data were organized into cross-tabulated tables relating sample well locations to each constituent in each analytical group (i.e., water chemistry parameters, inorganics, organics, and gases). The clustering software we used did not report a function relating multiple independent variables to a single dependent variable. Likewise, the software did not quantify a measure by which the data fit together (coefficient of correlation). However the cluster analysis did provide some logical order to the data so that patterns could be more easily recognized.

After processing, cluster results were reviewed for functional relationships within groundwater data and between groundwater and potential source material data (e.g., inorganic parameters in water wells versus inorganic parameters in production water, flowback fluid, and drilling mud). In some cases, patterns emerging from cluster analyses can be investigated further using multivariate regression analyses. However, the SAP was not designed to provide a sufficient number of samples and comprehensive representation of analyte concentrations to supply enough data points for multivariate regression analysis.

3.3.4 Chromatogram Pattern Matching

Chromatographic profiles generated from gas chromatography, specifically for the GRO and DRO fractions, were reviewed and evaluated using gas chromatogram pattern matching (**Section 2.1.3.4**).

GC chromatograms from groundwater samples were compared to chromatograms from samples of potential source materials and to standard reference chromatograms to help identify possible sources of organic constituents detected in water wells.

Because it is difficult to consistently quantify or even qualify individual organic constituents depending on the nature of the sample matrix, chromatograms generated by mass spectrometry were used to identify individual constituents indicative of potential sources. The presence of compounds that were not included in the calibration list for EPA Method 8260 and Method 8270 were reported. These compounds, referred to as TICs, were identified by comparing their retention times and mass spectra to a database of compounds with similar retention times and mass spectra.

Laboratory personnel assisted with the review and interpretation of chromatograms, and provided standard reference chromatograms of petroleum substances for comparison purposes. Representative chromatograms reviewed for this study are presented in **Appendix F**.

3.3.5 Stable Isotope Geochemistry

Stable isotope compositions of elements, such as oxygen, hydrogen, and carbon, are normally reported as a difference (i.e., δ values) relative to an accepted standard of known composition (Kendall and Caldwell, 1998). The δ values are reported in units of parts per thousand (denoted as ‰ or per mil) and are calculated by:

$$\delta = (R_x / R_s - 1) \times 1000$$

where:

R denotes the ratio of the heavy to the light isotope (e.g., $^{18}O/^{16}O$), and
R_x and R_s are the ratios in the sample and the standard, respectively.

A positive δ value means that the ratio of the heavy to the light isotope (i.e., the isotopic ratio) of the sample is higher than that of the standard; a negative δ value means that the isotopic ratio of the sample is lower than that of the standard. For example, a $\delta^{18}O$ value of +20‰ means that the $^{18}O/^{16}O$ ratio of the sample is 20 parts per thousand or 2 percent higher than the $^{18}O/^{16}O$ ratio of the standard.

The comparison of δ values between two samples herein will be reported as more or less positive or more or less negative. The δ values of each of the standards have been defined as 0‰. Values of $\delta^{2}H$ and $\delta^{18}O$ in this study are reported relative to the Vienna Standard Mean Ocean Water standard. The $\delta^{13}C$ values are reported relative to the Vienna Pee Dee Belemnite standard.

3.3.5.1 *Stable Isotopes of Water and Dissolved Inorganic Carbon*

Stable isotopes of water (i.e., oxygen [^{18}O] and hydrogen [^{2}H]) and the stable carbon (^{13}C) isotope of DIC can be used for tracing groundwater, assessing water-rock interaction, and identifying biogeochemical reactions occurring in hydrogeologic systems. The isotopic composition of groundwater is initially determined by the isotopic composition of recharge water, which can vary based on the source of recharge (e.g., precipitation or surface water bodies). Differences in isotopic composition of groundwater can result from differing recharge sources and climatic conditions occurring at the time of recharge, evaporative processes and water-rock interactions occurring after recharge, or from mixing with another type of water.

Stable isotope values of water well samples were compared to those from produced water samples to evaluate possible impacts to groundwater from produced water or formation fluid. Hydrogen and oxygen isotope values measured in samples of produced water and groundwater collected for this study are plotted with respect to a local meteoric water line (LMWL), which is a standard plotting or graphical technique used to evaluate stable isotopes of water. An LMWL is a linear relationship of the ratios of $\delta^{18}O$ and $\delta^{2}H$ in precipitation that has not evaporated. The LMWL used in this study was developed specifically for southeastern Idaho, western Wyoming, and south-central Montana (Benjamin et al., 2004), and is based on values obtained from 68 snow-core and precipitation samples collected from 1999 to 2001.

3.3.5.2 *Stable Carbon (^{13}C) and Hydrogen (^{2}H) Isotopes of Methane*

Results for stable isotopes of carbon (^{13}C) and hydrogen (^{2}H or deuterium [D]) in methane can be compared to previously reported values for microbial versus thermogenic gas to help identify the sources of methane. Methane is created through microbial or thermogenic processes. Microbial methane is typically generated in low-temperature, near-surface environments by acetate fermentation of organic material (e.g., landfill gas) or microbial reduction of carbon dioxide in deeper sediments (Schoell, 1980). Thermogenic methane is formed by the thermal breakdown of organic matter at high temperature and pressure, conditions typically encountered during the deep burial of sediments. These alternative gas-generating processes lead to characteristic chemical and isotopic signatures of gas. Various researchers have determined commonly accepted stable isotope of carbon (^{13}C) and hydrogen (^{2}H or D) ratios in methane for microbial versus thermogenic gas (Schoell, 1980, 1983; Whiticar et al., 1986; Baldassare and Laughrey, 1997; Rowe and Muehlenbachs, 1999; Osborn and McIntosh, 2010).

Typically, $\delta^{13}C$ values for microbially generated methane are more negative. Conversely, $\delta^{13}C$ values for thermogenic methane are less negative. In this study, the degree of fractionation observed in the stable isotopes of carbon (^{13}C) and hydrogen (^{2}H or D) in methane was used to identify the origin of gas and differentiate between different sources or types of gas. Standard plotting or graphical techniques were used in this evaluation.

3.3.6 Hydrocarbon Gas Component Ratios

Hydrocarbon component ratios can be used to determine the *wetness* of a gas and provide an indication of the degree of biodegradation or alteration of a hydrocarbon gas mixture.

3.3.6.1 *Gas Component Ratios: Methane to Ethane + Propane*

The formation of thermogenic methane (C_1) involves the cracking of complex organic material into simpler hydrocarbon compounds, including ethane, propane, and butane (C_2 through C_4). Exploration geochemists have traditionally described the bulk composition of natural gases in terms of their *dryness* or *wetness* (Lundegard, 2006). A *dry* gas is characterized by a much greater proportion of methane (C_1) versus higher molecular weight compounds, or gases with two or more carbon atoms. These gases will be referred to in this report as C_{2+} gases. A *wet* gas has proportionally less methane (C_1) and a relatively greater fraction of C_{2+} gases.

A variety of gas dryness or wetness indices, or gas component ratios, have been used to differentiate between types of gases. For this study, the ratio of methane to ethane plus propane [$C_1/(C_2 + C_3)$] is used to differentiate between types of gases. Due to the greater proportion of C_{2+} gases in thermogenic methane, the $C_1/(C_2 + C_3)$ ratio is lower in thermogenic gas than in microbial gas.

3.3.6.2 *Gas Component Ratios: Alkanes to Isoalkanes*

Component ratios of isobutane to n-butane ($isoC_4/nC_4$) and isopentane to n-pentane ($isoC_5/nC_5$) are used to evaluate whether biodegradation of hydrocarbons has occurred. Saturated hydrocarbons (n-alkanes and C_1–C_5 gases) are removed first during biodegradation of crude oil and natural gas in petroleum systems (Wenger et al., 2002; Head et al., 2003). Propane, n-butane, and n-pentane components are the first C_1–C_5 gas components to be degraded. The differentiation between non-biodegraded and biodegraded gas using gas component ratios has been used to identify the source of hydrocarbons in aquifers in western Canada (Rowe and Muehlenbachs, 1999; Taylor et al., 2000).

The concentrations of C_1 through C_5 gas components (i.e., methane, ethane, propane, butane, isobutane, pentane, and isopentane) were normalized to the sum of these gas components to minimize the effects of dilution by air in a sample and to facilitate the comparison of the relative abundance of the gas components among all gas samples (i.e., dissolved gas in groundwater, casing gas, and natural gas samples). Gas component ratios were also normalized to the sum of the principal C_1 to C_5 hydrocarbon gas constituents (i.e., methane, ethane, propane, n-butane, isobutane, n-pentane, and isopentane).

4.0 POTENTIAL POINT AND NON-POINT SOURCES

This section presents the results of an evaluation of numerous point and non-point sources that have the potential to introduce organic constituents to groundwater or directly into water wells in the PAPA. A *point source* is a single, identifiable source of impact, which is typically localized. A *non-point source* is a diffuse source or source that cannot be identified based on specific location or isolated event. For this report, the terms *point source* and *non-point source* refer to the operation or activity rather than the specific source medium that was released, because several types of source media (e.g., drill mud, flowback fluid, produced water) could potentially be released from one type of point source, such as a tank or pit.

BDE and AMEC (AMEC Geomatrix, 2008, 2009a, 2009b) identified many potential point and non-point sources:

- Gas production well construction, completion, and abandonment activities;
- Facilities associated with natural gas production, such as reserve pits, production equipment, LGSs, and associated CGFs;
- Water supply well construction, use, and operation;
- Underground injection of produced water;
- Spills on gas production well pads (on-pad);
- Spills or release sites that are located off of gas production well pads (off-pad) and directly related to E&P operations, such as a release from a tanker truck in transit containing E&P materials;
- Known releases that have occurred in or near the PAPA that are *not* related to natural gas E&P activities (e.g., landfills or leaking underground storage tank sites);
- Sampling and laboratory issues/artifacts; and
- Natural, non-point sources of organic constituents.

Figure 4-1 shows locations of identified potential point sources within and in the immediate vicinity of the PAPA. The pre-1984 natural gas wells depicted on **Figure 4-1** represent locations where historic E&P activities have occurred. Potential point sources related to these historic E&P activities include gas production well construction, completion, and abandonment; historic facilities associated with E&P activity on pads (e.g., reserve pits, on-site tanks, and production equipment); and on-pad spills.

The locations of E&P activities conducted after 1984 are shown on **Figure 4-1** and labeled as surface disturbance. These locations represent areas of well pads, access roads, and related E&P infrastructure as of 2009 and are based on BLM's GIS data for disturbed areas. Point sources related

to recent (post-1984) E&P activities include the same sources listed above for pre-1984 gas wells, as well as water supply well construction, use, and operation; modern facilities associated with natural gas production (e.g., LGS and CGF); and underground injection of produced water.

Each of these potential point and non-point sources is described in this section.

4.1 Construction, Completion, and Abandonment of Gas Production Wells

Natural gas production wells are considered potential point sources for organic constituents in the PAPA. Based on available information and Operator interviews, SOPs for the construction, completion, and abandonment of natural gas wells have changed over the course of E&P activities in the PAPA. Best management practices were likely not established and instituted until more recent E&P activities after 1984. Only 20 pre-1984 gas wells exist, and these existing wells are distributed widely throughout the PAPA (**Figure 4-1**).

This section briefly describes the protocol for construction, completion, and abandonment of natural gas production wells and provides a contrast between past and more recent construction, completion, and abandonment procedures and practices. PAPA Operator standard operating procedures and practices are summarized in a previous technical memorandum (AMEC, 2011).

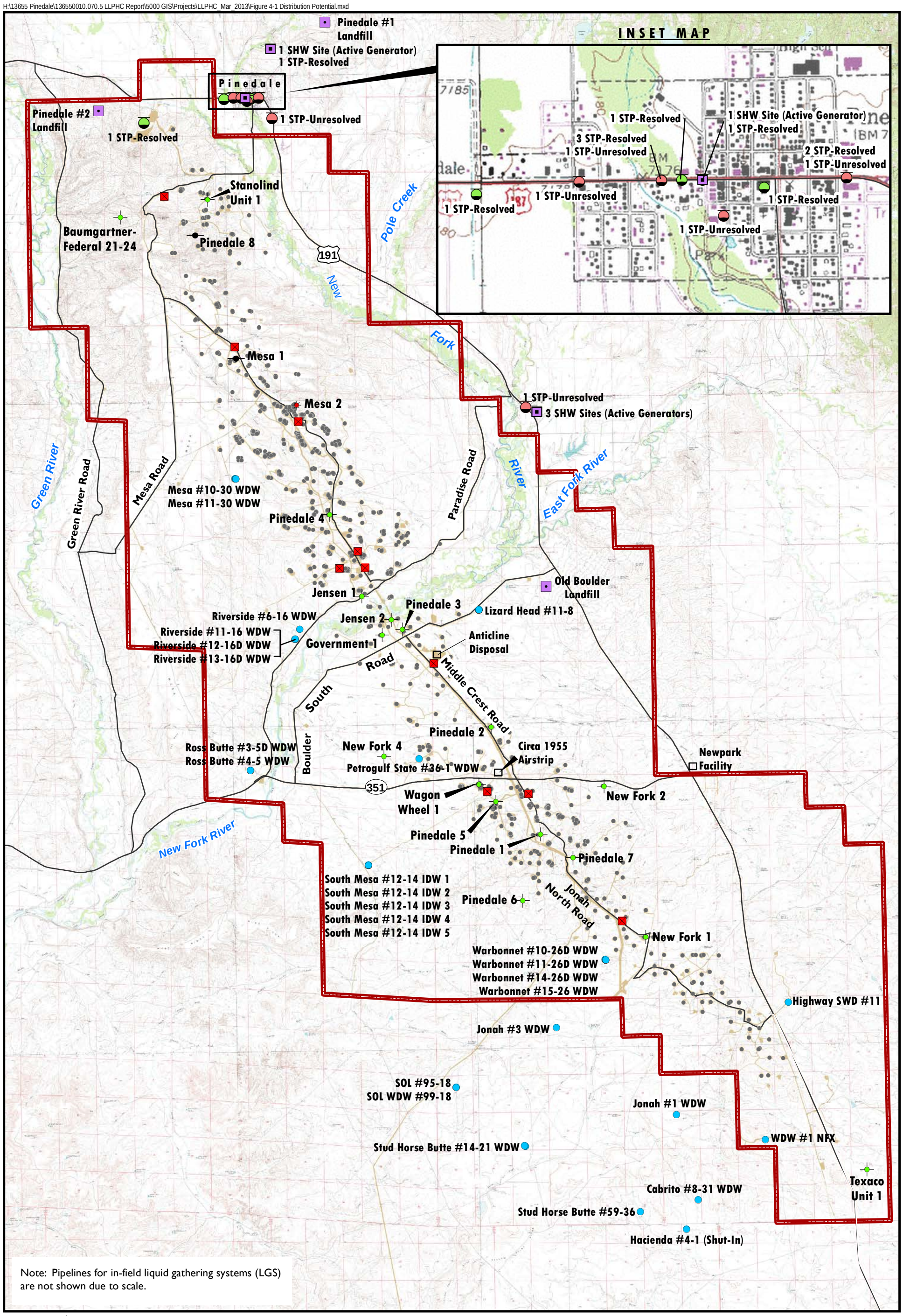
4.1.1 Well Construction

Natural gas wells are constructed to the standards set by the state and federal government, and every well drilled has been approved by one or both of those entities. Based on information provided by the Operators (PAPA Operators, 2012), the Operators adhere to WOGCC rules and regulations (i.e., Chapter 3, Operational Rules, Drilling Rules[4]) as well as applicable federal regulations when drilling, constructing, and completing natural gas production wells. Modern casing and cementing programs and more rigorous quality control measures are very different from early practices (AMEC Geomatrix, 2010). In addition to adhering to applicable state and federal requirements, Operators are voluntarily implementing new practices that are more protective of groundwater and the environment than prior practices (AMEC, 2011). For example, Operators employ advanced technologies, such as monitoring circulation volumes and conducting temperature and acoustic surveys, to further safeguard the integrity of cement in the top of the well casing (AMEC, 2011).

This section describes the construction of natural gas production wells, including descriptions of the drill muds used when drilling boreholes, the well casing and cementing program employed during the installation of natural gas production wells, and the procedures and testing protocols used to assess the integrity of the well casings and cemented intervals during well completions.

[4] Current WOGCC Rules and Regulations can be queried at http://soswy.state.wy.us/Rules/default.aspx.

H:\13655 Pinedale\136550010.070.5 LLPHC Report\5000 GIS\Projects\LLPHC_Mar_2013\Figure 4-1 Distribution Potential.mxd



Distribution of Potential Point Sources in the PAPA
Low Level Petroleum Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 4-1

4.1.1.1 *Drilling Muds*

Multiple natural gas production wells are generally installed on each pad using directional drilling technologies to minimize surface disturbance. Historically, all boreholes for natural gas wells were drilled using water-based drilling muds. Currently, fresh water-based mud is used for drilling the surface casing. Water-based mud may also be used to drill the borehole for the subsequent intermediate casing string. The depth where water-based mud is used corresponds to the depths where groundwater may be encountered that meets the WOGCC definition of "Fresh Water" and "Potable Water" or BLM's definition of "Usable Water." WOGCC defines *Fresh and Potable Water* as "water currently being used as a drinking water source or having a TDS concentration of less than 10,000 milligrams per liter (mg/L) and which can reasonably be expected to be used for domestic, agricultural, or livestock use" (WOGCC Rules and Regulations, Chapter 1, Section 2). Current BLM regulations require operators to "isolate fresh water-bearing and other usable water containing 5,000 ppm [parts per million] or less of dissolved solids and other mineral-bearing formations and protect them from contamination" [43 CFR 3162.5-2(d), October 1, 2012].

Beneath the depth where usable water can reasonably be expected, oil-based mud is generally used to drill wells. Oil-based mud is usually not used until reaching depths of around 7,000 feet below ground surface. In some cases, companies transition from water-based mud to oil-based mud at a depth shallower than 7,000 feet, but only if surface casing has been installed and cemented to a depth of at least 2,500 feet true vertical depth (PAPA Operators, 2013). In addition, pressure integrity testing of casing is conducted prior to changing over to oil-based mud, thereby providing confirmation that oil-based mud used in drilling is isolated from sources of usable or potable water.

4.1.1.2 *Well Casing and Cementing Program*

Historic natural gas production wells were often constructed with minimum lengths of surface casing and long intervals of uncemented open hole. For example, the Pinedale 2 natural gas production well was installed in 1955 with 450 feet of surface casing and an uncemented open borehole to a depth of 7,748 feet. Relatively lightweight steel casing (relative to modern casing) was typically used in these wells. This lighter weight steel casing may be susceptible to failure and corrosion.

In contrast, modern gas wells in the PAPA are constructed using continuous steel surface casing cemented into the borehole from ground surface to a depth below the interval of fresh groundwater (**Figure 2-9**). When used (i.e., below the depth of the surface casing), oil-based muds would not be in contact with fresh groundwater. Cement design is part of the approved permit to drill a natural gas production well. The cement slurry is designed to effect a permanent bond between the borehole and the steel casings, and the bonds are evaluated before well completion with a cement bond log (a sonic tool run on wireline).

Well bore construction entails installation of three to four cemented and pressure-tested steel casings. Casing pressure testing is performed after each casing schedule is cemented into the borehole prior to drilling the next casing schedule. The casing is pressure-tested to 10,000 psi, the maximum stimulation pressure used during hydraulic fracturing, and the pressure is held for 15-30 minutes to confirm integrity (see **Section 4.1.2**). The data from casing pressure testing are recorded and reported to the WOGCC and BLM.

A typical natural gas production well in the PAPA is constructed using the following casing schedules and testing protocols implemented to assess the integrity of the well casings:

- "Surface" casing is set to protect all known or reasonably estimated utilizable groundwater and to prevent blowouts or uncontrolled flows (WOGCC Rules and Regulations, Chapter 3, Section 22). PAPA operators generally set surface casing to a depth ranging between approximately 800 and 4,900 feet below the ground surface (PAPA Operators, 2013). The steel surface casing is typically 9-5/8 inches in diameter and is cemented into the borehole from the base of the casing to the ground surface. Pressure testing is then performed to assess the integrity of the casing and the cement bonded to the borehole wall and casing wall.
- "Intermediate" steel casing is 7 inches in diameter and is installed in an 8½-inch-diameter borehole to a depth of roughly 8,500 feet. After setting the casing, cement is added at the base of the casing and forced up the outside of the casing wall to seal it into the borehole. Pressure testing is then performed as described above.
- Steel "production" casing, which is 4½ inches in diameter, is then installed into a 6-inch-diameter borehole drilled to a permitted depth in the natural gas reservoir (i.e., Lance Pool). The steel production casing is also cemented into the borehole from the base of the casing up to at least 1,000 feet inside the intermediate casing. Cement bond logs are then typically performed to verify the top of the cement and to assess the cement bond. The production casing is then pressure-tested to the maximum stimulation pressure used during hydraulic fracturing (see **Section 4.1.2**).

The annulus between the surface casing and the borehole is sealed by circulating cement slurry from the bottom to the ground surface in order to seal the casing into the borehole. The remainder of the well is installed using subsequently smaller and overlapping casings that are cemented into their boreholes. Operators monitor the volume of cement slurry added for each cemented interval and add extra volume of slurry to adequately seal the casing to the borehole.

Operators commonly run cement bonding logs on all production casing strings, and cement bonding logs may be run after other casing installations for quality control purposes (i.e., to verify that no gaps are present). If gaps are found, that section of the casing is perforated, and additional cement slurry is squeezed through the perforations into the annulus. The adequacy of the repair is

typically checked with another cement bonding log, and the process is repeated, if necessary. According to PAPA Operators, field-wide, only 1-2 percent of gas production wells need cement repairs prior to the initial completion. As part of the well completion report issued to the appropriate regulatory agency, the post-cement top-of-cement elevation is reported. All well boring logs are also submitted to the appropriate regulatory agency. An additional check on the cement bond is made during hydraulic fracturing operations. Backside pressure is continuously monitored by Operators during hydraulic fracturing operations to detect any communication through the cement (see **Section 4.1.2**).

4.1.2 Well Completions

Well completion involves a number of steps to test the integrity of the well and then use of the well for natural gas production. Throughout the PAPA, hydraulic fracturing techniques are used to increase rates of gas production. *Hydraulic fracturing,* also referred to as *well stimulation*, involves pumping large quantities of fluids at high pressure down a well bore to fracture the targeted rock formation, thereby stimulating the flow of natural gas or oil. These fluids are referred to as both *hydraulic fracturing fluids* and *well completion(s) fluids*. Hydraulic fracturing of a natural gas well occurs in the producing zone of the well, which is approximately 8,000 to 14,000 feet below ground surface in the PAPA. Natural gas wells are typically fractured in 15 to 30 stages.

Field-wide, typical hydraulic fracturing pressures range from 6,000 to 10,000 psi, depending on the stage and depth of the producing zone. Pressures over 10,000 psi may occur but are usually instantaneous or of limited duration and occur only in the lower stages (e.g., depths in the range of approximately 14,000 feet). The duration of hydraulic fracturing for each stage in a well ranges from approximately 35 to 60 minutes. During each hydraulic fracturing operation, backside pressures are continuously monitored. Following the operation, hydraulic fracturing pressures are monitored for 5-15 minutes, and annulus and casing pressure may also be monitored. These monitoring data are used by the Operators to confirm each hydraulic fracturing operation was performed as designed.

The Operators are confident that materials from hydraulic fracturing are contained within the Lance Pool, based on well design, monitoring results, hydraulic fracture modeling, and geologic logs (PAPA Operators, 2013). The surface casing intervals for all natural gas and oil wells are cemented to the surface, and well casing integrity is scrutinized through pressure testing and verified with cement bond logs where necessary (**Section 4.1.1.2**). These testing and verification procedures are conducted prior to any completions activities to confirm the interior of the production casing is isolated from the annulus.

During hydraulic fracturing operations, annulus pressure is continually monitored and recorded (see **Section 4.1.2.3**). The dimensions of hydraulic fracturing are controlled by rock properties and stresses. It should be noted that the 7,000 feet of overlying rock (1.3 miles – the vertical distance between the Lance pool and groundwater resources) and overburden stress provide a barrier

between the zone of hydraulic fracturing and fresh water. According to PAPA Operators, monitoring and modeling analyses have shown that this barrier has not been compromised (PAPA Operators, 2013). Operators' practices and well designs meet or exceed all regulatory requirements, including BLM's Onshore Order No. 2 (BLM, 1988) and WOGCC Rules and Regulations (Chapter 3). In addition, all pipe specifications and cement designs are included in the application for permit to drill (APD) submittal to WOGCC (for permits on federal lands, BLM also receives the APD submittal).

Operators refer to procedures involved with hydraulic fracturing as "completions." This section describes the completions fluids used in hydraulic fracturing operations, the sources and quantities of water used in the completion process, and monitoring protocols used during hydraulic fracturing operations.

4.1.2.1 *Well Completions Fluids*

Hydraulic fracturing was performed on natural gas production wells in the PAPA as early as 1954. Well operators historically relied on the use of petroleum-based substances in completions fluids. Fuel oil, kerosene, natural gas condensate, and diesel and/or condensate emulsions were historically used in completions fluids based on review of BLM files and interviews with Operator personnel. Very little information is available based on the review of BLM files or interviews with Operator personnel regarding how historic hydraulic fracturing fluids or resulting waste fluids were handled or disposed.

Modern hydraulic fracturing fluids, or completions fluids, contain a variety of specialty chemicals and are often classified into water-based fluids, oil-based fluids, alcohol-based fluids, emulsion fluids, and foam-based fluids (Fink, 2003). A typical formulation of modern completions fluids contains greater than 99.5 percent by volume water, sand, and inert solids. Operators in the PAPA typically use a cross-linked gel only or employ a hybrid technique using both cross-linked gels and slick water treatments to reduce friction. Both systems would most likely include an agent to control bacterial growth. These completions fluids or techniques differ in several aspects:

- *Cross-linked fluid* is a fluid containing polymer additives, which increase the viscosity of the fluid. After adding the polymers, the consistency of the fluid resembles gel.
- *Slick water* is simply water with an added friction reducer. The friction reducer changes the surface tension of water, therefore reducing the friction it generates on the pipe.
- *Hybrid* typically indicates that the cross-linked and slick water fluids are used at separate times in the wellbore as individual treatments, and in some cases these fluids are utilized in the same treatment.

The use of large quantities of petroleum products to hydraulically fracture wells has been discontinued. Some Operators may use a small amount (less than 0.05 percent by volume) of hydro-treated petroleum distillate in hydraulic fracturing fluid. However, recycled water (e.g.,

produced water) used in completions fluids, or formation fluid found in the producing zone itself, would likely contain a greater percentage of petroleum hydrocarbons than the materials used in the makeup of hydraulic fracturing fluid. Based on information reported by the Operators in the PAPA (Groundwater Protection Council, 2012), additives that comprise less than 0.5 percent by volume of completions fluids may include a combination of one or more of the following substances:

- guar gum
- alkylated quaternary chloride
- ammonium acetate
- acetic acid
- EDTA/copper chelate
- sodium persulfate
- sodium chloride
- potassium metaborate
- sodium hypochlorite
- petroleum distillate blend
- hydro-treated light distillate
- 2-butoxyethanol
- phenol / formaldehyde resin
- potassium hydroxide
- potassium metaborate
- potassium formate
- chlorous acid / sodium salt
- ethoxylated nonylphenol
- isopropanol
- borate salts
- methanol
- potassium carbonate
- 2-bromo-2-nitro-1,3-propanediol
- ammonium persulfate
- sodium hydroxide
- white mineral oil
- magnesium hydroxide
- magnesium peroxide
- magnesium oxide
- naphtha, hydro-treated heavy
- sodium perborate tetrahydrate
- hexamethylenetetramine

After hydraulic fracturing ceases, the completions fluids are allowed to "flow back" up the well under natural pressures within the Lance Pool. The completions fluids ultimately flow back to the surface, where they are recovered. The resulting liquid is known as *flowback fluid*. The flowback fluid consists of both completions fluids and naturally occurring fluids present in the Lance Pool.

A typical natural gas production well is flowed back for about 5 to 10 days. Approximately 55 to 60 percent of hydraulic fracturing fluid is recovered from the natural gas production well upon completion of hydraulic fracturing. Although this distinct period of time during which the majority of flowback fluid is recovered (e.g., "flowback period") lasts approximately 10 days, fluids (naturally occurring water and condensate from the Lance Pool and the introduced hydraulic fracturing fluids) continue to be recovered throughout the production period of the natural gas well. Some amount of hydraulic fracturing fluid, however, may be unrecovered. As an example, a typical natural gas well in the Pinedale Anticline might produce more than 1 million cubic feet of natural gas per day, along with 10-100 barrels of water per day (see Nelson et al., 2010). The projected life of a typical natural gas well is on the order of 30 years. If, for instance, 1.5 million gallons of fluid is used for hydraulic fracturing of a well and 55 percent returns to the surface as flowback during the 10-day flowback period, approximately 675,000 gallons (16,071 barrels) would remain in the Lance Pool. At a water

production rate typical of natural gas wells (assume 34 barrels/day; see **Section 4.2.3**), this volume (675,000 gallons or 16,071 barrels) would be produced by the well in about 15-16 months (473 days). Over the production life of the typical natural gas well, the well might produce over 15 million gallons of water.

The SAP (AMEC Geomatrix, 2010) was designed to characterize flowback fluid as a potential source material. **Section 3.2.1.4** describes the procedures for sampling and analysis of flowback fluids, and **Tables B-1** and **B-4** (**Appendix B**) provide additional details on flowback fluid sampling and analysis.

4.1.2.2 *Water Sources and Usage*

Approximately 0.5 to 1.5 million gallons of water are currently used to hydraulically fracture a natural gas production well in the PAPA. Until approximately 2004, Operators used fresh water from industrial water supply wells installed on gas well pads as the water source for completions work. Currently, the water used for completions may include a combination of fresh water, produced water, flowback fluid, and/or treated water (i.e., recycled water). Treatment typically involves removal of liquid hydrocarbons (i.e., condensate) and solids. Operators began transitioning in 2005 to the use of produced water or treated produced water (i.e., recycled water) in the preparation of completions fluids. The water is either treated by Operators at centralized facilities or obtained from Anticline Disposal, a local wastewater treatment and disposal facility (**Section 4.6.2**). Operators may also re-use flowback fluid or use recycled flowback fluid in completions activities, as available. As of 2012, the usage of some combination of produced water and/or recycled water ranges from about 60 to 100 percent of water used in completion activities by the Operators.

4.1.2.3 *Monitoring Protocols during Well Completions Activities*

Well completion activities are regulated by the WOGCC and BLM. Many required and voluntary steps are taken during these activities to verify that the well bore construction provides an adequate barrier between fracturing fluids, produced fluids, and fresh groundwater so as to protect fresh groundwater resources. Completion activities (i.e., hydraulic fracturing operations) are not initiated until each well is confirmed to meet requirements for hydraulic fracturing based on pressure testing of the well casing, as described in **Section 4.1.1.2**.

Some of the important types of monitoring performed by the Operators that occur throughout each hydraulic fracturing operation to verify that hydraulic fracturing fluids are being placed in the target zone are summarized below.

- The surface casing is visually monitored to assess if excess pressure is present.
- The annulus pressure of the production casing is monitored and recorded continually at the well head during all completion activities to assess whether the fluid is being delivered to the targeted zone. Annulus pressure is monitored to confirm whether or not

communication occurs with the backside, or on the outside, of the production casing. Only one target zone (e.g., stage) is completed at a time. If only limited changes in pressure (increase from heating or decrease from cooling) occur on the production casing annulus or surface casing, then it can be concluded that all pressure and fluid were delivered to the single open target zone.

- Surface treating pressures are monitored and recorded continually during all completion activities. Changes in friction pressure and hydrostatic pressure will cause variations in surface treating pressures during hydraulic fracturing operations. These pressure variations, together with known volumes of fluid that were pumped, help establish if the hydraulic fracturing fluids are being placed in the target zone.

4.1.3 Well Abandonment

Relatively few natural gas wells associated with current operations (post-1984) have been abandoned, as most wells are still producing natural gas. However, when these wells are abandoned due to lack of production, appropriate rules and regulations are followed with respect to the procedures and protocol used for abandonment. For example, procedures for the work are documented in a Sundry Notice of Intent, and the Sundry is submitted to the appropriate agency for approval (BLM for federal lands and WOGCC for all lands). Plugging and abandonment activities are not performed until approved; once the approved work is completed, a Subsequent Report Sundry is issued to the appropriate agency.

Seventeen of the 20 pre-1984 gas wells have been abandoned, whereas the remaining three are either shut-in or flowing. Historically, operators tended to leave pre-1984 production wells shut-in for an extended period of time prior to abandonment. For example, available records indicate a history of intermittent production at the Pinedale 2 well. That well was plugged and abandoned on October 8, 2004, approximately 49 years after its spud date.

4.2 FACILITIES ASSOCIATED WITH NATURAL GAS PRODUCTION

This section briefly describes the facilities associated with natural gas production that are considered potential point sources in the PAPA. These facilities are located both at the gas well pad and at centralized locations within the PAPA. Facilities include reserve pits, production equipment and associated tanks, large aboveground storage tanks at the gas well pad, in-field fluid gathering systems (i.e., LGS), and tank batteries and other storage/transfer facilities at CGFs. This section describes these facilities and how their use in E&P operations in the PAPA has changed over time. **Figure 4-2** presents a timeline showing when key natural gas E&P infrastructure was introduced into the PAPA.

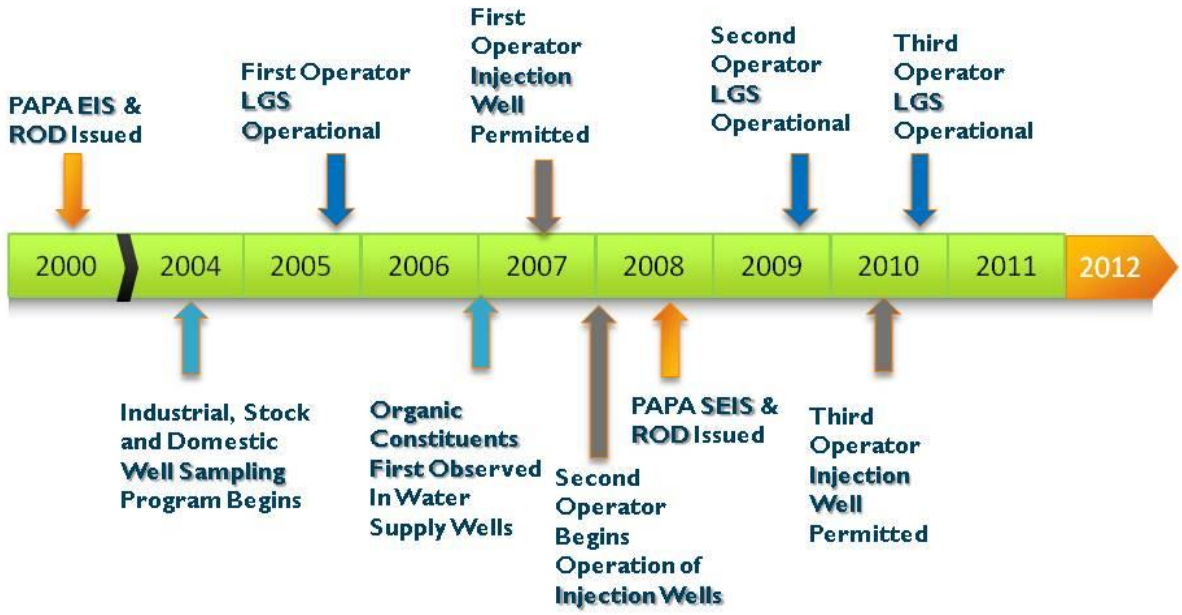


Figure 4-2 Timeline for Introduction of New Infrastructure in the PAPA since 2000

4.2.1 Reserve Pits

Historically, open reserve pits in the PAPA were used to contain oil- and water-based drilling fluids and cuttings, as well as completions and work-over fluids (e.g., hydraulic fracturing fluids, condensate, and produced water). The extent to which synthetic liners were utilized in these pits prior to 2000 is uncertain. The 2000 PAPA ROD (BLM, 2000) required produced water and reserve pits to be constructed in a manner that protects surface water and groundwater resources, including use of liners where warranted based on distances to surface water and groundwater resources and/or soil permeability. According to information communicated by BLM (Bill Lanning, personal communication, 2010), liners on containment pits have been a Condition of Approval for all APDs on federal lands since shortly after the 2000 PAPA ROD was issued. On state or fee lands in the Upper Green River Basin, the WOGCC currently requires all pits to be lined, with a separate lined pit required for completions fluids (WOGCC Rules and Regulations, Chapter 4).

The current trend is away from the use of open fluid pits and toward the use of closed-loop drilling and completions systems (AMEC, 2011). In closed or semi-closed mud systems, most drilling fluids are recycled, and the remaining oil-based and water-based cuttings are typically segregated in separate pits. Currently, Operators are using closed-loop drilling mud systems (e.g., pitless systems) on federal lands within the PAPA that negate the need for open fluid pits and facilitate the management of drill cuttings.

Cuttings from borings drilled using oil-based drilling fluids can be either disposed of at a permitted waste disposal facility or solidified and buried in on-site burial cells. For on-site burial, cuttings

containing oil-based drilling mud must be solidified and subsequently buried under a minimum of 3 feet of low-sodium, clean fill material and sufficient topsoil to allow revegetation of the former pit area. Cuttings from borings drilled using water-based drilling fluids are also typically buried on site in burial cells covered by a minimum of 3 feet of soil material in accordance with WOGCC regulations and BLM policy. Chapter 4 of the WOGCC rules defines pit closure and testing requirements.[5]

4.2.2 Production Equipment

Production equipment at gas well pads typically consists of oil/water separators and dehydration units, which are used to separate the formation fluids, such as condensate and produced water, from the natural gas at the ground surface. Modern production units typically include spill containment built into the system, or a high-density polyethylene (HDPE) liner is installed beneath the unit (AMEC, 2011). Operators manage fluids captured from drips or blowdown from production units/packs by temporarily storing the recovered fluids in drums with secondary containment or by transferring the fluids by hard-pipe connected directly to storage tanks on the well pad. Methanol for use in the gas production process is typically dispensed from polyethylene tanks constructed with built-in secondary containment.

4.2.3 Aboveground Storage Tanks at Gas Well Pads

The average production well in the PAPA produces 750 thousand cubic feet per day (MCFD) of natural gas. Approximately 5 barrels (bbl) of condensate and 34 bbl of water are produced daily along with the natural gas at each production well. Based on annual statistics compiled for the Pinedale Anticline field by the WOGCC for 2011,[6] daily total volumes for condensate and produced water are approximately 11,267 bbl and 52,125 bbl, respectively. Natural gas production wells in the south end of the PAPA tend to generate twice the volume of produced water compared to those in the north end. Condensate production does not vary much throughout the PAPA. Oil/water separators separate both the condensate and produced water from the natural gas stream at the ground surface. The natural gas stream is also run through a dehydration unit after the oil/water separator, where glycol is used to remove any remaining liquids from the natural gas prior to feeding the natural gas into the sales line.

Historically, condensate and produced water separated from natural gas at the ground surface were stored in aboveground storage tanks at the gas well pad. The fluids were ultimately transferred from the tanks to tanker trucks for disposition. It is unknown if tanks were monitored for leakage or if secondary containment was used.

[5] The WOGCC's pit closure guidelines are found at http://wogcc.state.wy.us/craig/pitclose.htm.
[6] http://wogcc.state.wy.us

Since 2004, lined secondary containment structures have been used to hold all tanks at gas well pads, CGFs, and injection facilities (see **Section 4.2.5**). On a daily basis, Operators inspect all tanks at all facilities and each well pad to assess for the presence of leaks/spills and to evaluate operational issues. Currently, aboveground storage tanks located on gas well pads are generally no longer used to store fluids generated during natural gas production at the pads (i.e., produced water and condensate), except on a temporary basis. Little storage of waste or materials currently occurs at gas well pads.

4.2.4 Liquid Gathering Systems

Fluids separated from the natural gas stream at the gas well pad are handled through the LGS and are recycled, reused, or disposed via permitted injection wells (see **Section 4.4**). An LGS is a network of buried pipelines emanating from each production pad that transports gas product, condensate, and produced water from multi-well pads via trunk pipelines to centrally located facilities (AMEC, 2011). The pipeline system has replaced the need for liquids to be hauled by tanker trucks. In general, the LGS pipelines in the PAPA consist of reinforced plastic pipe. These pipes are corrosion resistant. Liquids are piped to a CGF, where water and condensate are further separated, and the liquids are then piped to a refinery or disposal facility. Produced water is sent via pipeline to company-operated or third-party disposal facilities for treatment and disposal, treatment and re-use, or disposal via permitted Class II underground injection control wells (i.e., injection wells). Condensate is transferred to oil refinery markets by pipeline.

LGSs were installed by one Operator in the northern portion of the anticline beginning in 2005 and completed by May 2007. By 2010, LGSs were completed at established gas well pads for the larger Operators in the anticline throughout DA1 through DA4; DA5 does not contain LGS pipelines. The LGSs are continually expanded as new natural gas drilling and completion operations are brought on-line. Prior to establishment of the LGS, fluids generated during natural gas production were stored in lined pits (**Section 4.2.1**) and aboveground storage tanks on-pad and then trucked off-pad for treatment and/or disposal (**Section 4.2.3**).

The SAP, accepted by the BLM in consultation with the U.S. EPA and Wyoming DEQ, documents research into reported or recorded spills in the PAPA. No indications of spills or releases from LGS were reported. Most of the LGS infrastructure was installed after organic constituents were first observed in groundwater in 2006 (**Figure 4-2**).

Visual inspections aimed at detecting problems from the various components of the LGS are performed by operational personnel from multiple companies on a daily basis. Operators have implemented pipeline integrity programs whereby both external and internal inspections are conducted on a routine basis. The system pressure in the LGS is continuously monitored by supervisory control and data acquisition (SCADA) systems. Electronic pressure-measurement devices are installed throughout the LGS. These devices are continually monitored by the SCADA

systems and are a key component of the emergency shutdown system. The LGS has provisions for automatic shutdown at various valve locations throughout the pipeline network should there be pressure changes resulting from changes in flow volume.

Several procedures are regularly employed by the Operators to monitor the integrity of buried steel components in the PAPA. For LGS pipelines constructed with carbon steel, cathodic protection is used to protect the piping from corrosion caused by electrolysis. Bimonthly rectifier inspections and annual cathodic surveys are completed to assess proper function of the system. One company has also implemented a corrosion "coupon" program throughout its LGS. These coupons are pulled and analyzed monthly to determine whether pipe degradation is occurring. A "smart pig" is run in the condensate transport line every 5 years to measure the pipe wall thickness. Random inspections of buried piping have been performed by exposing the pipe with hydro-vac techniques to allow use of a sonar device to measure the cross-sectional thickness of the pipe wall.

Another company has a formalized asset integrity program that involves regular corrosion testing of tanks and lines, including wall thickness testing on tanks and buried pipes. Pipes are also periodically excavated and tested. Select facilities are sampled each year, and an annual ground surface survey of buried lines is conducted.

The in-field liquid gathering lines, as well as wastewater disposal wells (**Section 4.4**), were not part of historic (pre-1984) E&P operations and are a fairly recent addition to the infrastructure in the PAPA. The timeline in **Figure 4-2** illustrates key dates in the introduction of new infrastructure in the PAPA since 2000.

4.2.5 Tank Batteries and Other Storage/Transfer Facilities at CGFs

Currently, fluids in the field are handled through the LGS either by recycling, reuse, or injection. Fluids transferred by the LGS are stored in aboveground storage tank batteries at the CGF. Thus, aboveground storage tanks that have historically been located at the gas wells pads have been largely replaced by tank batteries at centralized locations, where fluids from the in-field liquid gathering pipelines are received (**Section 4.2.3**). Tankage will remain at many natural gas well pads for emergency use (i.e. hydrate removal), although the number of tanks may vary depending on need. In certain cases, tanks at gas well pads may be used for annual 24-hour liquid production testing for individual wells.

Older tank batteries were constructed within earthen dikes. In contrast, newer tank batteries at the CGFs are equipped with secondary containment structures that are typically constructed using corrugated steel firewall with an HDPE liner tied into the firewall (AMEC, 2011). The tank batteries and secondary containment facilities at the CGFs are monitored for leaks and inspected on a daily

basis. Tank integrity programs consisting of both external and internal inspections are conducted on a routine basis.

4.3 WATER SUPPLY WELL CONSTRUCTION, USE, AND OPERATION

The construction and use of on-pad water supply wells to support natural gas well drilling and completion operations have been in practice predominantly since 1984. Only two industrial water supply wells are known to have been constructed prior to 1984 to support gas drilling operations. Both of these wells were associated with the Wagon Wheel #1 natural gas production well, a pre-1984 gas well located in the central portion of the PAPA (**Figure 4-1**). These industrial water supply wells were installed to depths of 2,500 feet and 5,180 feet based on available records (AMEC Geomatrix, 2009a). Both wells were perforated over multiple intervals, and the lowest perforated interval of the shallower well coincided with the uppermost perforated interval of the deeper well. The current status of these wells is uncertain.

Up to 300 industrial water supply wells have been used to support modern E&P activities at or near the current natural gas production well pads in the PAPA (see **Photo C-1** in **Appendix C**). AMEC Geomatrix (2009c) presented an inventory of water wells and key available information regarding well location, depth, and completion. Industrial water supply wells were commonly installed using air rotary drilling techniques with an average depth of about 650 feet (AMEC, 2012). Water well casings are typically perforated adjacent to intervals of water-bearing sandstone. After well completion, wells are generally developed with compressed air from the drill rig to improve the hydraulic connection between the well and water-bearing units. The Wyoming State Engineers' Office sets the standards for the construction of water wells to protect the use of the state's groundwater resources.

