

SURFACE SPILLS AT UNCONVENTIONAL OIL AND GAS SITES:  
A CONTAMINANT TRANSPORT MODELING STUDY  
FOR THE SOUTH PLATTE ALLUVIAL AQUIFER

by

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## ABSTRACT

Hydraulic fracturing has revolutionized the U.S.'s energy portfolio by making shale reservoirs productive and commercially viable. However, the public is concerned that the chemical constituents in hydraulic fracturing fluid, produced water, or natural gas itself could potentially impact groundwater. Here, I present fate and transport simulations of aqueous fluid surface spills, the most likely pathway for groundwater contamination during oil and gas production operations, with four primary goals: (1) to evaluate whether or not these spills pose risks to groundwater quality in the South Platte aquifer system, (2) to identify the key hydrologic and transport factors that determine these risks, (3) to develop a screening level methodology that could be applied at other sites and for various pollutants, and (4) to demonstrate the potential importance of co-contaminant interactions using selected chemicals. I considered two types of fluid that can be accidentally released at oil and gas sites: produced water and hydraulic fracturing fluid. Benzene was taken to be a representative contaminant of interest for produced water because it is mobile, a known carcinogen, federally regulated, and a common constituent of produced water. Glutaraldehyde (biocide), polyethylene glycol (surfactant), and polyacrylamide (friction reducer) were the chemical additives considered for spills of hydraulic fracturing fluid because they represent different classes of common compounds used in hydraulic fracturing and experimental data were available. I focused on the South Platte Alluvial Aquifer, which is located in the greater Denver metro area and overlaps a zone of high-density oil and gas development. Risk of groundwater pollution was based on predicted concentration at the groundwater table.

For this screening level assessment, I considered a range of representative hydrologic conditions and chemical behavior for transport of benzene in a sandy loam. Results of the study showed that the risk of benzene contamination of groundwater from a single produced water spill, based on spill data, was relatively low in the South Platte aquifer. Spill size was the dominant factor influencing whether a contaminant reached the water table. Only statistically larger spills with spill volume per area of at least 12.0 cm posed a clear risk. Storm events following a spill were generally required to transport more typical sized spills (0.38 cm spill volume per area) to the water table; typical median-sized spills only posed risk to shallow

groundwater if a 500-year storm or if a 100-year storm (followed by little degradation or sorption) occurred right after the spill. However, for more typical storm intensities (1 year and 10 year), only the larger spills (with spill volumes per area  $\geq 6$  cm) posed risk to groundwater quality.

The purpose of the hydraulic fracturing fluid spill simulations was to assess the importance of accounting for co-contaminant interactions when modeling these spills. Co-contaminant interactions were largely considered in terms of biocidal and salt impacts on degradation of the three chemical additives glutaraldehyde, polyethylene glycol, and polyacrylamide. Results from the study showed that co-contaminant interactions are an important consideration when simulating spills of hydraulic fracturing fluid. Glutaraldehyde removal was impacted by the presence of salt, polyacrylamide, and its own concentration. Polyethylene glycol was affected by the presence of glutaraldehyde and salt. Polyacrylamide remained recalcitrant regardless of chemical composition of the hydraulic fracturing fluid. Because no EPA concentration standards exist for the three compounds, risk was evaluated by using a hazard quotient (HQ) risk evaluation approach based on potential exposure to a substance and the level at which no adverse effects are expected. Considering the highest predicted concentration of glutaraldehyde, the HQ was below 1, indicating relatively low risk associated with a spill of hydraulic fracturing fluid under these conditions.

Collectively, results demonstrated groundwater contamination potential due to produced water and hydraulic fracturing fluid spills is low in most areas of the South Platte system for the contaminants and spill conditions investigated. Substantial risk may exist in certain areas where the groundwater table is shallow (less than 10 ft below ground surface), soils contain high sand contents, and when large spills and large storms occur. By helping to identify locations in the Front Range of Colorado that are at low or high risk for groundwater contamination due to a surface spill, this research will aid in improving prevention and mitigation practices so that decision-makers can be better prepared to address accidental releases in Colorado. In addition, this research provides a methodology that could be used to evaluate risk of groundwater contamination due to spills for other aquifers. Future work could apply this methodology to study spills in other areas and to consider other compounds present in produced water and hydraulic fracturing fluid.

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## **WE<sup>2</sup>ST PUBLIC RELEVANCE AND BROADER IMPACTS EXECUTIVE SUMMARY**

The Conoco-Phillips Center for a Sustainable WE<sup>2</sup>ST at the Colorado School of Mines is a research-education-outreach institution dedicated to promoting the joint sustainability of water resources and energy production in arid regions. Initiatives of the center include educating water-energy literate graduate and undergraduate students, conducting research on topics related to the water-energy nexus, and facilitating discussion between communities, scientists, and industry. As a graduate fellow of the Conoco-Phillips Center for a Sustainable WE<sup>2</sup>ST, I am studying surface spills related to oil and gas development over the South Platte Alluvial Aquifer in the Front Range of Colorado. For my thesis, I focused on surface spills of hydraulic fracturing fluid and produced water. The objective is to model a range of spill scenarios that will inform decision-makers and allow them to create more informed prevention, mitigation, and remediation practices to address surface spills, particularly in high risk areas.

When considering the potential for unconventional oil and gas development to impact groundwater resources, there are several contamination pathways one can consider. One such pathway is an accidental surface spill that could transport fluid through the soil profile and potentially reach the groundwater table. The South Platte Alluvial Aquifer represents a high-risk region because the aquifer is relatively shallow and hydrologically connected to the South Platte River. Thus contamination of groundwater has the potential to also impact surface water quality. Colorado may increasingly turn to groundwater as a drinking water source as the population grows, shortages become more severe, and agriculture, municipalities, industry, and other western states compete for water. By choosing to focus on the more probable groundwater contamination pathway, this work aims to evaluate the risks associated with unconventional petroleum activities and focus on how these risks can be minimized and managed to allow for continued oil and gas development while maintaining water quality.

The goals of the produced water modeling study were to identify the minimum spill size which resulted in an impact to groundwater quality and to see how storm events would impact this “spill size threshold.” Results showed that areas with shallow groundwater tables less than 10 ft deep may be at risk for groundwater impacts due to large produced water spills or if a large storm occurs immediately following a produced water spill. Typical sized spills and typical

storms posed low risk. For the hydraulic fracturing fluid spills, I studied the chemical interactions between different additives and assessed the importance of accounting for these interactions when modeling these spills. I found that co-chemical interactions can have a substantial impact on transport of hydraulic fracturing fluid spills. The importance of accounting for these co-chemical interactions and the exact interactions that you would need to represent depends on the composition of the stimulation fluid, initial concentrations of the additives in the hydraulic fracturing fluid, the soil type of the spill site, depth to groundwater at the site, and spill size.

Previous work on groundwater contamination pathways due to oil and gas activity focused on methane and hydraulic fracturing fluid migration through the deep subsurface to shallow groundwater aquifers. While several studies have considered surface spills as a potential contamination pathway, I am not aware of any studies specific to Colorado that have gone beyond statistical analysis of spill data. This research provides advances in the field of groundwater modeling of surface spills associated with oil and gas activity through the shallow subsurface. By helping to identify the conditions under which a surface spill of produced water or hydraulic fracturing fluid would impact groundwater quality of the South Platte Alluvial Aquifer, this work will aid in improving best management practices so that decision-makers can be better prepared to address accidental releases in Colorado.

## **CHAPTER 1**

### **INTRODUCTION**

The powerful combination of hydraulic fracturing and directional drilling has revolutionized the energy portfolio of the United States. Beginning in 2004, these two technologies allowed oil and gas operators to extract hydrocarbons from shale reservoirs that were previously uneconomical and technically infeasible to access. Hydraulic fracturing, or the pumping of large volumes of engineered fluids into the subsurface to fracture rock, increases the permeability of shale and allows the oil and gas to flow from the formation to the surface. Directional drilling, the practice of installing wells in a variety of non-vertical orientations, allows petroleum engineers to contact a larger area of the subsurface and in turn, extract greater amounts of hydrocarbon. In general, these technologies target “unconventional” sources of hydrocarbon that would not be able to be extracted using traditional methods. As a result of these technologies, unconventional oil and gas “boomed” in the U.S. From 2004 to 2010, shale gas ballooned from several to 23% of all U.S. dry gas production; by 2035, shale gas production is expected to make up almost 50% of U.S. dry gas production (EIA, 2014).

Although there are clear economic and resource-security benefits to unconventional oil and gas development, intense scientific and public debate has arisen over the potential risks to water resources associated with this activity. Public concern seems to focus on risks to groundwater because it is outside the control of the average citizen and can be an expensive problem (Rahm and Riha, 2014). The major potential pathways for hydraulic fracturing and oil and gas activity to impact groundwater quality include methane and fluid migration from hydraulically fractured target formations (Flewelling and Sharma, 2014; Llewellyn et al., 2015; Reagan et al., 2015; Rutqvist et al., 2013), methane and fluid migration due to wellbore leakage (Burton et al., 2016; Darrah et al., 2014; Davies et al., 2014; Hildenbrand et al., 2016; Vidic et al., 2013; Zhang et al., 2014), buildup of toxic and radioactive materials in soil or stream sediment at discharge or spill sites (Akob et al., 2016; Lauer et al., 2016), and surface water or groundwater contamination due to accidental spills or leaks (Akob et al., 2016; Drollette et al., 2015; Gross et al., 2013; Lauer et al., 2016). There is still ongoing research assessing these contamination pathways and whether or not they warrant high public concern. Although there are

several ways for oil and gas activity to potentially impact groundwater quality, a surface spill and subsequent leakage into a shallow groundwater aquifer is the most likely groundwater contamination pathway (Groat and Grimshaw, 2012; Metzger, 2011). Over the last 13 years, 10,300 oil and gas related spills have occurred in New Mexico (Center for Western Priorities, 2015) and 3,900 brine<sup>1</sup> spills have been reported in North Dakota since unconventional oil activity surged in 2007 (Lauer et al., 2016). From 1993 to 2003, 16,906 fluid releases were reported to the Oklahoma Corporation Commission (Fisher and Sublette, 2005). 76.1% of the fluid releases involved oil or saltwater and 34% of recent oil or saltwater releases resulted in reported injury to environmental receptors (surface water, crops, livestock, soil, fish, or wildlife) (Fisher and Sublette, 2005).

## **1.1 Objectives and scope of work**

In this thesis, I present contaminant fate and transport simulations of surface spills, the most likely pathway for groundwater contamination during oil and gas production operations with four primary objectives: (1) to evaluate whether or not spills of aqueous fluids pose risks to groundwater quality in the South Platte aquifer system, (2) to identify the key hydrologic and transport factors that determine these risks, (3) to develop a screening level methodology that could be applied at other sites and for various pollutants, and (4) to demonstrate the potential importance of co-contaminant interactions using selected chemicals in hydraulic fracturing fluid. I focused on the South Platte Alluvial Aquifer, which is located in the greater Denver metro area and overlaps a zone of high-density oil and gas development.

I considered two different fluids that could be released during a surface spill at an oil and gas production site: produced water and hydraulic fracturing fluid. Produced water is water originally found in the geologic formation which flows to the surface, usually commingled with natural gas or oil. Hydraulic fracturing fluid is the engineered fluid pumped downhole to induce fractures in the target formation. For the produced water simulations, I sought to identify the spill-size risk threshold, the minimum spill volume per area required for there to be an impact on groundwater quality in the South Platte Alluvial Aquifer. I also considered how storm events changed this spill size risk threshold. Benzene was used as the marker contaminant for the

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<sup>1</sup> Here, brine and saltwater are equivalent to produced water. Produced water is water originally found in the geologic formation which flows to the surface, usually commingled with natural gas or oil.



produced water spills because of its relative abundance in produced water, known toxicity and MCL, and relatively high mobility. I acknowledge that there are other pollutants in produced water that are regulated and could pose risk to groundwater quality. Because this study is meant to develop a screening methodology useful for practitioners, I chose to explore one particular contaminant in-depth.

The purpose of the hydraulic fracturing fluid spill simulations was to assess the importance of accounting for co-contaminant interactions when modeling these spills. Co-contaminant interactions were largely considered in terms of biocidal and salt impacts on degradation of the three chemical additives glutaraldehyde, polyethylene glycol, and polyacrylamide. These three additives were chosen because they represent three different types of compounds (biocide, surfactant, and friction reducer), are common constituents of hydraulic fracturing fluid, and experimental data were available regarding their interactions. Because no U.S. Environmental Protection Agency (EPA) maximum contaminant levels (MCLs) exist for these three contaminants, risk was evaluated by using a hazard quotient (HQ) risk evaluation approach when toxicological data were available. I did not consider co-chemical interactions in produced water although previous studies suggest that the presence of salts and other hydrocarbons may impact the behavior of benzene.

In this study I assess factors and outputs that relate to risk; I define high risk as concentrations exceeding EPA limits reaching groundwater or corresponding to hazard quotients greater than 1. The inherent assumption is that infiltrating spill water that reaches the groundwater table at concentrations greater than regulatory standards will be of concern to policy makers and/or the general public, and thus these spills pose risk to groundwater quality. Subsequent mixing, dilution, and reactions in the aquifer are not considered in this research. The findings discuss what conditions control whether the spill reaches groundwater, and what processes are important to consider when modeling these spills.

Although this work focuses on one aquifer in Colorado, the results should be useful to those who wish to conduct similar studies in other regions since the modeling methodology would be similar. For example, I anticipate high interest in California, where containment requirements are far less strict than in Colorado, and thus the risk of spills infiltrating into the subsurface is greater.

The remainder of this chapter is organized as follows: Section 1.2 is a thorough literature review on topics of relevance to my thesis, Section 1.3 describes the study area, Sections 1.4 and 1.5 describes the occurrence and composition of spills, and Section 1.6 describes the organization of the thesis.

## **1.2 Literature review**

There have been several studies examining surface spills associated with oil and gas development and their potential to affect groundwater quality. These studies are summarized below.

U.S. EPA (2015b) analyzed spills relevant to hydraulic fracturing across the U.S.; the study utilized data on hydraulic fracturing-related spills, which they defined to be spills that occurred on or near the well pad site during pre-mixing, mixing and injection, or recovery of fluids after injection of hydraulic fracturing fluids. Although the spills were hydraulic fracturing-related, the actual released fluid could have been flowback water, produced water, hydraulic fracturing fluid, freshwater, recycled produced water, treated produced water, chemicals, or hydrocarbons. Flowback water is water immediately produced from the well following stimulation; it is mostly composed of the hydraulic fracturing fluid operators sent downhole. The spills occurred from January 2006 to April 2012 and the data came from nine states with online databases, nine hydraulic fracturing service companies, and nine oil and gas operators. From the original list of over 36,000 spills, about 12,000 spills contained insufficient information for the authors to determine whether or not the spill was related to hydraulic fracturing. Of the remaining spills, 457 hydraulic fracturing related spills were identified. The agency found that it was often difficult to determine whether or not the spill was related to hydraulic fracturing activities (U.S. EPA, 2015a). The 457 spills occurred in 11 different states, with the largest portion (38%) of spill data coming from Colorado, which provided reports with the most detail. After analyzing these 457 spills, U.S. EPA (2015a) found that the most common fluid released was flowback and produced water and there were many low volume (up to 1,000 gallon) spills and few high volume (greater than 20,000 gallon) spills. About 90% of these spills reported whether or not the released fluid reached an environmental receptor — soil, surface water, or groundwater. Of the 457 spills, 32 hydraulic fracturing fluid spills (7%) reached surface water while only one spill (0.2%) reached groundwater.

Gross et al., 2013 studied 77 surface spills of oil and produced water that occurred at oil and gas sites in Weld County, Colorado over a 1-year period (July 2010 to July 2011). The authors only examined spills that reported impact to groundwater. 62 out of the 77 studied spills had measurements of benzene, toluene, ethylbenzene, and xylene (BTEX) concentrations in groundwater prior to or in the beginning stages of the remediation process. Groundwater samples taken within the spill excavation area on the first date of sampling displayed BTEX concentrations 90%, 30%, 12%, and 8% above their respective MCLs. Mean concentrations of benzene and toluene dropped significantly for samples taken outside the excavation area and for later sampling dates. As of May 2012, 84% of the spills were successfully remediated and reported reduced BTEX concentrations.

The U.S. Geological Survey (USGS) has conducted field studies on a couple of sites in the western United States that were impacted by oil and gas development. One study in 2009-2010 conducted electromagnetic geophysical surveys and a surface-water and shallow groundwater sampling campaign in the Prairie Pothole Region over the Williston basin, a top domestic oil and gas producing region located in parts of Montana, North Dakota, South Dakota, and Canada (Gleason and Tangen, 2014). The Prairie Pothole Region contains permanent and seasonal wetlands that serve as ecologically important habitats for a majority of North America's migratory waterfowl. The USGS conducted field studies at three different oil and gas production sites near U.S. Fish and Wildlife Service Waterfowl Production Areas to investigate subsurface migration of brine-contaminated groundwater and to assess the potential for brine contamination to impact wetlands and streams in the study area. These sites contained varying configurations of active and abandoned wells, produced water storage pits, transport lines, and tank batteries. Two of the three sites had previous documented incidents of produced water or brine contamination. Surface water samples were taken from wetlands that were about 1.5 m deep and groundwater samples were taken from monitoring wells. Geophysical methods had exploration depths of 2-7 m and 7.5-60 m, depending on the site.

Geophysical surveys found elevated apparent conductivities near the majority of oilfield equipment and facilities. Groundwater samples taken from several areas with elevated apparent conductivity observations displayed high chloride and high specific conductivity measurements, indicating likely brine contamination. Strontium isotope data also confirmed that the contamination source was produced water brines. 34 of the 48 surface water and shallow

groundwater samples taken from wetlands and monitoring wells were moderately or extremely contaminated with brine while another 7 were potentially contaminated. Lateral migration of the brine plume was partly controlled by the type of near-surface sediments; at two of the sites, the brine plume migrated 600-800 m through coarse-grained glacial outwash deposits and 400 m through fine-grained clay-rich glacial till. The extent of vertical migration varied at the different sites depending on the structure of the sediment profile. Studies at the two sites with a known history of brine contamination (sampling in 1988-1990 and 2004-2006), showed that brine contamination persisted for at least 20 years at one site and 6 years for another. The source of the brine is thought to be leaching from buried produced water storage pits installed in the mid to late 1960s; therefore, brine contamination has persisted for four to five decades. Because environmental regulations did not require pits to be lined until 1970, it is likely that these pits were unlined.

From 2004 to 2009, the USGS conducted geophysical and groundwater sampling studies to assess the extent of brine contamination in an alluvial aquifer near the East Poplar oil field on the Fort Peck Indian reservation in Montana (Thamke and Smith, 2004). 3,000 people who live near the city of Poplar depend on groundwater from the Quaternary alluvium, lying from a few feet to 130 ft below ground surface, as a drinking water source. The city lies down-gradient from the East Poplar oil field. Brine contamination was first identified in the early 1990s; this follow-up study found that the city's public water supply wells were enriched with brine constituents and brine contamination extended 17.9 square miles. In certain areas of the aquifer, the entire vertical extent (up to 45 feet thick) contained water with high salinity. Water quality varied depending on proximity to potential contamination sources including storage tanks, oil wells, brine-injection wells, pipelines, and pits; because many of these facilities were co-located it was difficult to determine an exact source of leakage.

The USGS intensively studied the hydrogeology at two contaminated oil and gas production and wastewater disposal sites on Skiatook Lake in Osage County in northeastern Oklahoma from 2001 to 2007 (Kharaka et al., 2007; Otton et al., 2007). Osage County is also known as the Osage Indian Reservation. The Osage-Skiatook Petroleum Environmental Research (OSPER) project involved field and modeling studies to characterize the sites and determine the extent of contamination. One site (site A) was actively producing oil and gas from 1913 to 1999 and contained unlined produced water pits, tank battery facilities, a central power

unit (machinery that supplied pumping action to oil wells), other tanks, injection wells, and trenches to convey produced water to pits (Otton et al., 2007). Oil production on the other site (site B) began in 1938 and continues to this day. At site B, there are two injection wells, ten producing wells, and two unlined produced water pits. The unlined pits also receive hydrocarbon releases from accidental leaks. Brine is pumped from the pits to collection tanks, but these pumps occasionally fail (Kharaka et al., 2007).

Field studies at these sites revealed extensive groundwater contamination (beyond surface evidence) due to produced water leakage. At site A, produced water from unlined pits, accidental spills, and intentional surface discharge percolated through permeable sand and colluvium, sandstone, shales, and mudstone and migrated along contacts between permeable and less permeable units. Chloride concentrations were highest near the produced water pits and in low lying areas; subsurface chloride concentrations ranged from less than 30 mg/L to over 1500 mg/L at 15.6 to 20.5 m below ground surface. Contamination also extended into sediment and bedrock beneath the nearby lake (Otton et al., 2007). At site B, produced water from unlined pits and accidental spills penetrated through 3-7 m thick shale and siltstone units creating three interconnected plumes of brine in the subsurface that extended throughout the site. Contamination also extended beneath Skiatook lake. TDS levels were highest closest to the sources of leakage (produced water pits) and ranged from 1,590 to 26,600 mg/L at various monitoring wells drilled across the site. VOCs and BTEX were also present in a couple of wells across the site; of BTEX, benzene was the most dominant component and benzene concentrations ranged from 0 to 1 mg/L (Kharaka et al., 2007).

A couple of modeling studies have considered the potential for surface spills to impact groundwater quality. Fletcher (2012) developed a broad risk assessment framework to analyze the risk of groundwater contamination due to spills of hydraulic fracturing fluid at shale gas extraction sites in Pennsylvania targeting the Marcellus formation. The study defined hydraulic fracturing fluid spills as spills of hydraulic fracturing fluid after mixing and before it is injected downhole, spills of hydraulic fracturing fluid due to well blow outs, flowback water released due to pit overflows or leakage, and flowback water spilled during transportation to a treatment facility. The author surveyed oil and gas experts to gauge hydraulic fracturing fluid spill frequency and volume. From these surveys, Fletcher (2012) defined a moderate spill to be 5,000 gallons and a large spill as 50,000 gallons. Fletcher (2012) then used a stochastic analytical

modeling approach to estimate the potential for these spills to impact groundwater resources. The model was a 3D analytical solution to the advection-dispersion equation solving for the peak concentration at a groundwater well 200, 500, or 5,000 ft from the spill. The model assumes that these volumes were released directly into the aquifer and does not account for transport through the vadose zone. Degradation and sorption were not considered. Fletcher (2012) specified distributions for saturated hydraulic conductivity, hydraulic gradient, porosity, and dispersivity for 4 different aquifer types found in Pennsylvania. Monte Carlo simulations were run varying these four variables and solving for the peak concentration as a ratio of  $C_{\max}$  to  $C_0$  (initial concentration in the hydraulic fracturing fluid). The study did not consider specific chemical additives in the analysis. Results were presented as dilution factors (ratio of  $C_{\max}$  to  $C_0$ ) ranging from  $10^{-3}$  to  $10^{-2}$  for a 50,000-gallon spill for water wells 500-1000 ft from the point source. Because concentrations of chemical additives are generally  $<1\%$ , concentrations on the order of parts per million would be expected to reach water wells. Fletcher (2012) concluded that these levels are high enough to warrant additional research.

Gradient, an environmental consulting firm based in Massachusetts, prepared a report for Halliburton Energy Services, Inc. considering the potential for hydraulic fracturing fluid to affect drinking water sources and cause human health impacts (2013). The report considered a variety of scenarios including wellbore leakage, deep subsurface migration of hydraulic fracturing fluid from target formations to shallow groundwater aquifers, as well as potential impacts (from a drinking water human health perspective) to groundwater and surface water due to unintended surface releases of hydraulic fracturing fluid and flowback water. For their risk assessment of surface spills, Gradient (2013) conducted a broad probabilistic modeling study, adopting a modified version of the EPA soil screening levels methodology (U.S. EPA, 1996a, 1996b). In this model, the concentration of a particular contaminant at a drinking water well is modeled by calculating dilution factors for the unsaturated zone and saturated zones. In this case, dispersion was the only process working to decrease concentration magnitude; neither adsorption nor degradation were considered. Unsaturated zone dilution factors accounted for variability in depth to groundwater across the U.S., spill volume (based on spill data for Pennsylvania), spill depth (calculated from spill volume), and dispersivity. Saturated zone dilution factors accounted for variability in infiltration rates, depth of drinking water wells, source area, and aquifer properties (representing all possible groundwater conditions across the U.S.). The study derived unsaturated

zone dilution factors and relied on EPA derived dilution factors for the saturated zone. The paper utilized Monte Carlo simulations to generate distributions for dilution factors which were then applied to the initial contaminant concentration to estimate the final concentration at a groundwater drinking water receptor. The distribution of concentrations was then used to calculate hazard quotients, indicators for human health risk associated with exposure to a particular chemical.

Overall, the Gradient (2013) authors attempted to be as risk-conservative as possible and model input data were chosen to generate results that would apply to unsaturated and saturated zone conditions all across the country. The modeling study found that the human health risks associated with surface spills related to hydraulic fracturing activity were insignificant based on agency risk management guidelines. Even with their risk-conservative assumptions, dilution seemed to be sufficient to reduce concentrations. In the event a spill occurred, the highest hazard quotient calculated was 0.01, 100 times lower than the level at which health effects would be expected.

This literature review demonstrates that surface spills are clearly a common occurrence during oil and gas production, that production has resulted in environmental impacts in certain cases, and that risk of groundwater contamination is low in certain cases. The two most relevant studies to my research are the Gradient (2013) and Gross et al., (2013) studies. The work by Gradient (2013) suggests contamination is unlikely when considering realistic spills and both vadose zone and ground water transport, although the data is applied at a very coarse scale. The study by Gross et al (2013) suggests that numerous incidents of groundwater contamination from surface spills have already occurred in Weld County, but they did not evaluate causative hydrologic or transport mechanisms. An in-depth study evaluating the factors that control the degree of risk associated with spills related to oil and gas development at scale of an oil or gas “play” (generally regional or sub-regional) has never been conducted. Furthermore, few studies have honed in on Colorado, a major oil and gas state in an arid region with scarce water resources.

For my thesis, I chose to investigate surface spills associated with the Niobrara formation in the Colorado Front Range and to evaluate the relative importance of hydrologic and transport factors that impact whether spills pose risks to groundwater quality. I use conditions representative of the unconfined South Platte Aquifer to ground the study in reality; however, the

primary purpose is to determine the most important factors that impact the risks to groundwater associated with oil and gas spills. A secondary purpose is to present a screening level model that could later be applied at specific sites deemed most vulnerable.

