

**A RECOMMENDED ORGANIC ANALYTE SAMPLE SET FOR  
GROUNDWATER SAMPLING AROUND OIL AND GAS DEVELOPMENT**

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*Cover photo: Sampling groundwater at monitoring well 3772 south of Dagmar, Montana.*

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**CONTENTS**

Abstract..... 1

Introduction..... 3

    Hydrogeologic Setting..... 3

    History of Oil Development in the Prairie Pothole Region..... 3

    Potential for Modern Oil Field Waste Spills..... 5

    Identifying the Presence of Oil Field Waste in Groundwater..... 5

Purpose..... 6

Methods..... 6

    Well Selection..... 6

    Analyte Selection..... 9

    Sample Collection..... 9

Results..... 9

    Aquifers Representing Background Conditions..... 10

    Aquifers Known to Have Oil Field Waste Constituents..... 10

    Results from Sites of Unknown Condition..... 10

Discussion..... 10

    Quality Assurance/Quality Control Evaluation..... 11

Recommendations..... 12

Acknowledgments..... 13

References..... 13

Appendix A: Analytical Suite..... 17

Appendix B1: Detected Organic Compounds..... 21

Appendix B2: 2015–2016 Sampling Results from Selected Wells..... 25

## FIGURES

Figure 1. The sampled wells are a subset of a sampling program undertaken in eastern Montana in 2015-2016 .....	4
Figure 2. Groundwater sampled at site 221691 near Medicine Lake Wildlife Refuge.....	11

## TABLES

Table 1. Example organic compounds from microbial metabolism of organic contamination in groundwater .....	7
Table 2. Sample site summary .....	8

## ABSTRACT

Organic compounds occur naturally in groundwater systems and through unintentional release of fluids during oil and gas drilling and production activities. The presence of chemical indicators traditionally associated with oil field waste could hinder current and future oil and gas development if landowners interpret their water resources as impaired. However, contamination from oil development is rare, unpredictable, and dispersed across the oil field. Robust, cost-effective methods are needed to differentiate between naturally occurring and oil field sources of organic compounds. This study evaluates the utility of three organic-constituent analyses as potential distinguishing methods.

The study included sample collection from 11 wells and one lake chosen to represent a diversity of conditions, including groundwater known to have oil field waste constituents, groundwater outside of potential oil field impact, and unconsolidated and bedrock aquifers. All sites had detections of organic constituents during an earlier investigation. Three analytical methods, EPA 8260, EPA 8270, and RSK, were applied to each sample. Fifteen of the 138 compounds that can be identified with these methods were detected. Thirteen of the 15 compounds were measured with EPA 8260, indicating that this method is the most likely to identify organic compounds associated with oil field waste and the aerobic and anaerobic degradation of that waste. Based upon a comparison of results from contaminated and uncontaminated sites, tetrahydrofuran, xylene, and, in some cases, toluene are the most likely indicators of oil field waste in groundwater. EPA 8260, a lower-cost method that includes these three compounds, is the recommended analytical method. Results also suggest that organic analyses alone may not identify all groundwater affected by oil field waste; organic analyses should be supported with inorganic analyses. Quality control samples collected during this investigation were positive for organic compounds, indicating that some sample contamination occurred in the field or laboratory. This underscores the importance of quality control and quality assurance procedures in investigations of organic constituents.



## INTRODUCTION

Recent sampling of groundwater and surface water around areas of oil and gas development has shown that traditional fingerprints of oil field waste (e.g., chloride concentration, presence of organic constituents, high radioactivity, and high methane concentrations) also occur naturally in aquifers used for domestic and stock purposes (Meredith and Kuzara, 2018). The presence of chemical indicators traditionally associated with oil field waste could hinder current and future oil and gas development if landowners interpret their water resources as impaired by these activities. Defining a chemical fingerprint that confidently identifies chemical constituents associated with oil brines would reduce the possibility of misidentifying and misattributing naturally occurring organic compounds to oil and gas development.

Organic compounds include any molecule that has a base of carbon atoms in a chain (aliphatic) or ring (aromatic) structure. Common analytical methods measure the total concentration of organic compounds within certain weight ranges. Total purgeable hydrocarbons (TPH), gasoline range organics (GRO), total extractable hydrocarbons (TEH), and diesel range organics (DRO) are typical assays. TPH is approximately equivalent to GRO, which measures weight ranges of approximately  $nC_6$  to  $nC_{10}$  (subscript refers to the number of carbon atoms in the molecule). TEH is approximately equivalent to DRO, which measures weight ranges from approximately  $nC_{10}$  to  $nC_{23}$ .

The work presented here builds upon an earlier study of groundwater quality in areas of oil and gas development. Meredith and Kuzara (2018) identified 48 groundwater sample sites in eastern Montana with detections of TPH and/or TEH: 14 from bedrock aquifers and 34 from unconsolidated aquifers. These detections came from groundwater sampled in areas known to have constituents from oil field waste, the Prairie Pothole region in northeast Montana, and from areas that are unlikely to have impacts from oil development activities. These results suggest that these assays do not provide unequivocal evidence of oil brine constituents in groundwater; however, the component compounds measured in the assays may identify naturally occurring organic constituents as distinct from constituents of oil field waste. More detailed analytical methods were needed to identify the specific organic compounds resulting in TPH and TEH detections to

distinguish sources of organic compounds in groundwater.

## Hydrogeologic Setting

Major aquifers in the study area include surficial, unconsolidated aquifers and underlying bedrock units within about 200 to 300 ft below ground surface. Bedrock aquifers include those within the Tertiary Fort Union Formation, primarily the Tongue River Member sandstone and sandstones within the Cretaceous Fox Hills/Hell Creek Formation. Unconsolidated aquifers consist of Tertiary and Quaternary terrace deposits, Quaternary glacial outwash deposits, and modern alluvial deposits. In the northern part of the study site (fig. 1), surficial material is predominantly glacial till and glacial outwash (Bergantino and Wilde, 1998a,b; Reiten and Tischmak, 1993; Vuke and Colton, 1998; Vuke and others, 2003). The southern extent of glacial till and outwash aquifers is coincident with the extent of Laurentide Ice Sheet glaciation along the eastern Montana border, close to what is now Interstate 94 (Vuke and others, 2007).