Over the last several years, Operators have increased the volume of fluids being recycled, which reduces the volumes of fresh water used in completions activities (**Section 4.1.2**). Where fresh water is needed for drilling or completions activities, Operators are, where practicable, using a centralized water supply well to provide fresh water to multiple drilling pads instead of using a water supply well at each pad (AMEC, 2011).

Construction, use, and operation of water supply wells have or may have employed the following activities and materials:

- Unfiltered compressed air from air rotary drill rigs;
- Well casing or drilling tools that may not be cleaned prior to installation;
- Drilling and/or well installation using equipment that contains hydraulic fluids;
- Fluids or foams used to aid in removing drill cuttings from boreholes;

- Pipe dope used on drill rods, tools, and bits during drilling, and on drop pipe threads and fittings during pump installation (**Photos C-3** and **C-4**, **Appendix C**);
- Submersible pumps, electrical cables, and/or drop pipe that may not be cleaned between uses in wells;
- Inadequate or absent backflow prevention devices when wells were connected to tanks or pits;
- Trucks and/or tanks that may be used for storage of fluids other than potable water; and
- Lubricants associated with submersible pumps.

Although Operators currently require water well contractors to use clean practices, this was not an explicit requirement in the recent past (AMEC Geomatrix, 2010). AMEC has observed grease and/or pipe dope on wellheads and pipe fittings, and has observed a substance similar to pipe dope discharging from pumping wells during sampling activities. Very little of the material is exposed to the aquifer, generally that which has squeezed out between joints of the pipe, as illustrated schematically in **Figure 4-3**. By the fall of 2008, Operators had implemented a best practice that requires contractors to clean all downhole materials and equipment used in pump installations by high pressure/hot water, and use silicone-based dope compounds. BLM's SEIS ROD (BLM, 2008b) states that no new BLM rights-of-way or other approvals for new industrial water supply wells will be allowed in the PAPA until the groundwater characterization is completed and the causes of hydrocarbon detections have been determined and effectively mitigated.

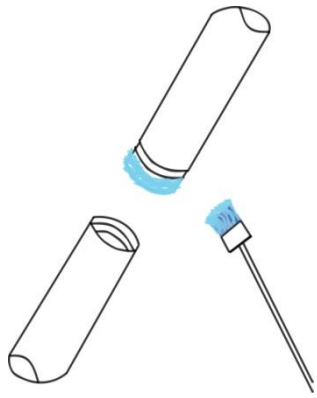


Figure 4-3 Schematic of Typical Use of Pipe Dope for Water Well Applications

The Operators have suspected or observed backflow of fluids containing organic constituents directly into industrial water supply wells. Prior to the issuance of the ROD in 2008 (BLM, 2008b), which required backflow prevention devices on all water supply wells, backflow is known or suspected to have occurred in the following industrial water supply wells: North Pinedale 14-8 (NP 14-8), North Mesa 4-7-32-109 (NM 4-7), WB 8-6, and RS 15-12. Organic constituents have

been removed from these wells by overpumping and/or implementing procedures to clean the inside of the well casing and remove contaminated water above the perforated intervals. SCCD annual monitoring data for wells NP 14-8 and NM 4-7 contained in **Appendix A** show that these corrective actions have resulted in non-detectable concentrations of TPH-GRO, TPH-DRO, and BTEX. SCCD data for wells WB 8-6 and RS 15-12 are also included in **Appendix A**. These wells were included in the SAP, and sampling results for these wells from this study are presented in **Section 7.0**. Well RS 15-12 was also enrolled in the Wyoming DEQ Voluntary Remediation Program in 2009. Through efforts of well cleaning, pumping, and additional sampling (see **Section 9.2.2.1.1**), the Wyoming DEQ determined that all remediation requirements have been successfully implemented or satisfied and issued a Certificate of Completion for well RS 15-12 on February 6, 2013.

4.4 UNDERGROUND INJECTION OF PRODUCED WATER

According to WOGCC records, permitted Class II water disposal wells have been used for subsurface injection of produced water in the PAPA since September 2005. All water disposal wells are completed in the Fort Union Formation at depths of 5,660 feet or deeper, and are cased and cemented through the overlying freshwater formations. At the end of 2007, only three produced water injection wells were active within the confines of the PAPA: Petrogulf State #36-1WDW, Highway SWD #11, and Riverside #6-16 WDW, with a total injection volume of 2,322,165 bbl for that year. These wells are located away from the main gas field development. The geographic positions of all active Class II injection wells in and adjacent to the PAPA are shown on **Figure 4-1** relative to the locations of gas well pads. Produced water injection wells are located predominantly downgradient of industrial water supply wells.

4.5 ON-PAD SPILLS

On-pad spills can occur from equipment or facilities temporarily constructed at the well pad to hold or process fluids from drilling and completions activities, or from more permanent fixtures commonly used during production activities. Historic spills of fuel and fluids used in E&P activities that may have occurred at some of the older well pad locations (pre-1984 gas wells) were not well documented. Apparent discharges of fluid of unknown composition from the Pinedale 2 and Pinedale 3 locations were observed on 1955 aerial photographs, which show the locations shortly after and during drilling, respectively. It is uncertain to what extent secondary containment measures were employed at well pads in the past; however, spill containment for production units and tanks was required by the BLM's SEIS ROD.

Currently, best management practices are employed at gas well pads. These practices include modern secondary containment systems for tanks, tank and pipeline integrity programs, and movement away from the use of pits or tanks at the gas well pad. It is uncertain to what extent secondary containment measures were employed at well pads in the past; however, spill

containment for production units and tanks is required by the BLM's SEIS ROD in the operator's Surface Use Plan of Operations under Onshore Order No. 1 (BLM, 2007). Operators participate in spill response training, and a spill response trailer is strategically located in the PAPA for use. Discussions regarding locating an additional spill response trailer(s) in the PAPA are ongoing among the Operators. Operators are required to report any surface releases that do occur to the appropriate regulatory agency(s) (BLM, WOGCC, and/or Wyoming DEQ), and these agencies provide regulatory oversight of cleanup efforts. The BLM "Undesirable Events" database documents numerous spills, many of which are related to E&P activities on BLM-administered lands. Regulatory oversight, including delineation of impacts to groundwater if necessary, was provided in resolving each of these reported releases.

4.6 OFF-PAD SITES

A review of public databases to evaluate potential sources of organic constituents not associated with natural gas E&P activities provided the following findings:

- No sites in Sublette County were listed in the EPA RCRA 2020 Corrective Action Universe.
- The EPA Envirofacts database did not return any entries for Sublette County that were not also found in State and Federal databases.
- The Wyoming DEQ Storage Tank Program database identified six unresolved sites and 11 resolved sites in the vicinity of the PAPA as of April 5, 2012 (**Figure 4-1**). One resolved site is located inside the PAPA boundary.
- The Wyoming DEQ Solid and Hazardous Waste Site listings identified eight sites in the towns of Pinedale and Boulder, which are located within or near the PAPA. Three of these sites are operating or historic municipal landfills, two of which are located inside the PAPA boundary (**Figure 4-1**).

Several facilities located in or proximal to the PAPA are discussed in detail below.

4.6.1 Landfills

Three existing or former landfills are located within or proximal to the PAPA: the Pinedale #1, Pinedale #2, and Old Boulder Landfill (**Figure 4-1**). Pinedale #1 is a historic municipal landfill located below Fremont Lake approximately 3 miles northeast of the PAPA. Pinedale #1 is located upgradient of the PAPA at a considerable distance. Pinedale #2 and the Old Boulder Landfill are located within the PAPA boundary. Pinedale #2 is a closed municipal landfill and the site of an active transfer station. It is located in the northern PAPA in Township 30 North, Range 110 West, Section 2. No additional information on this landfill was available to AMEC as a result of literature research and review of public databases conducted as part of preparing the SAP (AMEC Geomatrix, 2010).

The Old Boulder Landfill is located south of the New Fork River near the intersection of Boulder South Road and Highway 191. Information concerning the groundwater monitoring network at the landfill was obtained from the Wyoming DEQ during the preparation of the SAP in 2009-2010 and again as part of this study in 2013 (David Reid, personal communication, 2013). The landfill was closed in early 1985, and a closure permit for the landfill was never issued by the Wyoming DEQ. By 2009, funding became available, and four shallow (60- to 75-foot-deep) monitoring wells were installed. Sampling for various inorganic parameters, metals, nutrients and volatile organic compounds (EPA Method 8260B) occurred on two occasions: August 2009 and November 2010. Sampling results on file with Wyoming DEQ indicated that of the eight water samples analyzed, only two volatile organic compounds were detected (carbon disulfide in a sample from well MW-3 in 2010 and 1,1,2-trichloroethane in a sample from MW-4 in 2009). Concentrations of each compound were below 0.6 mg/L, and these analytes were detected only once. According to Wyoming DEQ, future monitoring of the Old Boulder Landfill is not currently scheduled.

4.6.2 Permitted Oil-Disposal Facilities

Two Wyoming DEQ-permitted oil-disposal facilities are located within or at the boundary of the PAPA: the Newpark Facility and the Anticline Disposal facility (**Figure 4-1**).

The Newpark Facility, located in Sand Springs Draw Industrial Park adjacent to the eastern boundary of the PAPA, was constructed in 2002. The facility was permitted to accept and treat produced water and petroleum-contaminated soil (PCS), but has not accepted waste since 2006. The facility is equipped with a double liner and interstitial monitoring system to detect leaks through the primary liner, as well as a groundwater-monitoring network associated with both the water and soil treatment facilities. A closure permit for the facility was issued by Wyoming DEQ in early 2012 (David Reid, personal communication, 2013).

The Anticline Disposal facility was constructed in 2002 to treat flowback fluid and produced water. The facility includes an oil/water separator, evaporation ponds, water treatment system, and fresh water storage pit. The facility maintains a Wyoming Pollutant Discharge Elimination System discharge permit for the New Fork River and Sand Draw. The cells of the water-evaporation system are triple-lined and have an interstitial leak-detection monitoring system. A groundwater monitoring network has been established at the facility. Groundwater monitoring data from the Wyoming DEQ provide no evidence that a release from the facility has occurred.

4.7 Sampling Methods and Laboratory Analytical Issues/Discrepancies

Groundwater samples can become compromised if correct sampling procedures are not employed. Correct sample-collection procedures include use of clean, new, disposable equipment or thoroughly decontaminated, reusable equipment. Since 2004, groundwater samples have been

collected by many individuals representing numerous entities using a variety of methods and analyzed by the laboratory using a variety of methods.

False positive laboratory results can result from the following procedural issues and conditions encountered during sample collection, sample handling, and/or laboratory analysis:

- Difficulty associated with decontaminating the braided steel cable previously used to retrieve bailers from the industrial water supply wells;
- Ineffective decontamination of pumping equipment prior to inserting the equipment into the water supply well for sample collection;
- Contamination of a sample due to oil residues on the industrial water supply wellhead or in ambient air at the time of sample collection;
- Use of laboratory analytical methodologies that are unable to distinguish interfering compounds from target analytes (e.g., EPA Method 8021 versus EPA Method 8260).

Biased analytical results can also arise due to the following improper sampling procedures:

- Inserting and retrieving a bailer through the stagnant water between the static water level and the perforated interval without first checking the top of the water column for substances (e.g., floating hydrocarbons) that may have been introduced into the water supply well;
- Retrieving a standard bailer equipped with a ball-seat check valve in an attempt to collect a grab sample of fresh formation water; movement of the ball-seat valve during bailer retrieval likely results in the sample actually being collected from near the top of the water column within the casing.

4.8 NATURAL SOURCES

Lacustrine and marginal lacustrine rocks in the Wasatch Formation in southwestern Wyoming are thermally immature, thus the potential for significant oil or thermogenic gas to be generated in situ in the Wasatch Formation is considered low (Roberts et al., 2005). Natural gas from the Wasatch Formation in southwestern Wyoming is produced via both conventional methods and by coal bed gas extraction methods (Clarey et al., 2010). Coal bed deposits are found in the Wasatch and Fort Union formations in areas southeast of the PAPA (Roberts, 2005a, 2005b), and the presence of gas has been documented in coal beds in the Fort Union Formation in this area (Roberts, 2005b). However, gas production is not documented in Wasatch and Fort Union Formations in the PAPA.

Natural gas is produced in the PAPA from the Lance Pool (**Section 2.2.3**). Natural gas fields are typically leaky (i.e., they contain imperfect seals, fractures, and other conduits that can allow natural gas to migrate vertically from the target formations). Therefore upward seepage of natural gas

from target formations through overlying strata to the ground surface can occur over geologic time. This seepage could occur as macroseepage (e.g., along geologic faults) or microseepage (e.g., diffusion through the overlying geologic material). Within the PAPA, natural gas and associated condensate is known to contain BTEX as well as other petroleum hydrocarbons.

The premise that all natural gas deposits have leaky seals to some degree is broadly supported in petroleum exploration literature. A notable memoir published by the American Association of Petroleum Geologists (AAPG) in 1996 comprehensively discusses the subject of hydrocarbon migration and its near-surface expression (AAPG Memoir 66; Schumacher and Abrams, 1996). In the early 1930s, German and Soviet investigators started near-surface exploration for petroleum with the development of methods to detect hydrocarbon gases, primarily methane, in soil gas. Over the decades since, the exploration community has improved near-surface prospecting methods with sophisticated detection, survey, and analytical techniques.

The essential requirement for a lithologic unit to act as a seal for buried natural gas accumulations is that the minimum displacement pressure of the lithologic unit be greater than the buoyant pressure of the accumulated natural gas. Grunau (1981) reported that almost all of the world's 176 giant gas fields depended on shale or evaporate seals. Folding and faulting that can accompany the formation of structural traps can put strain on the sealing unit. Depending on the ductile nature of the sealing lithologic unit and degree of strain, fractures can develop and promote leakage.

One of the principal causes of pressure buildup in reservoirs is the buoyancy of the hydrocarbon phase (Matthews, 1996). The driving force of natural gas migration is the upward buoyant force caused by the contrast in density between natural gas components and water. According to Matthews (1996), the dominant mechanism of leakage through a reservoir seal is bulk flow due to buoyancy, although diffusion plays a role in reservoir loss. Further, the presence of mature hydrocarbons at the surface is indisputable proof that an active source rock exists in the subsurface.

Authors contributing to AAPG Memoir 66 (Schumacher and Abrams, 1996) and the attendees at AAPG's 1984 Hedberg Research Conference were in general agreement on the following conclusions related to hydrocarbon gas or fluids, as presented in the Preface to Memoir 66:

- Hydrocarbon accumulations are dynamic; seals are imperfect.
- All petroleum basins have some type of near-surface hydrocarbon leakage.
- Surface expression of leakage is not always detectable by conventional means.
- Hydrocarbon seepage can be active or passive, and it can be visible (macroseepage) or only detectable by chemical methods (microseepage).
- Seepage expression, whether active or passive, is a function of many factors other than the mere presence or absence of active hydrocarbon generation and migration.

- Migration occurs mainly vertically, but it can also occur laterally over long distances.
- Hydrocarbons can move vertically through thousands of meters of strata in a relatively short time (weeks to years) without observable faults or fractures.
- Relationships between surface geochemical anomalies and subsurface accumulation can be complex; proper interpretation requires integration of seepage data with geological, geophysical, and hydrological data.
- Mechanisms of hydrocarbon migration are still poorly understood. Present evidence favors effusion as the process of macroseepage and buoyancy of microbubbles as the mechanism for microseepage.

The degree to which gas is altered as it moves through the subsurface during migration is not completely understood, with disagreement evident in the published literature. The transport of hydrocarbons through an entire stratigraphic section has been largely ignored (Matthews, 1996). It is generally believed that hydrocarbon gases do not undergo isotope fractionation during migration (Whiticar, 1994; Coleman et al., 1977), and that mixtures of different gas types could cause similar isotopic effects. However, others have suggested that thermogenic gas in which higher carbon gas components have been preferentially removed during migration may occur in conjunction with a shift in carbon and hydrogen isotope values of methane due to advective and/or diffusive processes (Prinzhofer and Pernaton, 1997; Prinzhofer et al. 2000).

Microbial activity is known to alter the isotopic composition of methane as microbes preferentially consume isotopically lighter (^{12}C) methane, which leads to the enrichment of heavy (^{13}C) methane (i.e., more positive carbon isotope values in the residual gas). Biological activity can also lead to the preferential depletion of certain gas components with respect to others (Whiticar, 1994). Chemical and mechanical diffusion is expected to alter hydrocarbon composition as gas moves through the subsurface. Adsorption of migrating hydrocarbons onto the mineral substrate as it passes through can lead to selective removal of hydrocarbons or selective retardation of hydrocarbons (Matthews, 1996). Phase separation or partitioning can also occur with changes in pressure and temperature during migration (England, 1994).

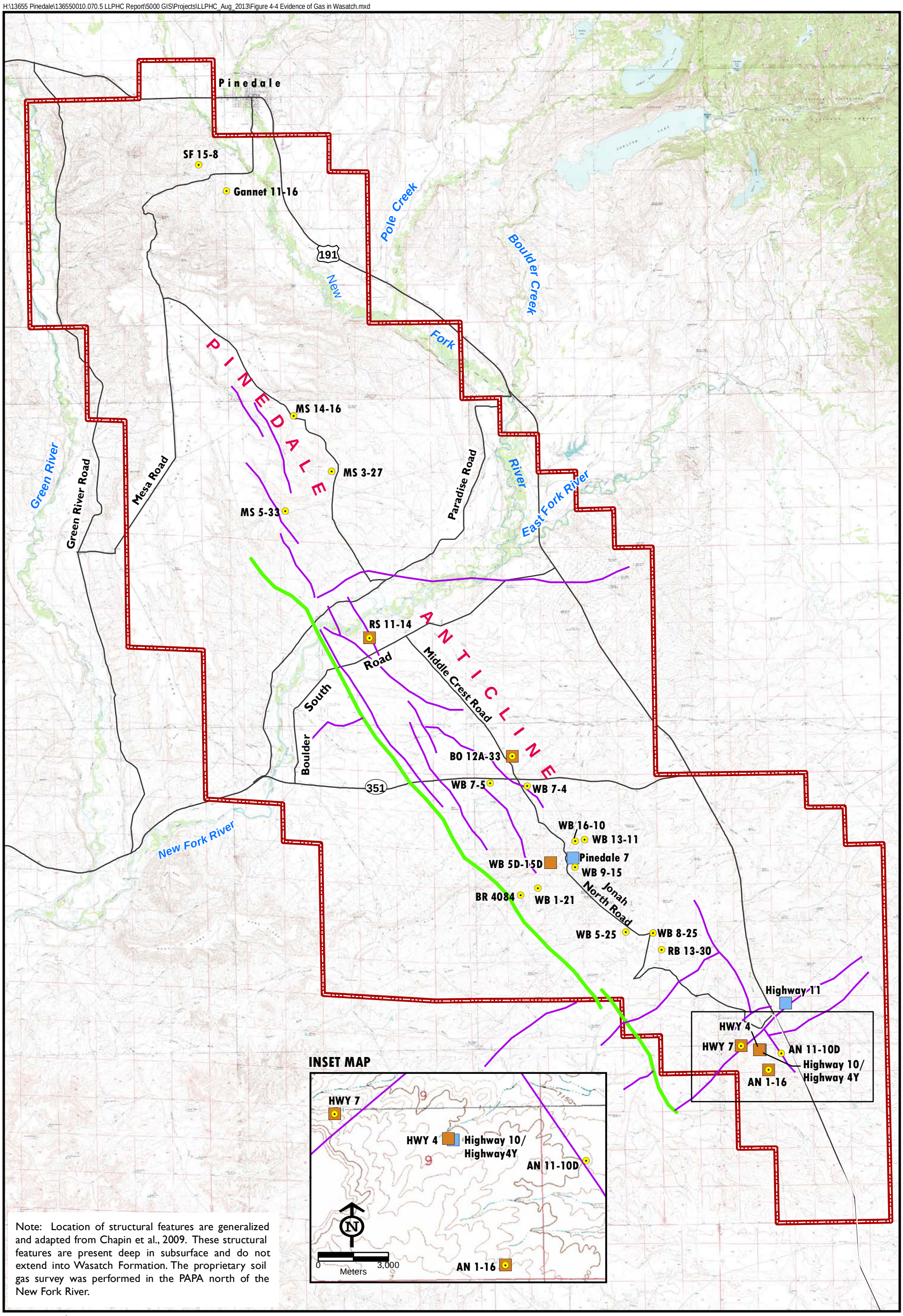
Numerous observations and other anecdotal information regarding the presence of hydrocarbon gas in the Tertiary Formations in the PAPA have been noted by others. Although none of these observations was made prior to the start of development in 1939, these observations were made prior to natural gas E&P activities in the immediate vicinity and include the following:

- A soil gas survey performed during 2003-2004 (prior to the SEIS) measured numerous hydrocarbons, including BTEX, normal alkanes, and branched alkanes, in the shallow subsurface (<12 feet) at several locations in the PAPA north of the New Fork River (proprietary document).

- Hydrocarbon gas was encountered at depths as shallow as approximately 185 feet in the Wasatch Formation, as documented on a driller's mud log while drilling the Highway 11 natural gas production well in 2001 (WOGCC, 2001).
- A letter report by the WOGCC documents hydrocarbon gas encountered while constructing the water supply well HWY 4 drilled in 2000 and presents analytical results of gas samples collected from a shallow gas well (Highway 10 drilled in 2002; total depth of 379 feet) (WOGCC, 2009a).
- A driller's mud log for the Highway 4Y natural gas production well drilled in 2000 documented a large gas show at a depth of 342 feet and a larger gas show (greater than 2,000 units) at a depth of 380 feet (WOGCC, 2009a).
- Searle Brothers Construction encountered hydrocarbon gas while drilling industrial water supply wells AN 1-16 and HWY 7 (prior to June 2003) at about 400 feet in depth. No water was encountered with the gas at AN 1-16 and the "gas burned the rig down" (WOGCC, 2009b). No natural gas production wells had been drilled yet at these pads.
- Searle Brothers Construction reported finding hydrocarbon gas when welding casing for industrial water supply wells RS 11-14 (drilled in 2003), BO 12A-33 (drilled in 2004), and WB 5D-15D (drilled in 2005). The depth of gas occurrence was not noted; however, these wells are installed to depths of 450 feet, 510 feet and 790 feet, respectively, in the Wasatch Formation. No natural gas production wells had been drilled yet on these pads (WOGCC, 2009b).
- A notation on the geologic completion report for the Pinedale 7 natural gas production well, which was installed in 1960, indicated that mud logging was commenced at a depth of 1,000 feet to evaluate for gas shows observed throughout the Wasatch Formation while drilling other natural gas wells in the Pinedale Anticline.

Locations where hydrocarbon gas was encountered at shallow depths in the PAPA while drilling natural gas production wells, constructing water supply wells, and screening well casings prior to groundwater sampling are shown on **Figure 4-4**. Based on these observations, it is plausible that hydrocarbon gas occurs naturally in the Tertiary Formations inside the PAPA.

H:\13655 Pinedale\136550010.070.5 LLPHC Report\5000 GIS\Projects\LLPHC_Aug_2013\Figure 4-4 Evidence of Gas in Wasatch.mxd



Note: Location of structural features are generalized and adapted from Chapin et al., 2009. These structural features are present deep in subsurface and do not extend into Wasatch Formation. The proprietary soil gas survey was performed in the PAPA north of the New Fork River.

N

0 Miles 3

amec

Methane Gas Detected in Well Casing by Well Samplers Prior to this Study

Gas Encountered or Monitored for in Wasatch Formation While Drilling Natural Gas Production Well by Operator

Methane Gas Encountered in Wasatch Formation While Drilling and Constructing Water Supply Well by Well Drilling Company

Structure - Bounding Reverse Fault

Smaller Faults

Pinedale Anticline Project Area

Observations of Gas Prior to Widespread Exploration and Production Activities in the Wasatch Formation
Low-Level Petroleum Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 4-4

5.0 ANALYTICAL RESULTS FOR POTENTIAL SOURCE MATERIALS

This section presents the results from sampling and analysis of potential source materials within the PAPA. A total of 34 representative samples of drill mud, natural gas condensate, produced water, flowback fluid, pump installation materials (e.g., pipe dope), LNAPL (i.e., free-phase material), and carbonaceous shale were collected and analyzed as part of implementing the SAP. The samples collected are listed in **Table 1**, and sampling methods are listed in **Table 2** and described in **Section 3.2.1**. Locations where samples were collected are shown on **Figure 3-1**.

Chemical testing results for various analytical groups are summarized in the following tables:

- **Table 3**: Volatile and Semivolatile Organic Fractions in Potential Source Material Samples;
- **Table 4**: Detected Volatile and Semivolatile Organic Compounds in Potential Source Material Samples;
- **Table 5**: Tentatively Identified Compounds in Potential Source Material Samples;
- **Table 6**: Total Metals in Potential Source Material Samples;
- **Table 7**: General Water Quality Parameters in Potential Source Material Samples; and
- **Table 8**: Isotopic Composition of Constituents in Groundwater, Produced Water, and Gas Samples.

The laboratory reports containing complete chemical testing results, including the testing and evaluation of the carbonaceous shale samples, are provided in **Appendix D**. The data validation and data quality review report is presented in **Appendix E**. Selected chromatograms from the TPH-GRO and TPH-DRO analyses for drill mud, condensate, produced water, flowback fluid, and selected pump installation samples (e.g., pipe dope) are included in **Appendix F**.

5.1 DRILL MUD

Three samples of oil-based, circulated drilling mud were collected and analyzed for volatile and semivolatile organic fractions, VOCs, SVOCs, and total metals (**Table 1**). Analytical results indicate that the samples are chemically similar, based on constituent concentrations, TICs reported in samples, and chromatogram responses. The results are summarized below.

5.1.1 Volatile and Semivolatile Organic Fractions in Drill Mud Samples

TPgH concentrations in the drill mud samples ranged from 170,000 to 223,000 milligrams per kilogram (mg/kg) (**Table 3**). Gasoline-range organics constituted less than 15 percent of the purgeable fraction, with concentrations ranging from 19,000 to 28,100 mg/kg. Most peaks in the

GRO chromatograms occur between a retention time of 16 and 24 minutes, which reflects the presence of volatile compounds in the diesel organics range (**Figures F-1** and **F-2** in **Appendix F**).

TEH concentrations in drill mud were slightly higher than TPgH concentrations, ranging from 249,000 mg/kg to 341,000 mg/kg. Diesel-range organics constitute greater than 95 percent of the TEH, with TPH-DRO concentrations ranging from 240,000 to 330,000 mg/kg. Peaks on the DRO chromatogram are mainly confined to the diesel range, with peaks concentrated between retention times of 6 minutes and 16 minutes (**Figures F-1** and **F-2** in **Appendix F**).

The appearance of the GRO and DRO chromatograms for the drill mud samples are quite similar (**Figures F-1** and **F-2** in **Appendix F**). The drill muds sampled for this study are diesel-based materials, and the chromatographic profiles in both the GRO and DRO chromatograms are consistent with diesel-based substances. Diesel and other middle distillates contain hydrocarbons that are primarily in the diesel organics range as defined by the method, with a smaller portion of material in the gasoline organics range. Although the analyses indicate a response in the gasoline organics range, no "gasoline" is present in the drill mud samples.

5.1.2 Volatile and Semivolatile Organic Compounds in Drill Mud Samples

Ethylbenzene, toluene, and xylenes were the only VOCs detected above the reporting limit in drill mud (**Table 4**). Concentrations ranged from 35 mg/kg toluene in RIV 4-10 MUD to 591 mg/kg total xylenes in JEN 1A MUD.

The individual SVOCs detected in drill mud, as well as the magnitude of SVOC concentrations, were relatively consistent between samples. The SVOCs detected in drill mud included:

- naphthalene;
- 1- and 2-methylnaphthalenes;
- phenanthrene; and
- pyrene.

Naphthalenes were detected at the highest concentrations (greater than 100 mg/kg) (**Table 4**). Phenanthrene and pyrene concentrations were roughly an order of magnitude lower than the concentrations of naphthalenes.

The total number of TICs reported in individual drill mud samples ranged from 26 (MS 12-16 MUD) to 41 (RIV 4-10 MUD) (**Table 5**). **Chart 5-1** presents the number of TICs reported from the respective chemical groups for each drill mud sample.

Chart 5-1 Number of TICs Reported in Drill Mud Samples by Chemical Group

TIC Chemical Group	Number of TICs		
	MS 12-16 MUD	RIV 4-10 MUD	JEN 1A MUD
Alkanes	11	13	14
Branched Alkanes	2	8	4
Alkylcycloalkanes	0	2	3
Alkylbenzenes	3	10	4
Indans/Indanes/Indenes	1	1	1
Naphthalenes	2	0	0
Decalins	1	3	0
Tetralins	6	4	5

The presence of numerous tetralins (i.e., tetrahydronaphthalenes) was characteristic of drill muds. No cycloalkanes, alkenes, branched alkenes, or cycloalkenes were reported in the drill mud samples.

5.1.3 Total Metals in Drill Mud Samples

Metals that were detected in drill mud samples included aluminum, barium, calcium, chromium, copper, iron, magnesium, manganese, nickel, potassium, silicon, sodium, strontium, titanium, and vanadium. Chromium, nickel, titanium, and vanadium were detected at concentrations equal to or just above the reporting limit of 5 mg/kg. Metals concentrations (total) detected in drill mud samples are listed in **Table 6**, and the ranges of concentrations for selected metals are summarized in **Chart 5-2**.

Chart 5-2 Range of Total Metals Concentrations in Drill Mud Samples

Total Metals	Concentration Range (milligrams per kilogram)
Aluminum	1,820 – 1,940
Barium	3,110 – 3,460
Calcium	22,400 - 32,400
Copper	13 - 33
Iron	2,180 – 2,420
Magnesium	806 - 1,750
Manganese	75 - 94
Potassium	559 - 804
Silicon	295 – 316
Sodium	409 - 937
Strontium	79 – 165

5.2 NATURAL GAS CONDENSATE

The natural gas condensate sample was analyzed for volatile and semivolatile organic fractions, VOCs, and SVOCs. The chemical composition of natural gas condensate, the TICs reported in the sample, and chromatogram responses are summarized below.

5.2.1 Volatile and Semivolatile Organic Fractions in Condensate Sample

The TPgH concentration in the condensate sample was 835,000 mg/kg, with gasoline-range organics (627,000 mg/kg TPH-GRO) comprising 75 percent of the reported TPgH (**Table 3**). The GRO chromatogram for the condensate sample is characterized by a spiky appearance due to the presence of alkanes (**Figure F-2** in **Appendix F**).

The TEH concentration in the condensate sample was 955,000 mg/kg, with diesel-range organics (373,000 mg/kg TPH-DRO) comprising only 40 percent of the reported TEH. The profile of the DRO chromatogram also has a spiky appearance; however, peaks are confined to the early retention time portion of the chromatogram (approximately 2 to 16 minutes, prior to the boiling point for C_{28} compounds).

5.2.2 Volatile and Semivolatile Organic Compounds in Condensate Sample

All BTEX constituents were detected in the condensate sample, and these were the only VOCs detected in this potential source material (**Table 4**). Toluene and total xylenes were the BTEX constituents detected at the highest concentrations, 33,400 and 41,500 mg/kg, respectively. Naphthalenes (i.e., naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene) were the only SVOCs detected in the condensate sample (**Table 4**). The naphthalene detected at the highest concentration was 2-methylnaphthalene (1,630 mg/kg).

Fifty-three TICs were reported in the condensate sample from the chemical groups listed in **Chart 5-3**. Condensate had the highest number of TICs reported over the smallest number of chemical groups among the source material samples. The condensate sample is characterized by numerous alkanes (C_4 through C_{21}), branched alkanes (C_4 through C_{12}, predominantly with single methyl groups), and numerous cycloalkanes (C_4 to C_6) and alkylbenzenes with multiple substitutions (e.g., dimethyl- and trimethyl-). No indan/indane/indene compounds nor naphthalenes (including decalins or tetralins) were reported in the condensate sample (**Table 5**).

Chart 5-3 Number of TICs Reported in Condensate Sample by Chemical Group

TIC Chemical Group	Number of TICs
Alkanes	17
Branched Alkanes	14
Cycloalkanes	1
Alkylcycloalkanes	14
Alkylbenzenes	7

5.3 PRODUCED WATER

Produced water samples were analyzed for volatile and semivolatile organic fractions, VOCs, SVOCs, total metals, other inorganic parameters, and isotopic composition (**Table 1**). The chemical composition of the samples, the TICs reported in samples, the chromatogram responses, and the results of isotopic analyses are summarized below.

5.3.1 Volatile and Semivolatile Organic Fractions in Produced Water Samples

TPgH concentrations in produced water samples ranged from 105 to 398 mg/L, with gasoline-range organics (102 to 362 mg/L TPH-GRO) comprising more than 90 percent of the reported TPgH. GRO chromatograms for produced water samples are characterized by a few distinct, relatively large peaks (**Figures F-3, F-4,** and **F-5** in **Appendix F**) that likely correspond to the peaks for benzene, toluene, ethylbenzene, and xylenes in the mass spectrometry chromatograms. The numerous smaller peaks at later retention times (16 to 22 minutes) on the GRO chromatograms likely correspond to the presence of volatile compounds in the diesel organics range.

Concentrations of semivolatile organics in produced water samples were more variable compared to other potential source materials sampled. TEH concentrations varied by more than three orders of magnitude across the samples collected, ranging from 48 to 44,400 mg/L (**Table 3**). The percentage of reported TEH in the diesel organics range varied from approximately 40 to 75 percent (19 to 17,100 mg/L TPH-DRO). This variation may be attributed to the degree of separation achieved by the oil/water separator at the drill pad.

Similar to the condensate samples, the DRO chromatograms for the produced water samples have a spiky appearance (**Figures F-3**, **F-4,** and **F-5** in **Appendix F**). Peaks in the DRO chromatograms are confined to the earlier retention time portion of the chromatogram, with most peaks occurring from approximately 4 to 12 minutes (prior to the boiling point for C_{20} compounds).

5.3.2 Volatile and Semivolatile Organic Compounds in Produced Water Samples

All BTEX constituents were detected in the produced water samples; these were the only VOCs detected above laboratory reporting limits in the samples (**Table 4**). Benzene and toluene were the VOC constituents detected at the highest concentrations in produced water samples, with maximum concentrations of 45.2 mg/L for benzene and 80.7 mg/L for toluene. Among the detected VOC constituents, ethylbenzene was detected at the lowest concentration in produced water (ranging from 0.552 to 1.86 mg/L).

SVOCs detected in produced water included:

- 2-4-dimethylphenol;
- phenol;
- naphthalene, 1-methylnapthalene, and 2-methylnapthalene;
- fluorene;
- cresols (m- and p-, o-); and
- phenanthrene.

SVOC concentrations varied only slightly among the produced water samples; moreover, the same SVOC compounds were detected among most of the samples. SVOC concentrations were generally below 1 mg/L in produced water samples, except for sample RS 15-12 PW, in which all three naphthalene constituents were each detected at concentrations greater than 1 mg/L (**Table 4**).

5.3.3 Tentatively Identified Compounds in Produced Water Samples

The number of TICs identified in produced water samples ranged from 35 (AN 1-9 PDW) to 53 (MS 14-16 PDW), and were relatively consistent among chemical groups (**Table 5**). **Chart 5-4** summarizes the number of TICs reported from each chemical group for each sample.

Chart 5-4 Number of TICs Reported in Produced Water Samples by Chemical Group

Chemical Group	Number of TICs in Produced Water Samples					
	AN 1-9 PW	RB 16-30 PW	WB 7-15 PW	RS 15-12 PW	MS 14-16 PDW	SP 13-33 PDW
Ketones	1	1	0	0	0	2
Alcohols	0	0	0	0	1	0
Alkanes	16	14	16	15	18	16
Branched Alkanes	3	7	5	8	13	10
Cycloalkanes	2	2	1	1	2	1
Alkylcycloalkanes	3	5	3	4	9	5
Alkylbenzenes	9	9	9	11	10	9
Tetralins	1	1	2	2	0	1

The produced water samples are characterized by numerous alkanes (C_5 through C_{23}), cycloalkanes and alkylcycloalkanes (C_4 to C_6), and branched alkanes (C_4 through C_{14}) and alkylbenzenes with multiple substitutions. Non-hydrocarbon TICs, ketones and an alcohol, were reported in some produced water samples. Cyclopentanone was reported in produced water samples SP 13-33 PDW, AN 1-9 PW, and RN 16-30 PW, and 2-methylcyclopentanone was reported in SP 13-33 PDW. One alcohol, 2-butoxyethanol, was reported in MS 14-16 PDW.

5.3.4 Total Metals in Produced Water Samples

Metals were detected in all produced water samples. The ranges of detected concentrations for selected metals are summarized in **Chart 5-5**.

The metal detected at the highest concentration was sodium. Aluminum, arsenic, copper, lead, mercury, and nickel were detected in some, but not all, produced water samples (**Table 6**).

Chart 5-5 Range of Total Metals Concentrations in Produced Water Samples

Total Metals	Concentration Range (milligrams per liter)
Barium	15.6 - 30.9
Boron	4 – 7.0
Calcium	35 - 129
Iron	5.84 – 60.6
Magnesium	6 – 15
Manganese	0.32 – 0.67
Potassium	25 – 115
Sodium	3,280 - 4,670
Silicon	27 - 52
Strontium	5.1 – 12.3

5.3.5 General Water Quality Parameters in Produced Water Samples

Produced water is characterized by high concentrations of TDS (8,190 to 12,000 mg/L) and chloride (5,030 to 6,880 mg/L). Produced water is predominantly a sodium-chloride water type. Bromide concentrations ranged from 66 to 123 mg/L; fluoride concentrations ranged from 1.0 to 1.2 mg/L **(Table 7**). General water quality parameters were generally consistent among produced water samples, with the following exceptions. The nitrate+nitrite concentration in produced water sample RS 15-12 PW sample was 7 mg/L, whereas low concentrations (less than 0.5 mg/L) of nitrate+nitrite were detected in the other produced water samples. Ammonia and total phosphorus were not detected in RS 15-12 PW; ammonia and total phosphorus concentrations ranged from 4.8 to 7.8 mg/L and 1.6 to 10.6 mg/L, respectively, in the other produced water samples.

5.3.6 Isotopes in Produced Water Samples

Hydrogen isotope values in five of the six produced water samples ranged from -70.5 to -64.6 per mil, and oxygen isotope values in these same samples ranged from -2.17 to -0.34 per mil. One outlier appeared in the produced water isotope data set. The hydrogen and oxygen isotope values for the produced water sample from the MS 14-16 pad were -137.0 and -6.87 per mil, respectively (**Table 8**). Carbon isotope values of dissolved inorganic carbon varied over a narrow range for all six of the produced water samples (-1.65 to 1.16 per mil) (**Table 8**).

5.4 FLOWBACK FLUID

Flowback fluid samples were analyzed for volatile and semivolatile organic fractions, VOCs, SVOCs, total metals, and inorganic constituents. The concentrations of analyzed constituents varied between the flowback fluid samples. These variations are likely related to the chemical makeup of the hydraulic fracturing fluid used and the duration of time that flowback had been occurring when the samples were collected. The composition of hydraulic fracturing fluid generally varies based on chemicals used to prepare the fluid, as well as the type of water used to prepare the fluid (e.g., fresh water, recycled water, or produced/flowback water). The composition of flowback fluid varies based on the properties of the hydraulic fracturing fluid used and the amount of formation fluid (i.e., produced water) that is flowing back from the well.

Formation fluids comprise an increasing percentage of flowback fluid over time as flowback of the gas well proceeds. Thus, the signature of the flowback fluid may resemble the signature of produced water depending on the type of hydraulic fracturing fluid used and the time elapsed since flowback began when collecting the sample. The time elapsed since flowback began and the type of hydraulic fracturing fluid employed for each flowback fluid sample collected are provided in **Table B-1** of **Appendix B.** The chemical composition of flowback fluid sampled, the TICs reported in samples, and chromatogram responses are summarized below.

5.4.1 Volatile and Semivolatile Organic Fractions in Flowback Fluid Samples

A wide range in TPgH concentrations (12.4 mg/L to 236 mg/L) was observed in the flowback fluid samples collected in the PAPA. This variability is mirrored by the range in TPH-GRO concentrations (9.0 mg/L to 125 mg/L) (**Table 3**). The percentage of reported TPgH that is made up of gasoline-range organics does not appear to be related to the magnitude of the TPgH concentration. GRO chromatograms for flowback fluid are presented in **Figures F-6** and **F-7** in **Appendix F**. The chromatograms exhibit a few single peaks earlier in retention time (less than 16 minutes) that appear to correspond with signals for BTEX compounds identified on the mass spectrometry chromatograms (**Appendix D**). A cluster of peaks occurring at retention times of approximately 16 to 24 minutes in the GRO chromatograms appear to correspond to volatile constituents in the diesel range.

Similar to the volatile organics, a wide range in TEH concentrations (26 to 5,080 mg/L) was observed in samples of flowback fluid, which is mirrored by the range in TPH-DRO concentrations (12 to 4,850 mg/L). Flowback fluid samples with a higher TEH concentration (greater than 1,000 mg/L) tended to also have a higher percentage of TPH-DRO. Samples of flowback fluid with higher concentrations of semivolatile organics were collected from wells where slick water hydraulic fracturing techniques were reportedly employed (MSD2-21 FBF and MS3C-33D FBF).

The DRO chromatograms from different flowback fluid samples tend to vary more than the GRO chromatograms, likely due to the type of hydraulic fracturing fluid used and the time elapsed since the start of flowback when samples were collected. The DRO chromatogram for MS3C-33D FBF shows a tight, broad peak between a retention time of 6 and 14 minutes, which is typical of a "diesel" type signature (**Appendix F, Figure F-6**). The DRO chromatogram for MSD2-21 FBF is similar to that for MS3C-33D FBF; however, the peaks have a lower response, and more tailing is evident beyond a retention time of 14 minutes (**Appendix F, Figure F-6**). The DRO chromatograms for MS 3-27 FBF and RS 9-2 FBF (**Appendix F, Figure F-7**) are different from the chromatograms for the other two samples in that several individual broad peaks are noted before a retention time of 6 minutes. These broad peaks are often indicative of highly polar compounds, such as glycols or phenols.

5.4.2 Volatile and Semivolatile Organic Compounds in Flowback Fluid Samples

The VOCs detected above the reporting limits in flowback fluid samples included the BTEX constituents and methyl ethyl ketone. BTEX compounds were detected in the four flowback fluid samples at concentrations ranging from 0.063 mg/L of ethylbenzene in sample MS 3-27 FBF to 31.7 mg/L total xylenes in RS 9-2 FBF. Detected concentrations were greatest in sample RS 9-2 FBF, with a minimum concentration of 2.10 mg/L of ethylbenzene. The BTEX concentrations were higher in the flowback fluid sample collected after the longest duration (36 hours) of flowback (RS 9-2 FBF) than in samples collected earlier in the flowback process (MS 3-27 FBF, MS3C-33D FBF, and MSD2-21 FBF), which is likely attributable to the greater amount of formation fluid (i.e., produced water) in sample RS 9-2 FBF compared to the other samples (**Table 4**). Methyl ethyl ketone was detected in two of the four flowback fluid samples at concentrations of 0.119 and 0.206 mg/L (**Table 4**).

The SVOCs detected in flowback fluid above laboratory reporting limits included:

- naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene;
- 2,4-dimethylphenol;
- phenol;
- cresols (m&p- and o-); and
- bis(2-ethylhexyl) phthalate.

The types and concentrations of SVOCs detected varied between samples (**Table 4**). Naphthalenes were detected in all flowback fluid samples. Concentrations of naphthalene constituents ranged between 2.10 mg/L and 5.98 mg/L in sample MSD2-21 FBF, but were all below 1 mg/L in samples RS 9-2 FBF, MS3-27-FBF, and MS3C-33D FBF. No other SVOCs were detected in samples MS3C-33D FBF and MSD2-21 FBF (**Table 4**). Detected SVOCs were mostly limited to naphthalenes in samples from wells where slick water hydraulic fracturing techniques were likely used (samples MSD2-21 FBF and MS3C-33D FBF), whereas cresols, phenols, and naphthalenes were detected in samples from wells where only cross-linked gels were likely employed (samples RS 9-2 FBF and MS 3-27 FBF) (**Table 4**; **Table B-1** of **Appendix B**). However, this finding may be an artifact of the variability in sample dilutions and the elevated report limits in some of the samples, rather than reflecting differences in the hydraulic fracturing fluid used.

5.4.3 Tentatively Identified Compounds in Flowback Fluid Samples

TICs from a wide variety of chemical groups were reported in the four flowback fluid samples. Samples were also characterized by varying numbers of reported TICs, which ranged from 22 (MS 3-27 FBF) to 77 (MSD2-21 FBF) (**Table 5-3**). **Chart 5-6** summarizes the number of TICs reported from each chemical group for each flowback fluid sample.