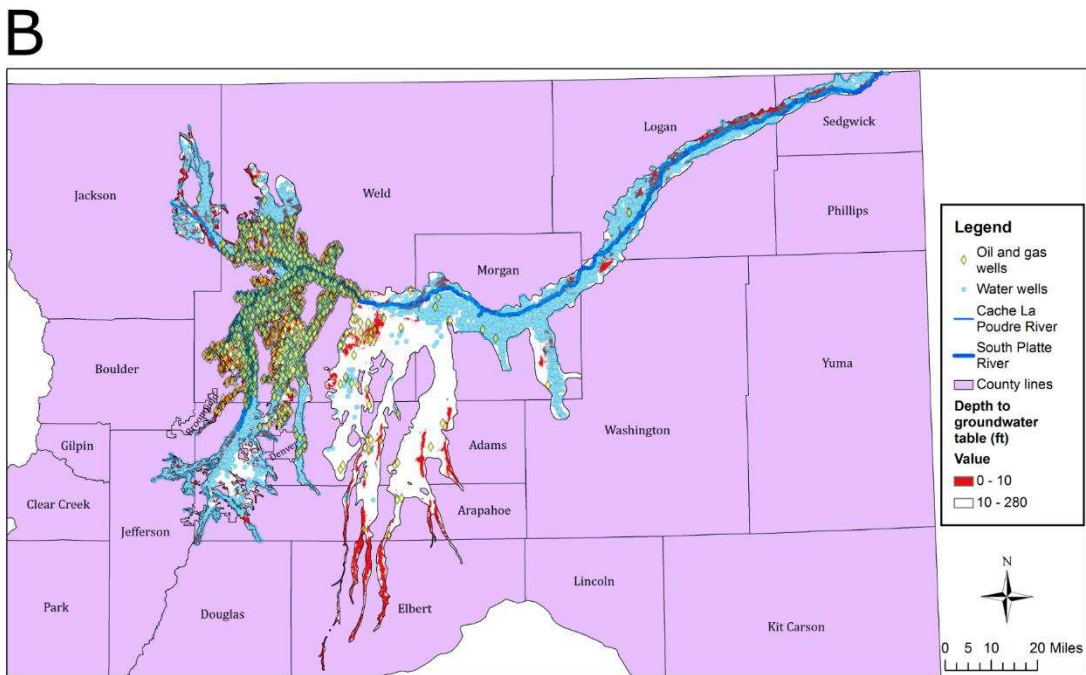
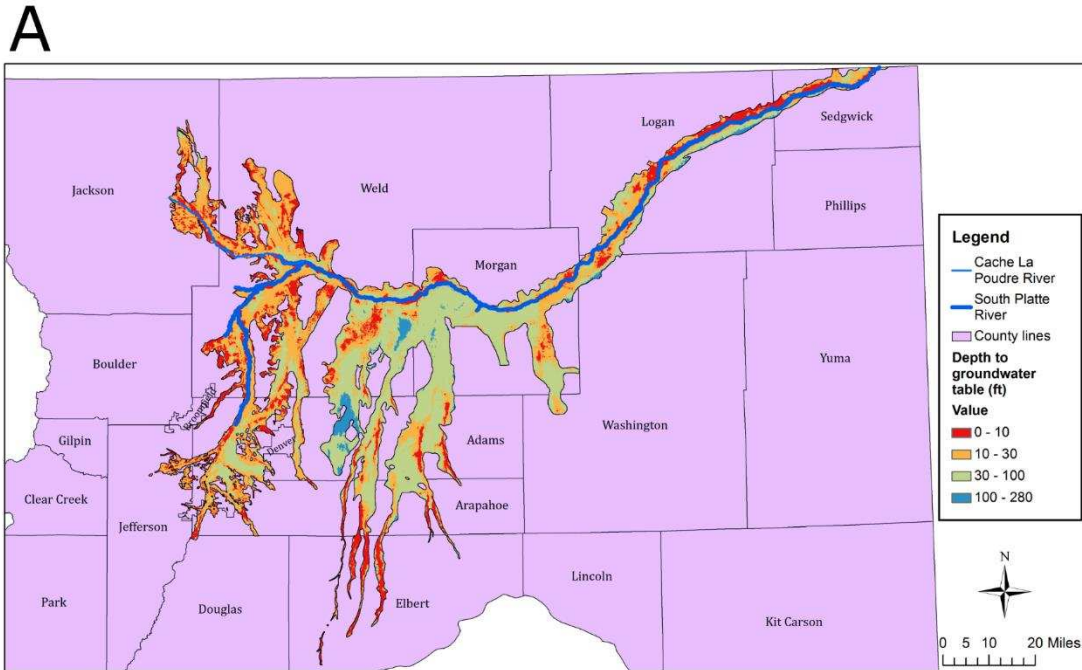
### **1.3 Study area**

Colorado is an interesting study area because discussion of the risks to groundwater resources associated with unconventional oil and gas activity is especially heightened in the arid western United States. According to Freyman, 2014, almost 50% of the wells hydraulically fractured since 2011 were in regions experiencing high or extremely high water stress and over 55% of the wells were located in areas affected by drought. In Colorado, 97% of wells are in regions with high or extremely high water stress (Freyman, 2014).

In addition, Colorado has seen a dramatic increase in oil and gas activity over the past decade. The number of active oil and gas wells increased from around 22,700 wells in January 2002 to 53,651 wells in July 2016 (COGCC, 2016a). Between 2004 and 2014, Colorado crude oil production more than quadrupled while marketed natural gas production increased by 51% (U.S. EIA, 2015). Much of this development is focused in Weld County, located in central-northeastern Colorado. In 2013, Weld County was the top oil producing county in the state (Hunt, 2013). The county contains most of the Wattenberg field, a major oil and gas field in Colorado, with wells commonly producing oil and gas from the Codell sandstone, Niobrara formation, and Muddy “J” sandstone (Higley and Cox, 2007; Nelson and Santus, 2011). Oil and gas activity in Weld County overlaps with the expanding suburban corridor along the Front Range of Colorado as well as agricultural interests towards the east.

The region of high density oil and gas activity in Weld County also intersects with the South Platte Alluvial Aquifer, a key aquifer with over 12,000 groundwater wells (Jones and Cech, 2009). The South Platte Alluvial Aquifer is also hydrologically connected to the South Platte River. Figure 1.1A displays a map of the South Platte Alluvial Aquifer showing depths to the water table (areas in red indicate regions where the groundwater table is less than 10 ft deep). Figure 1.1B also shows locations of drinking water wells in light blue and oil and gas wells in yellow. Clearly, there are many oil and gas wells in areas with shallow groundwater table depths.





**Figure 1.1:** Map of the South Platte Alluvial Aquifer in the Front Range of Colorado with counties of Colorado labeled and shown in light purple with A) depth to groundwater shown in color and B) showing overlap between presence of shallow groundwater tables, oil and gas activity, and water wells. Light blue circles represent water wells drilled into the South Platte Alluvium. The lack of drinking water wells in the South Platte Alluvial aquifer in Adams, Arapahode, Elbert, southern Weld and western Morgan counties may be due to the fact that these wells are administered by a separate Colorado groundwater management entity.

In addition, certain regions of the South Platte Alluvial Aquifer have observed decreases in depth to groundwater. During 2002-2003, an addendum to Colorado water law curtailed pumping from thousands of wells in the South Platte Alluvial Aquifer that lacked authorized augmentation plans, a court approved plan in which a party provides replacement water to the South Platte River to prevent injury to other downstream water users (Wellman, 2015). Reduced pumping, a set of wetter than average years starting in the mid-2000's, greater reliance on surface water sources, and local agricultural and recharge structures have likely led to 88% of wells and 81% of sub-watershed areas exhibiting rising water levels (when trends were significant) (Brown and Caldwell, 2015; Wellman, 2015). From 1993 to 2012, areas with groundwater levels within 20 ft of the land surface observed an average 0.6 ft shallowing of the water table (Wellman, 2015). Another report found on average 3 ft increases in groundwater levels across the lower South Platte River Basin alluvial aquifer from 2005 to 2015 (Donegan, 2015). Shallow groundwater tables are even occurring miles from the South Platte River channel (Donegan, 2015). One region experiencing particularly high water tables are areas near Greeley, La Salle, and Gilcrest, cities that all lie in the Wattenberg field (Brown and Caldwell, 2015; Wellman, 2015). This analysis indicates that there are many areas in the South Platte Alluvial Aquifer where a surface spill may pose a risk to groundwater quality, and where contaminants may also travel to the South Platte River. Overall, potential negative impacts to groundwater quality as a result of oil and gas activity are high-stakes issues in this water stressed region.

#### **1.4 Surface spills in Colorado**

The Colorado Oil and Gas Conservation Commission (COGCC) is an agency within the Colorado Department of Natural Resources (CDNR) that regulates oil and gas industry activities in the state. COGCC has many different functions which include handling permitting of oil and gas wells, conducting inspections of well sites, keeping track of production data, addressing any citizen complaints, and continuing to update regulations as it sees fit. Starting in about 1983, COGCC required spills 5 barrels (bbl, 1 bbl = 42 gallons) or greater in volume or any spill volume that impacted State waters to be reported (SSPA, 2013). In August 2013, the minimum reporting volume for spills occurring outside secondary containment (usually earthen or steel berms) decreased to 1 barrel (Mitsch Bush et al., 2013). There are many regulations and operator best management practices which work to prevent spills from occurring and to avoid spill

volumes from getting out of containment. Such practices include installing liners and steel or earthen berms, constructing surface water diversion structures to accommodate precipitation during storm events, training field truck drivers on ways to avoid leakage, compacting soil on site to limit infiltration, and visually inspecting sites on a regular basis.

Despite the various containment measures implemented at oil and gas sites, spills are still occurring. From 2010-2014, Colorado reported 3,449 surface spills related to oil and gas activity (COGCC, 2016b). During these spills, 18,925 bbl of oil and 142,457 bbl of produced water were released (COGCC, 2016b). Not only are these spills occurring frequently and potentially releasing large volumes, certain spills impact groundwater. In 2013, 22% of spills reported to the COGCC resulted in water contamination with 14% impacting groundwater (Center for Western Priorities, 2013). “Groundwater impacts”<sup>2</sup> are typically suspected if operators encounter saturated porous media while excavating impacted soil or water with an oil sheen. “Impacts” are later confirmed by taking groundwater samples and testing for benzene, toluene, ethylbenzene, total xylene, total dissolved solids, chloride, sulfate, and liquid hydrocarbons (COGCC, 2014, sec. 900). It is quite possible that other hazardous compounds are present but go undetected.

### **1.5 Composition of spills: produced water and hydraulic fracturing fluid**

There are many different fluids that can be accidentally released during these spills. In a study conducted by S.S. Papadopulos & Associates (SSPA) for the COGCC, SSPA found that from January 2010 to August 2013, 78% of oil & gas related spills in Colorado occurred during the production phase. These spills had an average volume of 104 bbls and likely released produced water. Along with oil, produced water is a commonly released fluid since it is usually produced at high rates and volumes, especially during the initial 2 months of production (Bai et al., 2013). Thus, produced water tanks are frequently emptied so that produced water can be transported and disposed of (U.S. EPA, 2015a). Accidental spills during the handling of produced water are very common (SSPA, 2013; U.S. EPA, 2015a). Although the composition of produced water varies by geologic formation, produced water is known for containing many different aliphatic, aromatic, resin, and asphaltene hydrocarbons (Maguire-Boyle and Barron, 2014; Orem et al., 2014). Hazardous volatile organic compounds, semi-volatile organic

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<sup>2</sup> “Groundwater” may refer to soil water or the groundwater table, depending on how the operator chooses to report it.

compounds, and polycyclic aromatic hydrocarbons are also commonly found in produced water (Akob et al., 2015; Lester et al., 2015; Orem et al., 2014). Produced water is also notorious for being very saline and having high values of total dissolved solids (TDS) (Akob et al., 2015; Barbot et al., 2013; Chapman et al., 2012; Maguire-Boyle and Barron, 2014). The Niobrara formation in Colorado with TDS at 22,500 mg/L (Lester et al., 2015) has relatively low TDS compared to other shale formations across the country.

The oil and gas operation phase reporting the second highest frequency of spills was stimulation (7.6% of spills) with an average spill volume of 86 bbls (SSPA, 2013). Spills occurring during the stimulation phase may result in releases of hydraulic fracturing fluid. Hydraulic fracturing fluid usually consists of gels, crosslinkers, breakers, friction reducers, pH adjusters, biocides, corrosion inhibitors, surfactants, clay stabilizers, scale inhibitors, and chemicals for iron control (Stringfellow et al., 2014). Studies have generated lists of the most commonly reported constituents of hydraulic fracturing fluid (Rogers et al., 2015; Stringfellow et al., 2014; U.S. EPA, 2015b). The toxicity of these compounds can vary but the toxicity of many chemicals cannot be evaluated due to a lack of data (Stringfellow et al., 2014; Yost et al., 2016). Waxman et al., 2011 identified 29 chemicals of concern in hydraulic fracturing fluid that included potential carcinogens, hazardous air pollutants, and compounds regulated by the Safe Drinking Water Act. Some of the listed chemicals included methanol, hydrochloric acid, ethylene glycol, acrylamide, phenol, dimethyl formamide, di (2-ethylhexyl) phthalate, and naphthalene (Waxman et al., 2011). However, not all the chemicals listed by Waxman et al., 2011 are regulated (i.e., through EPA maximum contaminant levels or state soil contamination standards); thus, the risk of these pollutants to water resources has not been evaluated.

## **1.6 Thesis organization**

This thesis describes research I have conducted over the past two years that will eventually become two papers. This first paper will discuss modeling produced water spills in the South Platte region of Colorado while the second paper will investigate the importance of accounting for co-contaminant interactions when modeling hydraulic fracturing fluid spills.

### **1.6.1 Evaluating risk to groundwater quality due to produced water spills**

Chapter 2 describes data analysis and simulations conducted to evaluate the risk produced water spills pose to groundwater quality in the South Platte Alluvial Aquifer, and demonstrates a screening level methodology that could be used in other geographic areas or for other shallow aquifer systems. The first step of the study involved determining the distribution of produced water spill volumes and areas for oil and gas sites relevant to the South Platte region. The results of this data analysis provided inputs to the model. Produced water spills were simulated with a vadose zone flow and transport model (HYDRUS) used to predict contaminant concentration in infiltrating water reaching the groundwater table. I determined the spill size risk threshold, minimum spill size necessary for concentrations at the groundwater table to exceed EPA standards. Finally, I considered how different hydrologic conditions, mainly storm events, can impact spill transport and risk.

### **1.6.2 The impact of co-chemical interactions on contaminant transport of hydraulic fracturing fluid spills**

Chapter 3 evaluates contaminant fate and transport of spills of hydraulic fracturing fluid. Because hydraulic fracturing fluids are often complex mixtures of many different compounds that have known impacts on microbial degradation, I investigated how co-chemical interactions impact transport of hydraulic fracturing fluid spills and assessed the importance of accounting for these co-chemical interactions in modeling these spills. For example, biocides are a common component of hydraulic fracturing fluid. If a spill of hydraulic fracturing fluid occurred, the presence of biocides would likely inhibit degradation of itself and other compounds. Furthermore, produced water is often recycled and reused for creating hydraulic fracturing fluid. Residual salinity could decrease degradation rates of hydraulic fracturing fluid constituents. To illustrate the potential importance of these interactions, I chose one particular spill size, representative of a large spill, and simulated transport of three constituents, glutaraldehyde (biocide), polyethylene glycol (surfactant), and polyacrylamide (friction reducer). These three chemical additives were chosen because they are common constituents of hydraulic fracturing fluid and experimental degradation rates accounting for co-chemical interactions were available. Then, I conducted a traditional risk analysis based on the hazard-quotient. With this work, we

help address high public concern and high uncertainty surrounding the chemical behavior and toxicity of the constituents in hydraulic fracturing fluid.

## **CHAPTER 2**

### **EVALUATING RISK TO GROUNDWATER QUALITY DUE TO PRODUCED WATER SPILLS**

#### **2.1 Methods**

I conducted a groundwater modeling study of produced water spills occurring in the South Platte region of Colorado. This study first involved analyzing spill data for produced water spills in Colorado to determine representative spill sizes then simulating spill transport considering a range of chemical behavior and different hydrological conditions.

##### **2.1.1 Data compilation and quality assurance-quality control**

I first analyzed spill data collected by COGCC regarding oil and gas related surface spills in Colorado. Operators are required to report spills to the COGCC whenever 1 barrel (bbl, 1 bbl = 42 gallons) or more of fluids are spilled outside of secondary containment, and for any spill of 5 bbl or more. The operators must fill out a series of forms recording the types of fluid released, spill volumes, spill areas, date of the incident, location, and a description of the event. This information is publically available through the Colorado Oil and Gas Information System (COGIS), an online database with a graphical user interface that allows a user to search for spills by date, location, well API ID number, etc. and download pdfs containing information about a particular spill. Because the COGCC does not offer a bulk download of all spill data available, I had to painstakingly extract data from various sources that had scraped COGIS data with varying degrees of success. The AirWaterGas NSF Sustainability Network Data Portal (AWG Sustainability Network, 2015), S.S. Papadopoulos and Associates dataset (SSPA, 2013), and the COGCC dataset (COGCC, 2016c) were the three datasets used for different parts of the spill analysis. In this data analysis, I only considered produced water spill volumes; I did not include oil spill volumes.

##### **2.1.1.1 Quality assurance-quality control methods for AirWaterGas Data Portal**

The AirWaterGas NSF Sustainability Network Data Portal (AWGDP) is a publically available tool developed by researchers at UC Boulder as part of the NSF Sustainability Network. Of the three datasets, the AWGDP is the most comprehensive including information on

7,729 spills that occurred in Colorado from 1990 to 2015. Quality assurance-quality control (QA/QC) methods for the AWGDP dataset involved removing all spills that happened after March 31, 2014. COGCC changed their spill reporting procedure, which created difficulties for the AWGDP automated scraping code and thus made spill data after March 31, 2014 largely incomplete. 908 spills were removed during this step. I also checked for duplicate spill reports within the AWGDP dataset and none were found.

Prior to late April 2014, the form that operators filled out to report spills to the COGCC required operators to categorize and report the fluid spilled as oil, water, or other. These limited options often lead to ambiguities regarding what fluid was released. For example, water can refer to produced water, fresh water, or hydraulic fracturing fluid. For the AWGDP dataset, produced water spills were defined as spills with nonzero values reported for water spilled. I studied 20 spill reports from the AWGDP dataset and 18 (90%) had sufficient information to determine that produced water was the released fluid; this test increases confidence that these spills were truly produced water spills. However, I was unable to differentiate between flowback water and produced water. I removed any spills that did not have sufficient information to categorize as a produced water spill (see Appendix A). Spills that did not have reported incident dates were removed; no reported incident date could indicate that the spill was historical (i.e., discovered after the release occurred and during unrelated activities) and thus reported volumes and areas are more likely to be inaccurate.

#### **2.1.1.2 Quality assurance-quality control methods for COGCC dataset**

The COGCC dataset is a publically available bulk download of more recent spill data prepared by the COGCC and updated every month. The data used for this analysis was last updated on January 4, 2016, and consisted of 2,738 Colorado spill records that occurred from 2009 to 2015. QA/QC of this dataset involved removing 1,512 duplicate spill reports.<sup>3</sup> The COGCC dataset contained detailed information about the type of released fluid; updated spill reporting at the COGCC required operators to specify the contents of the spill as oil, condensate,

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<sup>3</sup> To ease the spill reporting process for operators, around April 2014, COGCC changed its document management process. The COGCC began allowing operators to submit initial spill reports with a spill volume range and later submit final spill reports with a single number for the spill volume. Each spill is assigned a tracking number and each spill document (initial report, final report, supplementary material) is also assigned a number. Because the COGCC dataset includes the initial spill reports, one spill could have multiple entries in the dataset. Duplicate spill reports were disregarded and the information from the final spill report was used for data analysis.



flow back fluid, produced water, exploration and production waste, or drilling fluid. I used spills from the COGCC dataset that reported produced water as the released fluid. Additional information on the QA/QC procedure can be found in Appendix A.

#### **2.1.1.3 Quality assurance-quality control methods for SSPA dataset**

The SSPA dataset included spill reports that were downloaded and organized by S.S. Papadopoulos and Associates for a technical report the environmental consulting firm did for the Colorado Oil and Gas Conservation (COGCC, 2016b). The dataset was obtained from SSPA and consisted of 1,416 spills that occurred from 2010 to 2013. Consultants at S.S. Papadopoulos read the spill reports submitted to the COGCC and determined the phase of operations during which the spill occurred. In the SSPA dataset, spills designated as the “Production” phase and with nonzero values reported for water spilled were defined to be produced water spills. 641 spills met these requirements. After reading through 20 of these spill reports, I found that 17 reports had sufficient information to determine that the released fluid was produced water (see Appendix A for further information). Similar to the AWGDP dataset, I was unable to differentiate between flowback water and produced water. There were no duplicate spills within the SSPA dataset and all spills had a reported incident date.

#### **2.1.2 Produced water spill history**

To see how many produced water spills had occurred in Colorado annually over the past 50 years, I analyzed 3,724 unique quality-checked spills: 3,373 from the AirWaterGas Data Portal, 343 spills from the COGCC dataset, and 8 spills from the SSPA dataset. Table A.1 summarizes the number of spills removed from each dataset during the QA/QC process.

#### **2.1.3 Produced water spill characterization**

To get a sense of the range of spill sizes that occur in the field, I analyzed spill volume and spill area data from the SSPA and the COGCC datasets. I used these datasets because they both contained measurements and units of spill area; the AWGDP dataset had incomplete area information. Spill area is a necessary parameter for accurate vadose zone modeling, as described in more detail later.

I removed spills that did not have spill area measurements, did not report spill area units, or had incorrect units of measurement for area (e.g. feet, inches, yards, cubic feet). This QA/QC step resulted in the removal of 560 spills. After our QA/QC procedures, 424 produced water spills (123 spills from the SSPA dataset and 301 spills from the COGCC dataset) remained containing quality-checked information on spill volume and spill area. Following personal communication with practitioners in the oil and gas industry, it became clear that spill size (i.e., volume and area) may be correlated to the targeted geologic formation, flowrates, and onsite equipment. To capture a spill distribution that would be representative of spills that could impact the South Platte Alluvial Aquifer, I chose to only consider the spills that occurred in counties intersecting with the South Platte Alluvial Aquifer (i.e., geology, flowrates, and equipment used are similar for shale gas production in the Niobrara). The resulting subset of 90 unique surface spills (85 from the COGCC dataset and 5 from the SSPA dataset) was used for spill characterization (see Appendix A for additional information). While the goal was to only analyze spills of untreated produced water, and although I did my best to QA/QC the data, because of reporting uncertainty, I acknowledge the possibility that this data subset may contain a few spills of other fluids (e.g. frac water, treated produced water, flowback water). EPA ran into a similar issue when conducting their national study; the agency commented that it was often difficult to discern what fluid spilled and during what operational phase (2015a).

I calculated net spill volumes for the 90 spills using total volume spilled and recovered volume data. If a recovered water volume was not reported, I assumed no water was recovered. The net volume released was calculated by subtracting the recovered volume from the total volume spilled. If the calculated net volume was negative (more water was recovered than originally spilled), I assumed a net volume of 0. I divided the net spill volume by the area to get the spill volume per area, which yields a total depth of spill (useful for model input). The sorted spill volume per area or spill depths with linear interpolation were used to compute the 50<sup>th</sup> to 100<sup>th</sup> spill percentiles, in increments of 5. Percentiles smaller than the 50<sup>th</sup> were not computed because they were deemed to pose little or no risk to groundwater (explained in section 2.2). I note that these spill percentiles were calculated based on a limited dataset of spill observations and not based on a theoretical distribution.

#### **2.1.4 Model**

The model used in this study was HYDRUS-1D (Simunek et al., 1998). The model was set-up and parameterized to simulate produced water spills and represent areas overlying the South Platte Alluvial Aquifer.

##### **2.1.4.1 Description**

I chose to use HYDRUS-1D to model spill infiltration through the vadose zone. HYDRUS-1D is a one-dimensional finite element groundwater model capable of modeling water and solute flow through variably saturated porous media (Simunek et al., 1998). It is a cost-free, relatively easy to use (with a graphic user interface), and commonly used by practitioners who conduct vadose zone flow and transport analyses. Because this work presents a screening level model of risk associated with spills rather than a site-specific analysis and numerous simulations were required, use of a 1-D model was appropriate. The program numerically solves the Richard's equation for variably saturated flow using Galerkin-type linear finite element and implicit finite difference schemes (Simunek et al., 1998). It describes unsaturated soil hydraulic behavior using van Genuchten (1980) and Mualem (1976) constitutive equations and parameterizes these equations using soil hydraulic properties data for each of the U.S. Department of Agriculture (USDA)-based soil texture classes (Carsel and Parrish, 1988; Schaap et al., 2001). The advection-dispersion equation with linear, reversible partitioning between water, air, and soil phases, and first order transformation of contaminants, is used to model the solute transport.

##### **2.1.4.2 Model set-up**

The model domain consisted of a hypothetical but realistic unsaturated zone, soil surface to the groundwater table. Groundwater table depths of 2 ft and 10 ft were specified; these depths are representative of high-risk groundwater levels in the South Platte Alluvial Aquifer in the Front Range of Colorado. I assume that the unsaturated zone is homogeneous (soil type was based on realistic soil survey data as described below) and initially hydrostatic. I assumed a single porosity system with no hysteresis.

To specify the surface spill flux, I assume that the spill infiltrates at a rate equal to the long-term infiltration capacity of the soil (i.e., at a rate equal to the saturated hydraulic

conductivity). In other words, the initial impacts of dry-soil capillarity are neglected, which implies the soil surface saturates very quickly as the spill begins. Using the saturated hydraulic conductivity for the spill infiltration rate may underestimate the short-term water velocity through the vadose zone. Spill duration was determined using the assumed infiltration rate and the spill depth (i.e., volume per area). Fluid infiltrates through the top boundary for the duration of the spill. After the spill, no water or solute entered the system. The bottom boundary condition for water flow was set assuming a constant pressure head equal to the atmospheric pressure head (a head value of zero with the convention used) to represent the groundwater table. For solute transport, the upper boundary condition was specified using a concentration flux and a zero concentration gradient was used for the lower boundary condition. I assumed that no pollutants were present in the vadose zone before the spill. The Crank-Nicholson time weighting and Galerkin finite element space weighting schemes were used for the solute transport simulations.

Simulations were run for times varying from one month to one year with time steps varying from  $3.6 \times 10^{-12}$  s to 36 s depending on how quickly the solution converged. Run times were determined by studying model output and ensuring that both the water balance error and concentration balance error did not exceed 2%. Details on iteration criteria and model tolerances are shown in Table A.2. Profiles were spatially discretized into 0.01 ft elements for the 10-ft and 0.002 ft for the 2-ft simulations, which resulted in good numerical performance.

#### **2.1.4.3 Aquifer parameterization**

I assumed sandy loam soil type, which out of the 12 USDA-based soil texture classes, best represents the South Platte Alluvial Aquifer. Average soil hydraulic parameters representative of sandy loam soils were taken from Carsel and Parrish (1988) to parameterize the van Genuchten (1980) and Mualem (1976) equations. These soil hydraulic parameters include residual water content, saturated water content,  $\alpha$ , and  $n$ ; residual water content is the water content retained in the soil even at high suction, saturated water content is the water content of the soil at saturation,  $\alpha$  is an empirical parameter related to fluid interfacial properties and effective pore size, and  $n$  is an empirical constant related to pore size distribution.