## History of Oil Development in the Prairie Pothole Region

The Prairie Pothole region of the northern Great Plains is so named for the numerous small lakes that formed in Pleistocene glacial till and outwash deposits. This region, which extends into portions of northeast Montana, provides an ecosystem hospitable to a variety of wildlife. Oil development in this area began in the 1960s, and many lakes in the region have been impacted by oil field brines (Peterman and others, 2012; Reiten and Tischmak, 1993). Reiten and Tischmak (1993) reported that the history of uncontained coproduced oil brine discharges is based, in part, on residents reporting improper disposal of brines into sloughs, brine and oil pipeline leaks, brine spills, and overflowing evaporation pits. Plastic-lined reserve pits, excavated to hold drilling wastes (e.g., brine water and drill cuttings), were backfilled when drilling was completed. However, one method of backfilling included breaching the liner and pushing the drilling waste into unlined radial trenches. This created the potential for contamination of shallow aquifers. Oil field waste contamination in Prairie Pothole wetlands results in overall lower taxonomic richness of macro-invertebrates (Preston and others, 2018) and decreased aboveground biomass (Preston and Ray, 2017).

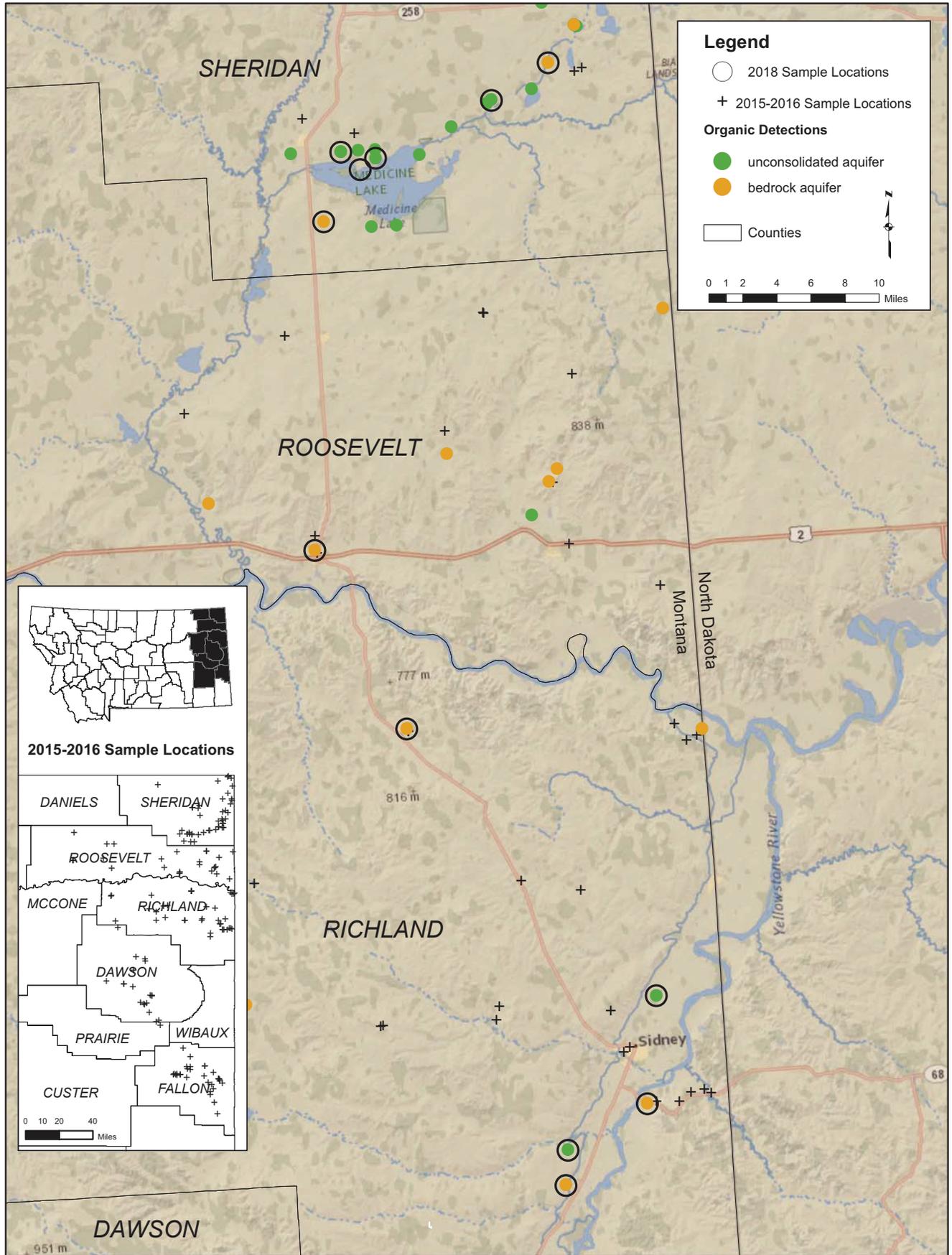


Figure 1. The sampled wells (open circles) are a subset of a sampling program undertaken in eastern Montana in 2015-2016 (Meredith and Kuzara, 2018). A subset of wells that had detectable TPH and/or TEH were resampled for a more detailed organic analysis.

The quality of coproduced oil brine water is a concern for soil, stock, and human health. Characteristics of produced water from the Bakken Formation include high salinity, with total dissolved solid concentrations ranging from 35,000 to 330,000 mg/L, and elevated levels of selenium, copper, lead, and radium (Lauer and others, 2016). Concentrations of naturally occurring radioactive isotopes ( $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ , and  $^{222}\text{Rn}$ ) in brine waters range up to 10,000 picocuries/L (pCi/L; Kharaka and others, 2013). The produced water from shale gas wells can include organic constituents such as polycyclic aromatic hydrocarbons [PAH; e.g., naphthalene, anthracene (appendix A)], heterocyclic compounds, aliphatic alcohols, phenols, aromatic amines, other aromatics, phthalates, fatty acids, nonaromatic compounds, and elevated total organic carbon (Orem and others, 2014).

### Potential for Modern Oil Field Waste Spills

In contrast to development practices of the 1960s, modern oil well construction prioritizes protecting shallow groundwater by requiring “surface casing to a depth below all fresh water located at levels reasonably accessible for agricultural and domestic use” [Administrative Rules of Montana (ARM) 36.22.1001], “the drilling, casing, producing and plugging of wells...that prevents the pollution of fresh water supplies by oil, gas, salt, or brackish water” [Montana Code Annotated 82-11-123(3)], and injection of produced water with concentrations greater than 15,000 parts per million total dissolved solids (ARM 36.22.1226). However, activities related to oil development may still affect the environment. For example, a 2015 pipeline leak spilled over 11 million liters of oil field wastewater (brine and flow-back water) into a North Dakota creek. This resulted in persistent, elevated levels of sodium, chloride, bromide, strontium, boron, lithium, ammonia, and hydrocarbons following remediation (Cozzarelli and others, 2017). Drollette and others (2015) identified unintentional surface releases of wastewaters from Marcellus Shale development as the source of trace amounts of GRO and DRO in private wells in Pennsylvania.

