

DISSERTATION

DON'T CRY OVER SPILLED WATER: IDENTIFYING RISKS AND SOLUTIONS FOR PRODUCED WATER

SPILLS

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## ABSTRACT

### DON'T CRY OVER SPILLED WATER: IDENTIFYING RISKS AND PRODUCING SOLUTIONS FOR PRODUCED WATER SPILLS

Resource requirements and future energy generation requires careful evaluation, particularly due to climate change and water scarcity. This thesis discusses one aspect of energy generation linked to water; oil-and-gas extraction and the large volumes of waste water produced, otherwise known as “produced water”. This research focuses on surface spills of produced water, their ramifications, safeguards against groundwater contamination at spill sites and potential remediation strategies. Produced water contains a variety of contaminants that include the group of known toxins, BTEX (benzene, toluene, ethylbenzene and xylene), and high salt concentrations. A combination of factors such as large volumes of generated produced water, the need for storage and transportation across large distances and the toxic-and-mobile nature of produced water constituents creates risks for spills that can pollute groundwater. Spills occur regularly, particularly in Weld County, Colorado, where the demand for natural gas is high.

To answer spill-related hypotheses, a multitude of methodology were employed: modeling, greenhouse experimentation, gas chromatography and summarization of spill reports and statistical analyses. Using publically available spill data, this research found that the frequency of oil-and-gas related spills and the average spilled volume has increased in Weld County from 2011–2015. Additionally, the number of spills that have resulted in groundwater

contamination has increased in the area. By focusing on the oil-and-gas operators responsible for these spills, a linear relationship was found between the volumes of oil-and-gas produced compared to the volumes of produced-water generated. However, larger oil-and-gas producers did not show a linear relationship between oil-and-gas produced and produced-water generated, such that larger producers were more efficient and generated less water per unit of energy. So while scale-up efficiency seems to exist for produced-water generation, no mitigation of spill volume would be obtained by utilizing larger producers. Regardless of which operator was responsible for the spill, the groundwater depth at a spill site significantly predicted when a spill would result in groundwater contamination. This result was also validated through modeling; shallow depths to groundwater as well as larger spill volumes and coarse soil textures contributed to higher concentrations of groundwater contamination. Previous research has shown that a large fraction of spills occur at well pads. Our results suggest that fracking-site selection should preclude areas where the groundwater is shallow and soil is coarsely textured. Additionally, precautions should be taken to reduce the volume of spilled produced water to reduce the risk of groundwater contamination.

This research additionally sought to reduce contaminant migration in soils towards groundwater at produced-water spill sites. In a greenhouse study it was shown that foxtail barley (*Hordeum jubatum*) and perennial ryegrass (*Lolium perenne*), can tolerate high salt concentrations in produced water while taking up minute levels of BTEX. The presence of plants changed the concentration of BTEX and naphthalene in the soil, but the direction of the change depended upon the particular plant and varied across contaminants. Additionally, the roots of either species saw no decrease of biomass upon exposure to BTEX and salt but shoots biomass

was significantly reduced for foxtail barley. These results suggest that these grasses would not be capable of addressing large concentrations of BTEX at spill sites; however, these plants would be useful near well pads that regularly experience smaller spills, thus being able to tolerate spills while continually removing small amounts of BTEX in the soil.

In conclusion, this thesis sought to identify holistic tools for produced-water spill prevention, mitigation and remediation to lessen environmental and health concerns while creating minimal disturbance to the natural landscape. The results lend themselves to important management information applicable to Weld County, CO but with lessons that others can draw upon elsewhere. This dissertation highlights areas for improved regulation and best management practices that can preemptively reduce the risk for groundwater contamination from produced water spills.

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## 1 PRELUDE

Oil-and-gas extraction is innately connected with water, a relationship commonly known as the “water-energy nexus”. Cogenerated “produced water”, waste water generated during oil-and-gas extraction, can represent significant losses to fresh water (as a fraction of produced water was used in the extraction process) and also present risks for groundwater contamination. Benzene, toluene, ethylbenzene, xylene (BTEX) and naturally occurring radioactive materials (NORM) are just a few of the hazardous contaminants found in produced water. The objective of this research was to characterize the overall chemical impact of produced-water spills, the risk for groundwater contamination at spill sites and evaluation of *in situ* remediation strategies. The dissertation is divided into three chapters with each chapter written as a separate manuscript that has been submitted to various journals.

This prelude section serves to briefly describe the main focus of each chapter and to present the hypotheses found in each chapter. The goal of this project was to produce science-based mitigation and restoration strategies for produced-water spill sites. Chapter 1, titled “Produced water surface spills: using past experiences to guide mitigation plans”, describes typical produced-water spills and to determine factors that could be of use for predicting the likelihood of a spill effecting groundwater. In Chapter 1, publically-available data were analyzed to characterize spills of produced water and oil-and-gas related material from 2015 in Weld County, Colorado. In this chapter I hypothesized that (1) oil-and-gas related spills, and more specifically produced water spills, were occurring more frequently and in larger volumes since 2011; (2) areas experiencing a spill has higher odds of groundwater contamination if larger

volumes of water, larger ground-surface areas affected and the depth to groundwater was shallow; (3) and that larger oil-and-gas producers had higher efficiency in regards to energy-to-water generation and energy-to-water spilled because of scale-up efficiencies. These questions were explored and the results of this analysis will be submitted for publication in a scientific journal.

In the second chapter, titled “Produced-water surface spills and the risk for BTEX-and-naphthalene groundwater contamination”, I evaluate spills typical of Weld County over a range of spill intensities and spill-site factors, like depth to groundwater and soil type, utilizing the modeling program HYDRUS. In this chapter I hypothesized that (1) benzene and toluene would be most problematic at spill sites; (2) the majority of spill scenarios would result in concentrations relevant to the EPA drinking water limit in groundwater and (3) higher-intensity spills, coarse soils and shallow groundwater would experience higher maximum groundwater concentrations. The results of this study were summarized into a quick reference guide for assessment of groundwater-contamination risk at potential spill sites. The results of this study have been accepted as a manuscript to *Water, Air and Soil Pollution*.

In Chapter 3 the ability to tolerate and remediate organic pollutants at a produced-water spill site were evaluated for two salt-tolerant grasses, while being exposed to typical salt concentrations found in produced water. I hypothesized that (1) each species would take up organic contaminants into their tissues; (2) the concentration in their tissue would decrease over time; (3) the organics and not the salt would be the limiting factor to plant growth and; (4) soil would have less contamination when treated with plants. The results of this study have been submitted to a scientific journal.

## **2 INTRODUCTION**

The extraction of natural gas through hydraulic fracturing (“fracking” or “hydro fracking”) has been suggested as a solution to our growing energy needs. Not only does natural gas release less carbon compared to coal upon ignition but natural gas meets peak energy demands that renewables cannot yet meet (Keer 2010, U.S. Energy Information Administration 2016). However, fracking is not without its own risks. Hydraulic fracturing for oil and gas creates large volumes of wastewater, also known as “produced water.” Known risks from fracking include seismic activity, stray gas migration into groundwater aquifers, and groundwater and surface water contamination from produced water spills (Torres et al. 2015; Vidic et al. 2013). This introduction provides an overview of produced water: what it is and how it is formed, laws regarding its disposal, and significance of spills. This research focuses on Weld County, Colorado, a region that has experienced rapid investment and development of fracking sites. Weld County is used as a case study to understand typical spill characteristics and to help identify methods for reducing the impact of fracking on the environment (Matthews 2011, Swain 2017).

### **2.1 OIL AND GAS EXTRACTION CREATES PRODUCED WATER**

Produced water is formed mainly from unconventional oil-and-gas extraction but is also employed at conventional wells for increased production. Both extraction techniques necessitate water and generate water. This section will focus on how produced water volumes vary across extraction techniques, resource type (oil or gas) and geological basin. This section will conclude with an overall discussion of produced water volumes generated across the United States and how those have changed over time.

Conventional drilling, the initial technique used to extract oil and gas, consists of drilling a vertical well directly into a basin from which the reserves were drawn. This method provides access to underground pools of oil and gas that can be pumped back to the surface. In the 1970's unconventional drilling became popular as conventional sources were on the decline. Unconventional drilling provided a method for extracting oil-and-gas reserves stored in tightly bound shale, sandstone and limestone, which was previously unfeasible. The method involved with unconventional drilling is a more sophisticated technique combining vertical and horizontal drilling with hydraulic fracturing. Unlike conventional drilling, unconventional drilling accesses relatively smaller volumes of oil and gas contained in different stratigraphic layers and a single unconventional well can be fracked multiple times and in different below-surface areas. Overall, unconventional drilling requires 3–4 millions of gallons of water (12–16 million liters) per well (Keer 2010). Water is needed for different purposes during the lifetime of the well. Water is used during the drilling process to reduce friction and also during the frack, which involves pumping pressurized water along with treatment chemicals and other materials, such as sand, to facilitate the recovery of tightly bound oil and gas (Keer 2010, Manuel 2010). The release of pressure pushes the combination of input water and source water to the surface in the form of “produced water” along with oil and gas (Keer 2010, Manuel 2010). Although the frack takes only a few days, water, oil and gas can be produced for up to 20 years thereafter (Bai et al. 2013). In the industry, the initial water returned to the surface is known as flowback water, which bares the chemical characteristics of the fracked basin and the treatment chemicals (Kondash et al. 2017). After two months, the water returned to the surface is called produced water and mainly reflects the chemistry of the fracked basin. Often there is no distinction made between flowback and

produced water. For the purposes of this introduction, “produced water” refers to both water types.

## **2.2 WATER-VOLUMES PRODUCED AND HOW THEY VARY ACROSS SPACE, TIME AND TECHNIQUE**

Determining statewide and national volumes of produced water generated can be difficult because of different reporting systems used by each state with varying levels of precision. Over the past two decades the trend shows produced water volumes increasing. In 1995 API estimated that 18 billion barrels of produced water was generated in onshore drilling in the United States. By 2007, this number increased to 21 billion barrels for all U.S. drilling, as estimated by Veil and Clark (2009). Although various projections show produced water volumes increasing through 2020, another analysis by Veil (2015) showed a 1% increase from 2007 to 2012. During that same period oil production increased by 29% and gas production increased by 22%, suggesting that perhaps the volume of produced water generated each year started to plateau.

The volume of water generated across space can vary greatly across multiple factors. Gas extraction is known to be more efficient than oil extraction in terms of units of water produced per unit of energy produced. For example, oil extraction requires over 9 units of water per unit of energy, where gas only requires 0.56 units of water per unit energy (Veil 2015). Additionally, unconventional drilling is more water efficient, producing less water per unit of energy generated (Scanlon et al. 2014, Veil 2015). The specific basin from which oil and gas is being extracted can influence the volumes of water being produced. With higher pressure and more naturally occurring water within the fracked region, more produced water can be returned to



the surface (U.S. Environmental Protection Agency 2017). Lastly, the volume of water used to fracture the formation influences the volume that comes back as produced water.

Volumes of produced water can vary according to the method of extraction used for fracking. Technology is being developed to utilize less water for the fracking injection so that lesser volumes of produced water waste are returned to the well head (Rodriguez 2015). Utilization of such technology, like non-water based gelling agents, could potentially make a company more efficient in terms of how much produced water is generated and spilled for every barrel of oil and gas produced, explaining the results observed by Veil (2012) (Mao et al. 2016). Additionally, if producers of oil and gas invested in the infrastructure, streamlined processes and reused water more frequently their process could become vastly more efficient. As a result they would realize significant monetary savings and reduce the amount of produced water generated and spilled. Anadarko, the second largest oil and gas producer in Colorado during 2016, asserts that water reuse is a priority (Anadarko 2015). One way in which they accomplish this is by having a closed loop system shunting water for reuse through 150 miles of pipeline (Anadarko 2015). Nobel Energy, the eighth largest producer in Colorado during 2016, reused 4 million barrels of water in 2015 and reduced water use by 24% from 2014 (Nobel Energy 2016). Colorado encourages water reuse in the COGCC rule 907(a)3. Reuse is financially beneficial for operators since 30% of the energy generated from hydraulic fracturing goes to disposal of produced water while treatment uses only 5–8 % of generated energy (Curtis 2014). If less water is produced, perhaps less is spilled, reducing remediation costs and creating additional benefits for water reuse.

Beyond reuse, the volume of water produced is also influenced by the characteristics of the basin from which oil and gas is being extracted. In Colorado, the majority of fracking wells are located in the Wattenberg Field within the Denver- Julesburg Basin mainly found within Weld County (Higley & Cox 2007, Matthews 2011). The majority of gas extracted is from the Codell-Niobrara reservoir and the Dakota-J reservoir in the Basin, all originating from the Cretaceous period (Nelson & Santus 2011). The Codell-Niobrara reservoir lies at 2161 m below the ground surface just above the Dakota-J reservoir which lies at 2405 m below the ground surface (Higley & Cox 2007, Nelson & Santus 2011). The two reservoirs are isolated from one another and the Codell-Niobrara reservoir has lower rates of water production. An average of 2,400 barrels of water are used for each frack in the Codell-Niobrara reservoir. This number is relatively low, especially compared to Texas with a median of 30,000 barrels of water used for one fracking event. The Codell-Niobrara returns only 1 barrel/day to the well head although 2,400 barrels of water were used for a single fracking event, thus the recovery period can take a significant period of time (Higley & Cox 2007, Nelson & Santus 2011). In contrast, the Dakota-J reservoir produces a median of 1.63 barrels/day of water at each well and this rate tends to decrease with time (Higley & Cox 2007). Both of these volumes are lower than the national average for shale gas and oil production, which is between 2–30 barrels of water/day (Gallegos 2015).

### **2.3 CHEMICAL COMPOSITION OF PRODUCED WATER AND TREATMENT OPTIONS**

Not only does the basin influence the volume of water produced during oil-and-gas extraction, it also impacts the chemical composition of produced water. During the process of oil-and-gas extraction, treatment chemicals like biocides, friction reducers, acids and gelling agents are used (Vidic et al. 2013). The chemical and physical characteristics of produced water

is mainly determined by the basin from which oil and gas is extracted whereas flowback water can additionally reflect the treatment chemicals used during drilling and recovery.

In this study, focus is mainly on BTEX, naphthalene and sodium chloride, but produced water often contains a complex mixture of constituents. Produced water has a high concentration of total dissolved solids (TDS), ranging from 1,000 mg/L to 400,000 mg/L, with a median of 32,300 mg/L over all basins within a subset of states in the central and western United States (Benko & Drewes 2008). Produced water from the Denver basin has, on average, 10,200 mg/L TDS, a fairly low level compared to other basins in the United States. Produced water is typically quite salty; sodium chloride comprised the majority of TDS observed in the Denver basin but other salt like sodium sulfate and sodium bicarbonate are also prevalent (Benko & Drewes 2008). Produced water can also contain heavy metals like lead, cadmium and mercury (Ozgun et al. 2013) and naturally occurring radioactive material (NORM) such as uranium, thorium and radon (Kargbo et al. 2010). The group of components generally considered to be the most hazardous are the volatile organic compounds (VOCs), including BTEX and phenol.

Produced water treatment needs are dependent upon how the water will be used in the future. Bromide and chloride found in produced water can form brominated or chlorinated disinfection products during treatment that are harmful to human health when present in drinking water (Sun et al. 2013). Cations found in produced water, such as calcium, barium and strontium can present challenges if water is to be reused for fracking because they can form scales and restrict flow (Barbot et al. 2013). If the water is to be stored in Class II Injection Wells, then the more simple approach of off gassing in a retention pond removes much of the VOCs, reducing the risk for stray gas migration into drinking water aquifers once the water has been

stored. Although most VOCs are readily photodegraded in the atmosphere, off gassing can also effect air quality. The cost versus benefit of using a particular treatment strategy needs to be thoroughly evaluated depending on how the water will be used.

## **2.4 HANDLING AND DISPOSAL OF PRODUCED WATER**

Produced water is often stored in either above ground or below ground storage tanks or lined pits at well sites (Murray 2013, Veil 2015). At the federal level, the Resource Conservation and Recovery Act subtitle C regulates hazardous-wastes, but produced water is excluded from those regulations and is subjected to the less strict subtitle D regulations for non-hazardous waste (Colorado Oil and Gas Conservation Commission 2012, Hammer et al. 2012). The main method for disposal is through Class II Underground Injection Control (UIC) wells, requiring an EPA permit, in which produced water is reinjected into a deep underground rock formation, (Gregory et al. 2011; U.S. Environmental Protection Agency 2016). Lesser volumes are disposed of in evaporation pits, discharged into waterways, used for dust suppression at fracking sites, reused, or recycled, but inevitably some produced water is inadvertently spilled into waterways or on the land surface (Colorado Oil and Gas Conservation Commission 2011b & 2012, Gross et al. 2013).

Colorado has established guidelines for exploration and production waste management (the 900 series Rules) established through the Colorado Oil and Gas Conservation Commission that regulates the various methods for disposal of oil-and-gas waste, among other relevant safety precautions (Colorado Oil and Gas Conservation Commission 2014b). The permitting of Class II UIC wells and other discharge of produced water is carried out by the Department of Public Health and Environment (CDPHE). (Colorado Department of Public Health & Environment

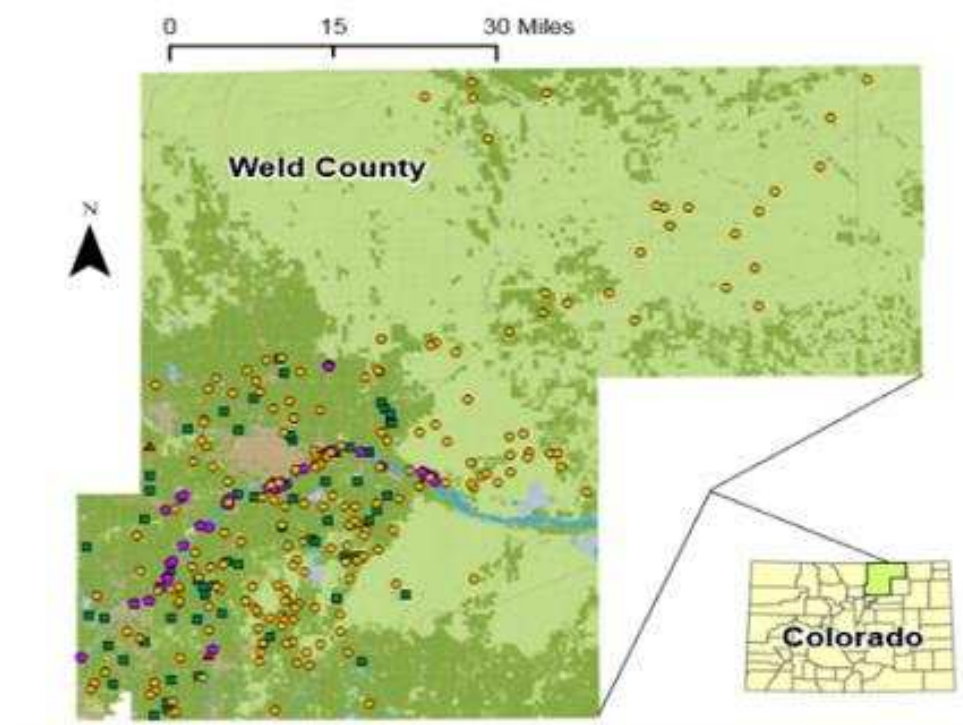
& Water Quality Control Commission 2017.; Colorado Oil and Gas Conservation Commission 2014a). Although the Colorado law suit Vance v. Wolf required for tributary oil-and-gas wells to maintain water quality and quantity to the standards for historic use by a senior appropriator, a state bill [37-90-137(7)(c)] allowed the State Engineer to make determinations for non-tributary status (Curtis 2014; Department of Natural Resources & Office of the State Engineer 2010). Non-tributary status has been granted for almost all oil-and-gas formations in Colorado so the water quality standards brought forth through Vance V. Wolf do not apply (Curtis 2014, Richardson, 2009) and Class II UIC wells can reduce the quality of groundwater.

Although approximately half of the water produced from fracking is disposed of in UIC wells (Colorado Oil and Gas Conservation Commission 2011), there are still on average seven spills of produced water every five days in Colorado (Colorado Oil and Gas Conservation Commission 2011a, Finley 2014). In the past, spills of five barrels or more spilled outside of a berm or secondary containment were required to be reported by oil-and-gas operators and handlers. In 2013 this volume was reduced to one barrel so perhaps current report reflects more accurate and complete spill details (Colorado Oil and Gas Conservation Commission 2014a & 2014b).

## **2.5 WELD COUNTY, COLORADO AND THE IMPACT OF SPILLS**

Spills of produced water are particularly important in Weld County, Colorado. Weld County makes up part of the densely-populated urban corridor to the east of the Rocky Mountains which coincides with 23% of oil and 58% of gas extraction sites in the state (Nelson & Santos 2011). The area is made up of more than 90% grasslands and agricultural/pastoral lands. It has two major rivers (the South Platte River and the Cache La Poudre River), a few cities, such

as Greeley, and numerous towns. There are over 15,000 oil and gas wells located within Weld County (Poulson 2013), and nearly all of the active wells use hydraulic fracturing (Gross et al. 2013). During a one-year period from 2010-2011, Gross et al. (2013) found that Weld County had the highest number of produced water spills in Colorado (Figure 2.1). Furthermore, Weld County utilizes roughly 25% groundwater to meet its water needs and certain areas rely completely on groundwater for drinking.



**Figure 2.1** Locations of oil-and-gas related spills on various land cover types in Weld County, Colorado, during 2013 (data from COGCC). Weld County received 312 oil-and-gas related spills in 2013. Colors in the map correspond to the land cover types in Figure 2.2. GIS data was retrieved from United States Geological Survey and Multi-Resolution Land Characteristics Consortium Projection. Projection: NAD\_1983\_UTM\_Zone\_13N. Geographic Coordinate System: GCS\_North\_American\_1983.

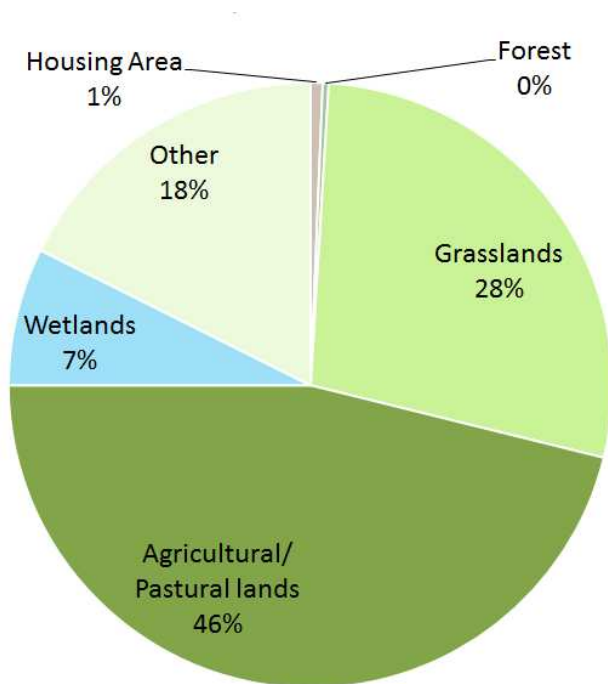


Figure 2.2 Percentage of oil-and-gas related spills on various land cover types in Weld County, Colorado, during 2013 (data from COGCC). Colors here are coordinated to the land cover types shown in Figure 2.1.

The depth to groundwater is very shallow in some areas, conceivably creating a high risk for leaching hazardous chemicals from produced water into underground aquifers from surface spills, however the extent to which this is an issue is unknown (Gross 2013, U.S. Geological Society et al. 2015). The lower South Platte Alluvial Aquifer is a shallow aquifer that stores 8.3 million acre-feet of water. The water table of the aquifer is less than five meters below the ground surface in many areas (U.S. Geological Society et al. 2015) and the water quality is known to be affected by the recharge water quality. Spills in this area could perhaps run the risk of degrading the quality of water in the aquifer.

In order to understand the extent of produced water spills in Weld County, a preliminary map (Figure 2.1 & 2.2) depicts the rate of occurrence and distribution of oil-and-gas related spills in the area. Out of the 312 oil-and-gas related spills self-reported from oil and gas companies to

the COGCC in Weld County during 2013, 22.4% affected groundwater, 11.5% affected surface water, and 0.64% affected both ground and surface water (Figure 2.1). The majority of spills, 65.4%, affected neither ground nor surface water. The bulk of oil-and-gas related spills occurred on agricultural/pastoral lands; lesser amounts occurred on grasslands, wetlands, and other land types like barren areas (Figure 2.1 & 2.2). The average spill area was approximately 34 acres (137,593 m<sup>2</sup>). The total area affected by spills was 5,655 acres (22.9 km<sup>2</sup>), with the majority of spills occurring in the southwest corner of Weld County near the South Platte River and the Cache La Poudre River.

According to the COGCC, the percentage of all produced water that is spilled every year is small relative to the total amount of water produced from fracking. For example, within the first eight months of 2011, two million gallons (47619 barrels) were spilled of produced water, although ten billion gallons ( $2.38 \times 10^8$  barrels) of produced water was generated (COGCC 2011). However, highly toxic organic contaminants in produced water, including benzene and radium, are mobile in soils (Todd et al. 1999, U.S. Environmental Protection Agency & Office of Air and Radiation 2004) and could migrate to the water table and render aquifer water undrinkable, even at low concentrations (U.S. Environmental Protection Agency 2013).

This preliminary assessment illustrates that although only a small percentage of all produced water is spilled (less than 1%), the land surface area affected by spills is nevertheless high, and the detrimental effects on humans and the environment might be substantial. These results underline the need to identify risk factors to determine the potential for groundwater contamination and for effective remediation methods to clean up spills after they have occurred.



The preliminary assessment (Figures 2.1 & 2.2) includes both oil-and-gas related spills. Gross et al. (2013) examined produced-water spills from oil-and-gas related activities in Weld County. They found that a produced-water spill, on average, releases seven barrels (294 gallons) of water and chemicals into the environment. The average produced-water spill affects 2120 ft<sup>2</sup> (197 m<sup>2</sup>) of land-surface area (a little less than 5% of an acre) in 2011, which is less average land-surface area than what is affected when looking at all oil-and-gas related materials spilled during 2013 as determined from the preliminary assessment, perhaps indicating that spills have become increasingly problematic for the area.

## **2.6 SITE REMEDIATION OF PRODUCED WATER SPILLS**

There is the potential for large land surface area to be affected from produced water spills. Most often surface spill sites have soil and groundwater removed to eliminate any health impacts from hazardous chemicals found in produced water. However effective this may be, excavation can be ecologically damaging and contribute to loss of habitat, thus making alternative remediation strategies preferable.

Phytoremediation is one such strategy that can be implemented to remove produced-water contaminants from soils, reducing the threat of those contaminants moving into groundwater. To determine if phytoremediation is an appropriate method for a certain location, site-specific parameters of the soil and the produced water spilled should be taken into consideration. When surface spills of produced water occur, high levels of sodium can affect soil parameters by altering the sodium absorption ratio (SAR). SAR compares the amount of sodium in soils to that of calcium and magnesium. Produced-water spills have the potential to increase SAR causing clay dispersion, reduced infiltration rate and loss of soil structure (Hendrickx et al.

2005). Compaction in soil reduces air space thus restricting the movement of volatile organics that travel mainly in the gaseous phase. While VOCs like benzene can rapidly travel in the soil this movement is restricted due to changes in soil SAR. Additionally, plant growth may be restricted from an increased SAR. However, the lower than average sodium levels from the Denver- Julesburg reduces the relevance of SAR-related effects in Colorado. Additionally, if the concentration of BTEX at produced-water spill sites is very high, soil may be excavated as the effectiveness of phytoremediation can take longer periods of time. For this reason that the suitability for grasses to remove contaminants like benzene from spill sites was evaluated.

## **2.7 GOALS AND PERSPECTIVE**

The volumes of produced water generated across the United States is high. Veil (2015) estimated over 21 trillion barrels of produced water was generated in 2012 from on-and-off shore drilling in the United States. In Colorado, although rules and regulations are relatively stringent regarding produced water management as compared to other states, over two spills occur every day (Finley 2014). By focusing on Weld County, Colorado we can bring to light the consequences of oil-and-gas drilling and produced-water spilling in populated areas with limited water resources. While there are many facets to the discussion of produced water, disposal, spills and remediation, the research presented in the next three chapters is an attempt to view the subject critically from a groundwater contamination perspective but also optimistically as opportunities for improvements become evident. In this way, I encourage implementation of responsible and science-based methods to reduce risks and help provide a balance between the water that we need and energy upon which we have come to depend.

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## 4 PRODUCED WATER SURFACE SPILLS: USING PAST EXPERIENCES TO GUIDE MITIGATION PLANS

### 4.1 SUMMARY

Natural gas and oil extraction, while providing much of our current energy needs, also generates large volumes of waste water (“produced water”) that creates risks for groundwater contamination when spilled. Weld County, Colorado, where the majority of extraction occurs in Colorado, was used as a case study to evaluate the current produced water volumes and spill locations. Publically-available produced-water production and spill data were analyzed to determine if improvements can be made to reduce the impacts of produced-water spills on the environment and human health. From 2011-2015 the frequency of spills that affected groundwater increased by 25 incidents and the average volume spilled at those sites increased by nine barrels, suggesting that the effects of produced water spills are becoming increasingly problematic. Evaluation of produced-water generation and produced-water spilled reveal that although larger-scale operations did generate less relative produced water per energy generated, the total volume of produced-water spilled by an operator was linearly correlated with the scale of the operation. Employing fewer, large-scale operators would help to reduce the overall volume of water generated but not the overall volume spilled. The depth to groundwater significantly affected the likelihood of groundwater contamination at spill sites. Since spills often occur at oil-and-gas well pads, extraction-site selection should preclude those areas that have shallow groundwater. The results from this research have important regulation and policy implications important for mitigating the increased threat of groundwater contamination from produced-water spills.

## 4.2 INTRODUCTION

Natural gas extraction rose 51% between 2005 and 2015 in Colorado (U.S. Energy Information Administration 2011). If extraction continues to increase at that rate, over 650 trillion cubic feet of natural gas per year will be generated in Colorado by 2030, promising to bolster our energy economy (U.S. Energy Information Administration 2011). Horizontal drilling and hydraulic fracturing (“fracking”), a process by which “unconventional” natural gas and oil can be extracted from underground formations, has greatly expanded the recoverability of oil and gas resources. However, hydraulic fracturing is a water-intensive procedure that generates large volumes of waste water known as “produced water” (Torres et al. 2015, Zoback et al. 2010).

Produced water is a mixture of water used in the fracking process and naturally occurring water released from the fracked rock formation (U.S. Environmental Protection Agency 2016). The chemical constituents of produced water, and their concentrations depend upon the fracking mixture used by the oil-and gas-operator, the attributes of the geological formation from which the produced water are generated, and the time since the fracturing event (Ozgun et al. 2013, J. A. Veil, Puder et al. 2004). In 2013, 7,700 million barrels of produced water are estimated to have been generated in Colorado (U.S. Environmental Protection Agency 2016).

To understand the water-to-energy relationship, Veil (2015) calculated the average produced water-to-oil ratio (WOR) and produced water-to-gas ratio (WGR) across the U.S. for 2012. Veil (2015) found a WOR of 9.2 barrels of water/barrel of oil and a WGR of 97 barrels of water/million cubic feet of gas. However, these two terms have different units and cannot be directly compared. Converting the gas volume in WGR from millions of cubic feet to barrels of oil equivalent (BOE), the national average WGR is 0.56 barrels water/barrel of oil equivalent,



indicating that gas extraction is a far more efficient method of energy generation, in terms of water production, than oil extraction.

The storage and disposal of produced water is state-regulated. In Colorado, produced water is disposed of mainly by pumping into deep underground wells (Colorado Oil and Gas Conservation Commission 2014, Stronger 2011, Torres et al. 2015, U.S. Environmental Protection Agency 2016), where a fraction of produced water is accidentally spilled onto the land surface (Patterson et al. 2017, Stronger 2011, Torres et al. 2015). Surface spills, often attributed to equipment malfunction or human error, typically occur from well-blowout events, storage leaks, pipeline leaks, and during transportation (Patterson et al. 2017, U.S. Environmental Protection Agency 2015). In addition to the problem posed by direct depletion of the water supply during energy extraction, surface spills pose major secondary threats to the water supply. In assessing that risk, it is particularly important to consider the toxic contaminants released into the environment by surface spills, which can pollute soils, groundwater, and surface water. Produced water contains a variety of hazardous contaminants; in particular, the contaminants known as BTEX (benzene, toluene, ethylbenzene, and xylene) are known to be mobile in soil, presenting a risk of groundwater contamination when produced water is spilled. While the economic value and energy independence gained by the projected increase in fracking production is enticing, there will likely be associated costs that will negatively affect society, the environment, and human health. To reduce these potential negative effects, mitigation plans will need to be implemented.

This issue is particularly important in Weld County, CO, which comprises much of the Denver-Julesburg basin, the geological formation from which the majority of oil and gas is

extracted in the state. Weld County is the top natural gas producer in Colorado even though it is located within the highly populated Front Range Urban Corridor (Higley & Cox 2007, Swain 2017). A quarter of Weld County's water requirements are met using groundwater, but many areas in the county have shallow groundwater that is highly susceptible to surface produced-water spills (Colorado Geological Survey 1995). Water supply depletion and subsequent produced-water spills stemming from energy-extraction operations present a dilemma for an area that is already water-limited, has a growing population of 28% per decade since the 1950s (Weld County Government 2016), and is projected to expand unconventional oil and gas production in the future.

