An Evaluation of the Potential for Ground Water Contamination by Transport of Petroleum Products over the Rathdrum Prairie Aquifer

Ground Water Investigation Report DEQ-CRO-01-16









State of Idaho Department of Environmental Quality

June 2016



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Printed on recycled paper, DEQ, June 2016, PID GWM 1004, CA 12153. Costs associated with this publication are available from the State of Idaho Department of Environmental Quality in accordance with Section 60-202, Idaho Code.

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Prepared by Gary R. Stevens P.G. Idaho Department of Environmental Quality Coeur d'Alene Regional Office 2110 Ironwood Parkway Coeur d'Alene, ID 83814

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Abbreviations, Acronyms, and Symbols

| 0 | degrees Fahrenheit or API gravity degrees |
|----------|--|
| API | American Petroleum Institute |
| bgs | below ground surface |
| BNSF | Burlington Northern Santa Fe |
| сс | cubic centimeter |
| ср | centipoise |
| d | day |
| DEQ | Idaho Department of Environmental Quality |
| dynes/cm | dynes per centimeter |
| EPA | US Environmental Protection Agency |
| G | gram |
| gal | gallon |
| HSSM | Hydrocarbon Spill Screening |
| I-90 | Interstate 90 |
| LNAPL | light nonaqueous phase liquids |
| m | meter |
| mi | miles |
| MOFAT | Multispecies Oil Fate and Transport |
| mpg | miles per gallon |
| PADD | Petroleum Administration for Defense Districts |
| RPA | Rathdrum Prairie aquifer |
| RVP | Reid Vapor Pressure |
| US | United States |
| wt | weight |
| yd | yard |
| yr | year |
| | |

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Executive Summary

The Rathdrum Prairie study area has a number of transport corridors that are used for transporting a variety of petroleum hydrocarbons, by truck, railcar, and pipeline. The recent significant increase of the rail transport of crude oil from the Midwest through the area has created a growing concern about the vulnerability of the Rathdrum Prairie aquifer (RPA) to potential releases.

The potential ground water impacts from a petroleum hydrocarbons release, the types of petroleum hydrocarbons, corridor locations, and mode of transport were determined, and potential release scenarios were evaluated by fate and transport modeling of petroleum hydrocarbons in the unsaturated and saturated zones.

Based on the scenarios evaluated in the investigation, potential releases from crude oil and gasoline tankers could occur over a relatively short period of time and would consist of a defined volume. The impact to ground water would be non-existent or limited given the significant depths to ground water from the surface over the RPA. Any release would be apparent, and remediation efforts could be initiated soon after the release, limiting the contaminated volume of soil.

Potential releases from a subsurface pipeline could consist of a small volume occurring over long periods of time, resulting in a greater risk for ground water impacts and difficulty identifying the releases in a timely manner. Subsequent remedial efforts could be more extensive.

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1 Introduction

The Rathdrum Prairie aquifer (RPA) is located in northern Idaho and is the sole drinking water supply for most of the residents in Kootenai County (Figure 1). The study area has a number of transport corridors that are used for transporting a variety of petroleum hydrocarbons, by truck, railcar, and pipeline. The recent significant increase of the rail transport of crude oil from the Midwest through the area has created a growing concern about the vulnerability of the RPA to potential releases.

To evaluate the potential ground water impacts from a petroleum hydrocarbons release, the types of petroleum hydrocarbons, corridor locations, and mode of transport were determined. Potential release scenarios were evaluated by fate and transport modeling of petroleum hydrocarbons in the unsaturated and saturated zones.

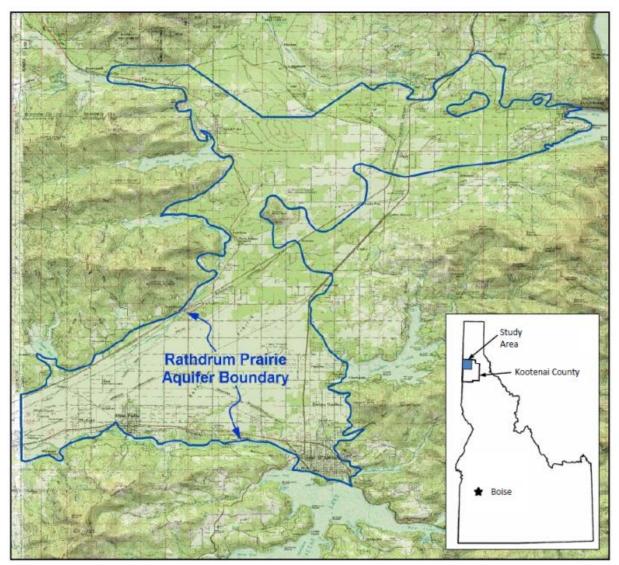


Figure 1. Vicinity map.

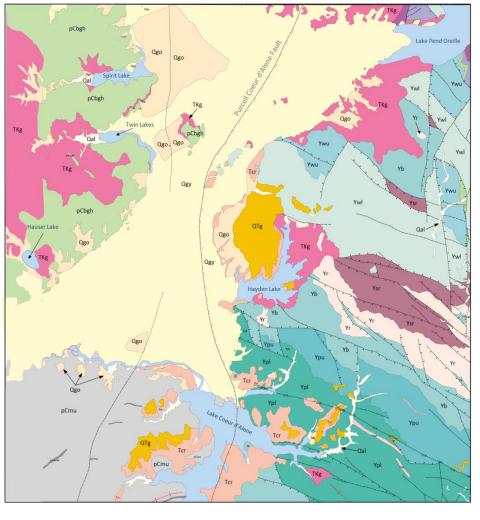
2 Rathdrum Prairie Aquifer

The RPA covers an area of about 211 square miles in Idaho and extends from Lake Pend Oreille southward to Coeur d'Alene and Post Falls and then westward to the Idaho-Washington state line (Figure 1). The RPA is part of the larger Spokane Valley-Rathdrum Prairie aquifer that extends into Washington. The water that recharges the RPA is mainly due to seepage from the Spokane River and adjacent lakes along with precipitation that falls on the Rathdrum Prairie. Ground water from the northern areas of the aquifer starts at a water elevation of about 2,100 feet and at the state line has a water elevation of about 1,970 feet. Depths to water from land surface range from approximately 150 to 550 feet.

The alluvium that forms the RPA was deposited 8- to 18 thousand years ago by southerly drainage from the continental Cordilleran Ice Sheet along with enormous catastrophic floods from Lake Missoula (Alt 2006). The flood water was derived from the failure of an ice dam blocking the flow of the Clark Fork River and creating Lake Missoula (Smith 2006). The ice dam formed when the continental Cordilleran Ice Sheet flowed far enough south to intercept the river. As the volume of water stored in Lake Missoula increased, there was a corresponding increase in stress on the ice dam. When the stress of the water exceeded the mechanical strength of the ice dam, a catastrophic failure released billions of gallons of water that flowed across the Rathdrum Prairie, through Washington, down the Columbia River, and eventually to the Pacific Ocean. The process of ice dam building and subsequent failure is believed to have been repeated approximately 40 times resulting in 40 catastrophic floods.

The large volume and flow rate of the floods deposited large gravel, cobbles, and boulders onto the Rathdrum Prairie and carried away most of the smaller silt and sand leaving behind the very permeable aquifer that is the source of drinking water today. The composition of the flood deposits reflects the bedrock lithology upgradient between Lake Missoula and the Rathdrum Prairie. The deposition of the significant volumes of gravel onto the Rathdrum Prairie blocked the tributary valleys forming Pend Oreille, Spirit, Twin, Hauser, Hayden and Coeur d'Alene Lakes (Alt 2006). The lakes recharge the aquifer through seepage into coarse alluvium and into the underlying aquifer.

A geologic map of the area with descriptions of the unconsolidated deposits of the Rathdrum Prairie and surrounding bedrock is seen in Figure 2. The basement of the Rathdrum Prairie is shown as the Gneiss of the Priest River Complex on the west side and Wallace Formation on the east side, separated by the Purcell-Coeur d'Alene Fault (Lewis et al. 2002). The very permeable aquifer allows water to flow with velocities of 20 to 50 feet per day. Because of the permeable nature of the unsaturated material between the aquifer and the land surface, it can be susceptible to land uses and contaminant releases. In 1978 the aquifer in Idaho and Washington was given a sole source aquifer designation by the US Environmental Protection Agency (EPA) (Federal Register, Vol. 43, No. 28) and in 1996 was given a designation as a sensitive resource aquifer by the State of Idaho (IDAPA 58.01.11). These designations provide additional protections to prevent water quality impacts.



Complied and modified from USGS Digital Geologic Map of the Coeut d'Alene 1:100,000 Quadrangle, Idaho and Montana, OFR 00-135 and USGS Digital Geologic Map of the Spokane County and Vicinity, OFR 98-503 and Idaho Geological Survey, Surficial Geologic Map of the Rathdrum Quadrangle and Part of the Newman Lake Quadrangle, Kootenai County, Idaho, SGM-6

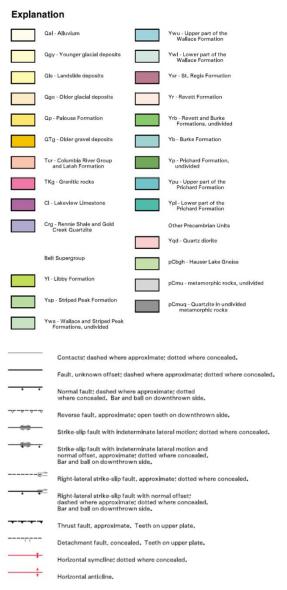


Figure 2. Bedrock geology map of the Rathdrum Prairie aquifer and surrounding area.

3 Petroleum Types and Transport

The study area has a number of transportation corridors that are used to transport petroleum hydrocarbon products. These products can consist of crude oil, along with refined products such as heating oil, gasoline, and diesel fuels. The three transportation corridors consists of (1) major roadways, (2) rail lines, and (3) pipelines (Figure 3).

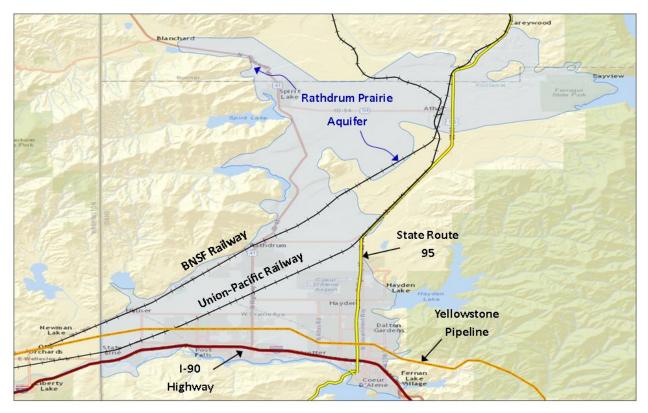


Figure 3. Petroleum transportation corridors over the Rathdrum Prairie.