Chart 5-6 Number of TICs Reported in Flowback Fluid Samples by Chemical Group

Chemical Group	Number of TICs in Flowback Fluid Samples			
	RS 9-2 FBF	MS3-27-FBF (MS15C2-22D)	MS3C-33D FBF	MSD2-21 FBF
Acids	1	1	0	0
Alcohols	0	3	0	1
Ketones	0	3	0	2
Phenols	2	0	0	0
Alkanes	13	2	7	23
Branched Alkanes	9	2	3	24
Alkenes	1	1	0	0
Branched Alkenes	0	0	0	1
Cycloalkanes	1	1	0	2
Alkylcycloalkanes	7	1	2	10
Cycloalkenes	2	0	0	2
Alkylbenzenes	8	6	14	8
Naphthalenes	1	1	0	3
Decalins	0	1	0	0
Tetralins	1	0	3	1

The flowback fluid samples were characterized by a greater number of non-hydrocarbon TICs (e.g., acids, alcohols, ketones, and phenols) reported compared to other potential source materials. Compounds that are typical of refined petroleum products, such as alkenes, branched alkenes, and cycloalkenes, were also reported in flowback fluid samples (**Table 5**). The branched alkanes, alkylcycloalkanes, and alkylbenzenes reported for these samples typically have multiple substitutions. Naphthalenes, decalins, and tetralins were also tentatively identified in one or more samples of flowback fluid.

The same formulation of hydraulic fracturing fluid was used at both gas well pads where samples RS 9-2 FBF and MS3-27-FBF were collected. Thus, the difference in the number of TICs reported between samples, as well as in the magnitude of organic constituent concentrations, is likely attributable to the amount of time that had elapsed since flowback began when samples were collected. Sample MS3-27-FBF was collected 45 minutes after flowback began, whereas sample RS 9-2 FBF was collected 36 hours after flowback began.

More alkanes, branched alkanes, alkylcycloalkanes, cycloalkanes, and alkylbenzenes were tentatively identified in sample RS 9-2 FBF, which is likely due to the greater proportion of formation fluid in the flowback fluid as this process proceeds.

5.4.4 Total Metals in Flowback Fluid Samples

Metals detected above their respective reporting limits in all flowback fluid samples included aluminum, arsenic, barium, boron, calcium, chromium, iron, magnesium, manganese, nickel, potassium, silicon, sodium, and strontium (**Table 6**). These metals were detected in flowback fluid samples at the ranges of concentrations listed in **Chart 5-7**.

5.4.5 General Water Quality Parameters in Flowback Fluid Samples

Similar to produced water, flowback fluid is predominantly characterized as sodium-chloride water type with high concentrations of TDS (9,450 to 13,900 mg/L) and chloride (5,750 to 7,520 mg/L) (**Table 7**). Bromide concentrations ranged from 49 to 133 mg/L; fluoride concentrations ranged from 1.1 to 1.4 mg/L. Ammonia concentrations (8.4 to 18 mg/L) exceeded nitrate+nitrite concentrations (0.1 to 0.7 mg/L) by more than an order of magnitude in flowback fluid samples.

Chart 5-7 Range of Total Metals Concentrations in Flowback Fluid Samples

Metals in Flowback Fluid	Total Concentration Range (milligrams per liter)
Aluminum	0.3 – 4.8
Arsenic	0.027 – 0.069
Barium	12.4 – 44
Boron	5.9 – 64
Calcium	137 – 1,050
Chromium	0.02 – 0.29
Iron	22.1 – 63.8
Magnesium	15 – 83
Manganese	0.48 – 0.96
Nickel	0.02 – 0.14
Potassium	33 – 98
Silicon	32.8 – 48.0
Sodium	3,930 – 4,870
Strontium	11.2 – 13.0

5.5 PUMP INSTALLATION MATERIALS

Samples of materials associated with pump installations (i.e., pipe dope, pipe grease, black film, Teflon tape) were analyzed for volatile and semivolatile organic fractions, VOCs, and SVOCs. Chemical characteristics varied only slightly among the sampled materials. The chemical composition of samples of pipe dope taken fresh from the container (PD Baseline) was similar to that of samples of used pipe dope (e.g., removed from pipe threads). The chemical composition of the samples, the TICs reported in samples, and chromatogram responses are summarized below. Volatile and semivolatile organic constituents were detected in all pump installation material samples, except for the two samples of black film. Detected TPgH, TPH-GRO, and VOC concentrations are considered estimated because the holding times at the laboratory prior to analysis exceeded quality control criteria (**Tables 3** and **4**; see data quality review in **Appendix E**).

5.5.1 Volatile and Semivolatile Organic Fractions in Samples of Pump Installation Materials

TPgH was detected in 12 samples of pump installation materials. The detected concentrations ranged from 28 to 2,340 mg/kg. Only half of the samples with detectable TPgH (6 of 12 samples) also had detectable levels of TPgH as gasoline-range organics (35 to 196 mg/kg TPH-GRO). Generally, few to no peaks are present on the GRO chromatograms for samples of pump

installation materials (**Figures F-8** and **F-9**, **Appendix F**). A broad complex of peaks centered on a retention time of 21 to 22 minutes is present on some of the GRO chromatograms (e.g., pipe dope sample BO 1-32-1; **Figure F-8**, **Appendix F**), which is likely representative of volatile components in the diesel range.

TEH was detected in all samples except the black film samples. Detected concentrations generally exceeded TPgH concentrations by two orders of magnitude or more. TEH concentrations also varied among samples by an order of magnitude or more, ranging from 6,170 mg/kg to 343,000 mg/kg (**Table 3**). Diesel-range organics constituted approximately 20 to 40 percent of TEH in samples of pump installation materials. When detected, TPH-DRO concentrations ranged from 1,350 to 107,000 mg/kg. DRO chromatograms for pipe dope samples are typically characterized by a baseline hump of unspecified material, frequently referred to as an unresolved complex mixture (UCM) (**Figures F-8** and **F-9** in **Appendix F**). A UCM-type signature is typical of biodegraded petroleum, uncombusted petroleum, lubricating oils, or asphalts (Stout and Wang, 2008). The UCM in the chromatograms for pump installation materials, particularly pipe dope, is likely related to the chemical makeup of the material itself, which is more typical of lubricating oil.

DRO chromatograms for the pipe dope samples generally display one of two types of responses:

- A broad cluster of peaks at retention times ranging between 10 and 28 minutes, with the highest response observed at 17 minutes (corresponding to C_{29} and C_{30} compounds) (**Figure F-8** in **Appendix F**); and
- A similar broad cluster of peaks, but punctuated with more distinct peaks at retention times of roughly 17.8, 18.5, 19.3, 20.3, 21.6, 23.2, 25.5, and 28.2 minutes (±0.5 minute) (**Figure F-9** in **Appendix F**).

The latter type of DRO chromatogram is consistent with the chromatogram for the "environmentally safe" pipe dope sample (PD-Baseline) recently employed by pump installation contractors in the PAPA.

5.5.2 Volatile and Semivolatile Organic Compounds in Samples of Pump Installation Materials

VOCs were detected above laboratory reporting limits in only 2 of the 17 samples of pump installation materials (WB 7-15-Pump and Riverside 1-4-Pump). Xylenes (m- and p-) were detected at low concentrations (less than 2 mg/kg) in these samples. The xylenes in the Riverside 1-4-Pump sample may be related to the grease that was observed with the pipe dope when collecting the sample.

Two phthalate compounds, bis(2-ethylhexyl) phthalate and di-n-octyl phthalate, were detected at concentrations of 37 and 54 mg/kg, respectively, in a sample of pipe dope (Riverside 1-4-Pump) (**Table 4**). No other SVOCs were detected above reporting limits in any samples of pump

installation materials. The phthalate detections may not be attributable to the presence of plasticizers in the pipe dope itself, but instead represent contamination from gloves used during sample collection, or plasticizers in the containers used to store the pipe dope prior to application.

5.5.3 Tentatively Identified Compounds in Samples of Pump Installation Materials

TICs were reported in 10 of the 17 samples of pump installation materials, with relatively few TICs reported in these samples as compared to other samples of potential source materials (**Table 5**). TICs were not reported in the following pipe dope samples: WB 16-5 Pump, WB 16-5 Pump 2, WB 7-5-2, MS 12-28-1, MS 12-28-2, MS 15-16-1, and MS 15-16-2. Peaks were observed at late retention times on the mass spectrometry chromatogram for several samples. However, the spectra could not be matched to spectra for known reference compounds.

5.6 LIGHT NONAQUEOUS-PHASE LIQUID

The LNAPL sample was analyzed for volatile and semivolatile organic fractions, VOCs, SVOCs, and total metals. The chemical composition of the LNAPL sample, the TICs reported in the sample, and chromatogram responses are summarized below.

5.6.1 Volatile and Semivolatile Organic Fractions in the Light Nonaqueous-Phase Liquid Sample

The LNAPL sample was characterized by high concentrations of TEH (906,000 mg/kg) and TPgH (127,000 mg/kg) (**Table 3**). Approximately 80 percent of the TEH falls within the diesel range (717,000 mg/kg TPH-DRO), whereas only 2 percent of the TPgH falls within the gasoline range (2,780 mg/kg TPH-GRO).

The DRO chromatogram for the LNAPL sample displays a UCM-type signature, characterized by a broad complex of peaks at retention times between 7 and 22 minutes (**Figure F-10** in **Appendix F**). The apex of the response in the DRO chromatogram is observed between 10 and 11 minutes. The GRO chromatogram for the LNAPL sample is characterized by a cluster of peaks at late retention time (18 to 24 minutes), which corresponds to the broad cluster of peaks observed between 7 and 22 minutes in the DRO chromatogram.

5.6.2 Volatile and Semivolatile Organic Compounds in the Light Nonaqueous-Phase Liquid Sample

No VOCs or SVOCs were detected above the laboratory reporting limits in the sample of LNAPL (**Table 4**).

5.6.3 Tentatively Identified Compounds in the Light Nonaqueous-Phase Liquid Sample

Seventeen TICs were reported in the LNAPL sample, as summarized in **Chart 5-8**.

Chart 5-8 Number of TICs Reported in LNAPL Sample

Chemical Group	Number of TICs
	AN 1-16 PHC
Ketones	2
Branched Alkanes	3
Cycloalkanes	1
Alkylcycloalkanes	1
Decalins	2
Terpenoids	8

The presence of numerous terpenoids, including adamantane compounds, but absence of straight-chain alkanes is characteristic of this sample.

5.6.4 Total Metals in the Light Nonaqueous-Phase Liquid Sample

Iron (20 mg/kg), sodium (73 mg/kg), and silicon (33 mg/kg) were the only metals detected in the LNAPL sample (**Table 6**). All other metals were below laboratory reporting limits.

5.7 CARBONACEOUS SHALE

The results of the thermal maturity assessment with respect to percent kerogen type, the thermal alteration index (TAI), and vitrinite reflectance values for the two carbonaceous shale samples are summarized in **Chart 5-9**.

Chart 5-9 Summary of Thermal Maturity Analyses

	Kerogen Type (%)				Thermal Maturity		
	Amorphous		Structured			Vitrinite Reflectance Value	
Sample ID	Fluorescent	Non-Fluorescent	Exinite	Vitrinite	TAI	Mean	Mode
T-3-SW	---	95	trace	5		---	---
T-4-RW-b	---	20	5	75	2.2-2.4	0.41	0.36

Intertek concluded that the two samples of carbonaceous shale were immature and had not reached the initial stages of hydrocarbon generation (**Appendix D**). The organic material in the carbonaceous shale drill cuttings from study well T-3-SW consisted primarily of non-fluorescent amorphous material, which is generally not a good source for hydrocarbons. The small amount of vitrinite present in the sample was judged to be reworked (non-indigenous, or not originally part of the parent sample) and therefore not representative of the maturity of the sample. The TAI

suggests that the sample is low maturity and has not reached the initial stages of hydrocarbon generation.

The organic material in carbonaceous shale drill cuttings collected from study well T-4-RW-b is primarily vitrinite with a smaller amount of non-fluorescent amorphous material. While not generally a good source for liquid hydrocarbons, it may represent a potential source for gas. However, the maturity based on the TAI and the vitrinite reflectance values was consistent, which suggests that the sample is of low maturity and has not reached the initial stages of hydrocarbon generation.

Thus, it is unlikely that the gas observed in groundwater at the wells is thermogenic gas generated in situ from the organic matter present in sediments of the Wasatch Formation. This analysis does not rule out the possibility that microbial gas could be generated in situ from organic matter present in these sediments.

5.8 POTENTIAL SOURCE MATERIAL DISTINCTION

All samples of potential source materials are hydrocarbon based. Thus differentiating between the samples involves looking at the types of hydrocarbons detected, the magnitude of hydrocarbon detection(s), and the proportions of the different organic compounds and fractions detected. Chemical characteristics of potential source materials are differentiated in this section with respect to inorganic and organic constituents (where applicable). Indicators that can be used to distinguish between the potential source materials are summarized in **Table 9**.

5.8.1 Inorganics

Inorganic constituents, which include basic anions (alkalinity, chloride, fluoride, sulfate), nitrogen compounds, total phosphorus, TDS, and total metals, were not analyzed in all potential source materials based on the target analytes specified in the SAP. The inorganic constituents in different potential source material samples were evaluated to assess whether these constituents could be used as potential indicators for that source material.

5.8.1.1 *General Water Quality Parameters*

Chart 5-10 summarizes the range of concentrations of general water quality parameters in produced water and flowback fluid samples. These potential inorganic indicators are likely not distinct enough from one another to distinguish between a potential impact in groundwater from produced water versus flowback fluid.

5.8.1.2 *Total Metals*

The range in concentrations of metals that were elevated in drill mud, flowback fluid, and/or produced water samples are summarized in **Chart 5-11**.

Chart 5-10 Range of Concentrations of General Water Quality Parameters in Produced Water and Flowback Fluid Samples

Analyte	Produced Water	Flowback Fluid
	milligrams per liter[1]	
Total Alkalinity (as $CaCO_3$)	423 – 767	600 – 972
Bicarbonate	516 – 936	732 – 1,190
Carbonate	ND	ND
Bromide	66 – 123	49 – 133
Chloride	5,030 – 6,880	5,750 – 7,520
Fluoride	1.0 – 1.2	1.1 – 1.4
Sulfate	ND	<50 – 289
Ammonia as Nitrogen	<5 – 7.8	8.4 – 18
Nitrate +Nitrite as Nitrogen	0.07 – 7	0.1 – 0.7
Total Phosphorus	<5 – 10.6	0.27 – 2.26
Total Dissolved Solids	8,190 – 12,000	9,450 – 13,900

[1] ND = not detected in any sample.
< indicates analyte not detected at the indicated reporting limit.

Chart 5-11 Range of Elevated Total Metals Concentrations in Flowback Fluid Samples

Metal	Drill Mud	Produced Water	Flowback Fluid
	mg/kg	milligrams per liter	
Aluminum	1,820 – 1,940	<0.1 – 0.1	0.3 – 4.8
Barium	3,110 – 3,460	15.6 – 30.9	12.4 – 44
Boron	ND	4 – 7	5.9 – 64
Calcium	22,400 – 32,400	35 – 129	137 – 1,050
Chromium	6	<0.01 – 0.04	0.02 – 0.29
Copper	13 – 33	<0.01 – 0.07	<0.01 – 2.44
Iron	2,180 – 2,420	5.84 – 60.6	22.1 – 63.8
Magnesium	806 – 1,750	6 – 15	15 – 83
Manganese	75 – 94	0.32 – 0.67	0.48 – 0.96
Potassium	559 – 804	25 – 115	33 – 98
Silicon	295 – 316	27 – 52	32.8 – 48
Sodium	409 – 937	3,280 – 4,670	3,930 – 4,870
Strontium	79 – 165	5.1 – 12.3	11.2 – 13
Titanium	9 – 13	ND	<0.01 – 0.06
Vanadium	4 – 5	ND	ND

ND = not detected in any sample; mg/kg = milligrams per kilogram.
< indicates analyte not detected at the indicated reporting limit.

With the exception of boron and sodium, metals were detected at higher concentrations in drill mud samples compared to flowback fluid or produced water samples. Barium, calcium, iron, magnesium, potassium, silicon, and strontium concentrations were elevated in all of the above-listed potential source materials, albeit more so in drill mud; thus, differentiation between groundwater impacts from these potential source materials based on metals concentrations alone may be difficult.

Drill mud contains elevated concentrations of aluminum, chromium, copper, manganese, titanium, and vanadium with respect to produced water and flowback fluid. Produced water and flowback fluid contain elevated concentrations of boron and sodium; but again, the presence of these metals at elevated concentrations in groundwater would not allow us to differentiate between an impact from produced water versus flowback fluid.

If inorganic constituents are detected at significantly elevated concentrations in groundwater samples with respect to what is typical in groundwater, these constituents could be used to narrow down the list of potential source materials that might be influencing groundwater quality (**Table 9**). However, an approach using multiple lines of evidence is needed to conclusively identify the potential source material, which would mean the incorporation of one or more organic indicators.

5.8.2 Organics

Organic constituents analyzed included volatile and semivolatile organic fractions (i.e., TPH-GRO, TPH-DRO, TPgH, and TEH), VOCs, SVOCs, and associated TICs. The presence of volatile and semivolatile organic constituents whether alone or in combination can provide an indication of the type of potential source material that may be impacting a well. The presence of certain VOCs and SVOCs, particularly BTEX, as well as the magnitude of concentrations detected, can also provide an indication of the presence of potential source materials. Comparison of chromatographic profiles from the GRO and DRO analyses provides additional information, because many organic constituents are not identified and/or quantified during VOC or SVOC analyses. TICs identified individually or in chemical groups can provide an indication of a potential source or provide an additional line of evidence as to the potential source material.

This section presents a discussion of individual organic constituents that can be used to differentiate between potential source materials.

5.8.2.1 *Volatile and Semivolatile Organic Fractions*

The presence and relative abundance of volatile organic fractions (i.e., TPH-GRO and TPgH) is more characteristic of condensate and produced water. The presence and relative abundance of semivolatile organic fractions (i.e., TPH-DRO and TEH) is more characteristic of drill mud or pump installation materials. The percentage of TPgH as TPH-GRO falls within a distinct range for condensate, produced water, and drill mud sampled for this study (**Table 3**). In contrast, the

percentages of these constituents varied over a wide range in samples of both flowback fluid (19 to 73 percent) and pump installation materials (8 to 70 percent, where detected), which makes it difficult to differentiate between these potential source materials based on this ratio.

Selected gas chromatograms for different potential source material samples are presented in **Appendix F**, **Figures F-1** through **F-10**. The constituents observed at late retention times in the GRO chromatograms for drill mud and pump installation materials appear to be generally the same constituents observed in the DRO chromatogram. The profiles in the DRO chromatograms for drill mud and pump installation materials are characteristic for these potential source materials. A large complex of mid-range peaks typical of a diesel signature occurs in drill mud, whereas a broad UCM-type signature eluting at late retention time is characteristic of pump installation materials. DRO chromatograms for some flowback fluid samples appear to have a slight diesel-like signature.

The profile in the GRO chromatograms for condensate, produced water, and flowback fluid predominantly falls in the gasoline organics range. The chromatographic profile for condensate has an overall spiky appearance due to the presence of alkanes, whereas produced water is characterized by several distinct, larger peaks at early retention times, which are related to the presence of more soluble BTEX constituents. The appearance of the profile in the GRO chromatogram for flowback fluid falls between the profiles for condensate and produced water.

The percentage of TEH as TPH-DRO is a better indicator for drill mud and pump installation materials than for the other potential source materials. Drill mud has a tight range (96 to 97 percent), and this percentage is much higher than that observed in other potential source materials. The percentage TPH-DRO in TEH in pump installation materials ranges from 20 to 38 percent, which generally does not overlap the percentage in other potential source materials. The percentage of TPH-DRO in TEH in produced water and flowback fluid samples fell within a broader range, which overlaps the corresponding percentage in condensate (**Table 3**).

As indicated by the TPH-DRO/(TPH-GRO + TPH-DRO) ratio, condensate tends to have a proportionally higher concentration of volatile constituents (i.e., TPH-GRO), whereas drill mud and pump installation materials tend to have a proportionally higher concentration of semivolatile constituents (i.e., TPH-DRO) (**Table 9**). This ratio varied over a greater range of values for the produced water and flowback fluid samples. However, the large range in this ratio for produced water is likely skewed toward the presence of a higher concentration of semivolatile organic compounds due to the one produced water sample that contained an abundance of free-phase product. C_{40+} compounds are commonly detected in pump installation materials, whereas the predominant carbon number range starts at C_6 for condensate and produced water samples (**Table 9**).

5.8.2.2 *Volatile and Semivolatile Organic Compounds*

The VOCs detected in potential source material samples were predominantly BTEX constituents (**Table 9**). The complete suite of BTEX constituents were detected in condensate, produced water, and flowback fluid. Benzene was absent in the drill mud, and only xylene constituents were occasionally detected in well/pump installation materials. Flowback fluid was the only potential source material with detectable levels of a VOC other than BTEX (i.e., methyl ethyl ketone). The types of SVOCs detected may allow differentiation between potential source materials. Only naphthalenes were detected in condensate. Naphthalenes, phenanthrene, and pyrene were consistently detected in drill mud. Cresols were present only in produced water and flowback fluid.

5.8.2.3 *Tentatively Identified Compounds*

Source distinction based on an individual TIC alone is difficult as the compound has only been tentatively identified, and its presence has not been quantified by calibration. However, the presence of multiple TICs within chemical groups, such as alkanes, alkenes, alkylbenzenes, and ketones, can be compared among samples of potential source materials to identify chemical signatures unique to a specific potential source material (**Table 9**).

Few TICs were observed in pump installation materials, and in several of the samples, the specific compounds corresponding to the individual peaks in the chromatogram could not be identified by the laboratory. The TICs common to condensate, produced water, flowback fluid, and drill mud included alkanes, branched alkanes, cycloalkanes, and alkylbenzenes, as these are all hydrocarbon-containing materials. Distinction of potential source materials based on these commonly reported TICs is limited to the predominance of compounds within a certain carbon number range or level of substitution for branched alkanes and alkylbenzenes. For example, in drill mud sampled for this study, alkanes and branched alkanes with lower numbers of carbon atoms (C_4 to C_8) were absent, and alkylbenzenes tended to be more heavily substituted (e.g., tri-substituted and tetra-substituted benzenes). In contrast, condensate tended to have both lower carbon number (C_4 to C_8) alkanes and higher carbon number alkanes. Condensate and produced water were characterized by more cycloalkanes, as well as alkylcycloalkanes and alkylbenzenes with light substitution (mono- and di-substitutions).

In addition to differences among chemical groups, the presence or absence of TICs in certain chemical groups is characteristic. While drill mud samples were characterized by the presence of decalins and tetralins, no TICs within these chemical groups were identified in the condensate sample. Adamantanes were found only in the LNAPL sample collected from industrial water supply well AN 1-16.

Trends with regard to the commonly detected TICs are not evident in flowback fluid samples, which is likely due to the variable composition of hydraulic fracturing fluids and differences in the time of contact with the formation. However, flowback fluid samples are characterized by the presence of

non-hydrocarbon TICs, such as ketones, phenols, organic acids, and alcohols. Of the sources sampled for this study, alkenes were detected predominantly in flowback fluid samples. Most natural systems contain only trace amounts of alkenes, but alkenes can be quite abundant in refined products (Prince and Walters, 2007).

6.0 ANALYTICAL RESULTS FOR GAS SAMPLES

Chemical testing results for gas samples are presented in this section. Gas samples included samples of gas dissolved in groundwater (i.e., dissolved gas), gas accumulating in well casings of industrial water supply wells and SAP study wells (i.e., casing gas), and gas collected from natural gas production wells. Results of chemical and isotopic composition testing for the gas samples are summarized in the following tables:

- **Table 8**: Isotopic Composition of Constituents in Groundwater, Produced Water, and Gas Samples;
- **Table 10**: Composition of Gas Samples from Water Well Casings and Natural Gas Production Wells; and
- **Table 11**: Composition of Dissolved Gas in Groundwater Samples.

Sampling locations for casing gas and natural gas well samples are shown on **Figure 3-2.** Dissolved gas samples were collected from the 34 industrial water supply wells and SAP study wells at locations shown on **Figure 3-3**. The analytical results for follow-up samples of casing gas collected at T-3-SW in 2011 for isotope analysis, dissolved gas collected at WB 7-4 in 2012 for hydrocarbon composition and isotope analysis, and casing gas and dissolved gas collected at BO 12A-33 in 2012 for hydrocarbon composition and isotope analysis are also reported in **Table 8**, **Table 10,** and **Table 11**. The laboratory reports containing complete chemical testing results are provided in **Appendix D**. The data quality review report is presented in **Appendix E**.

Normalized hydrocarbon concentrations are provided in **Table 10** and **Table 11** for the C_1 through C_5 gas components (i.e., methane, ethane, propane, butane, isobutane, pentane, and isopentane). Concentrations of these hydrocarbons were normalized to minimize the effects of dilution by air in a sample, and to facilitate the comparison of the relative abundance of the gas components among all gas samples (i.e., dissolved gas, casing gas, and natural gas samples). Normalization was performed through the C_5 gas components because concentrations for these individual compounds were reported in all gas samples.

The integrity of the primary dissolved gas sample collected at MS 14-16 in November 2010 for analysis of gas composition and isotopic composition of methane was compromised because the cap on the sample container was cracked in transit to the laboratory. Therefore, data associated with the duplicate sample for dissolved gas that was collected at MS 14-16 at that time is used for evaluation purposes in this report.

6.1 NATURAL GAS

The hydrocarbon composition of natural gas and isotopic composition of methane in natural gas samples collected from the six production wells sampled for this study are similar among samples.

Standard C_1 through C_6 gas components (i.e., methane, ethane, propane, n-butane, isobutane, n-pentane, isopentane, and n-hexane) were detected in all six natural gas samples. Methane is the dominant hydrocarbon gas component, ranging from 89.3 to 93.2 mole percent in the samples (**Table 10**). The *wetness* of the gas is the sum of the hydrocarbon gas components excluding methane (in other words all gases with two or more carbon atoms, designated C_{2+} gas components). Wetness of the natural gas samples ranged from approximately 5 to 10 mole percent. Ethane and propane concentrations in natural gas ranged from 4.0 to 5.9 and 1.1 to 2.0 mole percent, respectively. Benzene, ethylbenzene, and toluene were detected in all natural gas samples at concentrations below 0.1 mole percent. One or more xylene congeners were detected in four of the six natural gas samples. Benzene and toluene were detected at higher concentrations than ethylbenzene and xylenes in the natural gas samples.

Stable carbon (^{13}C) and hydrogen (^{2}H) isotope values of methane in samples from natural gas production wells varied within a narrow range (**Table 8**). Carbon isotope values of methane in natural gas samples ranged from -37.47 to -34.36 per mil; hydrogen isotope values of methane ranged from -178.7 to -189.1 per mil.

6.2 CASING GAS

The gas composition and isotopic composition of methane in casing gas samples collected from the water wells was more variable than that of natural gas samples collected from natural gas wells.

Methane is the dominant component in casing gas sampled from three water wells: BO 12A-33, AN 1-16, and T-4-RW-a (**Table 10**). Methane concentrations in these well casings ranged from 85.4 to 93.6 mole percent. Nitrogen, a non-hydrocarbon gas that is naturally prevalent in the atmosphere, is the dominant component of casing gas in the other seven wells sampled. Methane concentrations in six of these seven samples in which nitrogen gas is the predominant component ranged from 2.01 to 16.6 mole percent. In contrast, the other casing gas sample in which nitrogen gas is the predominant component (well WB 7-4) in 2010 contained a much lower methane concentration (0.449 mole percent). An attempt was made in 2012 to collect a follow-up sample of casing gas at this well to duplicate this finding. An insufficient volume of gas was present in the capped well casing at WB 7-4 in 2012. With the absence of corroborating evidence, the initial result at this well is considered anomalous, and may be an artifact of the low concentration of hydrocarbon gas that was observed in the well casing in 2010. The hydrocarbon composition results from this sample are reported in **Table 10**; however, these results are not used in data evaluation.

Methane concentrations normalized to C_1 through C_5 gas components ranged from 75.3 to 98.1 mole percent (range excludes the casing gas sample from WB 7-4) (**Table 10**).

All of the gas components up through C_6 (hexanes) were detected in 7 of the 10 casing gas samples, and all samples contained detectable levels of at least three of the components (**Table 10**). Ethane concentrations ranged from below the detection limit to 4.62 mole percent (4.79 mole percent when normalized to C_1 through C_5) in casing gas samples; propane concentrations ranged from 0.20 to 2.7 mole percent (0.25 to 45.4 mole percent normalized to C_1 through C_5). Benzene, ethylbenzene, and toluene were detected in casing gas samples from each of the 10 water wells sampled, and at least one xylene congener was detected in samples from eight of the wells (**Table 10**). The highest BTEX concentrations in casing gas were detected in the sample collected from BO 12A-33 in December 2010 (**Table 10**).

A broader range of isotope values was observed in casing gas samples as compared to natural gas samples. Carbon (^{13}C) isotope values of methane in casing gas ranged from -53.23 per mil in water supply well WB 7-5 to -32.72 per mil in SAP study well T-3-SW. Hydrogen (^{2}H) isotope values in casing gas samples ranged from -256.2 per mil in WB 7-5 to -171.0 per mil in WB 7-4 (**Table 8**). Although the isotopic composition of methane theoretically should not vary with methane concentration in the sample, results of carbon and hydrogen isotope analyses in the casing gas sample from WB 7-4 could not be duplicated because insufficient gas volume was present in the well casing during follow-up sampling in 2012. The results from the analyses for the 2010 samples are reported in **Table 8** but are not used in data evaluation.

6.3 DISSOLVED GAS

Methane was detected in all groundwater samples analyzed for dissolved gas for this study (**Table 11**). Dissolved methane concentrations ranged from 0.0009 mg/L at T-1-SW to 120 mg/L at T-4-RW-a. Dissolved methane concentrations exceeded the solubility of methane at standard atmospheric pressure (28 to 32 mg/L) in 11 of the 34 wells sampled, all of which are located south of the New Fork River.

Dissolved saturated hydrocarbon gas components up through hexanes (C_{6+}) were detected in 9 of the 34 wells sampled; C_{2+} gas components were detected in 21 of the 34 wells sampled (**Table 11**). Detected ethane concentrations ranged from 0.0017 to 5.56 mole percent (0.03 to 5.67 mole percent normalized) in dissolved gas samples; detected propane concentrations ranged from 0.0009 to 1.36 mole percent (0.002 to 1.54 mole percent normalized). Ethene was detected in dissolved gas from only one groundwater sample (RB 16-30).

Stable carbon (^{13}C) and hydrogen (^{2}H) isotope values of methane were determined in groundwater samples that contained sufficient dissolved methane concentrations for analysis. Isotope values could not be determined in samples collected from 10 wells located north of the New Fork River

and 6 wells located south of the New Fork River due to low methane concentrations in the samples. Carbon isotope values of methane in the samples analyzed ranged from -35.69 per mil in T-3-SW to -73.63 per mil in RS 11-25. Hydrogen isotope values of methane ranged from -193.9 per mil in T-3-RW to -303.1 per mil in T-5-RW (**Table 8**).

Dissolved gas samples collected from the LEL wells have the most consistently high concentrations of hydrocarbon gas, which includes dissolved methane, in groundwater (**Table 11**). No LEL wells sampled for this study had hydrocarbon gas accumulating in water well casings but little to no dissolved gas in groundwater. This is consistent with the finding that only water wells with sufficient dissolved hydrocarbon gas concentrations in groundwater will off-gas and result in the accumulation of hydrocarbon gas in the well casings. Control wells generally have lower concentrations of hydrocarbon gas, which consists primarily of dissolved methane, in groundwater as compared to LEL wells. Methane concentrations were so low in five of six control wells that the isotopic composition of methane could not be determined.

7.0 ANALYTICAL RESULTS FOR GROUNDWATER SAMPLES

Chemical testing results for groundwater samples collected from 25 industrial water supply wells and the 9 SAP study wells for this study are presented in **Section 7.1** for inorganic constituents and in **Section 7.2** for organic constituents.

Chemical testing results for organic constituents in groundwater samples collected from the 18 HDG study wells that were sampled as part of the companion HDG investigation are also presented in **Section 7.2**. Thus, results from laboratory tests for organic constituents are presented for a total of 27 study wells, although the SAP study wells were analyzed for a broader spectrum of analytes than the HDG study wells (**Section 3.2.3)**. Chemical testing results for inorganic constituents at the HDG study wells were reported in a separate report (AMEC, 2012) and are not repeated here.

Methods of sample collection were the same for both the HDG study wells and the SAP study wells (**Section 3.2.3**); however, the suite of organic analytes collected from the HDG study wells was more limited (i.e., BTEX, TPH-DRO, TPH-GRO). SGT was applied to the extract of samples that contained detectable TEH in all 27 study wells (SAP study wells and HDG study wells) and the results are presented herein.

Chemical testing results from follow-up sampling performed in 2012 are presented in the data tables together with the results from the initial samples collected in 2010 and 2011. Chemical testing results for groundwater samples collected from the top of the water column in two industrial water supply wells, RS 11-25 and RS 15-12 (samples RS 11-25 PHC and RS 15-12 PHC), are discussed in the text along with the results from groundwater samples collected from the perforated or screened interval. The hydrocarbon composition of dissolved gas samples collected during groundwater sampling were presented previously in **Section 6.3.**

Sampling locations are illustrated by well group (i.e., control, LEL, PHC, SAP study, and HDG study) on **Figure 3-3**.

7.1 INORGANIC CONSTITUENTS

Inorganic constituents analyzed in groundwater samples for this study included general water quality parameters, total metals, and stable isotopes of water and dissolved inorganic carbon. Chemical testing results for inorganic constituents are summarized in the following tables:

- **Table 8**: Isotopic Composition of Constituents in Groundwater, Produced Water, and Gas Samples;
- **Table 12**: General Water Quality Parameters in Groundwater Samples; and

- **Table 13**: Total Metals in Groundwater Samples.

The laboratory reports containing complete chemical testing results are provided in **Appendix D**. The data quality review report is presented in **Appendix E**.

7.1.1 General Water Quality Parameters

General water quality parameters analyzed for this study included total alkalinity (as calcium carbonate, bicarbonate, and carbonate), chloride, sulfate, fluoride, bromide, nitrate+nitrite and ammonia (as nitrogen), total phosphorus, and TDS.

Concentrations of general water quality parameters typically varied within an order of magnitude between sampled wells, except for sulfate and chloride concentrations, which varied over two orders of magnitude between sampled wells. Bromide was detected in a single groundwater sample from well WB 8-6 (1.2 mg/L) at a concentration slightly above the laboratory reporting limit of 0.5 mg/L (**Table 12**). Low concentrations (<0.1 mg/L) of nitrate+nitrite were generally measured in samples; however, a relatively high level of nitrate+nitrite (estimated concentration of 77 mg/L) was detected in the groundwater sample collected from WB 8-6 in November 2010 (**Table 12**). The nitrate+nitrite concentration was less than the laboratory reporting limit (0.01 mg/L) in the follow-up sample collected from the same well in 2012. Because the initial nitrate+nitrite concentration was not duplicated in the follow-up sample, the initial result is considered anomalous and is not considered further in data evaluation. The initial high concentration of nitrate+nitrite in this well could be an artifact of sample preservation.

Chart 7-1 summarizes the range of concentrations of general water quality parameters in groundwater samples from all 34 wells identified in the SAP and sampled for this study, and in groundwater samples from only the six control wells. General water quality parameters in selected categories of potential source material samples are included in **Chart 7-1** for comparison.

Except for sulfate, fluoride, and carbonate, concentrations of general water quality parameters in flowback fluid and produced water samples are elevated compared to concentrations observed in groundwater samples from all wells sampled for this study, as well as concentrations observed in control wells only. Chloride, bromide, and TDS concentrations are significantly higher in produced water and flowback fluid samples than in groundwater samples collected in the PAPA, and thus could serve as indicators of potential impacts to groundwater from these sources.

Chart 7-1 Range of Concentrations of General Water Quality Parameters in Potential Source Material and Groundwater Samples

Analyte	Produced Water	Flowback Fluid	Groundwater (Control Wells Only)	Groundwater (All Wells)
	milligrams per liter[1]			
Total Alkalinity (as $CaCO_3$)	423 – 767	600 – 972	117 – 221	71 – 276
Bicarbonate	516 – 936	732 – 1,190	111 – 261	63 – 318
Carbonate	ND	ND	<4 – 37	<4 – 70
Bromide	66 – 123	49 – 133	ND	<0.5 – 1.2
Chloride	5,030 – 6,880	5,750 – 7,520	5 – 40	2 – 405
Fluoride	1.0 – 1.2	1.1 – 1.4	0.4 – 7.0	0.4 – 13
Sulfate	ND	<50 – 289	3 – 969	<1 – 969
Ammonia (as Nitrogen)	<5 – 7.8	8.4 – 18	<0.05 – 0.22	<0.05 – 0.22
Nitrate +Nitrite (as Nitrogen)	0.07 – 7	0.1 – 0.7	0.02 – 0.05	<0.01 – 0.08[2]
Total Phosphorus	<5 – 10.6	0.27 – 2.26	0.011 – 0.067	0.010 – 0.78
Total Dissolved Solids	8,190 – 12,000	9,450 – 13,900	267 – 1,780	226 – 1,780

1 ND = not detected in any sample.
< indicates analyte not detected at the indicated reporting limit.

2 Result for sample collected from well WB 8-6 in November 2010 is considered anomalous and is not included in this range.

7.1.2 Total Metals

The following metals were detected in one or more groundwater samples collected during this study: aluminum, antimony, arsenic, barium, boron, calcium, chromium, copper, iron, lead, magnesium, manganese, nickel, potassium, selenium, silicon, sodium, strontium, thallium, and titanium (**Table 13**). The five metals detected most frequently in groundwater samples were boron, iron, manganese, sodium, and silicon. Barium, chromium, copper, lead, nickel, and titanium were generally detected in samples from wells with the higher concentrations of iron. Selenium and thallium were detected only in the sample from AN 11-10D at concentrations at or slightly above the reporting limit.

Concentrations of metals in industrial water supply wells appear to be consistent among categories of wells (i.e., control, LEL, and PHC). Aluminum, arsenic, chromium, iron, manganese, nickel, silicon, and titanium tended to be detected more frequently and/or at higher concentrations in SAP study wells compared to industrial water supply wells. In contrast, lead, which was detected at very low concentrations in four industrial water supply wells, was not detected above the reporting limit in any SAP study well.

Chart 7-2 presents a comparison of the range in concentrations of metals that were elevated in drill mud, flowback fluid, and/or produced water samples relative to concentrations in groundwater samples from the six control wells and from all 34 wells sampled as part of the SAP.

Drill mud samples generally contained elevated concentrations of metals with respect to groundwater. The presence of metals at elevated concentrations in groundwater may indicate an impact from drill mud. Similarly, elevated concentrations of boron and sodium in groundwater could serve as a potential indicator of impacts from either produced water or flowback fluid. However, the presence of these metals at elevated concentrations in groundwater would not allow us to differentiate between an impact from produced water versus flowback fluid.

7.1.3 Isotopes

Hydrogen and oxygen isotope values of groundwater in 33 of the 34 wells sampled for this study ranged from -149.2 to -165.3 and -18.39 to -21.37 per mil, respectively (**Table 8**). One SAP study well, T-4-RW-a, had hydrogen and oxygen isotope values outside this range (-137.6 and -17.32 per mil, respectively). T-4-RW-a is co-located with SAP study wells T-4-SW and T-4-RW-b and industrial water supply well AN 11-10D on an Operator gas well pad (**Figure 3-3**).

Chart 7-2 Range of Concentrations of Selected Metals in Potential Source Material and Groundwater Samples

Analyte	Drill Mud	Produced Water	Flowback Fluid	Groundwater (Control Wells Only)	Groundwater (All Wells)
	mg/kg[1]	milligrams per liter[1]			
Aluminum	1,820 – 1,940	<0.1 – 0.1	0.3 – 4.8	<0.1 – 1.8	<0.1 - 18.3
Barium	3,110 – 3,460	15.6 – 30.9	12.4 – 44	<0.1 – 2.1	<0.1 – 2.1
Boron	ND	4 – 7	5.9 – 64	0.2 – 0.3	<0.3 – 0.4
Calcium	22,400 – 32,400	35 – 129	137 – 1,050	<1 – 21	<1 – 47
Chromium	6	<0.01 – 0.04	0.02 – 0.29	<0.01 – 0.02	<0.01 – 0.09
Copper	13 – 33	<0.01 – 0.07	<0.01 – 2.44	<0.01 – 0.02	<0.01 – 0.13
Iron	2,180 – 2,420	5.84 – 60.6	22.1 – 63.8	2.24 – 50.1	0.09 – 138
Magnesium	806 – 1,750	6 – 15	15 – 83	ND	<1 – 17
Manganese	75 – 94	0.32 – 0.67	0.48 – 0.96	0.02 – 0.4	0.01 – 0.65
Potassium	559 – 804	25 – 115	33 – 98	<1 – 1	<1 – 3
Silicon	295 – 316	27 – 52	32.8 – 48	4 – 14.7	0.6 – 30.9
Sodium	409 – 937	3,280 – 4,670	3,930 – 4,870	112 – 587	102 – 587
Strontium	79 – 165	5.1 – 12.3	11.2 – 13	<0.1 – 0.6	<0.1 – 1.1
Titanium	9 – 13	ND	<0.01 – 0.06	<0.01 – 0.09	<0.01 – 0.51
Vanadium	4 – 5	ND	ND	ND	ND

1. ND = not detected in any sample; mg/kg = milligrams per kilogram.
< indicates analyte not detected at the indicated reporting limit.

Hydrogen and oxygen isotope values measured in samples of produced water and groundwater collected for this study are plotted in **Figure 7-1** with respect to a local meteoric water line (LMWL) (Benjamin et al., 2004). Hydrogen and oxygen isotope values measured in groundwater samples in the vicinity of the PAPA as reported by Chafin and Kimball (1992) are also plotted on **Figure 7-1** for reference. Hydrogen and oxygen isotopes values measured in groundwater collected for this study are similar to values reported by Chafin and Kimball (1992), but significantly different from values measured in produced water sampled for this study. The produced water samples collected for this study originated from the gas-producing formations in the PAPA. Water from these formations was likely recharged under climatic conditions different from conditions that exist today, and has likely undergone more evaporation. In addition, this formation water has likely experienced significant water-rock interaction, which would shift the isotope composition away from the LMWL. These deviations from the LMWL could allow stable isotopes of water to be used to assess impacts to groundwater from produced water in the PAPA.

A wide range in stable carbon isotope values of DIC was observed in groundwater (+2.12 to -20.23 per mil) (**Table 8**). The positive DIC values occurred in samples collected from industrial water supply wells HWY 7 and AN 1-16, which are located at the south end of the PAPA (**Figure 3-3**). Carbon isotope values of dissolved inorganic carbon in produced water varied over a more narrow range as compared to groundwater; however, the ranges in groundwater and produced water values overlap.

7.2 ORGANIC CONSTITUENTS

Chemical testing results for groundwater are presented in this section for the following volatile and semivolatile organic constituents:

- Volatile organic fractions as defined by Method 8015, specifically TPH-GRO and TPgH;
- Semivolatile organic fractions as defined by Method 8015, specifically TPH-DRO and TEH;
- VOCs including BTEX by Method 8260; and
- SVOCs by Method 8270.

Results for volatile and semivolatile organic fractions include both hydrocarbons and non-hydrocarbons detected within a specified carbon number range under analytical conditions defined by the method (see **Section 2.1**). The compounds detected using these methods may not necessarily represent petroleum or petroleum products.

Dissolved gases are not quantified as part of the analysis of the volatile organic fraction by Method 8015 (**Section 2.1.4**) or as part of VOC analysis by Method 8260, but are still considered volatile organic constituents for purposes of interpreting the results in later sections of this report. Results of these analyses for light hydrocarbon gases that are dissolved in groundwater samples

(i.e., dissolved gases) are discussed in Section 6.3. Although not quantified by Methods 8015 or 8260, the presence of these gases can also be inferred from the presence of early-eluting peaks in GRO chromatograms or by tentative identification from mass spectra generated from VOC analysis.