Oil-and-gas extraction and spills are mainly regulated at the state level. In Colorado, they are regulated by the Colorado Oil and Gas Conservation Commission (COGCC) and the Colorado Department of Public Health and Environment (CDPHE). The COGCC publicly discloses a variety of documentation about reported surface spills that has been used to characterize aspects of surface spills occurring in Weld County. For example, Gross et al. (2013) utilized COGCC spill/release reports to determine the number of surface spills that resulted in groundwater contamination by BTEX from oil and produced-water spills. They summarize the causes for surface spills occurring in Weld County during a one-year period spanning 2010-11. Their study found 77 spill sites with affected groundwater, across different types of spilled materials. 54 groundwater-affected sites involved spills of produced water, and when produced water was spilled, an average of seven barrels was released per site (range 1–28 barrels). Equipment failure was the main reason cited for the spills that affected groundwater. Other aspects of spill sites were also summarized by Gross et al. (2013), such as the depth to groundwater and the area

affected, but they did not attempt to use their data to predict the likelihood for groundwater contamination at a site. Since their study, additional oil-and-gas extraction wells have been added and the quantity of produced water generated has increased concomitantly, thus underlining the need for more current and detailed evaluation of spills and their effects on groundwater.

To summarize the current state of affairs, we data-mined spill/release reports and supplementary materials available through the COGCC for spills occurring during 2015 in Weld County. Given the known increase in fracking, we hypothesize that oil-and-gas related spills increased in frequency and average spill volume in Weld County since the Gross et al. (2013) study. We characterize produced-water spills by examining other metrics noted within the COGCC's documentation, and hypothesize that for produced-water spills, the likelihood of groundwater contamination would increase with larger volumes, larger affected surface areas, and shallower depths to groundwater.

In Colorado, a large fraction of oil and gas is produced by only a few operators, whereas the vast majority of operators produce much smaller volumes. Economic theory suggests that efficiency increases as the scale of an operation increases, allowing a higher profit margin and/or lower prices for consumers (so-called "economies of scale") (Molinos-Senante & Sala-Garrido 2017)). These improved efficiencies could apply to the oil-and-gas sector, such that larger producers would exhibit streamlined energy production, higher levels of expertise within the field, and perhaps more efficient reuse of produced water for subsequent fracking operations. If so, the question is whether these efficiencies would translate into a lower volume of produced water generated and spilled per unit of energy produced. We hypothesize that larger oil-and-gas

production operations would experience more spills, but that larger production would correlate with higher “generation efficiency” and “spill efficiency”, meaning that a larger oil-and-gas producer would generate a smaller amount of produced water per unit of production (generation efficiency) and would spill less produced water per unit of production (spill efficiency).

There are important limitations to our approach of utilizing COGCC surface-spill reports. In 2010-11, only spills of five barrels or more were required to be reported by operators, so Gross et al. (2013) may have underestimated spill frequencies. More recently, the reporting threshold for spills dropped to one barrel. Additionally, since the COGCC’s documentation is based upon self-reporting of spills by operators, their accuracy is limited by the accuracy of self-reporting. Lastly, these self-reports can be incomplete, failing to report the spill volume or the affected area size, perhaps because those variables can be difficult to accurately measure. Despite these important limitations, the COGCC’s data might nonetheless provide important information that can inform future management of produced water and highlight the most prominent risks for groundwater contamination.

Through these analyses, we hope to clarify a path forward for mitigation of the effects of fracking in Weld County. In particular, variables that can be used to predict the likelihood of groundwater contamination could inform the choice of location for fracking wells, which make up a large percentage of all spill sites. By evaluating the fate of produced water for each individual operator, we can highlight those companies with higher generation efficiency and spill efficiency, and promote “best practices” that could be promulgated across the industry to lower the environmental and health impacts of produced water. In this way, perhaps the benefits from

unconventional oil-and-gas extraction can outweigh the risks to the environment and human health.

#### 4.3 METHODS

COGCC spill/release reports (Form 19) (Colorado Oil and Gas Conservation Commission 2014b & 2017b) from 2015 in Weld County, CO, were analyzed, including both initial and supplementary reports (if supplied), site and topographic maps, analytical results, and site restoration and remediation workplans (Form 27) (Colorado Oil and Gas Conservation Commission 2014). The rectangular affected area was noted as written in the release report, or – if this value was not supplied in the report but a map and scale were included (as provided to the COGCC by the operator) – the rectangular area affected was estimated from the map. The volume of waste spilled was noted, or if a range was given the average of the range was used. If more than one type of material was spilled at a site, the volume of all materials spilled were summed. Individual spill intensity for a site was calculated by dividing the volume of any spilled material by the affected surface area, such that a higher spill intensity would be calculated for spills of large volumes of material spanning small surface areas.

Different types of materials were spilled across sites, not just produced water. Spills of produced water or produced water mixed with other materials (hereafter called “produced-water related” spills) were examined. Averages and ranges across all spill sites were calculated for the volume of produced water spilled at each site, the ground surface area affected, and the depth to groundwater. It was noted if soil and groundwater were impacted, and if so, the employed remediation technique was noted. A logistic regression was computed to determine if the odds of groundwater and soil contamination (both binary response variables) could be

explained by the depth to groundwater, the amount of produced water released, and the size of the surface area impacted.

Operator-related differences in produced-water generation and spill trends were assessed by tallying the total volume of produced-water related materials spilled and the frequency of spills by operator in Weld County during 2015. Spills were summarized for each operator (Colorado Oil and Gas Conservation Commission 2014b) and this information was linked with the operators' total energy production (oil and gas) and total produced water generated within Colorado during 2015 (Colorado Oil and Gas Conservation Commission 2017). In the U.S. oil production is usually denoted in units of barrels while gas production is often denoted in million cubic feet (mmcf); to standardize the units, gas production was converted BOE. A given operator's "total energy production" is denoted in BOE and is calculated by summing oil (bbl) and gas (BOE) generated within the state. A linear model was used to determine whether the total volume of produced water spilled by an operator in Weld County was explained by the operator's total energy production in Colorado, their total volume of produced water generated in Colorado, or their frequency of spills in Weld County. Generation efficiency was determined by the slope of the linear model relating the total energy production of an operator to the volume of water generated by the operator. Spill efficiency was determined as the slope of a linear model relating the total energy production of an operator to the total volume of produced-water related material spilled by the operator in Weld County. All statistical tests were assessed for significance at  $\alpha=0.05$ .

## 4.4 RESULTS

### 4.41 SPILLS OF OIL-AND GAS-RELATED MATERIALS

Different types of oil-and-gas related material was spilled alone or in combination across sites (Figure 4.1). This section focuses on spills across all material types whereas the subsequent section focuses on only those spills that are associated with produced water. Across all types of spilled material, there were a total of 316 oil-and-gas related spills or releases reported in Weld County during 2015 (Figure 4.1). There were 205 reports (65%) that included the volume of material that was spilled, either as an exact value or a range. Across all spill sites and spilled materials, an average of 37 barrels were released (range 0.5–3821 barrels, median 5 barrels); however, the distribution of spill volumes was skewed towards larger volume spills. Across all types of materials, 7,571 total barrels were reported to be spilled. Of the 316 reports, 242 (76%) either included the operator-determined rectangular area affected or included interpretable maps with delineated affected areas. An average rectangular area of 602 m<sup>2</sup> was affected at each site (range 0–17540 m<sup>2</sup>, median 91.3 m<sup>2</sup>), again with a skewed distribution towards larger areas. Across all of these reports, the total rectangular spill area affected was 138,488 m<sup>2</sup> (34 acres).

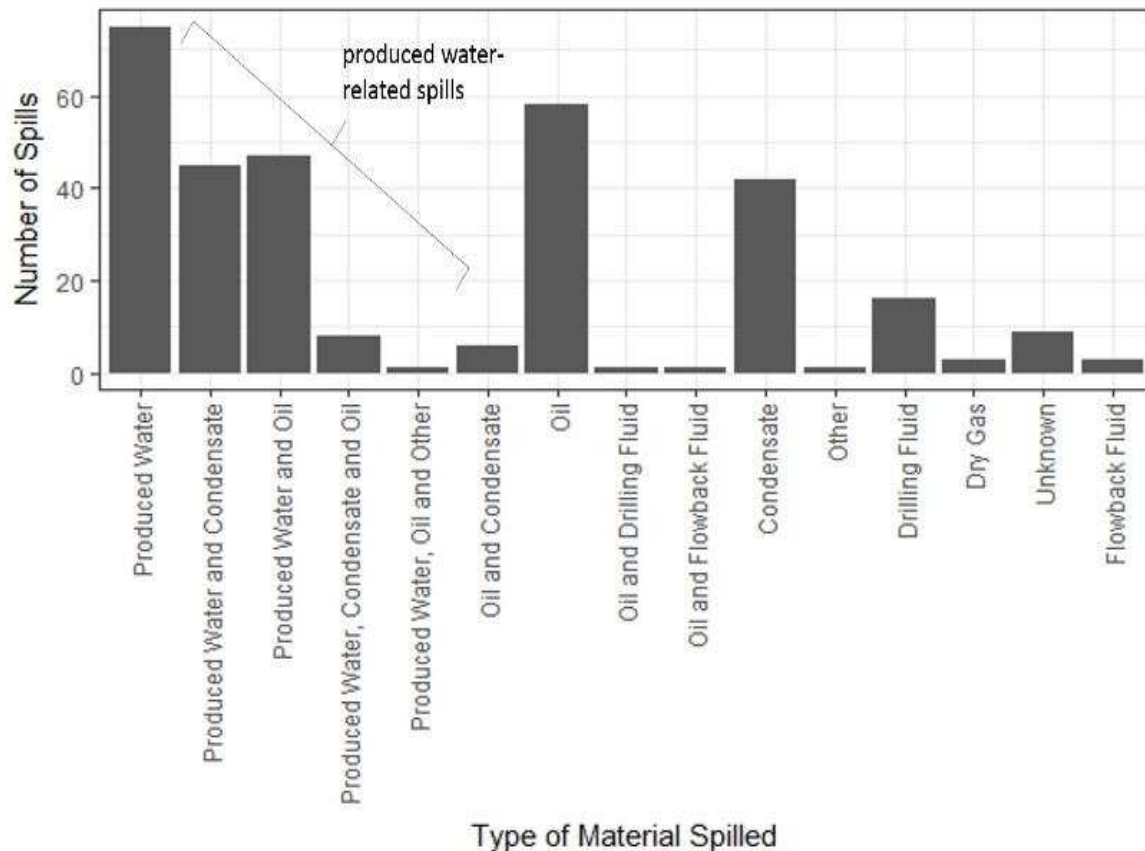


Figure 4.1 Various types and combinations of oil-and-gas related material that was spilled across sites in Weld County, CO during 2015. Produced water-related spills comprised the largest fraction of spill types (128/316, 40.5%).

Across all spilled materials, soil was impacted at 285 sites (90.2%) and groundwater at 102 sites (32.3%). In almost all cases in which groundwater was contaminated, soil was additionally impacted. Among sites where soil was impacted, excavation was the main method used to remove contaminated soil (70% of sites). Among sites where groundwater was contaminated, that contamination was addressed by extracting water by vacuum (43% of sites), and by *in-situ* remediation (21% of sites) such as groundwater oxygenation. In fewer cases, groundwater contamination was either monitored by subsequent testing, naturally attenuated, or any mitigation was not explicitly stated. At spill sites with groundwater contamination, the



average depth to groundwater was 2.3 m (range 0.3–4.6 m, median 1.5) and the average rectangular area affected was 171.6 m<sup>2</sup> (range 4.2–2222 m<sup>2</sup>, median 91.3 m<sup>2</sup>).

#### **4.42 GROUNDWATER CONTAMINATION FROM PRODUCED-WATER RELATED SPILLS**

This section provides summaries of only produced-water related spills. Overall, a total of 6,073 barrels of produced-water related materials were spilled, affecting a total rectangular spill area of 37,255 m<sup>2</sup> within Weld County in 2015. An average volume of 15.2 barrels was spilled per site (range 0.5–3821 barrels, median 6 barrels). Out of 176 sites with produced water-related spills, 63 sites (35.8%) experienced groundwater contamination; at these sites, an average of 16 barrels was spilled per site (range 2–102 barrels, median 6 barrels). The reported site-specific spill characteristics like rectangular affected spill area, volume of produced-water-related material spilled and the depth to groundwater showed signs of skew Therefore, a Mann-Whitney U Test was employed to test for differences in median and the Kolmogorov-Smirnov test were used to test for differences in distribution at sites with contamination versus without.

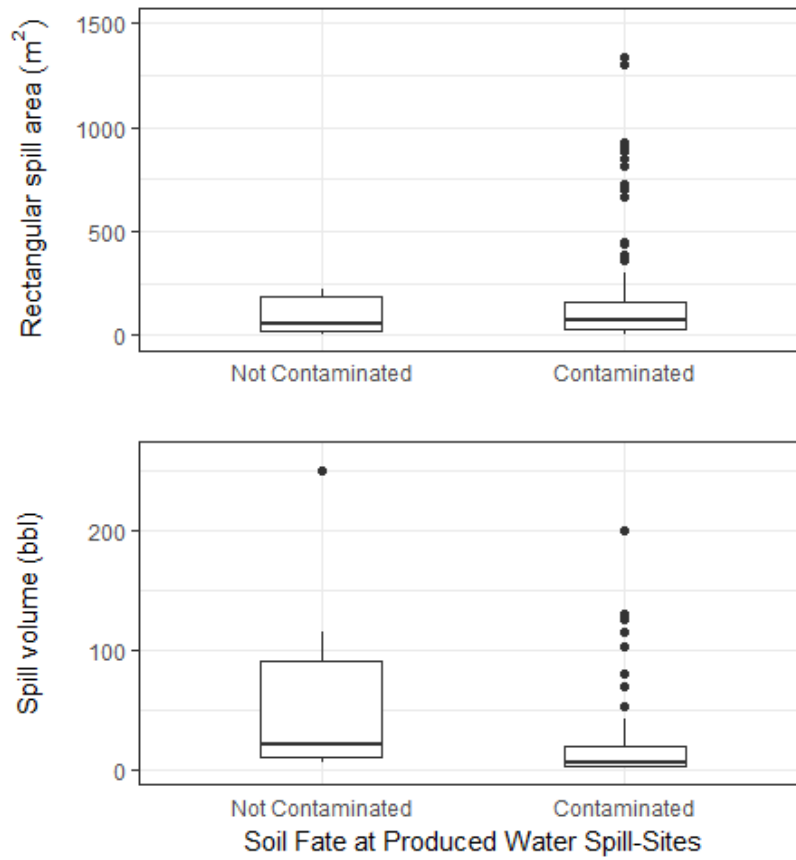


Figure 4.2 The distribution of produced-water spill volumes and rectangular-spill areas at spill sites that did or did not experience soil contamination. One spill volume was removed at a site that did not result in soil contamination (3821 barrels spilled).

Logistic regression showed no significant increase in the log-odds for soil contamination with increasing volume spilled ( $p = 0.55221$ ) or increasing rectangular spill area ( $p = 0.65160$ ). There was no significant difference between the median rectangular spill area at sites with soil contamination versus without (Mann-Whitney U test,  $p = 0.5472$ ) (Figure 4.2). However, the median spilled volume of water was significantly different at sites with soil contamination versus without (Mann-Whitney U test,  $p = 0.008036$ ). There was no significant difference in the distributions of rectangular spill areas at sites with soil contamination versus without (Kolmogorov-Smirnov test,  $p = 0.9119$ ) (Figure 4.2). However, the distribution of spill volumes

were significantly different at sites with soil contamination versus without (Kolmogorov-Smirnov test,  $p = 0.04245$ ).

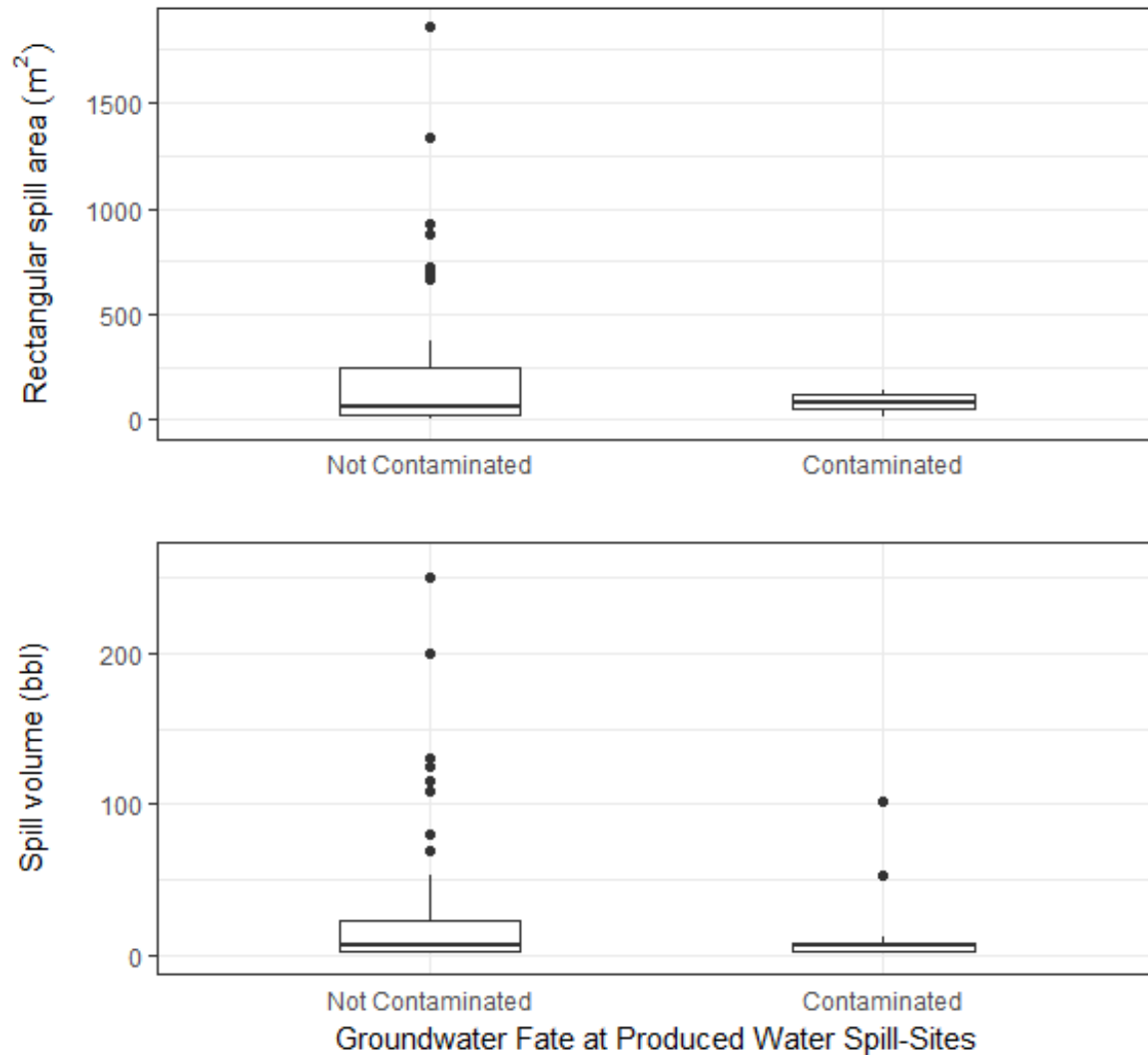


Figure 4.3 The distribution of produced-water spill volumes and rectangular-spill areas at spill sites that experience groundwater contamination. One spill volume was removed at a site that did not result in soil contamination (3821 barrels spilled).

Logistic regression showed no significant difference in the log-odds for groundwater contamination with volume spilled ( $p = 0.5265$ ) or the rectangular spill area ( $p = 0.3223$ ). There was no significant difference between the median spill volume (Mann-Whitney U test,  $p = 0.4016$ ) or median rectangular spill area (Mann-Whitney U test,  $p = 0.2076$ ) at sites with

groundwater contamination versus without (Figure 4.3). There was no significant difference in the distributions of volume spilled (Kolmogorov-Smirnov test,  $p = 0.4051$ ) or in the rectangular spill area (Kolmogorov-Smirnov test,  $p = 0.06707$ ) at sites with groundwater contamination versus without (Figure 4.3).

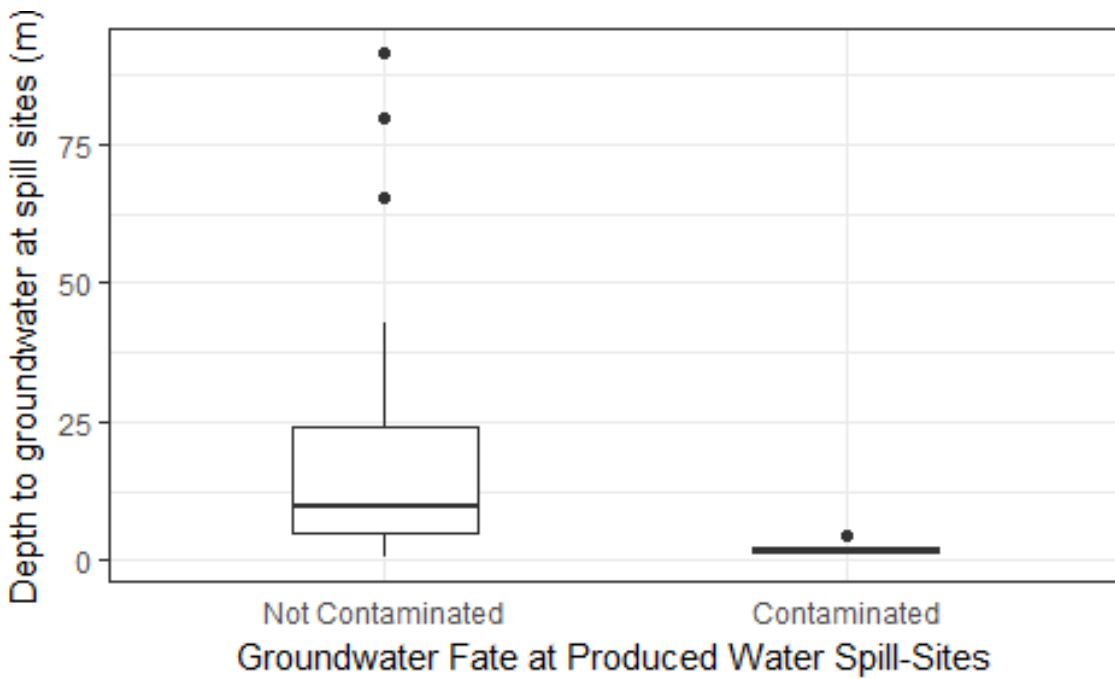


Figure 4.4 The distribution of groundwater depths at spill sites that did or did not experience groundwater contamination.

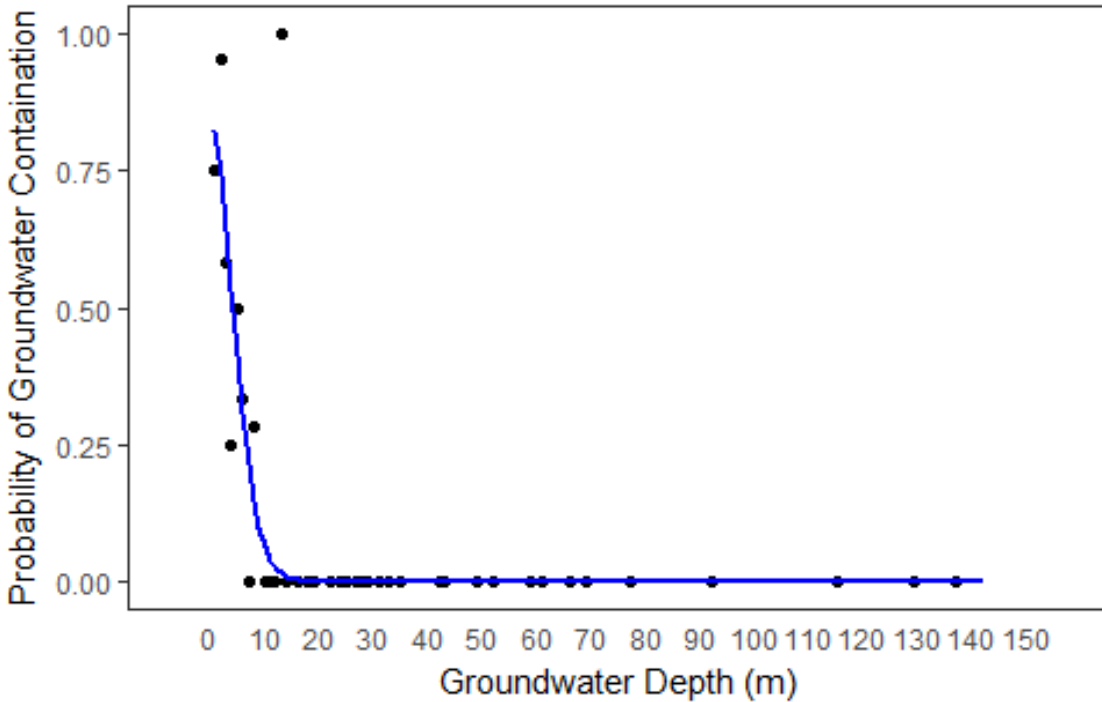


Figure 4.5 The probability of produced-water spills resulting in groundwater contamination as a function of depth to groundwater (logistic regression,  $p = 2.2 \times 10^{-16}$ , McFadden pseudo- $R^2 = 0.688$ ). Each dot represents the proportion of spills at a certain groundwater depth that resulted in groundwater contamination. The blue line represents the predicted probability of groundwater contamination at a certain depth as determined from the logistic regression fit. For every unit increase in the depth to groundwater, the log-odds for groundwater contamination decreased by a factor of 0.4671 and the odds for groundwater contamination decreased by a factor of 0.627.

The median depth to groundwater at sites with groundwater contamination versus without was significantly different (Mann-Whitney U test,  $p < 2.2 \times 10^{-16}$ ) as was the distribution of groundwater depths (Kolmogorov-Smirnov test,  $p < 2.2 \times 10^{-16}$ ) (Figure 4.4). The depth to groundwater did significantly affect the log-odds for groundwater contamination (Figure 4.5). The probability of groundwater contamination dropped to 50% with a depth of 4.1 m to groundwater, and to 1% at a depth of 12.5 m.

#### 4.43 OPERATOR-RELATED PRODUCED-WATER GENERATION AND SPILLS

This section focuses on only those companies that spilled oil-and-gas related material in Weld County during 2015. Each company's total energy production and produced water generation is evaluated in terms of their production across the whole state of Colorado. Out of the 56 operators that produced oil and gas in Colorado (DrillingEdge 2017), 18 reported spilling oil-and gas-related material in Weld County (Figure 4.6). Over 70% of spilled oil-and gas-related material can be attributed to three companies, two of which are within the 10 top energy producers in Colorado.

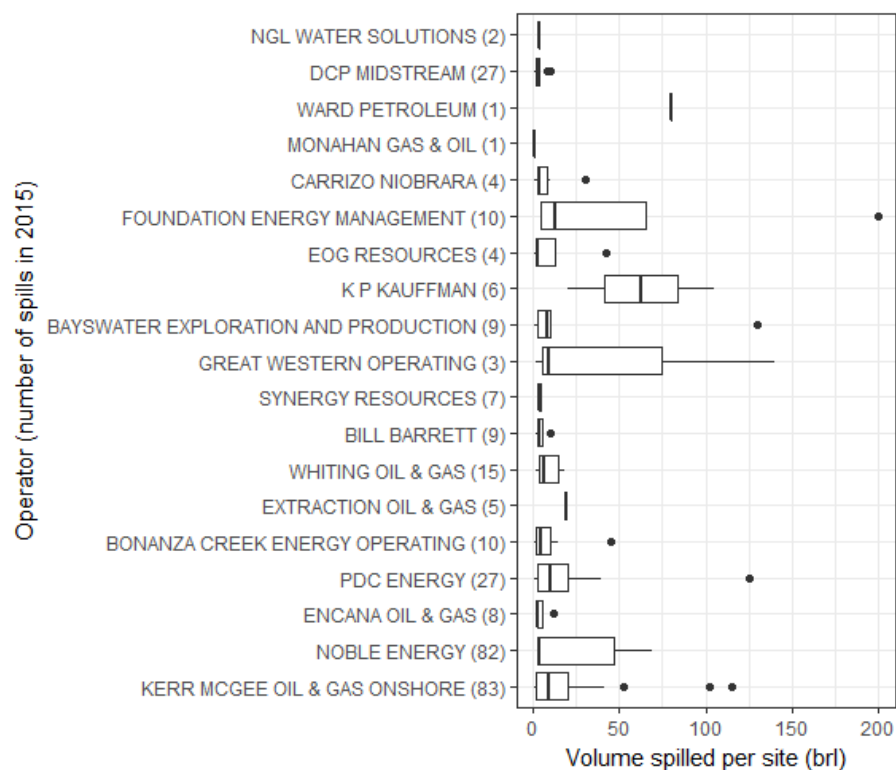


Figure 4.6 The distribution of spill volumes per site, grouped by operator. Operators are listed in order by energy production from top to bottom of the figure, with the largest producer at the bottom; the uppermost two operators do not produce oil and gas at all. The number of times an operator spilled in Weld County is shown in parentheses. Business entity abbreviations such as “LLC” were removed from operator names, as were the words “business” and “corporation”. One spill by NGL Water Solutions was removed from the plot because the spill volume was far larger than all others plotted (3821 barrels).

Three companies did not produce any oil or gas, but nevertheless reported spills in Weld County. One of these companies provides gas transportation; since its parent company does produces oil and gas, the data for the subsidiary and parent company were combined. The other two companies are involved with other processes related to oil and gas but unrelated to extraction (they are still referred to as an “operator” and “company”). The first of these companies transports and disposes produced water; it is responsible for spilling the largest total volume of produced water in Weld County. The second company is a mid-level processing corporation, and is responsible for the third-highest frequency of spills in Weld County.

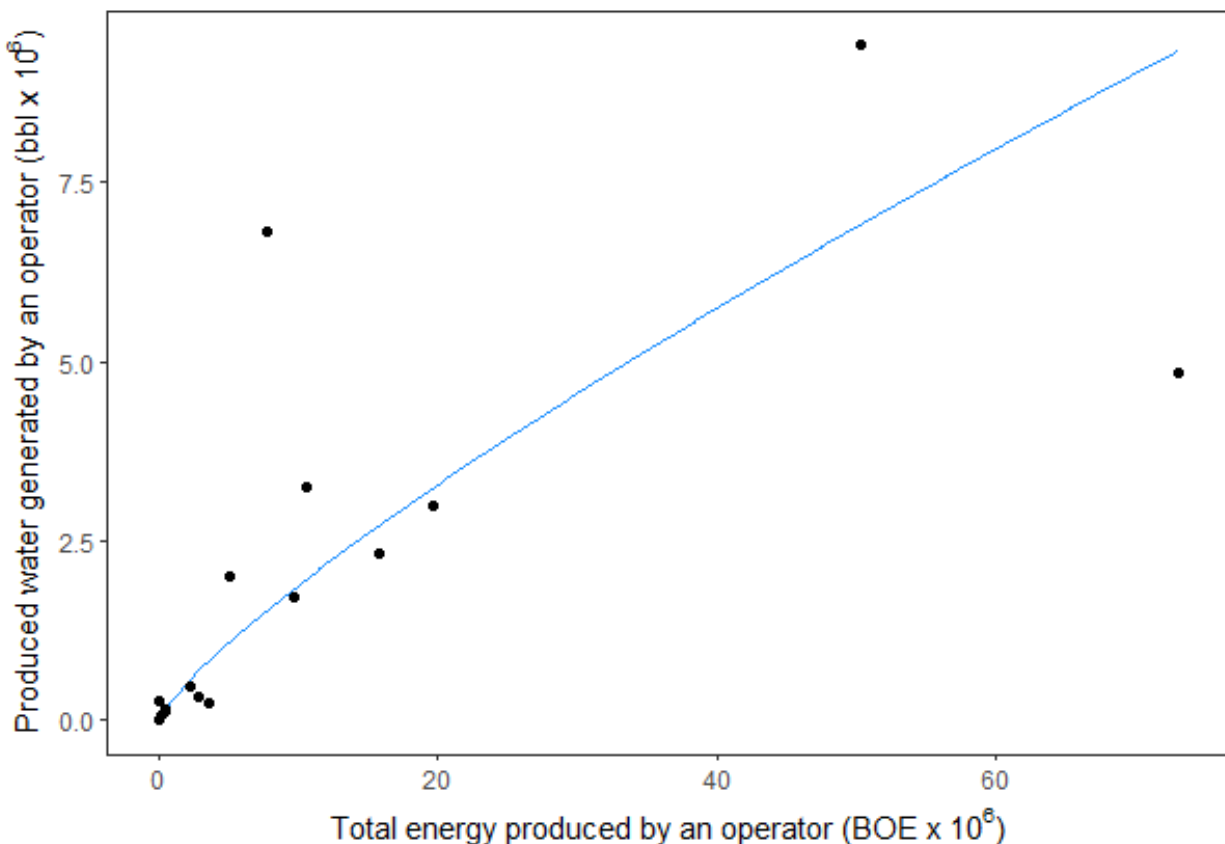


Figure 4.7 The relationship between the total energy produced and produced water generated by an operator in Weld County during 2015. Larger total energy producers generated less produced water per barrel generated than did smaller total energy producers. The model equation is  $y = x^{0.80577} * 0.295$  ( $p = 8.645 \times 10^{-9}$ , adjusted  $R^2 = 0.8563$ ). Both x and y are in units of BOE x 10<sup>6</sup>, as seen in the graph.

Across operators that spilled in Weld County during 2015 there was an average generation efficiency of 5.5 BOE/bbl of water, with a range of 0.02–15.07 BOE/bbl of water. Operators that generated more total energy also generated more produced water (Figure 4.7); however, the relationship was non-linear (as determined by model comparison with AIC). A smaller relative fraction of produced water was generated with increased total energy production (p value of the natural logged slope term =  $8.65 \times 10^{-9}$ ), indicating that generation efficiency increased with higher total energy production. This relationship was non-linear by AIC. The total energy produced by each company was positively correlated with the total number of spills by that company ( $p = 2.42 \times 10^{-8}$ , adjusted  $R^2 = 0.8379$ ), linear by AIC. There was one additional spill by an operator for every additional  $8.54 \times 10^5$  barrels of total energy produced.