3.1 Major Roadways

3.1.1 Transportation

Petroleum hydrocarbons are transported over roadways by tanker truck with volumes that range from approximately 1,000 to 9,000 gallons. The major roadways in the RPA area are Interstate 90 (I-90) and State Route 95. I-90 is a transcontinental freeway with the eastern terminus in Boston and the western terminus in Seattle. I-90 is an east-west freeway that crosses Kootenai County with approximately 15 miles of roadway over the RPA. The average daily traffic count for I-90 near Huetter (approximately 1.0 miles west of Coeur d'Alene) in 2014 was 54,006 vehicles (ITD 2016).

US Route 95 is a north-south highway with the southern terminus at the Idaho-Oregon border and the northern terminus at the Canadian border at Eastport, Idaho. Approximately 14 miles of

US Route 95 cross over the RPA. The 2014 average daily traffic count for US Route 95 just north of Coeur d'Alene, Idaho, was 33,057 and at Garwood, Idaho, was 14,635 (ITD 2016).

An estimate was made of the gasoline and diesel fuel that is transported within Kootenai County by determining the amount consumed. In 2015, 129,551 passenger cars, 11,968 light duty trucks, and 6,221 miscellaneous vehicles were registered in Kootenai County (ITD 2015). If we assume that passenger cars and miscellaneous vehicles travel an average of 12,000 miles per year (mi/yr) and obtain a gas mileage of 24.1 miles per gallon (mi/gal) (EPA 2008), then the fuel consumed would be 67,604,315 gallons per year (gal/yr). If we assume that light duty trucks travel an average of 15,000 mi/yr and obtain a gas mileage of 17.3 mi/gal (EPA 2008), then the fuel consumed would be 10, 376,879 gal/yr. The total fuel consumed would be approximately 77,981,194 gal/yr translating to about 8,665 nine-thousand gallon tanker trucks per year traveling over the RPA.

3.1.2 Releases

DEQ has no recorded tanker truck releases of petroleum hydrocarbons along the I-90 or State Route 95 corridors crossing over the RPA.

3.2 Yellowstone Pipeline

3.2.1 Transportation

Phillips 66 Pipeline LLC operates a 725-mile petroleum products pipeline system that originates from refineries in Billings, Montana, to markets in Montana, northern Idaho, and eastern Washington. The pipe carries fuel from the company's refineries in Billings, Montana, and is piped to Missoula, where it is loaded and taken by train to Thompson Falls. From there the product goes into the Yellowstone pipeline and on to Spokane, Washington. The Yellowstone pipeline is 10 inches in diameter and was constructed in 1954. Approximately 14 miles of pipeline that crosses over the RPA is used to transport refined petroleum products (gasoline and diesel). The pipeline transported approximately 66 thousand barrels per day in 2001 (Chevron 2002).

3.2.2 Releases

Seven significant releases were recorded from the Yellowstone pipeline in vicinity of the study area (Aspen Environmental Group 2000) that affected soil with one documented impact to ground water. The releases are described below and the locations are provided in Figure 4:

- In 1954 approximately 69,678 gallons of gasoline was released about 20 miles east of Coeur d'Alene. The release was caused by a dozer blade puncturing pipeline.
- On April 10, 1955, a release east of Coeur d'Alene was caused by a tractor crossing the pipeline releasing approximately 193,872 gallons of diesel.
- On October 16, 1965, approximately 5 miles east of Coeur d'Alene, a gunshot perforated the pipeline releasing 43,848 gallons.
- On May 2, 1973, near Murray, Idaho, a pipe split for a length of approximately 50 inches (Yellowstone Pipe Line Company 1973). Approximately 169,302 gallons of diesel was released.

- On May 4, 1983, the pipeline was impacted at a creek crossing while the gravel cover was being removed for bridge construction. Approximately 594 gallons of unleaded gasoline was released.
- On July 27, 1987, a grader widening a forest service road near the I-90 Fourth of July pass cut into the embankment and damaged the Yellowstone pipeline paralleling the road (DEQ 1988). The release of a gasoline and jet fuel mixture was approximately 27,048 gallons.
- On October 23, 1996, a pinhole size perforation in the Yellowstone pipeline was discovered in Spokane Valley, Washington. Both soil and ground water were contaminated with an unknown volume and type of petroleum hydrocarbon (Maxim Technologies 1997). The ground water plume of petroleum hydrocarbons extended downgradient approximately 200 feet.

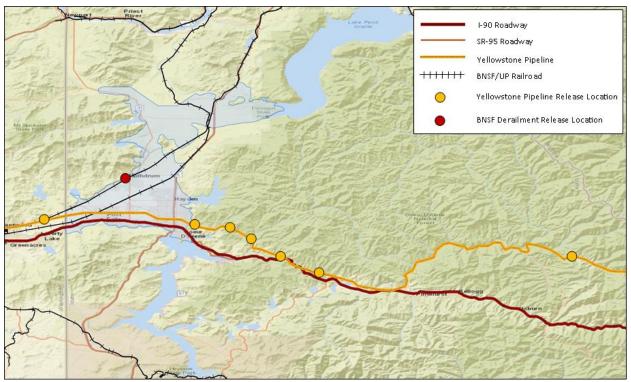


Figure 4. Petroleum release sources and locations near the Rathdrum Prairie.

3.3 Railroad

3.3.1 Transportation

The Bakken oil fields underlie the Williston Basin that occupies parts of Montana, North Dakota, Saskatchewan, and Manitoba (Figure 5). The oil field was discovered in 1951 but drilling technology that allowed for cost-effective drilling and oil removal became commonly used beginning in about 2000 resulting in dramatic oil production (Figure 6). The US Geological Survey calculated an expected 7.4 billion barrels of oil are available in the Bakken Formation (USGS 2013).



Figure 5. Boundaries of the Williston Basin and Bakken Formation.

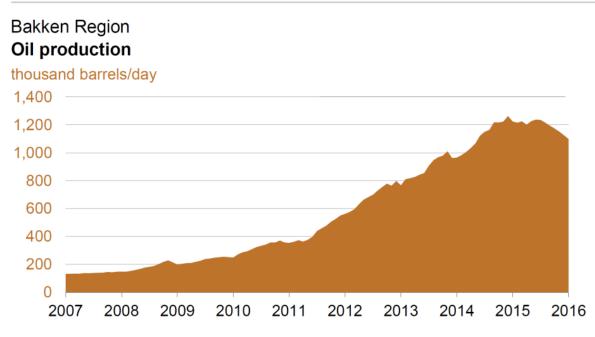


Figure 6. Bakken region oil production over time. (EIA, 2015a)

During World War II the United States was divided into different districts to help organize fuel distribution. The districts are referred to as Petroleum Administration for Defense Districts (PADD) and are still in use today (Figure 7). The Bakken oil fields are in PADD 2 and are the only significant oil producer in that PADD. The transport of Bakken crude oil through the Rathdrum Prairie area is for refineries on the West Coast that are in PADD 5. The volume of Bakken crude oil from PADD 2 to PADD 5 should account for most of the Bakken crude oil transported over the RPA.

The use of railcars to carry Bakken crude oil from the Midwest (PADD 2) to refineries on the West Coast (PADD 5) has increased significantly since 2010 (Figure 8). In 2010 the monthly transfer of crude oil from the Midwest to the West Coast was between approximately 20 and 200 barrels per month. In September 2015 the volume transported was 5,388 barrels—an increase of approximately 50 times. The typical rail train carrying Bakken crude has 80 to 120 tanker cars at approximately 20 to 30 thousand gallons per tanker car. The concern is with the increased oil by rail traffic there is a corresponding increase in risk of derailments with product release. The US Department of Transportation data indicate that more oil was spilled from railcars in the single year 2013 than the total spilled from railcars in the last 30 years (Lord et al. 2015).

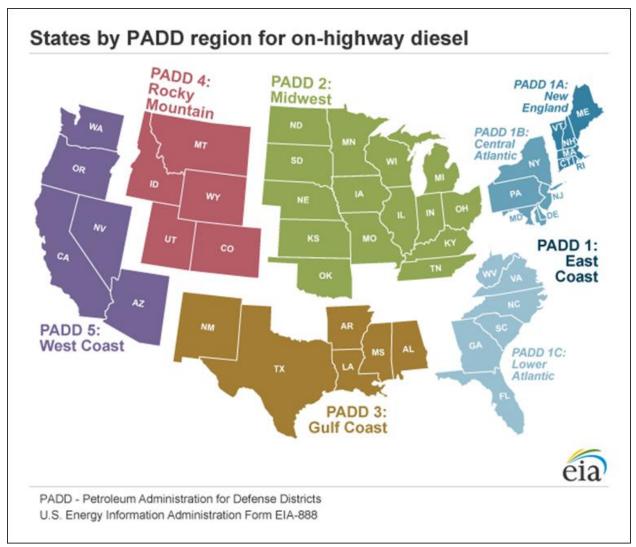
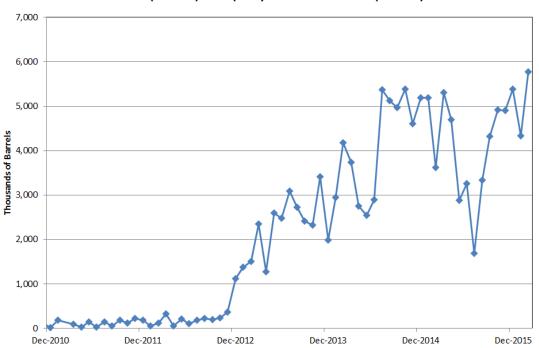


Figure 7. Petroleum Administration for Defense Districts.



West Coast (PADD 5) Receipts by Rail from Midwest (PADD 2) of Crude OII

Figure 8. Volume of crude oil transported by train from PADD 2 to PADD 5. (EIA, 2015b)

3.3.2 Releases

In the United States, a number of releases were caused by derailments of tanker cars carrying Bakken crude oil. Major derailments in the United States are described below, including one minor derailment and fuel oil release on the Rathdrum Prairie. The derailment descriptions and environmental impacts are also provided in Table 1.