Lauer and others (2016) reported approximately 3,900 brine spills in North Dakota since 2007. Such spills generally occur during transport (by pipeline or truck) of oil field wastewater to injection sites or from storage tanks. Investigations of accidental releases of

oil field wastewater into the environment in the Bakken region found that oil field waste constituents at spill sites can migrate through soil and groundwater and have been detected in surface water 4 years after the spill event.

A study of records from Colorado, New Mexico, North Dakota, and Pennsylvania found that North Dakota had the most unconventional wells (horizontal wells into shale targets) and the highest number of spills: 4,986 (Maloney and others, 2017). The number of spills differ from those reported by Laurer and others (2016) due to different databases and timeframes used in the respective analyses. While estimates of the spill numbers in Montana are not available in the scientific literature, the frequency of spills may be similar to these four states, ranging from 3 to 15 spills per 100 unconventional wells (Maloney and others, 2017). In Montana, 1,883 unconventional wells have been drilled into the Bakken and Three Forks Formations (MBOGC, 2019).

### Identifying the Presence of Oil Field Waste in Groundwater

The most common organic constituents present in flow-back water (water that returns to the surface during drilling and completion, including injected and formation waters) and produced water (formation water coproduced with oil, usually a brine) from shale formations are more aliphatic than aromatic, e.g., long chain fatty acids (Ferrer and Thurman, 2015). Of 986 compounds identified in Marcellus shale produced water, 61 percent were aliphatic, 24 percent cycloaliphatic, 13 percent aromatic, and 2 percent PAH (Leuk and Gonsoir, 2017). Of 163 groundwater samples collected in oil and gas development areas in Montana, there were no detections for aromatic ranges  $\text{C}_9$ – $\text{C}_{10}$  and  $\text{C}_{11}$ – $\text{C}_{12}$ , and 18 detections for aliphatic ranges  $\text{C}_5$ – $\text{C}_8$  and  $\text{C}_9$ – $\text{C}_{12}$  compounds (Meredith and Kuzara, 2018). However, light aromatic hydrocarbon BTEX [benzene ( $\text{C}_6\text{H}_6$ ), toluene ( $\text{C}_7\text{H}_8$ ), ethylbenzene ( $\text{C}_8\text{H}_{10}$ ), and xylene ( $\text{C}_8\text{H}_{10}$ )] compounds were the most frequently detected in water sampling conducted around oil development, but also the most frequently analyzed. Benzene concentrations in flow-back water were up to two orders of magnitude higher than toluene, ethylbenzene, and xylene (Luek and Gonsior, 2017). In a water-quality study in the Permian and Barnett Basins in Texas, groundwater contained BTEX compounds,

chlorinated solvents, and low molecular weight alcohols; however, only toluene and methanol were interpreted to be indicative of surface spills. Additionally, ethanol co-occurred with elevated bromide concentrations—an indication of brine water (Luek and Gonsior, 2017). Time series sampling showed increasing isopropyl alcohol, propargylic alcohol, acetaldehyde, cyclohexane, toluene, xylene, and ethylbenzene that the authors attribute to degradation of organic compounds associated with oil and gas development (Luek and Gonsior, 2017). Luek and Gonsior (2017) noted that our understanding of organic compounds in oil field wastewaters is limited to volatile and semi-volatile gas compounds because they can be measured through gas chromatography. Little is known about polar and non-volatile organic compounds.

Organic compounds, brought to the surface during drilling and production, are transformed through microbiological processes in soil and water. Aliphatic and aromatic compounds that contain functional groups, -OH, -Cl, -NH<sub>2</sub>, -NO<sub>2</sub>, and -SO<sub>3</sub>, act as electron donors for microbial oxidation. Oxidation can occur aerobically or anaerobically; however, benzene is recalcitrant under all anaerobic conditions (Bouwer and Zehnder, 1993). Aerobic conditions are generally more effective for removal (degradation) of organic constituents than anaerobic; however, some pollutants, such as halogenated aromatic compounds, are more readily degraded under anaerobic conditions (Ghattas and others, 2017).

It is often difficult to predict the products of microbial degradation of surface contamination from oil field waste because, in many cases, the source is unknown and local conditions, such as the groundwater pH, redox state, and other geochemical conditions, control the degradation (McNab and Narasimhan, 1994). Table 1 provides an example of possible microbial byproducts sequentially metabolized in groundwater downgradient from a site contaminated with organic products. Small organic acids were reported as byproducts of anaerobic degradation of flow-back water, including acetate, formate, and citrate (Luek and Gonsior, 2017); however, these are not measured in standard organic analytical methods such as EPA8260 or 8270. Acetone is an additive in enhanced oil production methods, but it may also be a product of anaerobic fermentation. Concentrations of acetone were

highly variable in the water-resource studies analyzed by Luek and Gonsior (2017).

## PURPOSE

The dispersed and unpredictable nature of potential oil field waste spills, in combination with the existing, historical spill sites, makes maximizing the efficiency of sampling programs a priority. The sampling program described here was designed to establish the most effective—based on cost and likelihood of detection—organic analyte suite for fingerprinting and distinguishing naturally occurring organic constituents from organic constituents in groundwater that are derived from oil field waste. Groundwater sampling programs should include analyses of organic and inorganic constituents; the work presented here only addresses the recommended analytical method for organic constituents.

## METHODS

### Well Selection

Meredith and Kuzara (2018) identified 48 groundwater samples with positive TPH and/or TEH detections out of the 168 samples they collected. Of these, 14 samples were from wells completed in bedrock aquifers and 34 from wells in unconsolidated aquifers (fig. 1). Eleven of the 48 wells were selected for this study, including wells in bedrock and unconsolidated aquifers from within and outside areas known to have oil field waste constituents in the groundwater (table 2, fig. 1). Medicine Lake was also sampled to investigate the veracity of a previous detection of total petroleum hydrocarbons in a sample collected by the Montana Department of Environmental Quality in June 2016 (Meredith and Kuzara, 2018).

Sample locations with documented oil field waste constituents were chosen in the vicinity of the Medicine Lake Wildlife Refuge in the Prairie Pothole region. This area has a history of groundwater contamination from oil field waste (Peterman and others, 2012; Preston and Ray, 2017; Preston and others, 2018; Rouse and others, 2013). Identifying sites representative of natural, background groundwater conditions was complicated by sample selection in the 2015–2016 groundwater sampling program (Meredith and Kuzara, 2018), which focused on a few select areas of historic oil development. All previously sampled wells were within 2 mi of an oil well due to the

Table 1. Example organic compounds from microbial metabolism of organic contamination in groundwater (modified from Bouwer and Zehnder, 1993 and Ghattas and others, 2017).