At most sites, surface soil is removed during well-pad construction (based on personal experience visiting well pads), so organic carbon is projected to be relatively low. I assumed a

fraction of organic carbon of  $10^{-4}$ , which is the value recommended by the EPA for aquifers containing low organic carbon (U.S. EPA, 2004; Wiedemeier et al., 1999). For most pollutants, higher organic carbon will cause transport retardation via sorption, so this assumption represents conservative transport with respect to risk to an underlying aquifer. Sandy loam dry bulk density values were taken from Linsley et al., 1982 and Yu et al., 1993. Dispersivity was set to 0.33 ft for the 10-ft simulations and 0.066 ft for the 2-ft simulations, based on dispersivity values suggested in Gelhar et al., 1992.

#### **2.1.4.4 Chemical-specific parameterization**

For the produced water simulations, I chose to focus on contaminant transport of benzene. Benzene is a common constituent of produced water (as previously discussed), known carcinogen, federally regulated, and mobile. Data for benzene is also relatively abundant compared to most organic pollutants in produced water. If high concentrations of benzene from surface spills reach the groundwater table, this finding would likely mandate remedial action. Benzene in terms of its chemical behavior can be representative of the other BTEX compounds. The initial benzene concentration in the spill was calculated by taking the average benzene concentration measured in produced water streams 90 days after hydraulic fracturing at 3 different well locations in southeastern Pennsylvania; benzene concentrations ranged from 0.2-0.36 mg/L and I used the average ~0.28 mg/L for the initial benzene concentration.

Simulations in this study, unless otherwise noted, accounted for first order aerobic microbial degradation and instantaneous, reversible partitioning to soil and air phases. Literature values of organic carbon-soil partitioning coefficients, aerobic microbial degradation rates (due to the aerobic nature of the unsaturated zone), and Henry's constants measured in aqueous environments were obtained from multiple sources (Howard et al., 1991; Mackay et al., 2006; Montgomery, 2007; Rifai and Newell, 1998) and median values were chosen for simulations. To consider conservative scenarios and account for variability in benzene's chemical behavior, in some cases, benzene was run as a conservative solute without any degradation or sorption. Benzene may not degrade or exhibit a very low degradation rate if microbes preferentially degrade other hydrocarbons or organics present in the produced water (Deeb et al., 2002) or the system goes anaerobic due to low diffusive flux of oxygen in saturated soil conditions. In this way, median aerobic benzene degradation rates (half-life of about 10 days) represent a best case

scenario in terms of benzene removal while conservative transport represents a worst case scenario. Benzene may sorb very little to soils with low organic carbon content. Thus, I considered scenarios in which benzene was highly mobile and did not sorb or degrade. Although conservative transport represents a worst-case scenario, conservative transport may be a reasonable assumption in certain cases (explained in section 2.2). Table 2.1 lists the chemical and aquifer specific parameters used for the produced water simulations.

**Table 2.1:** Chemical and soil-specific parameters used for HYDRUS spill size simulations

		Value	Source
Chemical-specific parameters	Initial benzene concentration (mg/L)	0.283 (median)	(Hayes, 2009)
	Organic carbon-soil partitioning coefficient (dimensionless)	0.771 (median)	(Mackay et al., 2006; Montgomery, 2007)
	Aerobic microbial degradation rate (d <sup>-1</sup> )	0.068 (median)	(Howard et al., 1991; Kappeler and Wuhrmann, 1978; Mackay et al., 2006; Montgomery, 2007)
	Henry's constant (dimensionless)	1.614 (median)	(Mackay et al., 2006; Montgomery, 2007)
Aquifer-specific parameters	Fraction of organic carbon (dimensionless)	10 <sup>-4</sup>	(U.S. EPA, 2004; Wiedemeier et al., 1999)
	Saturated hydraulic conductivity (m/hr)	0.0442083	(Carsel and Parrish, 1988)
Soil hydraulic parameters	Residual water content (dimensionless)	0.065	(Carsel and Parrish, 1988)
	Saturated water content (dimensionless)	0.41	(Carsel and Parrish, 1988)
	$\alpha$ (1/m)	7.5	(Carsel and Parrish, 1988)
	n (dimensionless)	1.89	(Carsel and Parrish, 1988)

#### 2.1.4.5 Storm simulations

Storm events can flush spills to locations deeper in the vadose zone, but also dilute concentrations. In the storm simulation scenarios, idealized storm events occurred for a realistic duration immediately following a spill, which would be the “worst-case” condition (i.e., prior to significant evaporation and redistribution). Driscoll et al., 1989 used precipitation gage data from across the U.S. to calculate statistics to characterize storms. Because the average storm in Fort Collins, CO is 10.36 hrs long (Driscoll et al., 1989), I chose to consider precipitation frequency data estimated for a 12 hour storm at the Greeley UNC station (ID 05-3553) in Greeley, CO

(Perica et al., 2013) (for additional information see Appendix A). I assumed a constant precipitation rate during the 12 hr storm. Below, Table 2.2 summarizes the precipitation rates used for the various storm frequencies.

**Table 2.2:** Precipitation rates and total precipitation depth for various storm frequencies used to represent storm events in the model simulations.

Storm frequency	Precipitation rate (mm/hr)	Total precipitation (mm)
1 yr	3	36
5 yr	4	48
10 yr	5	60
25 yr	7	84
50 yr	8	96
100 yr	9	108
500 yr	13	156

I note that the storm total precipitation depths are similar to monthly total precipitation data. Table 2.3 displays the average and 75<sup>th</sup> percentile of monthly total precipitation based on measurements taken at the NOAA Greeley UNC station (ID 05-3553) in Greeley, CO from 1981 to 2010. These data do not account for snow. Although I explore the impact of different storm intensities, it is possible that similar effects could be expected for sustained rainy periods over days, weeks, or months, disregarding evapotranspiration between storms. For context, total precipitation from a 5-year storm (48 mm) is similar to the average monthly precipitation for April. An average May, the wettest month of year for this station, is equivalent to a 10-year storm while total precipitation for an average spring (April to June) is very similar to a 500-yr storm.

**Table 2.3:** Average monthly total precipitation and 75th percentile of monthly total precipitation based on precipitation measurements taken at the NOAA Greeley UNC station 05-53553 from 1981 to 2010. The data below do not account for snow precipitation.

Month	Average monthly total precipitation (averaged from 1981 to 2010) (mm)	75 <sup>th</sup> percentile of monthly total precipitation (1982-2010) (mm)
January	12.19	19.56
February	10.16	15.49
March	28.45	33.78
April	45.97	68.33
May	60.71	75.18
June	49.02	60.45
July	42.67	61.98
August	37.08	45.97
September	28.19	43.43
October	25.65	36.32
November	18.8	26.42
December	14.22	19.56

## 2.2 Results and Discussion

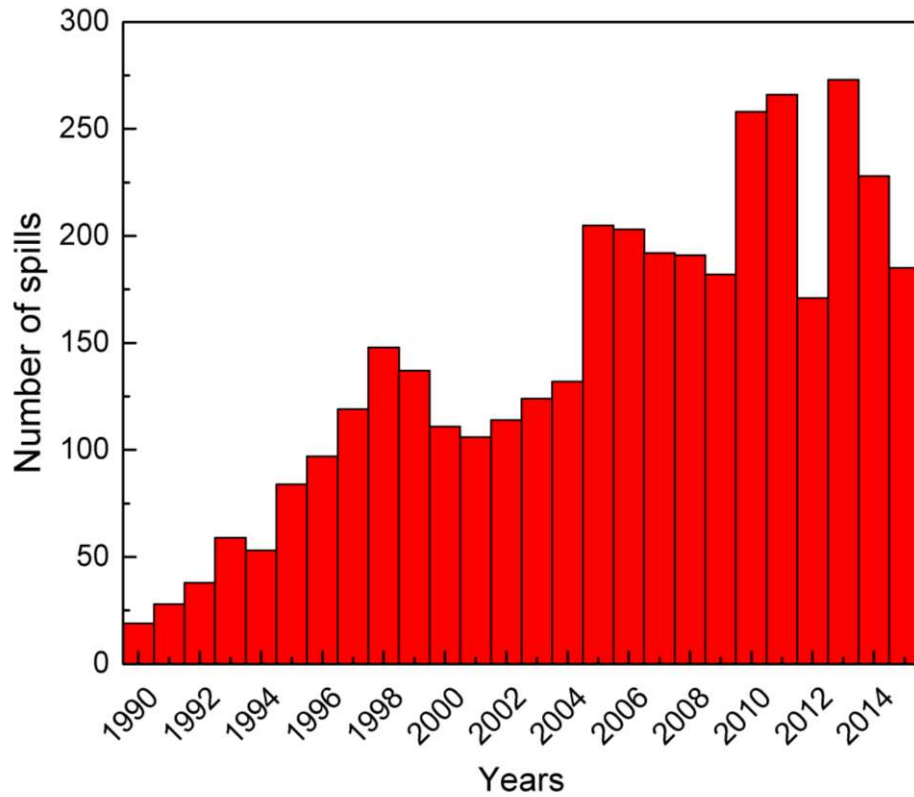
Produced water spill data were analyzed to determine the range of spill volumes and areas observed in regions overlying the South Platte Alluvial Aquifer. These data provided model inputs to simulate representative produced water spills and determine the risk these spills pose to groundwater quality. I also considered how storm events would impact risk of groundwater contamination.

### 2.2.1 Spill analysis

The number of spills has generally increased over time, and the number of spills increased drastically following the beginning of the shale gas boom in 2004, as shown in Figure 2.1. However, this trend may also be due to the fact that spill reporting has become more stringent over time; Colorado oil and gas regulations underwent major changes in 2008, 2012, and 2013 (Hunt, 2013). Overall, 185 produced water spills occurred in Colorado in 2015.

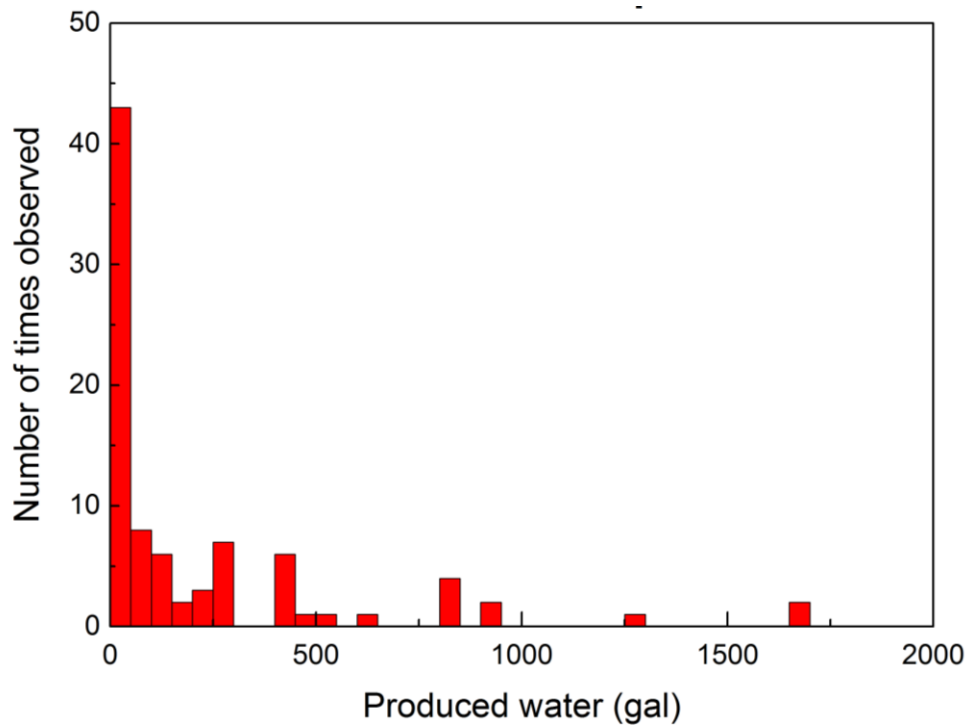
For produced water spills occurring in areas overlying the South Platte Alluvial Aquifer and reporting both spill volume and spill area data, net released spill volumes ranged from 0 to 8400 gallons (200 bbl) with an average of 387.8 gallons or ~9.2 bbl. A majority (62) of the 90 spills have volumes below 250 gallons, including 26 spills with net 0 volume spilled. 6 spills had





**Figure 2.1:** Number of produced water spills that occurred in Colorado from 1990 to 2015.

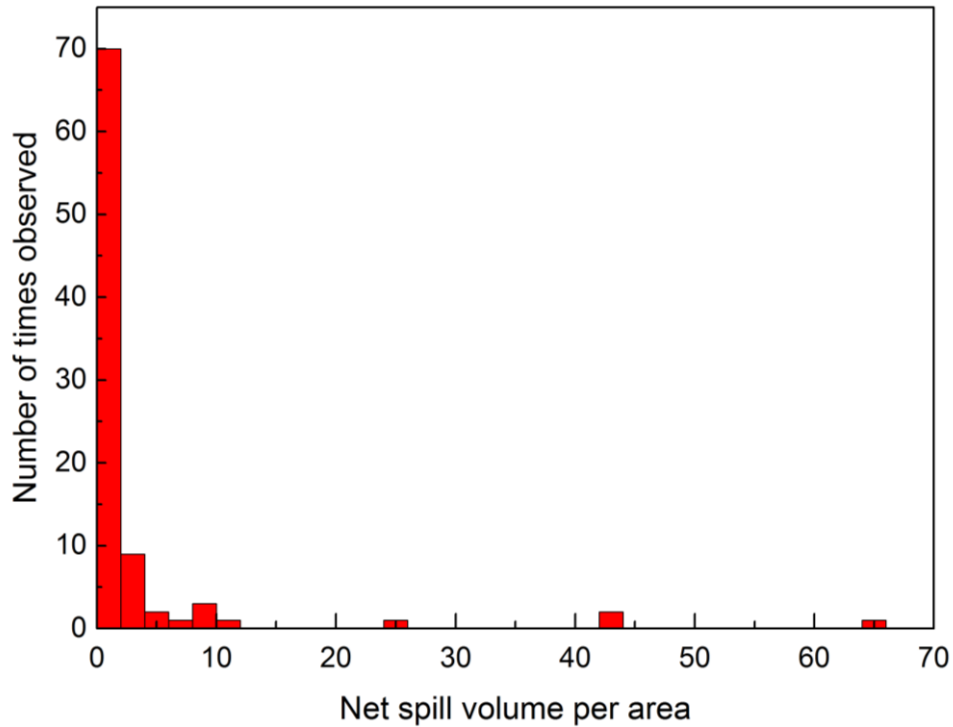
volumes exceeding 1000 gallons. The overall trend of many low volume and few high volume spills as shown in Figure 2.2, is consistent with conclusions from previous studies (Fletcher, 2012; U.S. EPA, 2015a). After analyzing 457 hydraulic fracturing related spills, (U.S. EPA, 2015a) found that the most common fluid released was flowback and produced water and there were many low volume ( $\leq 1,000$  gallon) spills and few high volume ( $>20,000$  gallon) spills. Out of the 1,148 Colorado spills SSPA (2013) analyzed with reported spill volumes, 332 spills (29%) had total spill volumes of 10 bbl (420 gallons) or less; differences between our analysis and SSPA (2013) are likely due to the fact that SSPA (2013) considered the total spill volume, not the net spill volume. In the Gross et al., (2013) analysis of 77 surface spills in Colorado, produced water spill volumes were reported for only 5 spills. The volumes ranged from 1 to 28 barrels with an average spill volume of 7 barrels. The maximum and average spill volumes in our dataset were higher, even though I accounted for recovered volumes. The differences are likely due to the fact that Gross et al., (2013) had volume data available for only 5 spills.



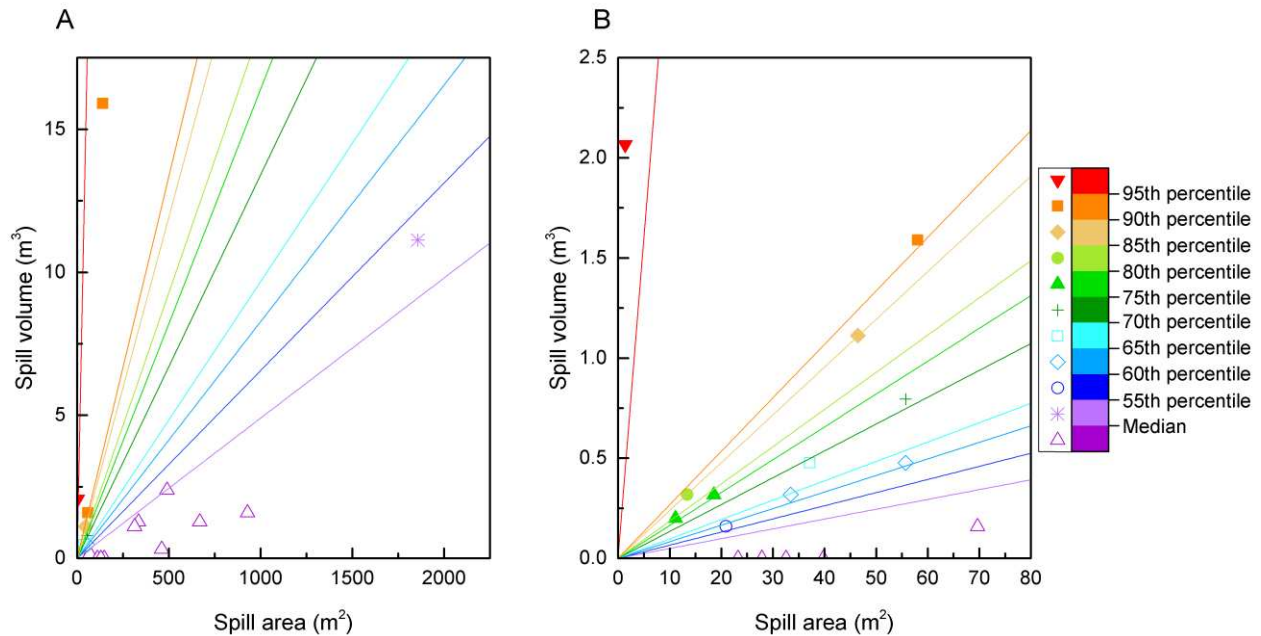
**Figure 2.2:** Histogram of the net (total volume – recovered volume) produced water spill volume for spills occurring in counties overlying the South Platte Alluvial Aquifer. These data exclude 3 spills with volumes above 2800 gallons for visualization purposes.

Net spill depth was similarly distributed to net volume spilled with many low values and a few high values, as shown in Figure 2.3. For the produced water spills, 80 out of 90 spills had net spill depths less than 5 cm. The average spill depth was ~3.1 cm and the median spill depth was 0.38 cm. Figure 2.4 displays the produced water spills in spill volume-spill area space. Similar to Figure 2.3, we can see many spills lower than the median spill depth. There are very few large volume spills and most spills tend to have low volumes. In comparison, spill depths (depth of impact) reported for 55 of 77 spills in Gross et al., 2013 ranged from 1 to 18 ft with a mean of 7 ft. In my analysis, I calculated an average spill depth (spill volume per area) significantly smaller than the depth of impact discussed in Gross et al., 2013. Spill areas in our dataset ranged from 4 ft<sup>2</sup> to 217,800 ft<sup>2</sup> with an average of 10,843 ft<sup>2</sup>. Out of the 77 spills Gross et al., 2013 analyzed, spill area was reported for 59 out of the 77 spills. Spill area ranged from 96 to 10,500 ft<sup>2</sup> with an average of 2,120 ft<sup>2</sup> (Gross et al., 2013). The range and average of spill

areas in our dataset were much larger than those in Gross et al., 2013. Differences between the analyses may be due to the fact that Gross et al., 2013 only considered a limited number of 5 spills with reported spill volume and spill area that impacted groundwater in Weld County while I accounted for 90 spills occurring across a longer time period and broader geographical space. In addition, Gross et al., 2013 included spills with unknown spill volumes (but known spill areas) and mixtures of released fluids (oil in addition to produced water); our study only considered produced water.



**Figure 2.3:** Histogram of spill volume per area or spill depth for produced water spills occurring in counties overlying the South Platte Alluvial Aquifer. These data were used for calculating the produced water spill percentiles.



**Figure 2.4:** Produced water spills occurring in counties overlying the South Platte Alluvial Aquifer plotted as a function of their spill volume and spill area. Plot A) represents a zoomed out view of plot B).

### 2.2.2 Individual spill simulations

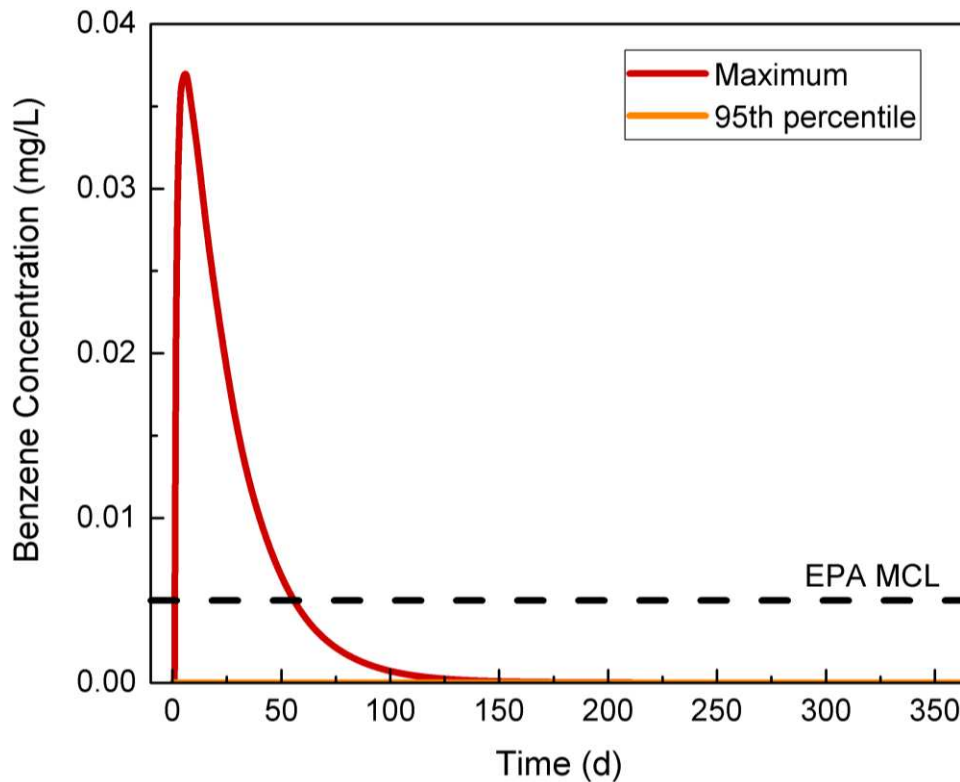
To see how spill size would affect the risk associated with the spill, I ran simulations of the different percentiles of produced water spills as described in section 2.1.4. Each percentile is associated with a different depth of water, which is then translated to an assumed spill infiltration duration. Table 2.4 lists the spill percentile, corresponding spill volume per area or spill depth, and the calculated spill duration (following methods described in sections 2.1.3 and 2.1.4). Again, I note that I calculated these spill depth percentiles using a limited number of observations and not a theoretical distribution. If I assumed an exponential distribution, the predicted 95<sup>th</sup> percentile spill would have spill depth of 9.4 cm compared to 12.0 cm from the data.

**Table 2.4:** Calculated spill volume per area (spill depth) and spill durations that correspond to a particular spill percentile. The spill durations serve as inputs to HYDRUS-1D.

Spill percentile	Spill depth (volume / area, cm)	Duration of spill (hr)
Median	0.38	0.0860
55 <sup>th</sup>	0.53	0.1199
60 <sup>th</sup>	0.69	0.1561
65 <sup>th</sup>	0.86	0.1945
70 <sup>th</sup>	1.08	0.2443
75 <sup>th</sup>	1.55	0.3506
80 <sup>th</sup>	2.65	0.5994
85 <sup>th</sup>	2.99	0.6763
90 <sup>th</sup>	5.99	1.3549
95 <sup>th</sup>	12.0	2.7076
Maximum	64.2	14.515

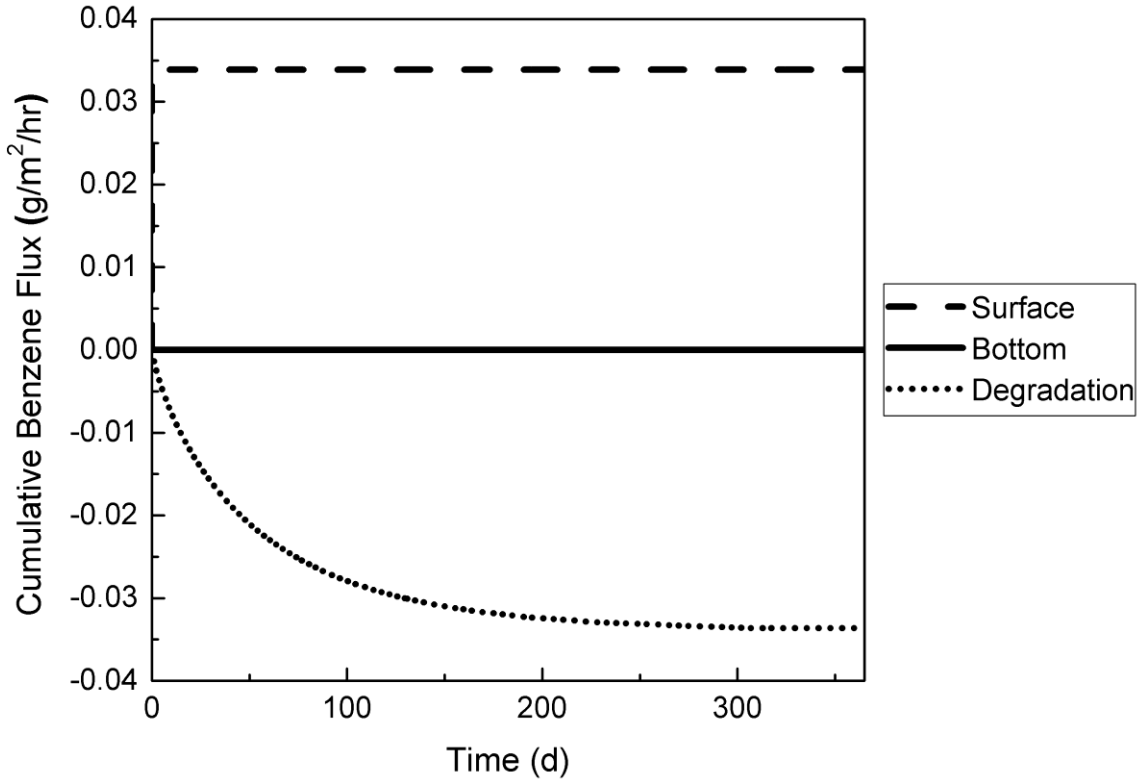
Figure 2.5 shows the concentration breakthrough curve expected at a 10-ft groundwater table depth following a maximum spill (64.2 cm of produced water released over ~14.5 hrs) and a 95<sup>th</sup> percentile spill (12 cm of produced water released over ~2.7 hrs). The maximum spill reaches the groundwater table relatively quickly, after 24 hrs, peaks at 0.037 mg/L and exceeds the EPA MCL (maximum contaminant level) for benzene (0.005 mg/L or 5 µg/L). Benzene exceeds the EPA MCL for 54.6 days. However, benzene concentrations from the 95<sup>th</sup> percentile spill are significantly lower than the EPA MCL. The benzene in the 95<sup>th</sup> percentile spill is completely biodegraded before it reaches the groundwater table 10 ft below. As shown in Figure 2.6, the bottom cumulative solute flux for the 95<sup>th</sup> percentile spill is 0 indicating that benzene is not exiting the soil profile from the bottom boundary. The model-reported degradation cumulative solute flux is the same magnitude as the surface cumulative solute flux indicating that benzene is completely removed.