- Galena, Illinois—On March 5, 2014, a Burlington Northern Santa Fe (BNSF) train carrying crude oil derailed near the city of Galena, Illinois. The derailment consisted of 21 railroad tanker cars, each containing about 30,000 gallons of Bakken crude oil. Five of the cars ruptured and caught fire and released crude oil into the surrounding area. The crude oil impacted soil, ground water, and surface water (BNSF 2015).
- **Casselton, North Dakota**—On December 30, 2013, a westbound BNSF train carrying grain derailed 13 cars near Casselton, North Dakota. One of the derailed grain cars fouled an adjacent track. An eastbound BNSF train carrying Bakken crude oil collided with the derailed grain car and subsequently derailed two locomotives and 20 tanker cars; 18 of the tanker cars were breached releasing approximately 464,000 gallons of crude oil (North Dakota Department of Health 2015a; Pinnacle Engineering 2015). A significant but unknown volume of crude oil was burned in the resulting fire.

- **Heimdal, North Dakota**—On May 6, 2015, a train carrying 107 cars of Bakken crude oil derailed near Heimdal, North Dakota. Six cars derailed and caught on fire. Approximately 94,000 gallons of oil was released with about 34,000 gallons consumed in the resulting fire (North Dakota Department of Health 2015b).
- **Culbertson, Montana**—On July 16, 2015, a train carrying 106 cars of Bakken crude oil derailed near Culbertson, Montana. Twenty-two tanker cars derailed with four cars breaking open and releasing approximately 27,210 gallons of crude oil into the surrounding area (Olympus Technical Services 2015)
- Hauser, Idaho—On February 27, 2001, 29 railcars on two trains on adjacent tracks derailed, including seven tanker cars containing Fuel Oil #5. Two of the tanker cars ruptured and one car leaked through the dome releasing an estimated 3,000 gallons of fuel oil (GeoEngineers 2001).
- Lac Megantic, Quebec—On July 5, 2013, a train carrying 72 tanker cars with Bakken crude oil derailed in the town of Lac Megantic, Quebec, Canada. Sixty-three of the tanker cars derailed and were breached releasing approximately 6 million gallons of crude oil. The subsequent fire consumed about 4.5 million gallons, and the remainder either infiltrated into the soil or flowed into nearby surface water bodies (Millette 2014).

Because of the series of railcar accidents described above and the related fire and explosion hazards associated with Bakken crude oil, the North Dakota Industrial Commission approved an order on December 9, 2014, requiring North Dakota oil producers to begin oil-conditioning all crude oil no later than April 1, 2015. Oil conditioning is a process performed at the well site that uses pressure and temperature to reduce the volatile content of the crude oil thus reducing its vapor pressure. The reduced volatility is an attempt to make the transport of the Bakken crude oil safer and in the case of derailment would potentially either eliminate or reduce the intensity of any subsequent fire consuming less of the released oil.

| Location | Release Date | Material | Estimated Oil Release Volume (gallons) | Estimated Oil Burned Volume (gallons) | Estimated Excavated Soil (cubic yard) | Ground Water Contamination | Surface Water Contamination | Fire |
|------------------|-----------------|--------------|--|---|--|-------------------------------|--------------------------------|------|
| Casselton, ND | 12/30/2013 | Bakken Crude | 400,000 | NA ^a | 7,479 | Yes | No | Yes |
| Heimdal, ND | 05/06/2015 | Bakken Crude | 94,000 | 34,000 | 1,929 ^b | No | No | Yes |
| Galena, IL | 03/05/2015 | Bakken Crude | 110,543 | 94,929 | 1,304 | Yes | Yes | Yes |
| Culbertson, MT | 07/16/2015 | Bakken Crude | 27,210 | 0 | 3,925 | Yes | No | No |
| Rathdrum, ID | 02/27/2001 | Fuel Oil #5 | 3,000 | 0 | 900 | No | No | No |
| Lac Megantic, QB | 07/05/2013 | Bakken Crude | 1,505,780 | 4,494,220 | 366,226 | No | Yes | Yes |

Table 1. Train derailments with remedial impacts and volumes.

^a Volume not calculated but a significant volume of crude oil was reported have been consumed in the fire. ^b 2,439.39 tons with density of 1.5 g/cc.

3.4 Ethanol

In 2015, about 13.7 billion gallons of fuel ethanol was added to motor gasoline produced in the United States, and fuel ethanol accounted for about 10% of the total volume of finished motor gasoline consumed in the United States (US Energy Information Administration 2015a). Ethanol (fermented corn) is added to motor gasoline to meet the requirements of the 1990 Clean Air Act and the Renewable Fuel Standard described in the Energy Independence and Security Act of 2007. Most ethanol is produced in the Midwest (PADD 2) and shipped by rail to oil refineries in other parts of the country (Figure 9). Most of the ethanol received on the West Coast (PADD 5) is from the Midwest. The volume of ethanol received in PADD 5 has increased significantly since 2009 as shown in Figure 10 (US Energy Information Administration 2015b). The volume received on the West Coast in 2015 was approximately 51 million barrels per year (2,134,000,000 gallons), which equates to about 71 thousand rail tanker cars. Not all ethanol rail traffic crosses over the RPA from PADD 2 to PADD 5. Approximately 1,830,000 barrels of ethanol were transported over the RPA in 2006 (Casavant et al. 2010). The significant volume of ethanol that is transported by rail makes this an additional risk in the event of a derailment but was outside the scope of this report.

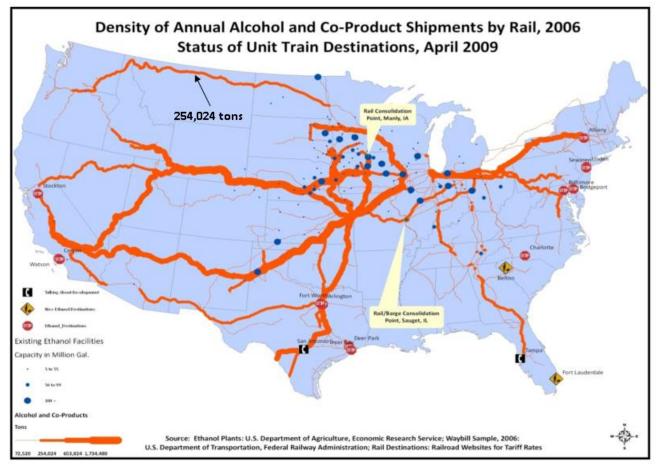
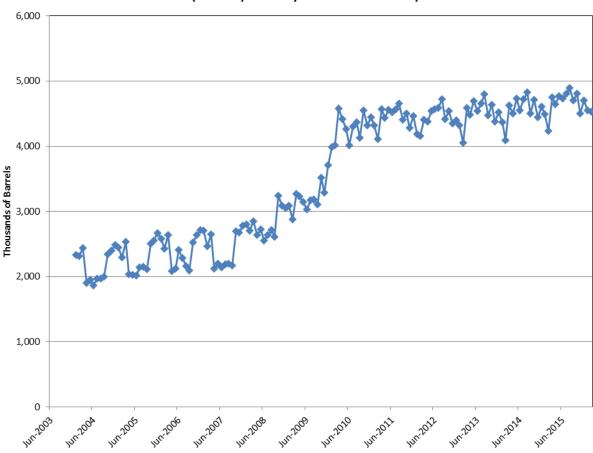


Figure 9. Sources and rail transport routes for alcohol and coproducts.

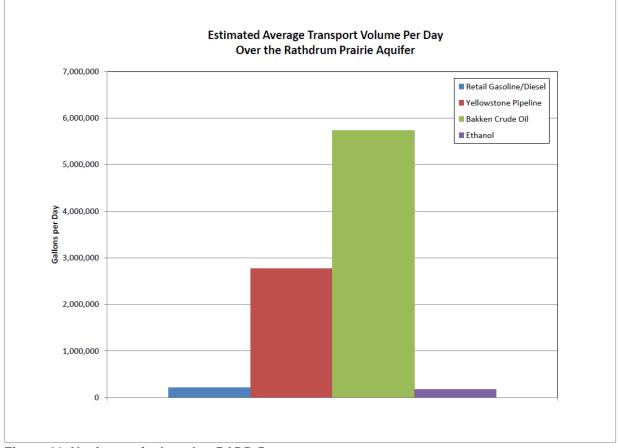


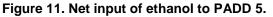
West Coast (PADD 5) Refinery and Blender Net Input of Fuel Ethanol

Figure 10. Net input of ethanol to PADD 5. (EIA, 2015c)

3.5 Volumes of Petroleum Transported over the Rathdrum Prairie Aquifer

Using the data presented above, an estimate was made of the daily volume of the various petroleum products that are transported over the RPA per day (Figure 11 and Table 2). The greatest volume of petroleum transported is Bakken crude oil, followed by refined petroleum products through the Yellowstone pipeline, retail gasoline and diesel supplied to the area, and rail transport of ethanol.





| Retail Gasoline/Diesel ^a | Yellowstone Pipeline ^b | Bakken Crude Oil ^c | Ethanol ^d | | | |
|--------------------------------------|-----------------------------------|-------------------------------|----------------------|--|--|--|
| Gallons per Day | | | | | | |
| 213,647 | 2,772,000 | 5,741,573 | 179,683 | | | |
| ^a Rasad on 2015 actimates | of fuel usage (section 3.1.1) | | | | | |

 $^{\rm a}$ Based on 2015 estimates of fuel usage (section 3.1.1) $^{\rm b}$ Transport during 2001

^c Based on Energy Information Administration data—2015 average crude oil transported from PADD 2 to PADD 5.

^d Based on volumes reported in US Transportation, Federal Railway Administration; Rail Destinations: Railroad Websites for Tariff Rates. Assume 15% by weight distilled dry grains with solubles.

Petroleum Properties 4

4.1 Petroleum Hydrocarbons

The principal constituents of petroleum hydrocarbons are hydrogen and carbon. The hydrogen and carbon are arranged in various structural configurations that form hundreds of different

compounds. These compounds can be very simple with only a few carbon and hydrogen atoms to very complex with many atoms. Petroleum hydrocarbons are classified into two major groups: aliphatics and aromatics. Aliphatic compounds are composed of carbon and hydrogen atoms in either chains or in a cyclic pattern and further divided into alkanes, alkenes, and alkynes based on their bonding and structure (Potter and Simmons 1998). Aromatic compounds are composed of one or more benzene rings (C_6H_6). The aromatic compounds are further subdivided into monoaromatics, diaromatics, and polynuclear aromatics depending on their bonding and structure (Potter and Simmons 1998).