<i>Increasing time and downgradient distance from a contamination source --&gt;</i>					
Process	Aerobic	Denitrification ( <i>both aerobic and anaerobic respiration</i> )	Mn(IV) and Fe(III) Reduction	Sulfate Reduction	Methanogenesis
Example Degraded Compounds			BTEX Halogenated aromatics Carbon tetrachloride	BTEX PAH Naphthalene Anthracene Alkanes Chlorinated compounds	Benzene Toluene Carbon tetrachloride Phenoxyethanol Halogenated aromatic compounds 1,1,2,2,-tetrachloroethane
Example Products of Microbial Degradation	Chlorobenzenes Chlorophenols Petroleum compounds PAHs Chlorobiphenyls Biphenyls Chloroanilines	Toluene m-xylene p-cresol Naphthalene Acenaphthalene Tetrachloromethane Bromoform Hexachloroethane	Toluene	Multiple halogenated aliphatics Chlorophenols Toluene	Multiple halogenated aliphatics PCBs Chlorophenols Trichlorobenzenes
Measured in method EPA 8260					
Measured in method EPA 8270					
Measured in both methods					

Table 2. Sample site summary.

	GWIC ID	Sample Date	Sample Site	Known Contaminated Site?	Aquifer Description
Bedrock Aquifer	279960	6/25/2018	In situ plumbing direct to bottles	No	Fort Union south of Sidney
	223679	6/26/2018	In situ plumbing direct to bottles	No	Fort Union south of Culbertson
	43095	6/26/2018	In situ plumbing direct to bottles	No	Fox Hills east of Homestake
	40257	6/26/2018	Pump & bailer	Unknown	Fort Union north of Culbertson
	79510	6/28/2018	In situ plumbing direct to bottles	No	Fox Hills south of Sidney*
	3772	6/27/2018	Whale & bailer	Yes	Fort Union south of Dagmar
Unconsolidated Aquifer	136651	6/26/2018	Bailer	No	Unconsolidated north of Sidney
	239702	6/25/2018	Whale & bailer	Unknown	Unconsolidated south of Sidney
	221691	6/27/2018	Bailer	Yes	Unconsol. north of Medicine Lake R/contaminated
	3767	6/27/2018	Whale & bailer	Yes	Unconsolidated north of Medicine Lake Refuge
	280641	6/28/2018	Whale & bailer	Yes	Unconsolidated north of Medicine Lake Refuge
Surface Water	262048	6/27/2018	Grab	No	Medicine Lake surface water
QA/QC Samples	3767	6/27/2018	Whale & bailer	Yes	Duplicate of 3767
	Equip. blank	6/28/2018	Bailer	No	Equipment/bailer blank Org.Free NW Sci water.
	Trip blank	n/a		No	Trip blank

\*Samplers could not verify water source. Could potentially be alluvial well 35881.

extensive development in the region, and these wells do not definitively represent background conditions. However, for our background sample set, we chose wells located at least 1 mi from a well pad and not connected by a highly transmissive aquifer (e.g., an unconsolidated aquifer). McMahon and others (2015) concluded that any contamination from Williston Basin oil wells would be 0.3 mi (0.5 km) or less from the wellhead, which supports our assumption that the chosen wells should represent background conditions.

Two wells were not categorized because their condition is unknown. Well 40257 is 0.6 mi from current

surface development and, in the 2015–2016 sampling (Meredith and Kuzara, 2018), this well had detectable BTEX, which was unusual compared to other wells sampled in the area. Well 239702 did not fit the definition of wells we classified as likely background in that it is in an unconsolidated aquifer within 0.3 mi of an oil well, but not within the Medicine Lake area.

Collecting similar numbers of bedrock and unconsolidated aquifer samples in the Medicine Lake area and background settings was difficult because of the geologic setting. The Prairie Pothole region is dominated by glacial till at the surface, and the major-

ity of monitoring wells in this region are shallow. In contrast, the majority of sites that fit our definition of likely background, including not connected by unconsolidated aquifers to drilling sites, were in Richland and Roosevelt counties, where private wells are generally completed in the Fort Union and Fox Hills aquifers. Each combination of setting and aquifer type has at least one sample location (table 2).

### Analyte Selection

An extensive suite of organic analytes was chosen to identify the specific compounds present in the TPH and TEH detections:

- Full volatile organic compounds (VOC) (low level) by method EPA 8260 (\$70/\$120)
  - o Volatile organic compounds by gas chromatography/mass spectrometry (GC/MS)
  - o Sample introduction through purge and trap by selected laboratories
  - o 69 analytes
- Full semivolatile organic compounds (SVOC) by method EPA 8270 (\$165/\$200)
  - o Semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS)
  - o Sample introduction by direct injection by selected laboratory
  - o 66 analytes
- Dissolved gases by method RSK 175 (\$75/\$100)
  - o Dissolved gases in water matrices using gas chromatograph headspace analysis
  - o 3 analytes (methane, ethane, ethene)

Prices quoted by commercial laboratories in Montana, June 2018 and January 2019. Analyte lists presented in appendix A.

### Sample Collection

Samples were collected using methods that minimize exposure of the water sample to sources of organic contamination (table 2). In four settings,

samples were collected directly from *in situ* plumbing and/or pumps. If possible, the spigot was cleaned with laboratory soap prior to flushing the plumbing system. No hoses or splitters were used during sample collection. Shallow monitoring wells were purged and sampled with a new, disposable, single-use PVC/poly bailer (two sites). Deep monitoring wells were purged with a submersible electric plastic pump (whale pump) followed by additional purging and sample collection with a single-use bailer (six sites). A grab sample from Medicine Lake was collected by wading away from the shore and direct-dipping bottles into the water (one site).

Field procedures included typical means to prevent sample contamination. Nitrile gloves were worn at all times during sample collection. Wells were purged until field parameters of temperature, pH, and specific conductance stabilized or three casing volumes had been removed. Sample bottles were provided by the laboratory and filled according to laboratory specifications. Samples were kept cool on ice until delivery to the laboratory. One blind duplicate sample was collected. An equipment blank sample was collected by rinsing a new bailer two times with certified organic-free water (purchased from Northwest Scientific Supply, shipped and stored in half-gallon amber glass bottles) and then collecting a sample of the certified organic-free water from the rinsed bailer. A trip blank, an unopened vial of water, was installed in one of the sample coolers by the laboratory and left in place throughout the 3 days of sample collection.