Chemical testing results for organic constituents detected in groundwater samples collected for this study as well as groundwater samples collected for the HDG investigation are summarized in the following tables:

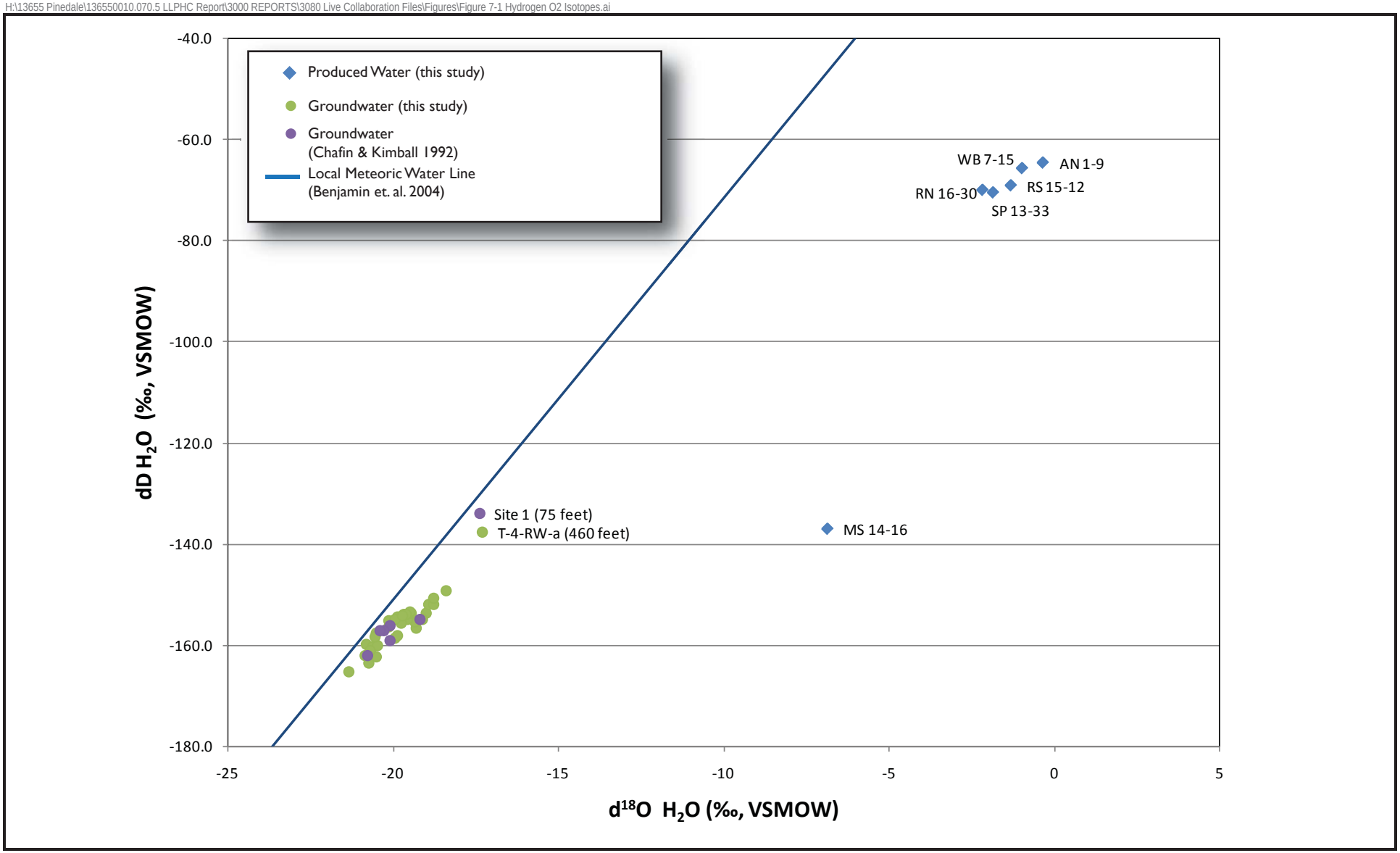
- **Table 14**: Detected Organic Constituents in Groundwater Samples; and
- **Table 15**: Tentatively Identified Compounds in Groundwater Samples.

Table 14 references the applicable groundwater standard for each organic constituent, which is the Wyoming DEQ groundwater cleanup level (Wyoming DEQ, 2012). The applicable groundwater standard for TPH-DRO varies depending on the presence of free-phase material in the well and/or the presence of other constituents of concern at concentrations above applicable groundwater standards. The applicable groundwater standard for TPH-DRO is 10 mg/L (10,000 micrograms per liter [µg/L]) when no free-phase material is detected in the well and when naphthalene and/or methylnaphthalenes, along with other constituents of concern, are detected at concentrations less than the applicable groundwater standard. If free-phase material is observed in the well and/or if naphthalene and/or 2-methylnaphthalene as well as other constituents of concern are detected above applicable groundwater standards, the applicable groundwater standard for TPH-DRO is 1.1 mg/L (1,100 µg/L). Concentrations of the semivolatile organic fraction after SGT treatment are also provided in **Table 14** for groundwater samples collected from all HDG and SAP study wells**.**

Table 15 summarizes the TICs reported in groundwater samples from the SAP study wells and industrial water supply wells specified in the SAP. Reports of TICs were not requested for groundwater samples collected from HDG study wells as part of the HDG investigation. The laboratory reports containing complete chemical testing results for organic constituents for both this study and the HDG investigation are provided in **Appendix D**. The data quality review report is presented in **Appendix E**.

Chemical testing results for organic constituents are discussed separately based on the concentrations of detected analytes. Groundwater samples collected from the relatively few locations where organic constituents were detected at concentrations greater than applicable groundwater standards are discussed in **Section 7.2.1**. A majority of groundwater samples had low-level detections, that is concentrations of organic constituents below applicable groundwater standards, which are the focus of this evaluation. The low-level detections of organic constituents are discussed separately in **Section 7.2.2.** The TICs reported in groundwater samples collected for this study are discussed in **Section 7.2.3.**

H:\13655 Pinedale\136550010.070.5 LLPHC Report\3000 REPORTS\3080 Live Collaboration Files\Figures\Figure 7-1 Hydrogen O2 Isotopes.ai



Note: delta D [H_2O] = Stable Isotope Composition of Deuterium (^{2}H) and Hydrogen (^{1}H) of Water
delta^{18} O [H_2O] = Stable Isotope Composition of Oxygen (^{18}O) and Oxygen (^{16}O) of Water
‰ = Parts per Thousand or per mil
VSMOW = Vienna Standard Mean Ocean Water

Hydrogen and Oxygen Isotope Values
In Groundwater and Produced Water
Relative to Local Meteoric Water Line
Low-Level Petroleum Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 7-1

amec

7.2.1 Detections of Organic Constituents above Applicable Groundwater Standards

Samples collected from three industrial water supply wells (WB 7-15, AN 1-16, and RS 11-25) and two SAP study wells (T-3-SW and T-3-RW) yielded detections of one or more organic constituents at concentrations greater than applicable groundwater standards. **Chart 7-3** summarizes the results for these five wells for those organic constituents that exceeded the applicable groundwater standard in at least one well.

Chart 7-3 Organic Constituents in Groundwater Samples with Concentrations Greater than Applicable Groundwater Standards

Well	Sample Depth	TPH-GRO	Benzene	Toluene	TPH-DRO
		micrograms per liter (µg/L)[1]			
T-3-SW	Perforated zone	340	**6.9**	18	< 300
T-3-RW	Perforated zone	**16,700**	**3,260**	**5,540**	< 300
WB 7-15	Perforated zone	707	**69**	150	< 310
AN 1-16	Perforated zone	197	< 1	2.1	**520,000**
RS 11-25	Top of water column	382	< 1	5.4	**18,000**
	Perforated zone	208	< 1	2.1	6,000

[1] **Bold type** indicates result that exceeds applicable groundwater standard.
< indicates analyte not detected at or above laboratory reporting limit shown.

Bis(2-ethylhexyl) phthalate was also detected in samples from several other wells at concentrations greater than the applicable groundwater standard, but detections of this compound are likely the result of cross-contamination and are not considered further (see **Section 7.2.2.4**).

Plots showing detected concentrations of organic constituents relative to the applicable groundwater standards and the laboratory reporting limits are presented in **Figure 7-2** for benzene and xylenes, **Figure 7-3** for ethylbenzene and toluene, and **Figure 7-4** for TPH-GRO and TPH-GRO. These plots provide a visual representation of the magnitude of the detected concentrations in low-level wells compared to groundwater standards and the concentrations observed in high-level wells.

Industrial water supply well WB 7-15 and SAP study wells T-3-SW and T-3-RW were the only wells with concentrations of volatile organic constituents above applicable groundwater standards. These wells are all located on the same natural gas production well pad, and are thus representative of groundwater conditions at one location.

LNAPL, or free-phase product, was present in industrial water supply well AN 1-16 when sampled for this study. The TPH-DRO concentration in the sample collected from the perforated zone of the well exceeded the applicable groundwater standard of 1.1 mg/L (1,100 µg/L) (**Table 14**). The standard of 1.1 mg/L is applicable due to the presence of LNAPL (product) in the well. Although the

sample was collected from the perforated zone of the well, based on solubility considerations, the high TPH-DRO concentration in the sample is potentially attributable to LNAPL that covered the outside of the Hydrasleeve™ and then entered the sample when the bag was punctured to draw the sample.

The TPH-DRO concentration in sample RS 11-25 PHC, collected from the top of the water column in industrial water supply well RS 11-25, exceeded the applicable standard of 10 mg/L (10,000 µg/L) for TPH-DRO in this well. The TPH-DRO standard of 10 mg/L applies to this well because LNAPL was not observed in the well at the time of sampling and other constituents of concern, such as naphthalenes and BTEX, were not detected above applicable groundwater standards (**Table 14**). The TPH-DRO concentration in the sample collected from the perforated zone in this well was below the applicable groundwater standard.

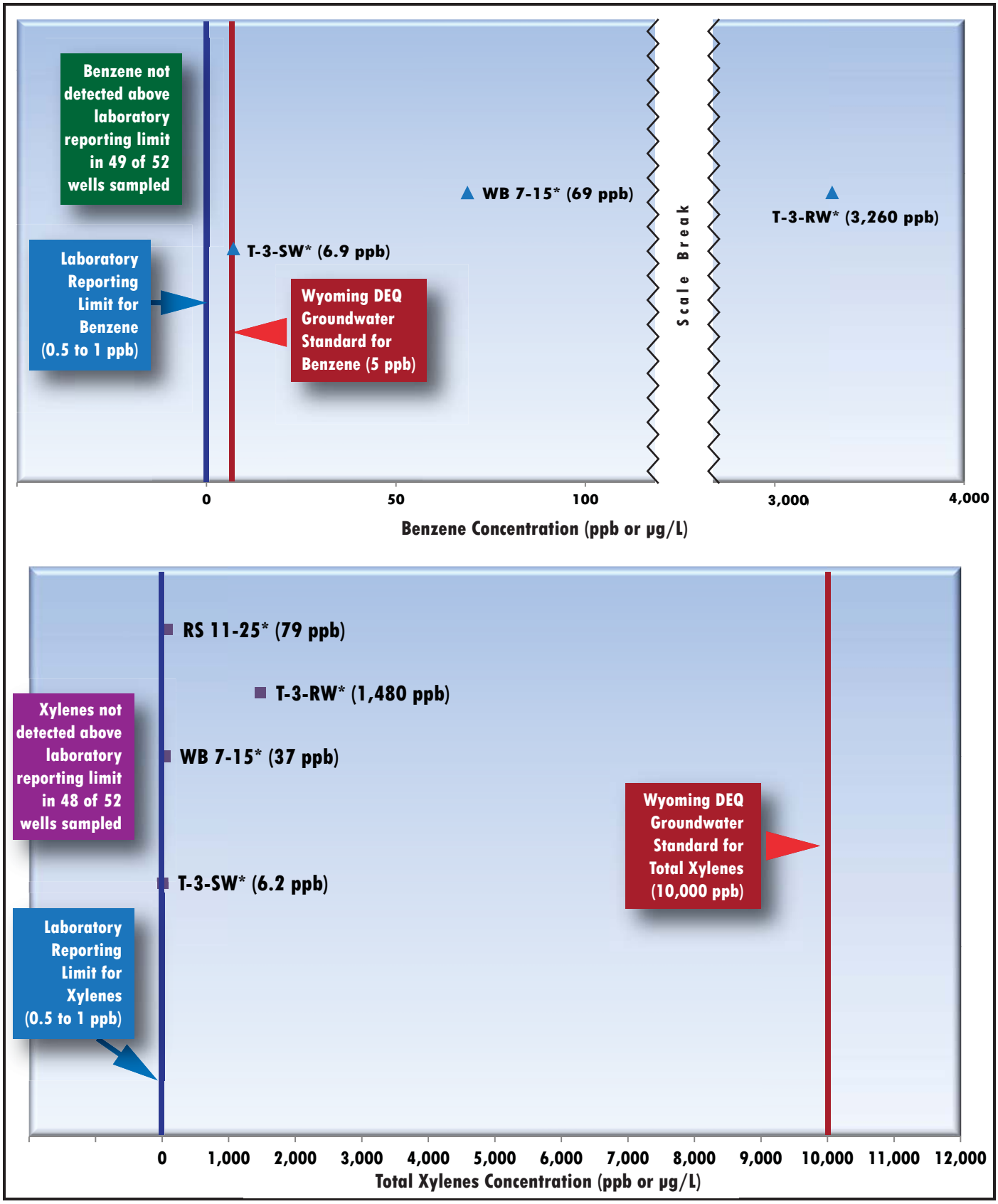
7.2.2 Detections of Organic Constituents in Wells with Low-Level Detections

Samples from the remaining wells sampled for this study had either no detections of organic constituents above reporting limits, or low-level detections of organic constituents in groundwater samples. Organic constituents were detected below the laboratory reporting limit in several low-level wells sampled for this study (**Appendix E**).

All wells sampled for this study had detections of volatile organic constituents in the form of dissolved hydrocarbon gas (**Section 6.3**). Only two of these wells, WB 16-5 and RS 2-24, had no other detections of organic constituents (i.e., purgeable or extractable organic fractions, VOCs, or SVOCs) besides the dissolved gas (**Table 14**). Eleven of the 18 HDG study wells sampled had no detections of organic constituents, although samples from the HDG study wells were not analyzed for the full suite of constituents that were specified for this study, which included dissolved gas composition.

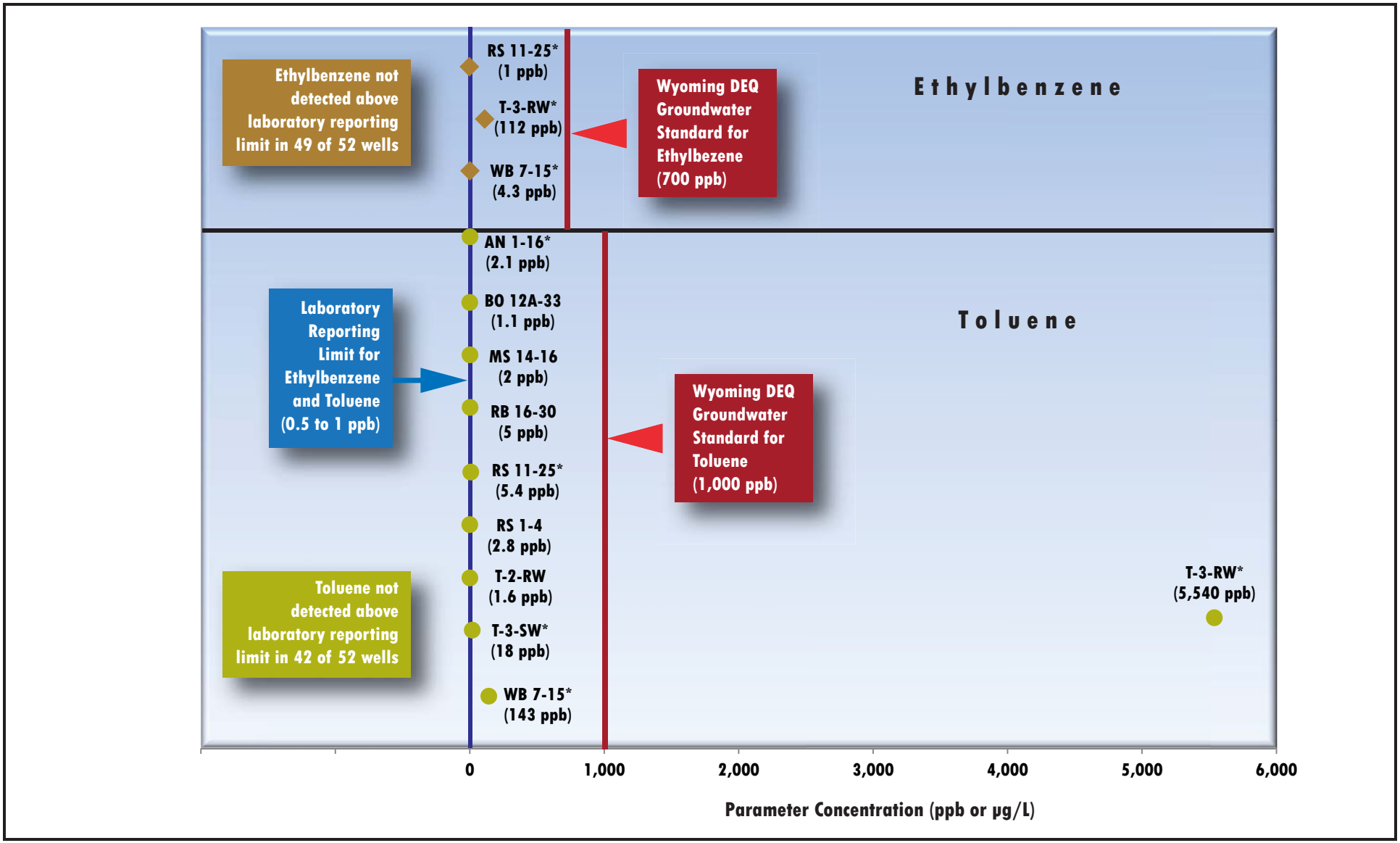
Chart 7-4 summarizes the number of wells in each well category in which organic constituents other than hydrocarbon gases were detected at concentrations above the laboratory reporting limit. **Chart 7-4** also shows the range of analytical results for those organic constituents that were detected above the laboratory reporting limit in at least one well. **Chart 7-4** includes only wells with low-level or non-detected concentrations of organic constituents for each well category, and does not include wells with high-level detections.

A majority of the study wells are co-located with one or two additional study wells at a given location and may also be located on a gas well pad with an industrial water supply well that yielded samples with low-level organic constituent detections. Thus, the number of water well samples producing low-level detections of organic constituents does not necessarily equal the number of distinct locations where samples yield low-level organic constituent detections. Rather, detections of organic constituents in samples from multiple wells may represent groundwater conditions at one single location.



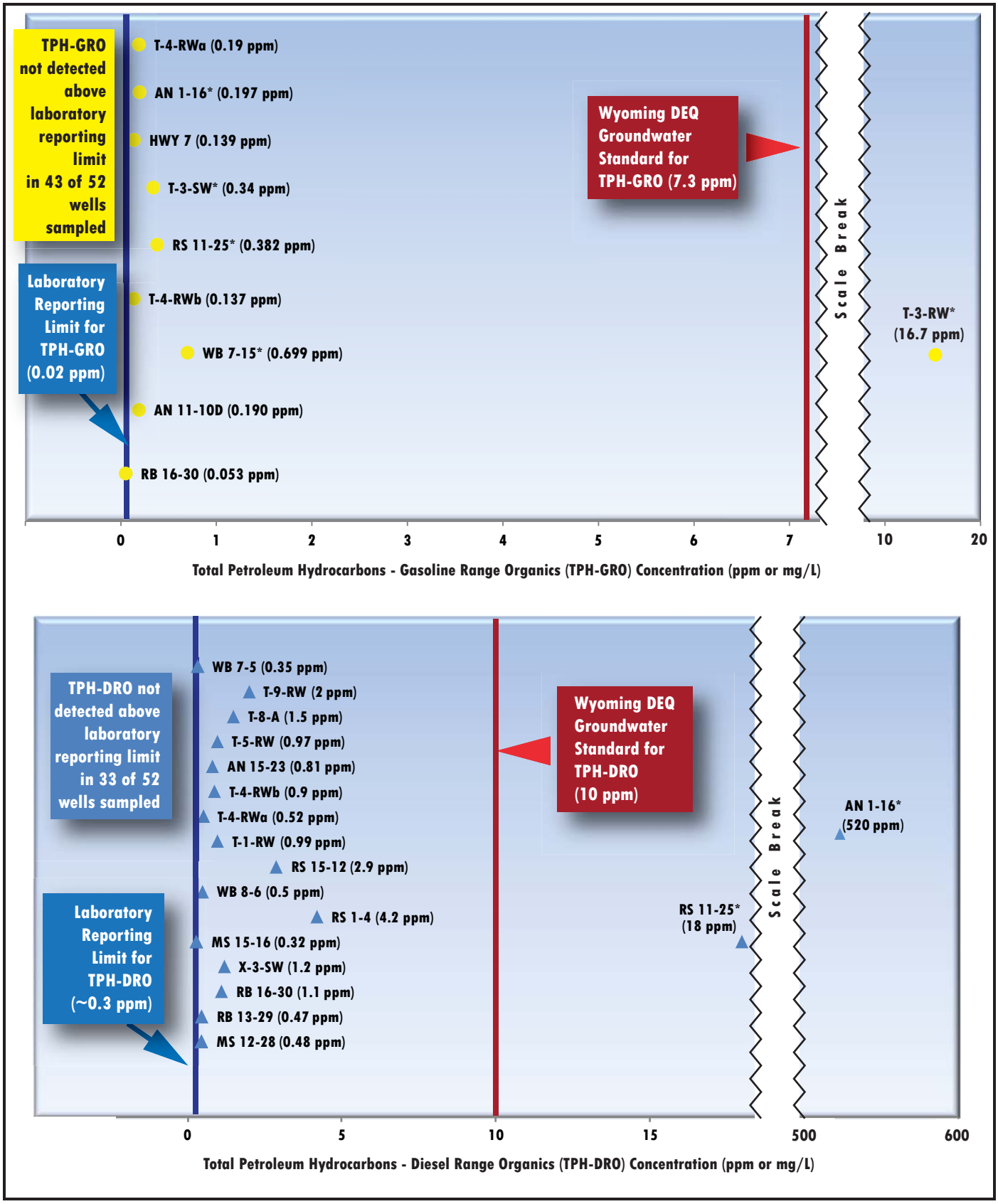
* = High Level Well
µg/L = Micrograms per Liter
ppb = Parts Per Billion

Benzene and Xylene Concentrations in Groundwater Samples
Low-Level Petroleum Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 7-2



* = High Level Well
µg/L = Micrograms per Liter
ppb = Parts Per Billion

Ethylbenzene and Toluene Concentrations in Groundwater Samples
Low-Level Petroleum Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 7-3



* = High Level Well
mg/L = Milligrams per Liter
ppm = Parts Per Million

TPH-GRO and TPH-DRO Concentrations in Groundwater Samples
Low-Level Petroleum Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 7-4

Chart 7-4 Numbers of Low Level Wells in Each Well Category with Organic Constituent Concentrations above the Laboratory Reporting Limit and the Concentration Ranges

Organic Constituent Data in Low-Level Wells [1]						
Analyte	**Summary of Results [2]**	**Control Wells (6)**	**LEL Wells (6)**	**PHC Wells (10)**	**HDG Study Wells (18)**	**SAP Study Wells (7)**
TPH-GRO	Detections	0	2	1	0	2
	Range (µg/L)	---	< 20 – 190	< 20 – 53	---	< 20 – 190
TPgH	Detections	0	4	5	0	2
	Range (µg/L)	---	<20 – 363	< 20 – 443	---	< 20 – 522
TPH-DRO	Detections	3	1	6	3	5
	Range (µg/L)	< 300 – 810	< 300 – 350	< 300 – 4,200	< 300 – 2,000	< 300 – 1,200
TEH	Detections	5	4	9	8	7
	Range (µg/L)	< 310 – 1,200	< 300 – 500	< 310 – 8,800	< 300 – 2,300	440 – 2,200
TEH after SGT	Detections	NA	NA	NA	3	4
	Range (µg/L)	NA	NA	NA	< 300 – 2,100	< 300 – 1,500
Toluene	Detections	0	1	3	0	1
	Range (µg/L)	---	< 1 – 1.1	< 1 – 5	---	< 1 – 1.6

[1] NA = silica gel treatment (SGT) was not applied to extracts of samples;
--- = not detected in any sample above laboratory reporting limit;
< = not detected at concentration equal to or greater than the laboratory reporting limit shown.

[2] Detections = number of samples in which analyte was detected above the laboratory reporting limit;
Range = range of concentrations of for each analyte in micrograms per liter.

7.2.2.1 *Volatile Organic Fractions*

Concentrations of volatile organic fractions as measured by EPA Method 8015, specifically TPH-GRO and/or TPgH, were below 600 µg/L in wells with low-level detections of organic constituents. TPH-GRO and/or TPgH were detected above the reporting limits predominantly in samples collected from wells located south of the New Fork River (**Table 14; Figure 3-3**). TPH-GRO and/or TPgH were not detected in control wells or HDG study wells.

Chromatograms from several of the analyses of the volatile organic fraction show characteristic, early-eluting peaks for samples with higher TPH-GRO and TPgH concentrations. These peaks at early retention times appear to correlate to reference spectra for hydrocarbon gases (e.g., propane,

isobutane, and pentane), which were identified on the mass spectrometry chromatograms. For example, the early-eluting peaks associated with these gases appear to comprise most of the TPgH at water wells HWY 7, AN 11-10D, T-4-RW-a, T-4-RW-b, and RS 11-14 (**Figure F-11** through **Figure F-13** in **Appendix F**). Early-eluting peaks on the GRO chromatogram for the sample collected from RB 16-30 appear to represent gases of alkenes based on the mass spectrum (**Figure F-19** in **Appendix F**).

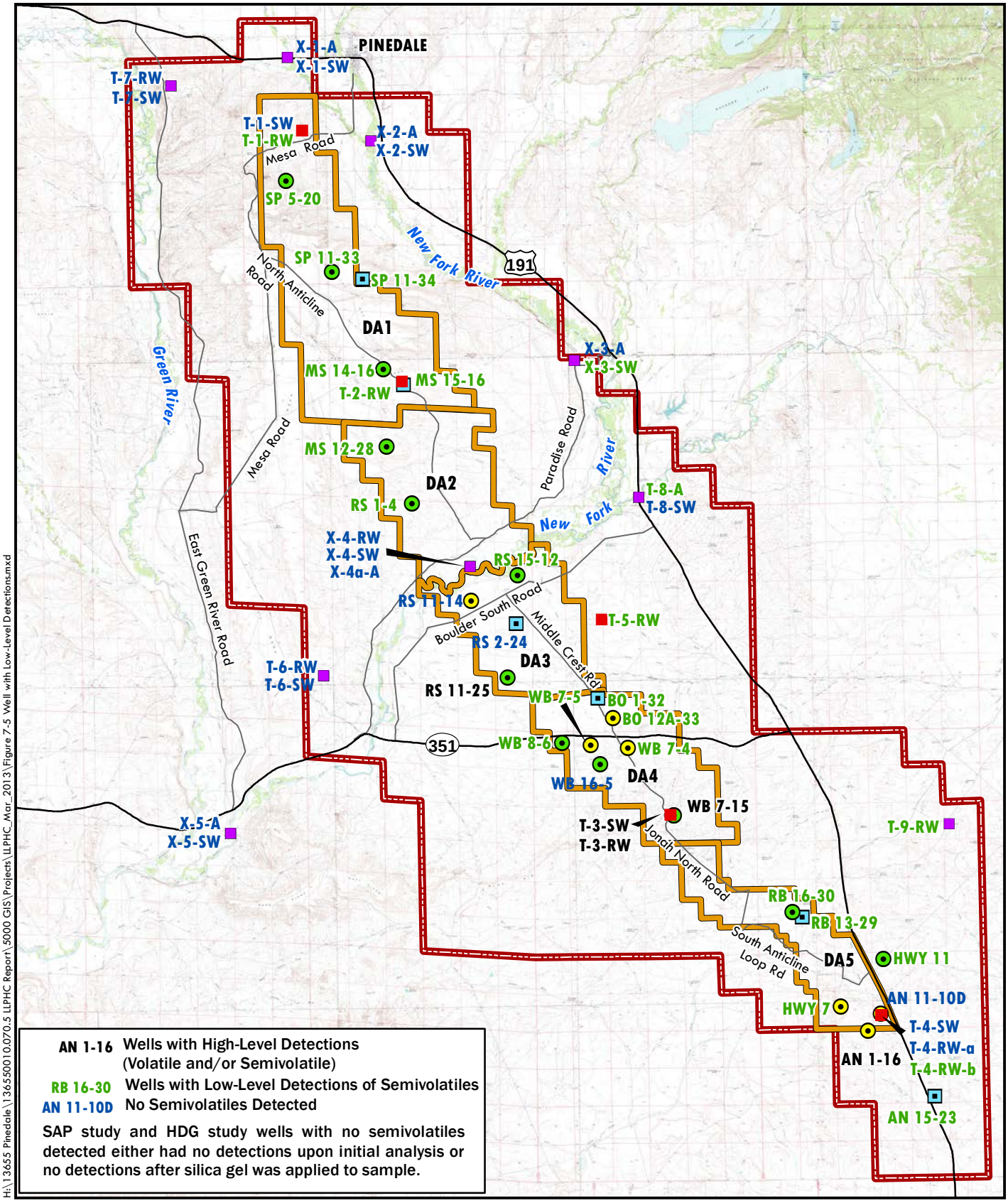
7.2.2.2 *Semivolatile Organic Fractions*

Figure 7-5 identifies the wells sampled for this study and the HDG investigation where low-level detections in the semivolatile organic fraction (TEH and TPH-DRO) were reported. **Figure 7-5** does not include wells with high-level detections. TPH-DRO and/or TEH were detected in samples from at least one water well in every well group, but less frequently in LEL wells and HDG study wells.

TEH was detected in five of six control wells. Although the semivolatile organic fractions were detected less frequently in HDG study wells, which are predominantly located away from E&P activities, the range of detected TPH-DRO and TEH concentrations were similar between study wells located on-pad versus off-pad. The detected concentrations of TEH were also similar in magnitude in samples from water wells located north and south of the New Fork River.

TPH-DRO was generally reported in samples with higher TEH concentrations (>1,000 µg/L). TPH-DRO concentrations were less than 1 mg/L (1,000 µg/L) in 11 of the 18 water wells where detected (**Table 14**). Only four water wells, RB 16-30, RS 1-4, T-4-RWa, and T-4-RWb, yielded detections of TPH-DRO with a complementary detection of either TPH-GRO or a BTEX compound (toluene) (**Table 14**).

Among the groundwater samples analyzed for the full suite of VOCs and SVOCs, the TPH-DRO concentrations in samples collected from industrial water supply wells RB 16-30, RS 1-4, and RS 15-12 and SAP study well T-4-SW were at or above a concentration of 1,100 µg/L. The applicable groundwater standard for TPH-DRO in these wells is 10 mg/L (10,000 µg/L), because LNAPL was not present in these wells and naphthalene, 2-methylnaphthalene, and other constituents of concern (e.g., BTEX) were not detected above applicable groundwater standards (**Table 14**). However, the chromatographic character of the samples collected from these three industrial water supply wells indicates the possible presence of non-dissolved petroleum. LNAPL was not observed when sampling these wells. Chromatograms from the analysis of the semivolatile organic fraction are often characterized by non-discriminate or UCM-type signatures in wells with low-level detections of organic constituents.



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Development Area (DA)

Pinedale Anticline Project Area

SAP Study Well

Control Well

PHC Well

LEL Well

HDG Study Well

amec

Wells with Low-Level Detections of Semivolatile Organic Fractions
Low-Level Petroleum Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 7-5

7.2.2.3 *Semivolatile Organics after Silica Gel Treatment*

Samples from all HDG and SAP study wells where TEH or DRO fractions were detected were treated with silica gel and then re-analyzed. After SGT, these fractions were no longer detected above the reporting limit in samples from more than half of study wells where TPH-DRO and/or TEH fractions had initially been reported (**Table 14; Figure 7-6**). Removal of the semivolatile organic fractions in these samples upon SGT may indicate that the organic constituents were either naturally occurring, or consisted of hydrocarbon constituents that had been degraded to the point that they have become polar and were retained on the silica gel upon treatment.

Low-level detections of the semivolatile organic fractions in study wells tended to vary by well depth and by location in the PAPA, particularly when considering detections of these fractions following SGT. **Figure 7-6** illustrates the spatial pattern of detections of the semivolatile organic fractions in groundwater samples both before and after SGT at all 27 HDG and SAP study wells. These wells include T-3-SW and T-3-RW, which are associated with high-level detections of volatile organic constituents, and T-4-RW-a and T-4-RW-b, which contain low levels of both volatile and semivolatile organic constituents.

Review of the pattern of low-level detections compared to the depth of the wells produced the following general findings.

- Study wells where semivolatile organic fractions (i.e., TPH-DRO and/or TEH) were not detected in samples prior to SGT generally represented the shallower well of well pair clusters installed in the New Fork River corridor or west of the crest of the anticline (i.e., X-1-A, X-2-A, T-6-SW, and T-7-SW). These semivolatile organic fractions tended to be detected in the sample from the deeper well at each of these well clusters prior to silica gel treatment, but not in the samples following SGT (i.e., X-1-SW, X-2-SW, T-6-RW, and T-7-RW).
- In general, the semivolatile organic fractions were not detected after SGT in samples from the shallower wells in well clusters located along the anticline crest (i.e., T-1-SW, T-3-SW, T-4-SW, and T-4-RW-a) or east of the anticline crest (i.e., X-3-A), but these fractions were detected following SGT in samples from the deeper wells in these well clusters (i.e., T-1-RW, X-3-SW, T-3-RW, and T-4-RW-b) and in the deeper unpaired study wells (i.e., T-5-RW and T-9-RW).
- The T-8 and X-5 well clusters were unusual in that semivolatile organic constituents were not detected in the deeper well (T-8-SW and X-5-SW), but were detected in shallower, alluvial wells (T-8-A and X-5-A). Semivolatile organic constituents continued to be detected following SGT in samples from HDG study well T-8-A, but not from HDG study well X-5-A.

Semivolatile organic constituents were not detected in the X-4 well cluster located at the intersection of the crest of the anticline and the New Fork River; therefore, SGT was not applied to extracts from these wells. Strong upward hydraulic gradients are present between the Wasatch Formation and the alluvial sediments at the X-4 well cluster (AMEC, 2012).

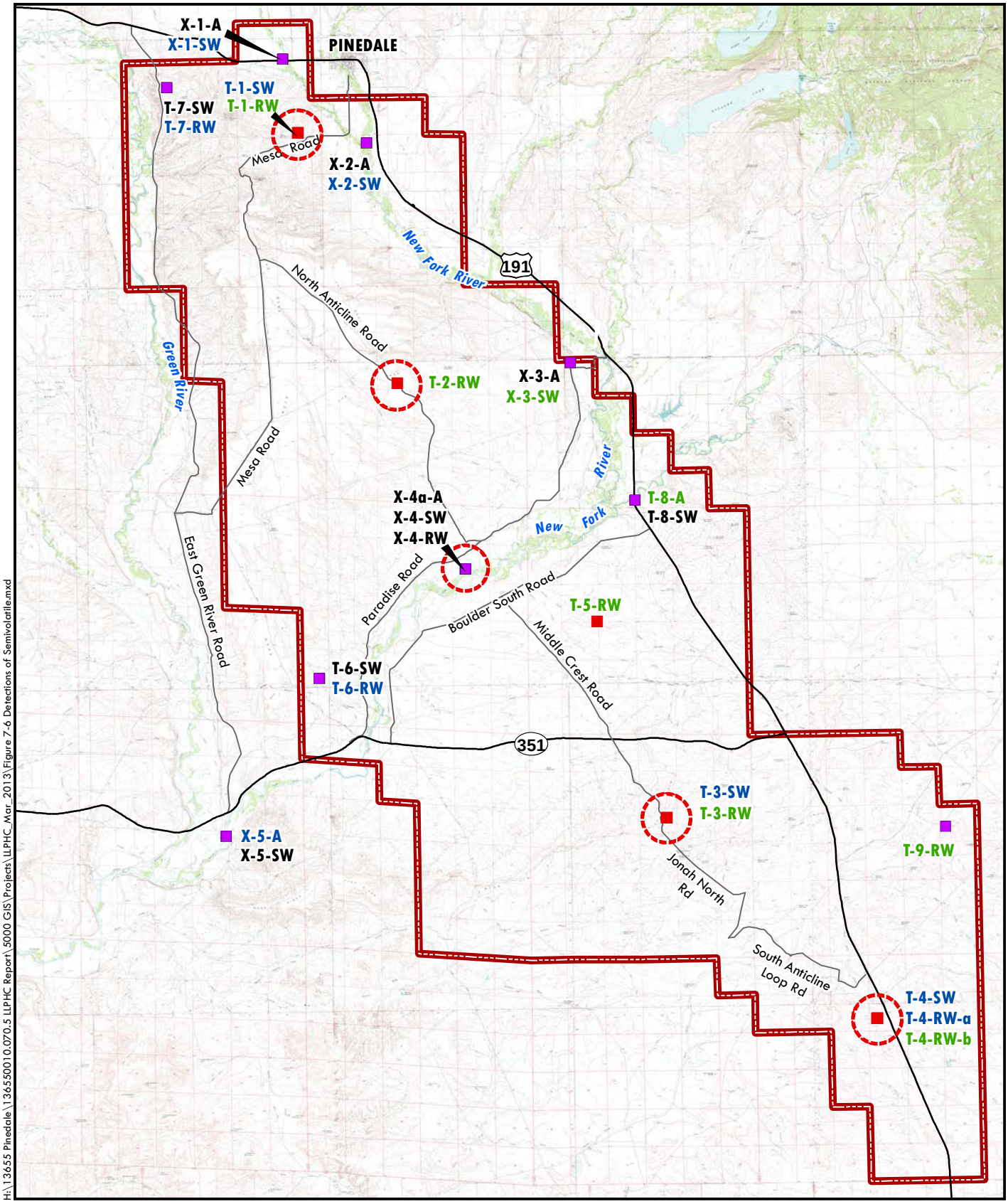
Three HDG study wells with TPH-DRO detected after SGT exhibited a characteristic hydrocarbon profile in the DRO chromatogram. A narrow complex of peaks is observed in these chromatograms (**Figure F-14** and **Figure F-15**, **Appendix F**).

7.2.2.4 *Volatile and Semivolatile Organic Compounds*

The absence of detected individual compounds above the laboratory reporting limit, such as VOCs and/or SVOCs, in wells with low-level detections of volatile and semivolatile organic fractions is notable (**Table 14**). For example, SVOC compounds that were detected in produced water and flowback fluid samples, such as naphthalenes, phenols, and cresols, were not detected above the laboratory reporting limit in samples collected from wells with low-level detections of organic constituents where analyzed. Neither benzene, ethylbenzene, nor xylenes were detected above the reporting limit in any well with low-level detections of organic constituents.

Toluene, the only BTEX compound detected above the laboratory reporting limit in samples with low-level detections of organic constituents, was not detected in any control wells or HDG study wells. Methyl ethyl ketone was the only other VOC detected above the laboratory reporting limit in groundwater samples analyzed for the full suite of VOCs. Methyl ethyl ketone was detected at a concentration of 30 µg/L in industrial water supply well MS 14-16 in November 2010 (**Table 14**). Methyl ethyl ketone was not detected above the laboratory reporting limit of 10 µg/L in the follow-up sample collected from this well in February 2012. Methyl ethyl ketone can be difficult to separate and quantify in the laboratory depending on the presence and concentrations of other VOCs in the sample. Because the presence of this constituent was not duplicated upon follow-up sampling, the detection of methyl ethyl ketone is not considered further in data evaluation for this study.

Two phthalate ester compounds were the only SVOCs detected above the laboratory reporting limit in groundwater samples with low-level detections of organic constituents (**Table 14**). Di-n-octyl phthalate was detected in the sample collected from RS 1-4 at a concentration of 18 µg/L. Bis(2-ethylhexyl) phthalate was detected in samples from four water wells (three of which were SAP study wells) at concentrations ranging from 16 µg/L to 174 µg/L, which are above the applicable groundwater standard of 6 µg/L for this compound. Phthalates are a common laboratory and sampling contaminant due to their ubiquitous presence in plastics found in laboratory and sampling equipment. These phthalate detections are likely the result of cross-contamination from plastics used during sampling or analysis and were not considered further during data evaluation for this study.



H:\13655 Pinedale\136550010.070.5 LLPHC Report\5000 GIS\Projects\LLPHC_Mar_2013\Figure 7-6 Detections of Semivolatile.mxd

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T-4-SW Semivolatile Organic Fractions Not Detected

T-4-SW Semivolatile Organic Fractions Not Detected After Silica Gel Treatment

T-4-SW Semivolatile Organic Fractions Detected After Silica Gel Treatment

Study Wells at Drill Pads Along Anticline (on-pad)

SAP Study Well

HDG Study Well

Detections of Semivolatile Organic Fractions in Study Wells Before and After SGT

Low-Level Petroleum Hydrocarbon Evaluation

Sublette County, Wyoming

FIGURE 7-6

7.2.3 Tentatively Identified Compounds

This section summarizes results for compounds tentatively identified by the laboratory in groundwater samples collected from the 25 industrial water supply wells and 9 SAP study wells for this study. Samples from selected wells collected during follow-up sampling in 2012 were analyzed for the targeted TICs reported for that well from the earlier sampling in order to verify the presence and quantify the concentrations of these TICs. Results for the follow-up sampling are presented in **Section 7.2.3.2**.

7.2.3.1 *Results from SAP Implementation in 2010 and 2011*

A summary of TICs categorized by chemical group that were reported in groundwater samples collected for this study is provided in **Table 15.** TICs were reported in 24 of 34 wells sampled for this study. No TICs were reported for the following wells: RS 2-24, MS 15-16, SP 11-34, T-1-SW, T-2-RW, T-4-SW, T-5-RW, HWY 11, WB 16-5, and SP 11-33.

More than 20 TICs were listed in samples from WB 7-15, RB 16-30, and RS 11-25. Organic constituents were detected at concentrations above applicable groundwater standards in two of these wells (RS 11-25 and WB 7-15) (see **Section 7.2.1**).

Samples with greater numbers of TICs reported typically had higher concentrations of purgeable and extractable organics, as well as VOCs. The total number of wells with TICs reported for each chemical group is tabulated in **Chart 7-5**.

TICs from hydrocarbon chemical groups were reported more frequently in groundwater samples than TICs from non-hydrocarbon chemical groups. The most frequently reported, individual TICs in sampled wells were:

- isobutane (13 wells);
- 2-methylbutane (12 wells);
- cyclic octaatomic sulfur (11 wells);
- propane (10 wells);
- cyclohexane (10 wells); and
- methylcyclohexane (10 wells).

Chart 7-5 Number of Wells with Reported TICs Listed by Chemical Group

TIC Chemical Group		Number of Wells with TICs Listed by Chemical Group	
		Wells with *Low-Level* Organic Constituent Detections (29)	**Wells with *High-Level* Organic Constituent Detections (5)**
Non-Hydrocarbon	Acids	1	0
	Alcohols	5	0
	Aldehydes	5	0
	Ketones	2	0
	Silanes	3	0
	Sulfur Compounds	11	2
Hydrocarbon	Alkanes	10	5
	Branched Alkanes	10	5
	Alkenes	2	0
	Branched Alkenes	4	1
	Alkynes	1	0
	Cycloalkanes	6	4
	Alkylcycloalkanes	8	5
	Cycloalkenes	1	0
	Alkylbenzenes	1	2
	Indans, Indanes, Indenes	1	1
	Naphthalenes/Tetralins	0	1
	Terpenoids	2	0

Cyclic octaatomic sulfur is considered a natural sulfur compound, and is often reported in wells with relatively high sulfate concentrations. Isobutane, 2-methylbutane, propane, cyclohexane, and methylcyclohexane are hydrocarbon compounds commonly associated with natural gas and condensate.

Indan/indane/indene compounds, 2-methylnaphthalene, and tetralins were reported only in two wells: RS 11-25 and RS 15-12. Alkylbenzenes were only reported in samples collected from T-3-RW, RS 11-25, and RS 15-12. Adamantane was reported in samples collected from T-4-RWa and T-4-RWb. Most natural petroleum systems contain only trace amounts of alkenes; however, alkenes can be quite abundant in refined products (Prince and Walters, 2007). Ten TICs from the alkene and branched alkene chemical groups, in addition to an alkyne (2-methyl-1-buten-3-yne), were reported in the sample collected from RB 16-30. These TICs were unusual as they are low in carbon number range (C_3 – C_6) (unsaturated hydrocarbon gas).

The TICs comprising non-hydrocarbon chemical groups (excluding sulfur compounds) were reported only in wells with low-level detections of organic constituents (**Chart 7-6**).

Chart 7-6 TICs Reported from Non-Hydrocarbon Chemical Groups in Groundwater Samples

Well	TICs Reported from Non-Hydrocarbon Chemical Groups
SP 5-20	Aldehydes
MS 14-16	Aldehydes, Ketones
MS 12-28	Alcohols, Aldehydes
RS 11-14	Alcohols
RS 1-4	Acids, Ketones
BO 12A-33	Alcohols
WB 8-6	Alcohols, Silanes
WB 7-5	Aldehydes, Silanes
RS 15-12	Silanes
RB 16-30	Alcohols, Aldehydes

7.2.3.2 *Follow-Up Sampling for Tentatively Identified Compounds*

Selected wells with low-level detections of organic constituents were re-sampled in 2012 to quantify concentrations of targeted TICs reported in samples collected from those wells in 2010 or 2011. The targeted TICs comprised alkenes and adamantane as well as non-hydrocarbons, including acid, alcohol, aldehyde, and ketone constituents.

A laboratory standard was not available for calibration of one non-hydrocarbon TIC (2-ethylhexanal) that was reported in groundwater samples collected in 2010 from industrial water supply well MS 12-28. The laboratory declined to analyze samples for fluorotrimethylsilane, which was reported as a TIC in groundwater samples collected from WB 8-6 and WB 7-5 in 2010, because of difficulty in quantifying this compound under standard laboratory conditions.

Results from follow-up sampling, which are quantified concentrations based on calibration to standards containing these compounds, are summarized in **Chart 7-7**.

Approximately half of the targeted TICs that were reported previously in the wells selected for follow-up sampling were not detected above the reporting limit. An alcohol, 2-ethyl-1-hexanol, was quantified in groundwater samples collected from three industrial water supply wells, BO 12A-33, WB 8-6, and MS 12-28. Nonanal was quantified in industrial water supply well SP 5-20, and n-hexadecanoic acid was quantified in industrial water supply well RS 1-4. An alkene, 2-methyl-1-pentene (1-heptene), and adamantane were quantified in SAP study well T-4-RWa; however, these constituents were not quantified in T-4-RWb. No applicable groundwater standards have been established for these compounds.