Crude oil is unprocessed petroleum hydrocarbons pumped from the oil-bearing formations at depth. The crude oil contains the full complement of the various petroleum hydrocarbon compounds along with other constituents such as sulfur and trace amounts of metals such as iron, nickel, and copper. The process of refining petroleum consists removing impurities and transforming the crude oil into other products such as gasoline, diesel, heating oil, and lubricants. Refineries use a distillation process for separating the various hydrocarbon compounds based on their different boiling points. The crude oil is heated and different products (fractions) boil off at different temperatures with light products, such as gasoline, boiling off at the lowest temperatures and heavier products, such as heating oil, boiling off at the higher temperatures. The different fractions are then further processed and in the case of gasoline various blending agents and additives are added such as antiknock and antioxidant compounds along with antirust agents and detergents.

4.2 Bakken Crude Oil

The chemical and physical properties of crude oil and gasoline vary significantly depending on the location. Typical properties used to describe crude oil include density, vapor pressure, viscosity, interfacial tension, and sulfur.

Bakken crude oil is described as light sweet crude. Light refers to a relatively low density, and sweet refers to the relatively low sulfur concentration. Density is measured in American Petroleum Institute (API) gravity degrees (°) with greater API gravity values representing less dense crude oils and lower API gravity values representing more dense crude oils. Heavy crude oils have an API gravity of less than 10° and light crude oils generally have an API gravity of greater than 31°. Bakken crude oils generally range between 40° and 43° (Auers et al. 2014; Lord et al. 2015). This would correspond to a specific gravity range of 0.81 to 0.83 grams per cubic centimeter (g/cc).

Crude oil typically containing compounds that volatilize easily are emitted by the crude oil as a vapor. Bakken crude oil can contain significant levels of methane, ethane, propane, butane, and pentane (Zhang et al. 2013). The Reid Vapor Pressure (RVP) is the pressure exerted in a closed container by the vapor on the crude oil that has obtained equilibrium at 100°F. RVP is a measure of crude oil's volatility. RVP for crude oils can range between approximately 4.0 and 9.3 pounds per square inch (psi); Bakken crude oil RVP ranges between 0.8 and 15.54 psi (AFPM 2014) with an average of 10.4 psi (Lord et al. 2015). Seasonal in nature, average RVP values for Bakken crude oil are 8.0 psi for warmer temperatures and 12.5 psi for colder temperatures.

North Dakota requires oil conditioning at the well site to remove volatiles for safer transportation. The volatile content is measured by the vapor pressure of the crude oil. National standards state that crude oil is stable at a vapor pressure of 14.7 psi. The North Dakota Oil and Gas Commission requires all Bakken crude oil to have a vapor pressure of 13.7 psi or less.

Dynamic viscosity is a measure of a liquids resistance to shear stress or flow. Liquids with low viscosity flow very slowly and liquids with high viscosity flow very rapidly. The unit of viscosity is the centipoise (cp), which is 1 gram per centimeter per second. Water has a viscosity of 1.0 cp and motor oil has a viscosity of about 250 cp. Crude oils typically have viscosities that range from approximately 2.0 to 300 cp. Bakken crude oil has viscosity of approximately 2.7 cp.

Interfacial tension is a measure of the adhesive forces between the two liquids (in this case crude oil and water). It is a measure of the force that holds the two together. The unit of measure is dynes per centimeter (dynes/cm). The oil/fresh water interfacial tension for crude oil generally ranges between 18.0 and 29.5 dynes/cm (Weaver 2004). Bakken crude oil interfacial tension has been measured as approximately 18.4 dynes/cm (Mahmoudkhani et al. 2015).

The sulfur content of a crude oil determines whether it is characterized as *sweet* or *sour*. Crude oil with low sulfur content (less than 0.5% by weight [wt]) is considered sweet and if greater than 0.5% by wt is considered sour. Sweet crude oil is preferable as it is easier to refine. Domestic sweet crude oils have a sulfur content that ranges between 0.0045% and 0.42% by wt. Bakken crude oil (Auers et al. 2014) has a sulfur content of about 0.1% by wt.

4.3 Gasoline

Gasoline is a distillation product of crude oil. About 19 gallons of gasoline can be made from a 42-gallon barrel of crude oil. The gasoline for automobiles has greater concentrations of benzene, toluene, ethylene, and xylene. Typical properties used to describe gasoline also include density, vapor pressure, viscosity, interfacial tension, and sulfur content. The physical and chemical characteristics of a composite gasoline are provided in Appendix A and Table 3.

Because of the distillation process and the composition of mostly the lighter carbon compounds, gasoline generally has a density between 0.73 to 0.75 g/cc. The density of gasoline is less than water (1.0 g/cc) and when it enters ground water it will be concentrated toward the top of the water table. EPA regulates the RVP of gasoline as per 40 CFR §§ 80.27. The maximum allowed RVP varies and depends on location and season. The allowable maximum RVP for gasoline ranges between 7.8 and 9.0 psi.

Again because of the distillation process and the composition of mostly the lighter carbon compounds, gasoline generally has a lower viscosity than crude oil. The dynamic viscosity of gasoline ranges between 0.37 to 0.54 cp (Irwin 1997a; Irwin 1997b).

Interfacial tension for gasoline and water is greater than Bakken crude oil with ranges from approximately 49 to 51 dynes/cm (Environment Canada 2016). The sulfur content of gasoline is regulated by EPA at 30 parts per million, which is a nearing 0.0% by wt.

5 Fate and Transport of Petroleum Hydrocarbons

Any petroleum hydrocarbon introduced at the ground surface will have the potential based on volume and duration to migrate through the unsaturated zone and enter into the ground water. The petroleum hydrocarbon then forms a pool at the water table and begins migrating downgradient as both a free phase and dissolved constituents.

Unsaturated flow occurs in the portion of the subsurface between the ground surface and the water table. The unsaturated zone is characterized by the pore spaces that contain both water and air. The saturated zone is the portion below the water table and is characterized by the pore spaces being completely filled with water and no air.

The rate that the petroleum hydrocarbon will migrate downward depends on the characteristics of the source along with a number of different properties of both the subsurface material and the petroleum hydrocarbon. Properties of the petroleum hydrocarbon that affect migration include density, viscosity, solubility, soil/water partition coefficients (ratio of petroleum hydrocarbon sorbed onto the soil to that in solution), and interfacial tension.

Properties of the subsurface material that will affect migration included grain size and grading, porosity, hydraulic conductivity, anisotropy (ratio of horizontal-to-vertical hydraulic conductivity), and degree of saturation. The hydraulic conductivity of the unsaturated zone depends on the degree of saturation of the pore spaces. The greater the degree of saturation the greater the hydraulic conductivity. The lower the degree of saturation the lower the hydraulic conductivity of the subsurface material. As the material becomes fully saturated, the hydraulic conductivity will approach the maximum value. This concept is described by various mathematical relationships including the Brooks-Cory and Van Genutchen equations (Radcliffe and Simunek 2010).

The concentration of petroleum hydrocarbons constituents can also be reduced with time through both biological degradation and volatilization. Biological degradation is largely through microbial processes that either uptake, where there is a physical-chemical removal by bacteria, or degradation where the bacteria chemically transform compounds to form new products (Lyman et al. 1992). Volatilization occurs largely in the unsaturated zone as the volatile components of the petroleum hydrocarbons are released to the atmosphere contained in the interstitial spaces of the subsurface material.

As petroleum hydrocarbons migrate downward through the unsaturated zone, a minimal volume, called residual, will remain in the aquifer material. Residual petroleum hydrocarbons are sorbed onto the unsaturated zone material rendering them immobile. The volume of residual petroleum hydrocarbon that remains depends on the sorption properties as defined by the specific hydrocarbon and characteristics of the unsaturated zone material. Typical residual petroleum hydrocarbon volumes in the unsaturated zone are between 10% and 20% (Mercer and Cohen 1990). Other studies indicate that the residual hydrocarbon volume depends on the initial hydrocarbon saturation (Charbeneau 2007). Areas with greater initial saturation may have residual values greater than indicated by Mercer and Cohen (1990). Brost et al. (2000) indicate that the residual petroleum concentration can be as low as 2% for coarse grained soils.

Petroleum hydrocarbons have a relatively low solubility and do not readily mix with water and are termed nonaqueous phase liquids. Molecular forces holding the water together are much stronger than the molecular forces holding the hydrocarbons together. As a result, when hydrocarbons are added to water, the hydrocarbons cannot separate the water molecules apart to mix. Hydrocarbons such as gasoline, diesel, and kerosene are less dense than water and will float on top; these hydrocarbons are termed light nonaqueous phase liquids (LNAPL).

6 Fate and Transport Models

The potential ground water quality impacts to the Rathdrum Prairie aquifer from three petroleum hydrocarbon release scenarios were modeled. The goal was to evaluate the rate of subsurface migration, and if an underlying aquifer would be impacted, to determine the extent of the resulting ground plume. The two models selected were the Multispecies Oil Fate and Transport (MOFAT) and the Hydrocarbon Spill Screening Model (HSSM). The three scenarios modeled include the following:

- 1. 30,000-gallon release of Bakken crude oil from a railroad tanker car
- 2. 9,000-gallon release of gasoline from a truck tanker car
- 3. 50-gallon per day release of gasoline from a transport pipeline

The following sections describe the models and modeling results.

6.1 Multispecies Oil Fate and Transport

MOFAT is distributed by EPA and is a two-dimensional finite element model for coupled multiphase and multicomponent transport in the unsaturated zone (Katyal et al. 1991). MOFAT can model all three phases of a LNAPL transport, water, oil, and air and can partition the chemical components. MOFAT uses the Van Genutchen models for capillary pressure-saturation and relative permeability relations in the unsaturated zone. MOFAT has been used successfully at different sites to model the subsurface migration of petroleum hydrocarbons (Farr 1999; Helweg and Hwang 1993; Jacobs Engineering Group 2005). MOFAT for Windows was used as a pre- and postprocessor to create input and grid files and to format output files. The petroleum soil saturation values were output as grid files that were then subsequently contoured using the Surfer software package for presentation in figures.

6.2 Hydrocarbon Spill Screening Models

HSSM is distributed by EPA and simulates the migration of petroleum hydrocarbons in the unsaturated zone and underlying aquifer (Weaver et al. 1994). HSSM models one-dimensional petroleum migration in the unsaturated zone using the Green-Ampt theory for ponded infiltration and a kinematic model to determine the redistribution and downward Darcy fluxes and the method of characteristics to solve the system of equations (Charbeneau and Weaver 1995). The capillary pressure-saturation and relative permeability relations in the unsaturated zone are solved using the Brooks-Corey model.