Running benzene transport as a conservative solute does not substantially change the smallest spill size that exhibits benzene concentrations exceeding the EPA MCL at the groundwater table or what I term here the spill size risk threshold. Assuming no degradation and no sorption, for a 10-ft groundwater table, both the 90<sup>th</sup> and 95<sup>th</sup> percentile spills displayed benzene concentrations that were far below the EPA MCL (not shown here). The 90<sup>th</sup> and 95<sup>th</sup> percentile spill fluids do travel to the groundwater table but velocities are so low that dispersion does not move the contaminant very far down the soil profile. Eventually, the vadose zone reaches hydrostatic conditions and benzene remains in the vadose zone.



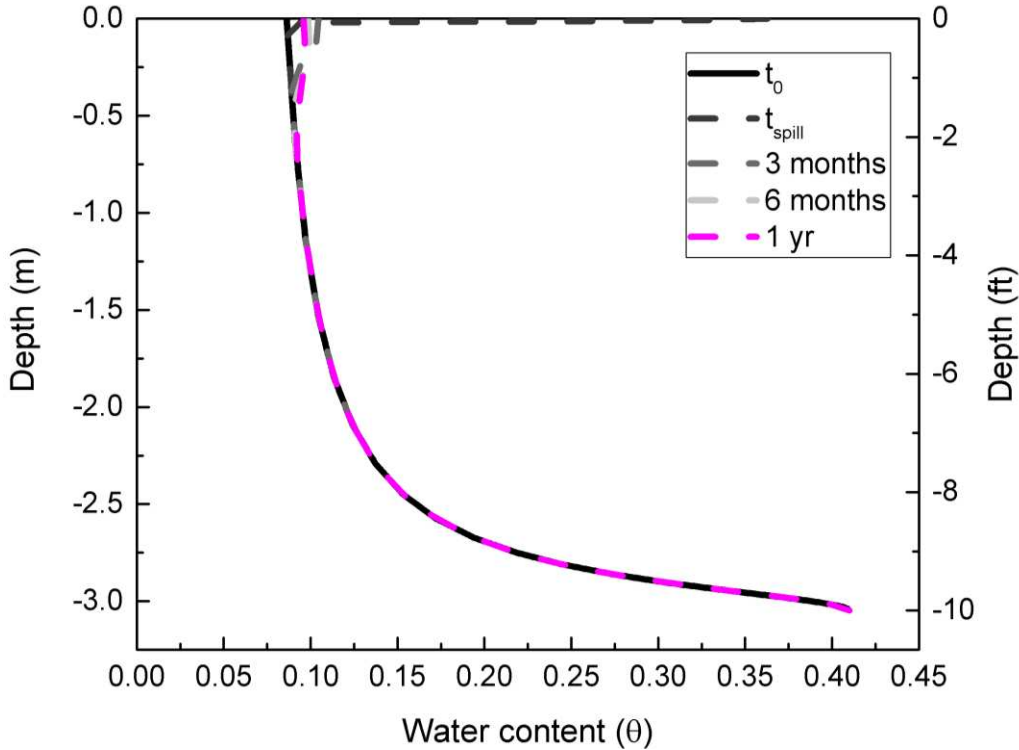
**Figure 2.5:** Concentration breakthrough curve for benzene predicted for a 10-ft groundwater table, accounting for degradation and sorption. The dashed line indicates the EPA MCL. Each curve represents a different spill percentile.

The median spill only impacts the first ~2.4 ft of the water content profile. Figure 2.7 displays profiles of water content with depth at different points in time for the median spill, accounting for degradation and sorption.  $t_{\text{spill}}$  indicates the water content profile immediately following the median spill. As seen in Figure 2.7, the median spill remains in the upper part of the soil profile and slowly drains allowing for long residence times and complete benzene removal before the contaminant reaches the groundwater table. Only the maximum spill exceeded the EPA standard for the 10-ft groundwater table case.



**Figure 2.6:** Benzene cumulative surface, bottom, and degradation fluxes for the 95<sup>th</sup> percentile spill for a 10-ft groundwater table, accounting for degradation and sorption.

With a 2-ft groundwater table, both the maximum and 95<sup>th</sup> percentile spills exhibit benzene concentrations higher than the EPA MCL, as shown in Figure 2.8. Breakthrough for the maximum spill occurs in 2.8 hrs and peaks at a concentration of ~0.28 mg/L. Benzene remains above the EPA standard for ~55.4 days. The 95<sup>th</sup> percentile spill reaches the 2-ft groundwater table in 2.7 hrs. The concentration breakthrough curve reaches a peak of ~0.038 mg/L and exceeds the EPA MCL for 34.3 days. However, the 90<sup>th</sup> percentile spill concentration breakthrough curve lies entirely below the EPA MCL. If benzene is run conservatively, the 90<sup>th</sup> percentile spill does exhibit benzene concentrations higher than the MCL (See Figure A.1). However, the 85<sup>th</sup> percentile spill output shows benzene concentrations below 0.005 mg/L (See Figure A.1).

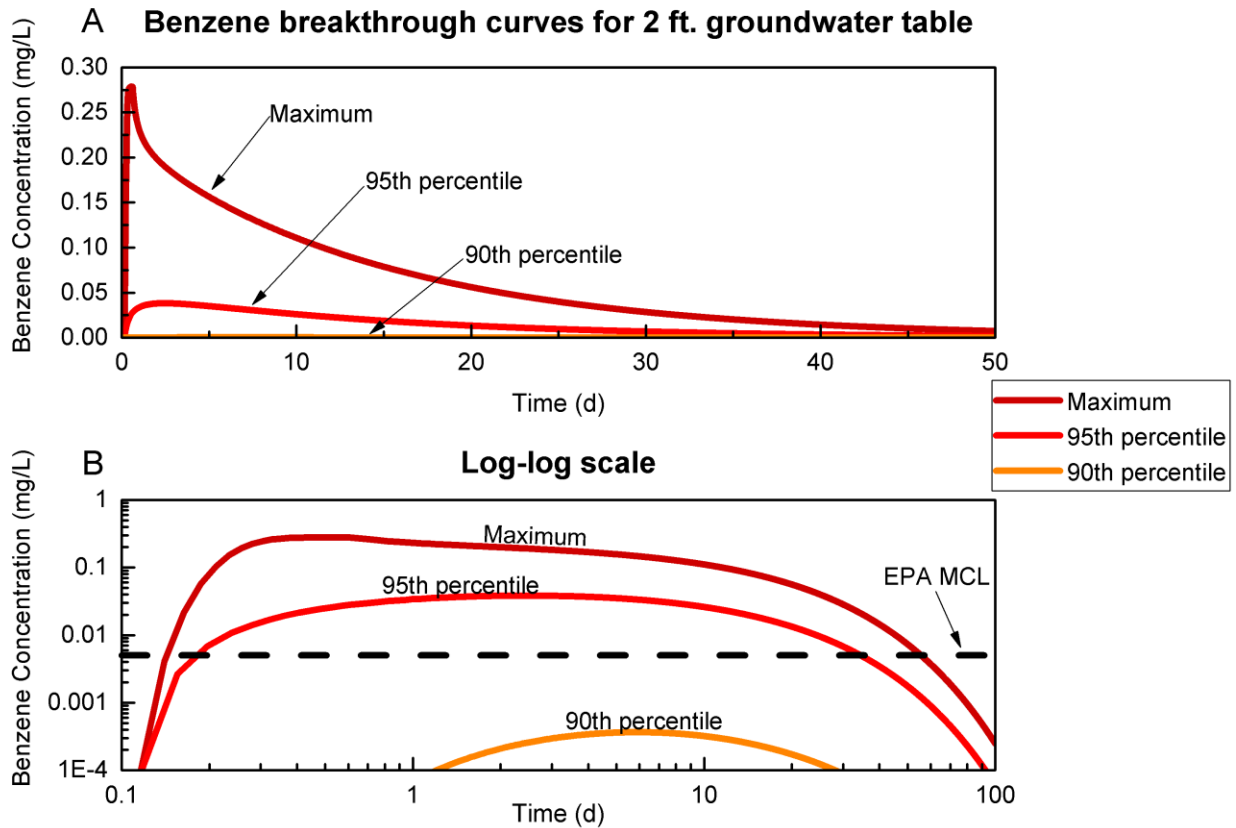


**Figure 2.7:** Water content vs. depth for the median spill over a groundwater table 10 ft below ground surface at different time points. This scenario accounted for degradation and sorption.

From these simulations of produced water spills, we can see that only very large spills, 90<sup>th</sup> percentile and larger for the case of a 2-ft groundwater table and the maximum spill for a 10-ft groundwater table, pose risks to groundwater quality even when assuming no degradation and no sorption. The primary driver is that, for reported typical spill volumes and areas, the spill is largely contained in the vadose zone for moderate time scales. For 2-ft depth to groundwater, the peak benzene concentration increased and concentration at the groundwater table exceeded the EPA limit for longer periods of time as the spill percentile increased. The maximum concentration was observed at later times as spill percentiles decreased. Although degradation is responsible for benzene removal, the biodegradation rate is not the most important factor controlling the degree of risk. Biodegradation does impact the spill size risk threshold for the 2-ft groundwater table case; conservative transport changes the spill size risk threshold from the 95<sup>th</sup> percentile spill to the 90<sup>th</sup> percentile spill. However, in these simulations, spills lower than the 90<sup>th</sup> percentile do not contain sufficient water to adequately saturate the vadose zone and create velocities to quickly transport the spill to the groundwater table. The spill drains slowly and the



soil profile approaches hydrostatic conditions, holding contaminated water in the vadose zone and allowing the benzene to degrade.



**Figure 2.8:** Benzene concentration breakthrough curves predicted at a 2-ft groundwater table, accounting for degradation and sorption on a A) linear scale and B) log-log scale. Each curve represents a different spill percentile.

### 2.2.2.1 Discussion for individual spill simulations

As discussed previously, spill depth and degradation rate are two factors controlling whether or not a spill reaches the groundwater table and exhibits benzene concentrations greater than the EPA MCL. A lower degradation rate would produce results intermediate between those for conservative and degrading spills, but would not enable smaller spills to reach the water table. Two other major factors that may control the spill size risk threshold are hydraulic conductivity and residual water content. A larger hydraulic conductivity (e.g., assuming a sandy soil or a larger value that might still be representative of a sandy loam), might cause the spill to travel faster and degrade less due to lower residence time in the vadose zone. On the other hand,

a smaller hydraulic conductivity or a larger degradation rate might eliminate the pollution risk from even the largest spills simulated above by enabling more degradation as the spill moves toward the water table. Increasing the hydraulic conductivity by an order of magnitude does not change the spill size risk threshold; the peak concentration predicted for the 90<sup>th</sup> percentile spill at a 2-ft deep water table increases by  $\sim 2.3 \times 10^{-4}$  mg/L relative to the base case but still remains below the EPA MCL. If the hydraulic conductivity is decreased ten-fold, then the peak benzene concentration for the 95<sup>th</sup> percentile spill for a 2-ft deep groundwater table decreases from  $\sim 0.038$  mg/L to  $\sim 0.020$  mg/L; more benzene degrades with longer residence time in the vadose zone.

It was somewhat surprising that only the largest spills are predicted to reach the water table. Given this result, another highly important factor must be the residual water content of the soil. This parameter determines how much water is retained in the vadose zone during an infiltration event. The value used in the simulations (0.065) was the mean value for a sandy loam calculated by Carsel and Parrish, 1988. Given the variability and difficulty in estimating residual water content (Schaap et al., 1998; Schaap and Leij, 1998), I simulated spills using a smaller residual water content for a sandy loam. I chose a residual water content of 0.039, an average value calculated from measurements on 481 sandy loam samples from three databases (Schaap and Leij, 1998). A smaller residual water content, that might still be reasonable for a sandy loam, could result in a smaller percentile spill reaching the water table. Simulations using this lower residual water content showed no change in the spill size risk threshold; there was only  $\sim 3\%$  difference in the peak concentration in the breakthrough curve for the 90<sup>th</sup> percentile spill over a 2 ft depth to groundwater. Of course, based on the databases given above, smaller residual water contents may be possible for a sandy loam, and site specific assessments for this parameter should be considered for more detailed modeling analyses of spills.

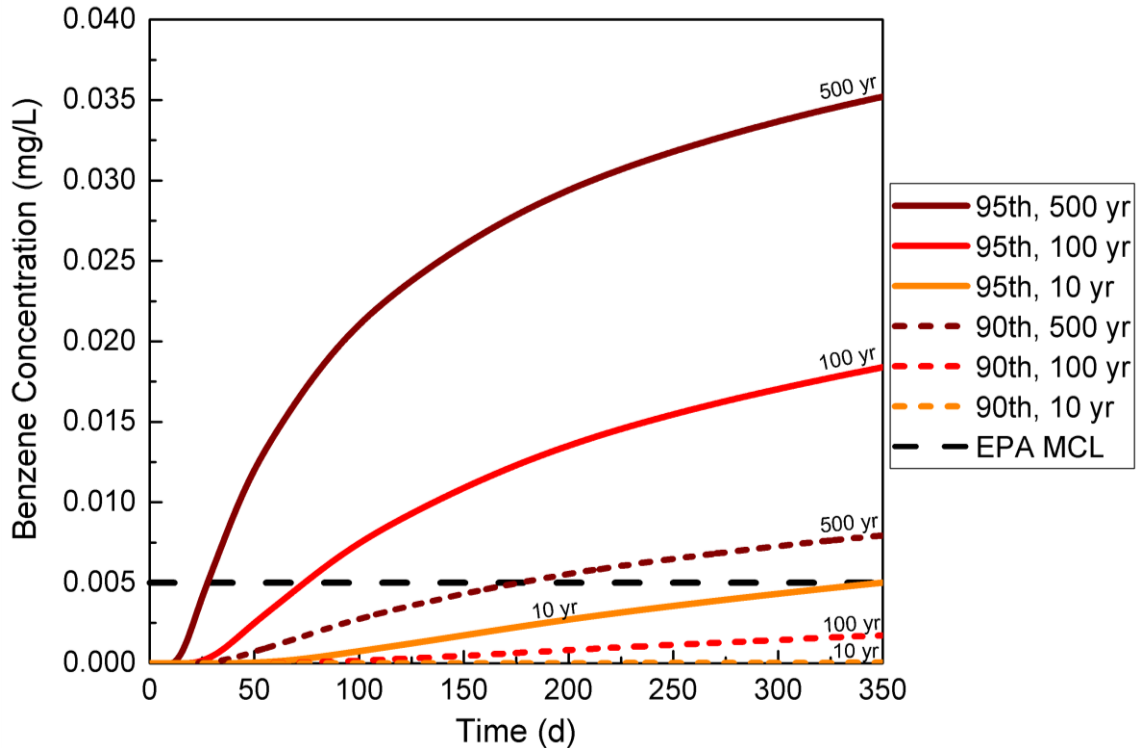
For the 2 spills Gross et al., 2013 considered in its analysis which resulted in a net release of produced water and oil that impacted groundwater, the spill volumes per area were  $\sim 1.56$  and  $\sim 0.76$  cm. These values correspond to 75<sup>th</sup> percentile and 60<sup>th</sup> percentile spills, respectively. It is possible that these smaller spills impacted groundwater because they occurred in areas with wetter soils or with sandy soils with smaller residual water contents. The Gross et al., 2013 spills also contained oil and condensate in addition to produced water; I did not consider transport of these NAPL mixtures in this study.

### **2.2.3 Storm simulations after a spill**

Because only very large (over 90<sup>th</sup> percentile) spills reached the groundwater table in conservative circumstances in the spill simulations, an obvious question to ask is how storm events would impact the spill size risk threshold. Results for the storm simulations are discussed below using base case chemical and aquifer properties as listed in Table 2.1 and considering 10- and 2-foot depths to the water table and both non-conservative (including representative sorption and degradation) and conservative transport.

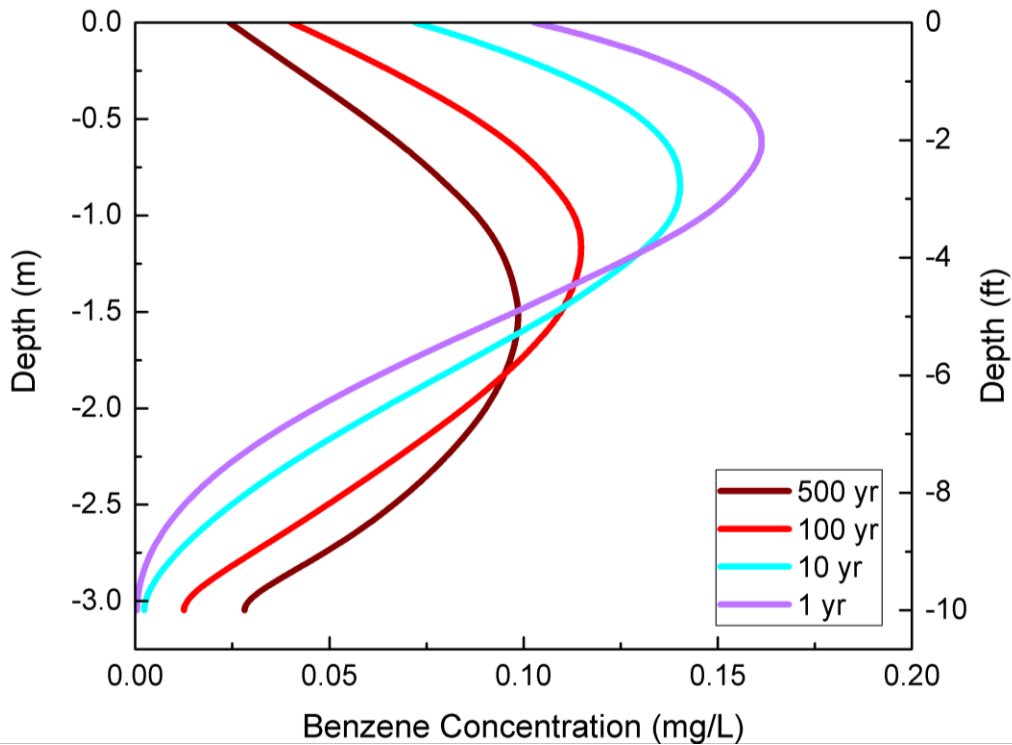
#### **2.2.3.1 Storm simulations after a spill for a 10-foot water table**

For a 10-ft groundwater table depth, all percentile spills smaller than the maximum spill did not display benzene concentrations greater than the EPA standard at the groundwater table, even following a 1000-year storm, when benzene sorption and degradation were considered. However, certain spills considering benzene as a conservative solute did reach the 10-ft deep groundwater table. Benzene may act as a conservative solute under certain conditions (discussed later). As shown in Figure 2.9, the concentration breakthrough curves gradually increase and plateau at steady state concentrations. Given a particular spill size, the highest benzene steady state concentrations are predicted for the 500-year storm and the final concentrations decrease with smaller storms. Recall that for both the 90<sup>th</sup> and the 95<sup>th</sup> percentile spills, assuming conservative transport, benzene concentrations stayed below 5 µg/L when only considering the spills. Benzene exceeds the EPA MCL at the groundwater table for the 95<sup>th</sup> percentile spill after 10, 100, and 500-year storms, assuming no degradation or sorption. These storms are large enough to flush this large spill to the water table. A 500-year storm is required to transport high concentrations of benzene from the 90<sup>th</sup> percentile spill to the aquifer 10 ft below ground surface (Figure 2.9). The 10 and 100-year storms do not provide sufficient water to flush the soil profile and transport benzene from 90<sup>th</sup> percentile spill to the groundwater table at high concentrations. After these storms, the soil profile slowly drains and benzene remains stored throughout the soil profile.



**Figure 2.9:** Benzene concentration breakthrough curves predicted at a 10-ft groundwater table assuming no degradation and no sorption. Solid lines indicate the 95th percentile spill and dashed lines indicate the 90th spill. Darker reds indicate a larger storm size and more yellow colors indicate a smaller storm size. The black dashed line shows the EPA limit at 5  $\mu\text{g/L}$ .

As expected, the storms provide additional water, which allows benzene to be conveyed further down the vadose zone. The larger storm intensities drive the benzene peak concentration for the 95<sup>th</sup> percentile spill deeper into the vadose zone, as shown in Figure 2.10. However, benzene's peak concentration in the soil profile increases as the storm size decreases. Higher velocities with the larger storms that transport more solute out the bottom boundary, greater dispersion, and more water for dilution, all result in less contaminant mass in the vadose zone.



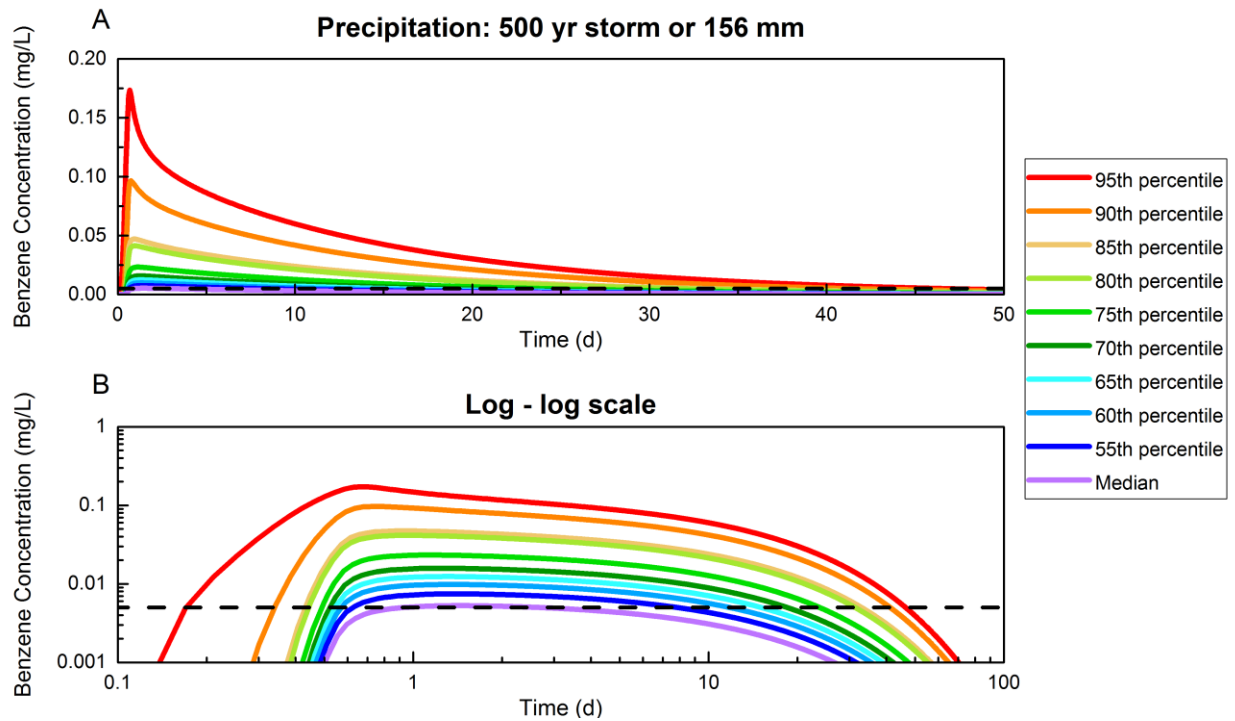
**Figure 2.10:** Benzene concentration vs. depth after 6 months for the 95th percentile spill, assuming no degradation and no sorption. Each curve represents a different storm frequency. Depth to water table was 10 ft.

### 2.2.3.2 Storm simulations after a spill for a 2-foot water table

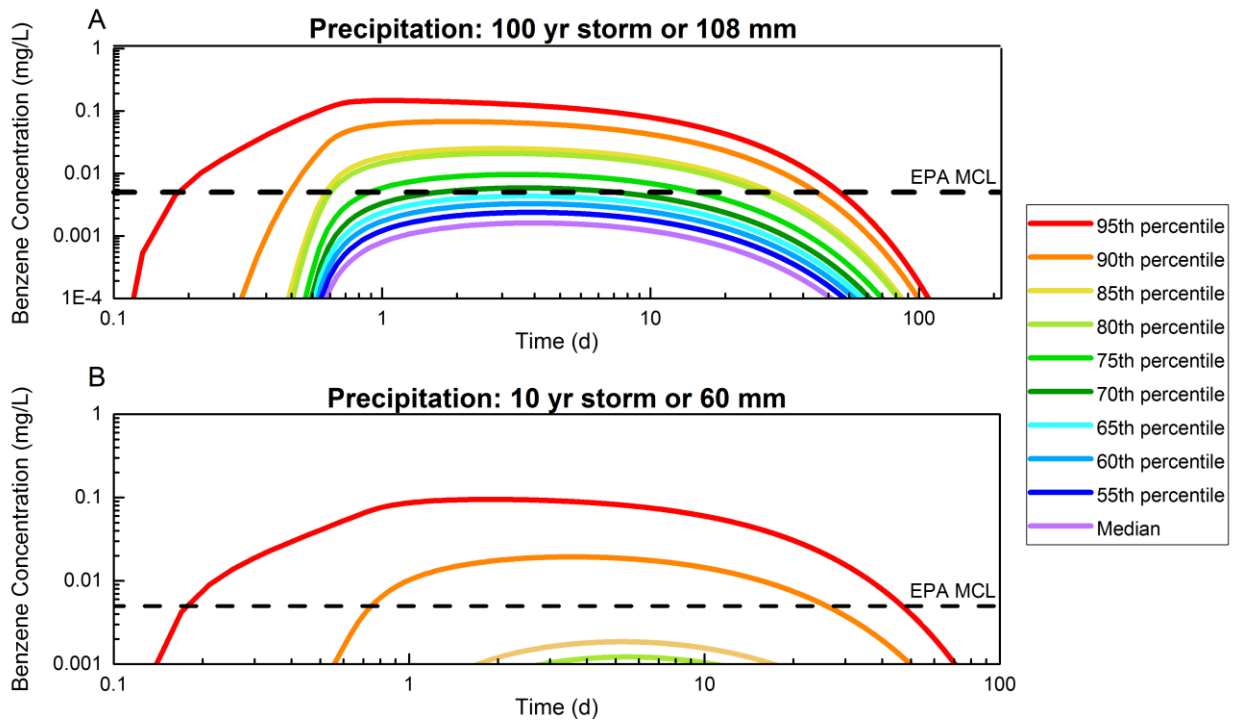
For 2-ft depth to groundwater, benzene concentrations at the water table for the 90<sup>th</sup> percentile spill without a subsequent rain event did not exceed the EPA MCL (Figure 2.8). Storms after a spill result in benzene concentrations greater than the MCL reaching the water table even for spill sizes smaller than the 90<sup>th</sup> percentile. A thorough discussion is provided below, and the results are summarized in Tables 4 and 5.