The total energy produced by an operator was also positively and linearly correlated (determined by model comparison with AIC) with the total volume of oil-and-gas related material spilled by that operator according to the linear model ( $p = 4.98 \times 10^{-3}$ ). The spill efficiency, however, does not increase with higher energy production; for every  $1.36 \times 10^6$  barrels of total energy produced 100 barrels of oil-and gas-related material was spilled by an operator. The intercept in this linear model, at 86.5 barrels, was also significant ( $p = 1.45 \times 10^{-3}$ ) indicating that even very small producers are expected to spill a baseline volume of produced water.

To determine which metrics (total energy produced by an operator, volume of produced water generated by an operator, and number of spills caused by an operator) best explained the spilled volume of oil-and-gas related material by an operator, model comparison with AIC was conducted. These three metrics were highly correlated with each other, so while all three



metrics individually correlated with the total volume of spilled produced water, according to AIC the number of spills by an operator was the best predictor of the total volume spilled. With each additional spill, the total volume of oil-and-gas related material spilled in the county by an operator increased by 7.92 barrels according to that linear model ( $p = 5.13 \times 10^{-4}$ , slope  $p = 5.13 \times 10^{-4}$ , adjusted  $R^2 = 0.4896$ ). Although energy production by an operator correlates to the total volume of produced water spilled, linear models showed no correlation between the total energy production by an operator and the average volume of oil-and-gas related material spilled per site by that operator ( $p = 0.2445$ ) or the median volume ( $p = 0.356$ ). The distributions of volume spilled per site by each operator were often highly skewed, as shown in Figure 4.7.

#### 4.5 DISCUSSION

This research provides some important findings that could help guide policy and inform the public about the future of oil-and-gas related spills and produced water. Our first hypothesis is that oil-and-gas related spills increased in frequency and average spill volume in Weld County since the Gross et al. (2013) study. During the 2015 period we studied there were 25 additional oil-and gas-related spills with affected groundwater, 9 of which were specifically additional produced-water related spills, compared to the one-year 2010–11 period studied by Gross et al. (2013). Average produced-water volumes spilled at a site increased by nine barrels, also in line with our hypothesis. This increased spill volume suggests that operators may have caught spills less quickly than before, perhaps due to increased automation and a resulting decrease in the monitoring of individual sites by workers (Jacinto 2014, Wethe 2017). Gross et al. (2013) reported equipment failure to be the main cause of spills that impacted groundwater. The U.S. Environmental Protection Agency (2015) found that among various causes considered, human

error was the largest cause of hydraulic fracturing-related spills (without consideration of groundwater contamination). Taken together, these results suggest that improved maintenance, equipment redundancy, more intensive worker training, and remote site monitoring might reduce the frequency of spills and average volume spilled.

Our second hypothesis is that the probability of groundwater contamination would be higher with larger volume of produced water spilled, larger affected surface area and shallow groundwater levels at spill sites. We have shown that the depth to groundwater at a spill site significantly and strongly affected the odds of groundwater contamination. Contrary to our hypothesis, however, the probability of groundwater contamination was not significantly correlate with the spill area or volume spilled. Patterson et al. (2017) found the majority of spills occur at storage facilities on well pads. Because depth to groundwater is such a strong determinant of the probability of groundwater contamination, our results underline the importance of preferring to locate fracking sites in areas with deep water tables when possible.

Our third hypothesis is that per barrel generated, larger total energy producers would generate less produced water (improved generation efficiency) and spill less oil-and-gas related material (improved spill efficiency) due to efficiencies of scale. Larger oil-and gas-producers did exhibit improved generation efficiency. Larger operators are able to reuse water and are often under greater public scrutiny to do so. Water treatment for reuse can often be costly, tending to limit it to larger operators with greater financial resources. Our finding is important because it shows that a shift towards larger producers might lower the impact of the oil-and-gas industry on limited water resources.

Contrary to our third hypothesis, however, there was no improvement in spill efficiency with larger total energy production; the amount of oil and gas produced by an operator correlated linearly with the produced water spilled. In addition, the number of spills by an operator was linearly correlated with that operator's total energy production, while the average and median volume spilled per site did not depend on total energy production. These findings indicate that perhaps the scale of an operator, rather than the specific practices of operators, are the primary determinant of how often spills will occur and therefore how much oil-and gas-related material is spilled. One interesting result that was surprising was that there was no significant difference between the average-and-median volumes of produced-water spilled across operators. This result would suggest that across all operators there could be improvement in catching spills earlier, thus reducing the average and total volume of produced-water spilled. The COGCC found in a recent study that the largest cause of spills across four states was due to equipment failure or human error. Early-warning spill-detection systems and multiple, redundant safeguards and employee training can help to minimize the volume of produced water spilled at a site. While these methods are available and put to use in Colorado, these results suggest that they are underutilized or under enforced. Colorado law does call for some such safeguards at sites when deemed necessary, but perhaps encouraging intensive and reoccurring training for operators and handlers would prove more effective (Colorado Oil and Gas Conservation Commission 2012).

While this research sought to provide insight into the state of produced water generated and spilled in Weld County, CO, we do not claim this to be an exhaustive analysis. It is important to point out that the data used for this study was heavily reliant upon reports created by the oil-

and-gas industry, and some underreporting of both the frequency and the volume of spills might be expected (and may vary by producer). Furthermore, this research only takes into consideration a one-year period, and does not account for any amount of oil-and-gas related material that was recovered before infiltration into the soil. A nationwide study conducted by the U.S. Environmental Protection Agency (2015) found that only 30% of oil-and-gas related fluid from hydraulic fracturing was recovered during 2012. Recovery efforts, although important, provide only limited mitigation of the environmental impacts of spills; nevertheless, accounting for recovery could still influence the results of this study.

Overall, if such biases are not too large, and remain reasonably consistent over time, the COGCC's public dataset could still be useful for detecting trends and patterns. Using that dataset, this study has provided some recommendations for reducing the possibility of groundwater contamination from produced-water surface spills. We have identified practices that could be enacted to increase producer spill efficiency, thereby lessening the overall impact of produced water on the environment and human health.

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## 6 PRODUCED-WATER SURFACE SPILLS AND THE RISK FOR BTEX-AND-NAPHTHALENE GROUNDWATER CONTAMINATION

### 6.1 SUMMARY

The widespread use of unconventional drilling involving hydraulic fracturing (“fracking”) has allowed for increased oil-and-gas extraction, produced water generation and subsequent spills of produced water in Colorado and elsewhere. Produced water contains BTEX (benzene, toluene, ethylbenzene, xylene) and naphthalene, all of which are known to induce varying levels of toxicity upon exposure. When spilled, these contaminants can migrate through the soil and contaminant groundwater. This research modeled the solute transport of BTEX and naphthalene for a range of spill sizes on contrasting soils overlying groundwater at different depths. The results showed that benzene and toluene were expected to reach human-health relevant concentration in groundwater because of their high concentrations in produced water, relatively low solid/liquid partition coefficient and low EPA drinking water limits for these contaminants. Peak groundwater concentrations were higher and were reached more rapidly in coarser textured soil. Risk categories of “low”, “medium” and “high” were established by dividing the EPA drinking water limit for each contaminant into sequential thirds and modeled scenarios were classified into such categories. A quick reference guide was created that allows the user to input specific variables about an area of interest to evaluate that site’s risk of groundwater contamination in the event of a produced water spill. A large fraction of produced-water spills occur at hydraulic-fracturing well pads, thus the results of this research suggest that the surface



area selected for a hydraulic-fracturing site should exclude or require extra precaution when considering areas with shallow aquifers and coarsely textured soils.

## 6.2 INTRODUCTION

Hydraulic fracturing, also known as “fracking”, is an extensively used process that releases unconventional natural gas and oil from shale formations or other tightly-bound rock formations (Keer 2010, Veil 2015, Zoback et al. 2010). Produced water is made up of water used in the fracking process and water derived from the fractured source rock. During 2007, the United States generated  $21 \times 10^9$  barrels of produced water, the volume of which would fit in 1.3 million Olympic size swimming pools (Veil 2015; Veil et al. 2004). With increasing use of hydraulic fracturing, this number is expected to continue to rise (Skalak et al. 2014, Torres 2015, Vengosh 2014, Zoback et al. 2010). Produced water contains a variety of constituents such as dispersed oil, soluble or dissolved organic constituents, bacteria, natural occurring radioactive material and a variety of salts (Gregory 2011, Torres 2015, Veil et al. 2004, Vidic et al. 2013). Concentrations vary within produced water according to the source rock from which the water was extracted (Benko & Drewes 2008, Guerra et al. 2011, Veil et al. 2004). Within the organics constituents, BTEX (benzene, toluene, ethylbenzene and xylene) as well as naphthalene, have higher concentrations in gas-related produced water (Benko & Drewes 2008, Todd et al. 1999). These contaminants have varying degrees of toxicity that can have additive effects when combined (Crouse et al. 2002, Todd et al. 1999, Veil et al. 2004). Thus produced water requires careful disposal or treatment (Colorado Oil and Gas Conservation Commission 2012, Gregory et al. 2011; Kargbo et al. 2010, Goodwin et al. 2012, Todd et al. 1999). However, unintentional surface spills of produced water often occur (Finley 2011 & 2014, Gross et al. 2013, Hammer et al. 2012, U.S.

Environmental Protection Agency 2016). BTEX, and to a lesser extent, naphthalene, can rapidly volatilize into the atmosphere or move through the soil towards groundwater (European Chemicals Bureau 2003, 2007b & 2008, Otton et al. 2007, Salanitro et al. 1997, Todd et al. 1999). However, when a surface spill occurs many variables determine the fate of BTEX and naphthalene. Produced water surface spills present a risk for groundwater contamination and subsequently, time-and cost-intensive remediation efforts (Pinedo et al. 2013, Todd et al. 1999, Vaezihir et al. 2012). EPA drinking water limits of these contaminants are low, particularly for benzene (0.005 µg/mL). Water is often vacuum extracted from groundwater aquifers to remove the threat to drinking water (Colorado Oil and Gas Conservation Commission 2011, Gross et al. 2013; Unger 1995). Determining which combination of factors present risks for groundwater contamination, such as the depth to groundwater, amount of fluid spilled and site-specific properties could help stakeholders weigh the risk for groundwater contamination at fracking sites, areas known to experience produced water spills often (Patterson et al. 2017, U.S. Environmental Protection Agency 2015a, 2015b & 2016).

One such area that stands to gain insight from such an analysis is Weld County, Colorado. Weld County is made up of mainly grassland and agricultural/pastoral land and is an area with intensive hydraulic fracturing activity (DrillingEdge 2017, O'Neill & Thorp 2014, U.S. Forest Service 2013, U.S. Geological Survey 2010). Natural gas production more than doubled there from 2013 to 2016 and it has more than 13,000 oil-and-gas producing wells (DrillingEdge 2017). Weld County also experiences a high frequency of produced water surface spills that is continuing to increase over time (U.S. Geological Society et al. 2015, Colorado Geological Survey 1995, Patterson et al. 2017). New spills have a higher likelihood of occurring in areas that

previously experienced a spill, meaning that one site may see accumulative impacts over time (Patterson et al. 2017). The region is at risk for groundwater contamination, particularly in the South Platte River Alluvial Aquifer that has groundwater at very shallow levels (less than 5 m in many regions) (Grigg 2005, U.S. Geological Society et al. 2015). Nearly 25% of the water needs in Weld County are satisfied through groundwater so understanding the movement of BTEX and naphthalene through the soil and its ultimate fate is a critical human health issue (U.S. Geological Society et al. 2015, Colorado Geological Survey 1995, Gross et al. 2013).

Given the above-mentioned characteristics of Weld County, the question remains whether produced water spills can be modeled over typical areas in Weld County to predict the risk for groundwater contamination of BTEX and naphthalene. The transport and fate of agricultural and industrial chemicals through the soil can be described by numerical models such as HYDRUS that allow multiple chemicals to be simulated simultaneously (Simunek 2013). Kasaraneni et al. (2014) modeled transport of polycyclic aromatic hydrocarbons (like naphthalene) through pervious material using this technique, obtaining results that accurately reflected results found in the lab. Others have accurately modeled BTEX leachability using similar modeling techniques but have not used initial concentrations relevant to produced water (Jin & Ray 2015). Lab testing using soil columns have also evaluated the leachability of BTEX, but not with the variability that would be encountered across an area like Weld County, such as varying water-table depths and soil types (Balseiro-Romero 2016). The time since the spill occurred can significantly impact BTEX and naphthalene concentration in groundwater; often the time since the spill is unknown in the field, making modeling a more informative method for determining peak concentrations reached at the water table at spill sites (U.S. Geological Survey 2006; Davis

et al. 2005). The model provides an efficient way to test the migration behavior of organic chemicals like BTEX and naphthalene found in produced water at multiple sites with a variety of site-specific variables and spill sizes, the results of which could inform decision making and policy.

## **6.21 APPROACH**

To garner site specific and realistic typical produced water spills in Weld County, we evaluated the spill and incident reports made available through the oil and gas regulatory agency in Colorado, the Colorado Oil and Gas Conservation Commission (COGCC). The COGCC has been cited with having the most comprehensive details regarding surface spills in the U.S. (Colorado Oil and Gas Conservation Commission 2013, Gross et al. 2013, U.S. Environmental Protection Agency 2015b). In the reports we noted the volume of produced water spilled at a site and the rectangular surface area affected by the spill. This allowed us to calculate a spill intensity that represents the hydraulic head of a spill ( $\text{spill intensity} = \text{spill volume} / \text{rectangular surface area}$ ). We modeled a range of typical spill intensities over varying soil types and depths to groundwater that represent the range found in Weld County. Our goal with the model was to predict the maximum concentration of BTEX and naphthalene reaching groundwater and compare this to EPA drinking water limits. EPA limits provide a guideline for unacceptable concentrations for human exposure, however even when below the limits human health can be affected. For this reason we established risk categories encompassing smaller fractions of the EPA limit for each contaminant that are still relevant for human health (U.S. Environmental Protection Agency 2009). We first hypothesized that benzene and toluene would be the more problematic contaminants that would dominate the risk categories because they have the lowest EPA

drinking water limits and are often highly concentrated in produced water (Benko & Drewes 2008, U.S. Environmental Protection Agency n.d.). Second, we hypothesized that the majority of spill scenarios would fall within the established risk categories, meaning that the majority of scenarios would have at least one contaminant that would reach the water table with concentrations of  $\geq 1\%$  of the EPA drinking water limit. Lastly, we hypothesized that groundwater would have higher peak concentrations and reduced times to reach the peak concentration at high-intensity spill sites overlaying coarse soil textures and shallow depths to groundwater. This is hypothesized because high-intensity spills would have a larger hydraulic head pushing the water and contaminant into the soil over shorter distances. Additionally, coarse textured soils (compared to clays) have higher water flow rates to carry contaminants and typically have greater air filled porosity to serve as diffusion avenues for contaminants in the vapor phase. We modeled all scenarios in both HYDRUS 1D and 3D to determine if the additional dimensions produced different peak concentrations at the top of the water table. If large differences in peak concentration were determined, we used the more conservative 3D model. HYDRUS 1D is a free program whereas 3D is not. The difference between the modeled values generated from 3D and 1D were explored so that other users who wished to replicate these methods in the free version could determine if those values were realistic.

In a user-friendly format, a quick reference guide was constructed in order to summarize the risk for groundwater contamination over various modeled parameters and spill scenarios. We hope this product will be of use for stakeholders evaluating the risk for groundwater contamination when deciding upon fracking sites, produced water storage facilities and transport routes for produced water, all of which commonly experience spills.

### 6.3 METHODS

To evaluate the likelihood of groundwater contamination in Weld County from spills of BTEX-and naphthalene-laden produced water, we first analyzed the COGCC spill data from 2015 to create realistic spill scenarios to simulate within HYDRUS. From this data, we calculated three spill intensities (low, medium and high) by dividing the median volume of produced water spilled at a site by three affected spill areas (from within the range reported in Weld County), creating three hydraulic heads for the simulated spill sites. These calculations are described in Table 1. The time frame over which the simulated spill took place varied across spill intensity, with the low-intensity spill occurring within a fraction of a day, the medium-intensity spill occurring over one day and the high-intensity spill occurring over three days (Table 6.1). Each spill intensity scenario was modeled in a grassland with either of two soil types, sandy loam or clay loam, which were often cited qualitatively in spill and release reports (Colorado Oil and Gas Conservation Commission 2013). The soil hydraulic parameters for clay loam and sandy loam were selected from the library of values provided with HYDRUS. These soils were further assumed to overlay groundwater depths of 30, 150, and 300 cm which represent a typical range (1<sup>st</sup> quartile, median and 3<sup>rd</sup> quartile, consecutively) of groundwater depths at sites that were reported to have experienced an oil-and-gas related spill during 2015 in Weld County. We modeled 18 total spill scenarios. We included root-water uptake in the grassland assuming a simple linear decrease in root density to a depth of 30 cm in the case of the 30 cm vadose zone and 50 cm rooting depth for the deeper water-table scenarios. The zone of groundwater saturation was modeled as 30 cm deep to allow for contaminant mixing. Since the spill intensity scenarios implicitly involve different spill areas (Table 6.1), we modeled the BTEX and

naphthalene movement in both 1D (downward) and 3D to assess the effect of subsurface lateral movement from a small spill area reducing the contaminant concentration reaching groundwater.

Table 6.1 Spill intensity calculation and period of time over which the spill took place. Values used to calculate spill intensity were based on a summary of the 2015 Weld County spill/incident reports made publically available through the Colorado Oil and Gas Conservation Commission. Spill intensity was determined by dividing the median volume of oil-and gas-related material spilled at a site (5 US barrels or  $7.95 \times 10^5 \text{ cm}^3$ ) by the range of rectangular surface areas affected at spill sites in Weld County during 2015.

Parameter	High Intensity	Medium Intensity	Low Intensity
Spill intensity calculation ( $\text{cm}^3/\text{cm}^2$ )	$7.95 \times 10^5 / 3.7 \times 10^3$	$7.95 \times 10^5 / 3.7 \times 10^4$	$7.95 \times 10^5 / 9.3 \times 10^4$
Spill Intensity (cm)	214	2.14	0.856
Length of time (day)	0.1	1	3

To execute the model, we used three year average climatic data from Greeley, Co for precipitation inputs and evapotranspiration losses (Colorado State University & U.S. Department of Agriculture 2017). A 45 day pre-spill period was modeled to help initialize realistic soil water conditions. Based off the real precipitation and evaporation inputs the modeled spill would have taken place in mid-September. Although we planned to simulate uncontained spills, we assumed micro topography would allow for pooling up to 10 cm. For the upper boundary condition that affects chemical movement from the soil to the atmosphere, we used a stagnant boundary layer of 2 cm to represent a fairly well-mixed environment. The relatively high volatility of the BTEX components results in peak solute concentrations reaching the groundwater that are sensitive to the assumed boundary layer thickness (discussed in conclusions). The concentrations calculated are for the aqueous phase only thereby being relevant to EPA drinking water limits and does not include vapor and adsorbed phases. A complete listing of the solute transport and reaction

parameters used are provided in Table 6.2. The initial concentrations of BTEX and naphthalene in the simulated produced water spill were the high range of values reported by Benko and Drewes (2008) as those concentrations more closely reflect that of gas-related produced water. Typical degradation rates for BTEX and naphthalene in soils were considered reflecting a combined physical and biodegradation rate as shown in Table 6.2. Risk categories were established by dividing the EPA drinking water limit for each contaminant into thirds. A scenario was classified as having a high risk for groundwater contamination if the peak reached at the top of the water table was above 67% of the EPA drinking water limit, medium risk if between 66–34% of the limit and low risk if between 33 –1% of the limit (Table 6.3). Naphthalene is not currently regulated by the EPA, however there is a recommended maximum level (100 µg/mL) which was used in lieu of an EPA drinking water limit (U.S. Environmental Protection Agency 2003b). The highest risk category reached by any of the contaminants in each scenario was used to generalize that scenario, such that if only one contaminant was in a high risk category, that scenario would overall be deemed a high risk for groundwater contamination.



Table 6.2 Chemical properties and relevant parameters for BTEX and naphthalene subsurface modeling. <sup>a</sup>From ASTM 2015, Table X1.2, X2.7 and text. <sup>b</sup>Modified from the U.S. National Library of Medicine 1993. Koc values calculated assuming 58% carbon in organic matter and 0.66% organic matter in soil. <sup>c</sup>Modified from Collins et al. 2002. <sup>d</sup>From the European Chemicals Bureau 2008. <sup>e</sup>From the European Chemicals Bureau 2003. <sup>f</sup>From the European Chemicals Bureau 2007. <sup>g</sup>From Lawrence 2006. <sup>h</sup>From European Chemicals Bureau 2007a. <sup>i</sup>From Benko et al. 2008. <sup>j</sup>From U.S. Environmental Protection Agency n.d. \*Naphthalene is not currently regulated in the United States. The value presented is the recommended limit (U.S. Environmental Protection Agency, 2003a).

Parameter	Benzene	Toluene	Ethylbenzene	Xylene	Naphthalene
Diffusion coefficient in liquid (cm <sup>2</sup> /d) <sup>a</sup>	0.9504	0.81216	0.7344	0.7344	0.81216
Diffusion coefficient in gas (cm <sup>2</sup> /d) <sup>a</sup>	8035.2	7344	6566.4	6220.8	6220.8
Koc (mL H <sub>2</sub> O/g C) <sup>b</sup>	85	107.5	520	58	870
Kd (cm <sup>3</sup> /g) <sup>b</sup>	0.317724	0.41151	1.99056	0.222024	3.33036
Henry's constant (unitless) <sup>c</sup>	0.19792	0.23391	0.28789	0.260899	0.0441648
First order rate constant for liquid, solid and gas (day <sup>-1</sup> )	0.0231 <sup>d</sup>	0.0077 <sup>e</sup>	0.0231 <sup>f</sup>	0.0231 <sup>g</sup>	0.3465 <sup>h</sup>
Concentration in produced water (µg/cm <sup>3</sup> ) <sup>i</sup>	27	37	19	0.611	0.556
EPA drinking water limits (µg/cm <sup>3</sup> ) <sup>j</sup>	0.005	1	700	10	100*

Table 6.3 Risk categories for various levels of groundwater contamination. Contamination equaled to or higher than 67% of the EPA drinking water limits signifies a high risk to groundwater, 66-34% of the limit signifies a medium risk and 33-1% signifies a low risk. \* Naphthalene is not currently regulated by the EPA, however drinking water has a recommended maximum level (U.S. Environmental Protection Agency, 2003b).

Contaminant	EPA Maximum Drinking Water Limits (µg/mL)	High Risk (µg/mL)	Medium Risk (µg/mL)	Low Risk (µg/mL)
Benzene	$5 \times 10^{-3}$	$3.3 \times 10^{-3}$ - $5 \times 10^{-3}$	$1.66 \times 10^{-3}$ - $3.3 \times 10^{-3}$	$5 \times 10^{-5}$ - $1.65 \times 10^{-3}$
Toluene	1	$6.7 \times 10^{-1}$ -1	$3.3 \times 10^{-1}$ - $6.6 \times 10^{-1}$	$1 \times 10^{-2}$ - $3.3 \times 10^{-1}$
Ethylbenzene	700	463-700	232-462	7-231
Xylene	10	6.6-10	3.4-6.6	0.1-3.3
Naphthalene	100	67-100	34-66	1-33

## 6.4 RESULTS

### 6.41 OVERALL TRENDS

To evaluate which of the contaminants were problematic, the 1D model was used to evaluate scenarios that were thought to result in reaching the highest peak concentration in groundwater (high-intensity spill overlying a shallow water table) in both soil types (Figure 6.1). In sandy loam soil, benzene and toluene were the only contaminants that exceeded the EPA drinking water limits; in clay loam soil only benzene exceeded the limit. Ethylbenzene, xylene and naphthalene never reached EPA limits or sufficiently high concentrations to be labelled within the risk categories, regardless of soil type (Figure 6.1). We decided to focus on benzene and toluene for the remaining analysis.

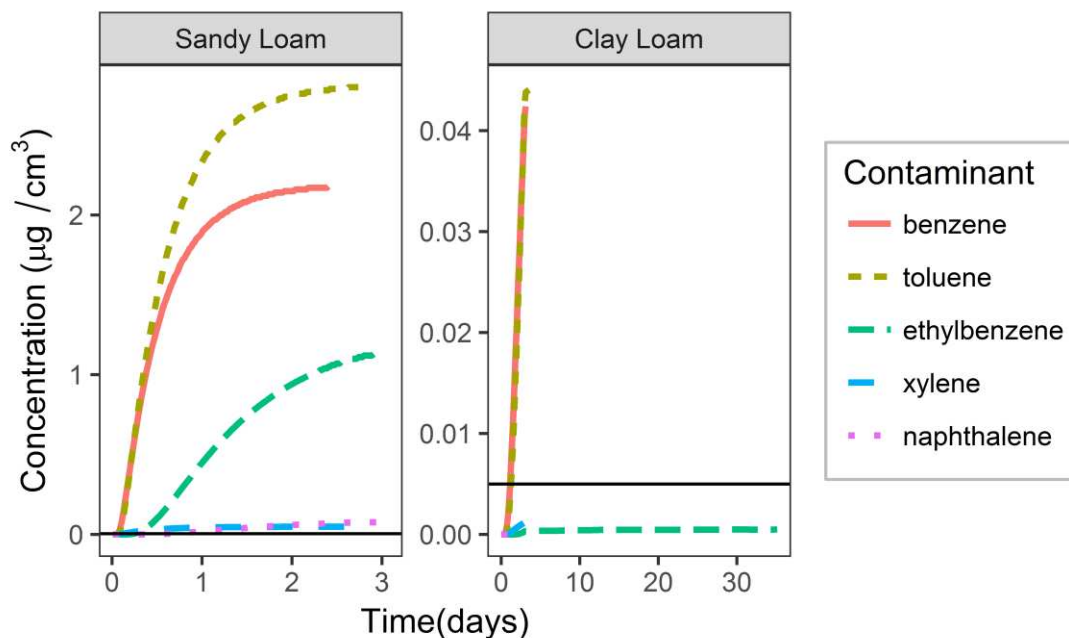


Figure 6.1 Concentration of all contaminants simulated at the top of a 30 cm (shallow) water table found below sandy loam (left) and clay loam (right) in HYDRUS 1D. Horizontal black lines represent the EPA limits for benzene (0.005 µg/cm³). Toluene has a limit of 1 µg/cm³ but is not shown here.

Table 6.4 Percent difference from 1D and 3D modeling for peak concentrations reached at the water table in sandy loam soils. The numbers in bold represent the conditions where 3D simulations rather than 1D were deemed the more conservative value and was used for further analysis.

Spill Intensity:		Low Intensity		Medium Intensity		High Intensity	
Depth (cm)		Benzene	Toluene	Benzene	Toluene	Benzene	Toluene
30		18	13	2	2	1	1
150		31	20	<b>21</b>	<b>35</b>	<b>97</b>	<b>131</b>
300		33	28	<b>437</b>	<b>525</b>	<b>30,273</b>	<b>17,553</b>

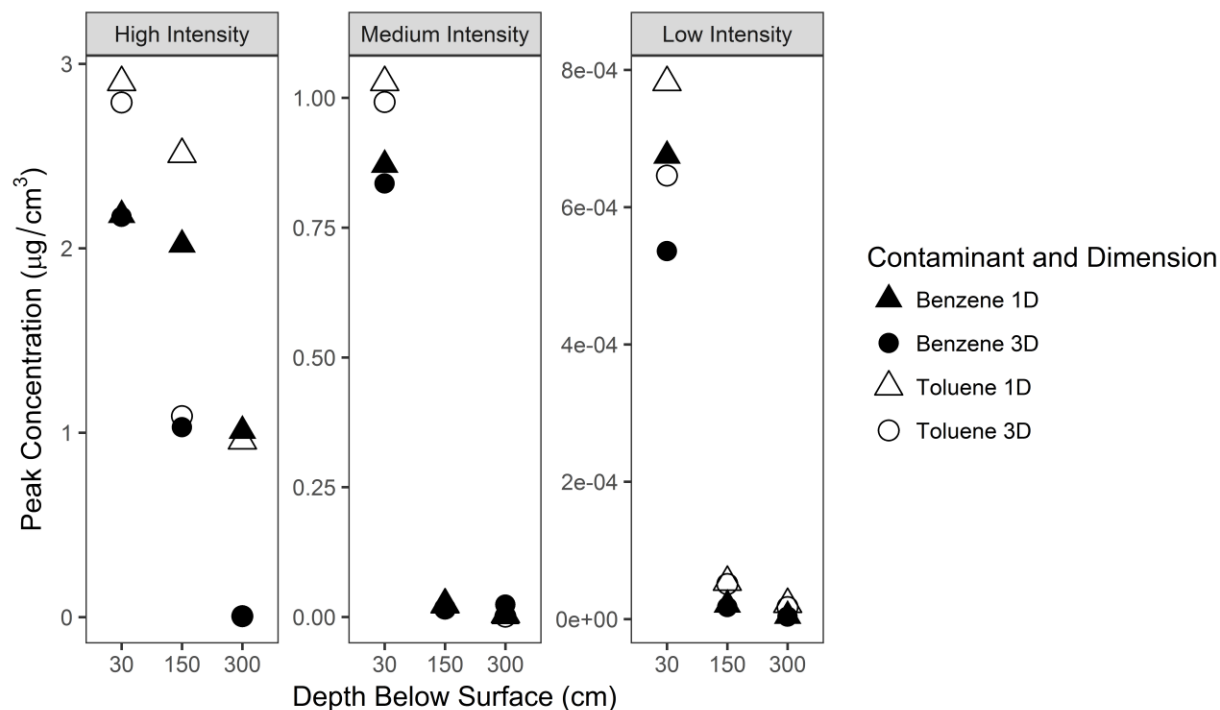


Figure 6.2 Comparison of 1D and 3D benzene concentrations simulated across water table depths in sandy loam soil. Results are divided into panels according to the three modeled spill intensities.

The effect of small spill areas on subsurface lateral movement of the contaminants is demonstrated in Figure 6.2 and Table 6.4. The 1D and 3D modeling showed large differences in the predictions of benzene and toluene concentrations when modeling high-and-medium intensity spills overlying sandy loam soil with groundwater at 150-and-300 cm deep (Figure 6.2 & Table 6.4). It is evident that one-dimensional flow analysis overestimates the hazard to groundwater from small area spills (which are higher intensity in these simulations) unless the vadose zone is very shallow. This prompted us to report the more conservative results from HYDRUS 3D for sandy loam soil with the water table at medium and deep depths and report HYDRUS 1D concentrations for all other scenarios (Table 6.4). Spills taking place over clay loam soil were not able to be simulated in HYDRUS 3D if the spill intensity was medium or high

(because of lateral surface runoff negating meaningful boundaries of the spill area) and thus the results presented for the clay loam are from HYDRUS 1D only.

The time to reach benzene and toluene peak concentration increased with depth as seen in Figures 6.3-6.6. However, the various times to reach peak concentration at the three depths had less variance when experiencing higher-intensity spills. In both soil types, peaks were reached faster with higher-intensity spills. Medium-and-high intensity spills with shallow water tables reached peak concentrations for benzene and toluene within 1 to 3 days in sandy loam soil (Figure 6.1, 6.3 and 6.4) whereas clay loam reached peak concentrations within 4 to 52 days (Figure 6.1, 6.5 and 6.6).

#### **6.42 SANDY LOAM**

Groundwater benzene is expected to exceed EPA limits ( $0.005 \text{ ug/cm}^3$ ) at all groundwater depths tested with a high-intensity spill, and at shallow or intermediate groundwater depths when exposed to a medium-intensity spill (Figure 6.3). However, the low-intensity spill is expected to have no risk for groundwater contamination at medium and deep depths to the water table and only a low risk for groundwater contamination at the shallow water table. Toluene concentrations in excess of EPA limits ( $1 \text{ ug/cm}^3$ ) are reached at the water table less often than for benzene. The toluene EPA limit is exceeded in scenarios with high-intensity spills and shallow or intermediate water table depths and in scenarios with medium-intensity spills at shallow water table depths (Figure 6.4).