Chart 7-7 Results from Follow-up Sampling for Tentatively Identified Compounds (TICs)

Well	Previously Reported TIC	Quantified Concentration Micrograms per liter (µg/L)[1]
BO 12A-33	2-Ethyl-1-hexanol	**24**
WB 8-6	2-Ethyl-1-hexanol	**5.3**
MS 12-28	2-Ethyl-1-hexanol	**9.1**
WB 7-5	Hexanal	< 2
MS 14-16	Hexanal	< 2
	Acetone	< 20
SP 5-20	Hexanal	< 2
	Nonanal	**2.4** JM%
RS 1-4	2-Ethylhexanoic acid	<10
	n-Hexadecanoic acid	**44** JM%
	2,4-Dimethyl-3-pentanone	< 1
T-4-RW-a	1-Heptene	**4.1**
	2-Methyl-1-pentene	< 1
	Adamantane	**2.1**
T-4-RW-b	2-Methyl-1-pentene	< 1
	Adamantane	< 1

1. Results in **BOLD** indicate analyte detected above reporting limit.
   JM% = Results from laboratory matrix spike/matrix spike duplicate sample were outside of control limits in associated batch. Associated result is qualified as an estimate.
   < indicates compound not detected at or above laboratory reporting limit specified.

8.0 DATA ANALYSIS

This section presents an overview of data analysis conducted for the study. Data analysis focused on evaluating the composition and origin of gases analyzed for this study and assessing relationships that may exist between various water quality indicators and the presence of low levels of organic constituents detected in wells sampled for this study. Evaluation of gas focused on evaluating the gas composition and methane isotope data (**Section 8.1**). Evaluation of water quality data included determining and mapping the ionic groundwater types observed in wells sampled for this study (**Section 8.2**) and analyzing trends in inorganic and organic groundwater data and dissolved gas data (**Section 8.3**). The analyses in **Sections 8.1** through **8.3** are then summarized in **Section 8.4**, which presents comprehensive matrices of indicators for both groundwater samples and potential source material samples. Finally, **Section 8.5** presents a brief assessment of the few wells sampled for this study that contained organic constituents detected at concentrations greater than applicable groundwater standards.

8.1 COMPOSITION AND ORIGIN OF GASES

Dissolved hydrocarbon gas (i.e., methane) was present in groundwater samples collected from all 34 water wells sampled for this study. Hydrocarbon gas had accumulated in the well casings of 10 water wells sampled for this study when capped. Distinct differences in the occurrence, hydrocarbon composition, and origin of dissolved gas and casing gas were observed.

This section:

- Provides a brief description of indicators used to identify the origin of gases;
- Describes the composition of hydrocarbon gas, including methane, in groundwater and in well casing gas samples;
- Discusses the origin, or possible origins, of hydrocarbon gas in groundwater, in well casings, and from natural gas production wells; and
- Discusses possible sources of gas in groundwater and well casings based on the origin of the gas.

8.1.1 Indicators of Origin in Gases

Methane is created through microbial or thermogenic processes. The origin of gas, whether microbial or thermogenic, can be evaluated based on the molecular composition of gas and the stable isotopic signature of carbon and hydrogen in the methane (Schoell, 1980, 1983; Whiticar et al., 1986; Baldassare and Laughrey, 1997; Rowe and Muehlenbachs, 1999; Osborn and McIntosh, 2010).

The *wetness* of a gas is a measure of the amount of higher molecular weight hydrocarbon gases, such as ethane, propane, butane, and pentane, in the gas (**Section 3.3.6.1**). These higher molecular weight gas components (i.e., C_{2+} gases) are often referred to as *wet gas* components. The wetness of a gas can be expressed as the ratio of methane to ethane plus propane [$C_1/(C_2 + C_3)$]. The greater the ratio, the greater the proportion of methane and the drier the gas. The primary components of microbial gas are methane and carbon dioxide (Schoell, 1980; Rice and Claypool, 1981), with very little or no C_{2+} gases. Thus, microbial gas is considered a dry gas. Microbial methane, often referred to as *biogenic gas* in the literature, is typically generated in low-temperature, near-surface environments by acetate fermentation of organic material (e.g., landfill gas) or by microbial reduction of carbon dioxide in deeper sediments (Schoell, 1980).

Thermogenic methane is formed by the thermal breakdown of organic matter at high temperature and pressure, conditions typically encountered during deep burial of sediments. Thermogenic gas typically contains a greater proportion of higher molecular weight hydrocarbon gas components than microbial gas.

Gas is generally considered of microbial origin if the $C_1/(C_2 + C_3)$ ratio is greater than 1,000 (Bernard et al. 2001; Waseda and Iwano, 2008). The $C_1/(C_2 + C_3)$ ratios of thermogenic gas are typically less than 50 (Bernard et al., 2001). Ratios of $C_1/(C_2 + C_3)$ for gases with an intermediate signature are typically between 50 and 1,000.

Stable isotope values of carbon and hydrogen in methane can be used to further constrain the origin of methane (**Section 3.3.5**). Generally, gas is considered of microbial origin if the carbon isotope value of methane is less than -60 to -64 per mil. Gases with a thermogenic origin have carbon isotope values of methane more positive than approximately -57 per mil based on a standard genetic classification scheme illustrated by Coleman et al. (1995). Methane isotope values for gases with an intermediate signature, which are often referred to as "mixed" gases in the literature, generally plot between thermogenic and microbial ranges on the standard genetic classification scheme for gases (i.e., Coleman et al., 1995).

Distinguishing the origin of gas, particularly thermogenic gas, can frequently be complicated by environmental processes, such as microbial production of hydrocarbons with higher carbon numbers (e.g., ethane and propane), diffusive fractionation, microbial oxidation, and mixing of gases. A gas with an intermediate signature may represent a combination of gases from different origins, such as a combination of microbial and thermogenic gases.

Migration of gases over varying distances and time scales can result in the loss of C_{2+} gas components through absorption of the higher molecular weight components to geologic materials (Matthews, 1996). The loss of these higher molecular weight gas components can result in thermogenic gas taking on a molecular composition similar to microbial methane. Some authors have suggested that diffusive migration could induce negative isotopic fractionation, whereby the

carbon isotope value of methane becomes more negative during gas migration due to fractionation (Prinzhofer and Pernaton, 1997; Prinzhofer et al., 2000); however, others have suggested that the carbon isotope values of methane remain relatively constant during gas migration (Rice and Claypool, 1981; Waseda and Iwano, 2008).

Oxidation of methane causes stable carbon and hydrogen isotope of methane values to shift toward more positive values because the lighter ^{12}C isotope is oxidized at a higher rate than the heavier ^{13}C isotope (Coleman et al., 1981). Thus, oxidation of biogenic methane can result in residual gas with an isotopic composition more typical of thermogenic methane. Microbial production of higher carbon gas components is reported to occur in near-surface sediment in oceans (Schoell, 1980; Bernard et al., 2001) and in aquifers (Taylor et al., 2000).

Component ratios of isobutane to n-butane ($isoC_4/nC_4$) and isopentane to n-pentane ($isoC_5/nC_5$) are used to evaluate whether biodegradation of hydrocarbons has occurred. Saturated hydrocarbons (n-alkanes and C_1–C_5 gases) are removed first during biodegradation and therefore these gas component ratios can be used to assess the degree of alteration of natural gas (**Section 3.3.6.2**).

8.1.2 Occurrence and Composition of Hydrocarbon Gas in Groundwater

The spatial pattern in dissolved methane concentrations and isotopic composition of dissolved methane in groundwater is illustrated on **Figure 8-1.** Dissolved methane concentrations are generally highest in groundwater in the southern half of the PAPA with concentrations in groundwater generally decreasing moving north in the PAPA (**Figure 8-1**). Dissolved methane concentrations in groundwater at all wells sampled north of the New Fork River were less than 1.0 mg/L. Dissolved methane concentrations in groundwater south of the New Fork River ranged from less than 1 mg/L to 120 mg/L.

In general, the chemical and isotopic signature of hydrocarbon gas in groundwater south of the New Fork River is different from that north of the New Fork River. In addition to increasing methane concentrations, the composition of the dissolved hydrocarbon gas becomes progressively wetter, or has a greater proportion of higher carbon component gases (C_{2+} gases), moving south in the PAPA. Gas component ratios, including the ratios of $C_1/(C_2 + C_3)$ in dissolved gas from wells sampled for this study, are presented on **Figure 8-2**. The ratios of $C_1/(C_2 + C_3)$ in dissolved gas in the PAPA decrease toward the south, which indicates an increase in gas wetness, or hydrocarbon gas with proportionally more C_{2+} gas components, toward the south end of the PAPA (**Figure 8-2**). Dissolved gas in groundwater samples collected north of the New Fork River in the PAPA is limited predominantly to methane. Thus, dissolved methane concentrations in groundwater are lower and C_{2+} gas components are absent in dissolved gas north of the New Fork River, except for a very low concentration of ethane (less than 0.0017 mole percent) detected at MS 12-28.

In groundwater samples with appreciable concentrations of C_{2+} gases, dissolved hydrocarbon gas shows evidence of alteration, particularly in samples collected in the south end of the PAPA (e.g., Antelope area). Normal alkanes in the dissolved hydrocarbon gas, such as n-butane and n-pentane, appear to be depleted preferentially with respect to concentrations of branched alkanes, such as isobutane and isopentane. The alteration of the gas is evidenced by the increasing ratios of isobutane to n-butane ($isoC_4/nC_4$) and isopentane to n-pentane ($isoC_5/nC_5$), as illustrated on **Figure 8-2**.

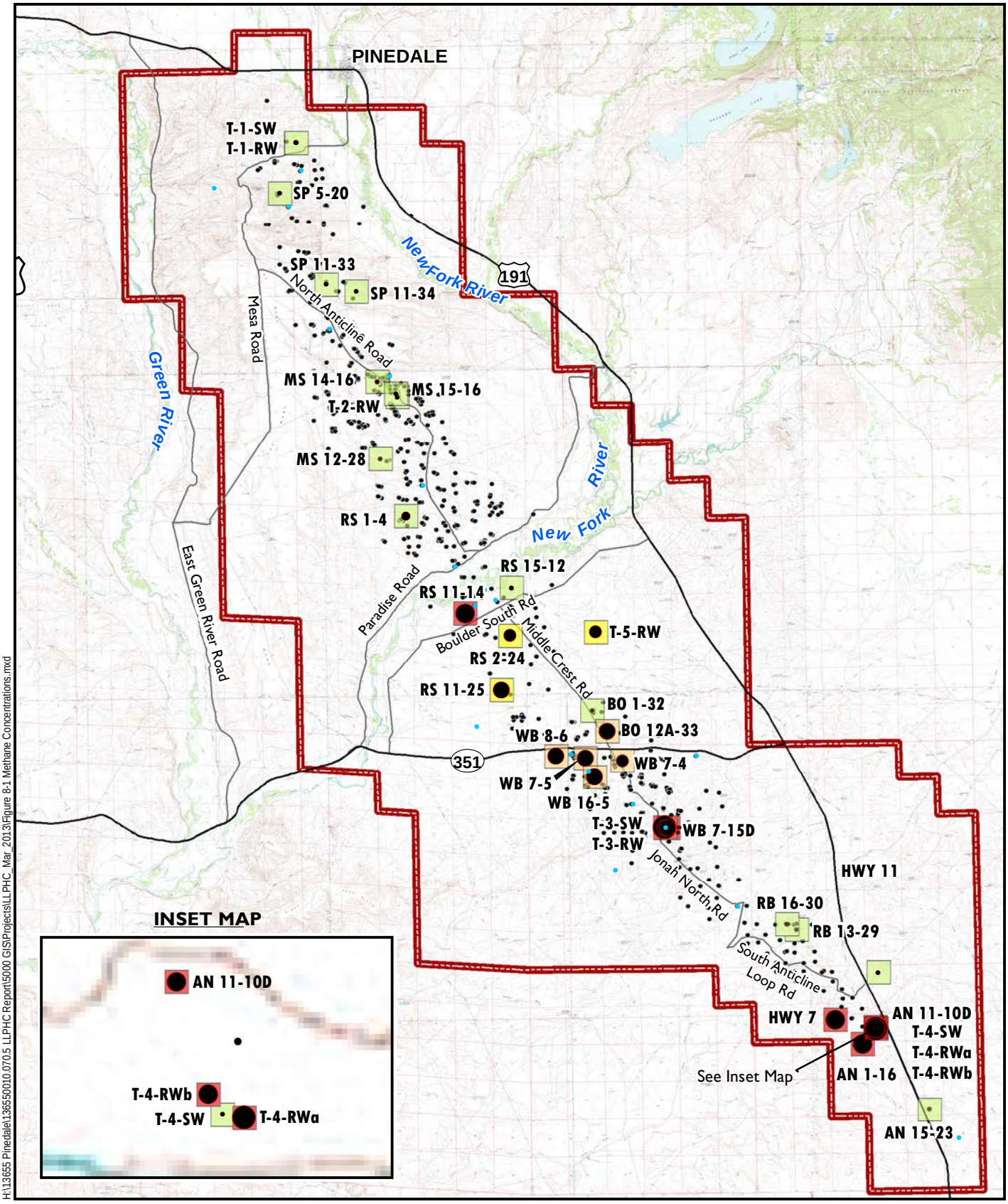
Higher concentrations of dissolved methane in groundwater in the PAPA are also associated with more positive stable carbon isotope values of methane, as illustrated in **Figure 8-3**.

Stable carbon isotope values of methane become progressively more negative moving north toward the New Fork River in concert with decreasing dissolved methane concentrations in groundwater. Values around -70 per mil are observed in groundwater samples collected immediately south of the New Fork River (**Figure 8-1**). Dissolved methane concentrations in groundwater were not sufficient for isotopic analysis in wells located north of the New Fork River.

Some exceptions exist to these overall trends in gas occurrence, hydrocarbon gas composition, and isotopic composition of methane. The dissolved hydrocarbon gas sample collected at RS 11-14, which is located immediately south of the New Fork River, had hydrocarbon composition and isotopic composition of dissolved methane in groundwater similar to values observed for samples collected in the Antelope area at the south end of the PAPA (**Figure 8-1**). In addition, samples from several wells located south of the New Fork River had low dissolved methane concentrations (less than 1 mg/L) (**Figure 8-1**). The dissolved gas in samples from these water wells had similar hydrocarbon composition as dissolved gas in groundwater samples collected north of the New Fork River.

8.1.3 Occurrence and Composition of Hydrocarbon Gas in Well Casings

Casing gas samples collected for this study represent the hydrocarbon gas that displaced the atmospheric gas in well casings while the wells were capped. Hydrocarbon concentrations in these samples are generally not directly comparable to hydrocarbon concentrations in other samples of well casing gas or dissolved gas in groundwater due to varying levels of dilution by air in the samples. Nevertheless, normalization of gas concentrations to a specific carbon range (e.g., C_1 to C_5) and calculation of gas component ratios based on these normalized concentrations can be used as a tool to compare hydrocarbon composition among casing gas samples and between casing gas and dissolved gas collected from the same well.



H:\13655 Pinedale\136550010.070.5 LLPHC Report\5000 GIS\Projects\LLPHC_Mar_2013\Figure 8-1 Methane Concentrations.mxd

N

0 Miles 4

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Pinedale Anticline Project Area

Pre-1984 Natural Gas Production Wells

Post-1984 Natural Gas Production Wells (Through March 17, 2012)

Methane (mg/L)

- <0.1
- 0.1 - 1.0
- 1.0 - 10
- 10.0 - 50.0
- 50.0 - 100
- >100

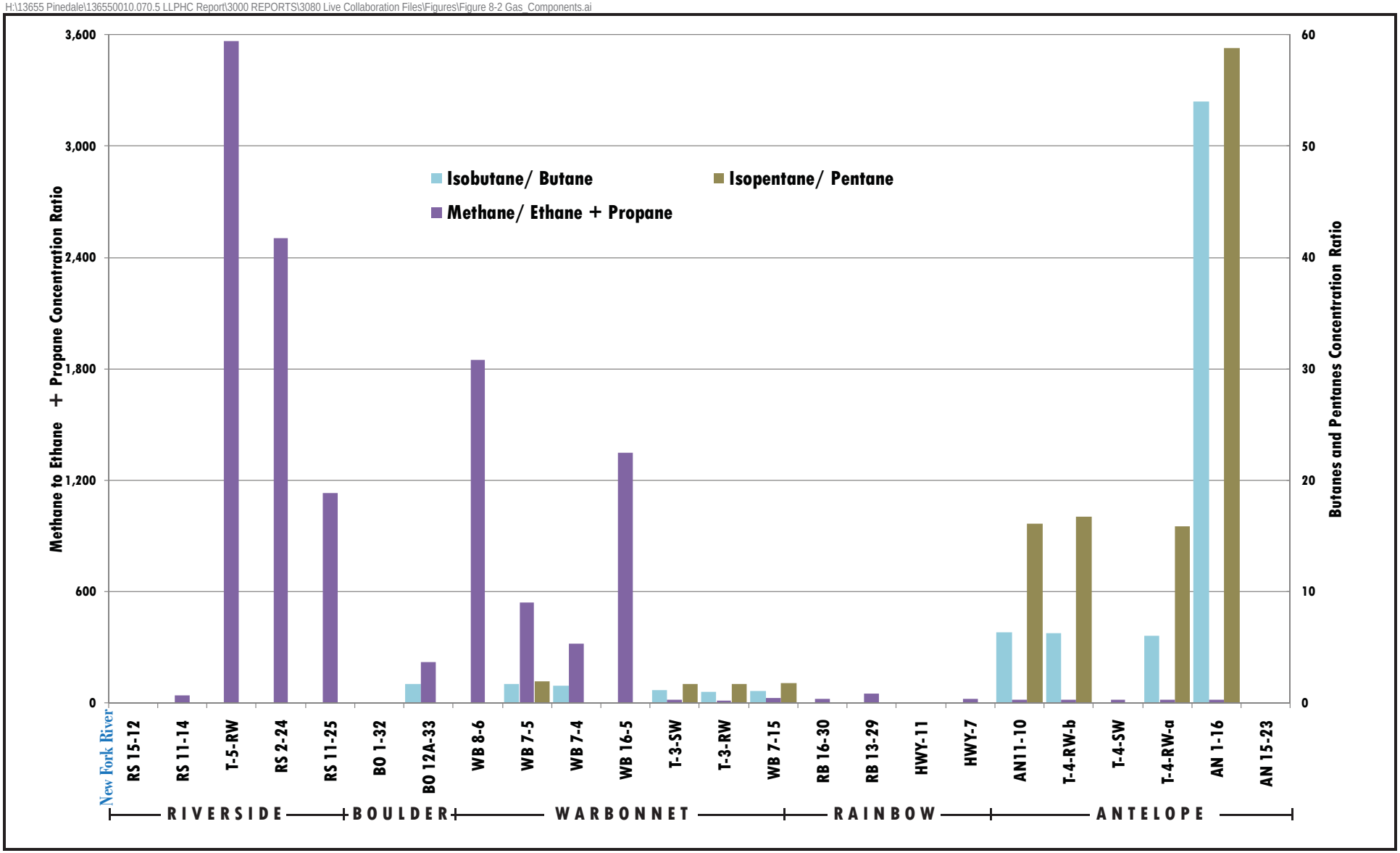
Carbon Isotope Value of Methane (per mil)

- $-100 < {}^{13}C < -64$
- $-64 < {}^{13}C < -50$
- $-50 < {}^{13}C < -30$
- No Isotope Data

Methane Concentration and Isotopic Composition of Methane in Groundwater Low-Level Petroleum Hydrocarbon Evaluation Sublette County, Wyoming

FIGURE 8-1

H:\13655 Pinedale\136550010.070.5 LLPHC Report\3000 REPORTS\3080 Live Collaboration Files\Figures\Figure 8-2 Gas_Components.ai



Gas Component Ratios in Groundwater
Low-Level Petroleum Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 8-2

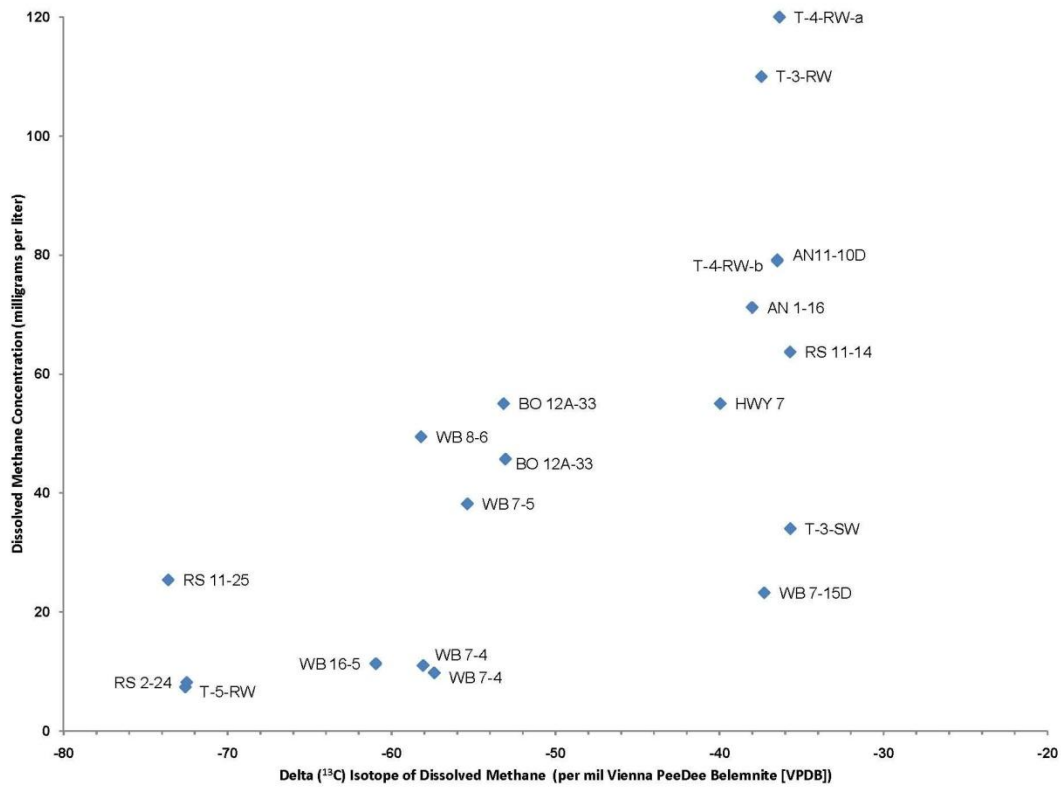


Figure 8-3 Methane Concentrations versus Stable (^{13}C) Isotope Values of Dissolved Methane

Only wells located south of the New Fork River for this study had sufficient quantities of gas accumulating in the well casings for sampling (**Figure 3-2**). This situation is generally consistent with observations made by the SCCD and others during groundwater sampling conducted prior to this study (**Figure 4-4**). Higher dissolved gas concentrations in groundwater, which are observed south of the New Fork River, would increase the likelihood of gas accumulating in water well casings if out-gassing of groundwater is the primary mechanism for the gas accumulation in well casings. In general, the hydrocarbon composition of casing gas and the isotopic composition of methane in casing gas are similar to values in dissolved gas from the same well, and thus follow the same general compositional trends observed in dissolved gas in the PAPA. The wetness of casing gas increases toward the south in the PAPA [i.e., $C_1/(C_2 + C_3)$ ratios decrease], and the stable carbon isotope value of methane becomes more positive toward the south. In addition, the $isoC_4/nC_4$ and $isoC_5/nC_5$ ratios in casing gas in the Antelope area are similar to those observed in groundwater (i.e., evidence of biodegradation).

8.1.4 Origin and Source of Natural Gas, Casing Gas, and Dissolved Gas

Natural gas produced from gas production wells in the PAPA is thermogenic. The hydrocarbon composition and isotopic composition of methane in natural gas samples collected from gas production wells for this study are consistent with a thermogenic origin based on the following findings:

- Higher carbon number gas components up through C_{10} (decanes) (i.e., wet gases) are present in the natural gas.
- $C_1/(C_2 + C_3)$ ratios in natural gas are less than 20.
- Carbon isotope of methane values in natural gas are more positive than -50 per mil.

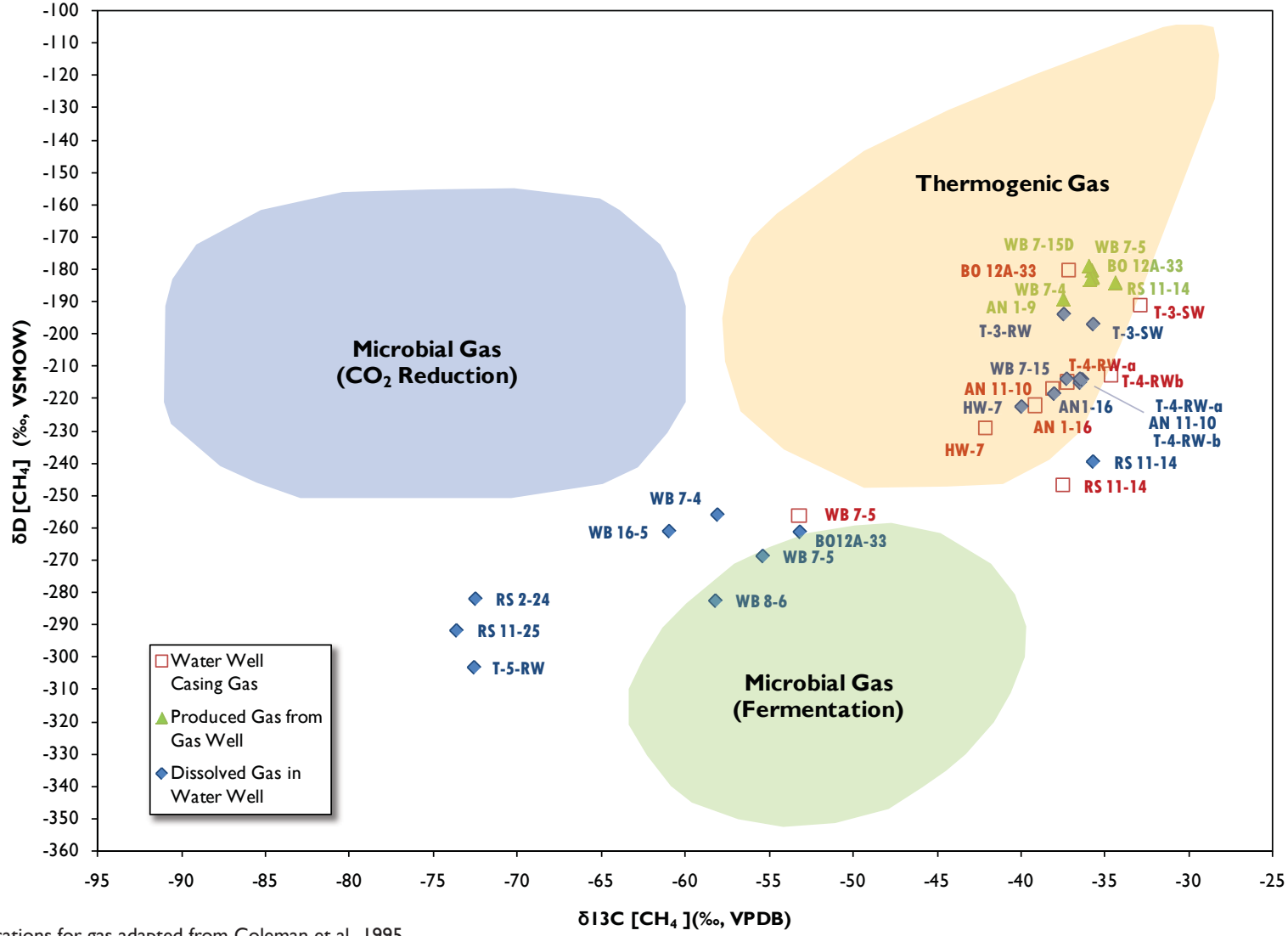
The source of the natural gas produced in the PAPA is the Lance Pool, the over-pressurized, tight-gas reservoir that collectively consists of Cretaceous sediments of the Lance Formation and Upper Mesaverde Group and Paleocene sediments of the Unnamed unit (see **Section 2.2.3**).

Gases with thermogenic, microbial, and intermediate signatures were observed in samples of groundwater (i.e., dissolved gas) collected for this study. Casing gas samples predominantly had a thermogenic signature. Stable carbon and hydrogen isotope values of methane in dissolved gas, casing gas, and natural gas samples are plotted on standard gas genetic classification fields for microbial and thermogenic gases on **Figure 8-4** to facilitate comparison. The following sections discuss the origin of dissolved gas and casing gas in water wells with respect to the hydrocarbon composition and isotopic composition of methane.

8.1.4.1 *Hydrocarbon Gas with a Thermogenic Signature*

Dissolved gas and casing gas in samples from the following water wells were of thermogenic origin based on both hydrocarbon composition and the isotopic signature of methane: HWY 7, AN 1-16, AN 11-10D, T-4-RWa and T-4-RWb, T-3-SW, T-3-RW, WB 7-15, and RS 11-14. These wells are all located south of the New Fork River, and samples from these wells contained dissolved methane concentrations greater than 50 mg/L. Typical of a thermogenic signature, the $C_1/(C_2 + C_3)$ ratios were less than 50, and stable isotope values of methane were more positive than -50 per mil (**Figure 8-1**).

Based on differences in hydrocarbon composition, the dissolved gas and casing gas in some wells is not the same gas that is currently being produced from the Lance Pool at the gas well pads. Thus, the presence of dissolved gas and casing gas in these wells is not an indication that natural gas is leaking from natural gas production wells or other associated gas production facilities.



Note: Genetic classifications for gas adapted from Coleman et al., 1995

Note: δ**D** [**CH4**] = Stable Isotope Composition of Deuterium (^{2}H) and Hydrogen (^{1}H) of Methane

δ^{13} **C**[**CH4**] = Stable Isotope Composition of Carbon (^{13}C) and Carbon (^{12}C) of Methane

‰ = Parts per Thousand or Per Mil

VSMOW = Vienna Standard Mean Ocean Water Standard

VPDB = Vienna PeeDee Belemnite Standard

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Carbon and Hydrogen Isotope Values
of Methane in Natural Gas,
Casing Gas, and Dissolved Gas Samples
Low-Level Petroleum Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 8-4

Carbon isotope values of methane in dissolved gas samples from the wells in the Antelope area (HWY 7, AN 1-16, AN 11-10D, T-4-RWa, and T-4-RWb) and from RS 11-14 fell within the range of values observed for natural gas samples from the Lance Pool; however, the hydrogen isotope values of methane in samples of dissolved gas and casing gas collected from the water wells were generally more negative than those observed in the natural gas sample collected from a nearby natural gas production well (**Figure 8-4**). In addition, relatively high $isoC_4/nC_4$ and $isoC_5/nC_5$ ratios of 2 to over 20 (or approximately 0.6 when ratios are normalized to the sum of the isomers) were observed in dissolved gas and casing gas from these wells, indicating preferential removal of n-butane and n-pentane compared to their respective isomers (**Table 10** and **Table 11**, **Figure 8-2**). Roughly equal concentrations of these gas components were found in natural gas samples, with $isoC_4/nC_4$ and $isoC_5/nC_5$ ratios between 1 and 1.5 (approximately 1.0 when ratios are normalized to the sum of the isomers; **Table 10**).

Taken together, these results suggest that the dissolved gas in Wasatch Formation groundwater in these areas has been altered relative to the source of natural gas produced from the Lance Pool (possible mechanisms for alteration of thermogenic gas signatures are discussed in **Section 9.1**). Thus, dissolved gas and casing gas in these water wells is not directly sourced from natural gas production at the drill pads in this area. The gas originates from a deep gas reservoir, most likely the Lance Pool, but has been altered, possibly during migration through the Tertiary rock units.

Dissolved gas in SAP study wells T-3-SW and T-3-RW and industrial water supply well WB 7-15, as well as the casing gas sample collected from T-3-SW, differed in composition from gas in the wells in the Antelope area. Wells T-3-SW, T-3-RW, and WB 7-15 are all located on the same gas well pad and have yielded water samples with concentrations of organic constituents exceeding applicable groundwater standards (see **Section 8.5.1.1**). Carbon isotope values of dissolved methane in groundwater samples collected at T-3-SW, T-3-RW, and WB 7-15 were very close to the carbon isotope value of methane in the natural gas sample collected from the natural gas production well (WB 7-15D) at this pad (**Figure 8-4**).

The hydrocarbon composition of dissolved gas samples from T-3-SW, T-3-RW, and WB 7-15 with respect to $C_1/(C_2 + C_3)$, $isoC_4/nC_4$, and $isoC_5/nC_5$ ratios was also very similar to that observed in the natural gas sample from WB 7-15D (**Table 10** and **Table 11**). Gas concentrations normalized to C_1 to C_5 gas components in casing gas and dissolved gas samples from these wells were very similar to the normalized gas concentrations in the natural gas sample (**Figure G-5** and **Figure G-6** in **Appendix G**). In contrast, normalized gas concentrations in casing gas and dissolved gas samples from the water wells in the Antelope area were different from the normalized gas concentrations in the natural gas sample collected from a nearby natural gas production well (**Figure G-3** and **Figure G-4** in **Appendix G**). The source of gas in wells T-3-SW, T-3-RW, and WB 7-15 could potentially be the natural gas produced at the well pad, or a gas very similar to that produced at the well pad.

These gases with a thermogenic signature do not appear to be generated in situ in the Wasatch Formation. Vitrinite reflectance and TAI analyses of carbonaceous shale samples collected while drilling study wells T-3-RW and T-4-RWb indicate that the shale is either not a good source for oil and gas generation, or if adequate for gas generation, not thermally mature enough to generate gas (see **Section 5.7**; **Appendix D**). The results of these thermal maturity analyses are consistent with findings by others (Roberts et al., 2005).

8.1.4.2 *Hydrocarbon Gas with an Intermediate Signature*

The dissolved gas in water wells WB 7-4, WB 16-5, WB 7-5, WB 8-6, and BO 12A-33, located in the central PAPA, is characterized by mostly an intermediate signature with respect to both hydrocarbon composition and the isotopic signature of methane. Carbon isotope values of methane at these five wells ranged from approximately -53 to -61 per mil. The more negative values in this range are considered representative of intermediate signatures between thermogenic and microbial gases (i.e., WB 16-5 and WB 8-6). The more positive values in this range (i.e., those for WB 7-4, WB 7-5, and BO 12A-33) are at the boundary of that representative of thermogenic gases (**Figure 8-4**).

Samples of dissolved gas with more negative carbon isotope values of methane typically had fewer detected hydrocarbon gas components and $C_1/(C_2 + C_3)$ ratios more typical of microbial gas. Dissolved hydrocarbon gas samples collected from WB 16-5 and WB 8-6 show a microbial-type signature, with only methane and ethane detected in the groundwater samples and $C_1/(C_2 + C_3)$ ratios greater than 1,000. C_{3+} gases were detected in the dissolved gas samples collected from WB 7-4, WB 7-5, and BO 12A-33, and the $C_1/(C_2 + C_3)$ ratios in these wells ranged from 221 to 609, which is typical of an intermediate gas signature.

Carbon isotope values of methane in dissolved gas at wells WB 7-5 and BO 12A-33 were at the boundary of the thermogenic range. The carbon isotope values of methane in both the casing gas and dissolved gas sampled from WB 7-5 were similar; however, the value in casing gas from BO 12A-33 was considerably more positive than the value in dissolved gas, similar to observations for casing gas and dissolved gas samples from the south end of the PAPA. Casing gas samples from both of these wells show preferential removal of n-alkanes as compared to their respective isomers ($isoC_4/nC_4$ and $isoC_5/nC_5$ ratios of approximately 2), whereas roughly equal concentrations of these gas components are found in natural gas samples from these wells ($isoC_4/nC_4$ and $isoC_5/nC_5$ ratios between 1 and 1.5) (**Table 10**). This removal of n-alkanes relative to their respective isomers is also evident when plotting normalized gas concentrations at wells BO 12A-33 and WB 7-5 (**Figure G-2** and **Figure G-5** in **Appendix G**, respectively).

The source of the dissolved gas with this intermediate signature in groundwater samples from these wells is unknown, but it is clearly not the same natural gas that is currently being produced at

gas well pads in the PAPA because of the isotopic and compositional differences between the gases. Gas with an intermediate signature could arise in several ways:

- Mixing of gases of different origins (e.g., microbial and thermogenic gas);
- The presence of a dissolved gas of differing origin, for example, a gas associated with coal-bearing strata (e.g., coal-bed methane) (Horşgörmez et al., 2002; Laughrey and Baldassare, 1998; Bartos and Ogle, 2002); or
- Mixing of thermogenic gases with different maturities or complicated thermogenic histories (Waseda and Iwano, 2008; Laughrey and Baldassare, 1998).

The most likely origin of gas with an intermediate signature in groundwater in the PAPA is either the mixing of microbial gas with altered thermogenic gas, or an increasingly altered thermogenic gas. Gas with an intermediate signature was present in wells located between wells containing gas with a microbial-type signature toward the north and wells containing gas with an altered thermogenic signature located toward the south. In wells with sufficient gas for analytical testing, gas with the intermediate signature exhibits the depletion of n-alkanes with respect to isoalkanes, as was observed in wells that contained altered thermogenic gas.

8.1.4.3 *Hydrocarbon Gas with Microbial Signature*

Dissolved gas in three water wells, T-5-RW, RS 2-24, and RS 11-25, which are located south of the New Fork River, fall within the genetic field for microbial origin based on carbon isotope values of methane more negative than -64 per mil (**Figure 8-4**) and $C_1/(C_2 + C_3)$ ratios greater than 1,000 (**Figure 8-2**).

No casing gas samples had a microbial signature.

The source of this gas with the microbial-type signature is unknown; however, again it is not the same gas that is being produced at the natural gas pads. Gases with the microbial-type signature could be the result of:

- Microbial methane produced through biodegradation of natural organic material present in Wasatch Formation sediment;
- Microbial methane produced through biodegradation of hydrocarbon-containing compounds present in the Wasatch Formation, whether from natural or anthropogenic sources; and/or
- An extremely altered thermogenic gas or a mixture of predominantly microbial gas with some thermogenic gas.

Although this gas may be predominantly microbial in origin, it could be mixed with a minor amount of the altered thermogenic gas. The gas in these wells appears to represent further

movement on a compositional and isotopic continuum with respect to the dissolved gas with intermediate signature observed in the central portion of the PAPA and altered thermogenic gas at the south end of the PAPA (**Figure 8-4**).

8.1.4.4 *Gas with an Indeterminate Signature*

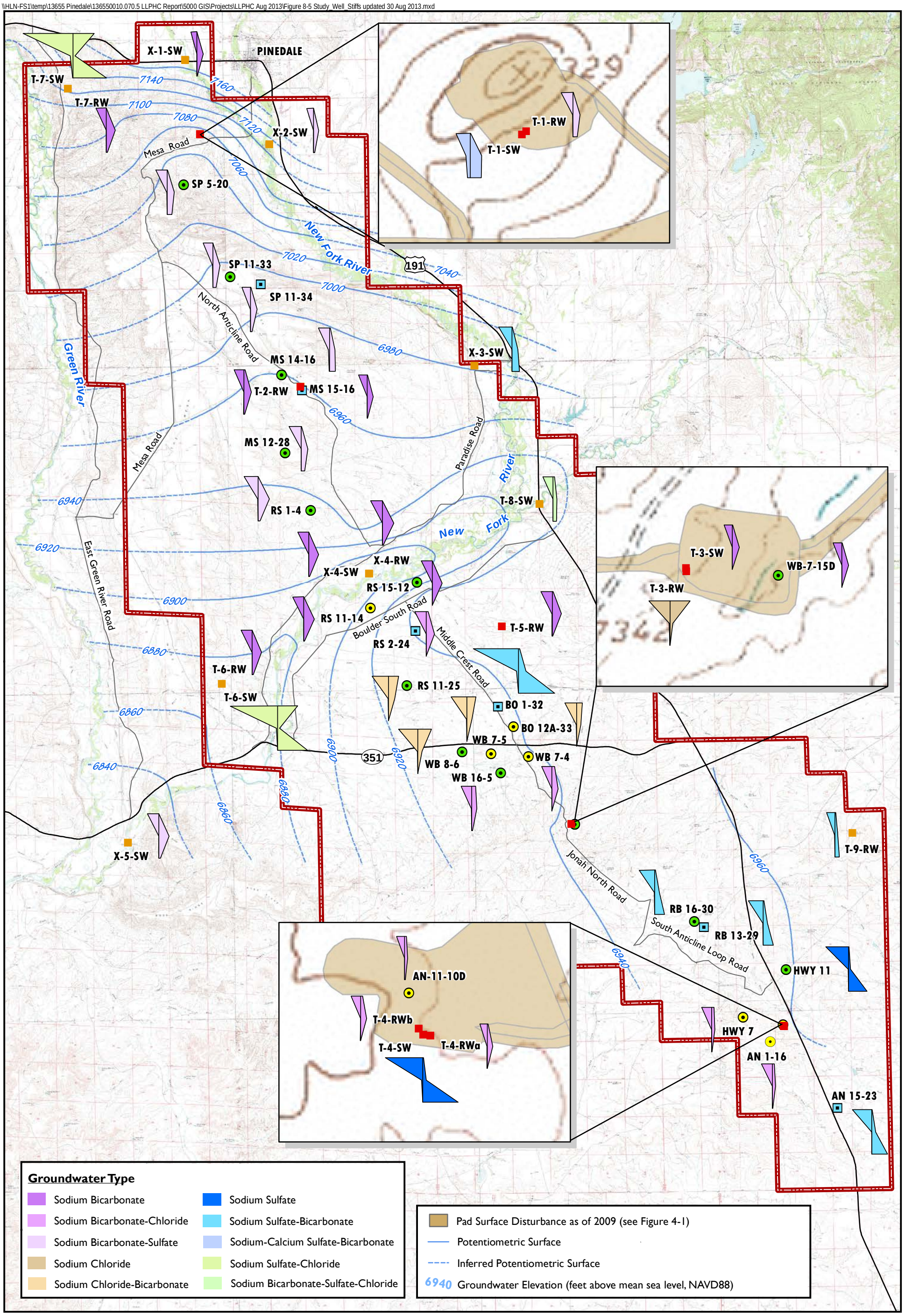
Dissolved gas with low concentrations of hydrocarbons typically had insufficient methane concentrations for isotopic analysis, and thus is referred to in this report as a gas with an indeterminate signature. All sampled wells located north of the New Fork River (RS 1-4, MS 12-28, T-2-RW, MS 15-16, MS 14-16, SP 11-34, SP 11-33, SP 5-20, T-1-SW, and T-1-RW) contained dissolved gas with an indeterminate signature. Several wells sampled south of the New Fork River, RS 15-12, BO 1-32, AN 15-23, HWY 11, T-4-SW, RB 13-29, and RB 16-30, also contained dissolved gas with an indeterminate signature.

Hydrocarbon components in dissolved gas in most wells with an indeterminate signature were limited to methane and ethane. The possible sources or origin of this gas would be similar to those gases with a microbial signature (see **Section 8.1.4.3**). Ethane has been shown to be produced by bacteria in aquifers along with methane (Taylor et al., 2000) and cannot be considered a gas produced only under thermogenic conditions. The sample collected from industrial water supply well RB 16-30 represents an exception to this general trend of few to no C_{2+} gases in dissolved gas with an indeterminate signature. Although dissolved methane concentrations were low in RB 16-30, unsaturated hydrocarbon gases through C_6 were reported as TICs in the groundwater sample from this well, and ethene was quantified in the dissolved gas sample.

8.2 MAJOR IONS IN GROUNDWATER

Stiff diagrams were prepared to show the major ionic signatures of groundwater samples collected for this study and the HDG investigation. The Stiff diagrams are plotted on a map of the PAPA in **Figure 8-5** to show the distribution of the major groundwater types for wells in the Wasatch Formation throughout the PAPA. Stiff diagrams are a useful way to illustrate general patterns of ionic chemistry in groundwater. The ionic chemistry of groundwater varies because of many complex factors, such as the composition and solubility of rock materials in the soil or aquifer, water temperature, partial pressure of carbon dioxide, acid-base reactions, oxidation-reduction reactions, loss or gain of constituents as water percolates through clay layers, and mixing of groundwater from adjacent strata, all of which can change with depth in the subsurface and with the residence time of water along a groundwater flow path (Indiana Department of Natural Resources, 2002).

\\HLN-FS1\temp\13655 Pinedale\136550010.070.5 LLPHC Report\5000 GIS\Projects\LLPHC Aug 2013\Figure 8-5 Study_Well_Stiffs updated 30 Aug 2013.mxd



Note: Inorganic data used to generate Stiff diagrams for HDG study wells and the potentiometric surface of Wasatch Formation obtained from hydrogeological data gaps investigation report (AMEC, 2012).

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0 Miles 3

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Pinedale Anticline Project Area
T-5-RW SAP Study Well
AN 15-23 Control Well
WB 16-5 PHC Well
HWY 7 LEL Well
X-5-SW HDG Study Well

Milliequivalents per Liter

Sodium
Calcium
Magnesium

Chloride
Bicarbonate+Carbonate
Sulfate

25 0 25

Groundwater Stiff Diagrams
Wasatch Formation
Low-Level Petroleum
Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 8-5

Sodium is the dominant cation in groundwater samples from wells installed in the Wasatch Formation, whereas no single anion was predominant in groundwater in the Wasatch Formation across the entirety of the PAPA. It is generally accepted that, as groundwater moves along a flow path, water type with respect to anions undergoes an evolution in the following sequence: bicarbonate to sulfate to chloride (Freeze and Cherry, 1979). The stiff diagrams plotted on **Figure 8-5** display a distinct geographic influence on ionic composition of groundwater in the PAPA, which is likely related to the area where the water was recharged, the lithology of units encountered along the groundwater flow path, and the residence time of groundwater within the aquifer. However, the ionic chemistry of groundwater sampled for this study does not appear to conform to the traditional evolutional model along a groundwater pathway.