If the petroleum hydrocarbon is of sufficient volume, downward migration will reach the aquifer and spread laterally into a pool. The thickness and size of the pool is calculated through a volume balance with the subsequent downgradient contaminant plume determined in two dimensions through a Gaussian-plume model. HSSM was used to model the ground water impacts in Scenario 3 (section 7.3). HSSM has been used successfully at different sites to model the subsurface migration of petroleum hydrocarbons (Citro and Gagliardi 2012; Exponent 2013; Yoon et al. 2009).

6.3 MOFAT Model Construction

The modeled unsaturated zone and underlying aquifer was constructed to represent the Rathdrum Prairie subsurface material. The modeled area extended 70 meters vertically and 100 meters horizontally. The modeled unsaturated zone is 60 meters thick (197 feet) with 10 meters (33 feet) of saturated material below it. No soil layer was included in the model. The aquifer has a horizontal hydraulic conductivity of 350 meters per day (m/d) (1,148 feet per day), a horizontal-to-vertical anisotropy of 2:1 and a porosity of 0.35. Three-hundred and fifty meters per day was used as the horizontal hydraulic conductivity as values significantly greater than this resulted in numerical model instability and non-convergence. The 350 m/d is lower than the typical hydraulic conductivity values (1,880–5,212 m/d) as determined through model calibration of the RPA (Hsieh et al. 2007). The variably saturated conditions and dependent relative permeability of the unsaturated zone are most likely the limiting factors of the hydraulic conductivity and would be a function of the saturated hydraulic conductivity. No degradation of the petroleum hydrocarbon or infiltration of precipitation was assumed.

A variable density grid was used with refinements both horizontally and vertically near the center surface spill area (Figure 12). The MOFAT model does not have a maximum residual oil value below which the petroleum hydrocarbon will cease downward migration in the unsaturated zone. The petroleum hydrocarbon saturation values were evaluated at the model grid nodes defining the center line of the mass in the unsaturated zone. If all the petroleum hydrocarbon saturation values were less than 0.02, the downward migration rate was defined as zero and assumed to be the maximum depth of infiltration.

Scenarios 1 (section 7.1) and 2 (section 7.2) were simulated with the construction of two MOFAT models for each. The first model (infiltration model) included a constant head boundary condition over the spill area that was terminated when the spill volume was infiltrated. The second model uses the results from the first model with a no-flow boundary condition for the petroleum hydrocarbon and calculates the redistribution over time (redistribution model) of the subsurface petroleum hydrocarbon volume. Scenario 3 (section 7.3) was simulated with only the infiltration model with a single constant head boundary condition representing a constant leakage rate. The three petroleum release scenarios were modeled using the water and oil phases and air phase was assumed to be stationary. No multicomponent transport was simulated; the released petroleum hydrocarbon was treated as a singular chemical mass. The releases were allowed to migrate unabated, and no remediation was assumed for the model duration.

The modeled parameters for both the subsurface material in the unsaturated zone and the Bakken crude oil and gasoline are provided in Table 3.

| | | | Bakken | - " |
|--|------|---|-----------|----------|
| Soil Properties | | Bulk Fluid Properties | Crude Oil | Gasoline |
| Porosity φ | 0.35 | Petroleum density pro (g/cc) | 0.82 | 0.73 |
| Van Genutchen alpha α (m ⁻¹) | 16 | Petroleum dynamic viscosity ηro (centipoise) | 2.69 | 0.45 |
| Van Genutchen n | 2.6 | Surface tension (dynes/cm) | 27 | 20 |
| Horizontal hydraulic conductivity kswx (m/day) | 350 | Interfacial tension (dynes/cm) | 18.4 | 50 |
| Vertical hydraulic conductivity kswz (m/day) | 175 | Capillary pressure curve scaling factor #1 βao | 2.67 | 3.6 |
| Residual water saturation S_m | 0.1 | Capillary pressure curve scaling factor #2 βow | 1.6 | 1.38 |
| Maximum residual petroleum saturation $S_{\rm or}$ | 0.1 | | | |

The MOFAT input data sheet for each scenario is provided in Appendix B. The MOFAT model was only used to model the unsaturated zone. One of the limitations of the MOFAT model is that the model cannot exceed 1,500 nodes. Expanding the model to adequately incorporate both the unsaturated zone and the downgradient portion of the aquifer that would include the contaminant plume would have exceeded this limit.

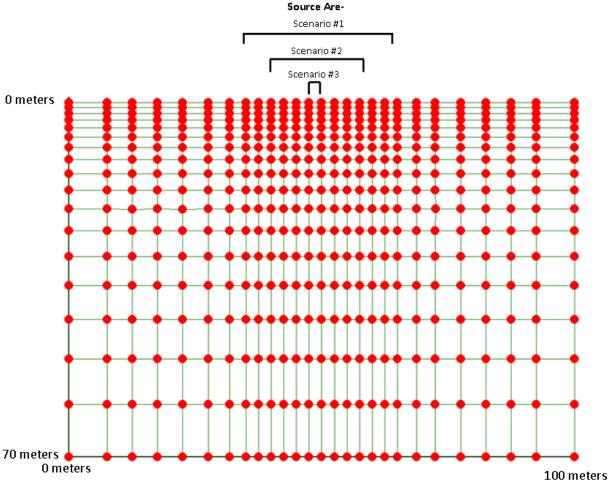


Figure 12. MOFAT model grid and source area locations.

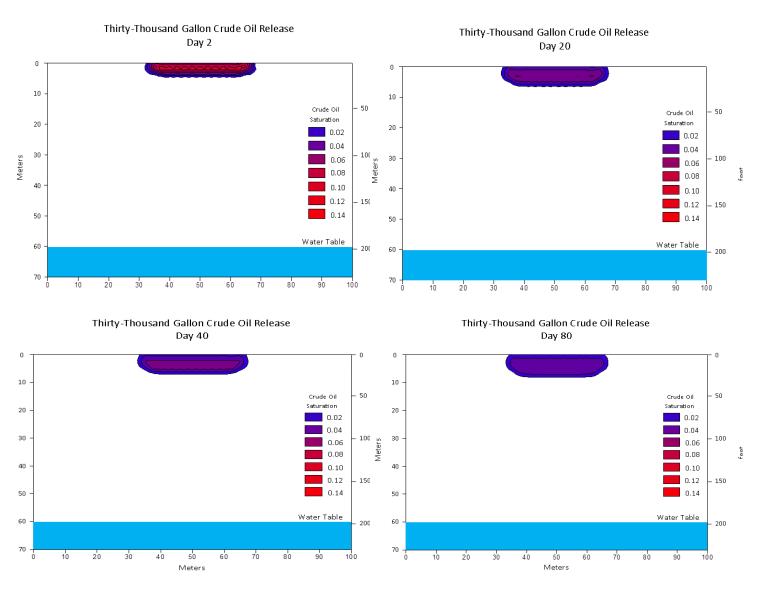
6.4 HSSM Model Construction

The HSSM model included developing a free product lens and a ground water plume of benzene so additional parameters of longitudinal and vertical dispersity were defined. Degradation of the petroleum hydrocarbon was included. No infiltration of precipitation was assumed. The modeled parameters for both the Bakken crude oil and gasoline were also identical to the MOFAT model (Table 3). The HSSM input data sheet for each scenario is provided in C.

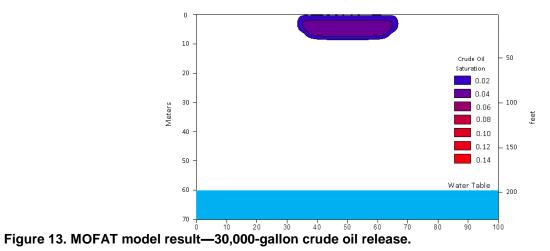
7 Model Results

7.1 Scenario 1—30,000-Gallon Release of Bakken Crude Oil

Scenerio 1 was modeled using a circular infiltration area with a diameter of 30 meters (98 feet). The two-dimensional MOFAT model simulated a 1-meter wide strip across the diameter of the infiltration area. The crude oil volume across a 1-meter wide strip (4.80 cubic meters) was infiltrated and then redistributed with time (Appendix B—calculations and Appendix C— MOFAT input files). The model results indicate that downward infiltration continues for approximately120 days to about 9 meters (\approx 29 feet) below ground surface (bgs) (Figure 13). Downward migration will continue past 9 meters but at a very slow rate.



Thirty-Thousand Gallon Crude Oil Release Day 120



7.2 Scenario 2—9,000- Gallon Release of Gasoline

Scenerio 2 was modeled using a circular infiltration area with a diameter of 15 meters (49 feet). The two-dimensional MOFAT model simulated a 1-meter wide strip across the diameter of the infiltration area (Appendix B). The gasoline volume across a 1-meter wide strip (2.85 cubic meters) was infiltrated then redistributed with time (B—calculations and Appendix C—input files). The model results indicate that downward infiltration continues for approximately 60 days to about 10 meters (\approx 33 feet) bgs (Figure 14). Downward migration will continue past 10 meters but at a very slow rate.

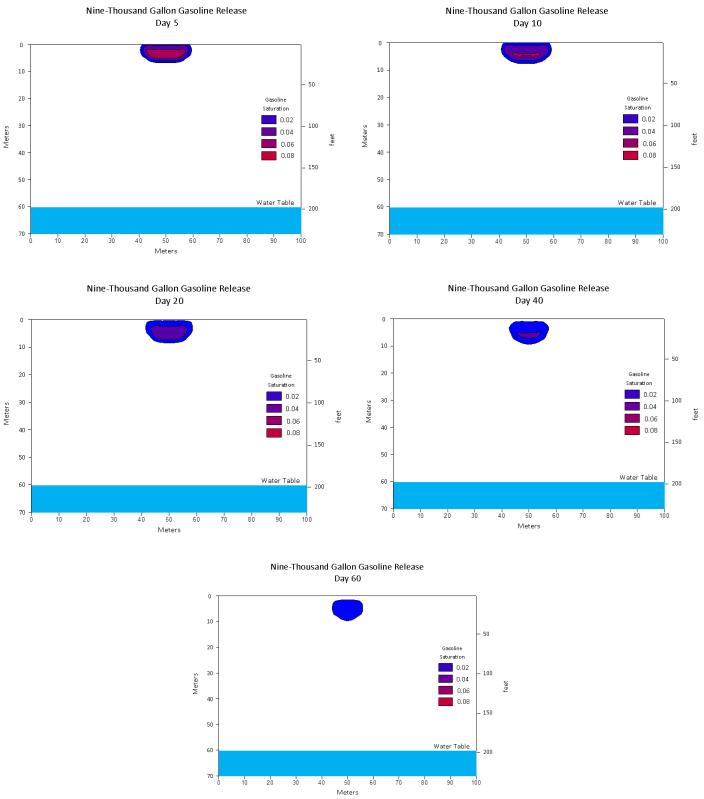


Figure 14. MOFAT model result—9,000-gallon gasoline release.