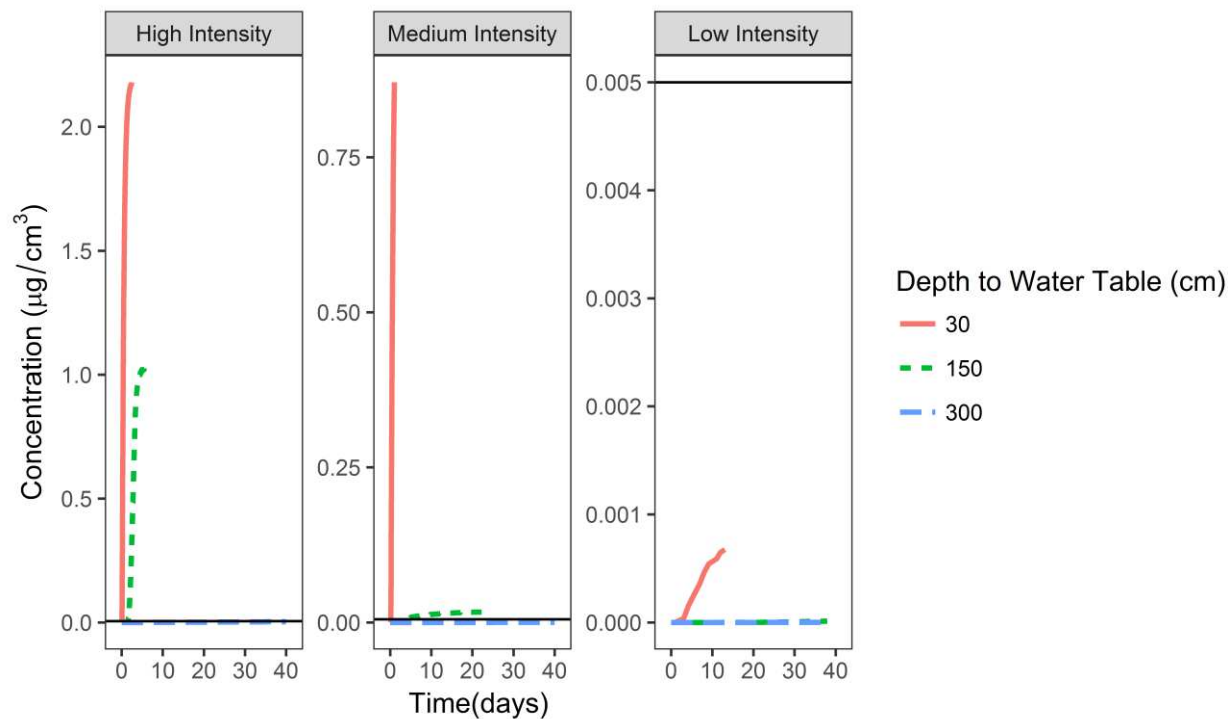


Figure 6.3 Modeled benzene concentration at the water table in sandy loam soils (with a mixture of 1D and 3D modeled concentrations as stated in Table 4.4). The black line marks the EPA drinking water limit for benzene.

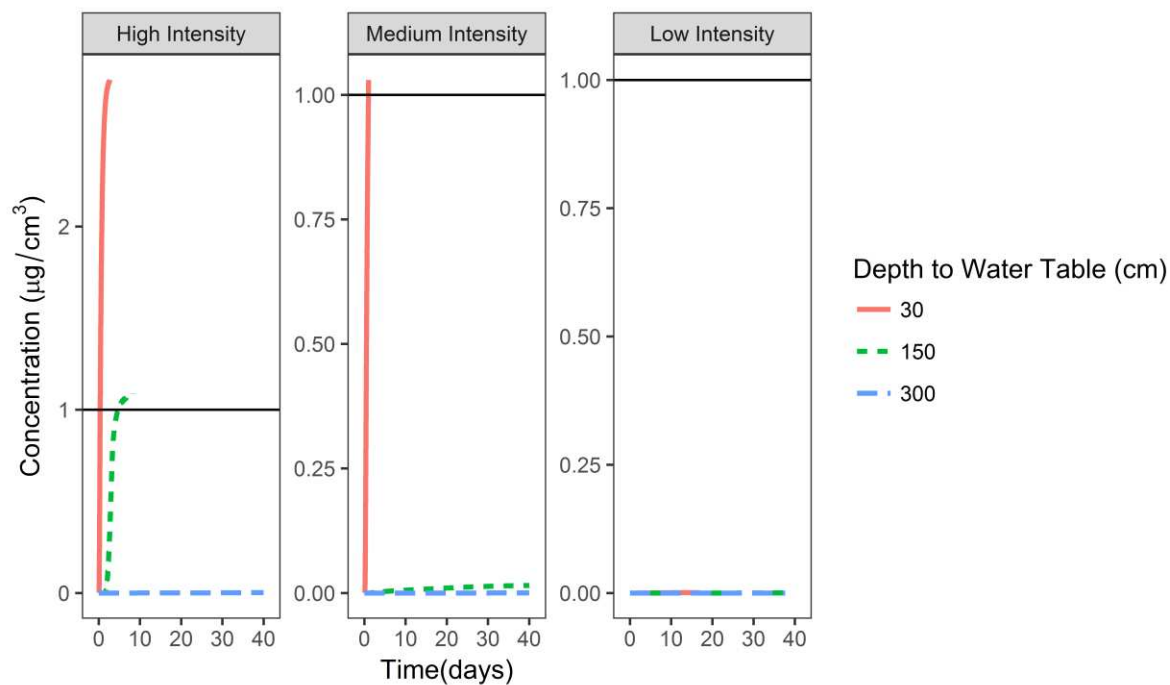


Figure 6.4 Modeled toluene concentration found at the water table in sandy loam soils (1D and 3D combinations as stated in Table 4.4). Black line marks the EPA drinking water limit for toluene.

### 6.43 CLAY LOAM

When subjected to the high-intensity spill scenario, HYDRUS 1D predicted very large pooling ( $\approx 100$  cm) on the clay loam due to its low hydraulic conductivity. Such high pooling would only be realistic when a spill was contained with surface features such as soil berms, which we did not simulate. We present the results for high-intensity spills on clay loam soils and pooling to a maximum of 10 cm. The leftover produced water from a high-intensity spill overlying clay loam does not infiltrate in our simulations. Surface runoff and subsequent infiltration and volatilization would be a potential pathway for BTEX flux and our results should be viewed with this knowledge. The peak concentration reached across all spill intensities and water table depths show that only the high-intensity spill overlying clay loam soil and shallow water table results in groundwater contamination exceeding the EPA drinking water limit for benzene (Figure 6.5). Benzene is not predicted to reach the 150 and 300 cm depth water tables for any of the spill intensity scenarios (Figure 6.5). In low-intensity spills, peak benzene concentrations at the shallow water table are a tenth of the EPA drinking water limit, putting it at low risk for groundwater contamination (Figure 6.5). Toluene is not predicted to reach the water table in other than the high-or-medium intensity spill with a shallow water table and in those scenarios the concentration reached is not high enough to be labelled within the risk categories (Figure 6.6).

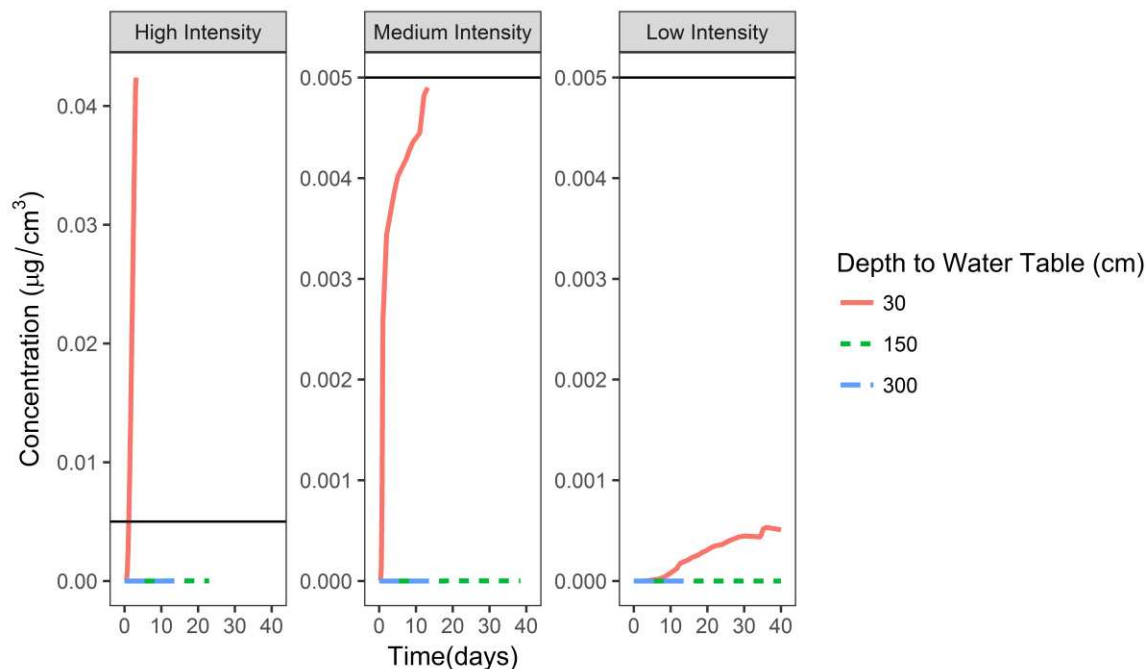


Figure 6.5 Modeled concentrations of benzene at the water table in clay loam soils (derived from 1D simulations). The black line marks the EPA drinking water limit for benzene.

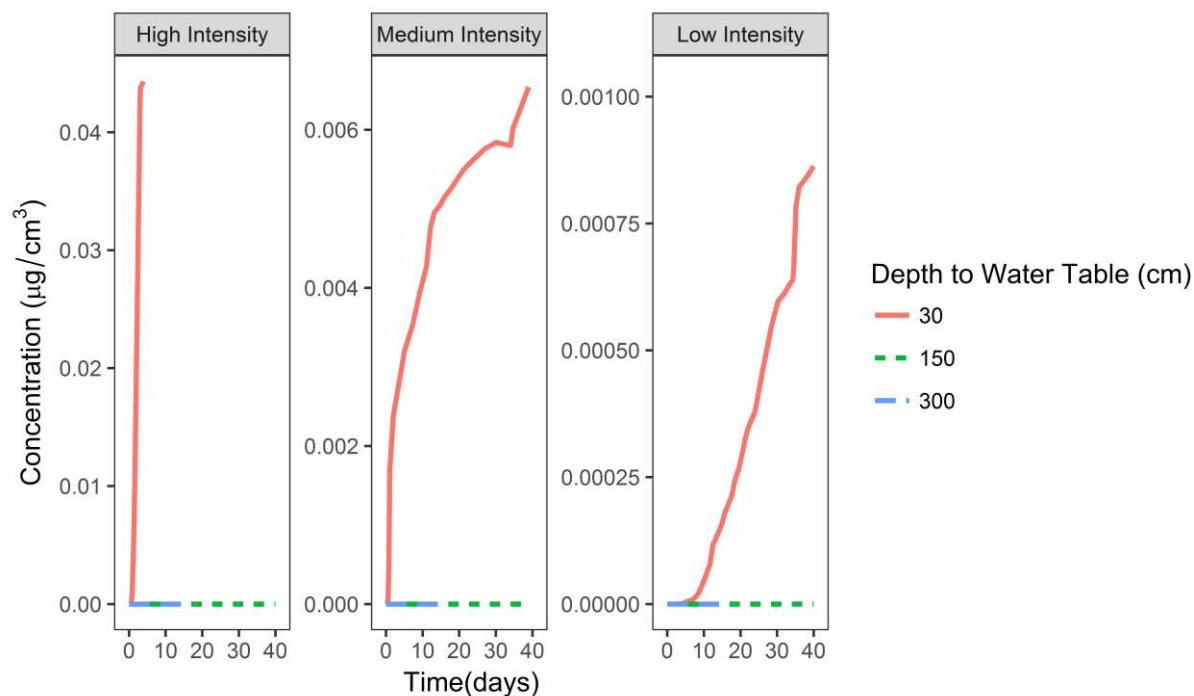


Figure 6.6 Modeled concentrations of toluene at the water table in clay loam soils (derived from 1D simulations). Note that the EPA drinking water limit for toluene has been excluded ( $1 \mu\text{g}/\text{ml}$ ) because all values were far below this limit.



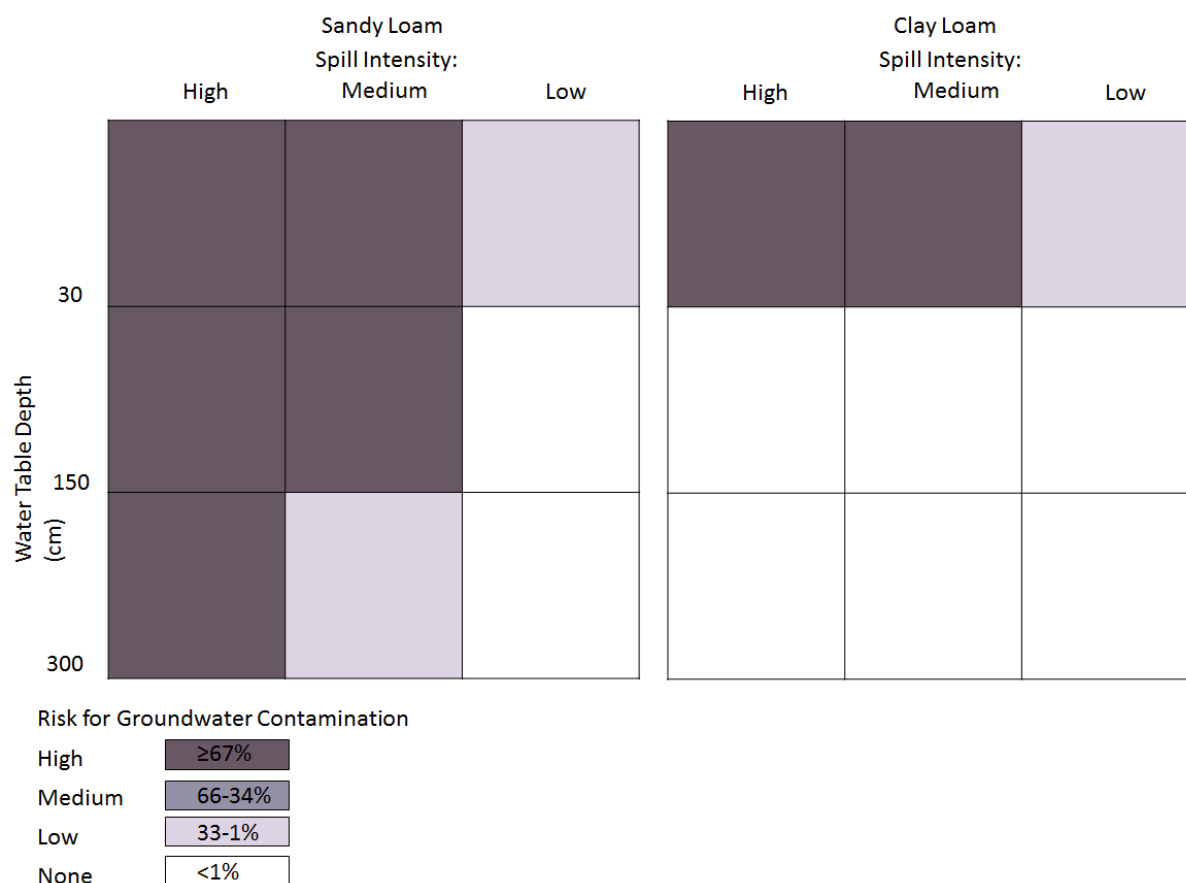


Figure 6.7 Quick reference guide to assess the risk of groundwater contamination at surface spill sites across multiple scenarios. The left panel depicts risks in sandy loam and right panel depicts risks in clay loam. The legend details the varying risk categories and outlines within each box the percentage range of EPA drinking water limit-concentrations by which each scenario was categorized as compared to the peak concentration of a contaminant. Benzene concentrations always reached the highest risk category of any modeled contaminant so this diagram represents the risk for benzene groundwater contamination. Refer to Table 6.3 for more information about the peak concentration ranges used for each contaminant and risk category.

## 6.5 CONCLUSION

Our results suggest that there is a risk for groundwater contamination from a subset of BTEX and naphthalene components within the modeled scenarios of soil type, depth to groundwater and spill intensity. The majority of BTEX and naphthalene movement and dissipation was through the gaseous phase. Our first hypothesis asserted that benzene and toluene would be the most problematic contaminants and would dominate the risk categories.

In support of our hypothesis in both sandy loam and clay loam soils, only benzene and toluene concentrations reached concentrations sufficient to be within a risk category and neither ethylbenzene, xylene nor naphthalene reached such concentrations. Our second hypothesis stated that the majority of scenarios would fall within the risk categories, such that the peak concentration of at least one contaminant would reach to 1% of that contaminants EPA drinking water limit. Contrary to this hypothesis, in clay loam soils benzene reached concentrations that qualified it for the established risk categories in three out of the nine simulations. In clay loam soil there was only one scenario out of nine that resulted in even a low risk for toluene contamination: a high-intensity spill with shallow groundwater depth. Supporting our hypothesis, in sandy loam soils peak concentrations reached levels that qualified it for a risk category seven times out of nine simulations for benzene and five times out of nine simulations for toluene. Overall, these results suggest that benzene and toluene are the primary contaminants out of the ones modeled here that should be addressed at produced water-spill sites. Furthermore, benzene and toluene are at risk for reaching the risk categories more often in sandy loam soils than in clay loam soil.

Our third hypothesis stated that higher peak concentrations and reduced times to reach these peaks would occur at high-intensity spill sites overlaying coarse-textured soils with shallow depths to groundwater. Supporting this hypothesis, we always found higher peak concentrations and reduced time to reach the water table for benzene and toluene in coarser sandy loam soils compared to clay loam soils. The scenario that resulted in the maximum peak concentration of benzene had the following characteristics: a high-intensity spill with a 30 cm deep water table in sandy loam soil. The maximum amount of benzene that reached the water table in that scenario

was 8% of the original mass found in produced water, whereas less than 0.2% of benzene reached the water table under the same conditions in a clay loam soil.

Although not presented in this work, attempts were made to compare the modeling results to concentration data from the field for specific spills as reported to the COGCC. Many important details were lacking for this comparison however, such as time since the spill occurred and the volume of water spilled. Qualitatively, the range of peak concentrations reached in this simulations were within typical analytical concentrations of BTEX reported to the COGCC. This research sought to provide rough estimates for BTEX and naphthalene groundwater-contamination risk across many parameters. Thus model validation of BTEX and naphthalene peak concentrations under similar conditions in the lab was not considered.

There are many considerations when evaluating the applicability of this work to other areas. It is important to recognize that produced water generated from different areas can have varying concentrations of BTEX and naphthalene. When utilizing this model for other areas, perhaps adjusting the BTEX and naphthalene concentrations to the relevant local levels would be advisable. Also, the main pathway for BTEX and naphthalene movement was through the vapor phase, meaning that soils with high water content would have lower air space and reduced movement of BTEX and naphthalene. In our simulations, we assumed an average  $K_d$  value across soil types. Different soil types would likely vary in  $K_d$  values such that clay soils would likely have a higher  $K_d$  than sandy soils because of higher surface area. In the future, utilizing soil specific  $K_d$  values for each contaminant would be advisable. Another consideration is that these results consider only one spill at a site. Research has shown that if a site experiences a spill, it is more likely to experience repeat spills and therefore would likely have increased peak concentrations

or prolonged periods of time for which peaks last (Patterson et al. 2017). An important determinant of the peak concentration reached was the thickness of the surface boundary layer because these contaminants are volatile. Using realistic boundary layer measurements will help to ensure accurate results. Lastly, HYDRUS 3D does provided lower peak concentrations than 1D with increase in the depth to groundwater, so if these methods are replicated in HYDRUS 1D, the user must assume the peak concentrations are overestimated for the actual 3D flow field.

Overall, this research provides a frame work for understanding the factors that contribute to the risk for groundwater contamination of benzene and toluene found at produced water-spill sites. Spills often occur at fracking well pads so we recommend avoiding coarse soil textures for fracking sites or add extra precautions to minimize spills as they often result in high risk for groundwater contamination, regardless of spill intensity (Patterson et al. 2017). Finer-textured soils have less risk for groundwater contamination and are thus a preferable choice for fracking locations. Catching spills early would reduce the volume of produced water spilled and reduce overall spill intensity. Lower spill intensities combined with deeper water tables underlying fine textured soils provides the most protection against groundwater contamination at produced-water surface-spill sites.

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## 8 PHYTOREMEDIATION OF BTEX AND NAPHTHALENE FROM PRODUCED-WATER SPILL SITES USING *POACEAE*

### 8.1 SUMMARY

Surface spills of water produced from hydraulic fracturing can expose soil and groundwater to organics such as BTEX and naphthalene (BTEX&N) as well as high concentrations of salt. As an alternative to soil excavation, we evaluated the effectiveness of BTEX&N soil remediation using two grasses present in Colorado. Perennial ryegrass (*Lolium perenne*; native to Colorado) and foxtail barley (*Hordeum jubatum*; present in Colorado) were grown separately in pots in the greenhouse and exposed to NaCl or a synthesized produced-water slurry containing relevant levels of salt and BTEX&N. Plant biomass was measured 14 days post-spill, and levels of BTEX&N were quantified using GC/MS for soil, roots, and shoots at day 7 and 14 post-spill. Foxtail barley shoot growth was reduced by BTEX&N, whereas perennial ryegrass shoot growth was enhanced by salt but not BTEX&N. While BTEX&N in soil associated with foxtail barley mainly decreased over time, the soil associated with perennial ryegrass mainly saw an increase in extractable BTEX&N with time. However, further research is needed to determine the fate of BTEX&N within grasses and soil.

### 8.2 INTRODUCTION

Hydraulic fracturing (often called fracking) generates waste called “produced water” that contains a complex mixture of chemicals, some of which are toxic (Veil et al. 2004, Gross et al. 2013, Hammer et al. 2012, Rahm et al. 2012, Rahm et al. 2013, Kargbo 2010). Constituents of produced water include dispersed oil, soluble organics, treatment chemicals, naturally occurring

radioactive materials and high concentrations of salt (Veil et al. 2004, Hammer et al. 2012, Kargbo et al. 2010). One potential and wide-spread conduit for the release of these contaminants into the environment is through surface spills of produced water (Gross et al. 2013, Hammer et al. 2012). In particular, Weld County, CO is one such areas that is intensively fracked (Matthews 2011), generates large volumes of produced water and subsequently experiences frequent produced-water surface spills (Matthews 2011, Vengosh et al. 2015, Finley 2011, Finley 2011a & 2014). The number of individual spills has increased over time; in 2011 there were 179 reported spills (Gross et al. 2013), but in 2015 that number had increased to 316 (Finley 2014, Center for Western Priorities n.d.). Cleanup of a produced water spill is often performed by excavating large quantities of soil at the spill site (Colorado Oil and Gas Conservation Commission 2012, Millano 1999), but this treatment causes significant detrimental effects to ecosystems through deterioration of the soil structure and removal of habitat for native species (Foster et al. 2003, Ako et al. 2014). New methods of non-invasive cleanup might be equally efficient at removing harmful chemicals (Singh & Jain 2003, Gerhardt et al. 2009) and preferable in light of the many drawbacks to excavation (Gross et al 2013, Ako et al. 2014, Saviour 2012). As an alternative to chemical-and-mechanical remediation methods, phytoremediation is a widely accepted and less invasive measure used to remove toxins from the environment (Singh & Jain 2003), including other oil-and-gas related compounds such as polycyclic aromatic hydrocarbons (PAHs) (Pilon-Smits 2005, Dietz & Schnoor 2001, Boonsaner et al. 2011, Muratova et al. 2008, Sun et al 2010, Lalande et al. 2003). Previous studies have focused on using phreatophytic trees such as willow and poplar to remove organic contaminants from groundwater (Ferro et al 2013, Burken & Schnoor 1998, Schwitzguébel et al. 2011,

Interstate Technology & Regulatory Council 2009), but many produced-water spills occur in more arid regions, such as the grasslands in Weld County, that would not support those species in many areas. The possibility that phytoremediation could be useful in cleaning up produced-water spills in the soils of more arid regions has received less attention.

One type of threat posed by produced water comes from BTEX (benzene, toluene, ethyl benzene, and xylene) and naphthalene (U.S. National Library of Medicine 1993), a group of toxic compounds together referred to as “BTEX&N” in this chapter. If produced-water surface spills occur, BTEX&N can either move through the soil subsurface as a liquid or gas or volatilize directly from solution (Figure 8.1). This is particularly true of BTEX and to a lesser extent, naphthalene given their tendency to have a relatively high partition in the gaseous phase compared to the aqueous phase as indicated by their associated Henry’s constant values,  $H_i$  (Table 8.1) (U.S. National Library of Medicine 1993). If BTEX&N volatilizes to the atmosphere then those compounds will be readily degraded through photodegradation (European Chemicals Bureau 2008, European Chemicals Bureau 2003 & European Chemicals Bureau 2007). If BTEX&N infiltrates into the soil, BTEX compounds can be highly mobile (as indicated by their associated  $K_{oc}$  values), as is naphthalene to a lesser extent (Table 8.1) (U.S. National Library of Medicine 1993, Lovanh et al. 2000). What is left of these compounds in the soil can reversibly adsorb to soil particles and roots (Dietz 2001), resulting in relatively longer-term storage of toxic chemicals in the system (Figure 8.1). Once in the soil, varying levels of oxygen (Vaezihir et al 2012) or other electron acceptors (Chakraborty & Coates 2005, Lovley 2000) and soil microbiota (Collins et al. 2002) determine the rate of degradation. The main mechanisms for BTEX&N loss from soil are thought to be volatilization and leaching through the soil subsurface, but the partitioning

between these two mechanisms is site-specific, dependent upon multiple factors and thus will have an effect on the amount left in the soil that is able to be taken up into plant root and shoot tissue (Figure 8.1).

Phytoremediation of these low-to-medium molecular weight aromatic compounds is plausible, because the hydrophobicity (Table 8.1) of these compounds should allow diffusion through root cellular membranes and into plant tissues (Burken & Schnoor 1998, U.S. National Library of Medicine 1993). The contaminants can be translocated to the shoot tissue where they can be either modified and bound within tissues (sequestered), fully degraded, or lost through the plant's transpiration stream. As  $\log K_{ow}$  falls below 1, compounds are increasingly too hydrophilic to bypass the lipid bilayer of the root cellular membrane, indicating that the chemicals will not enter or be stored in the plant. As  $\log K_{ow}$  rises above 2, on the other hand, compounds become so hydrophobic that they can be irreversibly adsorbed to the surface of soil and roots, so that the plant will not sequester the chemicals (Dietz & Schnoor 2001, Briggs et al 1983, Briggs et al 1982). Beyond uptake, plants can also enhance the degradation of BTEX&N in the soil through rhizodegradation (Wilson et al 2013), through symbiotic relationships with soil microbiota or through root excretions that break down the chemicals (Balseiro-Romero et al 2014, Kvesitadze et al. 2006).

In addition to sequestration of toxic organic compounds, to remediate a produced-water spill, plant species also must withstand extremely high salt concentrations known to be associated with produced water, which can exceed that of seawater (Benko & Drewes 2008). Species such as foxtail barley (*Hordeum jubatum*) (Israelsen et al. 2011, Natural Resource Conservation Service 2015) and perennial ryegrass (*Lolium perenne*) (Natural Resource

Conservation Service 2015, Nichols 2008) are salt tolerance and are both currently present in Colorado (Natural Resource Conservation Service 2015, U.S. Department of Agriculture 1999). Foxtail barley has been found to grow with high abundance in hydrocarbon-contaminated soils in Saskatchewan, Canada (Robson et al. 2004), making it an ideal candidate for further evaluation. However, foxtail barley was introduced to Colorado whereas perennial ryegrass is native and possibly preferable as a remediation candidate (Natural Resource Conservation Service 2015, U.S. Department of Agriculture 1999). For the current study, we tested the ability of these two species to take up BTEX&N in the presence of typical produced-water salt concentrations. We hypothesized that (1) foxtail barley and perennial ryegrass would take up BTEX&N in their tissues; (2) concentrations of the contaminants in plant tissue would decrease with time due to volatilization and degradation within the plant, out competing plant uptake; (3) because salt-tolerant species were used, BTEX&N would be the limiting factor for growth; and (4) the soil in which these plants were grown would contain less BTEX&N than soil in control pots containing no plants.

Table 8.1 Characteristics of the produced water slurry containing BTEX&N and salt that was applied to the treatment group. Lower  $K_{oc}$  values indicate higher mobile in the soil. Higher  $H_i$  indicate reduced volatility. Higher values of  $\log K_{ow}$  indicate higher hydrophobicity. The range of  $K_{oc}$  values encompasses what has been reported by various authors (U.S. National Library of Medicine 1993). <sup>a</sup> Modified from the European Chemicals Bureau (2008). <sup>b</sup> Modified from the U.S. Environmental Protection Agency (2011).

Chemical	Concentration <sup>a</sup>	$K_{oc}$	$H_i$	$\log K_{ow}$	EPA Drinking Water Limit <sup>b</sup>
Unit:	ng/L	ratio	atm $\times$ m <sup>3</sup> /mol	ratio	ng/L
Benzene	$2.7 \times 10^7$	85	$5.56 \times 10^{-3}$	2.31	$5 \times 10^3$
Toluene	$3.7 \times 10^7$	37-178	$6.64 \times 10^{-3}$	2.73	$1 \times 10^6$
Ethyl benzene	$1.9 \times 10^7$	520	$5.88 \times 10^{-3}$	3.13	$7 \times 10^5$
<i>m</i> -xylene	$6.11 \times 10^5$	48-68	$5.18 \times 10^{-3}$	3.12	$10 \times 10^6$
Naphthalene	$5.56 \times 10^5$	440–1300	$4.40 \times 10^{-4}$	3.29	NA
Sodium chloride	$1 \times 10^{10}$	NA	NA	NA	NA

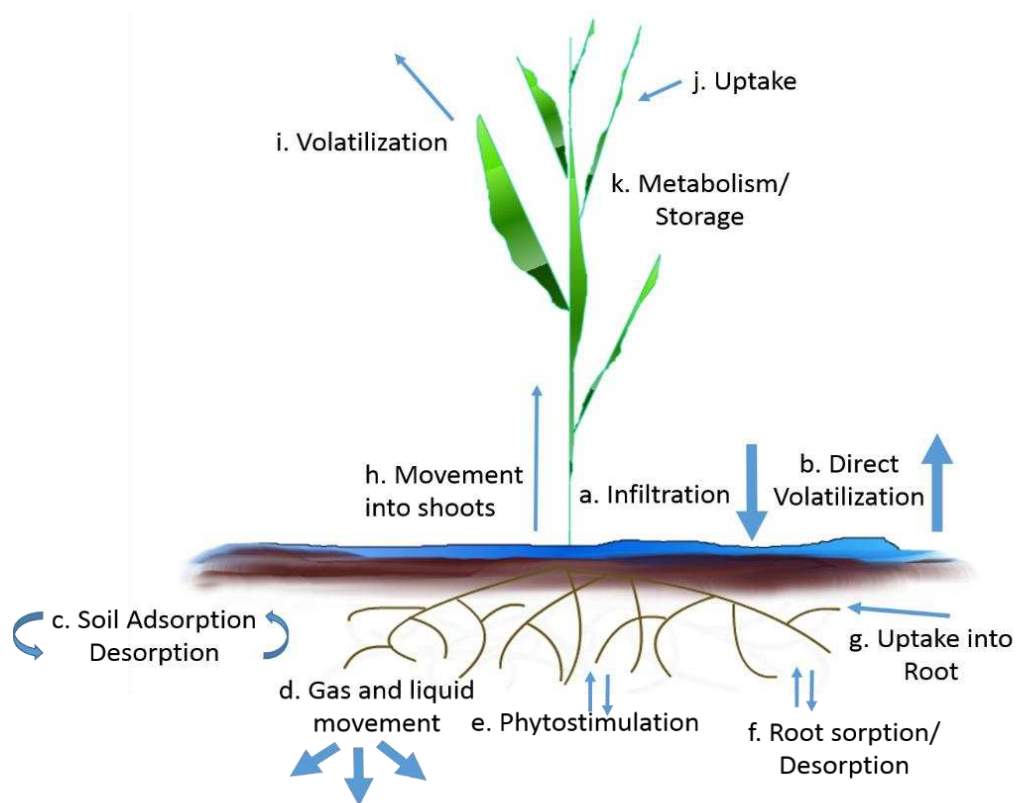


Figure 8.1 Potential processes and fates of BTEX&N from a produced-water spill in a soil-plant-atmosphere system. Modified from Collins, 2002, Figure 1. Arrow thickness symbolizes theorized relative importance within the system.

### 8.3 METHODS

In a greenhouse experiment, historical produced-water spills in Weld County, CO were simulated to test the efficacy of BTEX&N remediation by foxtail barley and perennial ryegrass. We collected soil from Pawnee National Grasslands, which currently has 60 active oil-and-gas wells and is located in Weld County (U.S. Forest Service 2013). The amount of organic matter in the soil was assessed through incineration (Schulte & Hopkins 1996) and roughly determined the soil's texture through the "feel method" (Thien 1979). Soil was sieved to 2 mm and mixed with 1/3 volume coarse perlite, a volcanic glass used to improve drainage to match field soil structure (Fields et al. 2014). The soil mixture was not sterilized, preserving the native soil organisms.

120 g of the soil mixture was filled to 2 cm from the top of 164 cm<sup>3</sup> 'cone-tainer' pots. Prior to sowing seeds, soil was saturated with water and allowed to drain. In separate pots either foxtail barley, perennial ryegrass or no seeds were sown for a total of 40 total pots of each species and 30 pots with no seeds. A pinch of approximately 30 seeds were mixed with the upper cm of the soil mixture. 10–30 individual plants were grown in each pot depending on germination. Plants were cultivated in the warm-bay greenhouse at 30°C for 30 days before being subjected to a simulated spill of produced water. The "treatment" group contained 20 pots of each species and received a salt and BTEX&N produced-water treatment ("salt + BTEX&N"); 10 pots of each species were harvested for soil, roots, and shoots at day 7 and 14 post-spill. The "salt-only" treatment contained 10 pots of each species; all pots were harvested for roots and shoots at day 14 post-spill. A "water-only" control group contained 10 pots of each species and received only water, no salt or BTEX&N; all pots were harvested for roots and shoots at day 14 post-spill. The "control soil" group contained 30 pots with no plants and received a salt +



BTEX&N treatment; 10 pots in this group were harvested at days 3, 7 and 14 post-spill. An additional measurement was taken in the control soil at day 3 to understand how BTEX&N was reduced prior to day 7 and 14 post-spill, whereas further time post-spill was of interest for plants.