The inorganic chemical data collected at water wells sampled for this study appear to be consistent with the historical inorganic chemical data gathered by the SCCD at these water wells. The inorganic chemical data from this study also appear to be consistent with the findings of other studies in the Green River Basin (Chafin and Kimball, 1992; Zimmerman and Collier, 1985). Those previous studies reported inorganic data from water wells in the Wasatch Formation that are generally installed at shallower depths and along river corridors in and near the PAPA. The deepest well sampled in the Chafin and Kimball (1992) study was 450 feet deep and located in the New Fork River corridor.

8.2.1 Ionic Chemistry of Groundwater North of the New Fork River

Sodium bicarbonate-sulfate and sodium bicarbonate-type groundwaters are the predominant water types north of the New Fork River, particularly along the crest of the Pinedale Anticline and at depth in the Wasatch Formation. Chafin and Kimball (1992) have noted that a sodium bicarbonate-type groundwater with low TDS develops within short distances of recharge zones in the northern Green River Basin. Development of this sodium bicarbonate groundwater is augmented in a downgradient flow direction by ion exchange occurring in the interbedded mudstone and shale units in the Wasatch Formation. In general, groundwater evolves from sodium bicarbonate-sulfate to sodium bicarbonate–type along the north/south groundwater flow path observed north of the New Fork River in the PAPA. This trend is contrary to what would be expected if groundwater followed a typical groundwater evolutional pathway. In addition, some shallower Wasatch Formation wells, such as X-3-SW along the New Fork River in the eastern portion of the PAPA and T-1-SW along the crest of the Pinedale Anticline, are sodium-calcium sulfate-bicarbonate to sodium sulfate-bicarbonate groundwaters. Groundwater upgradient and/or at shallower depths in the Wasatch Formation appears to contain a higher sulfate content. Shallower wells in the Wasatch Formation nearer to the Green River toward the west have sodium sulfate-chloride type water (T-6-SW and T-7-SW). The reason for the presence of this type of groundwater in these wells is unknown. The deeper Wasatch Formation wells at these well clusters (T-6-RW and T-7-RW) are of sodium bicarbonate type.

8.2.2 Ionic Chemistry of Groundwater South of the New Fork River

Sodium was the predominant cation in groundwater south of the New Fork River, which was consistent with groundwater north of the New Fork River. However, the predominant anion(s) in groundwater south of the New Fork River varied and appeared to be dependent on location in the PAPA. In general, groundwater evolves from sodium sulfate to sodium chloride-bicarbonate-type moving from east to west in the PAPA in the downgradient groundwater flow direction. Sodium bicarbonate-type water predominates in areas of groundwater discharge to the New Fork River (e.g., RS 15-12, RS 11-14, and the X-4 well cluster).

As was observed north of the New Fork River, groundwater with a higher sulfate content tends to occur in the upgradient groundwater flow direction (e.g., T-9-RW, RB 16-30, RB 13-29, and HWY-11) and/or at shallower depths within the Wasatch Formation (i.e., T-4-SW). Sodium sulfate-type water tends to have the highest TDS concentrations (**Table 12**). Chafin and Kimball (1992) report that sodium sulfate-type groundwater with higher TDS concentrations is common in the area that corresponds with the south end of the PAPA.

Groundwater appears to evolve to sodium bicarbonate-chloride (e.g., WB 16-5 and WB 7-4) and sodium chloride-bicarbonate type (e.g., WB 8-6 and WB 7-5) in the downgradient groundwater flow direction and/or with depth in the Wasatch Formation in the central portion of the PAPA. Three of the four wells with the sodium chloride-bicarbonate-type water are wells with some of the deepest perforated zones sampled for this study (elevation of the base of perforated zone ranging from about 6,300 to 6,400 feet above mean sea level). Chafin and Kimball (1992) did not report any sodium chloride water types; however, the results of their study are more representative of near-surface groundwater in the Wasatch Formation that is predominantly located in river corridors. The only sodium chloride-type groundwater that had a chloride concentration clearly elevated with respect to what is observed elsewhere in the PAPA was encountered in well T-3-RW, which appears to be affected by natural gas E&P activities (see **Section 8.5**).

8.2.3 Ionic Chemistry of Groundwater in Other Gas Fields

Variable water types have been observed in groundwater above other gas fields. In studies performed in Garfield County, Colorado, the geographical distribution of water types was variable and not explained by principal component and cluster analysis (URS, 2006). SSPA (2008) further concluded that a simple, gradual evolution of groundwater was not occurring and that other complex mechanisms may be at play, such as the possibility that geochemically distinct water types reflect significantly different conditions in the shallow subsurface or that water from depth was mixing with near-surface groundwater to contribute to the observed pattern. An analysis of methane with respect to groundwater type in the same area indicated that groundwater samples containing low methane concentrations (less than 1 mg/L) were associated with sulfate-bicarbonate and bicarbonate-sulfate waters, and groundwater samples containing higher concentrations of

methane (greater than 1 mg/L) were sodium bicarbonate to sodium chloride-type waters (McMahon et al., 2010). These findings are consistent with the findings of this study.

A relationship between ionic composition and well depth and proximity to suspected recharge area has been noted in the Wasatch Formation in the Powder River Basin in both Wyoming and Montana (Bartos and Ogle, 2002). Groundwater in the upper Wasatch Formation is characterized by water with a mixed cation composition and either sulfate or bicarbonate as the dominant anion. Deeper groundwater in the Wasatch Formation and underlying coal bed aquifers in the Fort Union Formation are characterized solely by a sodium bicarbonate-type groundwater. This zonation reportedly appears to be related to geochemical processes, such as dissolution and precipitation of minerals, ion exchange, sulfate reduction, and mixing of waters. Although coal bed aquifers have not been identified in the Fort Union Formation in the PAPA, the presence of methane that has migrated into Tertiary Formations may be conducive to setting up the same type of geochemical environment.

8.3 CORRELATION AND CLUSTER ANALYSIS OF GROUNDWATER AND GAS DATA

This section presents the results of analyses performed to evaluate relationships among constituents present in groundwater and gas samples. The purpose of these analyses was to identify individual constituents that could serve as potential indicators for sources of low-level organic constituents detected in water wells in the PAPA. This section focuses on the observed trends among groundwater samples and gas samples based on correlation and cluster analyses.

8.3.1 Results of Correlation Analysis

No discernable relationships were observed in the study dataset between the following groups of parameters:

- Inorganic constituents in groundwater and geographical location (i.e., northing coordinate of wells in the PAPA);
- Most inorganic constituents and dissolved methane concentrations in groundwater;
- Inorganic constituents and detections of individual organic constituents or groups of constituents (e.g., BTEX) in groundwater; or
- Inorganic constituents in groundwater and inorganic constituents in potential source material samples.

A positive correlation was observed between methane and chloride concentrations in groundwater; a negative correlation was observed between methane and sulfate concentrations in groundwater. No apparent correlations were observed between individual organic constituents, or between groupings of organic constituents and gases. As such, no consistent

relationship was observed between dissolved methane and organic constituents, such as BTEX, in groundwater.

8.3.2 Results of Cluster Analysis

Results of the cluster analysis substantiated the results from the correlation evaluation with respect to trends in groundwater samples:

- Higher chloride concentrations tend to occur with higher methane concentrations; and
- Lower sulfate concentrations tend to occur with higher methane concentrations.

These relationships are best demonstrated graphically by comparing groundwater type to the presence of dissolved methane in groundwater from water wells sampled for this study, as illustrated in the Piper diagram on **Figure 8-6**. The Piper diagram in **Figure 8-6** also reveals the following relationships:

- Groundwater is mixed sodium-bicarbonate-sulfate type water in wells north of the New Fork River with less than 1.0 mg/L of dissolved methane.
- Groundwater is mixed sodium-sulfate-bicarbonate type water in wells located south of the New Fork River with less than 1.0 mg/L of dissolved methane.
- Groundwater ranges from sodium-bicarbonate to sodium-chloride type water in wells located south of the New Fork River with dissolved methane concentrations greater than 1.0 mg/L (17 of 24 water wells sampled).

The isotopic composition of methane, where it can be determined in groundwater, also appears to be related to groundwater type. Groundwater with sodium-chloride-bicarbonate type water and methane concentrations greater than 1.0 mg/L has dissolved methane with an intermediate signature, whereas sodium-bicarbonate type groundwater with methane concentrations greater than 1.0 mg/L has dissolved methane with an altered-thermogenic signature. It is not known if groundwater with elevated chloride concentrations relative to groundwater in the rest of the PAPA and with dissolved methane of intermediate origin is consistent with background conditions in this area.

While relationships between inorganic constituents and dissolved gas were observed upon the clustering of individual constituents during evaluation, in general, no consistent relationship was observed between dissolved methane and low-level detections of organic constituents in groundwater. In addition, chloride and sulfate concentrations could not be consistently related to concentrations of organic constituents in groundwater.

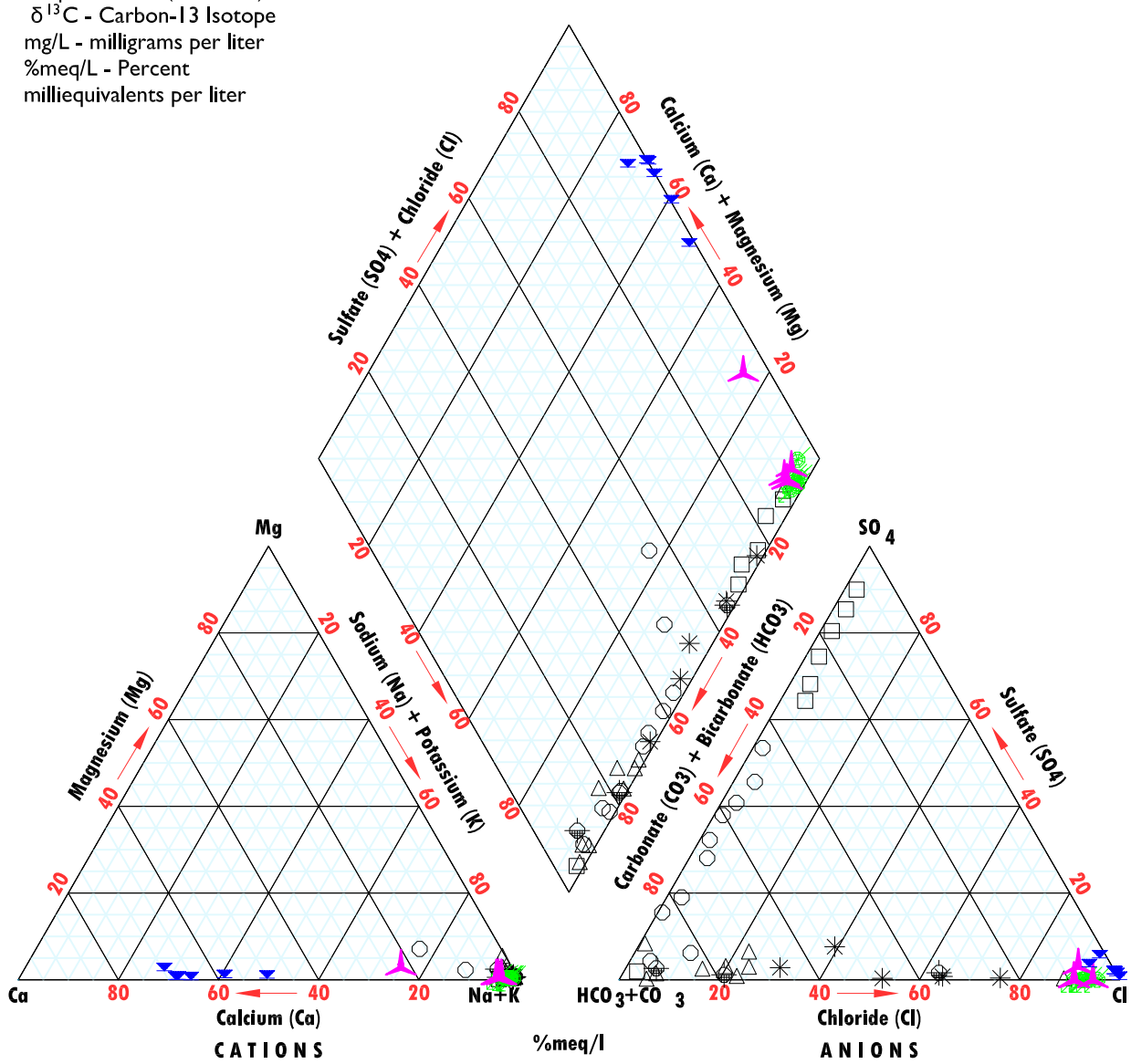
Groundwater

- ○ Wasatch, North of New Fork River, <1 mg/L CH_4
- □ Wasatch, South of New Fork River, <1 mg/L CH_4
- △ Wasatch, >1 mg/L CH_4, $-50 < \delta^{13}C < -30$
- ✳ Wasatch, >1 mg/L CH_4, $-64 < \delta^{13}C < -50$
- ⌖ Wasatch, >1 mg/L CH_4, $-100 < \delta^{13}C < -64$
- Fort Union

Natural Gas Production Fluids

- Produced Water
- Flowback Fluid

Note: CH_4- Methane (dissolved)
$\delta^{13}C$ - Carbon-13 Isotope
mg/L - milligrams per liter
%meq/L - Percent milliequivalents per liter



H:\13655 PAPA\Cadpro\LLPHC_Fall_2010\Piper_Diagram.dwg

Piper Diagram of Groundwater from Wasatch and Fort Union Formations, Flowback Fluid, and Produced Water Samples
Low-Level Petroleum Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 8-6

amec

8.4 CHEMICAL DATA SUMMARIES FOR SOURCE MATERIALS AND GROUNDWATER

A comprehensive matrix of chemical and chromatographic indicators was generated to facilitate comparison of the chemical and isotopic signatures between potential source materials and water wells. The chemical matrix is provided in **Appendix H**. The chemical matrix summarizes analytical results for potential source material samples and samples collected from water wells for this study and the HDG investigation. The chemical matrix includes a summary of the following potential indicators:

- Detections of volatile organic fractions (TPH-GRO and TPgH) and semivolatile organic fractions (TPH-DRO and TEH) above the laboratory reporting limit;
- Range in percentages of TPgH that is TPH-GRO and TEH that is TPH-DRO;
- General and specific attributes of chromatographic profiles;
- VOC detections above the laboratory reporting limit (BTEX and methyl ethyl ketone);
- SVOC detections above the laboratory reporting limit (phenols, naphthalenes, cresols, and other polycyclic aromatic hydrocarbons);
- TIC chemical groups present and total number of TICs reported in sample;
- TICs quantified by VOC and SVOC analysis upon re-sampling (acids, alcohols, aldehydes, ketones, alkenes, terpenoids);
- Inorganic constituents (general water quality parameters and total metals) at concentrations 10 times their respective reporting limits;
- Range in stable isotope values of water, dissolved inorganic carbon, and methane; and
- Hydrocarbon gas composition and range in gas component ratios.

Data for each potential source material sample and groundwater sample are displayed as a series of symbols in the chemical matrix. Results for multiple samples of a single potential source material were also summarized in the matrix as a material summary. Symbols on the matrix generally note detected constituents or groups of constituents or the ranges of measured values for a specified parameter. Symbols for source material summaries indicate if the parameters were consistently detected above the reporting limit. Symbols for inorganic parameters in samples of potential source materials and groundwater indicate whether the detection was elevated with respect to typical groundwater. Symbols were also used to identify general and specific attributes of GRO and DRO chromatograms. A more detailed explanation of the chemical matrix is presented in **Appendix H**.

To more easily evaluate each of the individual potential source materials, a series of smaller matrices were developed to compare summary indicators for each type of potential source material

with indicators for each of the water wells sampled for this study. These indicator matrix tables were generated from the comprehensive chemical matrix presented in **Appendix H** and are presented in **Tables 16–22** for each of the following potential source materials:

- Condensate (**Table 16**);
- Produced Water (**Table 17**);
- Flowback Fluid (**Table 18**);
- Drill Mud (**Table 19**);
- Pump Installation Materials (**Table 20**);
- LNAPL (**Table 21**); and
- Natural Gas (**Table 22**).

The potential indicator parameters for source materials in **Tables 16–22** were selected as those that were consistently detected among the samples for the respective potential source material or those that are characteristic of that particular potential source material in comparison to other potential source materials. If more than one sample was collected per source material type, the material summary from **Appendix H** was used for comparison to the indicators for individual water wells. The indicator matrix tables provide a visual guide to the parameters that could serve as potential indicators for each of the source materials with respect to the constituents detected in each water well.

Table 23 presents a summary of the sources or likely sources of organic constituents detected in each of the water wells based on the comparison of chemical signatures as shown in the indicator matrix tables as well as other evidence gathered for this study (i.e., spatial, chemical, temporal, physical or operational). The sources or likely sources identified in **Table 23** include the source materials that were sampled for this study as listed above, as well as source materials that were not directly sampled but were identified or inferred based on other evidence presented in this report. The sources that were not directly sampled for this study include altered thermogenic and/or microbial gas, naturally occurring organic matter, and well drilling and installation materials. The source or likely source determinations are based on multiple lines of evidence that will be discussed further for high-level wells in **Section 8.5** and low-level wells in **Section 9.0**.

8.5 DETECTIONS OF ORGANIC CONSTITUENTS ABOVE APPLICABLE GROUNDWATER STANDARDS

This section describes the characteristics of detections of organic constituents at concentrations above applicable groundwater standards (e.g., high level), as well as the specific chemical characteristics of the few wells sampled for this study with high-level detections.

The focus of this report is the evaluation of *low-level* detections of organic constituents in groundwater. Most detections of organic constituents in groundwater samples collected from wells sampled within the PAPA are considered low-level, with constituent concentrations well below applicable groundwater standards. This generalization is evident based on the results of annual sampling conducted by SCCD (**Appendix A**), as well as the results of groundwater sampling conducted for this study and for the HDG investigation (**Section 7.2.2**).

The wells targeted for sampling in this study were biased toward wells where organic constituents had previously been detected in samples collected by the SCCD. Despite this bias in well selection, only 5 of the 34 water wells sampled for this study had concentrations of organic constituents above applicable groundwater standards. Three of these five water wells are located within 500 feet of each other on the same gas well pad and are therefore indicative of groundwater conditions at a single location. While high-level detections of organic constituents in water wells are not the focus of this report, the analysis of high-level detections presented in this section provides context for wells with low-level detections with respect to identifying potential source media present in the wells. This evaluation may also provide insight into the likely mode of transport for organic constituents into the well. Sources or potential sources of low-level detections of organic constituents are evaluated in detail in **Section 9.0.**

Samples with high-level detections, that is wells in which organic constituents were detected at concentrations above applicable groundwater standards, typically contain significant detections in both the volatile and semivolatile organic fractions, although one organic fraction may dominate. The associated chromatographic profiles from these samples are characteristic and resemble chromatograms of known petroleum-based substances.

Often individual VOCs and/or SVOCs, such as BTEX constituents and naphthalene, are detected, which complement the results for the volatile and semivolatile organic fractions. These constituents are associated with most of the potential source material samples that contain petroleum substances. If included in the analyses, numerous TICs were reported for these samples. These TICs are characteristic of petroleum-containing substances and represent a variety of chemical groups, such as alkanes, alkylbenzenes, cycloalkanes, and adamantanes. The presence of numerous compounds with carbon–carbon double bonds (e.g., alkenes) or triple bonds (e.g., alkynes), especially those compounds in the lower carbon number ranges, may be indicative of refined petroleum products rather than naturally occurring, or unrefined, petroleum substances.

Results showing high-level detections of organic constituents are often repeatable between groundwater sampling events; multiple lines of evidence, such as described above, can then be used to ascertain potential sources of these high-level detections. The locations of high-level detections appear to be isolated with respect to one another based on the results of SCCD's annual monitoring of numerous wells in relatively close proximity (average distance between wells is 1,500 feet) in the PAPA. There is no evidence that these few high-level detections are linked to the low-level detections found sporadically in the PAPA. Water supply wells with high-level detections are overseen under existing regulatory frameworks in Wyoming (e.g., Voluntary Remediation Program).

Data used to identify and evaluate potential sources for the high-level detections in water wells WB 7-15, T-3-SW, T-3-RW, AN 1-16, and RS 11-25 are discussed briefly below for each of these wells.

8.5.1 High-Level Detections in Water Wells T-3-SW, T-3-RW, and WB 7-15D

The types of organic constituents detected in samples collected from WB 7-15, T-3-SW, and T-3-RW at the Warbonnet 7-15D drill pad most closely match those found in the produced water and natural gas samples (i.e., production gas) analyzed for this study (**Tables 17** and **22**).

TPH-GRO and BTEX were the predominant constituents detected in groundwater samples collected at this well pad (**Table 14**). Although low levels of TEH were detected, TPH-DRO was not detected in groundwater samples. The chromatographic profiles from the GRO analysis for groundwater samples collected from T-3-RW and WB 7-15 match the chromatographic profile for produced water sampled at this pad (**Figure F-16** in **Appendix F**). The elevated chloride concentration in T-3-RW is consistent with an impact from produced water; the numbers of TICs and TIC chemical groups represented in T-3-RW are similar to those in the produced water sample. SVOCs characteristic of produced water sampled for this study, such as naphthalenes, phenols, and cresols, were not detected above reporting limits in groundwater samples from these wells, possibly due to dilution by groundwater.

Hydrocarbon gas is present in these wells as evidenced by:

- The results of dissolved gas and casing gas analyses (**Table 10** and **Table 11**);
- The presence of hydrocarbon gas components reported as TICs in groundwater samples (**Table 15**); and
- The presence of early-eluting peaks in the GRO chromatograms from some of the wells (**Figure F-16** in **Appendix F**).

The hydrocarbon gas composition and isotopic composition of methane in dissolved gas and casing gas sampled at this gas well pad are notably similar to the values observed in natural gas

produced from the Lance Pool. Dissolved and casing gas samples at this location do not show any evidence of n-alkane depletion with respect to isoalkanes, which is evident in gas with an altered thermogenic signature (**Figure G-5** and **Figure G-6** in **Appendix G**).

A historic (pre-1984) gas well (Pinedale 7), which is plugged and abandoned, is located at this gas well pad (**Figure 4-1**). The chemical signatures of gas and groundwater from well T-3-RW, the nearest water well to Pinedale 7, match the chemical signatures of produced water and natural gas produced at the well pad. These matching signatures suggest that the Pinedale 7 well could be the source of groundwater impacts present at the pad. The Operator previously submitted a Sundry Notice (SN) to the BLM and WOGCC to enhance the plugging and abandonment (P&A) of the Pinedale 7; BLM and WOGCC subsequently approved the P&A enhancement procedure, and the work was completed during the summer of 2012. It is noted that a section of compromised casing had previously been identified and addressed during the initial P&A of this well in 2004; whether or not this section of casing is the source of the elevated concentrations has not been definitively determined. The site has been enrolled in the Wyoming DEQ Voluntary Remediation Program since 2007 and is subject to ongoing investigations at the pad location to assess the extent of the impact to groundwater. All ongoing work is occurring under the direction of Wyoming DEQ in cooperation with the Operator and BLM.

8.5.2 LNAPL in AN 1-16

The hydrocarbon profile and chemistry of the LNAPL sample collected from well AN 1-16 (sample AN 1-16 PHC) does not match any other single potential source material sampled for this study (i.e., drill mud, produced water, flowback fluid, or condensate) (**Table 9**). The LNAPL sample is composed mainly of TPH-DRO (**Table 3**), and no VOCs or SVOCs were detected in the LNAPL sample (**Table 4**). TICs reported in this sample included decalins and numerous adamantanes; however, no alkanes or alkylbenzenes were reported in the LNAPL sample, which were detected in several other potential sources sampled for this study (**Table 5**). The DRO chromatogram shows a smooth progression of C_{10} through C_{28} compounds, with some compounds present up through C_{40} (**Figure F-10** in **Appendix F**). Based on its UCM-type signature, the LNAPL in AN 1-16 appears to be rather weathered and degraded. The chromatographic profile of the LNAPL most closely resembles a standard reference chromatogram for crude oil used for general reference by the laboratory (**Appendix D**). The chemical signature of the semivolatile fraction in water well AN 1-16 matches the chemical signature of the LNAPL sample, which was collected from the top of the water column in this well (**Table 21**).

The source of this LNAPL is unknown; however the presence of compounds with a broad carbon-number range is not characteristic of a refined product, such as diesel fuel or motor oil. Polymethyl-substituted decalins and adamantanes are characteristic of heavier crude oils (Wang and Stout, 2007). Adamantanes are reported to be naturally occurring in many crude oils, gas condensates,

and natural gas reservoirs (Stout and Douglas, 2004). Further action should be considered with regard to this well under oversight by a State of Wyoming regulatory program.

8.5.3 High-Level Detections in RS 11-25

The types of organic constituents detected in samples collected from RS 11-25 are typical of a diesel-based substance. TPH reported in both groundwater samples collected from this well (i.e., samples from the perforated interval and top of the water column in well) are predominantly TPH-DRO (**Table 14**). This material is too heavy to be present completely in the dissolved phase and resembles a diesel-based hydrocarbon material based on the DRO chromatographic profiles (**Figure F-18** in **Appendix F)**. Benzene was not detected above reporting limits in either groundwater sample; however, ethylbenzene, toluene, and xylenes were detected above the laboratory reporting limit in at least one of the two samples. TICs reported for the groundwater samples included multiple indan/indane/indene compounds and tetralins (**Table 15**), which are not characteristic of all potential source materials sampled for this study. The TEX compound detections, chromatographic profile, and types of TICs reported in the samples, particularly the tetralins and indan/indane/indene compounds, are consistent with any diesel-based substance, and most closely resemble that of drill mud sampled for this study (**Table 19**). Elevated concentrations of metals, which could be a potential indicator of drill mud impact, were not observed in the groundwater samples. Elevated concentrations of inorganic constituents, such as chloride or TDS, and detections of benzene, phenols, and cresols, which could be a potential indicator of impact by flowback fluid or produced water, were not observed in groundwater samples (**Tables 17** and **18**).

Since the SAP was issued in 2010, the Wyoming DEQ accepted an approach to clean the interior well casing and pump in the RS 11-25 water well in a letter dated July 5, 2011. After the cleaning procedure, the Wyoming DEQ required four consecutive quarters of sampling and analysis to confirm that TPH-DRO levels were below regulatory standards. The well was cleaned in October 2011, and samples were taken and analyzed post-cleaning in October 2011, February 2012, May 2012, and September 2012. A report was issued to Wyoming DEQ (dated January 2013) that demonstrated the effectiveness of the well cleaning action, as all sampling results are significantly below Wyoming DEQ regulatory standards for TPH-DRO. The investigation did not confirm a specific source for the organic constituents detected in samples from the well.

9.0 SOURCES OF LOW-LEVEL ORGANIC CONSTITUENTS DETECTED IN WELLS

This section presents a detailed evaluation of low-level detections of organic constituents in groundwater samples in the PAPA. Analytical results presented in **Section 5.0** through **Section 7.0,** and the evaluation of analytical results presented in **Section 8.0,** are synthesized and interpreted to identify and evaluate the sources of low-level detections, both the potential source materials and the pathways by which the materials could be released to groundwater or directly into the well. For the purpose of this analysis, wells with detections of organic constituents at concentrations below applicable groundwater standards will be referred to as *low-level wells*.

The constituents detected in low-level wells sampled for this study can be grouped into two general classes of organic constituents (**Table 14**):

- *Volatile organic constituents* comprise the constituents reported as TPgH and TPH-GRO by EPA Method 8015 (**Section 7.2.2.1**), hydrocarbon gases detected in the dissolved gas analysis (**Section 6.3**), and individual VOCs detected using EPA Method 8260 (**Section 7.2.2.4)**.

- *Semivolatile organic constituents* comprise the constituents reported as TEH and TPH-DRO by EPA Method 8015 (**Section 7.2.2.2**) and individual SVOCs detected by EPA Method 8270 (**Section 7.2.2.4)**.

The sources or potential sources identified for most volatile organic constituent detections are different from the sources or potential sources identified for most semivolatile constituent detections. The sources for these two classes of organic constituents are therefore evaluated in separate sections, **Section 9.1** for volatile organics and **Section 9.2** for semivolatile organics. The few exceptions to this rule are elaborated upon in the appropriate sections. Moreover, although potential sources of volatile and semivolatile organic constituent detections are discussed separately in the sections below, the nature of the semivolatile fraction was considered when evaluating the potential sources of the volatile fraction in groundwater samples. Similarly, the volatile fraction was considered when evaluating the potential sources of the semivolatile fraction in groundwater samples.

The interpretations presented in this section are based on two main sources of information:

- Analytical results from samples of potential source materials and samples of groundwater and gas collected from water wells in the PAPA selected for this study (i.e., data presented in **Section 5.0** through **Section 7.0**); and
- Findings from research conducted for this study on potential point and non-point sources in the PAPA (**Section 4.0**).

Further information and context were also gleaned from the following additional sources:

- Historical chemical testing results from domestic, stock, and industrial water supply wells sampled annually in the PAPA were used to provide context to the timing of organic constituent detections in water wells and the spatial and temporal nature of these detections (**Section 2.5.3**; SCCD, 2009, 2010, 2011, 2012, 2013).
- The direction and velocity of groundwater flow determined as part of the HDG investigation (AMEC, 2012) were used in concert with the chemical data from this study to evaluate the occurrence of the observed low-level detections of organic constituents in groundwater in the PAPA.
- Results of the fate and transport modeling study (AMEC, 2013) were used to evaluate the predicted fate and transport of organic constituents in the event of a release and to assess the likelihood of certain sources and scenarios of release to result in low-level impacts to groundwater in the PAPA.
- Findings for detections of semivolatile organic constituents in study wells sampled as part of the HDG investigation (AMEC, 2012) were used to assess the likelihood that impacts to water quality in water wells are brought about by natural sources or originate from practices employed in the drilling, installation, and/or operation of water wells.
- Inorganic water quality data from the HDG investigation were used in concert with inorganic water quality data from this study to evaluate the influence of hydrogeologic factors on inorganic geochemistry.

Assessment of potential sources for low-level detections of organic constituents is complicated by several considerations:

- The water-soluble fraction of potential source material samples was not analyzed (i.e., the material itself was analyzed rather than water that had been placed in contact with the material).
- Only very low levels of many constituents were typically detected in groundwater samples. Therefore, caution was exercised when comparing the chemical signatures of potential source materials with chemical signatures in groundwater samples due to the potential for false positive analytical results or to minimize uncertain interpretations.
- Petroleum hydrocarbons weather (degrade) by three primary mechanisms: evaporation, solubilization, and oxidation (typically biodegradation), which can confound source interpretation (Zemo, 2007). Thus, the nature of the constituents detected in groundwater samples can reflect weathering conditions and may not be entirely representative of the source material itself.

9.1 DETECTIONS OF VOLATILE ORGANIC CONSTITUENTS IN LOW-LEVEL WELLS

All low-level wells sampled for this study contained volatile organic constituents. Based on assessment of the available evidence generated by this study, low-level detections of volatile organic constituents consist largely of dissolved hydrocarbon gas that has seeped upward from depth by natural processes that have occurred over geological time. The source of the gas is a deep gas reservoir, the Lance Pool; however, the hydrocarbon gas has been altered during migration as evidenced by the isotopic and chemical composition of the hydrocarbon gas in low-level wells. Because the hydrocarbon gas in low-level wells has a different isotopic and/or chemical composition from natural gas produced from the Lance Pool, it cannot be sourced from leaks of natural gas from natural gas production wells or associated E&P infrastructure (e.g., piping) in the PAPA.

Figure 9-1 presents a schematic diagram depicting the key findings that led to this conclusion and the evidence for these findings. The findings are indicated by larger white circles on **Figure 9-1**. Multiple lines of evidence for these findings are presented in smaller circles surrounding each finding that are color-coded to indicate the type of evidence (spatial, temporal, chemical, physical, or operational). The findings and evidence are summarized below:

- Hydrocarbon gases in low-level wells are not the same as natural gas produced in the PAPA, as evidenced by:
  - The hydrocarbon gas in low-level wells exhibits chemical and isotopic signatures that indicate the gas is altered thermogenic or microbial, and these signatures change moving from south to north in the PAPA (**Table 22**; **Figure 8-1**). In contrast, the chemical and isotopic signature of natural gas produced in the PAPA indicates the gas is unaltered thermogenic (**Table 22**).
  - The chemical and isotopic signatures of natural gas may be altered during migration by microbial activity, diffusion, phase separation, and adsorption. Gas that has been altered by biodegradation may show a preferential depletion of n-alkanes relative to isoalkanes, which was observed in low-level wells sampled for this study that displayed an altered thermogenic signature or intermediate signature (**Figures G-1** through **G-5** of **Appendix G**).
- Natural gas likely migrates to the ground surface over geologic time in the PAPA, which is illustrated in the conceptual model for gas generation and seepage on **Figure 9-2** and supported by the following evidence:
  - Natural gas was observed at the ground surface during a soil gas survey performed in the northern portion of the PAPA (**Section 4.8**).

— Hydrocarbon gas was observed at shallow depths during the drilling of natural gas production wells early in development of the gas field in the PAPA (**Figure 4-4**; **Section 9.1.3.4**).

— Hydrocarbon gas has been encountered during the drilling of water wells at gas well pads prior to gas well installation (**Figure 4-4**; **Section 9.1.3.4**).

— The gradual change in hydrocarbon gas signatures across the PAPA is more consistent with a non-point source (upward seepage) versus a point source (leaking natural gas production well).

— According to published literature, natural gas that has accumulated beneath other geological traps similar to the Pinedale Anticline is known to migrate to the ground surface over time (**Sections 4.8** and **9.1.3**).

In addition, the detection of individual, dissolved-phase VOCs (e.g., toluene) is not consistent with the chemical signatures of potential source materials sampled for this study (e.g., condensate, produced water, drill mud, flowback fluid, LNAPL) (**Tables 16-21**; **Section 9.1.2**). Thus, these potential source materials are not sources of the volatile organic constituents detected in low-level wells in the PAPA.

This section presents a summary of the evidence to support these findings and the ultimate conclusion.

9.1.1 Chemical Signature of Volatile Organic Constituents in Low-Level Wells

The chemical signatures of volatile organic constituents in low-level wells sampled for this study displayed the following general characteristics:

- All low-level wells contained dissolved methane in groundwater, and approximately half of these wells also contained higher molecular weight (C_{2+}) hydrocarbon gas components along with the methane in groundwater.
- Generally, no higher molecular weight gases (i.e., C_{2+} gases) were present in wells with low concentrations (<1 mg/L) of methane in groundwater.
- Volatile organic fractions reported as TPgH and TPH-GRO were detected above the laboratory reporting limit in less than half of the low-level wells at low concentrations (<600 µg/L). Detections of TPH-GRO tended to be associated with samples containing C_{3+} gases, based on the results of dissolved gas analyses.

* Based directly on chemical data collected for this Study

Evidence to Support Findings

Finding

Physical

Chemical

Spatial

Temporal

Source of Low-Level Detections of Volatile Organic Constituents in Water Wells
Low-Level Petroleum Hydrocarbon Evaluation
FIGURE 9-1

- The isotopic composition of methane in groundwater generally changed moving from south to north in the PAPA. Thermogenic gas was present at the south end of the PAPA. Methane concentrations in groundwater were too low in wells north of the New Fork River to perform isotope analysis.

- Individual VOCs, when detected in the low-level wells sampled for this study, were limited to toluene at very low concentrations equal to or less than 5 µg/L.

9.1.1.1 *Chemical Signature of Dissolved Gas*

All low-level wells sampled for this study contained dissolved methane, and approximately half of the low-level wells also contained higher (C_{2+}) hydrocarbon gas components, such as ethane, propane, butane, and pentane, as quantified by the analysis of dissolved gas in groundwater. Dissolved methane concentrations in groundwater generally decreased from south to north, ranging from below 0.1 mg/L in samples from wells at the northern end of the PAPA to 120 mg/L in a sample from a well at the southern end of the PAPA (**Table 11**; **Figure 8-1**). Groundwater samples with higher methane concentrations typically also contained a greater number of C_{2+} gases, whereas samples with the lowest methane concentrations generally contained no C_{2+} gases.

As discussed in detail in **Section 8.1.4.1**, the origin of dissolved hydrocarbon gas in many low-level wells at the south end of the PAPA is decidedly thermogenic. The stable carbon isotope values of methane in groundwater samples collected from these wells were similar to those observed in natural gas being produced in the PAPA. However, hydrogen isotope values of methane in groundwater (and casing gas) were shifted relative to those in natural gas (**Figure 8-4**). Moreover, both the dissolved gas and casing gas samples from these wells displayed a preferential loss of straight-chain alkanes (n-alkanes) relative to branched alkanes (isoalkanes), indicating that the thermogenic gas has been altered (**Figure 8-2**; **Figures G-1** through **G-4** in **Appendix G**). Hydrocarbon gas in wells located in the central portion of the PAPA has an intermediate signature, with influence from thermogenic gas that appears to be altered in a similar fashion as observed in low-level wells farther south (**Section 8.1.4.2**; **Figure 8-1**). Dissolved gas with a microbial-type signature is found near the New Fork River (**Section 8.1.4.3**; **Figure 8-1**). The methane isotope signature in groundwater samples from all wells located north of the New Fork River, as well as some wells located south of the New Fork River, could not be determined due to low dissolved methane concentrations in groundwater (i.e., insufficient methane volume for isotope analysis).

9.1.1.2 *Other Volatile Organic Constituents Detected in Groundwater Samples*

BTEX constituents, if detected above the laboratory reporting limit, were limited to toluene at very low concentrations (equal to or less than 5 µg/L) at the following low-level wells sampled for this study: T-2-RW, BO 12A-33, RS 1-4, RB 16-30, and MS 14-16 (**Table 14**). Benzene, ethylbenzene, and xylenes were not detected above laboratory reporting limits in any low-level wells. Although no relationship was apparent during data analysis, toluene was predominantly detected above the

laboratory reporting limit in samples where TPH-DRO and/or TEH were reported as compared to TPH-GRO and/or TPgH (**Table 14**). Toluene was not preferentially detected above the laboratory reporting limit in samples containing high concentrations of dissolved gas. The detection of an individual volatile organic constituent was not characteristic of the potential source materials sampled for this study; detection of multiple volatile organic constituents was generally observed.

Low concentrations (less than 600 µg/L) of the volatile organic fractions (i.e., TPgH and TPH-GRO) were also detected in low-level wells. These detected constituents appear to be related to the presence of hydrocarbon gas in some of these wells. Hydrocarbons that are gases at room temperature are not typically quantified when analyzed using standard analytical methods for analysis of groundwater, such as EPA Methods 8015 and 8260. Although not directly comparable due to differences in methodology, calibration, or instrumentation (**Section 2.1.3**), inferences can be made when comparing the hydrocarbon composition data from the dissolved gas analyses to the data and chromatograms generated from the analyses using these standard groundwater analytical methods. Early-eluting peaks between retention times of 2 to 4 minutes in GRO chromatograms may indicate the presence of hydrocarbon gas components in the C_3 to C_4 range, which would be measured as TPgH. The presence of C_5 to C_7 compounds associated with hydrocarbon gas would be captured as part of the measurement of the TPH-GRO fraction.

The TPgH detections in several low-level wells (T-4-RW-a, T-4-RW-b, AN 11-10D, HWY 7, WB 7-5, and RS 11-14) are related to the hydrocarbon gas present in the wells. A series of early-eluting peaks were found on the GRO chromatograms, and TICs commonly associated with natural gases, such as propane, butane, isobutane, and cyclohexanes, were reported in the mass spectrometry chromatograms. TPH-GRO was also reported in most of these wells. GRO and mass spectrometry chromatograms for low-level wells T-4-RW-a, T-4-RW-b, AN 11-10D, HWY 7, and RS 11-14 are provided in **Figure F-11** through **Figure F-13** in **Appendix F** to show these relationships.

Volatile organic fractions (i.e., TPgH and TPH-GRO) were also detected in industrial water supply well RB 16-30. Although the methane concentration in the sample from RB 16-30 was too low to determine isotopic composition of methane, higher molecular weight gases (e.g., propane, isobutane, isopentane, and hexanes) were present in groundwater from this well, and the $C_1/(C_2 + C_3)$ ratio of dissolved hydrocarbon gas was 20.8 (typical of thermogenic gas). TICs reported in the groundwater sample from this well included numerous low-molecular-weight compounds from the alkene/alkyne chemical groups, such as propene, 2-methyl-1-propene, 1-butene, 2-butene, 2-methyl-1-butene, and 2-methyl-1-buten-3-yne (**Table 15**; **Figure F-19** in **Appendix F**). Dissolved ethene was also quantified in the sample from this well (**Table 11**), as was toluene at a concentration of 5 µg/L (**Table 14**). It is not known why the composition of the hydrocarbon gas in RB 16-30 is different from the nearby wells with higher concentrations of methane, but the TPH-GRO and TPgH detections in this well appear to be primarily the result of the presence of these low-molecular-weight compounds in the groundwater sample.

The detections of TPgH in low-level wells RS 15-12, SP 5-20, MS 12-28, and WB 8-6 are not due to the presence of hydrocarbon gas. The TPgH detection at RS 15-12 is related to the presence of purgeable diesel-range organics that elute beyond the laboratory-specified range for TPH-GRO (**Figure F-18** in **Appendix F**). The TPgH reported in water wells WB 8-6, MS 12-28, and SP 5-20 appears to be related to one or two individual peaks that elute much later than is typical with gases in the GRO chromatograms. Although not conclusive, the peaks in the GRO chromatograms from water wells MS 12-28 and WB 8-6 likely correlate to one or more non-hydrocarbon TICs reported in each sample based on review of the mass spectrogram associated with the VOC analysis (**Figures F-26** and **F-31** in **Appendix F)**. The non-hydrocarbon TICs that are reported in these low-level wells do not appear to be related to the presence of gas, and are discussed further in **Section 9.2.1.2.**

9.1.1.3 *Dissolved Gas Interference in VOC Detection*

The presence of dissolved hydrocarbon gas in groundwater may affect the quantitation of other organic compounds analyzed using standard groundwater analytical methods. Benzene has been reported above the applicable groundwater standard of 5 µg/L in groundwater samples collected from industrial water supply wells AN 1-16, AN 11-10D, and HWY 7 during annual monitoring performed by the SCCD (**Appendix A**). These industrial water supply wells, as well as some of the study wells located on the AN 11-10D pad, had the highest concentrations of dissolved hydrocarbon gas in groundwater based on the results of the dissolved gas analysis performed during this study. As of 2010, groundwater samples collected annually from AN 1-16, AN 11-10D, and HWY 7 have been analyzed for BTEX by EPA Method 8021 and VOCs by EPA Method 8260 (SCCD, 2012). Groundwater samples collected from these wells for this study were analyzed for VOCs using EPA Method 8260 (**Table 2**). Results for groundwater samples collected for this study in 2010 from these wells, as well as those collected by SCCD in 2010, are summarized in **Chart 9-1**.

Benzene was detected in groundwater samples when analyzed by EPA Method 8021B (GC/FID), but not when analyzed by EPA Method 8260B (GC/mass spectrometry). This discrepancy is most likely a result of the mis-identification of benzene when using analytical methods (such as EPA Method 8021B) that do not include mass spectrometry to verify detections of individual compounds. To test this hypothesis, AMEC collected split samples of groundwater from AN 11-10D in 2009 for analysis of VOCs by both EPA Method 8021B and EPA Method 8260B to assess whether the benzene concentration exceeded the applicable groundwater standard at this well (AMEC Geomatrix, 2009b).

Chart 9-1 Analytical Results for VOCs for Selected Wells

Well	Sampler	Date	TPH-GRO (µg/L)[1]	BTEX/VOC Analytical Method[2]	Benzene (µg/L) [3]	Toluene (µg/L) [3]
AN 1-16	SCCD	10/29/10	0.2	8021B	8	2.4
AN 1-16	SCCD	10/29/10	not analyzed	8260B	not detected	2.6
AN 1-16	AMEC	11/19/10	0.197	8260B	<1	2.1 [4]
HWY 7	SCCD	10/28/10	0.17	8021B	6.3	<1
HWY 7	SCCD	10/28/10	not analyzed	8260B	not detected	not detected
HWY 7	AMEC	11/19/10	0.139	8260B	<1	<1
AN 11-10D	SCCD	10/6/10	0.17	8021B	5.9	<1
AN 11-10D	SCCD	10/6/10	not analyzed	8260B	not detected	not detected
AN 11-10D	AMEC	10/5/10	0.19	8260B	<1	<1

1. µg/L = micrograms per liter.
2. Methods are EPA method numbers from SW-846.
3. < indicates analyte not detected at or above laboratory reporting limit indicated.
4. Result qualified as estimated concentration based on data validation review.

The laboratory reported that the peak likely associated with benzene when analyzing the sample using EPA Method 8021B was not found in the method-specified retention time window for benzene. When analyzing the sample using Method 8260B, the peaks on the GRO chromatogram near the benzene retention time window were not specific to benzene, but rather to cyclohexane and methylcyclohexane, which are common constituents in hydrocarbon gas mixtures (AMEC Geomatrix, 2009b). This conclusion was confirmed by a library search conducted as part of the method. Based on this evaluation, benzene was likely not present in these wells. Consequently, the groundwater quality standard for benzene has likely not been exceeded in these wells as has been reported in the past.

9.1.2 Assessment of Potential Sources of Volatile Organic Constituents in Low-Level Wells

None of the potential source materials analyzed for this study is the likely source of low levels of volatile organic constituents detected in groundwater samples. The presence of hydrocarbon gas in low-level wells in the PAPA might be expected to originate from one or multiple point sources related to natural gas E&P, such as a leak from a natural gas production well or pipeline. However, the hydrocarbon gas detected in low level wells is different in isotopic and/or hydrocarbon composition from natural gas produced from the Lance Pool. Consequently, a direct, near-surface link cannot be made between gas observed in water wells and natural gas produced from the Lance Pool.