7.3 Scenario 3—50-Gallon Per Day Release of Gasoline

Scenario 3 was modeled using a circular infiltration area with a diameter of 2.5 meters (\approx 8 feet). The two-dimensional MOFAT model simulated a 1-meter wide strip across the diameter of the infiltration area. The gasoline volume was infiltrated at a head of 0.0625 meters (Appendix B—calculations and Appendix C—input files) for a total of 200 days when it reached the water table 60 meters bgs (Figure 15).

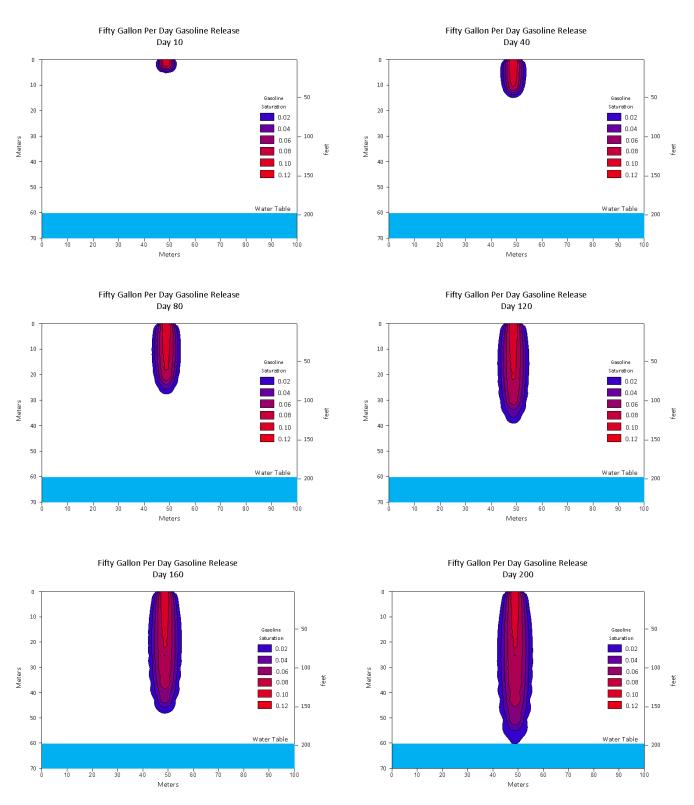


Figure 15. MOFAT model result—50-gallon per day gasoline release.

The HSSM model was then used to determine the impacts to ground water from the benzene component in gasoline from a constant 50-gallon per day source at the water table surface. The thickness and extent of the free product gasoline lens along with the length and concentration of the centerline benzene plume downgradient from the source was determined for 5 years. A limitation of HSSM is that the horizontal hydraulic conductivity of the modeled aquifer cannot exceed 500 m/d with a horizontal-to-vertical anisotropy of 2:1. Typical horizontal hydraulic conductivities of the RPA range between 1,880–5,212 m/d with very flat gradients (0.0006) that result in ground water velocities of approximately 6.0 m/d (\approx 20 feet per day). To achieve the magnitude of velocities typical of the RPA within the HSSM limitation of a hydraulic conductivity of 6.0 m/d. The centerline plume concentrations at 500 m, 750 m, 1,000 m, 2,000 m and 2,500 m are shown in Figure 16. The thickness and lateral downgradient extension of the free product pool can be seen in Figure 17.

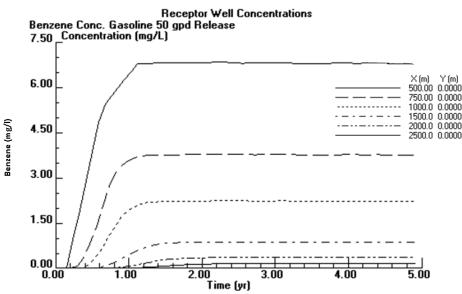


Figure 16. HSSM model result—50-gallon per day gasoline release. Concentration at downgradient receptors.

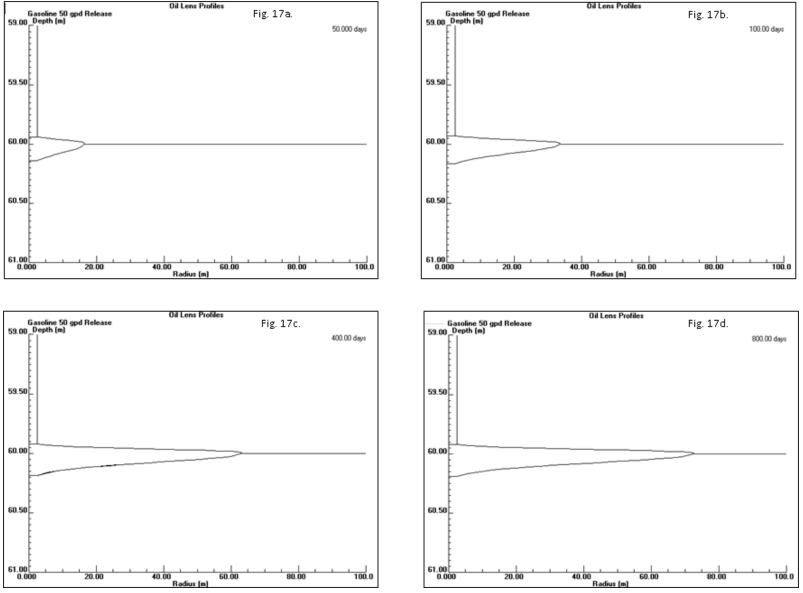


Figure 17. HSSM model result—50-gallon per day gasoline release. Gasoline lens profiles over time.

8 Model Limitations

The model scenarios presented in this report were constructed to estimate the distribution and migration of petroleum products in the subsurface. The distribution and migration rates depend on aquifer parameters, release rates, and other boundary conditions that can vary both over time and the geographic area of the study. No attempt was made to establish or determine these variations and is considered beyond the scope of this project. If a more detailed analysis is required or the model is used for another purpose, consult an appropriate ground water professional for the proper application limits of these models or the requirements for any additional studies or model construction.

9 Discussion

The direction of remedial efforts would differ depending on the release scenario. A release of a defined volume of petroleum hydrocarbon over a short period of time such as a crude oil or gasoline tanker release would result in the lateral spreading and infiltration of the volume. The vertical infiltration would be limited by the volume. As the volume of petroleum hydrocarbon migrated both laterally and vertically in the subsurface, saturation would decrease. The decrease in saturation would result in a decrease in the unsaturated hydraulic conductivity affecting migration rate and eventually reaching critical residual values resulting in the cessation of migration. As shown in Scenarios 1 and 2, the vertical rate and depth of migration varied between the two releases but slows significantly at a depth of approximately 10 meters (\approx 33 feet). The volume of release for a tanker truck would not exceed the volume of a singular truck. The release volume of crude oil from a train of tanker cars would depend on the number of cars breached and any crude oil that may be consumed by fire. Based on previous releases, this can vary to a large degree from a thousand to millions of gallons. The volume of contaminated soil and depth of migration will depend on the site specifics related to the release volume, lateral spreading (affects ponding depth), vertical hydraulic conductivity, and the elapsed time to the initiation of remedial efforts.

Remedial efforts for these types of releases that do not impact ground water could be achieved by excavating and removing the contaminated soil soon after the release. Any contaminated soil at depths that cannot be excavated can be remediated through various in-situ methods or a combination of methods, such as soil vapor extraction and bioventing, chemical oxidation, or surfactant flushing and vacuum extraction.

A release described in Scenario 3 that is characterized by a small volume that continues for an extended period of time such as an undetected release from a pipeline has much more potential to impact ground water. The continued source of petroleum hydrocarbon will saturate the subsurface material creating elevated hydraulic conductivities and a driving head, which results in relatively rapid downward migration to an underlying aquifer. The continued source will generate a lens of petroleum and a dissolved plume that could migrate downgradient significant distances. The concern is that if these small release rates were not detected, the release could occur for substantial periods of time. Contaminated ground water may impact the safety of the drinking water supplies in the vicinity of the release.

Remedial efforts for Scenario 3 releases would likely have to address both contaminated soil and ground water. Soil remediation would proceed as described above; treating the contaminated ground water can be time consuming and costly. Cost would include ground water characterization through the completion of multiple wells, analytical costs associated with sampling, and the associated treatment methods.

10 Conclusion

A significant volume of petroleum hydrocarbons are transported over the RPA every year. Potential releases from crude oil and gasoline tankers could occur over a relatively short period of time and would consist of a defined volume. Given the significant depths to ground water from the surface over the RPA, the potential to impact ground water is limited. The release would be apparent, and remediation efforts could be initiated soon after the release, limiting the contaminated volume of soil.

Potential releases from a subsurface pipeline could be a small volume occurring over long periods of time resulting in a greater risk for ground water impacts and difficulty identifying the releases in a timely manner. Subsequent remedial efforts could be more extensive.

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Appendix A. Physical and Chemical Characteristics of Bakken Crude Oil and Gasoline

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|---|--|

Report of Analysis

| Client: Job Location: Our Reference Number: Lab Reférence Number: | b Location: San Francisco, CA, USA ur Reference Number: US410-0012129 | | |
|--|--|---------------------------------|--------------------------|
| Sample ID: | 2014-SANF-000316-018 | Date Taken: Date Submitted: | 1-Mar-2014 5-Mar-2014 |
| Sample Designated As: | Bakken Crude Fairview, MT | Date Submitted: Date Tested: | 7-Mar-2014 |
| Vessel/Location: Representing: | Composite | Date Testeu. | 7-11101-2014 |
| Method | Test | Result | Unit |
| ASTM D323 | Test Temperature | 122 | ۹F |
| ASTM D323 | Reid Vapor Pressure (Proc A) | 16.30 | psi |
| ASTM D4294 | Sulfur Content | 0.0868 | Wt % |
| ISM TM0172 | NACE Corrosion Rating | E | |
| ASTM D86 | IBP Recovery | 44.1 | °C |
| ASTM D5705 | Test Temperature | 77 | ۴ |
| ASTM D5705 | Average H2S Result | < 5 | ppm v/v |
| ASTM D56 | Corrected Flash Point | <21 | °C |
| ASTM D6730 | Light Ends | See Attached Report | |
| ASTM D5002 | Density 15.56 °C/ 60 °F | 0.8079 | g/mL |
| ASTM D5002 | API Gravity @ 60 °F | 43.5 | °API |
| ASTM D4928 | Water Content | 0.05 | Mass % |
| ASTM D4928 | Water Content | 0.04 | Vol % |
| ASTM D97 | Pour Point | <-54 | °C |
| ASTM D664 | Procedure Used | A | |
| ASTM D664 | Acid Number | < 0.10 | mg KOH/g |
| IP 501 | Sodium | 37 | mg/kg |
| IP 501 | Vanadium | < 1 | mg/kg |
| IP 501 | Nickel | < 1 | mg/kg |
| IP 501 | Iron | 7 | mg/kg |
| ASTM D445 | Kinematic Viscosity @ 60 °F | 3.337 | cSt |
| ASTM D445 | Dynamic Viscosity @ 60 °F | 2.696 | kg/m*s |