The volume of solution spilled onto the surface of each pot was scaled based on the surface area affected by average produced-water spills in Weld County, CO, equaling 30 mL per container. Pre-and-post spill, all pots were watered with 30 mL of deionized water every 4 days. The salt+BTEX&N solution was synthesized by mixing the high concentrations of BTEX&N (Table 8.1) as typically found in hydrofracking produced water and a median salt concentration of 10 g/L (Table 8.1) typical of produced water derived from the Denver basin (Benko & Drewes 2008), where the majority of fracking occurs in Colorado. The EPA drinking water limit for benzene was exceeded within the salt + BTEX&N solution, but no other contaminants exceeded their limit (Table 8.1) (U.S. Environmental Protection Agency 2011). The salt-only solution was created using the same median salt concentration but no BTEX&N. The salt + BTEX&N and salt-only solutions also contained 25% methanol used to increase solubility of naphthalene. Methanol is a main component of produced water, but is often overlooked (Smiley et al. 1995). Methanol has no effect on the growth of similar grass species (Smiley et al. 1995) and its uptake was not considered within this experiment. The water-only solution contained only deionized water and no methanol.

At harvest, the soil and plants were gently removed from the pots. Shoots were separated from roots, and roots were delicately removed by hand from the soil. Total root and shoot biomass for all plants in a pot (wet weight) was measured. The total weight of all roots and

shoots in a pot was divided by the number of individuals in the pot to get the average wet weight of an individual. Roots and shoots of plants that received a salt-only or salt + BTEX&N treatment were washed with methanol and the tissue was cut into smaller pieces then capped in gas chromatography vials. Soil was coarsely homogenized using a spatula and placed in vials within 5–10 minutes, the implications of which are explained in the discussion. The concentration of BTEX&N was measured in a subset of the soil in each pot (~3 g), from which the total mass of each contaminant in all of the soil in the pot was extrapolated. Vials were kept in a refrigerator until they could be analyzed (generally 3 days after harvest) at 1.6 °C to minimize microbial degradation of the contaminants.

Concentrations of BTEX&N were analyzed using headspace analysis with GC/MS (U.S. Environmental Protection Agency 1996). Each sample was analyzed with a Hewlett-Packard model 7694 headspace sampler (Agilent Technologies 2000). The headspace sampler was interfaced to a Restek column Rxi-624Sil MS and an Agilent 6890 GC (Agilent Technologies 1999). BTEX&N detection was via MS with electron impact ionization operated in single ion monitoring mode. Expected mass-to-charge ratios (and retention times) were 51 and 78 (11.98 and 11.98 min) for benzene, 91 and 92 (15.92 and 15.92 min) for toluene, 91 and 106 (17.61 and 17.59 min) for ethylbenzene, 91 and 106 (17.73 and 17.73 min) for xylene, and 128 (21.42 min) for naphthalene (Agilent Technologies 1999, Kamal & Klein 2010).

The change in biomass upon exposure to the water-only, salt-only or salt + BTEX&N solution was determined with ANOVA for roots and shoots. Statistically significant differences in contaminant total mass in soils were determined with ANCOVA using time and species as independent variables, with the number of plants in a pot (siblings) as a covariate. Changes in

root and shoot contaminant mass were determined using a three-factor repeated measures analysis, with time (day 7 or 14) and tissue type (roots or shoots) as independent variables and the number of siblings defined as a covariate. We treated as a repeated measure the contaminant mass in a specific tissue across time. The tissue concentrations of the two species were analyzed separately to satisfy normality assumptions of residuals. P-values were adjusted with a Bonferroni correction to account for conducting multiple comparisons (Ott & Longnecker 2010). Significance was assessed at  $\alpha < 0.05$ .

## **8.4 RESULTS**

### **8.41 LIMITATIONS ON GROWTH**

Roots of both species were unaffected by the salt-only or salt + BTEX&N treatment; root mass was not significantly different between treatments and the water-only control (Figure 8.2). Shoot growth, however, differed markedly among treatments (Figure 8.2). Shoots of perennial ryegrass significantly increased in biomass in the salt-only treatment relative to the water-only control, indicating that this grass is a halophile, not just salt-tolerant. However, the produced-water treatment resulted in lower shoot biomass for perennial ryegrass (significantly lower than the salt-only treatment, but not significantly different from the water-only control). The shoots of foxtail barley were not significantly affected by the salt-only treatment, indicating salt-tolerance, but the combined salt + BTEX&N treatment significantly reduced shoot biomass relative to both the water-only control and the salt-only treatment (Figure 8.2).

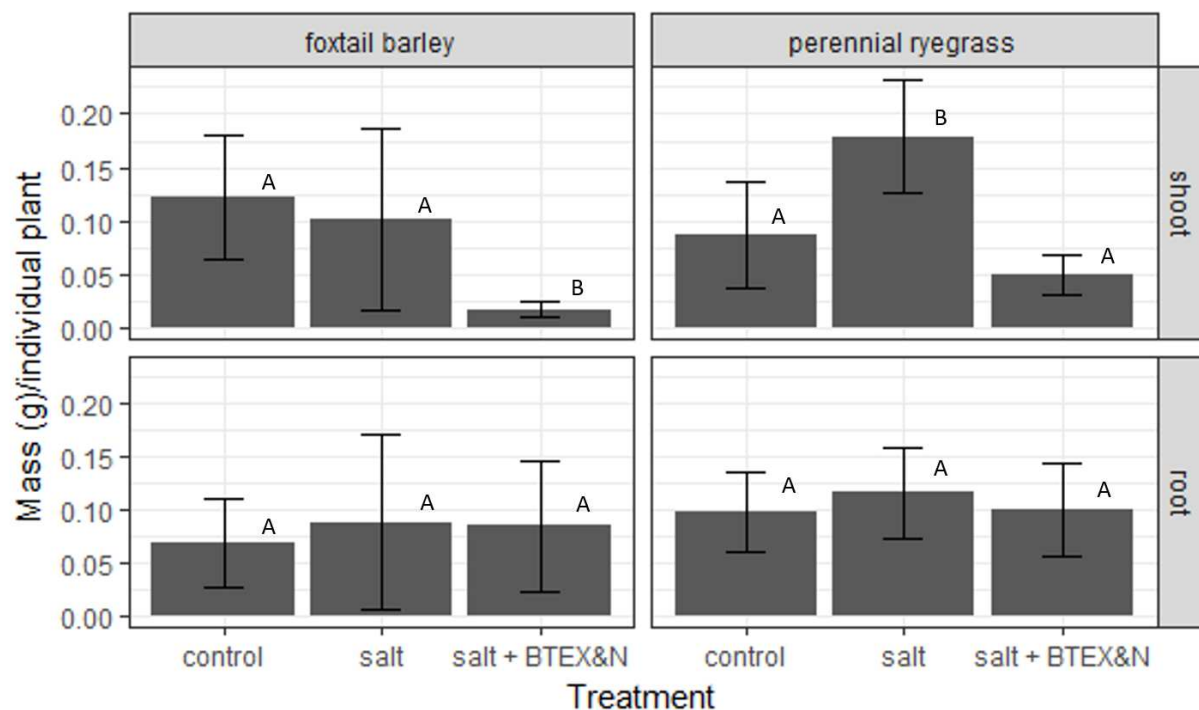


Figure 8.2 Changes in root and shoot wet biomass when seedlings were subjected to salt-only or to the salt + organic treatment at day 14. Different letters identify a statistically significant difference within one tissue type and species. Error bars are  $\pm$  one standard deviation,  $n=10$ .

#### 8.42 CONTAMINANT LEVELS IN SOIL

The soil was determined to be sandy loam and contain 3.5% organic matter. In the control soil, the initial soil concentrations of all observed contaminants at day 3 were significantly reduced by day 7 and 14 (Figure 8.3). The control soil and soil associated with either species often had significantly different total mass of each contaminant. (Figure 8.4). These results are broken down into the individual contaminant chemicals below. The raw data can be found in Table 8.2.

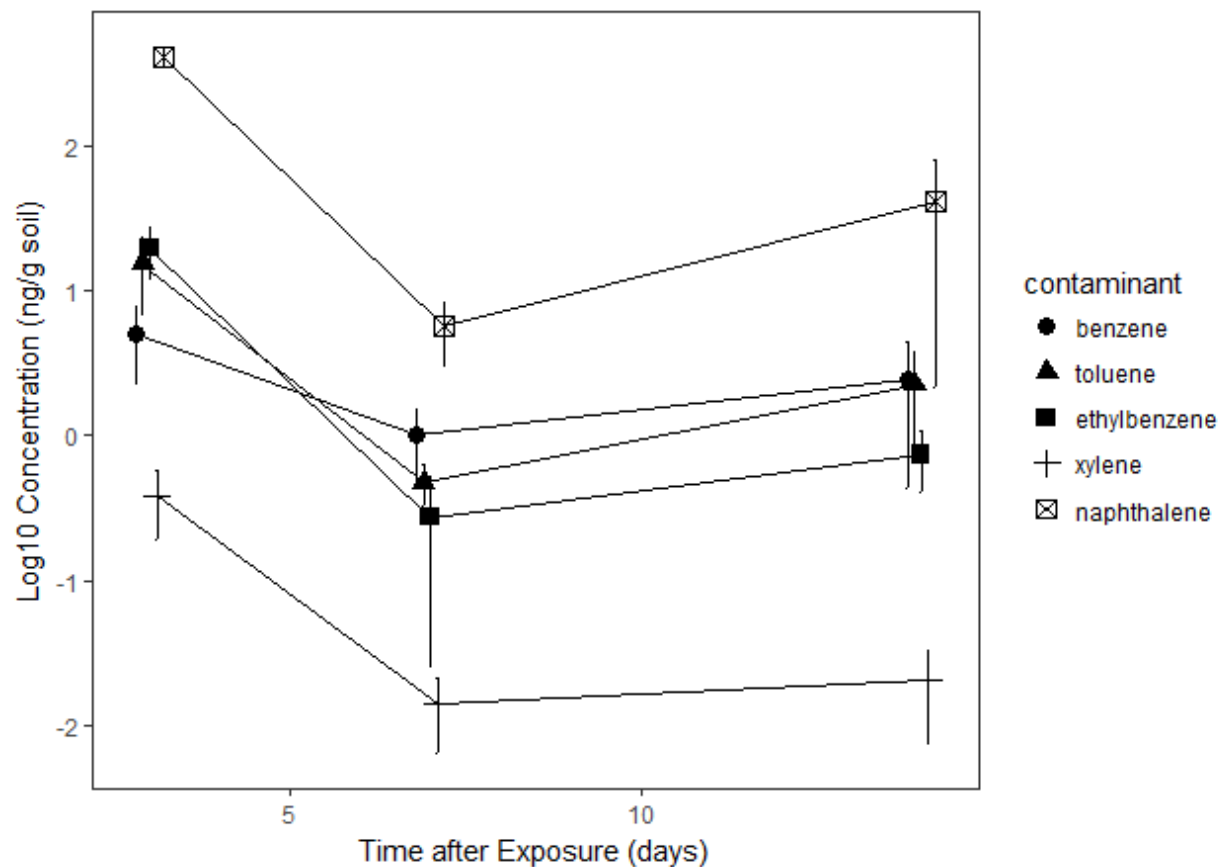


Figure 8.3 Change in soil concentration of contaminants in control pots (i.e., in the absence of plants). Note that the y-axis is on a log scale. Error bars represent  $\pm 1$  log10 standard deviation,  $n=10$ . From day 7 to 14 the concentrations of all contaminants slightly increased, but this difference was not significant and involved data below the detection limit. Accuracy of concentrations is limited below 10 ng/g soil (Log10 concentration = 1) with the method used. The values presented for day 3, 7 and 14 represent aqueous, gaseous and solid phase concentrations.

Table 8.2 The total contaminant mass of BTEX&N in 120 grams of soil treated with either foxtail barley, perennial ryegrass, or neither species (control soil). Total soil contaminant mass was extrapolated to the average number of siblings in a pot (9.8 individuals) to standardize across treatment species.

Soil treatment	Contaminant	Day post-spill	Total mass (ng)
Soil associated with foxtail barley	benzene	7	225.63
		14	300.36
	toluene	7	8.51
		14	49.07
	ethylbenzene	7	41.41
		14	46.29
	xylene	7	261.16
		14	267.81
Soil associated with perennial ryegrass	benzene	7	2651.56
		14	2407.76
	benzene	7	69.89
		14	212.61
	toluene	7	28.86
		14	538.35
	ethylbenzene	7	19.12
		14	93.25
Soil associated with no plants	xylene	7	219.13
		14	9432.08
	naphthalene	7	1490.19
		14	22504.32
	benzene	7	120.35
		14	293.82
	toluene	7	57.24
		14	270.73
Soil associated with no plants	ethylbenzene	7	33.08
		14	88.53
	xylene	7	1.69
		14	2.46
	naphthalene	7	684.44
		14	4950.26

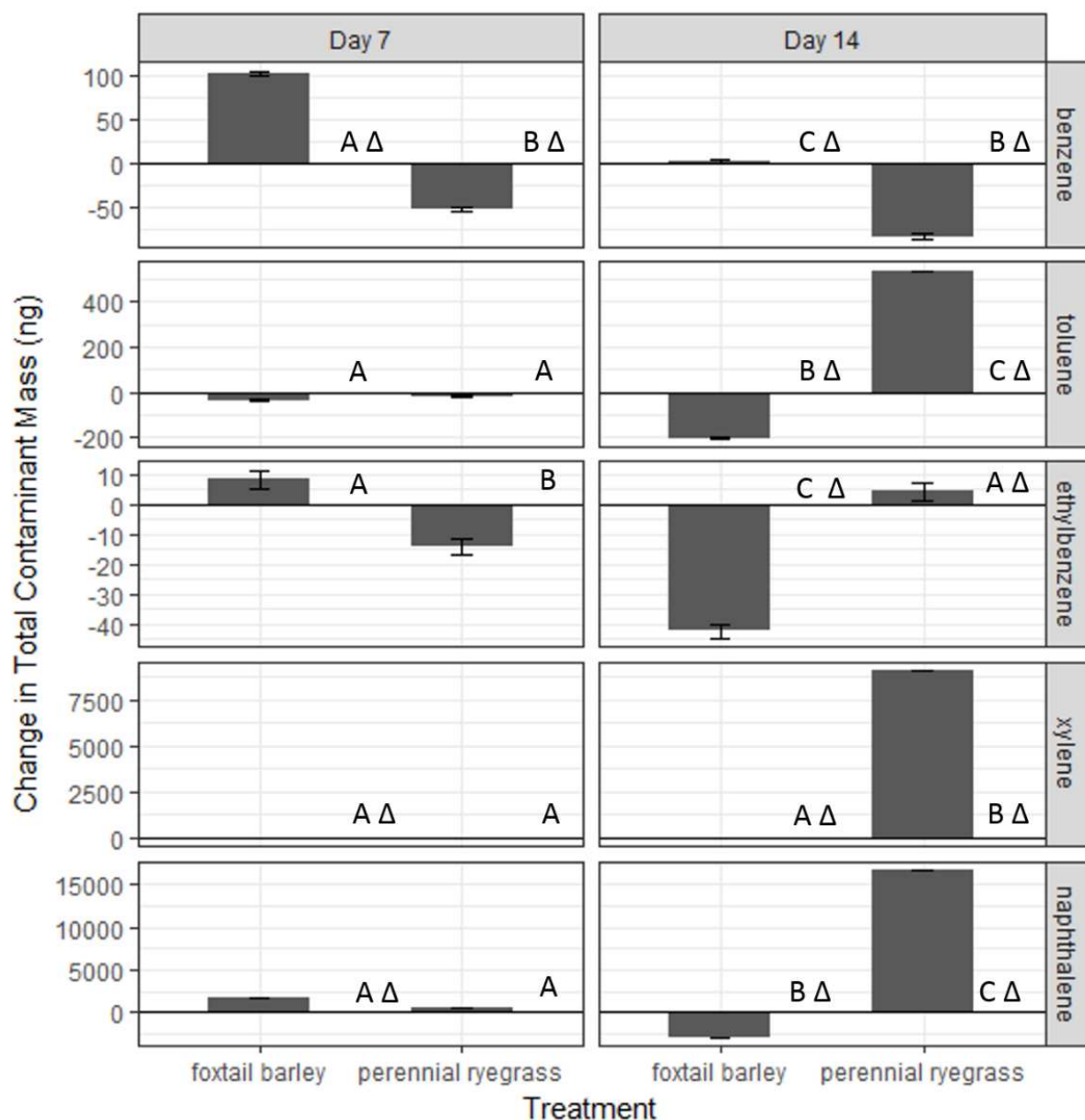


Figure 8.4 Difference between the total contaminant mass in the soil from treatment pots and the soil from control pots at different time points. Positive values indicate higher total mass of the contaminant in the treatment soil as compared to the control soil. Note that the y-axis is different for each row. Significance lettering is specific to each contaminant across time. Each Δ symbol indicates a significant difference between the treatment and the control soil at one time point.

Benzene: In soils planted with foxtail barley, benzene mass was significantly higher than the control soil at day 7, but there was a significant decrease in the difference over time such that at day 14 there was no statistical difference from the control soil. Soil containing perennial

ryegrass had significantly lower total mass of benzene than the unplanted control soil at day 7 and day 14 and the treatment further reduced these levels with time.

Toluene: Foxtail barley-treated soil had no statistical difference in total toluene compared to the control soil at day 7, but by day 14 the soil associated with foxtail barley had significantly reduced levels of toluene below that of the control soil. Soil associated with perennial ryegrass was not significantly different from the control soil at day 7. However, the difference between treated soil and control soil increased over time such that at day 14, perennial ryegrass-treated soil had significantly elevated total mass of toluene compared to the control soil.

Ethylbenzene: Soil associated with foxtail barley did not have a significant difference in the total mass of ethylbenzene compared to the control soil at day 7 but by day 14 there was a significant reduction in ethylbenzene compared to the control soil. Soil associated with perennial ryegrass did not have a significant difference in the total mass of ethylbenzene compared to the control soil at day 7 or 14.

Xylene: The soil planted with foxtail barley had significantly higher total mass of xylene compared to the control soil at day 7 and day 14, and the difference between the treatment and control soil did not significant change with time. The soil associated with perennial ryegrass did not have a significant change in the total mass of xylene at day 7. At day 14, xylene levels were significantly higher in the soil associated with perennial ryegrass than in control soil.

Naphthalene: Foxtail barley-treated soil had significantly elevated naphthalene compared to the control soil at day 7. At day 14, naphthalene was significantly lower than in the control soil. Perennial ryegrass had no significant effect on the total mass of naphthalene compared to



the control soil at day 7. However, at day 14 the total mass of naphthalene was significantly higher than the control soil, and had significantly increased compared to the control over time.

### 8.43 CONTAMINANT LEVELS IN TISSUE

We found BTEX&N from the synthesized salt + BTEX&N solution in root and shoot tissues of both species, but concentrations often varied significantly between species, between tissue types, and over time (Figure 8.5). However, only trace concentration of each contaminant (except for naphthalene) were found within the roots or shoots of either species, as levels were below accuracy detection limits. Results are broken down by contaminant below.

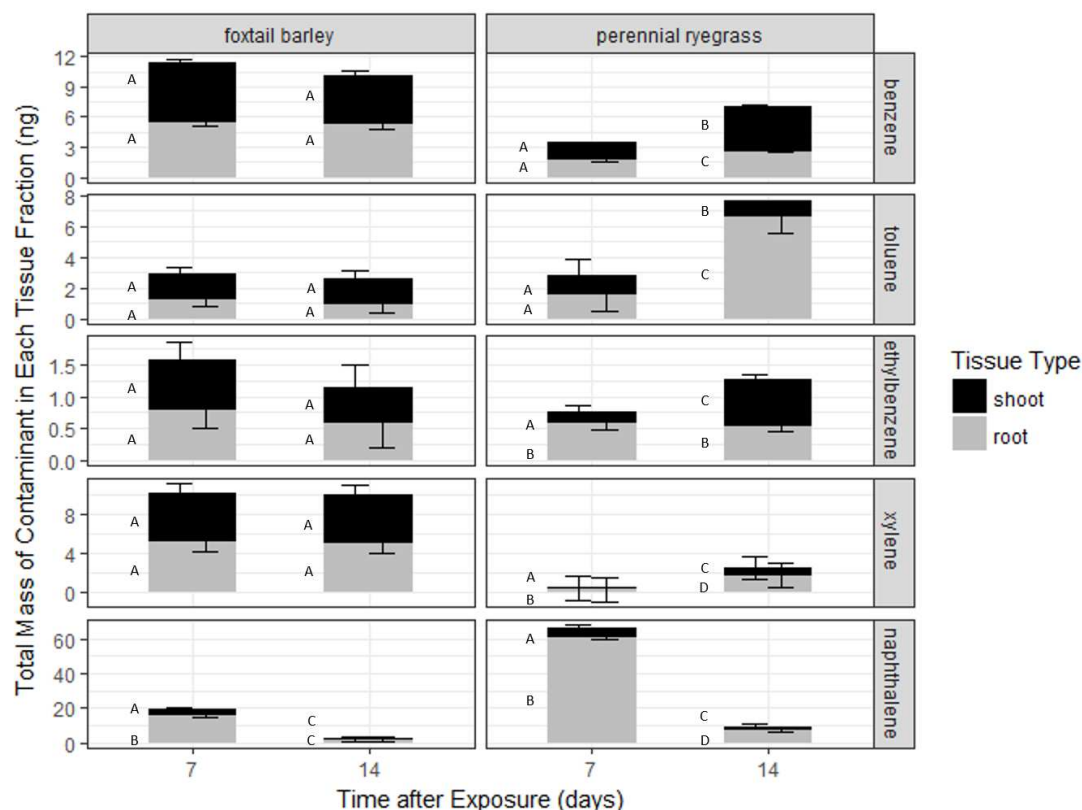


Figure 8.5 Total mass of organic contaminants in root-and-shoot tissue at day 7 and 14 post-spill. Across species, each treatment pot contained an average of 9.8 individual plants. Therefore, values shown are for the total mass of each contaminant extrapolated for 9.8 individual plants in a pot (determined through ANCOVA). Note that the y-axis is different for each row. Letters represent significant differences within a species for each contaminant. Significant differences were assessed between roots and shoots at each individual time point, as were changes for each individual tissue type over time (n=10).

Benzene: Perennial ryegrass had no significant difference between the levels of benzene in roots versus shoots at day 7. The amount of benzene increased in both tissue types over time, and by day 14 there was significantly more benzene in perennial ryegrass shoots than roots. Foxtail barley, on the other hand, had no significant difference between the tissue types at day 7 or 14, nor across tissue types over time. Adding the root and shoot data together, foxtail barley contained more benzene in the whole plant than did perennial ryegrass, at both day 7 and 14.

Toluene: Foxtail barley had no significant difference in toluene between roots and shoots at day 7 or 14, or for either tissue type over time. Perennial ryegrass showed no significant difference between levels of toluene in roots and shoots at day 7, but there was significantly more toluene in the roots than the shoots at day 14. There was a significant increase of toluene over time in the roots of perennial ryegrass. Overall, perennial ryegrass had higher total levels in the whole plant than foxtail barley at day 14.

Ethylbenzene: In perennial ryegrass, ethylbenzene was significantly higher in the root tissue compared to shoots at day 7, but by day 14 ethylbenzene was significantly higher in the shoot tissue than the roots. Levels in the roots showed no significant change over time, whereas ethylbenzene significantly increased in the shoots over time. In foxtail barley, however, there was no significant difference between the levels of ethylbenzene in roots or shoots at day 7 or 14, nor were there significant differences for either tissue type over time.

Xylene: In perennial ryegrass, there was significantly more xylene in the roots than shoots at day 7 and 14. Each tissue type in perennial ryegrass showed a significant increase in xylene over time. Conversely, foxtail barley had no significant difference either between tissue types or

over time. Foxtail barley had higher levels of xylene in the whole plant at both time points compared to perennial ryegrass.

Naphthalene: Naphthalene significantly decreased over time in roots and shoots for both species. However, both species always had significantly higher levels in root tissue compared to shoots. Although not statistically analyzed, the mass of naphthalene was higher in the whole plant of perennial ryegrass at both time points than in foxtail barley.

## **8.5 DISCUSSION**

### **8.51 CONTAMINANT LEVELS IN TISSUES AND EFFECTS ON GROWTH**

We first hypothesized that we would detect the presence of BTEX&N in each species' tissues. Partially supporting this prediction, we did detect naphthalene in the tissue of both plant species. All other contaminants were detected, but below limits for accurate quantification. One could either measure the concentration in each vial using larger amounts of biomass or utilize headspace detection methods with composite fibers for higher detection limits (Wilson et al. 2013) to avoid this issue in the future.

Our second hypothesis predicted the reduction of BTEX&N in the tissue over time. Contrary to our hypothesis, the level of most contaminants increased over time in perennial ryegrass and the levels mainly stayed the same in foxtail barley. The increase seen in perennial ryegrass over time suggests that bioaccumulation of BTEX&N is a key pathway for this species within the period tested. It is difficult with these results to determine pathways for BTEX removal with foxtail barley since the levels neither increased nor decreased. Naphthalene was the only contaminant that decreased in both tissue types over time in both species. This result suggests that naphthalene could possibly be degraded or lost through the transpiration stream. Research

by Burken and Schnoor (1998) showed that little BTEX was retained within the tissue of poplar trees and that the majority of the contaminant was lost through the transpiration stream. Perhaps with time all residual BTEX&N would be lost through mainly transpiration and to a lesser extent, degradation. Plants have been shown to break down BTEX to muconic and fumaric acid as well as phenol (Kvesitadze 2006). In future experiments, searching the mass spectra results for these degradation products could lend credence to the degradation mechanisms reported in other plant species, and clarify the mechanisms behind the results observed for the grasses studied here.

Our third hypothesis predicted that because both grass species are salt tolerant, BTEX&N would be the only limiting factor for growth. Supporting our hypothesis, BTEX&N were the limiting factor for shoot growth in foxtail barley and perennial ryegrass; salt was not limiting for either. Interestingly, growth of roots does not seem to be affected by BTEX&N or salt even though the majority of BTEX&N resides in the root tissue in both species. Perhaps these grasses possess protective capabilities within their roots but their shoot tissue is more susceptible to damage from BTEX&N. A study by Xu et al. (1995) found that root growth of foxtail barley was not affected by soil contaminated with oil until after 30 days of exposure. Perhaps the roots of foxtail barley and perennial ryegrass would be affected after more time had passed. An alternative explanation could be that the plant sacrificed shoot growth so it could grow new roots in areas with lower levels of contamination, thereby avoiding the stressor altogether.

#### **8.52 CONTAMINANT LEVELS IN THE SOIL**

Our fourth hypothesis was that BTEX&N would be reduced in the soil when treated with either species. This hypothesis was partially supported in soil treated with the foxtail barley,

which had reduced soil levels of toluene, ethylbenzene, and naphthalene below those of control soil over time, although the mass of benzene and naphthalene was higher than the control initially at day 7. Contrary to our fourth hypothesis, the majority of contaminants in the soil associated with perennial ryegrass were not reduced compared to the control soil. In fact, the total mass of toluene, xylene, and naphthalene increased over time in the soil treated with perennial ryegrass compared to the control. Of all the contaminants studied here, naphthalene had lowest concentration in the salt + BTEX&N solution, but it was nevertheless found in the highest concentration in the control soil at the end of the study. Naphthalene had the highest total mass of any contaminant within plant tissue at day 7, perhaps because this contaminant remained in the root zone for a relatively long time, providing a greater opportunity for uptake into the plant tissue.

Determining the effect of plants on BTEX&N in the soil is problematic in this experiment. Bulk soil analysis for volatile organic compounds like BTEX&N are sensitive to many factors. Soil moisture and organic carbon content can affect the recoverability of BTEX&N (U.S. Environmental Protection Agency n.d.). Plants can reduce soil moisture through transpiration and also contribute to higher organic carbon content of soil. Additionally, agitation of soil and longer times from collection to analysis can reduce the recoverability of BTEX&N (U.S. Environmental Protection Agency, 1993). With the removal of root tissue from soil, the time from collection to analysis took longer. Soil samples from pots were more agitated when associated with roots. These factors make it difficult to interpret the effect of plants on BTEX&N soil concentrations in this experiment. Future studies should reduce overall collection time and variations between soil samples collected from pots with and without plants.

## 8.6 CONCLUSIONS AND RECOMMENDATIONS

Results were mixed regarding the effectiveness of foxtail barley and perennial ryegrass for phytoremediation of produced-water spill sites. Both species showed varying levels of BTEX&N in their tissues. Our results show that perennial ryegrass and foxtail barley can absorb BTEX&N from produced-water spills. Perennial ryegrass maintains high shoot biomass, which is generally thought to be beneficial for maximum contaminant storage. Foxtail barley, on the other hand, was able to maintain relatively high levels of many contaminants even though it had lower individual biomass. Given these different benefits, a combination of the two species might most effectively provide phytoremediation of the multiple contaminants present in produced-water spills; further research into such mixed-species phytoremediation would be helpful. However, the relative low mass of BTEX&N found in the tissue of either species suggests that these grasses would only be capable of remediating smaller-sized produced-water spills. In this study, we could not determine the exact fate of the contaminants (degradation in plant tissue versus volatilization during transpiration), because our methods precluded accounting for the mass balance of these contaminants. Future research could involve radiolabeling the contaminants to identify degradation products, allowing a more complete understanding of the mechanisms of translocation, degradation, and volatilization. Additionally, future research could test a higher vegetation density, which would be more similar to the density in the field. Many questions remain and there is a great deal of future research to be conducted before the interactions between plants, soil, atmosphere, and produced-water contaminants are fully understood.

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## 10 CONCLUSIONS

Through this body of work I sought to bring insight to the hazards, fate and remediation of BTEX in produced water spills. Spills of produced water happens often in Colorado. Operators are charged with self-reporting spills. Contaminants found at produced-water-spill sites are generally removed through soil excavation and groundwater extraction via vacuum. Although spills are not perhaps altogether unpreventable, there are preemptive actions that could help potentially reduce their impact, such as catching spills earlier or sowing plant species with known BTEX-remediation capabilities. I sought to evaluate these sorts of mitigation techniques using multiple methods throughout this dissertation. In the first chapter I analyzed publically available data from the COGCC (Colorado Oil and Gas Conservation Commission) to determine both warning factors for groundwater contamination and the impact of operator scale on produced water generation and spills. In the second chapter I demonstrated the movement of BTEX and naphthalene through soil at a spill site and determined under various scenarios the effect on groundwater contamination. In the third chapter I tested the ability of two species of grass to remediate BTEX and naphthalene from soils affected by spills. Here, I restate the major findings from this body of work and tie them into the larger picture to draw conclusions and make recommendations for the future.

In the first chapter, I categorized all spills occurring in Weld County, CO, as available through the COGCC. Weld County, CO was an informative area of interest because of the large amount oil-and-gas related data available for the region. Weld County has the highest amount of oil-and-gas extraction in Colorado so it served as a sample representative for the whole state.

Within Weld County in 2015, there were 316 spill/release reports filed with the COGCC. Out of the many types of materials reported to be spilled, the largest fraction (40%) was composed of produced water or a combination produced water and other materials. Produced water is generated for oil, gas and coal bed methane extraction, all of which have varying concentrations of contaminants like benzene. There is no distinction made between the produced water generated by these different energy sources in Colorado. Differentiating between these produced water types would be useful when determining if there is a high risk for groundwater contamination, as much of that risk is based off initial concentrations of contaminants in produced water.

Surprisingly, the volume of produced water spilled did not affect the odds of groundwater or soil contamination. However, this research did not take into account any produced water that might have been recovered at the spill site and perhaps this explains why the volume spilled was not shown to be an important predictor for groundwater or soil contamination. Additionally, the reported volume spilled and recovered are estimates. Often times, COGCC spill reports give wide ranges of what might have been spilled at a site. Produced water-spill volumes are an imprecise measure. This is perhaps an area where operators can make improvements so that the risk for groundwater contamination can be accurately assessed. Not surprisingly, the depth to groundwater at a produced water-spill site was a significant indicator for the odds of groundwater contamination. The depth to groundwater is easier to measure after a spill occurred, whereas the volume spilled is not, and was most likely already known by an operator. While it is recommended that oil-and-gas extraction takes place well below the ground surface (at least 1 mile) to prevent contaminant stray migration(Jackson et al.,

2015), it is also important to have deep groundwater at fracking sites because such sites have frequent spills and spills pollute groundwater more often when groundwater is shallow.

Out of the 18 operators that spilled in Weld County during 2015, just two operators generated more than half of the total oil-and-gas produced. There was a non-linear correlation between the volumes of oil and gas that an operator generated and the generation efficiency of that operator. This suggests that having only a few larger-scale operators rather than numerous small scale operators in Colorado would result in lesser volumes of produced water generated overall. However, large operators did not show improved spill efficiency, suggesting that there would be no reduction in the total volume of oil-and-gas material spilled regardless of having many small operators or a few large operators. It is important to mention that these results only take into account one year and one county. The volumes of oil-and-gas produced are market-driven and so perhaps these same trends would not be seen in years of higher-or-lower demand for oil and gas. Overall, there are regulations in place encourage operators to use less water for oil-and-gas extraction, but improvements could be made to encourage operators to spill less. Doing so, particularly in a time where many view fracking as an unnecessary and dangerous form of energy, could help ease the dispute between such interested parties while maintaining high oil and gas yields/profit.