The chemical signature of the volatile organic constituents detected in groundwater samples did not match the chemical signature of any of the potential source materials sampled for this study, which included condensate (**Table 16**), produced water (**Table 17**), flowback fluid (**Table 18**), drill mud (**Table 19**), pump installation materials (**Table 20**), LNAPL (**Table 21**), and natural gas (**Table 22**). Relatively high concentrations of volatile organics reported as TPH-GRO and TPgH were detected in samples of condensate, produced water, and flowback fluid, as well as in the LNAPL sample. TPH-GRO was detected at low concentrations in only a few groundwater samples with an abundance of C_{3+} gas components. The detection of more than one BTEX constituent is characteristic of the potential source materials sampled for this study, except for pump installation materials. VOCs, when detected above the laboratory reporting limit in the low-level wells sampled for this study, were limited to toluene at concentrations equal to or less than 5 µg/L.

The profiles in GRO chromatograms of the condensate, produced water, flowback fluid, drill mud, and LNAPL samples do not resemble those in the groundwater samples with TPH-GRO and/or TPgH detections, except at well RS 15-12. GRO chromatograms of potential source materials, such as condensate, produced water, and flowback fluid, generally show numerous peaks, or the presence of numerous organic compounds in the sample, many of which are measured as TPH-GRO. The GRO chromatograms from several of the potential source material samples, such as drill mud and LNAPL, were characterized by heavier molecular weight compounds (i.e., higher carbon number compounds) that fall beyond the range of TPH-GRO. This response is typical of the more volatile compounds that comprise diesel-range organics. The GRO chromatogram from RS 15-12 was similar to the GRO chromatogram generated from drill mud samples (see **Section 9.2.1.3**). In contrast, GRO chromatograms from samples in low-level wells with volatile organic constituents showed either an abundance of early-eluting peaks (i.e., gases) or a few individual peaks that are not characteristic of the potential source materials sampled.

Volatile organic constituents in the form of hydrocarbon gas were detected in groundwater samples collected from every well sampled for this study. However, the composition of dissolved gas in groundwater samples (**Table 11**) is different from the composition of natural gas produced from gas wells in the PAPA (**Table 10**). This conclusion is also evident based on the chemical indicators and ratios compiled in **Table 22**. These data show that the chemical and isotopic signatures of natural gas produced in the PAPA differ from those of the dissolved gas observed in groundwater. If the dissolved gas and casing gases originated from a leak in a natural gas production well or associated E&P infrastructure (e.g., piping), or from off-gassing of open fluid pits in the near-surface, the composition of the dissolved gas would be the same as, or very similar to, the composition of the natural gas sample.

A leak of natural gas from a natural gas production well or associated natural gas processing or transport facility would likely also be associated with the presence of some condensate and/or

produced water, or perhaps flowback fluid, in addition to the presence of hydrocarbon gas in groundwater with the same chemical and isotopic signatures as the natural gas being produced in the gas field. Thus, groundwater impacted from such a leak would likely contain BTEX and other higher molecular weight organic compounds, such as naphthalenes, cresols, and/or phenols. Benzene, ethylbenzene, and xylenes were not detected in low-level wells; SVOCs characteristic of condensate, produced water, and/or flowback fluid were likewise not detected in these low-level wells (**Tables 16**, **17**, and **18**). Low-level concentrations of toluene were not detected preferentially in LEL wells or study wells with high hydrocarbon gas concentrations.

The isotopic composition of methane in some groundwater samples shows an intermediate or microbial signature, which differs from the thermogenic signature of methane in natural gas. Some groundwater samples do exhibit a thermogenic signature of methane that is similar to natural gas. However, the dissolved gas in groundwater shows the preferential depletion of straight-chain alkanes (n-alkanes) to branched alkanes (isoalkanes) relative to natural gas (**Figures G-1** through **G-4** of **Appendix G**) and is thus altered with respect to natural gas. The preferential depletion of n-alkanes relative to isoalkanes is also evident in some of the dissolved gas with an intermediate signature detected in groundwater samples with higher dissolved gas concentrations. The exact mechanism of the alteration of gas is unknown. However, certain gas components, such as n-alkanes, may be preferentially biodegraded or lost due to adsorption on mineral substrates, phase separation, or diffusive effects (**Section 4.8**). Changes in isotopic composition may also occur.

A clear trend is evident in the magnitude of dissolved gas concentrations in groundwater, the relative gas composition, and the isotopic composition of methane in groundwater samples from low-level wells proceeding from north to south in the PAPA, as illustrated in **Figure 8-1**. This pronounced spatial trend in isotopic and chemical composition is not characteristic of a point source, such as a leaking casing of a natural gas production well or associated gas processing facility. Thus, based on the chemical signature of hydrocarbon gas in low level wells that appears to have been altered with respect to natural gas produced in the PAPA and the regional trend in hydrocarbon gas signatures in the PAPA, the upward seepage of natural gas from depth by natural processes over the course of time is likely occurring.

9.1.3 Natural Gas Seepage

Dissolved hydrocarbon gas in groundwater can be present in the Wasatch Formation due to the natural migration of natural gas sourced from deeper geological units. All oil and gas fields are widely thought to leak to some extent, because geological seals on gas and oil accumulations are rarely perfect (e.g., Biddle and Wielchowsky, 1994; Schumacher and Abrams, 1996; Matthews, 1996; see also **Section 4.8**). The Pinedale Anticline is not an exception. Migration of natural gas from petroleum reservoirs to the near surface is a common occurrence in gas fields, although the rate of leakage and velocity of upward seepage vary depending on the geological conditions within the reservoir and overlying strata.

This section presents a comprehensive discussion on the presence of naturally occurring gas in near-surface strata in the PAPA. **Section 9.1.3.1** presents the conceptual model for natural gas generation and seepage in the PAPA. The remaining subsections further discuss naturally occurring sources of hydrocarbon gases, differences in gas occurrence in the PAPA, and other evidence of the presence of hydrocarbon gases in shallow strata and in groundwater in and near other natural gas fields.

9.1.3.1 *Conceptual Model of Natural Gas Generation and Seepage in the PAPA*

The conceptual model for natural gas generation and seepage in the PAPA is illustrated on **Figure 9-2**. Natural gas has been generated by heat and pressure in source rocks at great depth in the PAPA. The source rocks are considered to consist primarily of the Hilliard Shale and Lower Mesaverde, although there is some evidence that natural gas may also be generated in situ in the Upper Mesaverde and Lance Formation sediments. Gas generated over geologic time in the deeper source rocks has moved upward by buoyant forces into the Upper Mesaverde and Lance Formation, also referred to as the Lance Pool. The natural gas moves both laterally within sandstones comprising the Lance Pool and upward within the Lance Pool into a structural trap, the Pinedale Anticline.

The bulk of the natural gas has accumulated at the highest point of the anticline to form the gas field. Although a majority of natural gas in the Lance Pool is contained beneath the structural trap (anticline), some natural gas manages to move upward through the reservoir seal and into the overlying Fort Union Formation due to poor seal development and rock quality. Once the natural gas reaches the Fort Union and Wasatch Formations, it seeps upward more quickly due to the relatively higher porosity and permeability of these formations. Natural gas has likely been migrating from the Lance Pool to the surface over geologic time. Thus, the presence of this gas in near-surface water-bearing units can be expected based on geologic conditions.

9.1.3.2 *Likely Sources of Hydrocarbon Gas with Intermediate and Microbial Signatures*

The results of hydrocarbon gas composition and isotopic analyses of methane in this study suggest that dissolved hydrocarbon gas with an intermediate signature in groundwater in the central PAPA is the result of thermogenic gas from the Lance Pool that has been altered during migration and has mixed with gas derived microbially. The more negative stable carbon isotope value of methane in groundwater in the central PAPA is likely a result of this mix of gases. Hydrocarbon gas component ratios can be used to assess the degree of alteration (i.e., the preferential depletion of n-alkanes with respect to isoalkanes) if hydrocarbon gas concentrations (particularly C_{4+} gas components) in groundwater are high enough to calculate the ratio. Hydrocarbon gas with an intermediate signature in the central PAPA shows the same alteration as observed in altered thermogenic gas in the south PAPA in those wells with sufficiently high concentrations of hydrocarbon gases in groundwater to calculate the ratio. However, if concentrations of C_{4+} gas components in hydrocarbon gas with an intermediate isotopic signature in groundwater are below

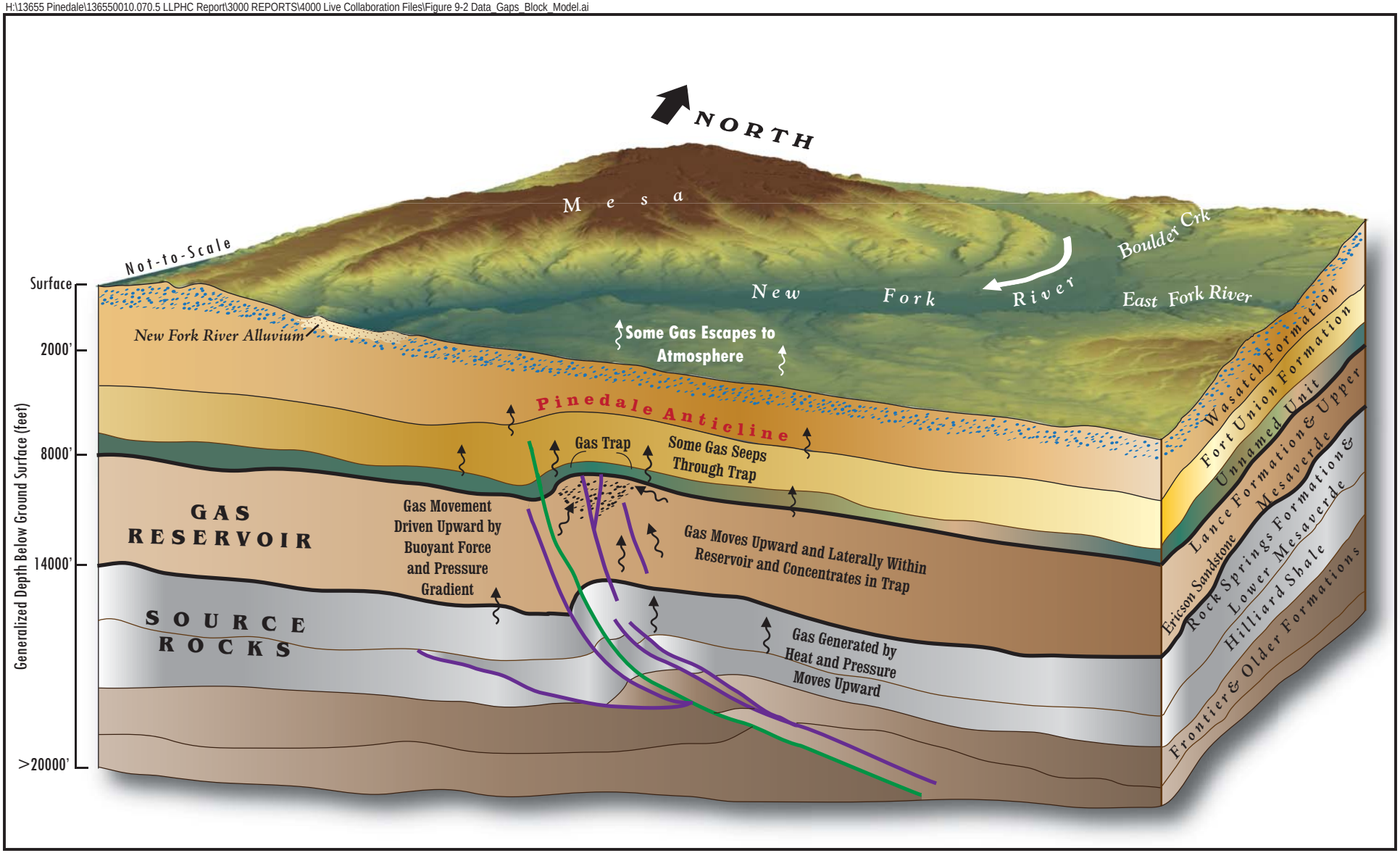
the reporting limit, the gas component ratios cannot be calculated and the degree of alteration cannot be determined.

The composition of natural gas can change during gas migration. For example, natural gas tends to preferentially lose the higher molecular weight gases (i.e., wet gases or C_{2+} gases) during migration (Whiticar, 1994; England, 1994; Matthews, 1996). It is possible that the C_{4+} gas components that would indicate alteration are lost during migration in the central portion of the PAPA. Therefore, this absence of C_{4+} gas components in groundwater from some low-level wells in the central PAPA does not represent an anomaly, and the observed chemical signatures are consistent with the overall trend in the magnitude of hydrocarbon gas concentrations and with the changes observed in the chemical signatures of hydrocarbon gas in groundwater moving north in the PAPA.

Alternatively, the intermediate hydrocarbon gas signatures observed in the central PAPA exhibiting a more negative stable carbon isotope of methane value and slightly different hydrocarbon gas composition could indicate the presence of thermogenically derived gas that originates from different source rocks, such as deeper Tertiary-age formations in this area. However, no evidence currently exists that thermogenically derived gas (e.g., natural gas) is generated in the lower Tertiary formations (e.g., Wasatch and Fort Union Formations) in or near the PAPA (Roberts, 2005b). According to Govert (2011), coal in the Fort Union Formation has not been buried deeply enough to generate significant gas in the area south of the Pinedale Anticline. The results of the thermal maturity analysis of carbonaceous shale in the Wasatch Formation (**Section 5.7**; **Appendix D**) from this study, as well as findings from previous reports (Roberts, 2005a; Roberts et al., 2005), indicate that the organic matter present in the Wasatch Formation is too immature to generate thermogenic gas. Consistent with the conceptual model for gas generation and seepage presented on **Figure 9-2**, any gas with a thermogenic signature present in the Wasatch and Fort Union Formations has arisen due to gas migration from below, and has not been directly sourced from within the formations.

Immature, naturally occurring organic material present in Wasatch Formation sediments or organic matter dissolved in groundwater may be producing low levels of microbially derived gas. Dissolved hydrocarbon gas with a microbial-type signature is present immediately south of the New Fork River. It is plausible that dissolved hydrocarbon gas in this area as well as the gas of indeterminate origin located north of, and at some wells south of, the New Fork River is derived predominantly from microbial sources.

H:\13655 Pinedale\136550010.070.5 LLPHC Report\3000 REPORTS\4000 Live Collaboration Files\Figure 9-2 Data_Gaps_Block_Model.ai



Upward Gas Seepage

Gas Accumulation

Zone of Groundwater Tapped by Water Wells

Faults

amec

Conceptual Model for Natural Gas Generation and Seepage in the PAPA
Low-Level Petroleum Hydrocarbon Evaluation
Sublette County, Wyoming
FIGURE 9-2

9.1.3.3 *Differences in Gas Occurrence in the PAPA*

The upward seepage of natural gas from depth to the near surface does not appear to be occurring in the northern portion of the PAPA to the same extent that it is occurring toward the south end of the PAPA based on the magnitude of dissolved hydrocarbon gas concentrations in groundwater. Previous studies have indicated that the magnitude of dissolved hydrocarbon gas concentrations in water wells can be linked to several factors, such as:

- Proximity of the wells to natural gas extraction or storage operations (Osborn et al., 2011);
- Hydrogeologic setting (Osborn et al., 2011; Breen et al., 2007); and
- Geologic features (McMahon et al., 2010).

All industrial water supply wells and SAP study wells sampled for this study (except T-5-RW) are located in close proximity to current natural gas E&P operations. Industrial water supply wells are located coincident with the main crest of the anticline and consequently with natural gas E&P activities as well. Nevertheless, no relationship is apparent between the magnitude of dissolved hydrocarbon gas in water wells and the proximity of the water well to natural gas E&P operations. A trend of decreasing dissolved hydrocarbon gas concentrations in groundwater is observed while moving along the crest of the anticline from south to north in the PAPA, whereas E&P operations are concentrated along the crest of the anticline throughout the PAPA. Some areas of concentrated E&P activity are present, for example, in development areas DA2 and DA4 (**Figure 2-8**); however, dissolved hydrocarbon gas concentrations in groundwater are not higher in those development areas as compared to others.

Subsurface geologic structures (e.g., faults) that are associated with the anticline at depth (i.e., greater than 5,000 feet) may exert a possible control on the presence of dissolved hydrocarbon gas in groundwater in the PAPA. Previous studies in the area have not shown that this faulting extends up into Tertiary sediments (Chapin et al., 2009). A generalized plan view depicting the relevant known geologic features at depth is displayed on **Figure 4-4**. These features were interpreted based on three-dimensional seismic studies in the Upper Cretaceous Lance Pool beneath the Tertiary-age Wasatch and Fort Union formations. The greater frequency of these geologic structures at depth in the subsurface (i.e., below the base of the Wasatch Formation) appears to be associated with the trend of higher concentrations of dissolved hydrocarbon gas south of the New Fork River.

9.1.3.4 *Other Evidence of Gas Occurring Naturally in the Shallow Subsurface*

Although baseline conditions for dissolved hydrocarbon gas in groundwater were not established prior to the commencement of E&P activities in the PAPA, anecdotal information suggests that dissolved hydrocarbon gas was present in groundwater in the PAPA prior to the start of natural gas

E&P operations, which is described in detail with relevant reference citations in **Section 4.8**. The locations where shallow hydrocarbon gases have been observed in the PAPA prior to large-scale E&P activities are depicted on **Figure 4-4**. Gas has been encountered in the Wasatch Formation while drilling natural gas production wells. Mud-logging was reportedly commenced at shallow depths while drilling natural gas wells early in gas field development to look specifically for shallow gas. Gas has been encountered in the Wasatch Formation while drilling water supply wells prior to drilling the natural gas production wells at gas well pads. Soil gas surveys (proprietary) performed in 2003 and 2004 (prior to the SEIS) for exploratory purposes have indicated the presence of organic constituents associated with natural gas, such as BTEX and alkanes (normal and branched), in soil gas in and near the PAPA. In the Antelope area, a shallow, exploratory gas well was completed in the Wasatch Formation at a depth of 379 feet, and gas from the well was tested for hydrocarbon composition (**Figure 4-4**). The WOGCC noted the presence of gas in the sample that had a different composition from natural gas produced from the Lance Pool (WOGCC, 2009a).

Dissolved hydrocarbon gas is commonly found in water wells at and near other gas fields. Methane with microbial and thermogenic signatures has been observed in aquifers located in gas fields in the Piceance and San Juan Basins of Colorado (McMahon et al., 2010; Gorody, 2005), although at lower concentrations than observed in this study. Wells with the highest methane concentrations in groundwater from the Wasatch Formation in the Mamm Creek area of the Piceance Basin contained methane of microbial origin based on molecular and isotopic compositional data (McMahon et al., 2010). Wells with the highest concentrations of methane in groundwater in the Wasatch Formation from this study contained methane that is thermogenic in origin, but altered relative to the natural gas from production wells in the PAPA (**Section 9.1.1.1**).

9.2 WELLS WITH LOW-LEVEL DETECTIONS OF SEMIVOLATILE ORGANIC CONSTITUENTS

Most potential source materials sampled as part of this study can be unequivocally ruled out as sources of semivolatile organic constituents detected in low-level wells, but in many cases, the specific source cannot be definitively identified. The source of semivolatile organic constituents detected at low levels in groundwater samples likely originate from substances introduced during the drilling, installation, and operation of the groundwater wells and/or from naturally occurring organic materials present in the aquifer. **Figure 9-3** presents a schematic diagram depicting the key findings and evidence that led to this conclusion:

* Based directly on chemical data collected for this study
** Based directly on hydrogeological data collected for the Hydrogeologic Data Gaps Investigation (AMEC, 2012)

Evidence to Support Findings

- Finding
- Spatial
- Chemical
- Operational

Source of Low-Level Detections of Semivolatile Organic Constituents in Water Wells
Low-Level Petroleum Hydrocarbon Evaluation
FIGURE 9-3

- The chemical signatures of groundwater samples from most of the low-level wells with detections of semivolatile organic constituents above laboratory reporting limits most closely resembled the signature of pump installation materials. This finding is supported by the following evidence:
  - No complementary VOCs or SVOCs were detected above the laboratory reporting limit in these wells (**Table 14**).
  - Few to no TICs were reported and, when reported, most TICs were not characteristic of sources sampled for this study or typically associated with petroleum substances.
  - TEH was always detected and TPH-DRO was detected along with TEH in some wells.
  - Chromatographic profiles were mostly non-characteristic and/or characterized by UCMs (**Section 9.2.1.3**).
  - Grease and/or pipe dope has been observed on pumps and/or pipe fittings during pump removal and well sampling.
  - One exception is RS 15-12. This well exhibited a chemical signature resembling drill mud, which is suspected to have resulted from the backflow of fluid via improper well/pump operation.
- Low-level detections of semivolatile organics in some low-level wells may be attributed to naturally occurring organic matter. This finding is based on the following evidence:
  - TEH was removed from the extract of samples collected from several study wells following treatment by silica gel.
  - Sediments containing organic matter (carbonaceous shale) are present in the Wasatch Formation.
  - Particulates of organic matter may be introduced to water wells during well drilling and installation and become entrained in groundwater samples. Suspended sediment was observed in several study wells prior to sampling in June 2011 (AMEC 2012).
  - Laboratory analysts have identified naturally occurring organic matter as a potential source of semivolatile detections based on the observed chromatographic response.
- The chemical signature in four study wells resembled the chemical signature of a refined petroleum-based substance, which may be attributable to well installation materials. This finding is based on the following evidence for these four wells:
  - TPH-DRO was detected and not removed upon silica gel treatment.
  - The chromatographic profiles exhibited a narrow, symmetrical response in the diesel-range organics, which most closely resembled the reference chromatogram for a mineral oil standard.

— The use of petroleum-based substances during water well drilling and installation may introduce semivolatile organic materials into the well.

— These study wells share a common history of well drilling and installation and are located upgradient of E&P activities.

This section presents a synthesis of evidence and findings from this study that lead to the interpretations regarding detections of semivolatile organic constituents in the low-level wells. The main objectives of this section are to:

- Summarize the chemical characteristics of the semivolatile organic constituents detected in low-level wells;
- Interpret the chemical testing data collected from this study to evaluate whether the sampled potential source materials are the sources of the low-level semivolatile organic constituents detected in low-level wells; and
- Identify and assess other potential source materials that were not sampled for this study but could also potentially be the source(s) of low-level semivolatile organic constituents detected in the PAPA.

9.2.1 Groundwater Chemistry at Low-Level Wells with Detections of Semivolatile Organic Constituents

Semivolatile organic constituents were detected in groundwater samples from low-level wells sampled for this study, as well as HDG study wells sampled as part of the HDG investigation (**Figure 7-5**). No relationship is apparent between the detection of volatile organic constituents versus semivolatile organic constituents in low-level wells. It is difficult to decipher the origin or sources of the semivolatile organic constituents detected in low-level wells, as they are generally limited to low concentrations of TPH-DRO and/or TEH. Other constituents amenable to source identification were not present in many samples.

Groundwater samples with low-level detections of semivolatile organic constituents collected from wells sampled for this study are generally characterized by:

- Detections of semivolatile organics by Method 8015 reported as TEH in most of the low-level wells, with TPH-DRO reported in approximately one-half of the samples with TEH (**Table 14**);
- Profiles in DRO chromatograms that are mostly non-characteristic and/or characterized by UCM-type signatures;
- No complementary detections of SVOCs above the laboratory reporting limit when analyzed using EPA Method 8270 (**Table 14**); and

- Few reported TICs, most of which are not characteristic of sources sampled for this study or typically associated with petroleum substances and which do not definitively implicate any specific potential source material (**Table 15**).

9.2.1.1 *Semivolatile Organic Constituents*

Detections of semivolatile organic constituents above the laboratory reporting limit were limited to TPH-DRO and/or TEH; individual SVOCs characteristic of petroleum-containing substances were not detected above the laboratory reporting limit in wells sampled for this study. Detected concentrations above the laboratory reporting limit reported as TEH in these low-level wells ranged from 320 µg/L (BO 1-32) to 8,800 µg/L (RS 1-4). Detections as TPH-DRO were reported in about half of the low-level wells with TEH detections. Detected concentrations above the laboratory reporting limit reported as TPH-DRO ranged from 320 µg/L (MS 15-16) to 4,200 µg/L (RS 1-4) (**Table 14**).

Low levels of semivolatile organics were not only detected in wells sampled for this study, which are predominantly located on natural gas well pads, but were also detected in HDG study wells, which are generally located outside of the core of E&P operations (i.e., off natural gas well pads, or off-pad). Detected concentrations in the TEH fraction in HDG study wells ranged from 300 µg/L (X-1-SW) to 2,300 µg/L (T-9-RW). Detections of TPH-DRO above the laboratory reporting limit were also reported in three of these wells at concentrations ranging from 1,200 µg/L (X-3-SW) to 2,000 µg/L (T-9-RW) (**Table 14**).

The extracts from groundwater samples collected from all study wells (i.e., SAP and HDG study wells) with TPH-DRO and/or TEH detections were treated with silica gel and re-analyzed. TPH-DRO and/or TEH were no longer detected following SGT in roughly half of these samples where they were initially detected (**Table 14**). This includes the sample from T-4-SW that had greater than 1 mg/L of TPH-DRO. Samples in which the semivolatile organic fractions were not removed by SGT tended to have:

- Higher TEH concentrations than those samples where TEH was removed upon SGT; and
- Semivolatile organics reported as diesel-range organics (TPH-DRO).

A trend in the detection of semivolatile organics in study wells was apparent with depth and by location in the PAPA (**Figure 7-6**; **Section 7.2.2.3**). TPH-DRO was detected above the laboratory reporting limit in samples from study wells located on-pad, as well as samples from wells located off-pad and upgradient of E&P operations based on the regional groundwater flow direction.

9.2.1.2 *Tentatively Identified Compounds*

Few (or no) TICs were generally reported in groundwater samples with low-level detections of semivolatile organic constituents, and many of the reported TICs in these samples are non-

hydrocarbons (**Table 15**). The exception to this generalization is low-level well RS 15-12, with numerous TICs reported, as discussed further in **Section 9.2.2.1.1**. No TICs were reported for the following wells with low-level detections of semivolatile organic constituents: T-1-SW, SP 11-33, SP 11-34, T-2-RW, MS 15-16, T-5-RW, HWY 11, and T-4-SW.

Chart 9-2 summarizes the number of TICs by major chemical groups reported in groundwater samples from wells with low-level detections of semivolatile organic constituents.

Chart 9-2 TICs Reported for Low-Level Wells Where Semivolatile Constituents Were Detected above the Reporting Limit

	Non-Hydrocarbons		Hydrocarbons				
Well No.	**Acids, Alcohols, Ketones & Aldehydes**	**Silanes & Sulfur Cmpds.**	**Alkanes & Branched Alkanes**	**Cycloalkanes & Alkyl-cycloalkanes**	**Alkenes & Branched Alkenes**	**Cycloalkenes & -alkynes**	**Terpenoids**
Number of Tentatively Identified Compounds (TICs) Reported							
T-4-RW-a			8	4	2		1
T-4-RW-b			4	5	2		1
HWY-7		1	7	6			
RB 16-30	2	1	3	6	10	2	
AN 15-23		1					
RB 13-29		1					
WB 7-4		1	5	1			
WB 7-5	1	1	8	3			
WB 8-6	1	2					
BO 12A-33	1		2				
BO 1-32		1					
RS 1-4	1	1					
MS 12-28	2						
MS 14-16	2						
SP 5-20	2						
T-1-RW		1	4				

For the discussion below, TICs that are hydrocarbons or closely associated with other hydrocarbons include TICs from the alkane, branched alkane, cycloalkane and alkylcycloalkane, alkene, branched alkene, cycloalkene, alkyne, and terpenoid chemical groups. TICs considered non-hydrocarbons include TICs from the acid, alcohol, ketone, aldehyde, silane, and sulfur compound groups. Hydrocarbon TICs were generally reported in wells located in the central and southern portions of the PAPA, whereas non-hydrocarbon TICs were generally reported in wells located in the central and northern portions of the PAPA.

9.2.1.2.1 Hydrocarbon TICs

Alkane, branched alkane, cycloalkane, and alkylcycloalkane compounds of lower molecular weight (e.g., C_3 to C_6) that are typically associated with dissolved hydrocarbon gas were tentatively identified in groundwater samples with low-level detections of semivolatile organic constituents (i.e., BO 12A-33, WB 7-5, WB 7-4, RB 16-30, HWY-7, T-4-RW-a, and T-4-RW-b). The presence of dissolved hydrocarbon gas does not appear to be related to the detection of semivolatile organic constituents in these wells. The exception is SAP study well T-1-RW, in which the alkanes and branched alkanes reported in the sample consist of compounds with higher molecular weights (C_{17} to C_{22}) than typically associated with gases (**Table 15**).

Multiple cyclopropane compounds were reported as TICs in the groundwater sample from only one well, industrial water supply well RB 16-30. As discussed in **Section 7.2.3.1**, TICs reported in the sample from RB 16-30 included alkanes typically associated with the dissolved hydrocarbon gas found in the PAPA, as well as a suite of lower molecular weight (C_3 to C_7) alkenes, branched alkenes, and cycloalkenes as well as one alkyne, which are not characteristic of any of the potential source materials sampled for this study. The presence of numerous alkenes in a sample may be indicative of a refined petroleum product, although the low-molecular-weight alkenes are unusual and not typically associated with most unrefined or refined petroleum products.

Adamantanes are reported to be naturally occurring in many crude oils, gas condensates, and natural gas sources (Stout and Douglas, 2004). Adamantane (a terpenoid) was reported as a TIC in groundwater samples from SAP study wells T-4-RW-a and T-4-RW-b. A few alkenes and branched alkenes, which were predominantly higher in molecular weight (C_5 to C_7) compared to those reported in the sample from RB 16-30, were also reported in these samples. These study wells were re-sampled in February 2012 to quantify adamantane and alkenes in groundwater samples from these wells. 1-Heptene and adamantane were quantified in SAP study well T-4-RW-a at concentrations of 4.1 and 2.1 µg/L, respectively. 2-Methyl-1-pentene (1-hexene), which was tentatively identified in samples from both wells in 2011, was not quantified during the follow-up sampling. The presence of a single alkene in groundwater from SAP study well T-4-RW-a is not conclusive evidence of the presence of a refined petroleum product, because the presence of additional compounds that are indicative of a refined petroleum product would also be expected.

9.2.1.2.2 Non-Hydrocarbon TICs

Cyclic octaatomic sulfur, which is considered a naturally occurring sulfur compound, was the only TIC identified in groundwater from industrial water supply wells AN 15-23 and BO 1-32. Sulfate concentrations in groundwater are relatively high (431 mg/L and 969 mg/L, respectively) at these two control wells (**Table 12**). Cyclic octaatomic sulfur was also reported in the following wells listed in **Chart 9-2**: T-1-RW, WB 7-4, RB 16-30, and RS 1-4.

One or two non-hydrocarbon TICs from the acid, alcohol, ketone, aldehyde, and silane chemical groups were reported in 10 wells with low levels of semivolatile organic constituents (**Chart 7-6**). With respect to potential source materials, TICs in the non-hydrocarbon chemical groups were most often reported in the flowback fluid samples (**Table 5**); however, none of the non-hydrocarbon TICs reported in flowback fluid samples was reported in groundwater samples (**Table 15**).

Wells with non-hydrocarbon TICs were re-sampled in 2012 to quantify the presence of these TICs and further evaluate the link between the TICs and potential source materials. Results of this follow-up sampling are presented in **Chart 7-7** in **Section 7.2.3.2**. These analyses produced the following key findings.

- Only three of the seven compounds tentatively identified in groundwater samples collected in 2010 (n-hexadecanoic acid, 2-ethyl-1-hexanol, and nonanal) were quantified in samples collected in 2012.
- Four compounds were not quantified in groundwater samples collected from wells where they were reported as TICs in 2010: acetone; 2-ethylhexanoic acid; 2,4-dimethyl-3-pentanone; and hexanal.
- The most commonly quantified TIC (2-ethyl-1-hexanol) was detected in follow-up groundwater samples collected from industrial water supply wells BO 12A-33, WB 8-6, and MS 12-28 at concentrations ranging from 5.3 to 24 µg/L. n-Hexadecanoic acid was quantified at a concentration of 44 µg/L in well RS 1-4. An aldehyde (nonanal) was quantified in a follow-up sample from SP 5-20 at a concentration of 2.4 µg/L.

The source of these non-hydrocarbon TICs that were quantified in groundwater samples is unknown. These compounds were not detected in potential source materials sampled for this study, including flowback fluid (**Table 18**), and the absence of other complementary detections of organic constituents precludes identification of a source for these compounds. In addition, these compounds have not been reported to have been used in hydraulic fracturing in the State of Wyoming (Groundwater Protection Council, 2012) and are not listed in the *Chemicals Used in Hydraulic Fracturing* prepared by the United States House of Representatives, Committee on Energy and Commerce Minority Staff (2011).

9.2.1.3 *Chromatographic Profiles*

This section compares the appearance of the DRO chromatograms from groundwater samples and potential source materials sampled for this study. Chromatographic profiles were evaluated from wells sampled for this study (i.e., LEL, control, PHC, and SAP study wells) as well as HDG study wells. The chromatographic profiles from groundwater samples were compared against chromatograms from potential source materials sampled for this study and standard reference chromatograms of

other potential source materials to assess if the chromatographic profiles of these potential source materials could match the chromatographic profile observed in the groundwater samples.

DRO chromatograms from most low-level wells exhibited only a slight response, which is insufficient to indicate a specific source material. The profiles in the DRO chromatograms vary somewhat between wells; however, because of the low response, it is not clear if the variations in the general appearance of the profiles are due to differences in degree of weathering, origin of the organic constituents, or an artifact of laboratory analysis. DRO chromatograms with slight responses tend to exhibit a profile characterized by a UCM or a hump lacking any diagnostic peaks. The UCM tends to occur within a range of retention times starting at 8 to 10 minutes and ending at 18 to 20 minutes, which correlates roughly to the range of response for C_{12} to C_{38} compounds. DRO chromatograms for these wells are provided in **Figures F-14** through **F-15**, **Figures F-18** through **F-29**, and **Figure F-31** in **Appendix F**. While these chromatographic profiles most closely resemble the DRO chromatograms for pump installation materials as compared to all other potential source materials sampled for this study, this interpretation is tenuous due to the low concentrations of semivolatile organic fractions, most of which are well below 1 mg/L.

For example, the chromatographic profiles in the DRO chromatograms are similar for groundwater samples collected from industrial water supply wells MS 14-16 and MS 15-16, with the apex of the UCM centered at a retention time of 17 minutes in both samples (**Figure F-25** in **Appendix F**). Samples of pipe dope removed from the pump discharge piping (i.e., drop pipes) for the pumps in MS 14-16 and MS 15-16 also exhibited a similar profile, most notably in that the apex of the UCM was also centered at a retention time of 17 minutes. Pipe dope appears to provide the best match for the detected constituents in wells MS 14-16 and MS 15-16; however, TPH-DRO was detected in the groundwater samples from these wells at concentrations only slightly above the reporting limit (**Table 14**). At these low concentrations, naturally occurring organic constituents associated with sediment or turbidity in the sample could just as well be the source of the detected organic constituents (William Brown, personal communication, 2011).

DRO chromatograms in a few low-level wells were characterized by a few distinct peaks instead of UCMs. The DRO chromatograms for the groundwater samples collected from industrial water supply wells RB 16-30 and MS 12-28 exhibited a few distinct peaks between retention times of 7 and 8 minutes, and a general absence of peaks or a hump in the diesel organics range (**Figure F-19** and **Figure F-26** in **Appendix F**). The DRO chromatogram for RS 1-4 also showed a few distinct peaks, albeit at later retention times (12 to 14 minutes) (**Figure F-26** in **Appendix F**). As was the case for GRO chromatograms, the peaks in DRO chromatograms cannot be definitively compared to the mass spectrograms generated during VOC and SVOC analysis; however, these peaks may be related to the acids, alcohols, and/or aldehydes reported as TICs in these samples (**Table 15**).

A UCM eluting between retention times of 12 to 13 and 16 minutes (C_{17} to C_{26}) is characteristic in DRO chromatograms for study wells X-3-SW, T-5-RW, T-8-A, and T-9-RW (**Figure F-14** and

Figure F-15 in **Appendix F**). This profile most closely resembles the reference chromatogram for a mineral oil standard (**Figure F-30** in **Appendix F**) (William Brown, personal communication, 2011). This type of response may also represent some type of grease. The study wells with this chromatographic profile are located east (upgradient) of E&P operations in the PAPA and share a common history of well drilling, installation, and operational practices, which may suggest a possible source arising from these practices rather than an impact from E&P activities. Again, naturally occurring organic material could also be the source of this response.

The DRO chromatogram from only one low-level well, RS 15-12, exhibited a sufficient response to identify the presence of a potential source material. The chromatographic profiles in the DRO chromatograms for the groundwater samples collected from RS 15-12 are characteristic of a diesel-based material (predominantly C_{12} to C_{26}) (**Figure F-18** in **Appendix F**). This chromatographic profile most closely resembles the DRO chromatograms for oil-based drill mud among the potential source materials sampled for this study.

9.2.2 Assessment of Potential Sources of Semivolatile Organic Constituents in Low-Level Wells

While multiple lines of chemical and physical evidence identifies the source of the low-level volatile organic constituents observed in water wells (**Section 9.1.2**), it is more difficult to connect the low-level detections of semivolatile organic constituents to their likely source(s). This section compares the chemical indicators identified in groundwater samples that contained detectable levels of semivolatile organic constituents above the reporting limit to the chemical signatures of each potential source material sampled, as well as other potential sources that might exhibit the same chemical signature as those found in groundwater samples. The results of this comparison are then used to evaluate the likelihood that these sources are contributing to the semivolatile organic constituents detected in groundwater.

9.2.2.1 *Materials Used or Generated during Natural Gas Exploration and Production Operations*

The chemical signature of samples from low-level wells with semivolatile organic constituent detections did not match the chemical signatures of the following sampled potential source materials that are used or generated during natural gas E&P operations: condensate (**Table 16**), produced water (**Table 17**), flowback fluid (**Table 18**), LNAPL (**Table 21**), and natural gas (**Table 22**). One low-level well (RS 15-12) appears to have a chemical signature consistent with a diesel-based material, such as drill mud (**Table 19**). The semivolatile organic constituents detected in groundwater samples most closely resemble the predominant semivolatile fraction in pump installation materials (**Table 20**), which are used in water well operations and are discussed in **Section 9.2.2.2**. The presence or absence of chemical signatures in groundwater that are attributed to the materials used or generated during natural gas E&P operations are discussed below.

9.2.2.1.1 Drill Mud

Oil-based drill mud is the most likely source of organic constituents in the groundwater samples collected from well RS 15-12 based on the presence of similar potential chemical indicators (**Table 19**) and the similar chromatographic profiles (**Figure F-18** in **Appendix F)**. The DRO chromatograms for the groundwater samples collected from RS 15-12 are characteristic of a diesel-based material (predominantly C_{12} to C_{26}). TPH-DRO comprised a high percentage of the total TEH in these groundwater samples. VOCs and SVOCs were not detected above the reporting limit in the groundwater samples collected from RS 15-12 during this study. However, this well also has a historical record of high-level detections of organic constituents in the past (**Appendix A**) that complement the identification of this source. Similar TIC chemical groups were reported in samples from RS 15-12 and in drill mud samples (**Table 19**).

The chromatographic profile for RS 15-12 is similar to the profile observed in the DRO chromatogram for the groundwater sample from industrial water supply well RS 11-25, in which high-level organic constituents were detected during this study (see **Section 8.5.3**). The chromatograms reveal a greater degree of weathering in the organic materials in well RS 15-12 as compared to RS 11-25 due to the smoother and less spiky appearance of the response in the DRO chromatogram for RS 15-12 (i.e., more closely resembles a UCM) (**Figure F-18** in **Appendix F)**.

The higher level detections reported historically in RS 15-12 most likely originated due to backflow of fluids containing organic constituents stored in a tank or reserve pit that was connected to the water well at the gas well pad (Wyoming DEQ, 2006) rather than from an impact to the Wasatch Formation while drilling a nearby gas well with oil-based drill mud. High organic constituent concentrations (i.e., above groundwater standards) were first detected in this well in July 2008 (**Appendix A**), and the well was subsequently entered in the Wyoming DEQ VRP. The well was cleaned in November 2008 using a procedure approved by Wyoming DEQ. A dramatic decrease in the organic constituent concentrations was observed at this well upon implementation of the well cleaning procedure and pumping at this well. For example, the concentrations of xylenes decreased from 25 mg/L on July 24, 2008, to below the reporting limit (less than 0.001 mg/L) on May 21, 2009 (**Appendix A**). Constituent concentrations, if detected, have been below applicable groundwater standards in this well since the cleaning procedure was implemented. These findings are consistent with an isolated, intra-well source of petroleum hydrocarbons versus a source resulting in a widespread impact to groundwater at this location. The Wyoming DEQ determined that all remediation requirements were met, and a certificate-of-completion was obtained from Wyoming DEQ VRP for this well in February 2013.

9.2.2.1.2 Natural Gas and Condensate

Natural gas is composed of volatile organic constituents, and is not contributing to the detections of semivolatile organic constituents in low-level wells. Fewer detections of semivolatile organic constituents occurred in wells with high concentrations of dissolved hydrocarbon gas (e.g., LEL

wells) as compared to wells with low concentrations of dissolved gas (e.g., control wells). Moreover, semivolatile organics (i.e., TPH-DRO and/or TEH) were detected in low-level wells without any apparent trend in concentration moving from north to south in the PAPA (**Figure 7-5**), whereas dissolved hydrocarbon gas concentrations increase substantially moving in this direction in the PAPA (**Figure 8-1**).

Condensate is not contributing to the detection of semivolatile organic constituents based on the chemical signatures observed in groundwater samples and the condensate sample (**Table 16**). It is expected that compounds with a molecular weight only slightly higher than gases would be detected in groundwater impacted by condensate versus the much higher molecular weight compounds that comprise the signature observed for the low-level semivolatile organic constituents detected in groundwater samples during this study. Volatile and semivolatile organic constituents that are characteristic of condensate, such as BTEX and naphthalenes, respectively, were not detected above the reporting limit in groundwater samples.

9.2.2.1.3 Produced Water and Flowback Fluid

Produced water and flowback fluid are not the source of organic constituents in groundwater based on the comparison of chemical indicators of produced water (**Table 17)** and flowback fluid (**Table 18)** versus the organic and inorganic constituents detected in groundwater for this study. Not only TEH and TPH-DRO, but also TPH-GRO and TPgH, were consistently detected in these potential source material samples (**Table 3**), which is not characteristic of the groundwater samples collected from low-level wells. Individual VOCs, such as BTEX, and SVOCs, such as naphthalenes, phenols, and cresols, were consistently detected above the reporting limit among these potential source material samples, but not in groundwater samples.

Non-hydrocarbon TICs were reported primarily in flowback fluid samples. The non-hydrocarbon TICs reported in some wells (**Table 15**) are not the same non-hydrocarbon TICs reported in flowback fluid samples (**Table 5**). Only half of the non-hydrocarbon TICs reported in groundwater samples were quantified upon re-sampling. The non-hydrocarbon TICs that were quantified in groundwater samples do not appear to be routinely used in hydraulic fracturing operations (see **Section 9.2.1.2.2**).

Inorganic constituents that are elevated in produced water and flowback fluid (e.g., sodium, chloride, TDS, etc.) were detected in groundwater samples from low-level wells, but at concentrations within the range typically observed in groundwater in the PAPA. It may be difficult to differentiate between an impact from produced water or flowback fluid in groundwater because these sources are often intermingled and their chemical signatures share many similarities. No groundwater samples in low-level wells contained signatures that could be assigned to either produced water or flowback fluid, or the combination thereof.

9.2.2.1.4 LNAPL

LNAPL, or free-phase organic material, was present in industrial water supply well AN 1-16. The LNAPL recovered from AN 1-16 does not appear to be related to any other potential source material sampled for this study. The DRO chromatogram for the LNAPL sample displays a UCM-type signature, characterized by a broad, asymmetrical complex of peaks between retention times of 7 and 22 minutes with the apex between 10 and 11 minutes (**Figure F-10** in **Appendix F**). The more volatile compounds in the diesel range are observed in the GRO chromatogram at late retention times (between 18 to 24 minutes). The carbon scan of this sample shows a range of compounds from C_{10} to greater than C_{40}, which resembles the carbon scan of a crude oil used by the laboratory as a reference standard (**Figure F-17** in **Appendix F**). No single potential source material sampled for this study exhibited this broad of a range in compounds.

The numerous terpenoid compounds (i.e., adamantanes) were reported as TICs only in the LNAPL sample. In contrast with other potential source materials sampled during this study, no alkylbenzenes or tetralins were reported as TICs in the LNAPL sample, and very few alkanes (i.e., alkanes, branched alkanes, and alkylcycloalkanes) were reported for the LNAPL sample. This suite of reported TICs was not observed in any other potential source material sampled (**Table 5**). The source of the LNAPL in this well is not known.