* Results obtained from the average of the individual samples from Fairview, Mt

Signed: _____ Date: _____ 3/7/2014 Intertek Nathaniel Preston, Chemist

Page 1 of 1 1572387 6050 Egret Court, Benicia, California 94510, USA Tel: +1 707 746 0556 3/7/2014 1:52:24 PM US410-0012129

| Detailed Hydrocarbon Analysis Summary Report - | Report Date: 3/7/2014 | 12:38:33 PM |
|---|--------------------------|------------------|
| RawFile: C:\Chem32\1\DATA\140306a\140306A 2014-03-06 15-55-00\204B0401.D\204B0401.CDF | Acquired: 03/07/14 01 | :05:15 |
| Sample: 316-018 | Analyzed: 3/7/2014 12 | 2:38:33 PM |
| Processed 335 Peaks | | |
| Reference File: C:\Chem32\DHARef\D6730_V1.DHA | | |
| Comments: | Yield: 52.65 | |
| | Int Std: methyl-t-butyle | ether |
| · · · · · · · · · · · · · · · · · · · | Int Std Amt: 0.21 | |
| | Sample Wt: 4.44 | Sample Den: 1.00 |

`、`

SUMMARY REPORT

| | Group Type | Total(Mass%) | Total(Vol%) | Total(Mol%) | |
|---|-----------------|--------------|-------------|-------------|--|
| | Paraffins: | 12.50 | 18.72 | 14.29 | |
| | I-Paraffins: | 11.63 | 16.77 | 11.37 | |
| | Olefins: | 1.36 | 1.85 | 1.27 | |
| • | Napthenes: | 11.27 | 14.69 | 11.41 | |
| | Aromatics: | 6.43 | 7.27 | 5.44 | |
| | Total C14+: | 7.30 | 9.57 | 3.89 | |
| | Total Unknowns: | 2.15 | 3.07 | 1.46 | |
| | | | | | |

| (| Oxygenates: | | | | | | | |
|---|------------------------|---------------|-------------|----------------|-----|--------|--|--|
| | Total: | | 0.00(Mass%) | 0.00(Vol% | 6) | | | |
| | Total Ox | ygen Content: | 0.00(Mass%) | | | | | |
| 1 | Multisubstituted Aroma | tics: | 4.69(Mass%) | 5.32(Vol% | 6) | | | |
| ļ | Average Molecular We | ight: 101.68 | | | | | | |
| F | Relative Density: 0.67 | | | | | | | |
| F | Reid Vapor Pressure @ | 0 100F: 3.74 | | | | | | |
| (| Calculated Octane Nun | nber: 56.05 | | | | | | |
| | | IBP | T10 | T50 | T90 | FBP | | |
| E | BP by Mass (Deg F) | 10.90 | 161.24 | 488.66 | T90 | 488.66 | | |
| | BP by Vol (Deg F) | -43.67 | 140.47 | 345.47 | T90 | 488.66 | | |
| F | Percent Carbon: 85.54 | | Percent H | ydrogen: 14.46 | | | | |
| E | Bromine Number (Calc |): 2.36 | | | | | | |

Gasoline (Unleaded)

| Pailing Paint Distribution (90) | | | | Reference |
|--|---------------------------------------|-------------------------|--------------------|------------------|
| Boiling Point Distribution (°C) | Weight % | Boiling Poir | | |
| | weight /s | (°C) | n. | |
| | 80 | 101 | | ESD 94 |
| | 85 | | | 230 84 |
| | 90 | | | |
| | 95 | | | |
| Boiling Range (°C) | | | | |
| | | 35 to 220 | | Shell 99a |
| Aqueous Solubility (mg/L) | | | | |
| | Temperature | | | |
| | (°C) | | | |
| | 20 (approx.) | 307 | (a) | MacLean 8 |
| | 22 | 112 | (a) | Suntio 86 |
| | 20 (approx.) | 261 | (b) | MacLean 8 |
| (a) fresh water; (b) salt water | | | | |
| Acute Toxicity of Water Soluble Fr | action (mg/L) | | | |
| | Test Organism | | | |
| 48h EC50 | Daphnia magna | 5 | (a) | MacLean 8 |
| | | 2 | (b) | EETD 89 |
| | Artemia spp. | 25 | (a) | MacLean 8 |
| | | 9 | (b) | EETD 89 |
| 48h LC50 | Daphnia magna | 50 | (a) | MacLean 8 |
| | | 18 | (b) | EETD 89 |
| | Artemia spp. | 51 | (a) | MacLean 8 |
| | | 18 | (b) | EETD 89 |
| | Rainbow trout larvae | 7 | (c) | Lockhart 87 |
| | | 5 | (d) | |
| (a) results based on fluorescence container | spectroscopy; (b) results based on GC | purge-and-trap analysis | s; (c) closed cont | tainer; (d) open |
| Threshold Limit Values (ppm) | | | | |
| | TWA | 300 | | ACGIH 99 |
| | STEL | 500 | | |

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Gasoline (Leaded)

| Synonyms: | Automotive Fuel | | Reference ID |
|----------------|---|--------|--------------|
| | Petrol | | |
| For additio | onal fuel specifications refer to ASTM D 4814. | | |
| API Gravity | | | |
| | | 62.4 | EETD 84 |
| Sulphur (weig | ght %) | | |
| | | 0.07 | EETD 84 |
| Density (g/mL | -) | | |
| | Temperature | | |
| | <u>(°C)</u> | | |
| | 0 | 0.7460 | EETD 84 |
| | 5 | 0.7501 | Maijanen 84 |
| | 15 | 0.7290 | EETD 84 |
| | 20 | 0.7340 | Maijanen 84 |
| Dynamic Visc | cosity (mPa-s or cP) | | |
| - | Temperature | | |
| | (°C) | | |
| | 0 | 0.8 | EETD 85 |
| | 5 | 0.5 | Maijanen 84 |
| | 15 | 0.6 | EETD 85 |
| | 20 | 0.5 | Maijanen 84 |
| Surface Tensi | ion (mN/m or dynes/cm) | | |
| oundoe rens | Temperature | | |
| | (°C) | | |
| | 0 | 20.9 | EETD 84 |
| | 15 | 19.8 | |
| Oil/Ealt Water | | | |
| Ull/Salt Water | r Interfacial Tension (mN/m or dynes/cm) Temperature | | |
| | the second se | | |
| | (<u>°C)</u> 0 | 19.8 | EETD 84 |
| | 15 | 18.6 | EETD 85 |
| | | 16.0 | EETD 60 |
| Oil/Fresh Wat | ter Interfacial Tension (mN/m or | | |
| | Temperature | | |
| | (°C) | | |
| | 0 | 19.7 | EETD 84 |
| | 15 | 18.0 | |
| Metals (ppm) | | | |
| | Barium | <0.3 | Cao 92 |
| | Chromium | <1.5 | |
| | Copper | <0.6 | |
| | Iron | 3 | |
| | Lead | 1750.0 | |
| | Magnesium | <1 | |
| | Molybdenum | <0.6 | |
| | Nickel | <1 | |
| | Titanium | 0.5 | |
| | Vanadium | <0.6 | |
| | Zinc | 0.5 | |

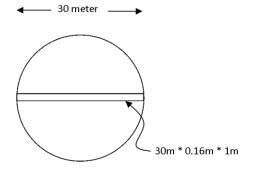
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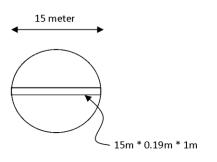
Gasoline (Leaded)

| | | | | Reference II |
|--|--|-------------------------|---------------------|----------------|
| Queous Solubility (mg/L) | | | | |
| | Temperature | | | |
| | <u>(°C)</u> | | | |
| | 20 (approx.) | 169 | (a) | MacLean 89 |
| | 22 | 240 | (a) | Suntio 86 |
| | 20 (approx.) | 132 | (b) | MacLean 8 |
| | 22 | 98 | (c) (d) | Maijanen 84 |
| | Unknown | 187 | (c) (e) | Murray 84 |
| (a) fresh water; (b) salt water; (c) summer gasoline; (e) reg | | | | |
| cute Toxicity of Water Solub | le Fraction (mg/L) | | | |
| | Test Organism | | | |
| 48h EC50 | Daphnia magna | 6 | (a) | MacLean 8 |
| | | 9 | (b) | EETD 89 |
| | Artemia spp. | 19 | (a) | MacLean 8 |
| | | 28 | (b) | EETD 89 |
| 48h LC50 | Daphnia magna | 14 | (a) | MacLean 8 |
| | | 19 | (b) | EETD 89 |
| | Artemia spp. | 21 | (a) | MacLean 8 |
| | | 31 | (b) | EETD 89 |
| (a) results based on fluoreso | ence spectroscopy; (b) results based on GC | purge-and-trap analysis | s; (c) fresh water; | (d) salt water |
| Threshold Limit Values (ppm) | | | | |
| | TWA | 300 | | ACGIH 99 |
| | STEL | 500 | | |

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Appendix B. MOFAT Input Data Sheet (Scenarios 1–3)





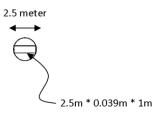


<u>Calculated depth</u> 30,000 gallons = 113.6 cubic meters Area = πr^2 = 3.14 * (15m)² =706.9 m² Depth = 113.6 m³ /706.9 m² Depth = 0.16 meters <u>2D Model Infiltrated Volume</u> 30m * 0.16 m * 1m = 4.8 m³

Scenario #2 Fixed volume release of gasoline

<u>Calculated Depth</u> 9,000 gallons = 34.1cubic meters Area = π r² = 3.14 * (7.5m)² =176.7 m² Depth = 34.1 m³ /176.7 m² Depth = 0.19 meters <u>2D Model Infiltrated Volume</u> 15m * 0.19m * 1m = 2.85 m³

Scenario #3 Constant rate release of gasoline



<u>Calculated Depth</u> 50 gallons = 0.189 cubic meters Area = π r² = 3.14 * (1.25m)² =4.91 m² Depth = 0.189 m³/4.91 m² Depth = 0.039 meters <u>2D Model Infiltrated Volume</u> 2.5m * 0.039m * 1m = 0.098m³ This page intentionally left blank for correct double-sided printing.