While the 2015 Weld County spill data was useful for providing predictors for groundwater contamination and operator-based spills, it was also used to as inputs for modeling of spills under a variety of realistic parameters. The solute flow equation in HYDRUS 1D and 3D was utilized to determine the peak concentration of BTEX and naphthalene at various water table depths. This research showed that soil texture highly affected the peak concentration

reached at the water table, with sandy loams having rapid movement of BTEX and naphthalene. Benzene was shown to be the most problematic because concentrations of benzene are high in produced water and the drinking water limit is very low. Under the scenario that resulted in the highest peak concentration of benzene, only 7% of the initial mass of benzene in produced water made up this peak. This result shows that even though the movement of benzene through the soil towards the groundwater is one important fate, the majority of benzene partitions elsewhere, mainly through volatilization to the atmosphere and degradation. Only one simulation that had the deepest water table (300 cm) resulted in a high risk for groundwater contamination. In accordance with the findings from “Produced Water Surface Spills: Using Past Experiences to Guide Mitigation Plans”, excluding shallow depths to groundwater at an oil-and-gas extraction site (where spills often occur) can be an important preemptive measure to reduce the threat of groundwater contamination from spills. This research suggests that when choosing locations for fracking or produced water storage, the depths to groundwater below 300 cm overlying clay-type soils are less likely to experience a high risk for groundwater contamination. Responding to spills faster so that less volumes are spilled would reduce the spill intensity, reducing the risk for groundwater contamination at that site as well. The time it took for benzene to reach groundwater was often rapid, on the order of one to two days. This makes rapid response for spills even more important because landowners are heavily reliant upon groundwater in Weld County; they would need to be informed of such spills immediately to reduce their exposure to the highest amounts of benzene.

Taking precautions, such as selection sites with deep groundwater depths and installing early warning detection systems and safety mechanisms to reduce the volume of water released,



would reduce the risk for groundwater contamination. However, land owners who are major stakeholders in this process do not have mineral rights and are not included when making these decisions. The quick reference guide provided in “Produced-Water Surface Spills and the Risk for BTEX-And-Naphthalene Groundwater Contamination” is an attempt to provide framework for land owners to understand the risks to groundwater on their property so that even though they do not have decision rights as such, they can be aware of the level of risk and can voice their concerns to operators and law makers.

In my last chapter, I sought to identify grass species relevant to the grasslands where spills often occur in Weld County, CO which would hinder the movement of BTEX and naphthalene and protect from groundwater contamination. This research showed that perennial ryegrass and foxtail barley differentially affected which contaminants were reduced or increased relative to the non-planted soil control. Although the tissue-bound concentrations of BTEX and naphthalene were relatively low, plants did alter the amount left in the soil. Although determining the mechanism for this difference was beyond the scope of my research, there is the possibility that plant root exudates alter the mobility of some contaminants or perhaps the roots of these species can reversibly bind BTEX and naphthalene. These findings provide a stepping stone for many other questions about applicability and mechanisms of using grasses for remediation of organics in arid regions.

Through the HYDRUS modeling it was shown that BTEX and naphthalene rapidly move towards groundwater. Planting grasses at spill sites, therefore, may not provide fast enough remediation to hinder BTEX and naphthalene movement. However, planting grasses at oil-and-gas sites could be a way to preemptively address produced water spills. Grasses would have

relatively longer roots with higher surface area pre-spill such that perhaps if a spill does occur, grasses would be established enough to reduce BTEX and naphthalene movement towards groundwater more than if seed was sown post-spill.

Overall, this research asserts that because produced water spills are frequently at fracking well pads, the depth to groundwater at such locations should be deep, below 12.5 m below the ground surface. It also shows that preemptive remediation techniques could be employed at fracking sites to slow the movement of BTEX and naphthalene in produced water to reduce the risk for groundwater contamination. Lastly, scaled up oil and gas operations could help reduce the amount of water spilled by an operator. Certain practices used by an operator could be helping to increase their generation efficiency. Transparency of practices and training could help new regulation to be instated that would increase all operators' generation efficiency. If we will continue to use hydraulic fracturing and generated produced water into the future, this research shows there is much work to be done to reduce the risk for groundwater contamination at spill sites and increase public safety.

## 11 REFLECTIONS ON GRADUATE SCHOOL

One would perhaps not think that getting a Ph.D. could be quite the wild ride, although that was my experience. Reflecting back on the past five years it seems fitting to feel rushed to get so much writing down on paper, to summarize five years' worth of study; that's how this all started. I had previously been in a Ph.D. program in a subject for which I had no passion. Out of obligation I applied to a grant program that would fund Ph.D. tuition and salary. I received an honorable mention but not the funding and so I moved on, finishing the Ph.D. program with a master's degree and feeling slightly lost. A week after I graduated in late December 2011 I was contemplating my next moves when the NSF contacted me to say funding had opened up, I was to receive the grant and I could take it to any university of my choosing. The only caveat was I had to start using the grant in the upcoming fall and the deadline to apply for academic programs had already past. This set of events would set me scrambling to find a school who would accept me past the deadline, an excellent a program at that school and a new field of study. This proved to be no easy task. What really set the stage for me to be writing this thesis, as I am now, was that my current advisor took a leap of faith and got me admitted into Colorado State University.

With this renewed attempt at pursuing a Ph.D. I decided to study what I viewed as the most interesting and important for the planet, rather than what an advisor saw as a vision for my study. My advisor, Melinda, encouraged me to take the reins on my research. With this flexibility, I took the first year to take classes and discover where I could best make my mark. Around this time hydraulic fracturing was big news and there was lots of ambiguity about the

risks it caused to the environment. The news and most research at the time were discussing stray gas migration from shale formations into groundwater. However, I was most interested in the vast volumes of wastewater generated from fracking, particularly in my new home of Colorado that is often water limited. I was interested in the fate of this generated water (known as “produced water”). Fracking was and still is big business in Colorado. Providing guidelines for best practices to mitigate risk could make a large impact in this area.

I focused on spills of produced water because they happen often and I thought that they perhaps could easily go undetected. At the beginning of this Ph.D., I was most interested in phytoremediation of produced water spills. Produced water is a complicated mixture of substances. Finding a non-destructive method for produced-water clean seemed an important endeavor. I knew that a project of this magnitude would be a time-and-money intensive process. After spending two years seeking out grants, I did find money for the project but only 1/3 of what was needed. Additionally, I did not have easily-accessible use of equipment for the experiment. The experimental design required GC/MS, a method with which I was not very familiar. This brings me to my first recommendation; if your research involves complicated methods, either find an expert to work with so you are not “reinventing the wheel” or outsource the work to an expert. Also, make sure that you have plenty of money for the project; cutting corners due to lack of money can be stressful and ultimately defeating. Had I known this, I could have avoided a few expensive mistakes. The work was not associated with any established lab and so even just purchasing chemicals and equipment and finding a working space was difficult. I had to switch work space in the middle of experiments and transfer equipment across campus. Working in an established lab with minimal movement of materials would have been helpful for

streamlining experiments and thoroughness, let alone chemical safety. Although I am still interested in phytoremediation, each setback made me realize that it would take another many years to get these sets of experiments correctly executed to answer the pertinent questions I wanted to answer. So while I made a small contribution to the study of phytoremediation for produced water spills, I also opened up many questions that I was not able to answer.

Unlike the phytoremediation research, modeling produced water spills turned out to be less fraught with obstacles. I took a class in the modeling program HYDRUS, taught by a committee member, Dr. Butters. While I acquired the inputs and programmed the model, Dr. Butters was there every step of the way to make sure that the values were realistic and that we set up the program accurately. This direct support proved to be invaluable and this portion of research flowed much more smoothly. So similar to my first recommendation, working with an expert in your needed method is a truly valuable step to be efficient with your work.

In preparation for the produced water modeling, I summarized the spill reports made available through the Colorado Oil and Gas Conservation Commission (COGCC). Little did I know that this information I gathered contained insights into produced water generation and spills that would lead to the construction of another paper. When sorting through every spill/release report in Weld County, CO during 2015, I ended up noting other information that perhaps was not of use for modeling but was none the less interesting. I came to wonder if any of the details in these reports could identify warning factors for groundwater or soil contamination. Also, spills were classified by the operator, making me wonder if large scale operations were more efficient and spilled less produced water relative to the amount of oil and gas that they produced, which could have policy implications. Using this publically-available data to answer such questions

seemed somewhat like a reconnaissance mission and perhaps because of that the results from that study felt very exciting and relevant. This brings me to my next two recommendations: (1) Record everything as you might find need for a piece of information that you originally did not know would be important later in your work. To that note, take a step back and look at the questions you are asking. Rather than letting the hypotheses drive the research, which is the sequence preached by the scientific method, sometimes letting the data drive the questions can lead you to interesting and important conclusions that you perhaps would never have pursued. I found in my case that letting the COGCC available data drive my questions, it took me towards a policy framework that I had not thought to explore but is now dominating my interests for the future.

So it seems that even though I was somewhat lacking in direction at the onset of this Ph.D., freedom and exploration had led me to believe that in my life after Ph.D., pursuing a career in energy policy and studying the ramifications of various energy-development practices perfectly fits with my desire to take us into an environmentally-sound future. This leads me to my last recommendation; pursuing a Ph.D. with lots of freedom can be challenging. If you are determine this freedom can open up opportunities to find your true calling, rather than always being under the wing of your adviser. Freedom lead me down an unknown path that often made me feel lost. It also allowed me to ask my own questions, making me into a strong and critical researcher capable of handling every aspect of my project from start to finish. With support from my mentors and determination I feel like I've made a positive contribution and have finally fulfilled a life-long dream of receiving my Ph.D.

## 12 APPENDIX

### 12.1 RAW DATA

#### 12.11 PRODUCED WATER SURFACE SPILLS: USING PAST EXPERIENCES TO GUIDE MITIGATION PLANS

Table 12.1 COGCC summary of spill reports. In the “soil”, “gw”, and “surface” columns, 0 represented no contamination and 1 represented contamination. The “volume” column recorded the volume of produced water spilled at a site and is recorded in barrels. The “Company” column recorded the company responsible for the spill. The “spilltype” column recorded the type of material spilled. The “gw.depth.m” column recorded the depth to groundwater in meters. The “area.m” column recorded the rectangular square area in m<sup>2</sup>. The “ranked. Production” column recorded the highest (1) and lowest (19) producers of oil and gas out of the operators who spilled in Weld County, CO during 2015. The “intensity” column calculated for each spill the volume of produced water spilled divided by the rectangular square area affected. The file named for this data was “lm spills.csv”, as seen in R code.

Order of record	soil	gw	surface	volume	Company	spilltype	gw.depth.m	area.m	ranked.production	intensity
189	1	0	0	1	DCP MIDSTREA M LP	2	na	15793.51	19	6.33E-05
311	1	0	0	2	BARRETT CORPORATI ON* BILL	3	9.144	5225.794	8	0.000383
23	1	0	0	3.8	NOBLE ENERGY INC	2	27.7368	8361.27	2	0.000454
305	1	0	0	10	BONANZA CREEK ENERGY OPERATING COMPANY LLC	3	10.668	13238.68	5	0.000755
309	1	0	0	3	BARRETT	3	13.716	2787.09	8	0.001076

					CORPORATI ON* BILL					
57	1	0	0	10	DCP MIDSTREA M LP	2	30.48	7432.24	19	0.001345
113	1	0	0	2	BAYSWATE R EXPLORATI ON AND PRODUCTIO N LLC	3	13.716	1045.159	11	0.001914
211	1	0	0	8	DCP MIDSTREA M LP	2	68.58	4180.635	19	0.001914
9	0	0	0	7	BONANZA CREEK ENERGY OPERATING COMPANY LLC	3	6.096	3367.734	5	0.002079
182	1	0	0	2	KERR MCGEE OIL & GAS ONSHORE LP	3	3.048	919.7397	1	0.002175
108	1	0	0	5	BONANZA CREEK ENERGY OPERATING COMPANY LLC	3	18.8976	2081.027	5	0.002403
178	1	0	0	1	KERR MCGEE OIL & GAS	3	1.8288	376.2572	1	0.002658



					ONSHORE LP					
221	1	0	0	1	BONANZA CREEK ENERGY OPERATING COMPANY LLC	3	28.956	313.5476	5	0.003189
8	1	0	0	3	DCP MIDSTREA M LP	2	na	929.03	19	0.003229
236	1	0	0	3	NOBLE ENERGY INC	1	32.6136	882.5785	2	0.003399
185	1	1	0	1	K P KAUFFMAN COMPANY INC	2	3.048	260.1284	13	0.003844
235	1	0	0	3	WHITING OIL & GAS CORPORATI ON	2	31.6992	754.8369	7	0.003974
290	1	0	0	3	K P KAUFFMAN COMPANY INC	1	3.6576	696.7725	13	0.004306
62	1	0	0	3	SYNERGY RESOURCES CORPORATI ON	1	6.096	661.9339	9	0.004532
285	1	1	0	3	DCP MIDSTREA M LP	2	1.524	557.418	19	0.005382

105	1	0	0	115	KERR MCGEE OIL & GAS ONSHORE LP	12	2.1336	17540.09	1	0.006556
127	1	1	0	1	KERR MCGEE OIL & GAS ONSHORE LP	3	5.1816	148.5519	1	0.006732
260	1	0	0	18	WHITING OIL & GAS CORPORATI ON	5	24.384	2406.188	7	0.007481
237	1	0	0	3	NOBLE ENERGY INC	3	3.6576	392.5152	2	0.007643
19	1	0	0	20	CARRIZO NIOBRARA LLC	3	4.572	2322.575	12	0.008611
124	1	0	0	2	DCP MIDSTREA M LP	2	na	209.0318	19	0.009568
165	1	0	0	105	CARRIZO NIOBRARA LLC	32	6.096	10730.3	12	0.009785
24	1	0	0	3	PDC ENERGY INC	1	10.9728	297.2896	4	0.010091
78	1	0	0	0.5	MONAHAN GAS & OIL INC	12	3.048	41.80635	16	0.01196
135	1	0	0	2	DCP MIDSTREA	2	na	167.2254	19	0.01196

					M LP					
134	1	0	0	10	KERR MCGEE OIL & GAS ONSHORE LP	3	5.1816	812.9013	1	0.012302
25	1	0	0	3.5	BARRETT CORPORATI ON* BILL	3	12.192	260.1284	8	0.013455
170	1	0	0	6	WHITING OIL & GAS CORPORATI ON	3	30.48	445.9344	7	0.013455
133	1	0	0	15	WHITING OIL & GAS CORPORATI ON	3	38.1	1045.159	7	0.014352
166	1	0	0	1	DCP MIDSTREA M LP	2	na	65.0321	19	0.015377
151	1	1	0	3	DCP MIDSTREA M LP	2	2.4384	195.0963	19	0.015377
239	1	0	0	2	KERR MCGEE OIL & GAS ONSHORE LP	13	1.8288	125.4191	1	0.015947
136	1	1	0	2	KERR MCGEE OIL & GAS ONSHORE LP	3	0.9144	117.0578	1	0.017086
214	1	1	0	4	DCP	2	3.3528	232.2575	19	0.017222

					MIDSTREA M LP					
192	1	0	0	1	PDC ENERGY INC	3	10.3632	55.7418	4	0.01794
175	1	0	0	7	KERR MCGEE OIL & GAS ONSHORE LP	12	17.3736	362.3217	1	0.01932
315	1	0	0	20	EXTRACTIO N OIL & GAS LLC	1	9.144	929.03	6	0.021528
261	1	1	0	3	NOBLE ENERGY INC	1	2.4384	130.0642	2	0.023066
177	1	1	0	3	DCP MIDSTREA M LP	2	0.6096	130.0642	19	0.023066
126	1	0	0	2	ENCANA OIL & GAS (USA) INC	2	1.524	83.6127	3	0.02392
204	1	1	0	2	DCP MIDSTREA M LP	2	3.048	81.29013	19	0.024603
146	1	0	0	35	KERR MCGEE OIL & GAS ONSHORE LP	1	42.672	1337.803	1	0.026162
191	0	0	0	5	EOG RESOURCES INC	13	10.668	185.806	14	0.02691
250	1	0	0	1	DCP	2	15.24	37.1612	19	0.02691

					MIDSTREA M LP					
222	1	0	0	13	KERR MCGEE OIL & GAS ONSHORE LP	5	4.572	455.2247	1	0.028557
114	1	0	0	4	NGL WATER SOLUTIONS DJ LLC	8	7.62	139.3545	20	0.028704
231	1	0	0	5	KERR MCGEE OIL & GAS ONSHORE LP	3	1.8288	165.8319	1	0.030151
18	1	0	0	1.5	WHITING OIL & GAS CORPORATI ON	1	41.148	46.4515	7	0.032292
287	1	1	0	2	FOUNDATI ON ENERGY MANAGEM ENT LLC	1	4.2672	59.45792	15	0.033637
47	1	0	0	2	DCP MIDSTREA M LP	2	9.144	55.7418	19	0.03588
112	0	0	0	3	BONANZA CREEK ENERGY OPERATING COMPANY LLC	5	3.048	81.75464	5	0.036695
312	1	0	0	25	PDC ENERGY INC	5	4.572	668.9016	4	0.037375

161	1	1	0	3	KERR MCGEE GATHERING LLC	12	1.8288	74.3224	1	0.040365
153	1	1	0	5	KERR MCGEE OIL & GAS ONSHORE LP	3	0.9144	110.3688	1	0.045303
210	1	0	0	2	BONANZA CREEK ENERGY OPERATING COMPANY LLC	3	7.62	41.80635	5	0.04784
41	1	1	0	13	KERR MCGEE OIL & GAS ONSHORE LP	2	0.9144	255.4833	1	0.050884
86	0	0	0	0.5	KERR MCGEE OIL & GAS ONSHORE LP	5	3.048	9.2903	1	0.05382
81	1	1	0	10	BAYSWATE R EXPLORATI ON AND PRODUCTIO N LLC	3	2.1336	185.806	11	0.05382
13	1	0	0	1	DCP MIDSTREA	2	na	17.65157	19	0.056652

					M LP					
104	1	0	0	6	WHITING OIL & GAS CORPORATI ON	3	48.768	104.0514	7	0.057664
251	1	0	0	22	KERR MCGEE OIL & GAS ONSHORE LP	1	0.9144	371.612	1	0.059202
115	1	0	0	3	NOBLE ENERGY INC	1	10.9728	46.4515	2	0.064583
186	1	0	0	3	ENCANA OIL & GAS (USA) INC	2	6.4008	46.4515	3	0.064583
3	0	1	1	52.5	NOBLE ENERGY INC	7	1.524	787.3529	2	0.066679
187	1	0	0	1	KERR MCGEE OIL & GAS ONSHORE LP	3	3.048	14.86448	1	0.067274
306	1	0	0	3	PDC ENERGY INC	3	3.048	42.92119	4	0.069896
252	1	0	0	3	ENCANA OIL & GAS (USA) INC	8	6.096	41.80635	3	0.071759
288	1	0	0	10	PDC ENERGY INC	5	1.8288	139.3545	4	0.071759
119	1	1	0	1	DCP	2	0.9144	13.93545	19	0.071759

					MIDSTREA M LP					
59	1	0	0	52.5	KERR MCGEE OIL & GAS ONSHORE LP	13	79.8576	725.6653	1	0.072347
38	1	1	0	6	BAYSWATE R EXPLORATI ON AND PRODUCTIO N LLC	3	0.6096	82.49786	11	0.072729
157	1	0	0	10	KERR MCGEE OIL & GAS ONSHORE LP	5	1.2192	132.3868	1	0.075536
280	1	0	0	3	NOBLE ENERGY INC	1	30.48	37.1612	2	0.080729
238	1	0	0	3	WHITING OIL & GAS CORPORATI ON	8	12.192	37.1612	7	0.080729
159	1	0	0	9	GREAT WESTERN OPERATING COMPANY LLC	5	9.144	111.4836	10	0.080729
284	1	0	0	2	K P KAUFFMAN COMPANY INC	13	7.9248	23.22575	13	0.086111



254	1	0	0	80	DCP MIDSTREA M LP	12	na	905.8043	19	0.088319
283	1	0	0	2	GREAT WESTERN OPERATING COMPANY LLC	1	2.1336	22.57543	10	0.088592
301	1	0	0	2	BONANZA CREEK ENERGY OPERATING COMPANY LLC	13	28.956	22.29672	5	0.089699
148	1	0	0	9	KERR MCGEE OIL & GAS ONSHORE LP	13	1.2192	92.903	1	0.096875
29	1	0	0	2	PDC ENERGY INC	13	24.384	18.5806	4	0.107639
291	0	0	0	6	NOBLE ENERGY INC	1	na	55.7418	2	0.107639
20	1	0	0	200	EOG RESOURCES INC	1	18.288	1858.06	14	0.107639
298	1	0	0	80	WARD PETROLEU M CORPORATI ON	3	42.672	668.9016	17	0.119599
206	1	0	0	7	WHITING	1	23.7744	58.06438	7	0.120556

					OIL & GAS CORPORATI ON					
253	0	0	0	18	EXTRACTIO N OIL & GAS LLC	3	6.096	139.3545	6	0.129167
218	1	1	0	52.5	NOBLE ENERGY INC	3	1.3716	371.612	2	0.141276
223	1	0	0	8	KERR MCGEE OIL & GAS ONSHORE LP	5	4.572	55.7418	1	0.143519
152	1	1	1	12	ENCANA OIL & GAS (USA) INC	1	1.524	83.6127	3	0.143519
164	1	0	0	15	BONANZA CREEK ENERGY OPERATING COMPANY LLC	1	65.532	97.54815	5	0.15377
176	1	0	0	3	BARRETT CORPORATI ON* BILL	2	na	18.5806	8	0.161459
273	1	0	0	15.5	WHITING OIL & GAS CORPORATI ON	38	11.2776	92.903	7	0.166841
65	1	0	0	7	KERR MCGEE OIL & GAS ONSHORE	5	6.096	41.80635	1	0.167439

					LP					
5	1	0	0	15	PDC ENERGY INC	1	6.096	89.27978	4	0.168011
314	1	0	0	19	NOBLE ENERGY INC	1	9.7536	92.903	2	0.204514
212	1	0	0	1	FOUNDATI ON ENERGY MANAGEM ENT LLC	3	64.008	4.64515	15	0.215278
307	1	0	0	25	KERR MCGEE OIL & GAS ONSHORE LP	3	3.048	107.303	1	0.232985
300	1	0	0	15	KERR MCGEE OIL & GAS ONSHORE LP	13	9.144	63.91726	1	0.234678
131	1	0	0	6	PDC ENERGY INC	13	6.4008	25.08381	4	0.239198
12	1	0	0	41	KERR MCGEE OIL & GAS ONSHORE LP	13	3.048	161.5583	1	0.253778
169	1	0	0	5	EOG RESOURCES INC	3	10.668	18.5806	14	0.269098
313	1	0	0	3	DCP	2	4.8768	11.14836	19	0.269098

					MIDSTREA M LP					
295	1	0	0	42	K P KAUFFMAN COMPANY INC	1	5.1816	141.0268	13	0.297816
140	1	0	0	5	WHITING OIL & GAS CORPORATI ON	2	73.152	16.72254	7	0.298998
110	0	0	0	140	GREAT WESTERN OPERATING COMPANY LLC	3	6.096	468.2311	10	0.298998
293	0	0	0	9	KERR MCGEE OIL & GAS ONSHORE LP	5	3.048	29.26445	1	0.30754
118	1	1	0	3	NOBLE ENERGY INC	1	1.2192	9.2903	2	0.322917
228	1	1	0	3	NOBLE ENERGY INC	2	1.524	9.2903	2	0.322917
299	1	0	0	9	KERR MCGEE OIL & GAS ONSHORE LP	3	15.24	27.8709	1	0.322917
17	1	0	0	125	PDC ENERGY INC	1	7.62	371.612	4	0.336372

316	1	0	0	45	BONANZA CREEK ENERGY OPERATING COMPANY LLC	5	6.096	133.7803	5	0.336372
52	1	1	0	52.5	KERR MCGEE OIL & GAS ONSHORE LP	13	0.9144	137.6822	1	0.381313
71	1	0	0	20	PDC ENERGY INC	1	91.44	46.4515	4	0.430557
66	1	0	0	0.5	KERR MCGEE OIL & GAS ONSHORE LP	5	5.1816	1.114836	1	0.448496
130	1	0	0	52.5	NOBLE ENERGY INC	2	19.2024	111.4836	2	0.470921
4	1	0	0	40	PDC ENERGY INC	1	24.0792	83.6127	4	0.478396
268	1	0	0	20	EOG RESOURCES INC	1	10.668	37.1612	14	0.538196
258	1	0	0	18	PDC ENERGY INC	5	3.048	32.51605	4	0.553573
160	1	0	0	5	SYNERGY RESOURCES CORPORATI	2	3.048	8.918688	9	0.560621

					ON					
61	1	0	0	130	BAYSWATER EXPLORATION AND PRODUCTION LLC	1	5.4864	226.3117	11	0.574429
196	1	0	0	32	NOBLE ENERGY INC	1	28.956	46.4515	2	0.688891
100	1	0	0	10	FOUNDATION ENERGY MANAGEMENT LLC	13	3.048	13.37803	15	0.747494
92	1	1	0	10	BAYSWATER EXPLORATION AND PRODUCTION LLC	1	2.4384	13.28513	11	0.752721
266	1	0	0	6	PDC ENERGY INC	1	0.6096	6.967725	4	0.861113
265	1	1	0	102	KERR MCGEE OIL & GAS ONSHORE LP	12	1.8288	111.4836	1	0.914933
158	1	0	0	3.5	FOUNDATION ENERGY MANAGEMENT LLC	13	3.6576	3.71612	15	0.941843

179	1	0	0	4.5	FOUNDATI ON ENERGY MANAGEM ENT LLC	13	9.4488	4.64515	15	0.968752
33	1	0	0	10	BARRETT CORPORATI ON* BILL	13	9.144	9.2903	8	1.076392
95	1	0	0	6	WHITING OIL & GAS CORPORATI ON	12	18.288	5.202568	7	1.153277
274	1	0	0	69	NOBLE ENERGY INC	1	3.6576	58.06438	2	1.188336
294	1	0	0	1	BAYSWATE R EXPLORATI ON AND PRODUCTIO N LLC	1	34.7472	0.371612	11	2.690979
137	1	0	0	30	FOUNDATI ON ENERGY MANAGEM ENT LLC	3	3.048	9.2903	15	3.229175
31	1	0	0	4	WHITING OIL & GAS CORPORATI ON	1	21.336	0.743224	7	5.381958
240	1	0	0	15	WHITING OIL & GAS CORPORATI ON	3	12.192	2.322575	7	6.458349
53	0	1	0	na	KERR MCGEE	1	2.4384	na	1	na

					GATHERING LLC					
68	0	1	0	na	KERR MCGEE GATHERING LLC	32	7.62	836.127	1	na
144	1	1	0	na	KERR MCGEE GATHERING LLC	3	1.524	33.44508	1	na
208	1	0	0	na	KERR MCGEE GATHERING LLC	2	3.6576	148.6448	1	na
244	1	0	0	na	KERR MCGEE GATHERING LLC	1	114.3	167.7828	1	na
245	1	1	0	na	KERR MCGEE GATHERING LLC	1	7.3152	2222.704	1	na
7	1	0	0	na	KERR MCGEE OIL & GAS ONSHORE LP	1	48.768	73.57918	1	na
10	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	12	1.2192	18.5806	1	na
15	1	1	0	na	KERR MCGEE OIL	312	0.3048	57.22825	1	na



					& GAS ONSHORE LP					
21	1	0	0	na	KERR MCGEE OIL & GAS ONSHORE LP	12	21.6408	148.6448	1	na
27	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	13	1.524	59.45792	1	na
34	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	312	1.524	27.8709	1	na
42	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	13	1.524	292.6445	1	na
54	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	312	1.2192	47.00892	1	na
58	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	2	0.9144	4.180635	1	na

60	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	312	0.6096	23.69027	1	na
67	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	13	1.524	13.93545	1	na
73	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	12	1.8288	78.03852	1	na
74	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	13	1.524	27.8709	1	na
84	1	0	0	na	KERR MCGEE OIL & GAS ONSHORE LP	12	76.5048	167.2254	1	na
87	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	13	1.2192	48.77408	1	na
88	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE	13	1.2192	46.82311	1	na

					LP					
93	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	13	2.1336	100.3352	1	na
101	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	13	2.4384	163.8809	1	na
103	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	12	0.6096	78.03852	1	na
121	1	0	0	na	KERR MCGEE OIL & GAS ONSHORE LP	13	4.8768	120.7739	1	na
122	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	12	1.8288	195.0963	1	na
125	1	0	0	na	KERR MCGEE OIL & GAS ONSHORE LP	13	26.2128	129.321	1	na
132	1	1	0	na	KERR MCGEE OIL	12	0.9144	24.52639	1	na

					& GAS ONSHORE LP					
145	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	13	1.524	117.0578	1	na
147	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	12	1.8288	88.25785	1	na
162	0	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	12	0.9144	20.90318	1	na
167	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	13	3.6576	18.5806	1	na
171	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	12	1.2192	14.30706	1	na
173	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	1	0.9144	37.1612	1	na

181	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	13	0.9144	50.16762	1	na
190	0	0	0	10	KERR MCGEE OIL & GAS ONSHORE LP	13	10.668	na	1	na
197	1	0	0	na	KERR MCGEE OIL & GAS ONSHORE LP	12	42.9768	80.82561	1	na
199	1	0	0	na	KERR MCGEE OIL & GAS ONSHORE LP	3	47.244	255.4833	1	na
202	0	0	0	na	KERR MCGEE OIL & GAS ONSHORE LP	12	2.1336	221.1091	1	na
207	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	12	1.524	20.90318	1	na
215	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE	12	1.524	76.92368	1	na

					LP					
225	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	12	0.9144	108.6965	1	na
226	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	12	5.4864	438.9667	1	na
233	1	0	0	na	KERR MCGEE OIL & GAS ONSHORE LP	12	10.668	448.7215	1	na
234	1	0	0	na	KERR MCGEE OIL & GAS ONSHORE LP	12	9.4488	278.709	1	na
241	1	0	0	na	KERR MCGEE OIL & GAS ONSHORE LP	13	9.144	37.1612	1	na
242	1	0	0	na	KERR MCGEE OIL & GAS ONSHORE LP	12	60.96	234.1156	1	na
259	1	1	0	na	KERR MCGEE OIL	12	1.8288	69.67725	1	na

					& GAS ONSHORE LP					
267	0	0	0	17	KERR MCGEE OIL & GAS ONSHORE LP	1	0.9144	na	1	na
278	1	0	0	na	KERR MCGEE OIL & GAS ONSHORE LP	13	32.6136	37.1612	1	na
281	1	1	0	na	KERR MCGEE OIL & GAS ONSHORE LP	13	1.8288	129.5997	1	na
296	1	0	0	na	KERR MCGEE OIL & GAS ONSHORE LP	13	48.1584	69.67725	1	na
6	1	0	0	3	NOBLE ENERGY INC	1	7.0104	na	2	na
14	1	1	0	3	NOBLE ENERGY INC	2	na	na	2	na
22	1	0	0	3	NOBLE ENERGY INC	1	9.144	na	2	na
26	1	0	0	na	NOBLE ENERGY INC	1	1.8288	na	2	na

30	1	1	0	3	NOBLE ENERGY INC	13	2.1336	na	2	na
35	1	1	0	6	NOBLE ENERGY INC	7	0.9144	na	2	na
37	1	0	0	3	NOBLE ENERGY INC	3	na	na	2	na
44	0	0	0	69	NOBLE ENERGY INC	3	51.816	na	2	na
45	1	0	0	3	NOBLE ENERGY INC	1	7.0104	na	2	na
46	1	0	0	14	NOBLE ENERGY INC	3	2.4384	na	2	na
48	1	1	0	3	NOBLE ENERGY INC	1	1.524	na	2	na
49	1	1	0	6	NOBLE ENERGY INC	12	1.524	na	2	na
50	1	0	0	6	NOBLE ENERGY INC	13	2.4384	na	2	na
55	1	0	0	6	NOBLE ENERGY INC	12	24.384	na	2	na
56	1	0	0	3	NOBLE ENERGY INC	1	3.6576	na	2	na



64	1	0	0	3	NOBLE ENERGY INC	1	128.016	na	2	na
70	1	0	0	3	NOBLE ENERGY INC	3	21.336	na	2	na
72	1	1	0	6	NOBLE ENERGY INC	13	4.2672	na	2	na
79	1	0	0	6	NOBLE ENERGY INC	12	6.096	na	2	na
83	1	0	0	na	NOBLE ENERGY INC	1	6.7056	na	2	na
89	1	0	0	na	NOBLE ENERGY INC	12	10.668	na	2	na
90	1	0	0	6	NOBLE ENERGY INC	32	1.2192	na	2	na
96	1	1	0	6	NOBLE ENERGY INC	13	2.4384	na	2	na
106	1	0	0	3	NOBLE ENERGY INC	1	na	na	2	na
107	1	0	0	3	NOBLE ENERGY INC	3	42.3672	na	2	na
109	1	0	0	3	NOBLE ENERGY INC	1	3.048	na	2	na
116	1	0	0	3	NOBLE	1	26.2128	na	2	na

					ENERGY INC					
128	1	0	0	na	NOBLE ENERGY INC	3	2.7432	na	2	na
139	1	0	0	2	NOBLE ENERGY INC	2	12.192	na	2	na
143	1	0	0	na	NOBLE ENERGY INC	1	136.8552	na	2	na
149	1	1	0	na	NOBLE ENERGY INC	1	3.048	113.8062	2	na
154	0	1	0	na	NOBLE ENERGY INC	2	0.9144	83.6127	2	na
156	1	1	0	na	NOBLE ENERGY INC	12	3.3528	37.1612	2	na
163	1	0	0	na	NOBLE ENERGY INC	1	30.48	na	2	na
168	1	0	0	3	NOBLE ENERGY INC	1	3.6576	na	2	na
180	1	1	0	na	NOBLE ENERGY INC	12	12.192	390.1926	2	na
183	1	1	0	na	NOBLE ENERGY INC	1	2.1336	29.72896	2	na
184	1	1	0	3	NOBLE ENERGY INC	1	2.4384	na	2	na