As would be expected, the chromatographic profile of the LNAPL sample collected from well AN 1-16 (**Figure F-10** in **Appendix F**) matches the chromatographic profiles found in the groundwater sample collected from this well (**Figure F-12** in **Appendix F**), except for the presence of dissolved hydrocarbon gas in the groundwater sample (**Table 11**). No other chemical signatures in groundwater definitively match the chemical signature of the LNAPL sample; however, DRO chromatograms in groundwater samples collected from the T-4 study well cluster faintly resemble the chromatographic profile for the LNAPL sample. Adamantane was also reported as a TIC in the groundwater samples from both T-4-RWa and T-4-RWb; however, adamantane was quantified in follow-up samples only in T-4-RWa (**Table 21**). This apparent link in chemical signature between the T-4 well cluster and the LNAPL sample is not conclusive, as SGT removed the DRO response in two of the three study wells (**Figure F-29** in **Appendix F**), and the industrial water supply well on the same pad as the T-4 study well (i.e., AN 11-10) did not exhibit any response in its DRO chromatogram. The LNAPL at the AN 1-16 pad is not likely a source of semivolatile organic constituent detections in the T-4 study well cluster as these wells are located about 0.5 mile away from the AN 1-16 pad in an upgradient groundwater flow direction.

9.2.2.2 *Materials Introduced during Operation of Water Wells*

Organic materials can be introduced during operation of industrial water supply wells, primarily during pump installation and removal, but also while filling tanks or pits without adequate backflow prevention devices. Samples of pump installation materials consisted predominantly of pipe dope, but also included a few samples of grease, as well as black film found on pump

housings. The black film appears to be mineral based since no organic constituents were detected in this sample (**Table 3**). Examples of pump installation and operational practices that might result in detections of organic constituents in groundwater samples were described in **Section 4.3**.

The chemical signatures of groundwater samples from most water wells with low-level detections of semivolatile organic constituents most closely resemble the chemical signature of pump installation materials among the potential source materials sampled for this study (**Table 20**). Pump installation materials sampled for this study are characterized predominantly by the presence of semivolatile organic constituents (i.e., TPH-DRO and/or TEH) and the almost complete absence of organic constituents, including tentatively identified compounds, in the volatile fractions. Most chromatographic profiles in wells with low-level detections of semivolatile organic constituents are characterized by a broad hump eluting between retention times of about 12 and 22 minutes (or longer), which is typical of a UCM signature and characteristic of the chromatographic profiles observed for pump installation materials sampled for this study (see **Figures F-8** and **F-9** in **Appendix F**).

Toluene was present in some wells at low concentrations without the other BTEX components detected above the reporting limit (e.g., T-2-RW, BO 12A-33 and RS 1-4), which was not characteristic of the potential source materials sampled for this study. Detections of toluene, as well as other single BTEX components, appear to be associated with the presence of the semivolatile organic fraction, and were not preferentially detected above the reporting limit in samples containing high concentrations of dissolved hydrocarbon gases in groundwater (**Section 9.1.1.2**).

Toluene is reported to be the most commonly detected VOC in Ohio public drinking water systems, and is often detected alone without the other BTEX components (Ohio EPA, 2009). This pattern of detections is also sometimes true for the other BTEX components. The Ohio EPA (2009) reports that benzene and toluene are commonly used individually as chemicals in industrial applications, and toluene, in addition to other BTEX components, have been detected in samples collected after water supply wells have been drilled. Toluene is found in substances such as paints, machine oils and greases, and release/de-rusting sprays, and has been associated with pipe dope compounds.

It is possible that some of the single, low-level detections of VOCs in groundwater samples collected for this study are associated with well and pump installation and/or operation. AMEC field personnel have observed grease and/or pipe dope on wellheads and pipe fittings, and have observed a substance similar to pipe dope discharging from wells during well sampling activities. Greasy films were observed on some pump housings when pumps were removed from industrial water supply wells in order to collect samples for this study. Pipe dope or greasy substances are confined mainly to pump housings or what has been squeezed out between the joints of the discharge piping for the pump (i.e., drop pipe); a minor amount of these substances are exposed to the groundwater (**Figure 4-3**). The use of "environmentally friendly" pipe dope has been required of pump contractors by Operators. However, the environmentally friendly pipe dope sampled for

this study (PD-Baseline) contains abundant higher molecular weight compounds that are reported in the semivolatile fraction.

Operators have identified the backflow of fluids containing petroleum hydrocarbons directly into industrial water supply wells as the source of some historical detections of organic constituents in wells (AMEC Geomatrix, 2010), including industrial water supply wells WB 8-6 and RS 15-12 that were sampled for this study. In these instances, organic constituents typically have since been removed from these wells by over-pumping and/or by implementing procedures to clean the interior of the well casing and remove impacted water above the perforated intervals. The success of well cleaning/pumping operations at WB 8-6 and RS 15-12 is evidenced in historic water quality data collected annually by the SCCD, which document historic high-level constituent concentrations that decrease abruptly after well cleaning, eventually reaching non-detectable levels (**Appendix A**). Operators are required by BLM's SEIS ROD (BLM, 2008b) to implement backflow prevention measures when filling any tanks or pits from an industrial water supply well, which should minimize or eliminate the occurrence of these types of impacts to water wells in the PAPA.

9.2.2.3 *Materials Introduced during Drilling and Installation of Water Wells*

The chemical signatures of the well drilling and construction materials used to install industrial water supply wells or study wells were not determined for this study, and thus are not available for comparison to the chemical signature in groundwater samples. However, based on the chemistry of the organic constituents that have been detected in low-level wells, it is plausible that substances used in well drilling and installation, as described in **Section 4.3**, are a source of low-level semivolatile organic constituents detected in some water wells in the PAPA.

The low-level semivolatile organic constituents detected in the PAPA are consistent with the types of petroleum-based substances that may be introduced while drilling or constructing a well (i.e., heavier oils or greases). For example, DRO chromatograms from four study wells (T-5-RW, T-9-RW, X-3-SW, and T-8-A) (**Figures F-14** and **F-15** in **Appendix F**) resemble the reference chromatogram for a mineral oil standard (**Figure F-30** in **Appendix F**) (William Brown, personal communication, 2011). This pattern may indicate the presence of a refined petroleum substance introduced while drilling or installing the study wells, as these wells share a common history of well drilling, installation, and operational practices. Natural gas E&P activities cannot be the source of semivolatile organic constituents detected in these four study wells, as these wells are located off-pad and east of the anticline (**Figure 3-3**) in an upgradient groundwater flow direction from E&P activities (**Figure 2-10**).

9.2.2.4 *Naturally Occurring Organic Matter in Water Samples*

In parallel with the possible presence of microbially generated gas in the Wasatch Formation, organic matter incorporated into Wasatch Formation sediments may be contributing to the semivolatile organic signature detected in water samples. The low concentrations of semivolatile

organic constituents and minimal response in chromatograms can just as well be attributed to naturally occurring organic material (William Brown, personal communication, 2011).

This organic matter and the resulting chromatographic response when tested using TPH methods for semivolatile organics could originate from organic matter dissolved in groundwater or sorbed on particulates from the hydrostratigraphic unit containing the groundwater (i.e., biogenic organic matter), and may not be associated with refined petroleum products or crude petroleum systems. Naturally occurring organic matter has been found at concentrations up to 1 mg/L in groundwater samples (Leenheer et al., 2001; Leenheer and Croue, 2003). Particles derived from coal or lignite can contain large amounts of semivolatile organic constituents, including hydrocarbons (Tissot and Welte, 1978; Lundegard and Sweeney, 2004). It is common for organic matter in groundwater samples to consist mostly of polar compounds, or non-hydrocarbon compounds. These polar, non-hydrocarbon compounds could be derived from biogenic organic matter (unrelated to petroleum), biodegradation of spilled petroleum (product of hydrocarbon degradation), or non-hydrocarbon components within spilled petroleum (original component of petroleum) (Lundegard and Sweeney, 2004; Zemo and Foote, 2003). On gas chromatograms, most of these non-hydrocarbon components are incompletely resolved and commonly comprise a substantial part of the UCM, similar to the chromatographic response observed at most wells in this study with low-level detections of semivolatile organic constituents.

Semivolatile organic constituents detected in low-level wells cannot be definitively attributed to naturally occurring organic matter in the Wasatch Formation because carbonaceous shale and other organic sediments from the Wasatch Formation were not analyzed for semivolatile organic constituents as was the case with the other sampled potential source materials. In addition, groundwater samples for volatile and semivolatile organics analysis were not filtered. Consequently, an evaluation of the difference in detections between filtered and non-filtered samples was not possible for this study. However, the removal of semivolatile organic constituents upon SGT is a strong indicator of the presence of naturally occurring organic matter.

Application of chemical adsorbents, such as silica gel, to extracts for analysis of semivolatile organic fractions is commonly used to remove polar compounds (non-hydrocarbons associated with biogenic organic matter) (**Section 2.1.3.3**). TPH-DRO and/or TEH detected slightly above the reporting limits in groundwater samples collected from study wells were typically removed by silica gel treatment (**Table 14**; **Figure 7-6**). Moreover, most of these study wells are located off-pad and away from any known or potential source of organic constituents, whether associated with natural gas E&P activities or other potential sources. As such, the semivolatile organic constituents detected in these study wells are likely attributable to naturally occurring organic matter dissolved in groundwater or sorbed on particulates in groundwater.

Although semivolatile extracts of samples collected from industrial water supply wells for this study were not treated with silica gel, the presence of very low concentrations of semivolatile organic

constituents in industrial water supply wells could be attributed to naturally occurring organic matter. Likely candidates for this phenomenon include industrial water supply wells in which only TEH was detected, such as SP 5-20, SP 11-33, SP 11-34, BO 1-32, BO 12A-33, WB 7-4, and HWY 11.

9.3 No Evidence of Widespread Impacts to Groundwater from E&P Activities in the PAPA

This study did not produce any evidence of widespread impact to groundwater in the PAPA as a result of E&P operations through the release of condensate, produced water, drill mud, flowback fluid, natural gas, or other materials used or generated during E&P operations from natural gas production wells or other E&P facilities (e.g., pipelines, produced water injection wells, pits, tanks, CGFs and LGS). A summary of the likely sources of low-level (and high-level) organic constituents detected in groundwater samples collected for this study is presented in **Table 23.**

Figure 9-4 presents a schematic diagram depicting the key findings that led to this conclusion:

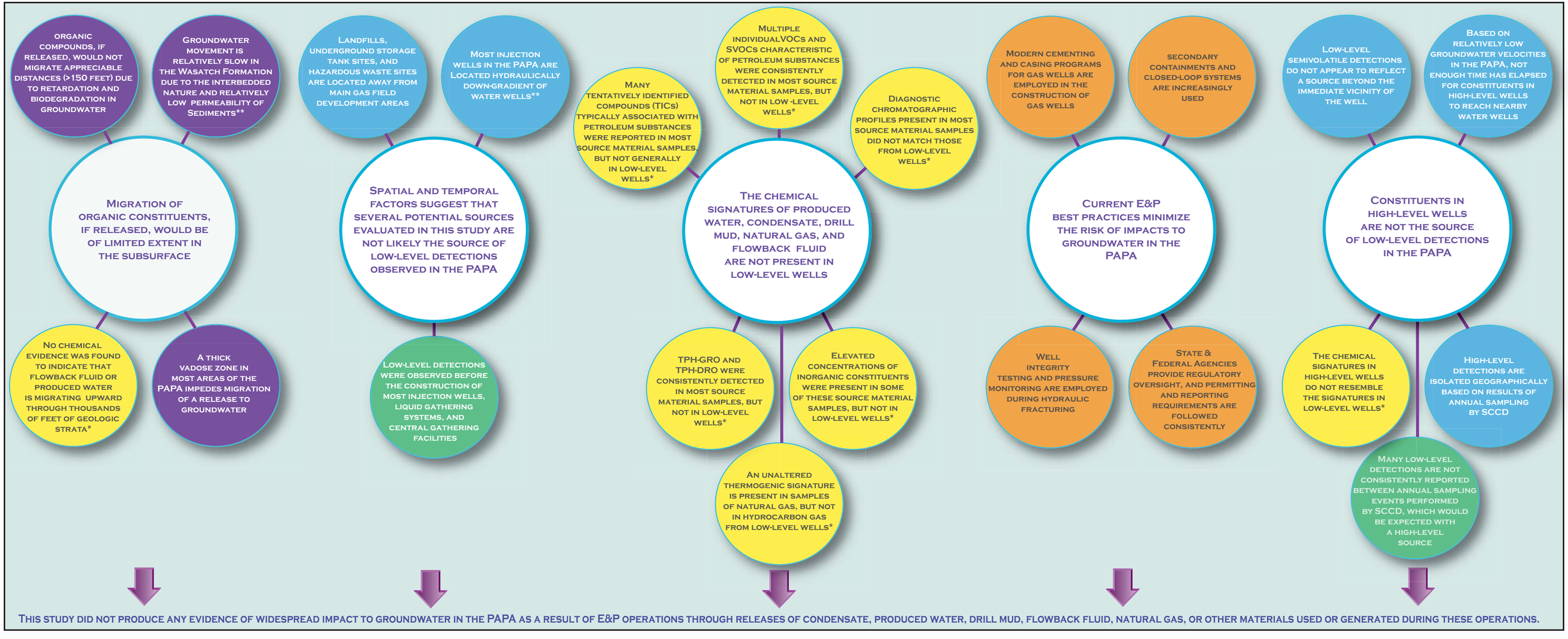
- The chemical signatures of most potential source materials sampled for this study, including produced water, condensate, drill mud, natural gas, and flowback fluid, are not present in low-level wells (**Table 23**; **Figure 9-4**). This finding is based on the following evidence:
  - Multiple individual VOCs and SVOCs characteristic of petroleum substances were consistently detected above the reporting limit in most potential source material samples, but not in low-level wells (**Tables 16–21**).
  - Both volatile and semivolatile organic fractions (e.g., TPH-GRO and TPH-DRO) were detected above the reporting limit in most potential source material samples, but not in low-level wells (**Tables 16–21**).
  - Many TICs typically associated with petroleum substances were reported in potential source material samples, but not generally in low-level wells (**Tables 16–21**).
  - Diagnostic chromatographic profiles present in most potential source material samples did not match those from low-level wells (**Tables 16–21**).
  - Elevated concentrations of inorganic constituents were present in some of these potential source material samples (where analyzed), but not in low-level wells (**Tables 16-21**).
  - An unaltered thermogenic signature is present in samples of natural gas, but not in dissolved hydrocarbon gas in groundwater from low-level wells (**Table 22**).

- Several potential sources evaluated in this study are not likely the source of low-level detections observed in the PAPA (**Figure 9-4**), as suggested by the following spatial and temporal factors:

  - Low-level organic constituent detections were observed in the PAPA before produced water injection wells, liquid gathering systems, and central gathering facilities were constructed or fully operational (**Section 9.3.2.1**).
  - Several potential off-pad sources, such as landfills, underground storage tanks, and hazardous waste sites, are located outside of the PAPA or away from the main gas field development area (**Section 9.3.2.4**).
  - Most produced water injection wells are located hydraulically downgradient of water wells in the PAPA (**Section 4.4**).

- Migration of organic constituents, if released, would be of limited extent in the subsurface due to the hydrogeology of the PAPA, as well as the fate and transport properties of organic and inorganic constituents in the unsaturated and saturated zones (**Section 9.3.3**; **Figure 9-4**). This finding is based on the following evidence:
  - Organic compounds, if released, would not migrate appreciable distances (>150 feet) due to retardation and biodegradation in groundwater.
  - Groundwater movement is relatively slow in the Wasatch Formation due to the interbedded nature and relatively low permeability of sediments.
  - A thick unsaturated (vadose) zone in most areas of the PAPA impedes the migration of a release to groundwater.
  - No chemical evidence was found to indicate that flowback fluid or produced water is migrating upward over thousands of feet of geologic strata.

- High-level wells are not the source of low-level detections in the PAPA (**Figure 9-4**). This finding is based on the following evidence:
  - The chemical signatures in high-level wells do not resemble the signatures in low-level wells (**Sections 8.5**, **9.1**, **9.2**, and **9.3.2.3**).
  - Not enough time has elapsed for impacts from high-level wells to reach nearby water wells based on the relatively low groundwater velocities in the PAPA.
  - Low-level detections of semivolatile organic constituents typically would not reflect groundwater conditions beyond the immediate vicinity of the well, based on potential sources identified (**Sections 9.2** and **9.3.2.3**).
  - High-level detections are isolated geographically in the PAPA, based on the results of annual groundwater sampling by SCCD.
  - Many low-level organic constituent detections are not consistently reported between annual groundwater sampling events performed by SCCD, indicating the absence of a high-level, continuous source (**Section 9.3.2.2**).



* Based directly on chemical data collected for this study
** Based directly on hydrogeological data collected for the Hydrogeologic Data Gaps Investigation (AMEC, 2012)

Finding

Evidence to Support Findings

Temporal
Spatial
Physical
Chemical
Operational

No Evidence of Widespread Impacts to Groundwater
From Natural Gas Exploration and Production
Low-Level Petroleum Hydrocarbon Evaluation
FIGURE 9-4

- Current E&P best practices minimize the potential for impacts to groundwater in the PAPA (**Sections 4.1, 4.2,** and **9.3.4**; **Figure 9-4**). This finding is based on the following evidence:
  - Secondary containments and closed-loop systems are increasingly used.
  - Modern well casing and cementing programs (**Section 4.1**) are employed in the construction of natural gas production wells.
  - Well integrity testing of natural gas wells and pressure monitoring are used during hydraulic fracturing operations.
  - State and federal agencies provide regulatory oversight of E&P operations, and permitting and reporting requirements are followed consistently.

The conclusions presented in **Figure 9-4** and summary of likely sources in **Table 23** are rooted in a suite of evidence related to the chemical, physical, temporal, spatial, and operational factors at play in the PAPA. This evidence is summarized in this section.

9.3.1 Chemical Evidence

The chemical signatures of most potential source materials sampled for this study, including produced water, condensate, drill mud, natural gas, and flowback fluid, are not present in low-level wells (**Table 23**; **Figure 9-4**). The key characteristics of the chemical signatures in these potential source materials are summarized on **Figure 9-4**.

These chemical signatures were not present in low-level wells, which indicate that widespread releases of potential source materials sampled for this study have not occurred. The study produced no chemical evidence of widespread releases of these materials from natural gas production wells or from other natural gas E&P facilities (pipelines, produced water injection wells, pits, tanks, CGFs, and LGS) (**Table 23**; **Figure 9-4**).

Volatile organic constituents detected in low-level wells are sourced primarily from the upward seepage of natural gas from depth by natural processes that have likely occurred over geologic time (**Section 9.1**; **Figure 9-1**). Low-level semivolatile organic constituents detected in water wells are likely sourced from substances used in the drilling, installation, and operation of water wells (**Section 9.2**; **Figure 9-3**; **Table 23**) or from naturally occurring organic matter present in the Wasatch Formation sediments (**Section 9.2.2.4**; **Figure 9-3**; **Table 23**).

The isolated, high-level detections of organic constituents observed at some gas well pads (see **Section 8.5**) are not the source of the low-level detections of semivolatile (or volatile) organic constituents in low-level wells in the PAPA. The chemical and chromatographic signatures of groundwater samples with high-level detections differ from the signatures of samples with low-level detections sampled for this study. There is no evidence that constituents detected at elevated

concentrations in high-level wells have affected nearby water wells, based on the results of annual sampling performed by SCCD (**Appendix A**). These observations complement what is known about the hydrogeology in the PAPA and the predicted fate and transport of dissolved constituents, which is discussed in further detail in **Section 9.3.3.2**.

9.3.2 Temporal and Spatial Evidence

Source identification, source pathways, and assessment of impacts to groundwater in the PAPA from natural gas E&P operations are informed by several temporal and spatial factors (**Figure 9-4**):

- Timing of the discovery of low-level detections with respect to the timing of E&P operations in the PAPA;
- Sporadic nature of many of the low-level organic constituent detections based on the historical groundwater sampling record;
- Spatial distribution of low-level organic constituent detections in the PAPA; and
- Location of sources with respect to water wells in the PAPA.

9.3.2.1 *Timing of Organic Constituent Detections and Development of E&P Infrastructure*

Based on the evaluation of the potential sources of organic constituents presented in **Section 4.0** and the timeline of key events in the development of the E&P infrastructure in the PAPA (**Figure 4-2**), low-level detections were reported before the development, establishment, or implementation of the following infrastructure or activities:

- Underground injection of produced water;
- Liquid storage/transfer at CGFs; and
- In-field fluid-gathering pipelines (LGS).

Most of the industrial water supply wells with low-level detections of organic constituents had been identified by mid-2007. At that time, installation and/or operation of in-field gathering pipelines, tank batteries, other liquid storage/transfer facilities at CGFs, and produced water injection well facilities in the PAPA either had not yet commenced or were not well established. In-field fluid-gathering pipelines were not part of historic (pre-1984) E&P operations and were installed beginning in 2005 by one Operator in the northern portion of the anticline. It was not until 2010 that the system of in-field fluid-gathering pipelines in the PAPA was substantially complete.

The same timeline of development occurred for facilities at CGFs that temporarily store and transfer fluids received from the system of pipelines prior to sale or disposition. At the end of 2007, only three produced water injection wells were active within the confines of the PAPA: Petrogulf State 36-1 (36-1 WDW), Highway SWD #11 (11), and Riverside 6-16 WDW (6-16 WDW) (**Figure 4-1**). Because low levels of organic constituents had already been detected before these facilities were

developed, these potential sources are not likely the sources of low-level detections of organic constituents in the PAPA.

9.3.2.2 *Temporal Nature of Organic Constituent Detections*

Many low-level organic constituent detections are sporadic in nature, or not consistently reported between annual sampling events performed by SCCD (**Appendix A**). These sporadic detections may result from cross-contamination during sampling or as a result of well operations prior to sampling, or may partly reflect changes in sampling methodologies or analytical methods through time. Whatever the cause, the nature of these detections is not consistent with a continuous source of organic constituents.

9.3.2.3 *Spatial Distribution of Organic Constituent Detections in the PAPA*

Complementary spatial trends have been observed in composition and concentration of low-level volatile organic constituents detected in the PAPA. In contrast, the composition and concentrations of low levels of semivolatile organic constituents displayed no particular trend across the PAPA with respect to magnitude of concentrations (e.g., areas with substantially higher or substantially lower concentrations of these constituents), or with respect to chemical composition (e.g., areas where greater numbers and/or types of semivolatile organic constituents are detected). The distribution of the low-level detections of semivolatile organic constituents is not indicative of a large, continuous plume of contaminants, or multiple plumes of contaminants originating from E&P activities in the PAPA. Low levels of semivolatile organic constituents were detected in study wells located away from E&P operations (off-pad) and off the crest of the anticline in the PAPA as well as in study wells and industrial water supply wells located on gas well pads in the immediate vicinity of active E&P operations (**Figure 7-5**).

The nature of the semivolatile organic constituent detections, in conjunction with chemical evidence indicating a likely source attributed to substances used in well drilling, installation, and/or operational practices, indicates that these detections are likely confined to the well casing or the immediate area of the perforated interval of a water well. An impact occurring in this manner would primarily affect the quality of water inside the well casing or wellbore with minimal impact to surrounding formation water. This type of impact is also consistent with a scenario whereby water containing organic constituents is accidentally back-siphoned into water wells, as appears to be the case at well RS 15-12. These isolated, intrawell impacts can typically be mitigated using well cleaning and pumping procedures.

9.3.2.4 *Location of Potential Point Sources with Respect to Water Wells*

Several potential sources are located away from the main gas field development areas and are thus not considered likely sources of organic constituents in industrial water supply wells and study wells in the PAPA. Landfills, permitted oil disposal facilities, and sites listed on Wyoming DEQ, BLM, or WOGCC databases within or proximal to the PAPA, as described in **Section 4.6**, are not considered

sources of low-level organic constituents detected in water wells mainly due to their distance from these wells in the PAPA and/or the degree of regulatory oversight or regulatory closure that these sites have received (AMEC Geomatrix, 2010). Although many of these facilities and sites are located in an upgradient groundwater flow direction with respect to water wells in the PAPA, a release, if it occurred, would likely not reach the wells due to the relatively low groundwater velocities reported by AMEC (2012) for the Wasatch Formation (see **Section 9.3.3.1**). In addition, a majority of water wells in the PAPA are located up-gradient relative to the direction of groundwater flow from most produced water injection well facilities (**Figure 2-10**), which are predominantly located west of the gas field development areas (**Figure 4-1**). Thus, these wells are not likely to be impacted from a release at a produced water injection well facility.

9.3.3 Physical Evidence

This section considers the hydrogeology of the PAPA and fate and transport characteristics of organic and inorganic constituents to assess potential sources of the observed low-level detections of organic constituents in groundwater in the PAPA (**Figure 9-4**).

9.3.3.1 *Hydrogeological Considerations*

The hydrogeology of the PAPA, as well as the fate and transport of solutes in the unsaturated and saturated zones, controls the likelihood that a release from any of these potential point sources would impact groundwater.

A majority of the natural gas well pads in the PAPA are located along the crest of the anticline and away from the river corridors. A hypothetical release at the ground surface in these areas would typically have to migrate vertically over 200 feet (and up to 500 feet in some places; see depth to water measurements in **Table B-3** in **Appendix B**) through the unsaturated (vadose) zone to reach the regional groundwater system in the Wasatch Formation. Assuming no preferential pathways exist in the Wasatch Formation, the volume of any spill or release would need to be substantial in order to reach groundwater in the Wasatch Formation at these locations. Only four gas well pads are located in the river corridors of the PAPA, where the alluvium is present at ground surface. A release at the ground surface in these areas would travel a shorter distance to enter the groundwater system as the depth to groundwater is shallower (less than 50 feet).

A spill or release large enough to reach groundwater, or a spill or release occurring directly in the Wasatch Formation, would migrate slowly in groundwater within the Wasatch Formation. The average linear velocity of groundwater in the Wasatch Formation ranges from 0.011 to 40 feet per year based on the observed range of hydraulic gradients and the range of hydraulic conductivity values determined from aquifer testing (**Section 2.4.3**). It would take at least 5 years for groundwater to travel the width of a typical gas well pad based on groundwater velocity estimates for the Wasatch Formation. A hypothetical spill or release of sufficient size within the river corridor would migrate at a much faster rate in the alluvium of the river corridors compared to a

hypothetical release in the Wasatch Formation. Average groundwater velocity in the alluvium ranges from approximately 1,390 to 4,270 feet per year based on the observed range of hydraulic gradients and range of hydraulic conductivity values determined from aquifer testing (**Section 2.4.3**).

Based on what is known about the hydrogeology in the PAPA, low levels of organic constituents detected in water wells are not the result of large releases from E&P activities, and the few locations with high-level detections are not the source of low-level detections in the PAPA. Not enough time has elapsed since the beginning of E&P operations in the PAPA (~1939) to the timing of this study (i.e., 2010) for a widespread plume of organic constituents to develop in groundwater, even if a release or several releases of large magnitude occurred at the ground surface and migrated to the groundwater system.

9.3.3.2 *Fate and Transport Considerations*

Numerical modeling of the groundwater system in the PAPA was undertaken as a companion study to this study (AMEC, 2013). The numerical model is appropriate for predicting flow and transport at an intermediate and regional scale, and is capable of simulating large-scale movement (>300 feet) of potential releases and travel times from potential sources to potential receptors. Model limitations are discussed in detail by AMEC (2013).

The groundwater flow model was constructed based on the data collected during the HDG investigation (AMEC, 2012). Advective and solute transport modeling was performed to assess the fate and transport of the organic and inorganic constituents (i.e., benzene, toluene, and chloride) that would most likely be released during E&P activities under hypothetical spill scenarios in the PAPA.

The fate and transport modeling produced the following key findings:

- A spill or release resulting from natural gas E&P activities in the PAPA would not be expected to affect groundwater in and around the town of Pinedale.
- A non-biodegradable constituent, such as chloride, dissolved in groundwater in the Wasatch Formation would travel less than 1.5 miles over a time period of 100 years in areas within the PAPA outside of the river corridors.
- Solute transport modeling of hypothetical spills of condensate generally demonstrated that concentrations of benzene and toluene in groundwater did not exceed applicable groundwater standards beyond the extent of the gas well pad.
- Hypothetical, individual releases of organic constituents from natural gas E&P activities are unlikely to impact large portions of the Wasatch Formation or alluvium due to relatively low groundwater velocities, and due to retardation and biodegradation of organic constituents in groundwater.

Results of five hypothetical release scenarios simulated within the area most susceptible to groundwater quality impacts (e.g., New Fork River corridor in the center of the PAPA) indicate that predicted concentrations of benzene and toluene in groundwater do not exceed applicable groundwater standards at distances greater than 150 feet away from simulated sources. Since most of the potential receptors in this area are greater than 150 feet from natural gas E&P activities, even if a major release to groundwater were to occur within this area, impacted groundwater would be unlikely to reach most of these receptors (AMEC, 2013). Widespread plumes of organic constituents did not develop in groundwater when these types of release scenarios were modeled, which is consistent with the hydrogeological data collected by AMEC (2012) as part of the HDG investigation, the chemical data collected annually by the SCCD (**Appendix A**), as well as the results of this study.

Based on model simulations of hypothetical releases, if free-phase material were released directly to groundwater, dissolved-phase organic constituents would not migrate far from the source based on groundwater velocities and due to retardation and biodegradation in groundwater (AMEC, 2013). There is only one known gas well pad in the PAPA where concentrations of organic constituents, such as benzene and toluene, have been consistently detected in groundwater at concentrations exceeding applicable groundwater standards. A historic (pre-1984) gas well located at this gas well pad may be contributing to the groundwater impacts present at the pad (see **Section 8.5.1**). In this case, a definable impact to groundwater has occurred, which does not resemble the low-level detections of organic constituents observed elsewhere in the PAPA. Although the extent of the impacts to groundwater have not been fully defined at this gas well pad, the impact to groundwater is likely isolated, as impacts such as these are not evident in water supply wells on nearby gas well pads (**Appendix A**).

9.3.4 Operational Evidence

Chemical evidence produced by this study indicates that past and current gas well construction has not caused widespread groundwater impacts in the PAPA. Organic constituents detected in groundwater at only one location may have been caused by well construction issues associated with a pre-1984 natural gas well (**Section 8.5.1**). Although the high-level detections at this location have not been fully delineated, they are not a source of the low-level detections in water wells sampled for this study nor do they appear to be affecting the water quality of nearby water supply wells, based on the results of annual sampling by SCCD (**Section 9.3.1**).

Based on the overview of current E&P operations presented in **Section 4.1**, the potential for impacts to groundwater are further minimized by the following current E&P best practices with respect to gas well construction:

- Natural gas wells are designed and constructed in compliance with existing regulations to achieve a high level of integrity of the wells (see **Sections 4.1.1.2** and **4.1.2**).

- Modern cementing and casing programs typically consist of three to four cemented and pressure-tested sets of telescoping, continuous steel casings.
- Surface casing is installed specifically to protect fresh water and potable groundwater, and oil-based drilling muds are used only below the depth of surface casing.
- Cement bonding logs are used on production casings to assess the integrity of the bond, and corrective measures are taken if needed to achieve an adequate bond.
- Advanced technologies and rigorous quality control measures are employed to minimize risk of releases from gas wells.
- Closed-loop systems are being increasingly used during gas well drilling, and pits (if used) must be lined and reclaimed shortly after drilling and completions operations cease at the gas well pad.

Chemical evidence produced by this study indicates that past and current well completions activities (i.e., hydraulic fracturing) have not caused widespread groundwater impacts in the PAPA. The potential for impacts to groundwater are further minimized by current E&P best practices described in **Section 4.1.2,** including:

- Natural gas wells are tested prior to and after completions operations to verify the integrity of the wells.
- High pressures (e.g., over 10,000 psi) are rare; when they occur, they are usually instantaneous or of limited duration and occur only at the greatest depths. The annulus pressure of the production casing is monitored and recorded continually at the wellhead to assess whether the fluid is being delivered to the targeted zone. Surface casing is visually monitored to assess if excess pressure is present.
- Operators advise that the results of proprietary microseismic studies in the PAPA provide an indication of the size of the zone of influence from hydraulic fracturing operations (including the vertical dimension), and confirm fracture containment within the intended zone.
- Once discrete zones in the producing formation are hydraulically fractured, the natural gas well serves as the pathway of least resistance for the naturally pressurized gas and liquids being liberated from the Lance Pool to reach the surface. Throughout the production period of the natural gas well, the introduced completions fluids and naturally occurring formation water and condensate from the Lance Pool continue to be recovered.

From a material (mass) balance standpoint, there is minimal risk of hydraulic fracturing fluids traveling upward to the Wasatch Formation. According to PAPA Operators, fluid volumes simply are not large enough in the upper stage(s) of the well for hydraulic fracturing fluid to travel the

thousands of feet from the zone of influence to the Wasatch Formation. In addition, stress differentials between the producing sands and the surrounding shales within the Lance Pool tend to contain the hydraulic fractures (and fluids) within the zone of interest. Designed pump rates and fluid viscosities also help keep the hydraulic fractures (and fluids) contained within the zone of interest.

Chemical evidence produced by this study indicates that past and current gas production activities have not caused widespread groundwater impacts in the PAPA. Based on current E&P operational practices discussed in **Section 4.2,** the potential for impacts to groundwater are further minimized by current E&P best practices, including:

- Modern production units are typically configured with spill containment built into the system or an HDPE liner installed beneath the unit.
- Lined secondary containment structures are in place for all tanks at gas well pads, CGFs, and produced water injection facilities.
- Tanks and containment units are inspected routinely, and tank integrity programs have been implemented.
- Pipeline integrity programs have been implemented throughout the PAPA.

Permitted Class II water disposal wells are permitted and strictly regulated through the WOGCC. The results of this study produced no evidence that injected produced water has migrated upward through more than 3,000 feet of geologic strata to produce low-level detections of organic constituents in groundwater in the PAPA. If this were occurring, organic constituents that are characteristic of produced water would be detected in groundwater. Although the disposition of the two water wells that supported operations at the Wagon Wheel #1 natural gas production well is not known (**Section 4.3**), the results of this study generated no evidence that these wells have produced a widespread impact to groundwater.

State and federal permitting and reporting requirements guide the oversight of gas field operations in such a way that it would be very unlikely that a widespread release in the PAPA could remain undetected. Although the exact composition of all fluids used and generated during historic operations is unknown, the fluids used on-record were petroleum-based and refined or unrefined. If widespread releases of these fluids had occurred from historical practices, SCCD's annual groundwater monitoring results would show more high-level detections in the PAPA than are currently observed, and these high-level detections would exhibit chemical signatures that could likely be traced to a particular fluid type.

10.0 CONCLUSIONS

This report documents the results of groundwater, gas, and potential source material sampling and evaluates potential point and non-point sources of low-level organic constituents detected in water wells in the PAPA. Low-level detections are considered those that are below applicable groundwater standards. The results of this study, which was designed and implemented in accordance with a SAP accepted by BLM in consultation with EPA and the Wyoming DEQ (AMEC Geomatrix, 2010), resulted in four primary conclusions (**Figures 9-1**, **9-3**, and **9-4**). These conclusions are supported by the findings of the HDG investigation and the hydrogeological conceptual model of the PAPA, which are summarized in **Section 2.0**.

Conclusion 1: The low-level detections of volatile organic constituents in water wells are largely attributable to the upward seepage of natural gas from the Lance Pool over geologic time by natural processes (see **Figure 9-1**).

This conclusion is based on the following findings and supporting evidence:

- Hydrocarbon gases in low-level wells are not the same as natural gas produced in the PAPA, as evidenced by:
  - The hydrocarbon gas in low-level wells exhibits chemical and isotopic signatures that indicate the gas is altered thermogenic or microbial, and these signatures change moving from south to north in the PAPA (**Table 22**; **Figure 8-1**). In contrast, the chemical and isotopic signature of natural gas produced in the PAPA indicates the gas is unaltered thermogenic (**Table 22**).
  - The chemical and isotopic signatures of natural gas may be altered during migration by microbial activity, diffusion, phase separation, and adsorption. Gas that has been altered by biodegradation may show a preferential depletion of n-alkanes relative to isoalkanes, which was observed in low-level wells sampled for this study that displayed an altered thermogenic signature or intermediate signature (**Figures G-1** through **G-5** of **Appendix G**).
- Natural gas likely migrates to the ground surface over geologic time in the PAPA, which is illustrated in the conceptual model for gas generation and seepage on **Figure 9-2.** This finding is based on the following evidence:
  - Natural gas was observed at the ground surface during a soil gas survey performed in the northern portion of the PAPA (**Section 4.8**).
  - Hydrocarbon gas was observed at shallow depths during the drilling of natural gas production wells early in development of the gas field in the PAPA (**Figure 4-4**; **Section 9.1.3.4**).

- Hydrocarbon gas has been encountered during the drilling of water wells at gas well pads prior to gas well installation (**Figure 4-4**; **Section 9.1.3.4**).
- The gradual change in hydrocarbon gas signatures across the PAPA is more consistent with a non-point source (upward seepage) versus a point source (leaking natural gas production well).
- According to published literature, natural gas that has accumulated beneath other geological traps similar to the Pinedale Anticline is known to migrate to the ground surface over time (**Sections 4.8** and **9.1.3**).

In addition, the detection of individual, dissolved-phase VOCs (e.g., toluene) is not consistent with the chemical signatures of potential source materials sampled for this study (e.g., condensate, produced water, drill mud, flowback fluid, LNAPL) (**Tables 16-21**; **Section 9.1.2**). Thus, these potential source materials are not sources of the volatile organic constituents detected in low-level wells in the PAPA (**Table 23**).

Conclusion 2. The source of low-level detections of semivolatile organic constituents in water wells is not readily apparent, but likely originates from substances introduced during the drilling, installation, and operation of the wells and/or from naturally occurring organic matter (see **Figure 9-3).**

This conclusion is based on the following findings and supporting evidence:

- The chemical signatures of groundwater samples from most of the low-level wells with detections of semivolatile organic constituents above laboratory reporting limits most closely resembled the signature of pump installation materials. This finding is based on the following evidence:
  - No complementary VOCs or SVOCs were detected above laboratory reporting limits in these wells (**Table 14**).
  - Few to no TICs were reported, and when reported, most TICs were not characteristic of sources sampled for this study or typically associated with petroleum substances.
  - TEH was always detected and TPH-DRO was detected along with TEH in some wells.
  - Chromatographic profiles were mostly non-characteristic and/or characterized by UCMs (**Section 9.2.1.3**).
  - Grease and/or pipe dope has been observed on pumps and/or pipe fittings during pump removal and well sampling.
  - One exception is RS 15-12. This well exhibited a chemical signature resembling drill mud, which is suspected to have resulted from the backflow of fluid via improper well/pump operation.

- Low-level detections of semivolatile organics in some low-level wells may be attributed to naturally occurring organic matter. This finding is based on the following evidence:
  - TEH was removed from the extract of samples collected from several study wells following treatment by silica gel.
  - Sediments containing organic matter (carbonaceous shale) are present in the Wasatch Formation.
  - Particulates of organic matter may be introduced to water wells during well drilling and installation and become entrained in groundwater samples. Suspended sediment was observed in several study wells prior to sampling in June 2011 (AMEC 2012).
  - Laboratory analysts have identified naturally occurring organic matter as a potential source of semivolatile detections based on the observed chromatographic response.
- The chemical signature in four study wells resembled the chemical signature of a refined petroleum-based substance, which may be attributable to well installation materials. This finding is based on the following evidence for these four wells:
  - TPH-DRO was detected and not removed upon silica gel treatment.
  - The chromatographic profiles exhibited a narrow, symmetrical response in the diesel-range organics, which most closely resembled the reference chromatogram for a mineral oil standard.
  - The use of petroleum-based substances during water well drilling and installation may introduce semivolatile organic materials into the well.
  - These study wells share a common history of well drilling and installation and are located upgradient of E&P activities.

Conclusion 3. This study did not produce any evidence of widespread impact to groundwater in the PAPA as a result of E&P operations through releases of condensate, produced water, drill mud, flowback fluid, natural gas, or other materials used or generated during these operations (see **Figure 9-4).**

This conclusion is based on the following findings and supporting evidence:

- The chemical signatures of most potential source materials sampled for this study, including produced water, condensate, drill mud, natural gas, and flowback fluid, are not present in low-level wells (**Table 23**; **Figure 9-4**). This finding is based on the following evidence:
  - Multiple individual VOCs and SVOCs characteristic of petroleum substances were consistently detected above the reporting limit in most potential source material samples, but not in low-level wells (**Tables 16–21**).

  - Both volatile and semivolatile organic fractions (e.g., TPH-GRO and TPH-DRO) were detected above the reporting limit in most potential source material samples, but not in low-level wells (**Tables 16–21**).
  - Many TICs typically associated with petroleum substances were reported in potential source material samples, but not generally in low-level wells (**Tables 16–21**).
  - Diagnostic chromatographic profiles present in most potential source material samples did not match those from low-level wells (**Tables 16–21**).
  - Elevated concentrations of inorganic constituents were present in some of these potential source material samples (where analyzed), but not in low-level wells (**Tables 16-21**).
  - An unaltered thermogenic signature is present in samples of natural gas, but not in dissolved hydrocarbon gas in groundwater from low-level wells (**Table 22**).

- Several potential sources evaluated in this study are not likely the source of low-level detections observed in the PAPA (**Figure 9-4**), as suggested by the following spatial and temporal factors:
  - Low-level organic constituent detections were observed in the PAPA before produced water injection wells, liquid gathering systems, and central gathering facilities were constructed or fully operational (**Section 9.3.2.1**).
  - Several potential off-pad sources, such as landfills, underground storage tanks, and hazardous waste sites, are located outside of the PAPA or away from the main gas field development area (**Section 9.3.2.4**).
  - Most produced water injection wells are located hydraulically downgradient of water wells in the PAPA (**Section 4.4**).

- Migration of organic constituents, if released, would be of limited extent in the subsurface due to the hydrogeology of the PAPA, as well as the fate and transport properties of organic and inorganic constituents in the unsaturated and saturated zones (**Section 9.3.3**; **Figure 9-4**). This finding is based on the following evidence:
  - Organic compounds, if released, would not migrate appreciable distances (>150 feet) due to retardation and biodegradation in groundwater.
  - Groundwater movement is relatively slow in the Wasatch Formation due to the interbedded nature and relatively low permeability of sediments.
  - A thick unsaturated (vadose) zone in most areas of the PAPA impedes the migration of a release to groundwater.

  - No chemical evidence was found to indicate that flowback fluid or produced water is migrating upward over thousands of feet of geologic strata.

- High-level wells are not the source of low-level detections in the PAPA (**Figure 9-4**). This finding is based on the following evidence:
  - The chemical signatures in high-level wells do not resemble the signatures in low-level wells (**Sections 8.5**, **9.1**, **9.2**, and **9.3.2.3**).
  - Not enough time has elapsed for impacts from high-level wells to reach nearby water wells based on the relatively low groundwater velocities in the PAPA.
  - Low-level detections of semivolatile organic constituents typically would not reflect groundwater conditions beyond the immediate vicinity of the well, based on potential sources identified (**Sections 9.2** and **9.3.2.3**).
  - High-level detections are isolated geographically in the PAPA, based on the results of annual groundwater sampling by SCCD.
  - Many low-level organic constituent detections are not consistently reported between annual groundwater sampling events performed by SCCD, indicating the absence of a high-level, continuous source (**Section 9.3.2.2**).

- Current E&P best practices minimize the potential for impacts to groundwater in the PAPA (**Sections 4.1**, **4.2**, and **9.3.4**; **Figure 9-4**). This finding is based on the following evidence:
  - Secondary containments and closed-loop systems are increasingly used.
  - Modern well casing and cementing programs (**Section 4.1**) are employed in the construction of natural gas production wells.
  - Well integrity testing of natural gas wells and pressure monitoring are used during hydraulic fracturing operations.
  - State and federal agencies provide regulatory oversight of E&P operations, and permitting and reporting requirements are followed consistently.

Although the exact composition of all fluids used and generated during historic operations is unknown, the fluids used on-record were petroleum-based and refined or unrefined. If widespread releases of these fluids had occurred from historical practices, SCCD's annual groundwater monitoring results would show more high-level detections in the PAPA than are currently observed, and these high-level detections would exhibit chemical signatures that could likely be traced to a particular fluid type.

Conclusion 4. The Interim Plan (AMEC Geomatrix, 2008) and the Plan of Study (AMEC Geomatrix, 2009a) stipulated that potential sources for the low-level detections be identified so that additional mitigation measures (beyond those in the 2008 ROD) may be developed and implemented, if necessary. Based on the findings of this study, no additional measures are necessary to mitigate the existing low-level volatile or semivolatile organic constituents detected in water wells in the PAPA.

This conclusion is based on the following findings:

- The source of the low-level detections of volatile organic constituents in groundwater is attributed to the upward seepage of natural gas by natural processes over geologic time. The presence of the gas in near-surface groundwater in the PAPA can be expected based on geologic conditions and cannot be mitigated.
- The low-level semivolatile organic constituents detected in groundwater likely originate from substances introduced during the drilling, installation, and operation of groundwater wells and/or from naturally occurring organic materials present in groundwater. By the fall of 2008, Operators had implemented a best practice that requires contractors to clean all downhole materials and equipment used in pump installations by high pressure/hot water, and use hydrocarbon-free pipe dope compounds. Although no water wells have been drilled on BLM-administered lands since the 2008 ROD, similar best practices would be required for well drilling and installation. As organic materials are inherent to the Wasatch Formation, naturally occurring organic matter in groundwater wells in the PAPA cannot be mitigated.

These findings and conclusions do not mean that releases from potential point sources researched for this study could not become sources of organic constituents in water wells in the future. The sustained application of best practices for E&P operations in the PAPA is necessary to protect groundwater resources. Implementation of the forthcoming Final Groundwater/Aquifer Pollution Prevention, Mitigation and Monitoring Plan will provide a mechanism for evaluating groundwater conditions over the long term, determining changes over time in water quantity and quality, and detecting potential responses to anthropogenic and non-anthropogenic stressors to the groundwater system.

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