For a detailed description of the sampling and analysis plan, see: <http://www.mbmgs.mtech.edu/pdf/SAP.pdf>

## RESULTS

Samples analyzed include 11 groundwater samples, one lake sample, one blind duplicate well sample, one equipment blank, and one trip blank (table 2, fig. 1, appendix B1). Fifteen of the 138 analytes were detected (appendix B1). Method RSK 175 identified methane; method EPA 8270D identified bis(2-ethylhexyl)phthalate; and method 8260B detected the remaining 13 analytes (acetone, 2-butanone, benzene, chloromethane, trans-1,2, dichloroethene, ethylbenzene, tetrahydrofuran, toluene, 1,2,4 and 1,3,5-trimethylbenzene, and m-, p-, and o-xylene).

### Aquifers Representing Background Conditions

Two of the six wells in the “uncontaminated” sample set were positive for organic compounds. Well 279960 contained trans-1,2 dichloroethene, and well 43095 contained toluene and methane. The source of the toluene in the sample from well 43095 is unknown; however, it is associated with high methane, and the presence of more than one organic constituent may indicate it is not a laboratory error. The trans-1,2 dichloroethene in the sample from well 279960 is at the reporting limit of 0.5 µg/L and may be from plumbing in the newly constructed house (appendix B1).

### Aquifers Known to Have Oil Field Waste Constituents

All four groundwater samples collected from aquifers known to have constituents from oil brine and drill cuttings had organic detections. These include methane (3 wells), bis(2-ethylhexyl)phthalate (2 wells), 2-butanone (MEK) (1 well), benzene (1 well), tetra-hydrofuran (3 wells), toluene (3 wells), 1,2,4-trimethylbenzene (1 well), xylene (total, m&p, and o; 2 wells) (appendix B1).

### Results from Sites of Unknown Condition

Both wells classified under unknown condition were positive for organic compounds. Groundwater from well 40257, which had previous detections of BTEX, contained methane, bis(2-ethylhexyl)phthalate, benzene, ethylbenzene, toluene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, and m&p and o-xylene. Well 239702, completed in an unconsolidated aquifer relatively close to an oil well, had a low-level detection of toluene, at 0.92 µg/L (detection limit is 0.5 µg/L) (appendix B1).

## DISCUSSION

Comparing detections in the background and Medicine Lake sample sets, and looking for common detections within the Medicine Lake sample set, we conclude the analytes that may indicate the presence of oil field waste constituents are: tetrahydrofuran, xylene, and, perhaps, toluene. Two studies point to the utility of toluene as a tracer of oil field waste in water. Bouwer and Zehnder (1993) cite toluene as a common byproduct of microbial degradation of organic compounds. Luek and Gonsior (2017) used toluene as

one indicator of spills of oil field waste at the surface. However, studies completed by the USGS recommend disregarding toluene concentrations below 0.69 µg/L due to the prevalence of detections of toluene in quality control blank samples (Bender and others, 2011; Fram and others, 2012; McMahon and others 2015). In this study, toluene was below the detection limit (0.5 µg/L) in well 3767 and detected at concentrations below 0.69 µg/L in the duplicate sample from this well. This low-level toluene on its own would be insufficient to conclude that groundwater at the well has constituents from oil field waste. However, other organic compounds are present in these samples. Similarly, taken on its own, the presence of toluene at low levels in samples from wells 43095 (in the Medicine Lake set, at 1.5 µg/L) and 239702 (in the unknown condition set, 0.92 µg/L) does not definitively indicate the presence of oil field waste. These interpretations represent a conservative approach to determining if oil field waste is present based upon the literature documenting quality control issues related to identification of toluene near the detection limit.

Comparing the results from the two wells of unknown condition to the results from the Medicine Lake and background sample sets can provide insight into whether these sites have been affected by oil field waste. Well 239702, completed in an unconsolidated aquifer in close proximity to an oil well, contained 0.92 µg/L toluene, just above the censor level of 0.69 µg/L. In the absence of other organic constituents or other evidence of oil field waste constituents from previous sampling, we interpret this site to be unaffected by the nearby oil well. Ten analytes, including BTEX, were detected in groundwater sampled from well 40257, completed in the Fort Union Formation and located approximately 0.6 mi from an oil well. These results indicate the presence of organic constituents that do not occur naturally in the aquifer, but additional sampling of nearby wells is necessary to determine if the source is related to oil development or the result of nearby surface spills unrelated to oil production.

It is important to note that organic analyses cannot be used alone to identify constituents from oil field waste. Groundwater sampled from well 221691 was the color of coffee (fig. 2), smelled strongly of hydrocarbons, and has a drill log that lists pit material and drilling mud, indicating this well was completed in a



Figure 2. Groundwater sampled at site 221691 near Medicine Lake Wildlife Refuge, was dark in color and smelled strongly of hydrocarbons despite having very few organic constituent detections using EPA methods 8260 and 8270.

reclaimed drill cutting impoundment. However, the only organic compounds detected were 2-butanone and methane. The inorganic geochemistry, including a specific conductance of 96,842  $\mu\text{S}/\text{cm}$  (appendix B1), radiochemistry, and previous GRO and DRO detections (appendix B2), clearly point to the presence of oil field waste constituents in the groundwater. In contrast, the total dissolved solids of the other samples collected in in the Medicine Lake area did not differ significantly from the range of total dissolved solids in background samples (appendix B1). This demonstrates the importance of multiple lines of evidence, in this case several geochemical indicators, to determine if groundwater is affected by oil production activities.

The one analyte detected using method EPA 8270, bis(2-ethylhexyl)phthalate, is a disclosed additive in hydraulic fracturing fluid (Drollette and others, 2015). This analyte was detected in wells 3767, 280641, and 40257. All wells are in Sheridan County, two near the Medicine Lake Wildlife Refuge. Most of the oil production in this area occurred before the introduction

of hydraulic fracturing; however, there have been 36 hydraulically fractured wells in Sheridan County since 2011 (horizontal wells into the Bakken or Three Forks Formation; FracFocus, 2019; MBOGC, 2019). The prevalence of bis(2-ethylhexyl)phthalate in natural waters is not well defined. However, it is used in many industrial practices and in PVC pipes commonly used in well construction and water distribution (Drollette and others, 2015). Unlike the findings of Drollette and others (2015), the detections of bis(2-ethylhexyl)phthalate in this study were correlated with earlier detections of DRO in just one of the three wells (well 3767; appendix B2). Overall, the detection of bis(2-ethylhexyl)phthalate on its own may be insufficient to definitively attribute contamination to oil field waste; however, all samples with bis(2-ethylhexyl)phthalate detections also had detections of other organic constituents that point to the presence of oil field waste.