188	0	0	0	80	NOBLE ENERGY INC	3	3.6576	na	2	na
194	1	1	0	3	NOBLE ENERGY INC	1	7.0104	na	2	na
195	0	0	0	115	NOBLE ENERGY INC	13	10.9728	na	2	na
203	1	1	0	na	NOBLE ENERGY INC	2	0.9144	20.90318	2	na
209	1	1	0	na	NOBLE ENERGY INC	2	1.8288	227.6124	2	na
216	1	0	0	na	NOBLE ENERGY INC	1	2.7432	na	2	na
217	1	1	0	na	NOBLE ENERGY INC	3	1.2192	na	2	na
220	1	1	0	na	NOBLE ENERGY INC	12	1.2192	na	2	na
227	1	0	0	na	NOBLE ENERGY INC	1	4.8768	27.8709	2	na
229	0	0	0	108	NOBLE ENERGY INC	13	na	na	2	na
230	1	0	0	3	NOBLE ENERGY INC	1	68.58	na	2	na

243	1	0	0	na	NOBLE ENERGY INC	1	51.816	na	2	na
246	1	1	0	na	NOBLE ENERGY INC	12	1.524	na	2	na
247	1	0	0	na	NOBLE ENERGY INC	12	27.432	na	2	na
248	1	0	0	3	NOBLE ENERGY INC	1	7.9248	na	2	na
249	1	1	0	6	NOBLE ENERGY INC	13	1.524	na	2	na
255	1	0	0	3	NOBLE ENERGY INC	1	2.4384	na	2	na
257	1	1	0	na	NOBLE ENERGY INC	12	2.1336	na	2	na
262	1	0	0	52.5	NOBLE ENERGY INC	13	27.7368	na	2	na
263	1	0	0	52.5	NOBLE ENERGY INC	1	13.716	na	2	na
271	1	1	0	3	NOBLE ENERGY INC	2	2.4384	na	2	na
272	1	1	0	52.5	NOBLE ENERGY INC	1	3.3528	na	2	na
275	1	0	0	3	NOBLE	1	6.096	na	2	na

					ENERGY INC					
282	1	1	0	6	NOBLE ENERGY INC	12	0.6096	na	2	na
289	na	0	0	na	NOBLE ENERGY INC	7	na	na	2	na
292	1	0	0	na	NOBLE ENERGY INC	7	na	na	2	na
297	1	1	0	na	NOBLE ENERGY INC	1	1.8288	27.8709	2	na
304	1	0	0	na	NOBLE ENERGY INC	12	30.48	58.06438	2	na
317	0	0	0	30	NOBLE ENERGY INC	4	5.1816	na	2	na
94	1	0	0	47.5	ENCANA OIL & GAS (USA) INC	2	na	na	3	na
98	0	0	0	24	ENCANA OIL & GAS (USA) INC	1	na	na	3	na
270	0	0	0	100	ENCANA OIL & GAS (USA) INC	2	na	na	3	na
310	1	0	0	2	ENCANA OIL & GAS (USA) INC	5	na	na	3	na
16	1	1	0	1	PDC ENERGY INC	3	3.9624	na	4	na

82	1	0	0	na	PDC ENERGY INC	1	24.384	845.4173	4	na
102	1	1	0	na	PDC ENERGY INC	32	0.9144	13.93545	4	na
117	1	1	0	na	PDC ENERGY INC	3	1.2192	69.67725	4	na
120	1	0	0	na	PDC ENERGY INC	3	9.144	69.67725	4	na
138	1	0	0	na	PDC ENERGY INC	1	10.0584	250.8381	4	na
142	1	0	1	na	PDC ENERGY INC	13	8.5344	817.5464	4	na
174	1	0	0	na	PDC ENERGY INC	12	11.5824	22.29672	4	na
213	1	0	0	na	PDC ENERGY INC	12	7.62	25.08381	4	na
219	1	0	0	na	PDC ENERGY INC	1	4.8768	89.7443	4	na
232	1	1	0	na	PDC ENERGY INC	1	2.4384	1300.642	4	na
276	1	1	0	na	PDC ENERGY INC	3	na	13.93545	4	na

277	1	1	0	na	PDC ENERGY INC	3	1.524	204.3866	4	na
279	1	0	0	na	PDC ENERGY INC	3	9.144	74.3224	4	na
172	0	0	0	na	BONANZA CREEK ENERGY OPERATING COMPANY LLC	7	5.7912	45.52247	5	na
28	0	0	0	250	EXTRACTIO N OIL & GAS LLC	13	11.8872	na	6	na
51	1	0	0	1	EXTRACTIO N OIL & GAS LLC	3	na	na	6	na
63	1	0	0	na	EXTRACTIO N OIL & GAS LLC	312	6.096	209.0318	6	na
2	0	0	0	15	WHITING OIL & GAS CORPORATI ON	7	na	na	7	na
76	1	0	0	na	WHITING OIL & GAS CORPORATI ON	7	na	na	7	na
123	1	0	0	na	BARRETT CORPORATI ON* BILL	3	15.24	195.0963	8	na
141	0	0	0	40	BARRETT CORPORATI	1	15.24	na	8	na

					ON* BILL					
302	1	1	0	na	BARRETT CORPORATI ON* BILL	3	4.572	232.2575	8	na
303	1	0	0	na	BARRETT CORPORATI ON* BILL	32	3.9624	9.2903	8	na
39	1	1	0	na	SYNERGY RESOURCES CORPORATI ON	7	na	na	9	na
40	0	0	0	2	SYNERGY RESOURCES CORPORATI ON	3	0.6096	na	9	na
80	1	0	0	3.5	SYNERGY RESOURCES CORPORATI ON	13	na	na	9	na
91	1	1	0	6	SYNERGY RESOURCES CORPORATI ON	13	na	na	9	na
264	1	0	0	0.5	SYNERGY RESOURCES CORPORATI ON	3	na	na	9	na
11	1	0	0	3	BAYSWATE R EXPLORATI ON AND PRODUCTIO N LLC	3	na	na	11	na



43	1	0	0	na	BAYSWATER EXPLORATION AND PRODUCTION LLC	13	8.5344	167.2254	11	na
224	0	1	0	na	BAYSWATER EXPLORATION AND PRODUCTION LLC	7	na	na	11	na
269	1	0	0	6	CARRIZO NIOBRARA LLC	35	na	na	12	na
308	1	0	0	30	CARRIZO NIOBRARA LLC	5	na	na	12	na
85	1	1	0	na	K P KAUFFMAN COMPANY INC	12	0.9144	97.54815	13	na
198	1	0	0	na	K P KAUFFMAN COMPANY INC	12	3.6576	na	13	na
99	1	0	0	na	FOUNDATI ON ENERGY MANAGEMENT LLC	1	3.048	16.72254	15	na
129	1	0	0	na	FOUNDATI ON ENERGY MANAGEMENT LLC	13	3.6576	27.8709	15	na

155	1	1	0	na	FOUNDATI ON ENERGY MANAGEM ENT LLC	12	1.8288	27.8709	15	na
201	1	0	0	na	FOUNDATI ON ENERGY MANAGEM ENT LLC	312	58.5216	na	15	na
200	1	1	0	na	SMITH OIL PROPERTIES INC	1	na	na	18	na
32	1	1	0	na	DCP MIDSTREA M LP	2	2.4384	55.7418	19	na
36	1	0	0	52.5	DCP MIDSTREA M LP	2	na	na	19	na
69	1	1	0	na	DCP MIDSTREA M LP	32	4.572	34.1883	19	na
75	0	0	0	12	DCP MIDSTREA M LP	12	na	0	19	na
77	1	0	0	3	DCP MIDSTREA M LP	2	na	na	19	na
97	1	1	0	na	DCP MIDSTREA M LP	6	10.668	125.4191	19	na
111	1	1	0	na	DCP MIDSTREA M LP	6	2.1336	557.418	19	na
150	0	0	1	1	DCP MIDSTREA	2	na	na	19	na

					M LP					
193	1	0	0	na	DCP MIDSTREA M LP	312	3.048	139.3545	19	na
256	1	0	0	na	DCP MIDSTREA M LP	6	na	148.6448	19	na
286	1	1	0	na	DCP MIDSTREA M LP	312	4.2672	139.3545	19	na
205	1	0	0	3821	NGL WATER SOLUTIONS DJ LLC	314	na	na	20	na

Table 12.2. Oil-and-gas related spills, total energy generated and total produced water generated in Weld County, CO during 2015 according to operator. The “x” column shows the name of the operator in question. The “freq” column shows the number of times an operator spilled in Weld County in 2015 and “freq.ln” shows the natural log of the frequency. The “ave.spilled” shows the average volume of oil-and-gas related material (in barrels) that was spilled in Weld County by an operator and “ave.spilled.ln” is the natural log of the average volume. The “median.spilled” shows the median volume (in barrels) of oil-and-gas related material spilled in Weld County by an operator and “median.spilled.ln” is the natural log of the median volume. The “total.spilled” column shows the total volume (in barrels) of oil-and-gas related material spilled in Weld County by an operator and “total.spilled.ln” is the natural log of the total volume. “gas.bbl”, “oil.bbl” and “waterproduced.bbl” shows the gas produced (barrels of oil equivalent), oil produced (barrel) and water produced by an operator (barrels) across all of Colorado, respectively. “water.produced.3” shows  $10^6$  barrels of produced water generated by an operator in all of Colorado and “water.produced.3.ln” is the natural log of this volume. “total.production” is the addition of an operator-generated gas (barrels of oil equivalent) and oil (barrel) and “total.production.6” is  $10^6$  of this volume. “total.production.6.ln” is the natural log of “total.production.6”.

x	fr e q	freq.l n	ave. spill ed	ave.s pilled .ln	media n.spill ed	media n.spille d.ln	total .spill ed	total. spille d.ln	gas. bbl	oil.b bl	water prod uced. bbl	water.p roduce d.3	water.pr oduced. 3.ln	total.p roducti on	total.pr oductio n.6	total.pro duction. 6.ln
KERR	8	4.418	22.4	3.109	9	2.1972	605	6.405	36,4	36,5	4,845	4,846	8.48590	73,049	73049.	11.1988

MCGE E OIL & GAS ONSH ORE LP	3	8406 08	2	9534 18		24577		2284 58	85,9 67	63,4 59	,972		3123	,426	425551 724	9155
NOBLE ENERG Y INC	8 2	4.406 7192 47	17.7 2	2.874 6939 45	3	1.0986 12289	1009 .8	6.917 5075 7	25,1 42,8 17	25,2 21,9 09	9,412 ,343	9,412	9.14977 7192	50,364 ,726	50364. 725724 138	10.8270 4632
ENCAN A OIL & GAS (USA) INC	8	2.079 4415 42	24.1 9	3.185 9393 25	7.5	2.0149 03021	193. 5	5.265 2775 12	9,90 4,83 7	9,71 7,64 3	2,988 ,864	2,989	8.00264 8661	19,622 ,480	19622. 479551 724	9.88443 1104
PDC ENERG Y INC	2 7	3.295 8368 66	19.6 4	2.977 5683 03	8	2.0794 41542	275	5.616 7710 98	7,91 1,85 7	7,87 9,36 8	2,321 ,750	2,322	7.75007 6491	15,791 ,225	15791. 225413 793	9.66720 9711
BONA NZA CREEK ENERG Y OPERA TING COMP ANY LLC	1 0	2.302 5850 93	10	2.302 5850 93	5	1.6094 37912	90	4.499 8096 7	3,89 5,14 6	6,71 5,18 1	3,259 ,463	3,259	8.08931 7737	10,610 ,327	10610. 327206 897	9.26958 3071
EXTRA CTION OIL & GAS LLC	5	1.609 4379 12	72.3	4.280 8241 29	19	2.9444 38979	289	5.666 4266 88	3,63 5,32 5	6,05 6,59 8	1,735 ,063	1,735	7.45879 9003	9,691, 923	9691.9 230000 00	9.17904 8137
WHITI NG OIL	1 5	2.708 0502	8.57	2.148 2677	6	1.7917 59469	120	4.787 4917	1,69 7,13	6,01 2,22	6,801 ,624	6,802	8.82491 6686	7,709, 363	7709.3 625862	8.95019 0789

& GAS CORP ORATI ON		01		33				43	8	5					07	
BARRE TT CORP ORATI ON* BILL	9	2.197 2245 77	10.2 5	2.327 2777 06	3.25	1.1786 54996	61.5	4.119 0371 75	1,65 2,38 2	3,44 8,12 9	2,015 ,583	2,016	7.60866 3763	5,100, 511	5100.5 105517 24	8.53709 5922
SYNER GY RESOU RCES CORP ORATI ON	7	1.945 9101 49	3.33	1.202 9723 04	3.25	1.1786 54996	20	2.995 7322 74	1,43 5,20 0	2,21 0,88 3	253,6 13	254	5.53580 9483	3,646, 083	3646.0 833448 28	8.20140 8814
GREAT WESTE RN OPERA TING COMP ANY LLC	3	1.098 6122 89	50.3	3.918 0050 77	9	2.1972 24577	151	5.017 2798 37	1,12 7,50 4	1,70 4,88 2	320,6 16	321	5.77024 4145	2,832, 386	2832.3 861379 31	7.94887 4794
BAYS WATE R EXPLO RATIO N AND PROD UCTIO N LLC	9	2.197 2245 77	23.1 4	3.141 5627 22	6	1.7917 59469	162	5.087 5963 35	978, 706	1,21 5,50 2	470,4 68	470	6.15372 7944	2,194, 208	2194.2 080344 83	7.69357 6456

CARRIZO NIOBRARA LLC	4	1.386294361	40.3	3.696351469	25	3.218875825	161	5.081404365	3,149	9,003	13,589	14	2.609260642	12,152	12.151965517	2.497490928
K P KAUFFMAN COMPANY INC	6	1.791759469	12	2.48490665	2.5	0.916290732	48	3.871201011	272,404	206,015	121,552	122	4.800342155	478,419	478.419482759	6.170487927
EOG RESOURCES INC	4	1.386294361	57.5	4.051784948	12.5	2.525728644	230	5.438079309	133,834	328,901	165,122	165	5.106684595	462,735	462.735137931	6.137154834
FOUNDATION ENERGY MANAGEMENT LLC	10	2.302585093	8.5	2.140066163	4	1.386294361	51	3.931825633	54,126	65,929	57,616	58	4.053800307	120,055	120.054689655	4.787947386
MONAHAN GAS & OIL INC	1	0	0.5	-0.693147181	0.5	-0.693147181	0.5	-0.693147181	8,628	1,222	783	1	-0.244622583	9,850	9.849931034	2.287464454
WARD PETROLEUM CORPORATION	1	0	80	4.382026635	80	4.382026635	80	4.382026635	5	7,136	2,793	3	1.027116287	7,141	7.141000000	1.965852823

ON																
SMITH OIL PROPE RTIES INC	1	0	0		0		0		0	4,37 8	263,0 07	263	5.57218 0648	4,378	4.3780 00000	1.47659 1999
DCP MIDST REAM LP	2 9	3.367 2958 3	9.02	2.199 4443 34	3	1.0986 12289	198. 5	5.290 7891								
NGL WATE R SOLUT IONS DJ LLC	2	0.693 1471 81	191 2.5	7.556 1665 66	1912. 5	7.5561 66566	3825	8.249 3137 46								

## 12.12 PRODUCED-WATER SURFACE SPILLS AND THE RISK FOR BTEX-AND-NAPHTHALENE

### GROUNDWATER CONTAMINATION

Data for chapter 2 can be found online only. The data set is too large to include here.

## 12.13 PHYTOREMEDIATION OF BTEX AND NAPHTHALENE FROM PRODUCED-WATER SPILL SITES

### USING *POACEAE*

Table 12.3 The total concentration of BTEX&N in soil treated with either foxtail barley or perennial ryegrass at day 7 or 14 after a produced water spill. Siblings represent the total number of individual plants that were present in the soil at time of harvest. Control.conc represents the total mass of each contaminant found in the soil. Control.diff was calculated by taking the average of each contaminant's total mass in a pot in the control soil at day 8.1 7 or 14 and subtracting that value from the total contaminant mass from the treatment soil in an individual pot at day 7 or 14. The excel file was named "longformat\_soil\_difference.csv" and the data was read into R with the name "soil", as seen in the R code.

contaminant	concentration	day after exposure	fraction.tested	species	total.conc	siblings	control.diff
benzene	1.6875	14	soil	PR	203.0063	13	-90.8138
benzene	2.0313	14	soil	PR	244.3654	13	-49.4547
benzene	1.2772	14	soil	PR	153.6472	24	-140.173
benzene	1.2772	14	soil	PR	153.6472	26	-140.173
benzene	1.55	14	soil	PR	186.465	24	-107.355
benzene	1.4583	14	soil	PR	175.4335	38	-118.387
benzene	1.2963	14	soil	PR	155.9449	48	-137.875
benzene	2.0625	14	soil	PR	248.1188	14	-45.7013
benzene	1.8421	14	soil	PR	221.6046	22	-72.2155
benzene	0.8333	14	soil	PR	100.246	22	-193.574
benzene	2.9167	14	soil	FB	350.879	3	57.05892
benzene	1.8927	14	soil	FB	227.6918	3	-66.1283



benzene	3.2895	14	soil	FB	395.7269	3	101.9068
benzene	2.0035	14	soil	FB	241.0211	3	-52.799
benzene	3.0891	14	soil	FB	371.6187	4	77.79864
benzene	2.4504	14	soil	FB	294.7831	2	0.963033
benzene	1.8519	7	soil	FB	222.7836	2	102.4387
benzene	2.4791	7	soil	FB	298.2357	3	177.8909
benzene	1.8123	7	soil	FB	218.0197	5	97.67485
benzene	1.6572	7	soil	FB	199.3612	4	79.01632
benzene	2.0556	7	soil	FB	247.2887	5	126.9438
benzene	2.0313	7	soil	FB	244.3654	3	124.0206
benzene	1.9076	7	soil	FB	229.4843	2	109.1394
benzene	2.0479	7	soil	FB	246.3624	2	126.0175
benzene	1.8686	7	soil	FB	224.7926	3	104.4477
benzene	2.1143	7	soil	FB	254.3503	3	134.0055
benzene	1.0313	7	soil	PR	124.0654	6	3.720551
benzene	0.492	7	soil	PR	59.1876	6	-61.1572
benzene	0.5722	7	soil	PR	68.83566	5	-51.5092
benzene	0.7775	7	soil	PR	93.53325	2	-26.8116
benzene	0.65	7	soil	PR	78.195	4	-42.1498
benzene	0.4985	7	soil	PR	59.96955	4	-60.3753
benzene	0.6715	7	soil	PR	80.78145	3	-39.5634
toluene	4.556075	14	soil	PR	548.0958	13	548.0958
toluene	5.05257	14	soil	PR	607.8242	13	607.8242

toluene	3.18976	14	soil	PR	383.7282	24	383.7282
toluene	3.697684	14	soil	PR	444.8314	26	444.8314
toluene	3.17757	14	soil	PR	382.2617	24	382.2617
toluene	2.912773	14	soil	PR	350.4065	38	350.4065
toluene	2.976809	14	soil	PR	358.1101	48	358.1101
toluene	5.023364	14	soil	PR	604.3107	14	604.3107
toluene	4.107231	14	soil	PR	494.0999	22	494.0999
toluene	2.09415	14	soil	PR	251.9263	22	251.9263
toluene	0.384827	14	soil	FB	46.29467	3	-224.44
toluene	1.32669	14	soil	FB	159.6008	3	-111.134
toluene	0.836203	14	soil	FB	100.5952	3	-170.14
toluene	0.846657	14	soil	FB	101.8529	3	-168.882
toluene	0.75196	14	soil	FB	90.46084	4	-180.274
toluene	0.535222	14	soil	FB	64.38717	2	-206.348
toluene	0.28845	7	soil	FB	34.70059	2	-22.5436
toluene	0.313267	7	soil	FB	37.686	3	-19.5582
toluene	0.330056	7	soil	FB	39.70573	5	-17.5385
toluene	0.336307	7	soil	FB	40.45773	4	-16.7865
toluene	0.373832	7	soil	FB	44.97196	5	-12.2723
toluene	0.642523	7	soil	FB	77.29556	3	20.05134
toluene	0.412866	7	soil	FB	49.66783	2	-7.57639
toluene	0.517001	7	soil	FB	62.19527	2	4.951047
toluene	0.272987	7	soil	FB	32.84035	3	-24.4039

toluene	0.833826	7	soil	FB	100.3092	3	43.06499
toluene	0.934579	7	soil	PR	112.4299	6	55.18569
toluene	0.463203	7	soil	PR	55.72328	6	-1.52094
toluene	0.542977	7	soil	PR	65.32019	5	8.075972
toluene	0.558959	7	soil	PR	67.24277	2	9.998547
toluene	0.429907	7	soil	PR	51.71776	4	-5.52646
toluene	0.401353	7	soil	PR	48.28278	4	-8.96144
toluene	0.463428	7	soil	PR	55.75037	3	-1.49385
ethylbenzene	0.906433	14	soil	PR	109.0439	13	20.51222
ethylbenzene	0.840643	14	soil	PR	101.1294	13	12.59775
ethylbenzene	0.762777	14	soil	PR	91.76201	24	3.230376
ethylbenzene	0.635647	14	soil	PR	76.46834	26	-12.0633
ethylbenzene	0.77193	14	soil	PR	92.86316	24	4.33152
ethylbenzene	1.091618	14	soil	PR	131.3216	38	42.79
ethylbenzene	0.888023	14	soil	PR	106.8291	48	18.29747
ethylbenzene	1.081871	14	soil	PR	130.1491	14	41.61749
ethylbenzene	0.800246	14	soil	PR	96.26962	22	7.737984
ethylbenzene	0.324886	14	soil	PR	39.08382	22	-49.4478
ethylbenzene	0.321064	14	soil	FB	38.62401	3	-49.9076
ethylbenzene	0.092239	14	soil	FB	11.09635	3	-77.4353
ethylbenzene	0.461681	14	soil	FB	55.54017	3	-32.9915
ethylbenzene	0.387147	14	soil	FB	46.57375	3	-41.9579
ethylbenzene	0.63857	14	soil	FB	76.81992	4	-11.7117

ethylbenzene	0.309143	14	soil	FB	37.18989	2	-51.3417
ethylbenzene	0.192525	7	soil	FB	23.16078	2	-9.92235
ethylbenzene	0.196021	7	soil	FB	23.5813	3	-9.50183
ethylbenzene	0.282615	7	soil	FB	33.99857	5	0.915436
ethylbenzene	0.265816	7	soil	FB	31.97767	4	-1.10546
ethylbenzene	0.259909	7	soil	FB	31.26706	5	-1.81607
ethylbenzene	0.41423	7	soil	FB	49.83187	3	16.74874
ethylbenzene	0.352286	7	soil	FB	42.38005	2	9.296917
ethylbenzene	0.497698	7	soil	FB	59.87309	2	26.78996
ethylbenzene	0.321537	7	soil	FB	38.68089	3	5.597765
ethylbenzene	0.500011	7	soil	FB	60.15131	3	27.06818
ethylbenzene	0.350877	7	soil	PR	42.21053	6	9.127397
ethylbenzene	0.102297	7	soil	PR	12.30628	6	-20.7769
ethylbenzene	0.14414	7	soil	PR	17.34	5	-15.7431
ethylbenzene	0.111923	7	soil	PR	13.46428	2	-19.6188
ethylbenzene	0.093567	7	soil	PR	11.25614	4	-21.827
ethylbenzene	0.143508	7	soil	PR	17.26402	4	-15.8191
ethylbenzene	0.072495	7	soil	PR	8.721183	3	-24.3619
xylene	47.95792	14	soil	PR	5769.338	13	5766.875
xylene	78.91399	14	soil	PR	9493.352	13	9490.89
xylene	118.2845	14	soil	PR	14229.63	24	14227.17
xylene	84.62118	14	soil	PR	10179.93	26	10177.47
xylene	77.29703	14	soil	PR	9298.833	24	9296.37

xylene	72.68977	14	soil	PR	8744.579	38	8742.117
xylene	91.64833	14	soil	PR	11025.29	48	11022.83
xylene	95.53218	14	soil	PR	11492.52	14	11490.06
xylene	75.45597	14	soil	PR	9077.353	22	9074.89
xylene	89.0264	14	soil	PR	10709.88	22	10707.41
xylene	0.007735	14	soil	FB	0.930538	3	-1.53209
xylene	0.012694	14	soil	FB	1.527037	3	-0.93559
xylene	0.010578	14	soil	FB	1.272531	3	-1.1901
xylene	0.014104	14	soil	FB	1.696708	3	-0.76592
xylene	0.01105	14	soil	FB	1.329341	4	-1.13329
xylene	0.008477	14	soil	FB	1.019768	2	-1.44286
xylene	0.020372	7	soil	FB	2.450801	2	0.76349
xylene	0.027656	7	soil	FB	3.327065	3	1.639754
xylene	0.009202	7	soil	FB	1.10696	5	-0.58035
xylene	0.009376	7	soil	FB	1.127925	4	-0.55939
xylene	0.022002	7	soil	FB	2.646865	5	0.959554
xylene	0.020627	7	soil	FB	2.481436	3	0.794125
xylene	0.019882	7	soil	FB	2.391745	2	0.704434
xylene	0.031599	7	soil	FB	3.801348	2	2.114037
xylene	0.025518	7	soil	FB	3.069817	3	1.382506
xylene	0.018403	7	soil	FB	2.21392	3	0.526609
xylene	0.111386	7	soil	PR	13.39975	6	11.71244
xylene	0.007216	7	soil	PR	0.868141	6	-0.81917

xylene	0.008716	7	soil	PR	1.048494	5	-0.63882
xylene	0.011843	7	soil	PR	1.424748	2	-0.26256
xylene	0.009901	7	soil	PR	1.191089	4	-0.49622
xylene	0.007593	7	soil	PR	0.913412	4	-0.7739
xylene	0.010228	7	soil	PR	1.230464	3	-0.45685
naphthalene	114.645	14	soil	PR	13791.79	13	8841.531
naphthalene	188.6464	14	soil	PR	22694.17	13	17743.91
naphthalene	282.7631	14	soil	PR	34016.4	24	29066.14
naphthalene	202.2897	14	soil	PR	24335.45	26	19385.19
naphthalene	184.7811	14	soil	PR	22229.16	24	17278.9
naphthalene	173.7673	14	soil	PR	20904.2	38	15953.94
naphthalene	219.0883	14	soil	PR	26356.32	48	21406.07
naphthalene	228.3728	14	soil	PR	27473.25	14	22522.99
naphthalene	180.3799	14	soil	PR	21699.71	22	16749.45
naphthalene	212.8205	14	soil	PR	25602.31	22	20652.05
naphthalene	7.007774	14	soil	FB	843.0352	3	-4107.22
naphthalene	11.92765	14	soil	FB	1434.896	3	-3515.36
naphthalene	24.60293	14	soil	FB	2959.732	3	-1990.53
naphthalene	7.112962	14	soil	FB	855.6893	3	-4094.57
naphthalene	21.76427	14	soil	FB	2618.241	4	-2332.02
naphthalene	14.88413	14	soil	FB	1790.561	2	-3159.7
naphthalene	9.253172	7	soil	FB	1113.157	2	428.7124
naphthalene	19.3382	7	soil	FB	2326.386	3	1641.942

naphthalene	19.13728	7	soil	FB	2302.215	5	1617.771
naphthalene	15.26358	7	soil	FB	1836.209	4	1151.765
naphthalene	15.51611	7	soil	FB	1866.588	5	1182.144
naphthalene	11.4645	7	soil	FB	1379.179	3	694.7348
naphthalene	15.85038	7	soil	FB	1906.801	2	1222.357
naphthalene	29.18293	7	soil	FB	3510.706	2	2826.262
naphthalene	22.2656	7	soil	FB	2678.552	3	1994.108
naphthalene	10.09657	7	soil	FB	1214.617	3	530.1727
naphthalene	19.97041	7	soil	PR	2402.441	6	1717.997
naphthalene	5.330619	7	soil	PR	641.2735	6	-43.1707
naphthalene	5.292108	7	soil	PR	636.6406	5	-47.8036
naphthalene	4.926248	7	soil	PR	592.6276	2	-91.8166
naphthalene	7.739645	7	soil	PR	931.0793	4	246.6351
naphthalene	7.351073	7	soil	PR	884.334	4	199.8898
naphthalene	5.061372	7	soil	PR	608.8831	3	-75.5611

Table 12.4 Raw data for the concentration of each contaminant found in the roots and shoots of foxtail barley and perennial ryegrass. File named Long\_format\_bt看\_tissue.csv. "Concentration" units are ng of contaminant/g of plant tissue. "Siblings" signify the number of individual plants in a pot. "Wet mass" is in grams. "Total.mass" is in ng of contaminant/g of tissue in one plant.

contaminant	concentration	day after exposure	fraction tested	fraction	species	siblings	wet mass	total.mass
benzene	5.3571	14	root	tissue	PR	13	0.56	2.999976

benzene	4.0865	14	root	tissue	PR	13	0.52	2.12498
benzene	5.4025	14	root	tissue	PR	24	0.59	3.187475
benzene	4.7379	14	root	tissue	PR	26	0.62	2.937498
benzene	5.1136	14	root	tissue	PR	24	0.44	2.249984
benzene	4.717	14	root	tissue	PR	38	0.53	2.50001
benzene	8.0128	14	root	tissue	PR	48	0.39	3.124992
benzene	7.6786	14	root	tissue	PR	14	0.35	2.68751
benzene	7.3661	14	root	tissue	PR	22	0.28	2.062508
benzene	5.5707	14	root	tissue	PR	22	0.46	2.562522
benzene	27.3438	14	shoot	tissue	PR	13	0.16	4.375008
benzene	35.4167	14	shoot	tissue	PR	13	0.12	4.250004
benzene	30	14	shoot	tissue	PR	24	0.15	4.5
benzene	34.6154	14	shoot	tissue	PR	26	0.13	4.500002
benzene	25.3472	14	shoot	tissue	PR	24	0.18	4.562496
benzene	45.4545	14	shoot	tissue	PR	38	0.11	4.999995
benzene	26.0417	14	shoot	tissue	PR	48	0.18	4.687506
benzene	46.875	14	shoot	tissue	PR	14	0.1	4.6875
benzene	28.9063	14	shoot	tissue	PR	22	0.16	4.625008
benzene	41.4773	14	shoot	tissue	PR	22	0.11	4.562503
benzene	139.0625	14	root	tissue	FB	3	0.04	5.5625
benzene	29.1667	14	root	tissue	FB	3	0.18	5.250006
benzene	71.0938	14	root	tissue	FB	3	0.08	5.687504
benzene	53.125	14	root	tissue	FB	3	0.08	4.25



benzene	9.6065	14	root	tissue	FB	4	0.54	5.18751
benzene	84.375	14	root	tissue	FB	2	0.06	5.0625
benzene	202.0833	14	shoot	tissue	FB	3	0.03	6.062499
benzene	75	14	shoot	tissue	FB	3	0.06	4.5
benzene	78.75	14	shoot	tissue	FB	3	0.05	3.9375
benzene	95.3125	14	shoot	tissue	FB	3	0.04	3.8125
benzene	66.4063	14	shoot	tissue	FB	4	0.08	5.312504
benzene	153.125	14	shoot	tissue	FB	2	0.04	6.125
benzene	168.75	7	root	tissue	FB	2	0.03	5.0625
benzene	27.3438	7	root	tissue	FB	3	0.16	4.375008
benzene	15.0641	7	root	tissue	FB	5	0.39	5.874999
benzene	8.4375	7	root	tissue	FB	4	0.8	6.75
benzene	26.9886	7	root	tissue	FB	5	0.22	5.937492
benzene	20.0893	7	root	tissue	FB	3	0.28	5.625004
benzene	14.0625	7	root	tissue	FB	2	0.36	5.0625
benzene	67.9688	7	root	tissue	FB	2	0.08	5.437504
benzene	38.3929	7	root	tissue	FB	3	0.14	5.375006
benzene	19.0018	7	root	tissue	FB	3	0.273	5.187491
benzene	134.375	7	shoot	tissue	FB	2	0.04	5.375
benzene	179.1667	7	shoot	tissue	FB	3	0.03	5.375001
benzene	78.5714	7	shoot	tissue	FB	5	0.07	5.499998
benzene	105	7	shoot	tissue	FB	4	0.05	5.25
benzene	67.1875	7	shoot	tissue	FB	5	0.08	5.375

benzene	78.125	7	shoot	tissue	FB	3	0.06	4.6875
benzene	293.75	7	shoot	tissue	FB	2	0.02	5.875
benzene	95	7	shoot	tissue	FB	2	0.05	4.75
benzene	90.2778	7	shoot	tissue	FB	3	0.09	8.125002
benzene	446.875	7	shoot	tissue	FB	3	0.02	8.9375
benzene	2.9481	7	root	tissue	PR	6	0.53	1.562493
benzene	4.9242	7	root	tissue	PR	6	0.33	1.624986
benzene	4.0541	7	root	tissue	PR	5	0.37	1.500017
benzene	4.4922	7	root	tissue	PR	2	0.32	1.437504
benzene	6.0185	7	root	tissue	PR	4	0.27	1.624995
benzene	3.8194	7	root	tissue	PR	4	0.36	1.374984
benzene	3.6458	7	root	tissue	PR	3	0.48	1.749984
benzene	7.0313	7	shoot	tissue	PR	6	0.24	1.687512
benzene	10.1563	7	shoot	tissue	PR	6	0.16	1.625008
benzene	9.9265	7	shoot	tissue	PR	5	0.17	1.687505
benzene	8.2031	7	shoot	tissue	PR	2	0.16	1.312496
benzene	7.5	7	shoot	tissue	PR	4	0.2	1.5
benzene	7.7381	7	shoot	tissue	PR	4	0.21	1.625001
benzene	8.8816	7	shoot	tissue	PR	3	0.19	1.687504
toluene	11.93258	14	root	tissue	PR	13	0.56	6.682243
toluene	11.68224	14	root	tissue	PR	13	0.52	6.074766
toluene	12.90987	14	root	tissue	PR	24	0.59	7.616822
toluene	11.07929	14	root	tissue	PR	26	0.62	6.869159