For a 2-ft depth to groundwater, the 500-year storm is sufficient to cause every spill size, from median to 95<sup>th</sup> percentile, to exceed the EPA MCL at the groundwater table, even when considering representative sorption and degradation. As seen in Figure 2.11, the peak benzene concentration decreases with spill size and ranged from ~0.17 mg/L to 0.0053 mg/L for the 95<sup>th</sup> percentile spill and median spill, respectively. The duration of time the benzene concentration is greater than the EPA standard is longer for larger spill percentiles. In general, the timing of the peak concentration as well as time of breakthrough increased as the spill size decreased, for reasons discussed previously. Compared to the 500-year storm, the 100-year and 10-year storms

do not contain adequate precipitation to cause the median spill to pose risk to groundwater quality. For a 100-year storm and non-conservative benzene transport, all spills greater than or equal to the 70<sup>th</sup> percentile result in benzene concentrations exceeding the EPA MCL (Figure 2.12A; shown on log-scale for clarity, plots on a linear scale can be found in Appendix A). As shown in Figure 2.12A, peak concentrations range from ~0.15 mg/L for the 95<sup>th</sup> percentile spill to ~0.002 mg/L for the median spill (recall the MCL is 0.005 mg/L). For more typical storm frequencies, only the larger spills seem to pose risk. Considering the 10-year storm, only the 90<sup>th</sup> and 95<sup>th</sup> percentile spills displayed concentrations exceeding the EPA standard (Figure 2.12B). Peak concentrations ranged from ~0.09 mg/L for the 95<sup>th</sup> percentile spill to  $\sim 9 \times 10^{-6}$  mg/L for the median spill (not shown in Figure 2.12B). Overall trends in magnitude of peak concentration, duration of time above the EPA standard, and timing for the 100-year and 10-year storms were similar to those seen for the 500-year storm.

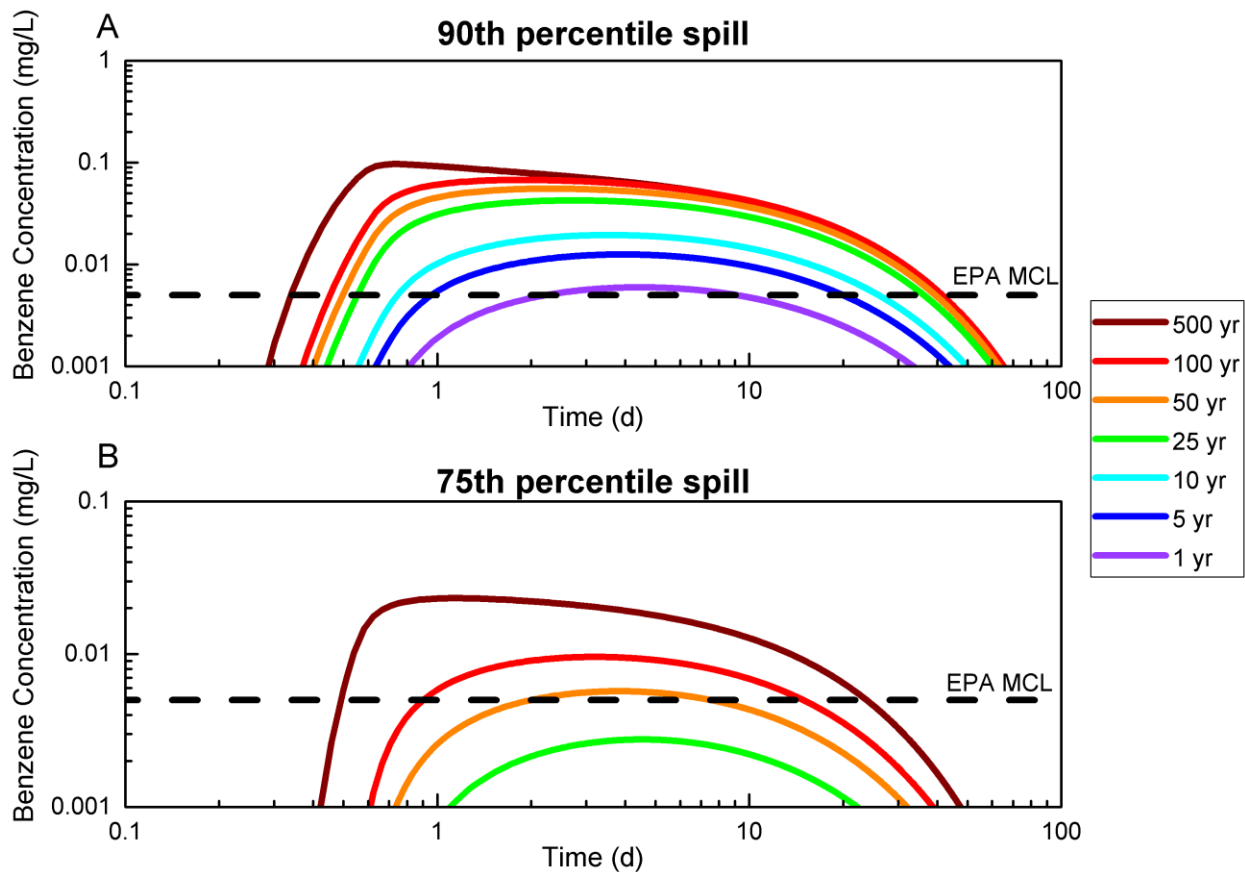


**Figure 2.11:** Benzene concentration breakthrough curves for a 2-ft water table and the 500-year storm on a A) linear scale and B) log-log scale. Each curve represents a different spill percentile with warmer colors representing larger spill sizes and cooler colors indicating smaller spill sizes.



**Figure 2.12:** Benzene concentration breakthrough curves for a 2-ft water table and the A) 100-year storm and B) 10-year storms. Each curve represents a different spill percentile with warmer colors representing larger spill sizes and cooler colors indicating smaller spill sizes.

Considering only the spill itself (without subsequent rainfall), and non-conservative benzene transport, benzene in the 90<sup>th</sup> and 75<sup>th</sup> percentile spills degraded before they could reach a 2-ft ground water table (Figure 2.8). However, when considering possible storms after a 90<sup>th</sup> percentile spill, all the storm frequencies considered — 1, 5, 10, 25, 50, 100, and 500-year — move the spill down the soil profile to groundwater and resulted in benzene concentrations that were higher than EPA standards (Figure 2.13A). Even storms with typical frequencies change the risk from the 90<sup>th</sup> percentile spill. For the 75<sup>th</sup> percentile spill, the 50, 100, and 500-year storms resulted in benzene concentration breakthrough curves which exceeded the EPA MCL, as shown in Figure 2.13B. The 25-year storm showed benzene concentrations consistently below 5  $\mu\text{g/L}$ . For a still quite large but more typical spill size at the 75<sup>th</sup> percentile, storm sizes of 50-year and greater are needed to make these spills pose risk to groundwater quality. For a particular spill percentile, larger storm sizes were consistently associated with higher peak concentrations and longer time periods during which benzene was above 5  $\mu\text{g/L}$ . Time of peak concentration and of breakthrough increased as storm size decreased.



**Figure 2.13:** Benzene concentration breakthrough curves for a 2-ft water table on log-log scales for the A) 95th percentile spill and B) 75th percentile spill. Each curve represents a different storm frequency with warmer colors representing higher intensity storms and cooler colors indicating lower intensity storms.

Table 2.5 summarizes the storm simulations for areas with a 2-ft groundwater table depth. Cells highlighted in red indicate scenarios which resulted in peak benzene concentrations higher than the EPA limit and contain the predicted peak concentration. Green cells indicate that the entire concentration breakthrough curve was below the EPA standard. For more typical storm frequencies of 10-year and 1-year, the 95<sup>th</sup> and 90<sup>th</sup> percentile spills are the only spills predicted to pose risk.

I also consider scenarios in which benzene may act as a conservative solute. Conservative transport of benzene following a storm event may occur if the soils are saturated and benzene degrades anaerobically (discussed in greater detail in section 2.2.3.3). Results from simulations run with a 2-ft groundwater table, different spill sizes, different storm frequencies, and



conservative benzene transport (no degradation or sorption) can be seen in Table 2.6. The cells highlighted in red indicate cases where the maximum benzene concentration changed from below to above the EPA MCL compared to the base case results (with degradation and sorption) summarized in Table 2.5. Maximum benzene concentrations corresponded to the concentration predicted at the 2-ft groundwater table when the soil profile returned to hydrostatic conditions. If benzene acts as a conservative solute, 100-year storms are expected to make all spills equal to and larger than the median spill pose risk to groundwater quality. For a 10-year storm, spills 75<sup>th</sup> percentile and larger result in benzene concentrations above EPA standards. In the case of a 1-year storm, the 85<sup>th</sup> percentile spill begins to pose concern. Even with this 2-ft shallow groundwater table, large storms (100-year and 500-year) need to occur for typical spills to begin to pose risk. Storms with more typical frequencies (1-year and 10-year) still do not provide sufficient water to the system to cause median spills to travel to the groundwater table at concerning concentrations. Similar to the results from the individual spills, it is still the large spills at the 90<sup>th</sup> and 95<sup>th</sup> percentile that pose risk.

**Table 2.5:** Summary of all produced water spill and storm simulations considering a 2-ft groundwater table, accounting for degradation and sorption. Each row represents a different spill percentile and each column represents a different storm frequency. Cells colored in red indicate spill-storm cases in which the peak concentration exceeded the EPA standard of 5 µg/L. The concentration values indicate the maximum concentration predicted. The green cells indicate spill-storm scenarios in which the entire concentration breakthrough curve was below the EPA limit.

Spill quantile	Storm frequency			
	1 yr	10 yr	100 yr	500 yr
Median				5.261 µg/L
55 <sup>th</sup>				7.432 µg/L
60 <sup>th</sup>				9.799 µg/L
65 <sup>th</sup>				12.36 µg/L
70 <sup>th</sup>			5.830 µg/L	15.76 µg/L
75 <sup>th</sup>			9.572 µg/L	23.21 µg/L
80 <sup>th</sup>			20.85 µg/L	41.39 µg/L
85 <sup>th</sup>			24.94 µg/L	47.11 µg/L
90 <sup>th</sup>	5.937 µg/L	19.34 µg/L	67.30 µg/L	96.51 µg/L
95 <sup>th</sup>	67.84 µg/L	94.73 µg/L	146.6 µg/L	173.6 µg/L

**Table 2.6:** Summary of all produced water spill and storm simulations considering a 2-ft groundwater table, assuming no degradation and no sorption. The table shows how considering benzene to be a conservative solute can change the risk of a particular spill-storm combination. Each row represents a different spill percentile and each column represents a different storm frequency. Cells colored in gray indicate simulations from Table 2.5 that resulted in concentrations at a 2-ft groundwater table greater than the EPA standard of 5 µg/L. Cells colored in red indicate spill-storm cases in which the concentration at the groundwater table exceeded 5 µg/L but only when benzene was set as a conservative solute. The concentration values indicate the maximum concentration predicted when the soil profile became hydrostatic. The green cells indicate spill-storm scenarios in which concentrations were consistently below the EPA limit.

Spill quantile	Storm frequency		
	1 yr	10 yr	100 yr
Median			7.306 µg/L
55 <sup>th</sup>			10.36 µg/L
60 <sup>th</sup>			13.70 µg/L
65 <sup>th</sup>			17.32 µg/L
70 <sup>th</sup>			
75 <sup>th</sup>		8.525 µg/L	
80 <sup>th</sup>		21.94 µg/L	
85 <sup>th</sup>	5.642 µg/L	27.23 µg/L	

### 2.2.3.3 Discussion for storm simulations

Similar to the individual spill simulations, the spill-storm results may change somewhat if degradation rate, hydraulic conductivity, and organic carbon content were different than the base case conditions represented in Table 2.1. For the spills where degradation was important relative to conservative transport, a higher degradation rate may reduce the risk of a certain spill size and storm frequency combination (resulting in a larger spill size risk threshold). Lower degradation rates would produce results intermediate between the conservative and non-conservative results discussed above. Although conservative transport of benzene represents a worst-case scenario, given the high precipitation associated with the large storms, soils could become saturated resulting in limited diffusion of air into the subsurface and anaerobic degradation of benzene. Anaerobic degradation rates for benzene can be orders of magnitude lower than aerobic degradation rates (Howard et al., 1991; Rifai and Newell, 1998). Preferential microbial degradation of other organics in produced water would also limit benzene degradation (Deeb et al., 2002). In these cases, conservative transport could reasonably occur.

Hydraulic conductivity is almost certain to vary over a couple orders of magnitude in the South Platte aquifer. For the spills where benzene concentrations exceeded the EPA limit at the

water table, a higher hydraulic conductivity would result in less degradation and cause results to be intermediate between the conservative and non-conservative results described above. A lower hydraulic conductivity would allow more time for degradation, and generally reduce the risk associated with a specific spill size; larger spills would impose risk. Sorption generally had a negligible impact in these simulations because of the small fraction of organic carbon and benzene's relatively low soil-organic carbon partitioning coefficient, compared to other pollutants. Sorption tends to reduce peak concentrations, but retard transport. Thus, higher sorption would likely produce results intermediate between the conservative and non-conservative results described above.

Multiple storms after a spill were not considered in these simulations because an infinite number of storm frequencies and durations exist. However, as one can see from Table 2.2, an unlikely case of 1-year storms in 5 successive days would provide about the same total volume as a 50-year storm, so the results above for a 500-year storm could be viewed as a reasonable worst case scenario for multiple storms soon after a spill. Although I simulated storm events, high precipitation events of short duration, it is possible for long term precipitation trends to also impact spill risk. For example, since the average total precipitation in May is very similar to a 10-year storm, monthly precipitation over time could be equivalent to the total precipitation of multiple storms, neglecting evapotranspiration and capillary redistribution between events.

Precipitation rate and total precipitation depth were both important factors in determining how precipitation events impacted the spill size risk threshold. Faster precipitation rates generally led to higher transport velocities and greater total mass of benzene reaching the groundwater table. A lower precipitation rate dissipating the same total precipitation over a longer time period changed the peak concentration predicted at the groundwater table and tended to increase the spill size risk threshold (reducing risk associated with more typical spills). The median degradation half-life of benzene used for these simulations was about 10 days. In scenarios assuming non-conservative transport, precipitation rate was an important factor in determining the benzene levels at the groundwater table; accounting for degradation and sorption, storms resulted in higher peak benzene concentrations and smaller spill sizes reaching the water table while monthly precipitation rates led to lower peak concentrations and larger spill size thresholds.

If we assume conservative transport — a reasonable assumption if soil microbial populations preferentially degrade other organics in produced water (Deeb et al., 2002) and there is low soil organic carbon content — then the relative importance of precipitation rate vs. total precipitation varies. It seems that very large precipitation depths provide sufficiently high hydraulic conductivities over the long term to outweigh the effect of the precipitation rate. For example, both the 500-year storm and average spring have total precipitation depths of about 156 mm. The 95<sup>th</sup> percentile spill over a 10-ft deep water table for a 500-year storm produces benzene concentrations similar to those predicted for an average spring (April-May-June),  $\pm 5$   $\mu\text{g/L}$  (results not shown here). However, for lower precipitation depths, precipitation rate increases in influence. Although average total precipitation depth for May is equivalent to the precipitation depth for a 10-year storm, the spill size risk threshold for a 2-ft water table for May is the 80<sup>th</sup> percentile spill and the spill size risk threshold for the 10-year storm is the 75<sup>th</sup> percentile spill. Long term precipitation could also impact the initial conditions of the soil profile when the spill occurs. Because certain areas near high density oil and gas development are known to be net recharge areas (Brown and Caldwell, 2015; Donegan, 2015; Wellman, 2015), initial conditions in the soil column may not be hydrostatic.

Overall, more intense storms and large total precipitation depths lead to more saturated soil conditions which increases the hydraulic conductivity and in turn, increases the transport velocity. In general, these higher transport velocities lead to lower residence times in the soil profile, less time for microbial degradation, greater mass of benzene advected to the aquifer, and higher concentrations of benzene at the groundwater table. However, it is important to note that Colorado has an arid climate. Numerous rains over several months or years may provide more rain than a 500-year storm, but it is likely that microbial degradation during this period would remove some benzene from the soil profile. Finally, this study tested a limited number of possible hydrologic, transport, climate and spill conditions possible in the future. Nonetheless, the modeling framework used here could be used to test any specific spill, site, or climate condition desired.

Although I quantify risk as exceeding the EPA limit as the spill is transported to the groundwater table, it is important to note that the actual risk to human health would be the contaminant concentration at the drinking water receptor. Understanding this risk would involve modeling groundwater flow in the aquifer to see if significant concentrations reach the

groundwater well after the spill enters the aquifer. Benzene has been shown to degrade more slowly in the water table than in the soil (ATSDR, 2007). This trend may be due to the fact that low oxygen levels in groundwater aquifers result in anaerobic degradation of benzene. However, dilution and dispersion effects in an aquifer would likely be significant.

The results of this study generally show that the risk due to typical surface spills is low for most areas of the South Platte Alluvial Aquifer, unless large storms occur immediately following a spill. Although field studies have found strong evidence of groundwater contamination due to produced water spills (Gleason and Tangen, 2014; Kharaka et al., 2007; Otton et al., 2007; Thamke and Smith, 2004), many of these sites were producing oil and gas prior to enforcement of strict environmental regulations. Contamination occurred before sites were upgraded or abandoned. Some of these sites likely experienced multiple large spill events and many rain events. Furthermore, pits used to store produced water and trenches dug to convey produced water around the sites were unlined (Gleason and Tangen, 2014; Kharaka et al., 2007; Otton et al., 2007). In Colorado, it is no longer common practice to use pits to store produced water and equipment handling produced water are usually surrounded by berms and lined. As a result, large volume spills do not occur frequently and are not commonly released into the environment. It seems that these best management practices and enforcement of Colorado's oil and gas regulations are working to minimize the occurrence of massive releases.

Fletcher (2012) and Gradient (2013) conducted stochastic modeling studies to evaluate the potential for spills to impact groundwater quality. Both studies calculated output contaminant concentrations as a dilution factor, or the ratio between the maximum concentration predicted and the original concentration in the released fluid. Fletcher (2012) calculated dilution factors of  $10^{-3.5}$  to  $10^{-5}$  for 5,000 gallon spills in unconsolidated sand and gravel aquifers (mean saturated hydraulic conductivity of  $8.8 \times 10^{-6}$  m/hr) at source-to-well distances of 200 ft. Dilution factors ranged from  $10^{-3.5}$  to  $10^{-4}$  for distances of 500 ft (Fletcher, 2012). Dilution factors for the 50,000 gallon spill ranged from  $10^{-3}$  to  $10^{-2}$  (Fletcher, 2012). For our analysis, any spills that reported benzene reaching the groundwater table at concentrations below the EPA MCL had dilution factors lower than  $10^{-1.75}$  (~0.018). Dilution factors for spills that exhibited benzene exceeding the EPA standard ranged from  $10^{-0.007}$  (~0.98) to  $10^{-1.73}$  (~ $1.9 \times 10^{-2}$ ). The longer travel distances, 3D dispersion, and groundwater aquifer flow considered in Fletcher (2012) explain the difference in dilution factors between our analysis and Fletcher (2012).

Gradient (2013) reported a distribution of dilution factors for the unsaturated zone, ranging from  $9.9 \times 10^{-3}$  to  $5.3 \times 10^{-2}$  from the 50<sup>th</sup> to 95<sup>th</sup> percentile of dilution factors, respectively. Furthermore, the dilution factors for the saturated zone were orders of magnitude lower, ranging from  $5.6 \times 10^{-5}$  to  $9.1 \times 10^{-27}$  (Gradient, 2013). The unsaturated zone dilution factors are much smaller than the values calculated in our analysis, possibly due to the broad range of conditions Gradient (2013) considered as well as the study's use of an analytical solution to represent groundwater flow.

### **2.3 Conclusions**

In this part of the thesis, I focused on produced water spills occurring in the Front Range of Colorado and evaluated the risk to South Platte Alluvial Aquifer groundwater quality. Data analysis of produced water spills showed that most spills released small net volumes and resulted in low spill volume per area. This result is consistent with what previous studies have found (U.S. EPA, 2015a). From the produced water spill and storm simulations, we can draw the following conclusions:

- Using representative hydrologic and contaminant transport values for transport of benzene in a sandy loam, which is appropriate for a screening level assessment, the risk of benzene contamination of groundwater from a produced water spill is relatively low in the South Platte aquifer (based on spill data).
- Only statistically larger spills pose a clear risk. Spills at the maximum spill size are the only spills to consistently pose risk in areas with groundwater tables 10 ft deep below ground surface. However, actual site conditions could enable smaller spills to reach ground water (i.e., soils with relatively higher sand contents).
- Spill size is the dominant factor influencing whether a contaminant reaches the water table.
- Residual water content, which impacts the vadose zone storage of spill water, was the dominant hydraulic or transport variable impacting whether a contaminant reaches the groundwater. However, using two representative values for sandy loam that varied by a factor of two did not significantly change the results. Areas likely to have lower residual water contents (i.e., with a higher sand composition) should be evaluated in additional detail.

- Storms events following a spill are generally required to flush spills to the water table. For a 10-ft depth to groundwater, higher storm intensities and higher spill sizes pose risk if little degradation or sorption occurs. Accounting for more typical storm frequencies and shallower water tables, 90<sup>th</sup> percentile and 95<sup>th</sup> percentile spills become a concern.
- Typical median-sized spills only pose risk to shallow groundwater if a 500-year storm (equivalent to 156 mm of rainfall) occurs right after the spill. A 100-year storm (108 mm of precipitation) may result in significant concentrations for a typical spill if little degradation or sorption occurs.

Overall, this study demonstrated that the large spills are the spills consistently posing risk in areas with shallow groundwater tables, primarily because most spills are small enough that the entire volume can be contained in the vadose zone, even under most rainfall conditions. Most areas of the South Platte Alluvial Aquifer with groundwater tables 30 ft below ground surface (Wellman, 2015), are not at risk for groundwater contamination due to surface spills. More typical sized spills can become a concern if 100-year storms or larger happen and little degradation and sorption occur. These results suggest that resources should focus on ensuring that oil and gas sites with shallow groundwater tables are properly lined and have additional measures in place to avoid leakage. I hope that this work will allow for decision-makers to be better prepared to address accidental releases in Colorado and help create more informed prevention, mitigation, and remediation practices for accidental surface spills, particularly in high risk areas.

## CHAPTER 3

### THE IMPACT OF CO-CHEMICAL INTERACTIONS ON TRANSPORT OF HYDRAULIC FRACTURING FLUID SPILLS

#### 3.1 Introduction

Because there is high public concern and high uncertainty regarding the chemical behavior and toxicity of hydraulic fracturing fluid constituents, I decided to study the fate and transport of contaminants in surface spills of hydraulic fracturing fluid (HFF). Large volume spills of hydraulic fracturing fluid have occurred in Pennsylvania — estimated at 6,900 gallons (Lustgarten, 2009) — and Texas, estimated at 42,000 gallons (Ciesco, 2015). Larger spills of flowback water — whose composition may be similar to HFF if it spent only a short time downhole — estimated at 84,000 gallons (Finley, 2013) have also been reported in Colorado. HFFs are often complex mixtures of many different compounds that would likely impact transport of other compounds in solution (Kekacs et al., 2015; Stringfellow et al., 2014). For example, biocides are a common component of HFF; if a spill of HFF occurred, a biocide could inhibit degradation of itself and other compounds (Kahrilas et al., 2014; Leung, 2001). Surfactants can potentially result in co-solvent effects and friction reducers can change the viscosity of the released fluid (Stringfellow et al., 2014). Furthermore, produced water is often recycled and reused for creating HFF. The presence of dissolved solids (salts) has been shown to decrease degradation rates of HFF constituents (Kekacs et al., 2015). For this chapter of my thesis, I chose to study how certain compounds influence degradation of other co-chemicals in HFF.

I chose to focus on the co-chemical interactions between three common chemical additives in hydraulic fracturing fluid, glutaraldehyde, polyethylene glycol, and polyacrylamide. These three chemical compounds represent three different categories of additives — biocide, surfactant, and friction reducer — and are widely used in HFF (Stringfellow et al., 2014). Data on these interactions exist in the literature (McLaughlin, 2016; McLaughlin et al., 2016). Glutaraldehyde is a biocide used to inhibit growth of microbes that can corrode steel casing, clog the well, and potentially release harmful gases. Glutaraldehyde has low acute dermal and inhalation toxicity, high acute oral toxicity, and is highly irritating to the eyes and skin (U.S.



EPA, 2007). LD<sub>50</sub> (lethal dose required to kill 50% of a population) ranged from 360 to 420 mg/kg for rats (U.S. EPA, 2007). Glutaraldehyde does not tend to bioaccumulate, is readily biodegradable in freshwater and marine environments, unlikely to be carcinogenic or mutagenic, and does not have neurotoxic, reproductive, or developmental effects (Leung, 2001; U.S. EPA, 2007). Polyethylene glycol is a surfactant which is often added to the stimulation fluid to reduce interfacial tension between oil and water in the formation and increase oil recovery (Stringfellow et al., 2014; Thurman et al., 2014). Polyethylene glycol is considered to be nontoxic. Polyacrylamide is a friction reducer which helps maintain laminar flow in the casing (Al-Muntasheri, 2014; Stringfellow et al., 2014; Vidic et al., 2013). Polyacrylamide has reported LD<sub>50</sub> values at >1000 mg/kg for rats, 12,950 mg/kg for mouse, and 11,250 mg/kg for rabbits (Lewis and Sax, 1996; U.S. EPA, 2013).

Similar to the produced water spills simulations, I chose to focus on the South Platte Alluvial Aquifer for the study area. As discussed previously, the South Platte Alluvial Aquifer is a great case study because there is significant oil and gas presence in areas with shallow groundwater table depths. Furthermore, the high density oil and gas activity in the area targets the Niobrara formation, a tight formation typically requiring hydraulic fracturing treatments. There are many areas in the South Platte Alluvial Aquifer where a HFF surface spill may pose a risk to groundwater quality, and where contaminants may also travel to the South Platte River.

This chapter examines the importance of accounting for co-chemical interactions and their impact on contaminant transport modeling of these HFF spills. I chose one particular spill size, representative of a large spill, and simulated spills of a model HFF composed of glutaraldehyde, polyethylene glycol, and polyacrylamide. I also considered the impact of salt on degradation of these three additives. The degradation rate model inputs and model set up were chosen to reflect how these three constituents interact. The focus of the study was to evaluate the importance of considering co-chemical interactions in modeling these HFF spills; I did not assess the risk different HFF spill sizes may pose to groundwater quality in the South Platte Alluvial Aquifer. I analyzed spill data and used model parameterization representative of the South Platte Alluvial Aquifer to ground the study in reality.