Appendix C. MOFAT & HSSM Input Files

| 1 9999 | 0 | k Release 0 1 1 1 10.39 52.66 67.84 7.53 37.5 | (Infiltrat 0 0 18 27 19.37 55.89 69. 12.53 40. | 2 1 0 0 27.12 58.67 70. 17.53 42.5 | 0 2 0 33.82 61.08 22.53 45. | 39.61 63.16 27.53 47.5 | 44.61 64.95 31.75 50. |
|------------|------------|--|---|--|--|---------------------------------|--------------------------------|
| | 52.5 | 55. | 57.5 | 60. | 62.5 | 65. | 68.75 |
| | | 77.48 | 82.48 | 87.48 | 92.48 | 100. | |
| | | 4.8 | 100 | 0 1 5 | 1 0 2 | 100 | |
| | 0. 2.67 | 0.0005 0.82 | 100. 2.67 | 0.15 1.6 | 1.03 | 120. | |
| | 1. | | 0.001 | 1. | | | |
| 0 | 1 | | | | | | |
| | 10. | 10. | -1. | | | | |
| | 350. | | 0.35 | 0.1 | 0.1 | 16. | 2.6 |
| 0 | | 0 | | | | | |
| 0 | 0 | 0 | | | | | |
| 144 | 1 | | | | | | |
| 162 | 1 | | | | | | |
| 180 198 | 1 1 | | | | | | |
| 198 216 | 1 | | | | | | |
| 234 | 1 | | | | | | |
| 252 | 1 | | | | | | |
| 270 | 1 | | | | | | |
| 288 | 1 | | | | | | |
| 306 | 1 | | | | | | |
| 324 | 1 | | | | | | |
| 342 | 1 | | | | | | |
| 360 | 1 | | | | | | |
| 4 | | | 0.05 | | | | |
| | | | 0.05 | | | | |
| | | | .025 | | | | |
| | 99 | 990 | .025 | | | | |

| Crude Oil 30 | k Release | (Redistrib | oution) | | | |
|--------------|-----------|------------|---------|-------|-------|-------|
| 1 1 | 0 1 | 0 0 | 2 1 | 0 | | |
| 9999 50 | 1 1 | 18 27 | 0 0 | 2 0 | | |
| 0. | 10.39 | 19.37 | 27.12 | 33.82 | 39.61 | 44.61 |
| 48.93 | 52.66 | 55.89 | 58.67 | 61.08 | 63.16 | 64.95 |
| 66.5 | 67.84 | 69. | 70. | | | |
| 0. | 7.53 | 12.53 | 17.53 | 22.53 | 27.53 | 31.75 |
| 35. | 37.5 | 40. | 42.5 | 45. | 47.5 | 50. |
| 52.5 | 55. | 57.5 | 60. | 62.5 | 65. | 68.75 |
| 72.48 | 77.48 | 82.48 | 87.48 | 92.48 | 100. | |
| 0 | 0. | | | | | |
| 0. | 0.0005 | 30. | 0.15 | 1.03 | 2. | |
| 2.67 | 0.82 | 2.67 | 1.6 | | | |
| 1. | 0.05 | 0.001 | 1. | | | |
| 350. | 175. | 0.35 | 0.1 | 0.1 | 16. | 2.6 |
| 0 0 | 0 | | | | | |
| 0 0 | 0 | | | | | |
| 4 | | 0.05 | | | | |
| | | 0.05 | | | | |
| | | .025 | | | | |
| 99 | 990 | .025 | | | | |

| Gasoli | ne 9.0 | k Relea | ase | (Infi | ltrat | e) | | | | | | |
|--------|--------|---------|-----|------------|-------|----|-----|----|-----|-----|----|-------|
| 1 | 0 | 0 | 1 | 0 | 0 | 2 | 1 | 0 | | | | |
| 9999 | 100 | 1 | 1 | 18 | 27 | 0 | 0 | 2 | 0 | | | |
| | Ο. | 10.3 | 39 | 19 | .37 | 27 | .12 | 33 | .82 | 39. | 61 | 44.61 |
| 4 | 8.93 | 52.6 | 56 | 55 | .89 | 58 | .67 | 61 | .08 | 63. | 16 | 64.95 |
| | 66.5 | 67.8 | | | 69. | | 70. | | | | | |
| | Ο. | 7.5 | 53 | | .53 | 17 | .53 | 22 | .53 | 27. | 53 | 31.75 |
| | 35. | 37. | - | | 40. | | 2.5 | | 45. | 47 | | 50. |
| | 52.5 | 55 | | 5 | | | 60. | | | 6 | 5. | 68.75 |
| | | 77.4 | | 82 | .48 | 87 | .48 | 92 | .48 | 10 | 0. | |
| 2 | | .85 | | | | | | | | | | |
| | 0. | | | | 00. | | 0.1 | 1 | .03 | 12 | 0. | |
| (| | 0.7 | | | | | .38 | | | | | |
| | 1. | 0.00 |)5 | 0. | 001 | | 1. | | | | | |
| 0 | 1 | | | | | | | | | | | |
| | 10. | 1 | | | | | | | | | | |
| | 350. | | 5. | 0 | .35 | | 0.1 | (| 0.1 | 1 | 6. | 2.6 |
| 0 | 7 | 0 | | | | | | | | | | |
| 0 | 0 | 0 | | | | | | | | | | |
| 198 | 1 | | | | | | | | | | | |
| 216 | 1 | | | | | | | | | | | |
| 234 | 1 | | | | | | | | | | | |
| 252 | 1 | | | | | | | | | | | |
| 270 | 1 | | | | | | | | | | | |
| 288 | 1 | | | | | | | | | | | |
| 306 | 1 | 0 | | 1 | | | | | | | | |
| 3 | | 0. | | -1. .05 | | | | | | | | |
| | | 005 | | | | | | | | | | |
| | 99 | 99. | - (| 0.2 | | | | | | | | |

| Gasoline 9. | 0k Release | (Redistrib | ution) | | | |
|-------------|------------|------------|--------|-------|-------|-------|
| 1 1 | 0 1 | 0 0 | 2 1 | 0 | | |
| 9999 50 | 1 1 | 18 27 | 0 0 | 2 0 | | |
| 0. | 10.39 | 19.37 | 27.12 | 33.82 | 39.61 | 44.61 |
| 48.93 | 52.66 | 55.89 | 58.67 | 61.08 | 63.16 | 64.95 |
| 66.5 | 67.84 | 69. | 70. | | | |
| 0. | 7.53 | 12.53 | 17.53 | 22.53 | 27.53 | 31.75 |
| 35. | 37.5 | 40. | 42.5 | 45. | 47.5 | 50. |
| 52.5 | 55. | 57.5 | 60. | 62.5 | 65. | 68.75 |
| 72.48 | 77.48 | 82.48 | 87.48 | 92.48 | 100. | |
| 0 | 0. | | | | | |
| 0. | 0.0005 | 150. | 0.1 | 1.01 | 5. | |
| 0.45 | 0.73 | 3.6 | 1.38 | | | |
| 1. | 0.01 | 0.001 | 1. | | | |
| 350. | 175. | 0.35 | 0.1 | 0.1 | 16. | 2.6 |
| 0 0 | 0 | | | | | |
| 0 0 | 0 | | | | | |
| 3 | 0. | -1. | | | | |
| (| | 0.05 | | | | |
| ç | 9999. | -0.2 | | | | |
| | | | | | | |

| Gasoline 50 gpd Release | | | | | | | | | | | | |
|-------------------------|------|-------|---------|-------|-------|---|-------|---|------|----|-----|-------|
| 1 | 0 | 0 | 1 | 0 | 0 | 2 | 1 | 0 | | | | |
| 99999 | 50 | 1 | 2 | 18 | 27 | 0 | 0 | 2 | 0 | | | |
| 0. | | 1 | 10.39 | | 19.37 | | 27.12 | | 3.82 | 39 | .61 | 44.61 |
| 48.93 | | Ľ | 52.66 | | 55.89 | | 58.67 | | 1.08 | 63 | .16 | 64.95 |
| 66.5 | | 6 | 67.84 | | 69. | | 70. | | | | | |
| 0. | | | 7.53 | | 12.53 | | 17.53 | | 2.53 | 27 | .53 | 31.75 |
| 35. | | | 37.5 | | 40. | | 42.5 | | 45. | 4 | 7.5 | 50. |
| 52.5 | | | 55. | | 57.5 | | 60. | | 62.5 | | 65. | 68.75 |
| 72.48 | | 7 | 77.48 | | 32.48 | 8 | 87.48 | | 2.48 | 1 | 00. | |
| 0 | | Ο. | | | | | | | | | | |
| | Ο. | 0. | 0005 | | 150. | | 0.1 | | 1.01 | | 5. | |
| | 0.45 | | 0.73 | | 3.6 | | 1.38 | | | | | |
| | 1. | | 0.05 | C | 0.001 | | 1. | | | | | |
| 0 | 1 | | | | | | | | | | | |
| | 10. | 10. | | -1. | | | | | | | | |
| | 350. | | 175. | | 0.35 | | 0.1 | | 0.05 | | 16. | 2.6 |
| 1 | 2 | 0 | | | | | | | | | | |
| 0 | 0 | 0 | | | | | | | | | | |
| 469 | 1 | | | | | | | | | | | |
| 234 | 2 | | | | | | | | | | | |
| 252 | 2 | | | | | | | | | | | |
| 2 | | 0. | | 10. | | | | | | | | |
| | 9 | 9999. | | 10. | | | | | | | | |
| 3 | 0. | | -1. | | | | | | | | | |
| | | .002 | | .0625 | | | | | | | | |
| | 9 | 999. | 90.0625 | | | | | | | | | |

HSSM Benzene Conc. Gasoline 50 gpd Release

```
250 2
         2
             16
                  0.35 0.1
    1
         2
             0.1 0.5 60
1
0.45 0.73 0.02 1
2.6 72
         20
0.039
         0.0 2500
8208
311 0.83E-1 0.083
                      1.89
2.5 1.001
             .1E-1
                      1 0.0042
                                  0.15
.3260
         1750 212
1825 20
         .1
             1
                  0.1E-2
10
50
    60
         70
             80
                  90
                      100
200 400 600 800
             .100E-2
100 10
         101
                      100 6
50
    1825 50
             1
500 0
750 0
1000 0
1500 0
2000 0
2500 0
```

0