#### Quality Assurance/Quality Control Evaluation

Organic analyses are prone to erroneous results, in part due to their low reporting limits. As in all water

sampling, care should be taken to avoid contaminating samples through handling and equipment. Although sampling procedures were adhered to, contamination of blank samples was detected in this study as well as in the groundwater and surface-water samples analyzed in Meredith and Kuzara (2018).

Results from the equipment and trip blanks in this study indicated the presence of organic compounds. Both had detections of acetone, and chloromethane was also found in the equipment blank (appendix B1). Acetone was detected in all samples except in Medicine Lake surface water, which was the only sample collected without using equipment (e.g., pumps, bailers, *in situ* plumbing). However, the trip blank, which was sealed in the laboratory and remained in the cooler, had detectable acetone. This suggests that the equipment was not the source, or at least not the only source, of the contamination.

The presence of acetone and chloromethane in quality control samples was further investigated by submitting samples for EPA 8260B analytes to a different laboratory. The same source of blank water, rinsed through a new bailer, was used to prepare the additional trip and equipment blanks. There were no detections of the EPA 8260 analytes, suggesting that the detections of acetone and chloromethane in blanks found by the first laboratory were unrelated to the source of the blank water. Acetone is a common laboratory glassware drying agent, and other studies suggest it may be related to a laboratory source (McMahon and others, 2015).

The sample and duplicate sample from well 3767 had two notable discrepancies. Bis (2-ethylhexyl) phthalate was detected in the duplicate sample only, at a concentration of 18.1  $\mu\text{g/L}$ , about twice the reporting limit of 9.5  $\mu\text{g/L}$ . Acetone, likely introduced through laboratory contamination, was much lower in the duplicate (87.8  $\mu\text{g/L}$ ) compared to the original sample (332  $\mu\text{g/L}$ ).

Several studies point to the difficulty in eliminating sample contamination by organic compounds. McMahon and others (2015) found acetone and toluene in groundwater samples collected in the oil development areas of the Williston Basin, but discounted the validity of these results based on an extensive evaluation of USGS VOC quality control data sets (Bender and

others, 2011; Fram and others, 2012). As discussed above with respect to toluene, the USGS recommends censoring all acetone results and toluene concentrations below 0.69  $\mu\text{g/L}$ . Extensive sampling by the EPA in northeastern and southwestern Pennsylvania found low-level and sporadic detections of phthalates, toluene, benzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, chloroform, acetone, phenol, 2-butoxyethanol, DRO, and GRO. These detections were considered contamination from the laboratory and sampling and inconsistent with oil field waste because there was no correlation with other indicators such as chloride, TDS, Ba or Sr (U.S. EPA, 2015a,b).

Given the history of oil field waste disposal in the Medicine Lake area, the samples collected from this area provide an example of the geochemistry of groundwater that contains oil field waste constituents. The detections of xylene and tetrahydrofuran—and possibly toluene—in these samples, are likely products of the decomposition of oil field waste constituents. However, the findings in this and other studies is that spurious organic detections are common in groundwater studies and therefore a conservative approach to interpreting the presence of oil field waste is warranted.

## RECOMMENDATIONS

The recommended analytical method for general groundwater sampling in response to oil and gas development is method EPA 8260B (full VOC, low-level detection). The majority (13 of 15) of detected analytes were measured using this method. The recommendation is also based, in part, on the relatively low cost (\$70 to \$120) of Method EPA 8260B, which is approximately half that of EPA 8270 and similar to RSK 175. This recommendation is also supported by the findings of Luek and Gonsoir (2017): of the 55 identified halogenated organic compounds associated with flow-back and produced waters, 9 were measured in EPA 8260B compared to 2 in EPA 8270C.

Methane analysis is recommended for groundwater quality characterization purposes only if measured in conjunction with methane isotopes ( $\text{d}^{13}\text{C}$  and  $\text{d}^2\text{H}$ ). Previous sampling showed methane occurs naturally in many aquifers in eastern Montana, and concentration results varied significantly by collection and analysis method (Meredith and Kuzara, 2018). Methane concentrations measured using different analytical

methods should not be compared. A comprehensive methane survey should use one method for concentration analysis in conjunction with the isotopic analysis (Bordeleau and others, 2015; McMahon and others, 2015).

The exception to this recommendation would be to measure methane concentrations where safety is a concern, such as in domestic wells or where wells are used in conjunction with a storage tank. Elevated concentrations of methane in groundwater can be found under natural conditions in many eastern Montana aquifers (e.g., well 43095; Meredith and Kuzara, 2018). Eltschlager and others (2001) recommend mitigating the explosive hazard at methane concentrations of 10 mg/L and above. While there is no established methane limit for human health (U.S. EPA, 2019), it is important for homeowners to know about the risk of fire and explosion related to methane in groundwater.

We recommend exceeding the minimum EPA-recommended number of quality assurance samples of 5 percent when designing groundwater sampling protocols for organic analytes. This recommendation stems from the results from the quality control samples collected during this sampling program and those presented in Meredith and Kuzara (2018). Specific recommendations include collecting a minimum of one duplicate per 10 sampling locations, using certified organic-free water as blank water, requesting matrix fortified samples and trip blanks from the laboratory, and sending sample splits to two or more laboratories.

A robust sampling program will need to evaluate additional, non-organic compounds related to oil field waste—particularly in produced and flow-back water—that are of concern when present in water resources. These include naturally occurring constituents in oil production target formations and other geologic formations, such as radioactive constituents (uranium, thorium, radium, radon, strontium, and potassium), and metals (e.g., aluminum, iron, zinc; Ferrer and Thurman, 2015).