## **3.2 Methods**

I conducted a groundwater modeling study of hydraulic fracturing fluid spills to assess the importance of accounting for co-chemical interactions when modeling these spills. This study first involved analyzing spill data for hydraulic fracturing fluid spills in Colorado to determine a representative spill size then simulating vadose zone transport of spills considering different co-chemical interactions.

### **3.2.1 Hydraulic fracturing fluid spill analysis**

For the purposes of this study, I define hydraulic fracturing fluid spills as releases of stimulation fluid prior to injection that likely contained some chemical additives. The EPA Hydraulic Fracturing Related Spills Table (U.S. EPA, 2015a) and the SSPA 2013 datasets were used to characterize HFF spills. These datasets were chosen because they contained spills that were specifically designated as being related to hydraulic fracturing. For the EPA dataset, I searched for spills that occurred in Colorado during which fracturing fluid or chemical and products were released. Spills without COGCC identification numbers were removed. I manually searched for the spills through the online COGIS database and read the individual spill reports to 1) confirm that they were spills of hydraulic fracturing fluid and 2) obtain spill area measurements. After the QA/QC process (described in more detail in Appendix B), 9 spills from the EPA Hydraulic Fracturing Related Spills Table were determined to be releases of HFF and were included in the spill analysis.

After reading through several individual spill reports listed in the SSPA dataset, it became clear that the 60 spills categorized as occurring during the “StimulationFrac” operational phase were more likely to be spills of HFF. From this subset, spills without volume or area data were removed. Following the QA/QC process described in Appendix B, I decided to include 18 spills from the SSPA dataset in the HFF spill analysis. Overall, I applied a similar QA/QC process to the HFF spills as I did to the produced water spills. Spills with no spill volume categorized under “water” or “other” as the type of fluid released were removed. Spills with no area measurements (magnitude or appropriate units) were also removed. All 27 spills used for this analysis had reported incident dates.

HFF spill net volumes, net spill volume per area or spill depth, and spill-size percentiles were calculated following the procedure described in section 2.1.3. The EPA dataset already had

net spill volumes pre-calculated. The 95<sup>th</sup> percentile HFF spill was chosen and kept constant throughout the HFF spill simulations. Because the focus of the study was to evaluate the importance of considering co-chemical interactions in modeling these HFF spills, I did not evaluate the risk these spills pose to groundwater quality and I did not consider how different HFF spill sizes would impact the degree of risk.

### **3.2.2 Hydraulic fracturing fluid spill simulations**

Hydraulic fracturing fluid spills were simulated using HYDRUS-1D and the model was set-up and parameterized to represent conditions in the South Platte region. Chemical-specific properties were chosen to best represent the type of co-chemical interactions we would expect to occur.

#### **3.2.2.1 Model set-up**

The model set-up used for the HFF spill simulations was the same as the structure used for the produced water spill simulations (see section 2.1.4). Only one depth to groundwater, 10 ft, was considered for the HFF spill simulations. I used HYDRUS-1D with the same upper and lower boundary conditions, temporal discretization, spatial discretization, dispersivity, soil type, and vadose zone properties as specified for the produced water spills. Simulation times varied from 1 to 1.5 years.

#### **3.2.2.2 Chemical-specific parameterization**

Simulations of HFF spills modeled the transport, degradation, and sorption of three constituents, glutaraldehyde, polyethylene glycol, and polyacrylamide. Three different scenarios were considered: 1) three constituents do not interact (Case A), 2) three constituents interact but salt is not present in the HFF (Case B) and 3) three constituents interact and salt is present in the HFF (Case C). Case C represents a HFF which used recycled produced water to create the stimulation fluid.

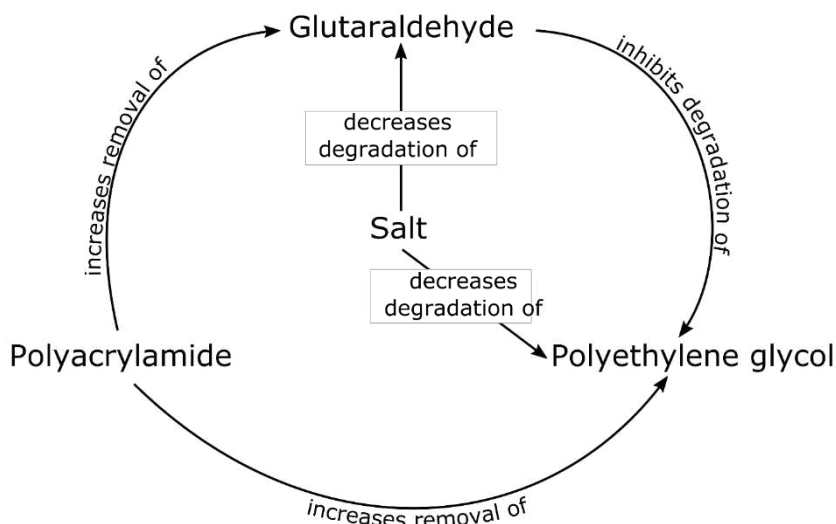
The HFF spill scenarios considered aerobic microbial degradation and soil sorption. The degradation rates for the three additives and the soil-organic carbon partitioning coefficient for glutaraldehyde were based on experimental data from McLaughlin, 2016. McLaughlin et al., 2016 added glutaraldehyde, polyethylene glycol, polyacrylamide, and salt in different

combinations to aqueous solutions with homogenized top soil and measured degradation rates for the three chemical additives. McLaughlin et al., 2016 chose the three additives because they are common constituents in hydraulic fracturing fluid and represent three different categories of additives: biocide, surfactant, and friction reducer. After examining McLaughlin et al., 2016 and determining how co-chemical behavior and spill conditions would affect degradation rates, I carefully chose the appropriate degradation rates for the model inputs.

Glutaraldehyde had the most complex interactions because as a biocide, it inhibits its own degradation and the degradation of other compounds (Leung, 2001; McLaughlin et al., 2016). Pseudo-first order removal rates for glutaraldehyde exhibited a lag phase —during which glutaraldehyde was above the minimum inhibitory concentration (MIC) and hindered its own degradation, — and a degradation phase, — during which glutaraldehyde removal was no longer deterred and the degradation rate increased. Struchtemeyer and Elshahed (2012) showed that the MIC for glutaraldehyde is 200 mg/L for biofilms of sulfate-reducing bacteria so I chose 200 mg/L to be the MIC for this modeling study. I note that this MIC level is likely an underestimate since biocidal MICs for planktonic cells have been shown to increase in the presence of organic matter such as humic acids (Struchtemeyer and Elshahed, 2012). Preliminary modeling results showed that glutaraldehyde concentrations dipped below 200 mg/L, after 3 days of the 1-1.5 year run time. Because glutaraldehyde would only be inhibiting its own removal for a short period of time relative to the total time span considered, I chose to use removal rates calculated for the degradation phase.

Polyethylene glycol degradation was significantly impacted by the presence of glutaraldehyde (McLaughlin et al., 2016). When glutaraldehyde and polyethylene glycol were both present, polyethylene glycol experienced an extended lag phase — during which glutaraldehyde impeded degradation — and a degradation phase when the degradation rate of polyethylene glycol increased (McLaughlin et al., 2016). Degradation of polyethylene glycol remained inhibited 62 days after glutaraldehyde had been completely removed (McLaughlin et al., 2016). After this point, polyethylene glycol degradation increased but 50% of the initial concentration still remained after an additional 78 days (McLaughlin et al., 2016). Preliminary modeling results showed that glutaraldehyde was completely removed from the soil profile in half a year. Because the presence of glutaraldehyde resulted in a significant lag in polyethylene glycol degradation, I chose to use a degradation rate for polyethylene glycol which represented

an average of the lag and degradation phases. McLaughlin et al., 2016 showed that polyacrylamide was very recalcitrant regardless of which compounds were also present in solution. Figure 3.1 is a diagram summarizing the co-chemical interactions (McLaughlin et al., 2016).



**Figure 3.1:** Co-chemical interactions between glutaraldehyde, polyethylene glycol, and polyacrylamide that can influence contaminant transport summarized from McLaughlin et al., 2016. The direction of the arrow indicates that one contaminant impacts another. The absence of arrows indicates that there were no observed impacts. For example, glutaraldehyde inhibits degradation of polyethylene glycol but polyethylene glycol does not impact glutaraldehyde.

Table 3.1 summarizes the chemical specific parameter values used for the HFF spill simulations. Glutaraldehyde was the only chemical additive that displayed sorption (McLaughlin et al., 2016). A soil organic carbon partitioning coefficient of ~578 L/kg was calculated from experimental data from McLaughlin et al., 2016. This value is on the higher end — likely due to the high fraction of organic carbon of the soil used in the experiments — but still within the range of soil-organic carbon partitioning coefficients calculated for glutaraldehyde from previous studies (Leung, 2001). I note that the top soil used in the experiments had a larger fraction of organic carbon of ~0.008 compared to the fraction of organic carbon used in the simulations. I also note that the degradation rates in Table 3.1 were not published in McLaughlin et al., 2016 and were provided by McLaughlin, 2016 as part of our collaboration. Initial concentrations were 250 mg/L for glutaraldehyde, 750 mg/L for polyethylene glycol, and 130 mg/L of

polyacrylamide following the concentrations studied by McLaughlin et al., 2016 and representative of typical concentrations observed in HFF.

**Table 3.1:** Pseudo-first order rate constants measured at  $23 \pm 1^\circ\text{C}$  and  $\text{pH} = 5.9\text{-}6.3$  and soil-organic carbon partitioning coefficients that served as model inputs for this study (Taken from McLaughlin et al., 2016 and McLaughlin, 2016).

Chemical additive combination	Pseudo-first order aerobic biotic decay rate ( $\text{d}^{-1}$ ) (McLaughlin, 2016)	Soil-organic carbon partitioning coefficient (L/kg) (McLaughlin, 2016)
<b>Glutaraldehyde</b>		
Case A - Glutaraldehyde	0.1152	577.7
Case B - Glutaraldehyde, Polyethylene glycol, Polyacrylamide	0.1343	577.7
Case C - Glutaraldehyde, Polyethylene glycol, Polyacrylamide, Salt	0.1164	577.7
<b>Polyethylene glycol</b>		
Case A - Polyethylene glycol	0.0339	0
Case B - Glutaraldehyde, Polyethylene glycol, Polyacrylamide	0.0043	0
Case C - Glutaraldehyde, Polyethylene glycol, Polyacrylamide, Salt	0	0
<b>Polyacrylamide</b>		
Case A - Polyacrylamide	0	0
Case B - Glutaraldehyde, Polyethylene glycol, Polyacrylamide	0	0
Case C - Glutaraldehyde, Polyethylene glycol, Polyacrylamide, Salt	0	0

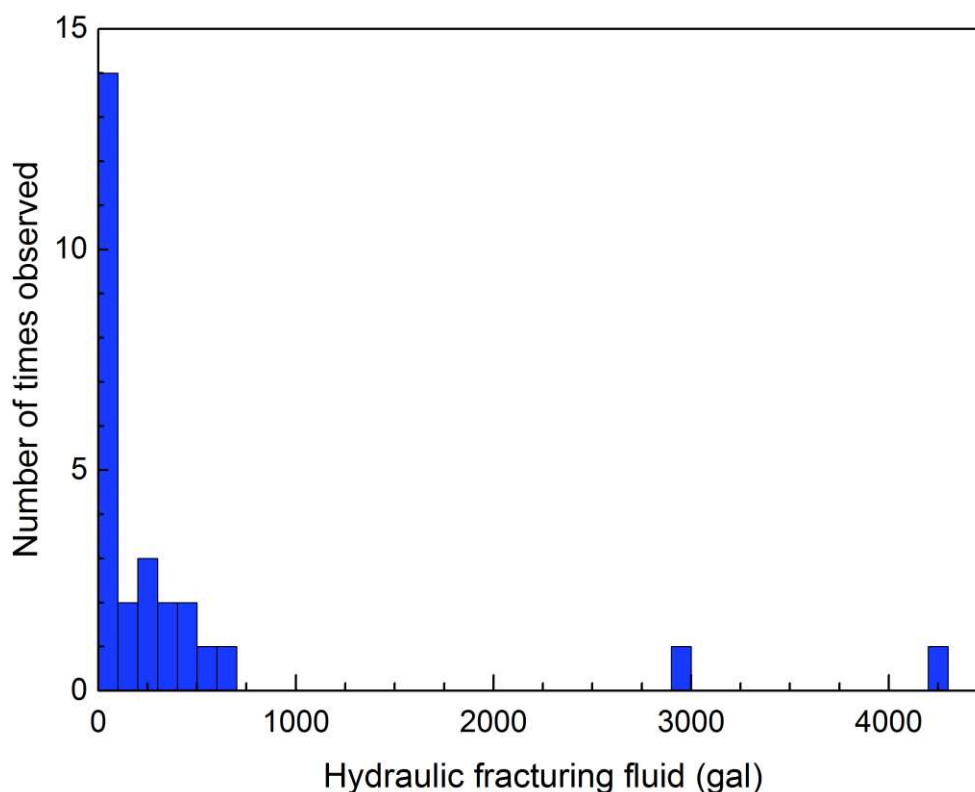
### 3.3 Results and Discussion

I analyzed hydraulic fracturing fluid spill data for the state of Colorado to determine the range of spill volumes and areas. These data provided model inputs to simulate a representative hydraulic fracturing fluid spill and determine the relative importance of accounting for co-chemical interactions when modeling spills of hydraulic fracturing fluid.

#### 3.3.1 Hydraulic fracturing fluid spill analysis

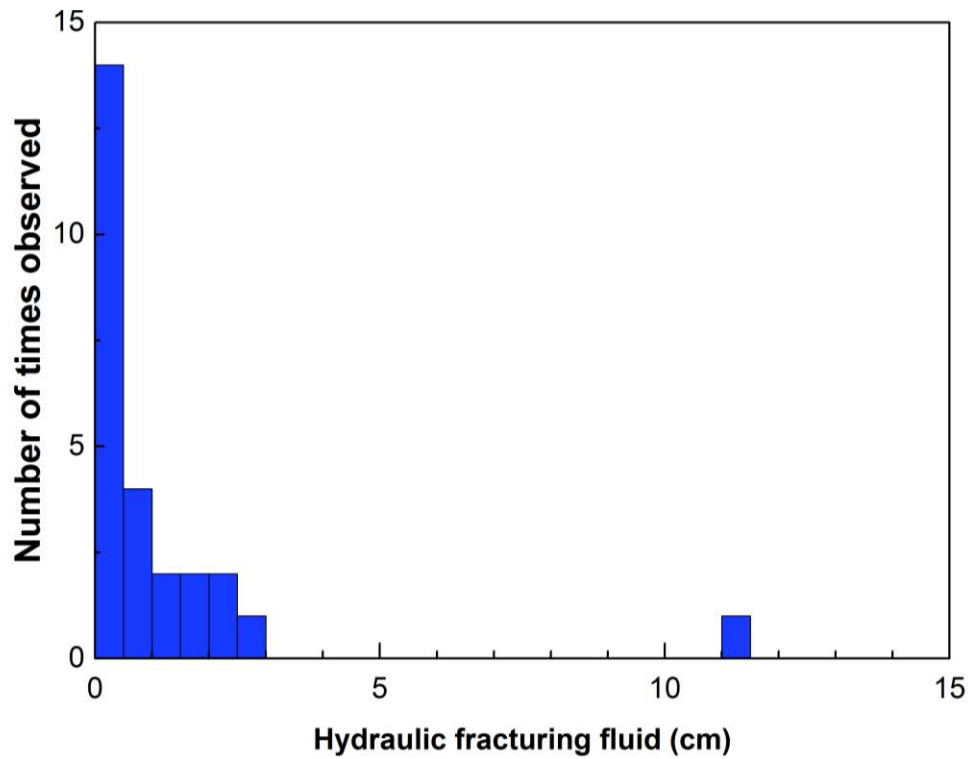
HFF spills were distributed similarly to the produced water spills with most of the spills (17 out of 27) having volumes less than 250 gallons, including 7 spills with net 0 volume, as seen in Figure 3.2. 2 spills had volumes greater than 1000 gallons. The ranges of spill volumes for produced water and HFF spills were also similar, as seen in Figure 2.2 and 3.2. However, the maximum produced water spill volume at 8400 gallons was twice as large as the maximum HFF spill at 4200 gallons. Given that HFF spills are expected to occur while service company crews

are on-site for the hydraulic fracturing operation, I anticipated HFF spills to be of smaller volumes than produced water spills. From our analysis, it is not clear if that is the case.

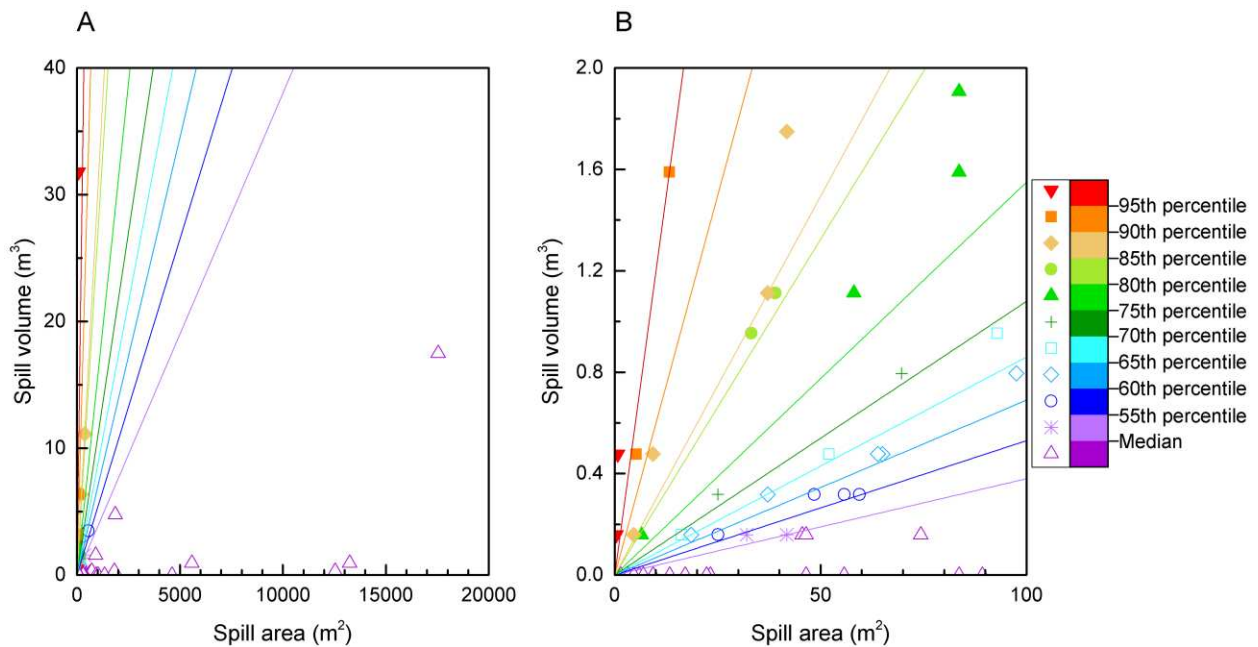


**Figure 3.2:** Histogram of the net (total volume – recovered volume) hydraulic fracturing fluid spill volume for spills occurring in Colorado.

Net spill volume per area was similarly distributed to net volume spilled with many low values and a few high values, as shown in Figure 3.3. 25 out of 27 HFF spills had less than 5 cm net spill volume per area. In general, HFF spills had lower net spill volumes per area compared to produced water spills. However, the maximum net spill volume per area for the HFF spills at ~148 cm was twice as large as the maximum 64 cm for produced water spills. Figure 3.4 shows the net spill volume per area plotted as points in spill volume-spill area space. Similar to Figure 2.4, we can see that the majority of spills are smaller than the median spill percentile. Table 3.2 summarizes the spill percentiles calculated for HFF spills. After this analysis, the 95<sup>th</sup> percentile spill of HFF was modeled to see how co-chemical interactions would affect the transport of the HFF additives through the unsaturated zone. The 95<sup>th</sup> percentile spill had a spill volume per area of about 32 cm and a spill duration of ~7.2 hrs.



**Figure 3.3:** Histogram of spill depth for hydraulic fracturing fluid spills occurring in Colorado. These data were used to calculate the hydraulic fracturing fluid spill percentiles.



**Figure 3.4:** Hydraulic fracturing spills occurring in Colorado plotted as a function of their spill volume and spill area. Plot A) is a zoomed out view of plot B).



**Table 3.2:** Calculated HFF spill volume per area and spill durations that correspond to a particular HFF spill percentile. The spill durations serve as inputs to HYDRUS-1D.

Spill percentile	Spill volume per area (cm)	Duration of spill (hr)
Median	0.49	0.1101
55th	0.66	0.1483
60th	0.83	0.1871
65th	0.97	0.2188
70th	1.34	0.3032
75th	1.64	0.3710
80th	1.86	0.4201
85th	2.39	0.5396
90th	2.67	0.6039
95th	31.9	7.2260
Maximum	148	33.548

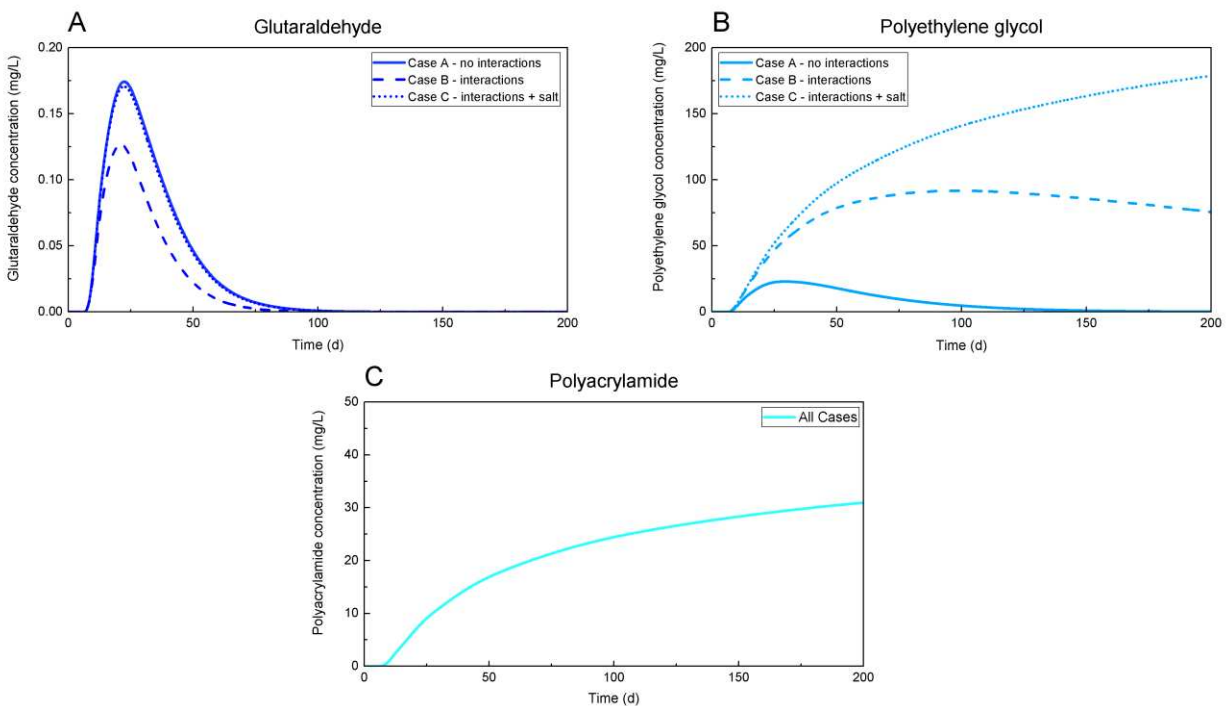
### 3.3.2 Hydraulic fracturing fluid simulations

In Figure 3.5, we see concentration breakthrough curves for the HFF spill simulations considering three chemical additives – glutaraldehyde, polyethylene glycol, and polyacrylamide – for three different cases: Case A disregarding interactions between the three contaminants, Case B accounting for co-chemical interactions, and Case C considering interactions and the presence of salt (which may be introduced to HFF if recycled produced water is used instead of freshwater). The behavior of the concentration breakthrough curves follows the degradation rates. The glutaraldehyde concentration breakthrough curve considering interactions (Case B) is substantially lower in magnitude compared to Case A, accounting for no interactions (Figure 3.5A). From Case A to Case B, the peak concentration of glutaraldehyde decreases from ~0.174 mg/L to ~0.127 mg/L and the timing of the peak decreases slightly from ~22 days to ~21 days. McLaughlin et al., 2016 suggests that glutaraldehyde and polyacrylamide or glutaraldehyde and ammonium in the polyacrylamide additive underwent cross-linking abiotic reactions which accounted for about 30% of glutaraldehyde removal. Accounting for these co-chemical interactions increases the removal rate of glutaraldehyde and in turn decreases the peak concentration glutaraldehyde exhibits at the 10-ft groundwater table. If salt is present, glutaraldehyde’s concentration breakthrough curve is very similar to Case A. Salt slightly inhibits degradation of glutaraldehyde; glutaraldehyde has been shown to biodegrade in seawater under certain conditions (Leung, 2001). Glutaraldehyde’s peak concentration under Case C at

~0.171 mg/L is slightly lower than the peak concentration under Case A at 0.174 mg/L. Salt delays degradation of glutaraldehyde at earlier times and then degradation increases. Time of breakthrough for all cases remains the same at ~5 days.

The maximum concentration for polyethylene glycol increases from about 23 mg/L to ~92 mg/L after accounting for co-chemical interactions, as seen in Figure 3.5B. Polyethylene glycol's predicted peak concentration increases as glutaraldehyde acts as a biocide and slows microbial degradation of polyethylene glycol. Maximum concentration in Case B is observed at ~97 days and is substantially delayed compared to the peak concentration in Case A seen at ~29 days. In the presence of salt, degradation of polyethylene glycol was completely inhibited. In Case C, the simulation ended before polyethylene glycol concentrations reached steady state to minimize the water balance error. The last concentration predicted at 1.5 years was ~222 mg/L. Time of breakthrough remained the same for all three cases at ~5 days.