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**APPENDIX A: ANALYTICAL SUITE**

**RSK 175 AIR Headspace**

	Unit	Report Limit
Ethane	µg/L	10
Ethene	µg/L	10
Methane	µg/L	10

**EPA 8270D MSSV. Preparation Method: EPA 3520**

	Unit	Report Limit		Unit	Report Limit
Phenol	µg/L	9.5	4-Nitrophenol	µg/L	9.5
bis(2-Chloroethyl) ether	µg/L	9.5	Dibenzofuran*	µg/L	9.5
2-Chlorophenol	µg/L	9.5	2,4-Dinitrotoluene	µg/L	9.5
1,3-Dichlorobenzene	µg/L	9.5	Diethylphthalate	µg/L	9.5
1,4-Dichlorobenzene	µg/L	9.5	4-Chlorophenylphenyl ether	µg/L	9.5
1,2-Dichlorobenzene	µg/L	9.5	Fluorene*	µg/L	9.5
2-Methylphenol(o-Cresol)	µg/L	9.5	4-Nitroaniline	µg/L	9.5
bis(2-Chloroisopropyl) ether	µg/L	9.5	4,6-Dinitro-2-methylphenol	µg/L	9.5
3&4-Methylphenol(m&p Cresol)	µg/L	9.5	N-Nitrosodiphenylamine	µg/L	9.5
N-Nitroso-di-n-propylamine	µg/L	9.5	4-Bromophenylphenyl ether	µg/L	9.5
Hexachloroethane	µg/L	9.5	Hexachlorobenzene	µg/L	9.5
Nitrobenzene	µg/L	9.5	Pentachlorophenol	µg/L	19
Isophorone	µg/L	9.5	Phenanthrene*	µg/L	9.5
2-Nitrophenol	µg/L	9.5	Anthracene*	µg/L	9.5
2,4-Dimethylphenol	µg/L	9.5	Di-n-butylphthalate	µg/L	9.5
bis(2-Chloroethoxy)methane	µg/L	9.5	Fluoranthene*	µg/L	9.5
2,4-Dichlorophenol	µg/L	9.5	Pyrene*	µg/L	9.5
1,2,4-Trichlorobenzene	µg/L	9.5	Butylbenzylphthalate	µg/L	9.5
Naphthalene*	µg/L	9.5	3,3'-Dichlorobenzidine	µg/L	47.6
4-Chloroaniline	µg/L	9.5	Benzo(a)anthracene*	µg/L	9.5
Hexachloro-1,3-butadiene	µg/L	9.5	Chrysene*	µg/L	9.5
4-Chloro-3-methylphenol	µg/L	9.5	bis(2-Ethylhexyl)phthalate	µg/L	9.5
2-Methylnaphthalene*	µg/L	9.5	Di-n-octylphthalate	µg/L	9.5
2,4,6-Trichlorophenol	µg/L	9.5	Benzo(b)fluoranthene*	µg/L	9.5
2,4,5-Trichlorophenol	µg/L	9.5	Benzo(k)fluoranthene*	µg/L	9.5
2-Chloronaphthalene	µg/L	9.5	Benzo(a)pyrene*	µg/L	9.5
2-Nitroaniline	µg/L	9.5	Indeno(1,2,3-cd)pyrene*	µg/L	9.5
Dimethylphthalate	µg/L	9.5	Dibenz(a,h)anthracene*	µg/L	9.5
Acenaphthylene*	µg/L	9.5	Benzo(g,h,i)perylene*	µg/L	9.5
2,6-Dinitrotoluene	µg/L	9.5	N-Nitrosodimethylamine	µg/L	9.5
3-Nitroaniline	µg/L	9.5	1,2-Diphenylhydrazine	µg/L	9.5
Acenaphthene*	µg/L	9.5	Carbazole	µg/L	9.5
2,4-Dinitrophenol	µg/L	9.5	1-Methylnaphthalene	µg/L	9.5

\* Polycyclic aromatic hydrocarbons (PAH)

## EPA 8260B MSV Low Level

	Unit	Report Limit		Unit	Report Limit
Acetone	µg/L	20	2,2-Dichloropropane	µg/L	1
Allyl chloride	µg/L	4	1,1-Dichloropropene	µg/L	0.5
Benzene	µg/L	0.5	cis-1,3-Dichloropropene	µg/L	0.5
Bromobenzene	µg/L	0.5	trans-1,3-Dichloropropene	µg/L	0.5
Bromochloromethane	µg/L	1	Diethyl ether (Ethyl ether)	µg/L	4
Bromodichloromethane	µg/L	0.5	Ethylbenzene	µg/L	0.5
Bromoform	µg/L	4	Hexachloro-1,3-butadiene	µg/L	1
Bromomethane	µg/L	4	Isopropylbenzene (Cumene)	µg/L	0.5
2-Butanone (MEK)	µg/L	5	p-Isopropyltoluene	µg/L	0.5
n-Butylbenzene	µg/L	0.5	Methylene Chloride	µg/L	4
sec-Butylbenzene	µg/L	0.5	4-Methyl-2-pentanone (MIBK)	µg/L	5
tert-Butylbenzene	µg/L	0.5	Methyl-tert-butyl ether	µg/L	0.5
Carbon tetrachloride	µg/L	0.5	Naphthalene	µg/L	1
Chlorobenzene	µg/L	0.5	n-Propylbenzene	µg/L	0.5
Chloroethane	µg/L	1	Styrene	µg/L	0.5
Chloroform	µg/L	1	1,1,1,2-Tetrachloroethane	µg/L	0.5
Chloromethane	µg/L	4	1,1,2,2-Tetrachloroethane	µg/L	0.5
2-Chlorotoluene	µg/L	0.5	Tetrachloroethene	µg/L	0.5
4-Chlorotoluene	µg/L	0.5	Tetrahydrofuran	µg/L	10
1,2-Dibromo-3-chloropropane	µg/L	4	Toluene	µg/L	0.5
Dibromochloromethane	µg/L	0.5	1,2,3-Trichlorobenzene	µg/L	0.5
1,2-Dibromoethane (EDB)	µg/L	0.5	1,2,4-Trichlorobenzene	µg/L	0.5
Dibromomethane	µg/L	1	1,1,1-Trichloroethane	µg/L	0.5
1,2-Dichlorobenzene	µg/L	0.5	1,1,2-Trichloroethane	µg/L	0.5
1,3-Dichlorobenzene	µg/L	0.5	Trichloroethene	µg/L	0.4
1,4-Dichlorobenzene	µg/L	0.5	Trichlorofluoromethane	µg/L	0.5
Dichlorodifluoromethane	µg/L	1	1,2,3-Trichloropropane	µg/L	4
1,1-Dichloroethane	µg/L	0.5	1,1,2-Trichlorotrifluoroethane	µg/L	1
1,2-Dichloroethane	µg/L	0.5	1,2,4-Trimethylbenzene	µg/L	0.5
1,1-Dichloroethene	µg/L	0.5	1,3,5-Trimethylbenzene	µg/L	0.5
cis-1,2-Dichloroethene	µg/L	0.5	Vinyl chloride	µg/L	0.2
trans-1,2-Dichloroethene	µg/L	0.5	Xylene (Total)	µg/L	1.5
Dichlorofluoromethane	µg/L	1	m&p-Xylene	µg/L	1
1,2-Dichloropropane	µg/L	4	o-Xylene	µg/L	0.5
1,3-Dichloropropane	µg/L	0.5			