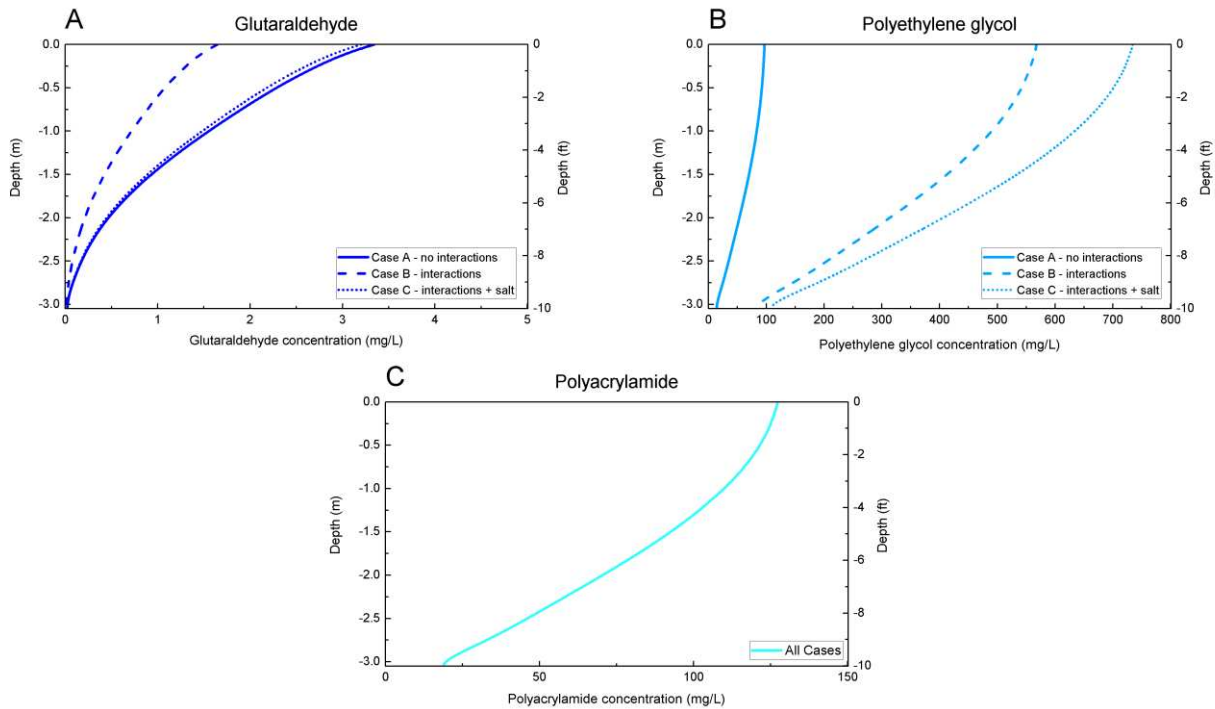
Co-chemical interactions did not affect degradation of polyacrylamide in McLaughlin et al., 2016's experimental study. Polyacrylamide was very recalcitrant and showed no evidence of



**Figure 3.5:** Concentration breakthrough curves predicted for a 10-ft groundwater table for A) glutaraldehyde, B) polyethylene glycol, and C) polyacrylamide.

removal, as shown Figure 3.5C. After 1.5 years, polyacrylamide reached a non-steady state concentration of about 38 mg/L. There was a slight difference of 0.04 mg/L between the final concentration calculated for Case B and Case C, likely due to numerical error. Breakthrough occurred at ~5 days for all cases.

Figure 3.6 shows concentration vs. depth profiles for glutaraldehyde, polyethylene glycol, and polyacrylamide after 2 months, comparing the three different cases. Figure 3.6 tells a similar story as Figure 3.5. Glutaraldehyde removal increases when considering co-chemical interactions but is similar to the base Case A when accounting for the presence of salt. Polyethylene glycol degradation is inhibited in the presence of glutaraldehyde and even more inhibited when both glutaraldehyde and salt are present. Polyacrylamide is not affected by contaminant interactions. Overall, concentrations are higher towards the soil surface. Glutaraldehyde and polyethylene glycol eventually degrade in the subsurface while polyacrylamide remains in the soil once the profile reaches hydrostatic conditions.



**Figure 3.6:** Profiles of concentration with depth for the hydraulic fracturing fluid spills over a 10-ft water table for chemical additives A) glutaraldehyde, B) polyethylene glycol, and C) polyacrylamide.

### 3.3.3 Discussion

The simulations show that under these conditions, co-chemical interactions affect the spatial distribution of contaminant concentrations in the soil profile and the contaminant concentrations predicted at the groundwater table. The degradation and concentrations of the biocide glutaraldehyde and the surfactant polyethylene glycol were particularly impacted by the presence of other compounds. Glutaraldehyde removal was likely enhanced in the company of polyacrylamide (in the absence of salt) because glutaraldehyde has been shown to form a covalent double bond between its aldehyde group and other amine groups (Dmitriev et al., 2015; McLaughlin et al., 2016; Migneault et al., 2004). Glutaraldehyde likely undergoes crosslinking reactions with amine groups on polyacrylamide or ammonia (present as ammonium sulfate), a component of the polyacrylamide mixture (Dmitriev et al., 2015; McLaughlin et al., 2016; Migneault et al., 2004). Polyethylene glycol degradation was inhibited by the presence of the biocide and even more so by the presence of salt.

Co-chemical interactions are an important consideration in certain scenarios. The types of co-chemical interactions that would need to be accounted for would likely change with the composition of the HFF, soil organic carbon content, and initial concentrations. I considered the co-chemical interactions for these three additives because data were available. However, this hydraulic fracturing fluid composition represents a small subset of possible chemical mixtures in hydraulic fracturing fluid. There may be other chemical compounds that play important roles in the contaminant transport of HFF that were not considered here. McLaughlin et al., 2016 used a soil-water ratio of 1:10 on a mass basis for their microcosm studies, which is much lower than the soil-water ratio in the simulations and in typical field conditions. A higher soil-water ratio or higher soil organic carbon content would likely result in greater sorption of glutaraldehyde. Greater sorption of glutaraldehyde would decrease mobility and keep glutaraldehyde sorbed near the soil surface. If a HFF spill were detected, glutaraldehyde containing soil could easily be excavated. Greater sorption would result in less risk in terms of glutaraldehyde exposure from an individual spill. This change in sorption would also impact degradation of other contaminants in the vadose zone; polyethylene glycol may experience a shorter lag in degradation. Co-chemical effects would also change with different initial concentrations; higher concentrations of glutaraldehyde in the HFF may result in a longer lag in degradation that would need to be considered.

None of the three chemicals considered in this study have EPA MCLs, so I used hazard quotients to estimate the human health risk of the predicted contaminant concentrations. Glutaraldehyde is the most likely public health concern with a dietary chronic reference dose of 0.16 mg/kg/day (U.S. EPA, 2007). Following standard EPA procedure (assuming recommended values for daily drinking water intake, life expectancy, exposure duration, etc.), the highest simulated peak concentration of glutaraldehyde results in a hazard quotient of 0.013. A hazard quotient greater than 1 indicates risk of adverse effects. A glutaraldehyde concentration of 13.7 mg/L would be necessary for the hazard quotient to be greater than 1 and generate concern. Shallower groundwater tables may possibly see higher concentrations of glutaraldehyde. Based on profiles of glutaraldehyde concentration, I would expect glutaraldehyde to pose risk for areas with groundwater tables <5.7 ft deep. I note that standard hazard quotient calculations are typically based on 30 years of exposure to a certain contaminant concentration. Considering that spills are pulse sources and not continuous sources, the hazard quotient and the overall risk would likely be much lower.

### **3.4 Conclusions**

In this part of the thesis, I considered how co-chemical interactions would affect the degradation and the predicted concentrations of three common chemical additives following a surface spill of hydraulic fracturing fluid. Data analysis of hydraulic fracturing fluid spills showed that most spills released small net volumes less than 750 gallons and resulted in spill depths less than 3 cm; a couple of spills had very high volumes greater than 2750 gallons and one spill had a spill depth greater than 11 cm. Hydraulic fracturing fluid spills were distributed similar to produced water spills. From the hydraulic fracturing fluid spill simulations, I can draw the following conclusions:

- Glutaraldehyde, polyethylene glycol, and polyacrylamide concentrations predicted at the groundwater table followed the specified aerobic degradation rates taken from McLaughlin 2016; higher degradation rates led to lower simulated concentrations and lower degradation rates led to higher predicted concentrations. Glutaraldehyde and polyethylene glycol were impacted by co-chemical interactions while polyacrylamide remained recalcitrant regardless of co-chemical interactions.

- For the representative conditions in the South Platte Alluvial Aquifer used in our simulations, glutaraldehyde concentrations did not result in a hazard quotient greater than 1, indicating that the 95<sup>th</sup> spill percentile of hydraulic fracturing fluid spills (from Colorado data) pose low risk to groundwater quality, from a human health perspective.

Overall, this study showed that co-chemical interactions are an important consideration in certain conditions when modeling hydraulic fracturing fluid spills. The specific interactions that need to be accounted for may differ depending on the research question, but in general, salt inhibits microbial degradation of HFF (Kekacs et al., 2015) and biocides can impact degradation of themselves and other compounds (Kahrilas et al., 2014; Leung, 2001; McLaughlin et al., 2016). Glutaraldehyde and polyacrylamide undergo cross-linking reactions, increasing the removal rate of glutaraldehyde (Dmitriev et al., 2015; McLaughlin et al., 2016; Migneault et al., 2004). Biocidal action likely only impacts degradation of hydraulic fracturing fluid spills but salt could also hinder degradation in produced water spills. Thus, chemical composition of the released fluids need to be considered to evaluate the significance of co-chemical interactions when modeling these spills and in turn, accurately determine the degree of risk surface spills pose to groundwater quality. With different initial concentrations of glutaraldehyde, soil types, soil organic carbon content, and depth to groundwater, the types of co-chemical interactions one would have to consider may change, increasing or decreasing the risk depending on the situation.

## CHAPTER 4

### CONCLUSIONS

With expansion of oil and gas development in the United States due to hydraulic fracturing and encroachment of this activity into suburban areas, public concern regarding the potential for oil and gas activities to impact groundwater resources has grown. The discussion of the risks is particularly heightened in the arid western United States where a negative impact to groundwater quality can have significant consequences for an already water stressed region. Although there are many possible ways for oil and gas stimulation and production to impact groundwater quality, an accidental surface spill is the most probable contamination pathway (Groat and Grimshaw, 2012; Metzger, 2011). I chose to focus on evaluating the risk of surface spills associated with oil and gas development to groundwater quality in the South Platte Alluvial Aquifer. Surface spills associated with oil and gas activity occur frequently in Colorado with about 690 spills happening each year (COGCC, 2016b). A study conducted on the spills occurring in Colorado in 2013 found that 14% of these spills impacted groundwater (Center for Western Priorities, 2013). The South Platte Alluvial Aquifer is a region particularly at risk due to oil and gas impacts because it overlaps with the Wattenberg field, an area of high density oil and gas activity in the Front Range of Colorado. Depth to groundwater in the alluvial aquifer varies but can be as shallow as 2 ft in some regions.

Spills related to oil and gas activity can release many different types of fluids but usually involve produced water. Produced water is water originally stored in the formation which flows to the surface along with oil or natural gas. Although composition of produced water varies over time and space, it often contains hydrocarbons, such as volatile organic compounds, semivolatile organic compounds, and polyaromatic hydrocarbons (Khan et al., 2016; Lester et al., 2015) and is very saline, ranging from a couple hundred to >300,000 mg/L total dissolved solids (seawater is typically ~35,000 mg/L total dissolved solids) (Hayes, 2009; NOAA, 2015). Another type of fluid that can be released at oil and gas sites is hydraulic fracturing fluid. Hydraulic fracturing fluids are often complex mixtures of biocides, crosslinkers, breakers, surfactants, and corrosion inhibitors (Stringfellow et al., 2014).

The goal of this thesis was to evaluate the risk of accidental surface spills and to determine the conditions under which they would affect groundwater quality in the South Platte

Alluvial Aquifer. I considered two types of fluid that could be released, produced water and hydraulic fracturing fluid. For the produced water spills, I determined the spill size risk threshold, the minimum spill volume per area necessary for a spill to reach the water table and exceed EPA limits. I then considered how storm events could affect this spill size threshold. Overall, this work set up a screening level methodology that could be applied at other sites and for various contaminants. For the hydraulic fracturing fluid spills, I was interested in how co-chemical interactions would impact degradation of the stimulation fluid as it moved through the subsurface. For the produced water and hydraulic fracturing fluid cases, research questions were addressed by conducting vadose zone simulations in HYDRUS-1D. Risk was assessed by studying the predicted concentration at shallow groundwater table depths and comparing this value to EPA limits, if they existed. Although previous work has studied spills in Pennsylvania (Fletcher, 2012) and on a broad national scale (Gradient, 2013), I am unaware of any scientific literature which has completed a specific study on spills in Colorado beyond spill data analysis.

Analysis of produced water and hydraulic fracturing spill volume data showed that they were similarly distributed. A majority of the spills had volumes less than 250 gallons while several spills exhibited volumes greater than 1000 gallons. This general trend of many small spills and a few large spills is consistent with previous studies (U.S. EPA, 2015a). Spill volume per area or spill depth was also similarly distributed with most of the spills displaying values less than 5 cm and several spills with spill depths greater than 10 cm. From the spill data analysis, I calculated spill percentiles of the spill depth. These spill percentiles served as model inputs.

The produced water spill simulations considered groundwater table depths of 2 ft or 10 ft. Benzene was chosen to be a representative contaminant in produced water. Accounting for sorption and degradation, only the maximum spill (spill depth of 148 cm) posed risk to a 10-ft groundwater table while a spill greater than the 95<sup>th</sup> percentile (12.0 cm spill depth) impacted a 2-ft groundwater table. If benzene acted as a conservative solute, then the 90<sup>th</sup> percentile spill (~6 cm spill volume per area) in addition to the 95<sup>th</sup> and maximum spill size exceeded the EPA limit for a 2-ft groundwater table. Overall the simulations showed that large spills, generally 90<sup>th</sup> percentile or above, posed risk to groundwater quality while a typical median (0.38 cm) spill involved little risk.

I also studied how storm events coupled with produced water spills would impact spill transport. For a 10-ft groundwater table depth, spills lower than the maximum percentile did not



exhibit concentration breakthrough curves with benzene concentrations exceeding 5 µg/L when accounting for degradation and sorption. If benzene acted conservatively, then the 95<sup>th</sup> spill percentile followed by 10-year, 100-year, and 500-year storms resulted in benzene concentrations higher than the EPA limit. The 90<sup>th</sup> percentile spill with a 500-year storm also exceeded 5 µg/L at the groundwater table. Lower percentile spills and lower storm intensities did not impact a 10-ft groundwater table. For a 2-ft groundwater table depth, a 500-year storm was necessary for the median spill percentile to involve risk. 100-year storms also caused all spill percentiles considered to pose risk if benzene acted as a conservative solute. For more typical storm intensities (1 yr and 10 yr), only the larger 90<sup>th</sup> percentile and 95<sup>th</sup> percentile spills consistently resulted in concentrations greater than the EPA limit at the groundwater table.

Previous work on surface spills associated with oil and gas development focus on spill data analysis or field work to assess groundwater quality impacts at oil and gas sites that likely represent worst-case scenario. Very few studies have simulated surface spills. Fletcher (2012) considered leakage directly into an aquifer and did not consider vadose zone transport while Gradient (2013) considered dilution effects from both the unsaturated and saturated zones. The results of this thesis differed from Gradient (2013) which predicted greater dilution from unsaturated zone transport. Possible differences between our study and Gradient (2013) could be due to the broad transport conditions (e.g. depth to groundwater, source area, dispersivity) considered in Gradient (2013) as well as the different spill data used to size the spills.

For the hydraulic fracturing fluid spills, I considered co-chemical interactions between glutaraldehyde, polyethylene glycol, and polyacrylamide under three different scenarios: Case A with no interactions represented, Case B accounting for co-chemical interactions, and Case C including co-chemical interactions and the presence of salt. Co-chemical interactions affected the degradation of these chemicals in the subsurface and the resulting concentration predicted at a 10-ft groundwater table. The presence of salt and polyacrylamide, the biocidal nature of glutaraldehyde, and time scale of interest affected degradation rates and how glutaraldehyde removal was represented. Polyethylene glycol was particularly impacted by the presence of glutaraldehyde and salt. Polyacrylamide's behavior stayed consistent despite changing conditions. Glutaraldehyde was the only toxic compound considered in this study. A representative hazard quotient calculated for the highest glutaraldehyde concentration predicted showed that the human health risk due to a spill in the conditions considered was low. The types

of co-chemical interactions that would need to be accounted for would likely change depending on the chemical composition of the hydraulic fracturing fluid, initial concentrations of the additives, soil type, soil organic carbon content, depth to groundwater, and spill size.

In this screening level assessment using representative hydrologic and contaminant-specific values for transport of benzene in a sandy loam, the risk of groundwater contamination due to benzene from a produced water spill is low in most areas of the South Platte Alluvial Aquifer. An accidental release may negatively impact areas with shallow groundwater if the spill is large and/or if the spill is followed by a large storm. Overall, spill depth was the dominant factor controlling whether the contaminant reached the water table. Actual site conditions (i.e., soils with high sand content) may allow smaller spills to reach groundwater. These results suggest that operator resources and state regulatory agencies should focus on ensuring that oil and gas sites with groundwater tables 10 ft deep or less are properly lined and have other measures in place to avoid leakage.

There are many other common pollutants and components of produced water (e.g., salt, polyaromatic hydrocarbons, other BTEX compounds) and hydraulic fracturing fluid (e.g., acetaldehyde, dodecyl dimethyl ammonium chloride, tetramethyl ammonium chloride) that may have human health concerns (Akob et al., 2015; Orem et al., 2014; Stringfellow et al., 2014). Future work can explore the transport of these constituents. Future work should consider modeling transport of produced water and hydraulic fracturing fluid constituents in the groundwater aquifer in addition to the vadose zone modeling conducted here to see if compounds reach drinking water receptors. This work endeavors to be site-specific in its consideration of and choosing parameters to be representative of a particular groundwater aquifer in Colorado. However, a coupled field-experimental-modeling study tracking a particular spill's movement through the subsurface would be interesting and help validate this study's modeling results. Stochastic modeling varying chemical-specific, unsaturated zone, and saturated zone properties could also reveal the range of concentrations possible for a particular spill and potentially help practitioners to make risk management-based decisions.

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## APPENDIX A

### 2.1.1. Data compilation and quality assurance-quality control

Spill reports that explicitly mentioned produced water as the released fluid remained in the dataset. If the terms “produced water,” “flowback water,” or “brine” were not in the spill description, I read spill reports to try to understand where the spill occurred on the site and what equipment failed. This information was used to infer if releases involved produced water. If insufficient information was available, the spill was removed from the dataset. I applied the same review criteria to the COGCC dataset and the SSPA dataset.

#### 2.1.1.2. Quality assurance-quality control methods for COGCC dataset

The COGCC dataset differentiated the data between “Recent” and “Historical” spills. However, the 18 “Historical” spills remaining in the dataset were not removed because they all included reported incident dates and specific spill volumes.

#### 2.1.1.3. Quality assurance-quality control methods for SSPA dataset

I acknowledge that during last minute QA/QC, I found a couple of spills in the SSPA dataset that may not have released produced water. These spills will be removed before the paper is submitted to a journal. Removal of these spills results in the spill depth percentiles shifting to slightly higher values.

### 2.1.2. Produced water spill history

**Table A.1:** Number of spills used for different parts of the spill data analysis after the QA/QC process.

	AWGDP dataset	COGCC dataset	SSPA dataset
Total number of produced water spills	3396	343	641
Number of produced water spills after QAQC	3373	343	8
Number of produced water spills used for spill history analysis	3373	343	8
Number of produced water spills that occur in counties above the South Platte Alluvial Aquifer and have spill volume and spill area data	0	85	5

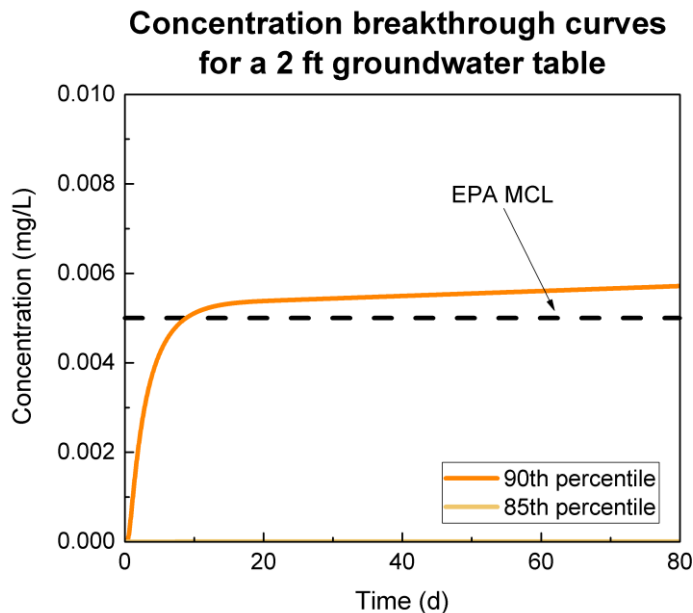
**Table A.2:** HYDRUS iteration criteria and model tolerances used for all simulations

Variable	Value
Maximum number of iterations allowed during any time step in solving the Richard's equation	30
Maximum tolerated absolute change in the value of the water content between two successive iterations during a particular time step for unsaturated region	0.001
Maximum tolerated absolute change in the value of the water content between two successive iterations during a particular time step for saturated region	0.01

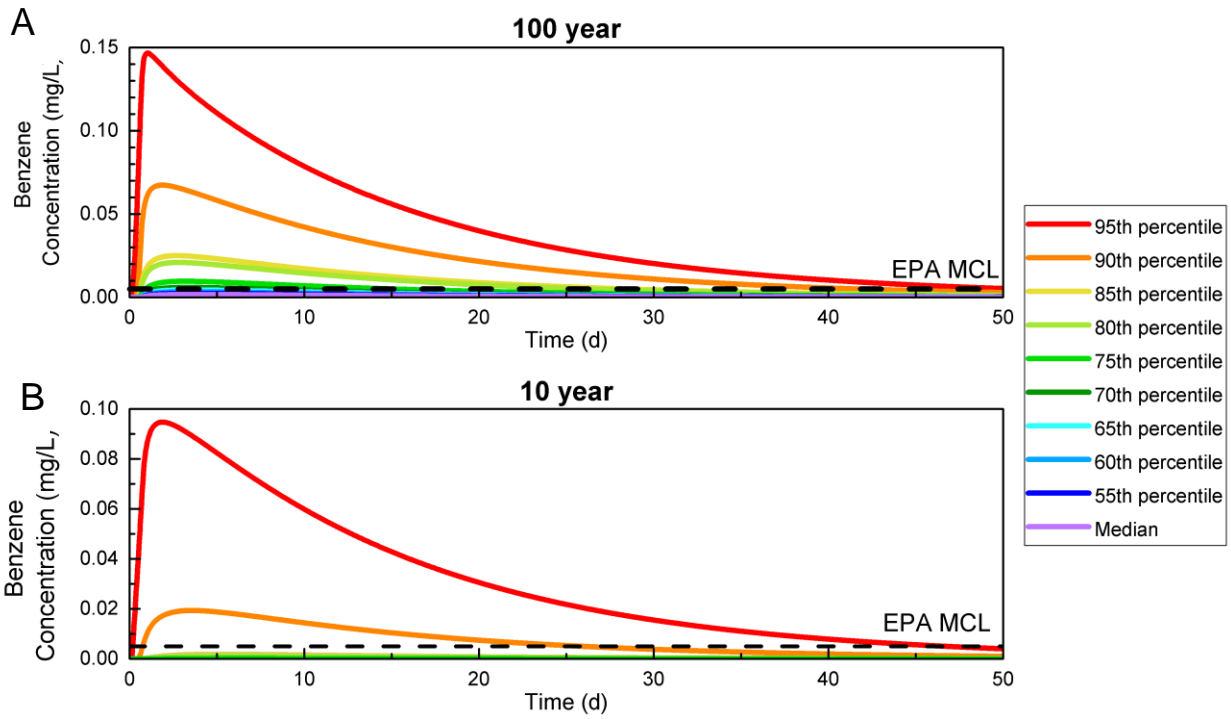
### 2.1.4.5. Storm simulations

Driscoll et al., 1989 only considered 2 precipitation gages in Colorado, Denver and Fort Collins. I chose to focus on storm statistics for Fort Collins because it was geographically closer to the area of interest and thus more representative of precipitation for areas overlying the South Platte Alluvial Aquifer. I chose to focus on precipitation frequency estimates calculated for Greeley, CO again, due to the station's close proximity to the area of interest.

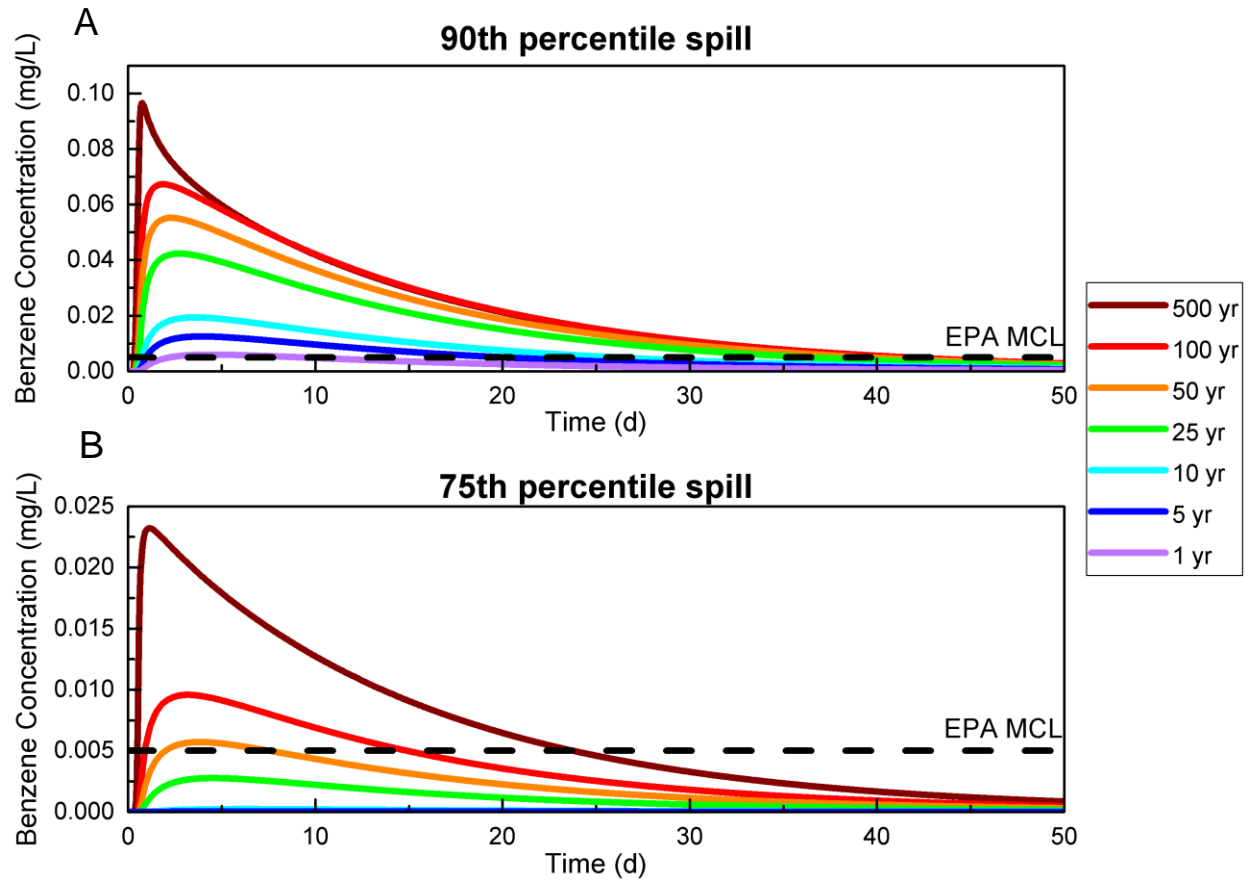
## 2.2 Results and Discussion: Additional figures



**Figure A.1:** Benzene concentration breakthrough curves for the 90<sup>th</sup> and 85<sup>th</sup> percentile spills considering a 2 ft groundwater table and assuming no degradation and no sorption. The 85<sup>th</sup> percentile concentration breakthrough curve lies at 0.



**Figure A.2:** Benzene concentration breakthrough curves on linear scales for the A) 100-year storm and B) 10-year storms. Each curve represents a different spill percentile with warmer colors representing larger spill sizes and cooler colors indicating smaller spill sizes.



**Figure A.3:** Benzene concentration breakthrough curves on linear scales for the A) 90th percentile spill and B) 75<sup>th</sup> percentile spill. Each curve represents a different storm intensity with warmer colors representing higher intensity storms and cooler colors representing lower intensity storms.

## APPENDIX B

### 3.2.1. Hydraulic Fracturing Fluid Spill Analysis

Quality-assurance-quality-control of the hydraulic fracturing fluid spill data was challenging. The most difficult problem was determining the type of fluid that was actually released. Spills claiming hydraulic fracturing fluid to be the released fluid could actually indicate flowback water, hydraulic fracturing fluid that had experienced downhole conditions for a short time period (days to months), freshwater that served as the base fluid, treated or recycled produced water that served as the base fluid, and hydraulic fracturing fluid that contained chemical additives but had not been injected. For this analysis, I wanted to focus on the last type of released fluid: hydraulic fracturing fluid that contained additives but had not been injected. Flowback water and hydraulic fracturing fluid that has experienced downhole conditions may contain some hydraulic fracturing fluid chemicals, but it is likely that some of the chemicals degraded under the formation's high temperature and high pressure conditions (Kahrilas et al., 2014). Thus, the composition and concentrations would be uncertain. Freshwater, treated produced water, or directly recycled produced water would not contain hydraulic fracturing chemicals.

Spill reports that explicitly listed hydraulic fracturing fluid compounds that were in the accidentally released fluid remained in the dataset. If no additives were mentioned, I read spill reports to try to understand during what stage of the hydraulic fracturing process the spill occurred, where the spill occurred on the site, and what equipment failed. I spoke to a previous hydraulic fracturing field engineer to determine what types of equipment failure at which locations on well pad sites would result in a spill of hydraulic fracturing fluid containing chemical additives. This information was used to infer if releases involved the correct type of fluid. For any of the spills I was uncertain about, I had the hydraulic fracturing field engineer review the report and give me her opinion. If insufficient information was available, the spill was removed from the dataset. I applied the same review criteria to the EPA dataset and the SSPA dataset.

## APPENDIX C

### SUPPLEMENTAL ELECTRONIC FILES

The supplemental electronic files include the HYDRUS-1D model input and output files for simulations shown in the figures of this thesis. There are two folders labeled “Individual spill simulations” and “Storm simulations.” The Individual spill simulations are organized into “Produced water” and “Hydraulic fracturing fluid” folders. The Storm simulations folder is broken down into “2ft” and “10ft” folders, indicating the depth to the groundwater table considered in the various simulations. The “2ft” folder contains simulations grouped into the “1 yr storm,” “10 yr storm,” “75thpercentile,other\_storms,” “90thpercentile,other\_storms,” “100 yr storm,” and “500 yr storm.” The produced water spill simulations were given the following naming convention: “pw\_##netflux\_Ksat.” The ## were replaced by numbers indicating the spill size (e.g. max for maximum, 95th for 95<sup>th</sup> percentile, 90th for 90<sup>th</sup> percentile, med for median). The simulations for a 2 ft groundwater table simulations had a “2ft” descriptor following “Ksat” in the filename while the 10-ft groundwater table had no descriptor; unless otherwise noted, the simulation considered a 10 ft depth to groundwater. The next set of letters (if present) indicated the storm size with “#yr.” For example, the 100-year storm had the description “100yr.” The final set of letters indicated if the simulation considered non-conservative or conservative transport. If the simulation assumed conservative transport, the filename contained “nodegnosorp” at the end of the filename. Simulations assuming non-conservative transport did not have a descriptor; unless otherwise noted, the simulation accounted for degradation and sorption processes. For example, “pw\_85thnetflux\_Ksat\_2ft\_1yr\_nodegnosorp” would indicate that this simulation considered an 85<sup>th</sup> percentile spill of produced water over a 2 ft groundwater table with a 1-yr storm immediately following the spill and assuming no degradation or sorption. “pw\_90thnetflux\_Ksat” is a 90<sup>th</sup> percentile produced water spill occurring over a 10-ft groundwater table.

The hydraulic fracturing fluid simulations were given the following naming convention: “hf\_95th\_aaaaaaa.” The first two letters stand for the type of fluid in the spill (“hf” for hydraulic fracturing fluid). “95th” refers to the 95<sup>th</sup> percentile spill size. The last group of letters indicated the different HFF co-chemical interactions considered: “GAPEGsPAM” for Case A, “GAPEGsPAMco” for Case B, and “GAPEGsPAMsalt” for Case C.



<b>Individual spill simulations</b>	Files and folders containing model run inputs and outputs for individual spill simulations. Includes “Hydraulic_fracturing_fluid” and “Produced_water” folders.
<b>Hydraulic_fracturing_fluid</b>	Files and folders containing model run inputs and outputs for individual spill simulations of hydraulic fracturing fluid. Contains 3 different simulations each representing a different type of co-chemical interaction (base case with no interactions, case B considering co-chemical interactions, and case C accounting for co-chemical interactions and salt) and each with its own folder.
hf_95th_GAPEGsPAM.h1d	HYDRUS-1D project file for the base case hydraulic fracturing fluid spill simulation considering no co-chemical interactions.
hf_95th_GAPEGsPAMco.h1d	HYDRUS-1D project file for the hydraulic fracturing fluid spill simulation considering co-chemical interactions.
hf_95th_GAPEGsPAMsalt.h1d	HYDRUS-1D project file for the hydraulic fracturing fluid spill simulation considering co-chemical interactions and the presence of salt.
<b>hf_95th_GAPEGsPAM</b>	Folder containing 14 model run input and output files for the base case hydraulic fracturing fluid spill simulation considering no co-chemical interactions.
<b>hf_95th_GAPEGsPAMco</b>	Folder containing 14 model run input and output files for the hydraulic fracturing fluid spill simulation considering co-chemical interactions.
<b>hf_95th_GAPEGsPAMsalt</b>	Folder containing 14 model run input and output files for the hydraulic fracturing fluid spill simulation considering co-chemical interactions and the presence of salt.

<b>Produced_water</b>	Files and folders containing model run inputs and outputs for individual produced water spill simulations. Contains 6 simulations of different produced water spill sizes and two different depths to groundwater; each simulation has its own folder.
pw_90thnetflux_Ksat_2ft.h1d	HYDRUS-1D project file for the 90 <sup>th</sup> percentile produced water spill and 2-ft depth to groundwater.
pw_95thnetflux_Ksat_2ft.h1d	HYDRUS-1D project file for the 95 <sup>th</sup> percentile produced water spill and 2-ft depth to groundwater.
pw_maxnetflux_Ksat_2ft.h1d	HYDRUS-1D project file for the maximum produced water spill and 2-ft depth to groundwater.
pw_mednetflux_Ksat.h1d	HYDRUS-1D project file for the median produced water spill and 10-ft depth to groundwater.
pw_95thnetflux_Ksat.h1d	HYDRUS-1D project file for the 95 <sup>th</sup> percentile produced water spill and 10-ft depth to groundwater.
pw_maxnetflux_Ksat.h1d	HYDRUS-1D project file for the maximum produced water spill and 10-ft depth to groundwater.
<b>pw_90thnetflux_Ksat_2ft</b>	Folder containing 14 model run input and output files for the 90 <sup>th</sup> percentile produced water spill and 2-ft depth to groundwater.
<b>pw_95thnetflux_Ksat_2ft</b>	Folder containing 14 model run input and output files for the 95 <sup>th</sup> percentile produced water spill and 2-ft depth to groundwater.
<b>pw_maxnetflux_Ksat_2ft</b>	Folder containing 14 model run input and output files for the maximum produced water spill and 2-ft depth to groundwater.
<b>pw_mednetflux_Ksat</b>	Folder containing 14 model run input and output files for the median produced

	water spill and 10-ft depth to groundwater.
<b>pw_95thnetflux_Ksat</b>	Folder containing 14 model run input and output files for the 95 <sup>th</sup> percentile produced water spill and 10-ft depth to groundwater.
<b>pw_maxnetflux_Ksat</b>	Folder containing 14 model run input and output files for the maximum produced water spill and 10-ft depth to groundwater.
<b>Storm simulations</b>	Files and folders containing model run inputs and outputs for spill-storm simulations. Includes “2ft” and “10ft” folders.
<b>2ft</b>	Files and folders containing model run inputs and outputs for spill-storm simulations and 2-ft depth to groundwater. Includes “1 yr storm,” “10 yr storm,” “75thpercentile,other_storms,” “90thpercentile,other_storms,” “100 yr storm,” and “500 yr storm” folders.
<b>1 yr storm</b>	Files and folders containing model run inputs and outputs for simulations of spills over groundwater tables 2 ft below the surface, followed by 1-yr storms. Contains 3 different produced water spill-storm simulations considering different spill sizes, conservative transport, and nonconservative transport; each simulation has its own folder.
<b>pw_85thnetflux_Ksat_2ft_1yr_nodgnosorp.h1d</b>	HYDRUS-1D project file for the 85 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface and considering conservative transport, followed by a 1-yr storm.
<b>pw_90thnetflux_Ksat_2ft_1yr.h1d</b>	HYDRUS-1D project file for the 90 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 1-yr storm.

pw_95thnetflux_Ksat_2ft_1yr.h1d	HYDRUS-1D project file for the 95 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 1-yr storm.
<b>pw_85thnetflux_Ksat_2ft_1yr_nodegnosorp</b>	Folder containing 14 model input and output files for the 85 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface and considering conservative transport, followed by a 1-yr storm.
<b>pw_90thnetflux_Ksat_2ft_1yr</b>	Folder containing 14 model input and output files for the 90 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface and followed by a 1-yr storm.
<b>pw_95thnetflux_Ksat_2ft_1yr</b>	Folder containing 14 model input and output files for the 95 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface and followed by a 1-yr storm.
<b>10 yr storm</b>	Files and folders containing model run inputs and outputs for simulations of spills over groundwater tables 2 ft below the surface and followed by 10-yr storms. Contains 5 different produced water spill-storm simulations considering different spill sizes, conservative transport, and nonconservative transport; each simulation has its own folder.
pw_75thnetflux_Ksat_2ft_10yr_nodegnosorp.h1d	HYDRUS-1D project file for the 75 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface and considering conservative transport, followed by a 10-yr storm.
pw_80thnetflux_Ksat_2ft_10yr_nodegnosorp.h1d	HYDRUS-1D project file for the 80 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface and considering conservative transport, followed by a 10-yr storm.

pw_85thnetflux_Ksat_2ft_10yr_nodegnosorp.h1d	HYDRUS-1D project file for the 85 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface and considering conservative transport, followed by a 10-yr storm.
pw_90thnetflux_Ksat_2ft_10yr.h1d	HYDRUS-1D project file for the 90 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 10-yr storm.
pw_95thnetflux_Ksat_2ft_10yr.h1d	HYDRUS-1D project file for the 95 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 10-yr storm.
<b>pw_75thnetflux_Ksat_2ft_10yr_nodegnosorp</b>	Folder containing 14 model input and output files for the 75 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface and considering conservative transport, followed by a 10-yr storm.
<b>pw_80thnetflux_Ksat_2ft_10yr_nodegnosorp</b>	Folder containing 14 model input and output files for the 80 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface and considering conservative transport, followed by a 10-yr storm.
<b>pw_85thnetflux_Ksat_2ft_10yr_nodegnosorp</b>	Folder containing 14 model input and output files for the 85 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface and considering conservative transport, followed by a 10-yr storm.
<b>pw_90thnetflux_Ksat_2ft_10yr</b>	Folder containing 14 model input and output files for the 90 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 10-yr storm.
<b>pw_95thnetflux_Ksat_2ft_10yr</b>	Folder containing 14 model input and output files for the 95 <sup>th</sup> percentile produced water spill over groundwater

	tables 2 ft below the surface, followed by a 10-yr storm.
<b>100 yr storm</b>	Files and folders containing model run inputs and outputs for simulations of produced water spills over groundwater tables 2 ft below the surface and followed by 100-yr storms. Contains 10 different produced water spill-storm simulations considering different spill sizes, conservative transport, and nonconservative transport; each simulation has its own folder.
pw_mednetflux_Ksat_2ft_100yr_nodegnosorp.h1d	HYDRUS-1D project file for the median produced water spill over groundwater tables 2 ft below the surface and considering conservative transport, followed by a 100-yr storm.
pw_55thnetflux_Ksat_2ft_100yr_nodegnosorp.h1d	HYDRUS-1D project file for the 55 <sup>th</sup> produced water spill over groundwater tables 2 ft below the surface and considering conservative transport, followed by a 100-yr storm.
pw_60thnetflux_Ksat_2ft_100yr_nodegnosorp.h1d	HYDRUS-1D project file for the 60 <sup>th</sup> produced water spill over groundwater tables 2 ft below the surface and considering conservative transport, followed by a 100-yr storm.
pw_65thnetflux_Ksat_2ft_100yr_nodegnosorp.h1d	HYDRUS-1D project file for the 65 <sup>th</sup> produced water spill over groundwater tables 2 ft below the surface and considering conservative transport, followed by a 100-yr storm.
pw_70thnetflux_Ksat_2ft_100yr.h1d	HYDRUS-1D project file for the 70 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 100-yr storm.
pw_75thnetflux_Ksat_2ft_100yr.h1d	HYDRUS-1D project file for the 75 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 100-yr storm.

pw_80thnetflux_Ksat_2ft_100yr.h1d	HYDRUS-1D project file for the 80 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 100-yr storm.
pw_85thnetflux_Ksat_2ft_100yr.h1d	HYDRUS-1D project file for the 85 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 100-yr storm.
pw_90thnetflux_Ksat_2ft_100yr.h1d	HYDRUS-1D project file for the 90 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 100-yr storm.
pw_95thnetflux_Ksat_2ft_100yr.h1d	HYDRUS-1D project file for the 95 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 100-yr storm.
<b>pw_mednetflux_Ksat_2ft_100yr_nodegnosorp</b>	Folder containing 14 model input and output files for the median produced water spill over groundwater tables 2 ft below the surface and considering conservative transport, followed by a 100-yr storm.
<b>pw_55thnetflux_Ksat_2ft_100yr_nodegnosorp</b>	Folder containing 14 model input and output files for the 55 <sup>th</sup> produced water spill over groundwater tables 2 ft below the surface and considering conservative transport, followed by a 100-yr storm.
<b>pw_60thnetflux_Ksat_2ft_100yr_nodegnosorp</b>	Folder containing 14 model input and output files for the 60 <sup>th</sup> produced water spill over groundwater tables 2 ft below the surface and considering conservative transport, followed by a 100-yr storm.
<b>pw_65thnetflux_Ksat_2ft_100yr_nodegnosorp</b>	Folder containing 14 model input and output files for the 65 <sup>th</sup> produced water spill over groundwater tables 2 ft below the surface and considering conservative transport, followed by a 100-yr storm.
<b>pw_70thnetflux_Ksat_2ft_100yr</b>	Folder containing 14 model input and output files for the 70 <sup>th</sup> percentile produced water spill over groundwater

	tables 2 ft below the surface, followed by a 100-yr storm.
<b>pw_75thnetflux_Ksat_2ft_100yr</b>	Folder containing 14 model input and output files for the 75 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 100-yr storm.
<b>pw_80thnetflux_Ksat_2ft_100yr</b>	Folder containing 14 model input and output files for the 80 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 100-yr storm.
<b>pw_85thnetflux_Ksat_2ft_100yr</b>	Folder containing 14 model input and output files for the 85 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 100-yr storm.
<b>pw_90thnetflux_Ksat_2ft_100yr</b>	Folder containing 14 model input and output files for the 90 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 100-yr storm.
<b>pw_95thnetflux_Ksat_2ft_100yr</b>	Folder containing 14 model input and output files for the 95 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 100-yr storm.
<b>500 yr storm</b>	Files and folders containing model run inputs and outputs for simulations of produced water spills over groundwater tables 2 ft below the surface and followed by 500-yr storms. Contains 10 different produced water spill-storm simulations considering different spill sizes; each simulation has its own folder.
<b>pw_mednetflux_Ksat_2ft_500yr.h1d</b>	HYDRUS-1D project file for the median produced water spill over groundwater tables 2 ft below the surface, followed by a 500-yr storm.



pw_55thnetflux_Ksat_2ft_500yr.h1d	HYDRUS-1D project file for the 55 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 500-yr storm.
pw_60thnetflux_Ksat_2ft_500yr.h1d	HYDRUS-1D project file for the 60 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 500-yr storm.
pw_65thnetflux_Ksat_2ft_500yr.h1d	HYDRUS-1D project file for the 65 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 500-yr storm.
pw_70thnetflux_Ksat_2ft_500yr.h1d	HYDRUS-1D project file for the 70 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 500-yr storm.
pw_75thnetflux_Ksat_2ft_500yr.h1d	HYDRUS-1D project file for the 75 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 500-yr storm.
pw_80thnetflux_Ksat_2ft_500yr.h1d	HYDRUS-1D project file for the 80 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 500-yr storm.
pw_85thnetflux_Ksat_2ft_500yr.h1d	HYDRUS-1D project file for the 85 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 500-yr storm.
pw_90thnetflux_Ksat_2ft_500yr.h1d	HYDRUS-1D project file for the 90 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 500-yr storm.
pw_95thnetflux_Ksat_2ft_500yr.h1d	HYDRUS-1D project file for the 95 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 500-yr storm.
<b>pw_mednetflux_Ksat_2ft_500yr</b>	Folder containing 14 model input and output files for the median produced water spill over groundwater tables 2 ft

	below the surface, followed by a 500-yr storm.
<b>pw_55thnetflux_Ksat_2ft_500yr</b>	Folder containing 14 model input and output files for the 55 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 500-yr storm.
<b>pw_60thnetflux_Ksat_2ft_500yr</b>	Folder containing 14 model input and output files for the 60 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 500-yr storm.
<b>pw_65thnetflux_Ksat_2ft_500yr</b>	Folder containing 14 model input and output files for the 65 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 500-yr storm.
<b>pw_70thnetflux_Ksat_2ft_500yr</b>	Folder containing 14 model input and output files for the 70 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 500-yr storm.
<b>pw_75thnetflux_Ksat_2ft_500yr</b>	Folder containing 14 model input and output files for the 75 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 500-yr storm.
<b>pw_80thnetflux_Ksat_2ft_500yr</b>	Folder containing 14 model input and output files for the 80 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 500-yr storm.
<b>pw_85thnetflux_Ksat_2ft_500yr</b>	Folder containing 14 model input and output files for the 85 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 500-yr storm.
<b>pw_90thnetflux_Ksat_2ft_500yr</b>	Folder containing 14 model input and output files for the 90 <sup>th</sup> percentile produced water spill over groundwater

	tables 2 ft below the surface, followed by a 500-yr storm.
<b>pw_95thnetflux_Ksat_2ft_500yr</b>	Folder containing 14 model input and output files for the 95 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 500-yr storm.
<b>75thpercentile,other_storms</b>	Files and folders containing model run inputs and outputs for simulations of the 75 <sup>th</sup> percentile spill over groundwater tables 2 ft below the surface and followed by different storm sizes (other than 1-yr, 10-yr, 100-yr, and 500-yr). Contains 2 different produced water spill-storm simulations considering different storm sizes.
pw_75thnetflux_Ksat_2ft_25yr.h1d	HYDRUS-1D project file for the 75 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 25-yr storm.
pw_75thnetflux_Ksat_2ft_50yr.h1d	HYDRUS-1D project file for the 75 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 50-yr storm.
<b>pw_75thnetflux_Ksat_2ft_25yr</b>	Folder containing 14 model input and output files for the 75 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 25-yr storm.
<b>pw_75thnetflux_Ksat_2ft_50yr</b>	Folder containing 14 model input and output files for the 75 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 50-yr storm.
<b>90thpercentile,other_storms</b>	Files and folders containing model run inputs and outputs for simulations of the 90 <sup>th</sup> percentile spill over groundwater tables 2 ft below the surface and followed by different storm sizes (other than 1-yr, 10-yr, 100-yr, and 500-yr).

	Contains 3 different produced water spill-storm simulations considering different storm sizes.
pw_90thnetflux_Ksat_2ft_5yr.h1d	HYDRUS-1D project file for the 90 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 5-yr storm.
pw_90thnetflux_Ksat_2ft_25yr.h1d	HYDRUS-1D project file for the 90 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 25-yr storm.
pw_90thnetflux_Ksat_2ft_50yr.h1d	HYDRUS-1D project file for the 90 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 50-yr storm.
<b>pw_90thnetflux_Ksat_2ft_5yr</b>	Folder containing 14 model input and output files for the 90 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 5-yr storm.
<b>pw_90thnetflux_Ksat_2ft_25yr</b>	Folder containing 14 model input and output files for the 90 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 25-yr storm.
<b>pw_90thnetflux_Ksat_2ft_50yr</b>	Folder containing 14 model input and output files for the 90 <sup>th</sup> percentile produced water spill over groundwater tables 2 ft below the surface, followed by a 50-yr storm.
<b>10ft</b>	Files and folders containing model run inputs and outputs for spill-storm simulations and 10-ft depth to groundwater. Contains 7 simulations considering different spill sizes and storm intensities; each simulation has its own folder.
pw_90thnetflux_Ksat_10yr_nodgnosorp.h1d	HYDRUS-1D project file for the 90 <sup>th</sup> percentile produced water spill over groundwater tables 10 ft below the

	surface and considering conservative transport, followed by a 10-yr storm.
pw_90thnetflux_Ksat_100yr_nodegnosorp.h1d	HYDRUS-1D project file for the 90 <sup>th</sup> percentile produced water spill over groundwater tables 10 ft below the surface and considering conservative transport, followed by a 100-yr storm.
pw_90thnetflux_Ksat_500yr_nodegnosorp.h1d	HYDRUS-1D project file for the 90 <sup>th</sup> percentile produced water spill over groundwater tables 10 ft below the surface and considering conservative transport, followed by a 500-yr storm.
pw_95thnetflux_Ksat_1yr_nodegnosorp.h1d	HYDRUS-1D project file for the 95 <sup>th</sup> percentile produced water spill over groundwater tables 10 ft below the surface and considering conservative transport, followed by a 1-yr storm.
pw_95thnetflux_Ksat_10yr_nodegnosorp.h1d	HYDRUS-1D project file for the 95 <sup>th</sup> percentile produced water spill over groundwater tables 10 ft below the surface and considering conservative transport, followed by a 10-yr storm.
pw_95thnetflux_Ksat_100yr_nodegnosorp.h1d	HYDRUS-1D project file for the 95 <sup>th</sup> percentile produced water spill over groundwater tables 10 ft below the surface and considering conservative transport, followed by a 100-yr storm.
pw_95thnetflux_Ksat_500yr_nodegnosorp.h1d	HYDRUS-1D project file for the 95 <sup>th</sup> percentile produced water spill over groundwater tables 10 ft below the surface and considering conservative transport, followed by a 500-yr storm.
<b>pw_90thnetflux_Ksat_10yr_nodegnosorp</b>	Folder containing 14 model input and output files for the 90 <sup>th</sup> percentile produced water spill over groundwater tables 10 ft below the surface and considering conservative transport, followed by a 10-yr storm.
<b>pw_90thnetflux_Ksat_100yr_nodegnosorp</b>	Folder containing 14 model input and output files for the 90 <sup>th</sup> percentile

	produced water spill over groundwater tables 10 ft below the surface and considering conservative transport, followed by a 100-yr storm.
<b>pw_90thnetflux_Ksat_500yr_nodegnosorp</b>	Folder containing 14 model input and output files for the 90 <sup>th</sup> percentile produced water spill over groundwater tables 10 ft below the surface and considering conservative transport, followed by a 500-yr storm.
<b>pw_95thnetflux_Ksat_1yr_nodegnosorp</b>	Folder containing 14 model input and output files for the 95 <sup>th</sup> percentile produced water spill over groundwater tables 10 ft below the surface and considering conservative transport, followed by a 1-yr storm.
<b>pw_95thnetflux_Ksat_10yr_nodegnosorp</b>	Folder containing 14 model input and output files for the 95 <sup>th</sup> percentile produced water spill over groundwater tables 10 ft below the surface and considering conservative transport, followed by a 10-yr storm.
<b>pw_95thnetflux_Ksat_100yr_nodegnosorp</b>	Folder containing 14 model input and output files for the 95 <sup>th</sup> percentile produced water spill over groundwater tables 10 ft below the surface and considering conservative transport, followed by a 100-yr storm.
<b>pw_95thnetflux_Ksat_500yr_nodegnosorp</b>	Folder containing 14 model input and output files for the 95 <sup>th</sup> percentile produced water spill over groundwater tables 10 ft below the surface and considering conservative transport, followed by a 500-yr storm.
A_level.out	Text file containing model output of pressure heads and cumulative fluxes at the boundary and in the root zone.
ATMOSPH.IN	Text file describing time dependent boundary conditions imposed at the top or bottom of the profile.

Balance.out	Water, heat, and solute mass balance output file containing the total amount of water, heat, and solute inside each specified subregion, inflow/ouflow rates to/from each subregion, absolute and relative errors in water and solute mass balances, as well as the mean pressure head, mean temperature, and mean concentration of each subregion.
DESCRIPT	Text file with project description
HYDRUS1D.DAT	Text file that enables communication between particular modules of the user-interface. The text file holds information about the processes being considered in the simulation, the profile setup, spatial discretization, and units.
I_Check.out	Text file describing the spatial discretization, soil hydraulic characteristics, and transport properties of each soil material.
Nod_Inf.out	Text file containing the pressure head, water content, fluxes, soil hydraulic information, solution and sorbed concentrations, and temperature at each node.
Obs_Node.out	Text file containing pressure head, water content, temperature, and solution and sorbed concentrations as a function of time at specified nodes.
PROFILE.DAT	Text file containing nodal information.
Profile.out	Text file describing input soil hydraulic properties.
Run_Inf.out	Text file containing time and iteration information.
SELECTOR.IN	Text file describing root water uptake input parameters.
solute.out	Text file with actual and cumulative concentration flux output for each solute.

T_Level.out	Text file containing output of pressure head and fluxes at the boundaries and in the root zone.
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