**APPENDIX B1: DETECTED ORGANIC COMPOUNDS**

EPA Analytical Method: RSK 175 8270D 8260B

GWIC ID	Sample Date	Sample Time	Sample Collection Method	Known Contaminated Site?	Aquifer Description	SC mS/cm	pH	Temp °C	Analyte (mg/L)	Methane	bis(2-Ethylhexyl)phthalate	Acetone
221691	6/27/2018	11:21	Bailer	Yes	Unconsol. north of Medicine Lake R/contaminated	96,842	6.85	11	22.1			44.2
3772	6/27/2018	14:47	Whale & bailer	Yes	Fort Union south of Dagmar	2534	8.18	8.9	7160			310
3767	6/27/2018	16:58	Whale & bailer	Yes	Unconsolidated north of Medicine Lake Refuge	2518	6.93	9.3	16.4			332
3767	6/27/2018	17:10	Whale & bailer	Yes	Duplicate of 3767	2518	6.93	9.3	12.8		18.1	87.8
280641	6/28/2018	9:53	Whale & bailer	Yes	Unconsolidated north of Medicine Lake Refuge	2040	7.19	8.8			14.2	319
239702	6/25/2018	15:30	Whale & bailer	Unknown	Unconsolidated south of Sidney	1107	7.21	12.3				544
40257	6/26/2018	14:48	Grundfos/whale pump & bailer	Unknown	Fort Union north of Culbertson	2322	9.07	10.8	121		10	585
279960	6/25/2018	14:27	In situ plumbing direct to bottles	No	Fort Union south of Sidney	909	7.48	14.6				638
136651	6/26/2018	8:54	Bailer	No	Unconsolidated north of Sidney	1402	7.89	11.6				336
223679	6/26/2018	10:42	In situ plumbing direct to bottles	No	Fort Union south of Culbertson	5742	7.84	10.3				283
43095	6/26/2018	17:18	In situ plumbing direct to bottles	No	Fox Hills east of Homestake	4145	8.46	9.6	49800			111
262048	6/27/2018	9:53	Grab	No	Medicine Lake surface water	2921	8.85	21.8				
79510	6/28/2018	13:27	In situ plumbing direct to bottles	No	Fox Hills south of Sidney*	1502	7.17	12.1				462
QA/QC Samples												
Equip. blank	6/28/2018	16:30	Bailer	No	Equipment/bailer blank Org. Free NW Sci water.							423
Trip blk	n/a		Trip blank	No	Trip blank							104

Unknown contamination level - blue  
 Known GW contamination sample location - yellow  
 Red indicates blank detections





**APPENDIX B2: 2015–2016 SAMPLING  
RESULTS FROM SELECTED WELLS**

GWIC ID	Analyte (µg/L)															
	Date Collected	Organic Carbon, Dissolved (DOC)	Gross Alpha precision (±)				Gross Beta precision (±)		Gasoline Range Organics (GRO)	Purgeable Hydrocarbons (as measured with GRO)	Methyl tert-butyl ether (MTBE)	Benzene	Toluene	Ethylbenzene	m+p-Xylenes	o-Xylene
			Alpha	Beta	Beta	Beta										
221691	8/19/2015 19:32	91	282	193	471	157	50	75	ND	ND	ND	ND	ND	ND	ND	ND
3772	9/21/16 13:27								ND	ND	ND	ND	ND	ND	ND	ND
3767	8/3/2015 17:03	23	3.0	6.1	1.3	5.4	ND	21	ND	ND	1.2	ND	ND	ND	ND	ND
280641	9/19/16 14:17								ND	ND	ND	ND	ND	ND	ND	ND
239702	9/15/2015 17:06	3.4	0.6	2.4	4.2	2.5	ND	ND	ND	ND	0.52	ND	ND	ND	ND	ND
40257	9/1/2015 12:03	3.3	13.5	7.2	4.9	4.1	22	26	ND	ND	8.7	ND	ND	1.3	0.57	
279960	5/12/2015 17:55	1.7	-0.1	1.8	4.0	2.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
136651	9/15/2015 12:11	3.1	6.6	3.7	6.6	2.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
223679	7/19/16 11:09															
43095	8/18/2015 8:15	8	1.6	11.0	-3	13.8	ND	ND	ND	ND	1.7	ND	ND	ND	ND	ND
262048	6/23/2016 9:08		7.6		25.5						ND					
79510	8/5/2015 9:32	4.2	-3	4.3	-0.2	6.6	ND	ND	ND	ND	0.58	ND	ND	ND	ND	ND
79510-dup	8/5/2015 9:32	4.1	-3	3.7	-9	6.1	ND	ND	ND	ND	0.50	ND	ND	ND	ND	ND
Unknown contamination level - blue																
Known GW contamination sample location - yellow																

GWIC ID	Analyte (mg/L)											
	Total		Purgeable		Hydrocarbons (as measured in VPH)		Diesel Range Organics (DRO)		Total Hydrocarbons		Ethane	Ethene
	Xylenes, Naphthalene	C9 to C10 Aromatics	C5 to C8 Aliphatics	C9 to C12 Aliphatics	Aromatic (C11-C22) (ug/L)	Aromatics measured in VPH	Diesel Range Organics (DRO)	Total Hydrocarbons	Methane	Ethane	Ethene	
221691	ND	ND	61	ND	ND	52	0.73	21	0.047	ND	ND	ND
3772	ND	ND	ND	ND	ND	ND	ND	0.35	8.6	ND	ND	ND
3767	ND	ND	ND	20	ND	28	0.97	1.7	0.0016	ND	0.0013	ND
280641	ND	ND	338	ND	ND	308	ND	0.678	ND	ND	ND	ND
239702	ND	ND	ND	ND	ND	ND	ND	ND	0.0015	ND	ND	ND
40257	1.9	ND	12	ND	ND	22	ND	0.82	0.23	ND	ND	ND
279960	ND	ND	ND	ND	ND	ND	ND	0.54	ND	ND	ND	ND
136651	ND	ND	ND	ND	ND	ND	ND	0.59	ND	ND	ND	ND
223679	ND	ND	ND	ND	ND	ND	ND	0.274	ND	ND	ND	ND
43095	ND	ND	ND	ND	ND	ND	0.63	0.86	21	0.0042	ND	ND
262048	ND	ND	ND	ND	ND	ND	ND	321	ND	ND	ND	ND
79510	ND	ND	ND	ND	ND	ND	ND	ND	4.9	0.0088	ND	ND
79510-dup	ND	ND	ND	ND	ND	ND	ND	ND	1.6	0.0071	ND	ND
Unknown contamination level - blue												
Known GW contamination sample location - yellow												