toluene	14.2311	14	root	tissue	PR	24	0.44	6.261682
toluene	12.16717	14	root	tissue	PR	38	0.53	6.448598
toluene	17.73305	14	root	tissue	PR	48	0.39	6.915888
toluene	19.89319	14	root	tissue	PR	14	0.35	6.962617
toluene	19.85981	14	root	tissue	PR	22	0.28	5.560748
toluene	15.74563	14	root	tissue	PR	22	0.46	7.242991
toluene	67.75701	14	shoot	tissue	PR	13	0.16	10.84112
toluene	93.06854	14	shoot	tissue	PR	13	0.12	11.16822
toluene	77.88162	14	shoot	tissue	PR	24	0.15	11.68224
toluene	85.19051	14	shoot	tissue	PR	26	0.13	11.07477
toluene	64.12253	14	shoot	tissue	PR	24	0.18	11.54206
toluene	121.4953	14	shoot	tissue	PR	38	0.11	13.36449
toluene	58.41121	14	shoot	tissue	PR	48	0.18	10.51402
toluene	132.243	14	shoot	tissue	PR	14	0.1	13.2243
toluene	66.00467	14	shoot	tissue	PR	22	0.16	10.56075
toluene	102.8037	14	shoot	tissue	PR	22	0.11	11.30841
toluene	25.70093	14	root	tissue	FB	3	0.04	1.028037
toluene	4.413292	14	root	tissue	FB	3	0.18	0.794393
toluene	14.6028	14	root	tissue	FB	3	0.08	1.168224
toluene	9.929907	14	root	tissue	FB	3	0.08	0.794393
toluene	2.422984	14	root	tissue	FB	4	0.54	1.308411
toluene	7.788162	14	root	tissue	FB	2	0.06	0.46729
toluene	59.19003	14	shoot	tissue	FB	3	0.03	1.775701

toluene	28.8162	14	shoot	tissue	FB	3	0.06	1.728972
toluene	35.51402	14	shoot	tissue	FB	3	0.05	1.775701
toluene	40.88785	14	shoot	tissue	FB	3	0.04	1.635514
toluene	18.10748	14	shoot	tissue	FB	4	0.08	1.448598
toluene	46.72897	14	shoot	tissue	FB	2	0.04	1.869159
toluene	23.36449	7	root	tissue	FB	2	0.03	0.700935
toluene	4.088785	7	root	tissue	FB	3	0.16	0.654206
toluene	5.391804	7	root	tissue	FB	5	0.39	2.102804
toluene	3.212617	7	root	tissue	FB	4	0.8	2.570093
toluene	2.548853	7	root	tissue	FB	5	0.22	0.560748
toluene	4.339119	7	root	tissue	FB	3	0.28	1.214953
toluene	8.17757	7	root	tissue	FB	2	0.36	2.943925
toluene	7.593458	7	root	tissue	FB	2	0.08	0.607477
toluene	4.672897	7	root	tissue	FB	3	0.14	0.654206
toluene	2.225189	7	root	tissue	FB	3	0.273	0.607477
toluene	16.35514	7	shoot	tissue	FB	2	0.04	0.654206
toluene	26.47975	7	shoot	tissue	FB	3	0.03	0.794393
toluene	12.01602	7	shoot	tissue	FB	5	0.07	0.841121
toluene	13.08411	7	shoot	tissue	FB	4	0.05	0.654206
toluene	8.17757	7	shoot	tissue	FB	5	0.08	0.654206
toluene	14.79751	7	shoot	tissue	FB	3	0.06	0.88785
toluene	46.72897	7	shoot	tissue	FB	2	0.02	0.934579
toluene	14.01869	7	shoot	tissue	FB	2	0.05	0.700935

toluene	79.95846	7	shoot	tissue	FB	3	0.09	7.196262
toluene	142.5234	7	shoot	tissue	FB	3	0.02	2.850467
toluene	3.262211	7	root	tissue	PR	6	0.53	1.728972
toluene	4.8145	7	root	tissue	PR	6	0.33	1.588785
toluene	4.420308	7	root	tissue	PR	5	0.37	1.635514
toluene	4.088785	7	root	tissue	PR	2	0.32	1.308411
toluene	5.711319	7	root	tissue	PR	4	0.27	1.542056
toluene	4.023884	7	root	tissue	PR	4	0.36	1.448598
toluene	2.433801	7	root	tissue	PR	3	0.48	1.168224
toluene	5.646417	7	shoot	tissue	PR	6	0.24	1.35514
toluene	8.761682	7	shoot	tissue	PR	6	0.16	1.401869
toluene	7.42166	7	shoot	tissue	PR	5	0.17	1.261682
toluene	7.301402	7	shoot	tissue	PR	2	0.16	1.168224
toluene	7.009346	7	shoot	tissue	PR	4	0.2	1.401869
toluene	6.23053	7	shoot	tissue	PR	4	0.21	1.308411
toluene	8.116085	7	shoot	tissue	PR	3	0.19	1.542056
ethylbenzene	1.566416	14	root	tissue	PR	13	0.56	0.877193
ethylbenzene	1.012146	14	root	tissue	PR	13	0.52	0.526316
ethylbenzene	0.991179	14	root	tissue	PR	24	0.59	0.584795
ethylbenzene	0.754575	14	root	tissue	PR	26	0.62	0.467836

e								
ethylbenzen	0.398724	14	root	tissue	PR	24	0.44	0.175439
e								
ethylbenzen	0.88271	14	root	tissue	PR	38	0.53	0.467836
e								
ethylbenzen	1.349528	14	root	tissue	PR	48	0.39	0.526316
e								
ethylbenzen	1.336675	14	root	tissue	PR	14	0.35	0.467836
e								
ethylbenzen	0.417711	14	root	tissue	PR	22	0.28	0.116959
e								
ethylbenzen	1.271294	14	root	tissue	PR	22	0.46	0.584795
e								
ethylbenzen	5.847953	14	shoot	tissue	PR	13	0.16	0.935673
e								
ethylbenzen	10.23392	14	shoot	tissue	PR	13	0.12	1.22807
e								
ethylbenzen	5.847953	14	shoot	tissue	PR	24	0.15	0.877193
e								
ethylbenzen	3.59874	14	shoot	tissue	PR	26	0.13	0.467836
e								
ethylbenzen	3.248863	14	shoot	tissue	PR	24	0.18	0.584795
e								

ethylbenzen e	5.847953	14	shoot	tissue	PR	38	0.11	0.643275
ethylbenzen e	2.923977	14	shoot	tissue	PR	48	0.18	0.526316
ethylbenzen e	3.508772	14	shoot	tissue	PR	14	0.1	0.350877
ethylbenzen e	5.116959	14	shoot	tissue	PR	22	0.16	0.818713
ethylbenzen e	5.316321	14	shoot	tissue	PR	22	0.11	0.584795
ethylbenzen e	19.00585	14	root	tissue	FB	3	0.04	0.760234
ethylbenzen e	3.573749	14	root	tissue	FB	3	0.18	0.643275
ethylbenzen e	1.461988	14	root	tissue	FB	3	0.08	0.116959
ethylbenzen e	9.502924	14	root	tissue	FB	3	0.08	0.760234
ethylbenzen e	1.082954	14	root	tissue	FB	4	0.54	0.584795
ethylbenzen e	8.77193	14	root	tissue	FB	2	0.06	0.526316
ethylbenzen	17.54386	14	shoot	tissue	FB	3	0.03	0.526316

e								
ethylbenzen	9.746589	14	shoot	tissue	FB	3	0.06	0.584795
e								
ethylbenzen	15.20468	14	shoot	tissue	FB	3	0.05	0.760234
e								
ethylbenzen	17.54386	14	shoot	tissue	FB	3	0.04	0.701754
e								
ethylbenzen	8.040936	14	shoot	tissue	FB	4	0.08	0.643275
e								
ethylbenzen	2.923977	14	shoot	tissue	FB	2	0.04	0.116959
e								
ethylbenzen	11.69591	7	root	tissue	FB	2	0.03	0.350877
e								
ethylbenzen	1.827485	7	root	tissue	FB	3	0.16	0.292398
e								
ethylbenzen	8.547009	7	root	tissue	FB	5	0.39	3.333333
e								
ethylbenzen	1.681287	7	root	tissue	FB	4	0.8	1.345029
e								
ethylbenzen	2.126528	7	root	tissue	FB	5	0.22	0.467836
e								
ethylbenzen	4.385965	7	root	tissue	FB	3	0.28	1.22807
e								



ethylbenzen e	4.548408	7	root	tissue	FB	2	0.36	1.637427
ethylbenzen e	5.847953	7	root	tissue	FB	2	0.08	0.467836
ethylbenzen e	2.506266	7	root	tissue	FB	3	0.14	0.350877
ethylbenzen e	1.285264	7	root	tissue	FB	3	0.273	0.350877
ethylbenzen e	10.23392	7	shoot	tissue	FB	2	0.04	0.409357
ethylbenzen e	13.64522	7	shoot	tissue	FB	3	0.03	0.409357
ethylbenzen e	4.177109	7	shoot	tissue	FB	5	0.07	0.292398
ethylbenzen e	5.847953	7	shoot	tissue	FB	4	0.05	0.292398
ethylbenzen e	4.385965	7	shoot	tissue	FB	5	0.08	0.350877
ethylbenzen e	7.797271	7	shoot	tissue	FB	3	0.06	0.467836
ethylbenzen e	26.31579	7	shoot	tissue	FB	2	0.02	0.526316
ethylbenzen	10.52632	7	shoot	tissue	FB	2	0.05	0.526316

e								
ethylbenzen	4.548408	7	shoot	tissue	FB	3	0.09	0.409357
e								
ethylbenzen	213.4503	7	shoot	tissue	FB	3	0.02	4.269006
e								
ethylbenzen	1.655081	7	root	tissue	PR	6	0.53	0.877193
e								
ethylbenzen	1.594896	7	root	tissue	PR	6	0.33	0.526316
e								
ethylbenzen	1.896633	7	root	tissue	PR	5	0.37	0.701754
e								
ethylbenzen	1.27924	7	root	tissue	PR	2	0.32	0.409357
e								
ethylbenzen	1.732727	7	root	tissue	PR	4	0.27	0.467836
e								
ethylbenzen	2.59909	7	root	tissue	PR	4	0.36	0.935673
e								
ethylbenzen	1.096491	7	root	tissue	PR	3	0.48	0.526316
e								
ethylbenzen	1.461988	7	shoot	tissue	PR	6	0.24	0.350877
e								
ethylbenzen	1.096491	7	shoot	tissue	PR	6	0.16	0.175439
e								

ethylbenzen e	1.719986	7	shoot	tissue	PR	5	0.17	0.292398
ethylbenzen e	1.461988	7	shoot	tissue	PR	2	0.16	0.233918
ethylbenzen e	1.169591	7	shoot	tissue	PR	4	0.2	0.233918
ethylbenzen e	1.39237	7	shoot	tissue	PR	4	0.21	0.292398
ethylbenzen e	1.231148	7	shoot	tissue	PR	3	0.19	0.233918
xylene	40.17857	14	root	tissue	PR	13	0.56	0.374329
xylene	2.475248	14	root	tissue	PR	13	0.52	1.287129
xylene	5.873469	14	root	tissue	PR	24	0.59	3.465347
xylene	6.068349	14	root	tissue	PR	26	0.62	3.762376
xylene	6.469397	14	root	tissue	PR	24	0.44	2.846535
xylene	5.604334	14	root	tissue	PR	38	0.53	2.970297
xylene	10.78954	14	root	tissue	PR	48	0.39	4.207921
xylene	5.304102	14	root	tissue	PR	14	0.35	1.856436
xylene	6.630127	14	root	tissue	PR	22	0.28	1.856436
xylene	4.789066	14	root	tissue	PR	22	0.46	2.20297
xylene	12.22153	14	shoot	tissue	PR	13	0.16	1.955446
xylene	6.394389	14	shoot	tissue	PR	13	0.12	0.767327
xylene	4.950495	14	shoot	tissue	PR	24	0.15	0.742574

xylene	5.140899	14	shoot	tissue	PR	26	0.13	0.668317
xylene	4.125413	14	shoot	tissue	PR	24	0.18	0.742574
xylene	5.850585	14	shoot	tissue	PR	38	0.11	0.643564
xylene	6.875688	14	shoot	tissue	PR	48	0.18	1.237624
xylene	4.950495	14	shoot	tissue	PR	14	0.1	0.49505
xylene	7.889851	14	shoot	tissue	PR	22	0.16	1.262376
xylene	6.750675	14	shoot	tissue	PR	22	0.11	0.742574
xylene	0.618812	14	root	tissue	FB	3	0.04	0.024752
xylene	0.137514	14	root	tissue	FB	3	0.18	0.024752
xylene	0.309406	14	root	tissue	FB	3	0.08	0.024752
xylene	0.309406	14	root	tissue	FB	3	0.08	0.024752
xylene	0.137514	14	root	tissue	FB	4	0.54	0.074257
xylene	0.412541	14	root	tissue	FB	2	0.06	0.024752
xylene	1.650165	14	shoot	tissue	FB	3	0.03	0.049505
xylene	0.412541	14	shoot	tissue	FB	3	0.06	0.024752
xylene	0.49505	14	shoot	tissue	FB	3	0.05	0.024752
xylene	0.618812	14	shoot	tissue	FB	3	0.04	0.024752
xylene	0.618812	14	shoot	tissue	FB	4	0.08	0.049505
xylene	1.237624	14	shoot	tissue	FB	2	0.04	0.049505
xylene	2.475248	7	root	tissue	FB	2	0.03	0.074257
xylene	0.154703	7	root	tissue	FB	3	0.16	0.024752
xylene	0.634679	7	root	tissue	FB	5	0.39	0.247525
xylene	0.340347	7	root	tissue	FB	4	0.8	0.272277

xylene	0.337534	7	root	tissue	FB	5	0.22	0.074257
xylene	0.353607	7	root	tissue	FB	3	0.28	0.09901
xylene	0.412541	7	root	tissue	FB	2	0.36	0.148515
xylene	0.928218	7	root	tissue	FB	2	0.08	0.074257
xylene	0.53041	7	root	tissue	FB	3	0.14	0.074257
xylene	0.181337	7	root	tissue	FB	3	0.273	0.049505
xylene	0.618812	7	shoot	tissue	FB	2	0.04	0.024752
xylene	0.825083	7	shoot	tissue	FB	3	0.03	0.024752
xylene	1.414427	7	shoot	tissue	FB	5	0.07	0.09901
xylene	1.980198	7	shoot	tissue	FB	4	0.05	0.09901
xylene	0.928218	7	shoot	tissue	FB	5	0.08	0.074257
xylene	1.237624	7	shoot	tissue	FB	3	0.06	0.074257
xylene	0.49505	7	shoot	tissue	FB	2	0.05	0.024752
xylene	0.550055	7	shoot	tissue	FB	3	0.09	0.049505
xylene	4.950495	7	shoot	tissue	FB	3	0.02	0.09901
xylene	0.420325	7	root	tissue	PR	6	0.53	0.222772
xylene	0.750075	7	root	tissue	PR	6	0.33	0.247525
xylene	0.93658	7	root	tissue	PR	5	0.37	0.346535
xylene	0.386757	7	root	tissue	PR	2	0.32	0.123762
xylene	1.10011	7	root	tissue	PR	4	0.27	0.29703
xylene	0.825083	7	root	tissue	PR	4	0.36	0.29703
xylene	0.515677	7	root	tissue	PR	3	0.48	0.247525
xylene	0.309406	7	shoot	tissue	PR	6	0.24	0.074257

xylene	0.928218	7	shoot	tissue	PR	6	0.16	0.148515
xylene	0.582411	7	shoot	tissue	PR	5	0.17	0.09901
xylene	1.237624	7	shoot	tissue	PR	2	0.16	0.19802
xylene	0.742574	7	shoot	tissue	PR	4	0.2	0.148515
xylene	0.589345	7	shoot	tissue	PR	4	0.21	0.123762
xylene	1.302762	7	shoot	tissue	PR	3	0.19	0.247525
naphthalen e	96.04818	14	root	tissue	PR	13	0.56	3.076923
naphthalen e	5.91716	14	root	tissue	PR	13	0.52	8.284024
naphthalen e	14.04072	14	root	tissue	PR	24	0.59	8.994083
naphthalen e	14.50659	14	root	tissue	PR	26	0.62	6.804734
naphthalen e	15.4653	14	root	tissue	PR	24	0.44	7.100592
naphthalen e	13.39734	14	root	tissue	PR	38	0.53	10.05917
naphthalen e	25.79275	14	root	tissue	PR	48	0.39	4.43787
naphthalen e	12.67963	14	root	tissue	PR	14	0.35	4.43787
naphthalen	15.84954	14	root	tissue	PR	22	0.28	5.266272

e								
naphthalen e	11.44842	14	root	tissue	PR	22	0.46	4.674556
naphthalen e	29.21598	14	shoot	tissue	PR	13	0.16	1.83432
naphthalen e	15.286	14	shoot	tissue	PR	13	0.12	1.775148
naphthalen e	11.83432	14	shoot	tissue	PR	24	0.15	1.597633
naphthalen e	12.28949	14	shoot	tissue	PR	26	0.13	1.775148
naphthalen e	9.861933	14	shoot	tissue	PR	24	0.18	1.538462
naphthalen e	13.98601	14	shoot	tissue	PR	38	0.11	2.95858
naphthalen e	16.43655	14	shoot	tissue	PR	48	0.18	1.183432
naphthalen e	11.83432	14	shoot	tissue	PR	14	0.1	3.017751
naphthalen e	18.86095	14	shoot	tissue	PR	22	0.16	1.775148
naphthalen e	23.66864	14	root	tissue	FB	3	0.04	0.946746

naphthalen e	11.17686	14	root	tissue	FB	3	0.18	2.011834
naphthalen e	16.27219	14	root	tissue	FB	3	0.08	1.301775
naphthalen e	11.83432	14	root	tissue	FB	3	0.08	0.946746
naphthalen e	7.341661	14	root	tissue	FB	4	0.54	3.964497
naphthalen e	32.54438	14	root	tissue	FB	2	0.06	1.952663
naphthalen e	29.5858	14	shoot	tissue	FB	3	0.03	0.887574
naphthalen e	9.861933	14	shoot	tissue	FB	3	0.06	0.591716
naphthalen e	9.467456	14	shoot	tissue	FB	3	0.05	0.473373
naphthalen e	17.75148	14	shoot	tissue	FB	3	0.04	0.710059
naphthalen e	6.656805	14	shoot	tissue	FB	4	0.08	0.532544
naphthalen e	11.83432	14	shoot	tissue	FB	2	0.04	0.473373
naphthalen	213.0178	7	root	tissue	FB	2	0.03	6.390533



e								
naphthalen e	25.14793	7	root	tissue	FB	3	0.16	4.023669
naphthalen e	107.5709	7	root	tissue	FB	5	0.39	41.95266
naphthalen e	43.04734	7	root	tissue	FB	4	0.8	34.43787
naphthalen e	103.5503	7	root	tissue	FB	5	0.22	22.78107
naphthalen e	244.9281	7	root	tissue	FB	3	0.28	68.57988
naphthalen e	97.14004	7	root	tissue	FB	2	0.36	34.97041
naphthalen e	173.8166	7	root	tissue	FB	2	0.08	13.90533
naphthalen e	65.51141	7	root	tissue	FB	3	0.14	9.171598
naphthalen e	17.55641	7	root	tissue	FB	3	0.273	4.792899
naphthalen e	36.98225	7	shoot	tissue	FB	2	0.04	1.47929
naphthalen e	100.5917	7	shoot	tissue	FB	3	0.03	3.017751

naphthalen e	71.00592	7	shoot	tissue	FB	5	0.07	4.970414
naphthalen e	46.15385	7	shoot	tissue	FB	4	0.05	2.307692
naphthalen e	30.32544	7	shoot	tissue	FB	5	0.08	2.426036
naphthalen e	50.29586	7	shoot	tissue	FB	3	0.06	3.017751
naphthalen e	82.84024	7	shoot	tissue	FB	2	0.02	1.656805
naphthalen e	48.52071	7	shoot	tissue	FB	2	0.05	2.426036
naphthalen e	21.03879	7	shoot	tissue	FB	3	0.09	1.893491
naphthalen e	54.19497	7	shoot	tissue	FB	3	0.02	1.083899
naphthalen e	166.9086	7	root	tissue	PR	6	0.53	88.46154
naphthalen e	148.2876	7	root	tissue	PR	6	0.33	48.93491
naphthalen e	165.2007	7	root	tissue	PR	5	0.37	61.12426
naphthalen	116.679	7	root	tissue	PR	2	0.32	37.33728

e								
naphthalen e	167.6529	7	root	tissue	PR	4	0.27	45.26627
naphthalen e	261.0125	7	root	tissue	PR	4	0.36	93.9645
naphthalen e	122.1647	7	root	tissue	PR	3	0.48	58.63905
naphthalen e	46.59763	7	shoot	tissue	PR	6	0.24	11.18343
naphthalen e	32.17456	7	shoot	tissue	PR	6	0.16	5.147929
naphthalen e	29.23773	7	shoot	tissue	PR	5	0.17	4.970414
naphthalen e	14.7929	7	shoot	tissue	PR	2	0.16	2.366864
naphthalen e	19.82249	7	shoot	tissue	PR	4	0.2	3.964497
naphthalen e	34.09411	7	shoot	tissue	PR	4	0.21	7.159763
naphthalen e	34.25724	7	shoot	tissue	PR	3	0.19	6.508876

## 12.2 R CODE

### 12.21 PRODUCED WATER SURFACE SPILLS: USING PAST EXPERIENCES TO GUIDE MITIGATION

#### PLANS

```
#general stats
tapply(spill$area.m, mean, na.rm=TRUE)
summary(spill$area.m, na.rm=TRUE)
summary(spill$volume, na.rm=TRUE)
summary(spillpw$volume, na.rm=TRUE)
summary(spill$gw.depth.m, na.rm=TRUE)
groundwater = spill[spill$gw == "1", ]
summary(groundwater$gw.depth.m, na.rm=TRUE)
summary(groundwater$volume, na.rm=TRUE)
sum(spillpw$volume, na.rm=TRUE)
sum(spill$volume, na.rm=TRUE)
sum(spillpw$area.m, na.rm=TRUE)
#What explains gw contamination
spill <- read.csv("C:/Users/arshores/Desktop/Hydrus paper/cogcc spills from about 2009 and
on/lm spills.csv", na.strings = " ")
str(spill)
spill$soil<-as.factor(spill$soil)
spill$gw<-as.factor(spill$gw)
spill$surface<-as.factor(spill$surface)
type1 = spill[spill$spilltype == "1", ]
type2 = spill[spill$spilltype == "12", ]
type3 = spill[spill$spilltype == "31", ]
type4 = spill[spill$spilltype == "312", ]
type5 = spill[spill$spilltype == "314", ]
type6 = spill[spill$spilltype == "13", ]
spillpw=rbind(type1, type2, type3, type4, type5, type6)
write.csv(spillpw, "C:/Users/arshores/Desktop/spillpw.csv")
str(spillpw)
spillpw$soil <- factor(spillpw$soil, levels = c("0","1"),labels=c("Not
Contaminated","Contaminated"))
spillpw$gw <- factor(spillpw$gw, levels = c("0","1"),labels=c("Not
Contaminated","Contaminated"))
spillpw$depth.bi<-cut(spillpw$gw.depth.m, seq(0,142,1), right=FALSE, labels=c(1:142))
spillpw$depth.bi2<-cut(spillpw$gw.depth.m, seq(0,142,1), right=FALSE)
# logistic regression of depth to watertable on groundwater contamination
summary(spillpw$depth.bi)
depthtable=table(spillpw$depth.bi2, spillpw$gw)
depthtable
```

```

depthtable <- cbind(depthtable, "observation"=1:nrow(depthtable))
depthtable <- as.data.frame(depthtable)
colnames(depthtable) <- c("no", "yes", "depth")
depthtable$totalobs <- depthtable[,1] + depthtable[,2]
depthtable$proportionyes <- depthtable[,2] / depthtable[,4]
glm.out = glm(cbind(yes, totalobs-yes) ~ depth, family=binomial(logit), data=depthtable)
plot(yes/totalobs ~ depth, data=depthtable)
lines(depthtable$depth, glm.out$fitted, type="l", col="red")
summary(glm.out)
1 - pchisq(25.6, df=38)
anova(glm.out, test="Chisq")
str(depthtable)
str(spillpw)
## odds ratios only
exp(coef(glm.out))
library(pscl)
pR2(glm.out)
pred = data.frame(depth=12.5)
predict(glm.out, pred, type="response")
predinc <- seq(1, 142, 1)
gwpred <- predict(glm.out, list(depth = predinc), type="response")
gwpred2
gwpred1 <- as.data.frame(gwpred)
gwpred2 <- cbind(gwpred1, "depth"=1:nrow(gwpred1))
total <- merge(gwpred2, depthtable)
total
depth.prop <- ggplot(depthtable, aes(depth, proportionyes, na.rm=TRUE))
depth.prop + geom_point(width=0.4)+
scale_x_continuous(limits = c(0,150), expand = c(.1,.1), breaks=seq(0,150,10))+
theme_bw()+
xlab("Groundwater Depth (m)")+
theme(axis.ticks.x=element_blank())+
ylab("Probability of Groundwater Contamination") +
geom_line(aes(y=gwpred), size=1, color="blue")+theme( panel.grid.major = element_blank(),
panel.grid.minor = element_blank())
# logistic regression of depth to watertable, area and volume on groundwater contamination
#area and volume don't effect the log odds of having contaminated gw but depth to gw does
glm.out1 = glm(gw ~ gw.depth.m+area.m+volume, family=binomial(logit), data=spillpw)
summary(glm.out1)
anova(glm.out1, test="Chisq")
exp(coef(glm.out1))
newdata = data.frame(gw.depth.m=13)
newdata = data.frame(gw.depth.m=3.7)
predict(glm.out1, newdata, type="response")

```

```

## odds ratios only
exp(coef(glm.out1))
library(pscl)
pR2(glm.out1)
library(rcompanion)
# logistic regression of area on soil contamination
spillpw$area.bi<-cut(spillpw$area.m, seq(0,2000,1), right=FALSE, labels=c(1:2000))
spillpw$area.bi2<-cut(spillpw$area.m, seq(0,2000,1), right=FALSE)
summary(spillpw$.bi)
areatable=table(spillpw$area.bi2, spillpw$soil)
areatable
areatable <- cbind(areatable, "observation"=1:nrow(areatable))
areatable <- as.data.frame(areatable)
colnames(areatable) <- c("no", "yes", "area")
areatable$totalobs <- areatable[,1] + areatable[,2]
areatable$proportionyes <- areatable[,2] / areatable[,4]
glm.out3 = glm(cbind(yes, totalobs-yes) ~ area, family=binomial(logit), data=areatable)
plot(yes/totalobs ~ area, data=areatable)
lines(areatable$area, glm.out3$fitted, type="l", col="red")
summary(glm.out3)
1 - pchisq(0.6, df=1)
anova(glm.out3, test="Chisq")
str(depthtable)
str(spillpw)
# logistic regression of volume on soil contamination
spillpw$volume.bi<-cut(spillpw$volume, seq(0,250,1), right=FALSE, labels=c(1:250))
spillpw$volume.bi2<-cut(spillpw$volume, seq(0,250,1), right=FALSE)
summary(spillpw$volume.bi)
volumetable=table(spillpw$volume.bi2, spillpw$soil)
volumetable
volumetable <- cbind(volumetable, "observation"=1:nrow(volumetable))
volumetable <- as.data.frame(volumetable)
colnames(volumetable) <- c("no", "yes", "volume")
volumetable$totalobs <- volumetable[,1] + volumetable[,2]
volumetable$proportionyes <- volumetable[,2] / volumetable[,4]
glm.out4 = glm(cbind(yes, totalobs-yes) ~ volume, family=binomial(logit), data=volumetable)
plot(yes/totalobs ~ volume, data=volumetable)
lines(volumetable$volume, glm.out4$fitted, type="l", col="red")
summary(glm.out4)
anova(glm.out4, test="Chisq")
## logistic regression of depth to watertable, area and volume on soil contamination
glm.out2 = glm(soil ~ area.m + volume, family=binomial(logit), data=spillpw)
summary(glm.out2)
anova(glm.out2, test="Chisq")

```

```

#groundwater contamination
glm.out2 = glm(gw ~ intensity, family=binomial(logit), data=spillpw)
summary(glm.out2)
#What explains gw contamination
spill <- read.csv("C:/Users/arshores/Desktop/Hydrus paper/cogcc spills from about 2009 and
on/lm spills.csv", na.strings = " ")
str(spill)
spill$soil<-as.factor(spill$soil)
spill$gw<-as.factor(spill$gw)
spill$surface<-as.factor(spill$surface)
type1 = spill[spill$spilltype == "1", ]
type2 =spill[spill$spilltype == "12", ]
type3 = spill[spill$spilltype == "31", ]
type4 = spill[spill$spilltype == "312", ]
type5 = spill[spill$spilltype == "314", ]
type6 = spill[spill$spilltype == "13", ]
spillpw=rbind(type1, type2, type3, type4, type5, type6)
write.csv(spillpw , "C:/Users/arshores/Desktop/spillpw.csv")
spillpw$soil <- factor(spillpw$soil, levels = c("0","1"),labels=c("Not
Contaminated","Contaminated"))
spillpw$gw <- factor(spillpw$gw, levels = c("0","1"),labels=c("Not
Contaminated","Contaminated"))
#methods for combining plots
library(gridExtra)
library(cowplot)
plot_grid(volumepw, areapw, labels=c("A", "B"), ncol = 2, nrow = 1)
#Different method to combine plots
library(grid)
library(dplyr)
grid.newpage()
grid.draw(rbind(ggplotGrob(areapw), ggplotGrob(volumepw), size = "last"))
library(ggplot2)
volumepw <- ggplot(spillpw, aes(gw,volume,na.rm=TRUE))+
geom_boxplot(width=0.4)+
scale_y_continuous(limits = c(0,260))+
theme_bw()+
theme(axis.title.y=element_text(margin=margin(0,20,0,0)))+
ylab("Spill volume (bbl)")+
theme(axis.ticks.x=element_blank())+
xlab("Groundwater Fate at Produced Water Spill-Sites")
volumepw
areapw <- ggplot(na.omit(spillpw), aes(gw, area.m,na.rm=TRUE))+
geom_boxplot(width=0.4)+
theme_bw()+

```

```

#scale_y_continuous(limits = c(0,1500))+
theme(axis.title.y=element_text(margin=margin(0,20,0,0)))+
ylab(bquote('Rectangular spill area'~(m^2)))+
theme(axis.ticks.x=element_blank())+
xlab(" ")
areapw
depthpw <- ggplot(na.omit(spillpw), aes(gw,gw.depth.m,na.rm=TRUE))+
geom_boxplot(width=0.4)+
theme_bw()+
ylab("Depth to groundwater at spill sites (m)")+
theme(axis.ticks.x=element_blank())+
xlab("Groundwater Fate at Produced Water Spill-Sites")
depthpw
#groundwater median and distribution analysis
yes.cont = spillpw[spillpw$gw == "Not Contaminated", ]
no.cont = spillpw[spillpw$gw == "Contaminated", ]
library(plyr)
wilcox.test(volume~gw, data=spillpw, na.rm=TRUE)
wilcox.test(area.m~gw, data=spillpw, na.rm=TRUE)
wilcox.test(gw.depth.m~gw, data=spillpw, na.rm=TRUE)
ks.test(yes.cont$volume, no.cont$volume)
ks.test(yes.cont$area.m, no.cont$area.m)
ks.test(yes.cont$gw.depth.m, no.cont$gw.depth.m)
library(ggplot2)
#soil contamination
volumepwsoil<- ggplot(spillpw, aes(soil,volume,na.rm=TRUE))+
geom_boxplot(width=0.4)+
theme_bw()+
scale_y_continuous(limits = c(0,260),breaks=seq(0,300,100))+
theme(axis.title.y=element_text(margin=margin(0,20,0,0)))+
ylab("Spill volume (bbl)")+
theme(axis.ticks.x=element_blank())+
xlab("Soil Fate at Produced Water Spill-Sites")
volumepwsoil
wilcox.test(volume~soil, data=spillpw, na.rm=TRUE)
#soil contamination area
str(spillpw)
areapwsoil <- ggplot(spillpw, aes(soil,area.m, na.rm=TRUE))+
geom_boxplot(width=0.4)+
theme_bw()+
theme(axis.title.y=element_text(margin=margin(0,20,0,0)))+
scale_y_continuous(limits = c(0,1500))+
ylab(bquote('Rectangular spill area'~(m^2)))+
theme(axis.ticks.x=element_blank())+

```



```

xlab(" ")
areapwsoil
yes.cont.soil = spillpw[spillpw$soil == "Not Contaminated", ]
no.cont.soil = spillpw[spillpw$soil == "Contaminated", ]
ks.test(yes.cont.soil$area.m, no.cont.soil$area.m)
ks.test(yes.cont.soil$volume, no.cont.soil$volume)
wilcox.test(area.m~soil, data=spillpw, na.rm=TRUE)
grid.newpage()
grid.draw(rbind(ggplotGrob(areapwsoil), ggplotGrob(volumepwsoil), size = "last"))
library(ggplot2)
#company
spill <- within(spill,
Company <- factor(Company,
levels=names(sort(table(Company),
decreasing=TRUE))))
groundwater.contamination = spill[spill$gw == "1", ]
count= count (groundwater.contamination)
count= count (soil.contamination)
soil.contamination = spill[spill$soil == "1", ]
tapply(groundwater.contamination$volume, spill$Company, sum, na.rm=TRUE)
summary(groundwater.contamination$area.m)
library(plyr)
count= count (spillpw)
count= count (spill$Company)
volume.med=tapply(spill$volume, spill$Company, FUN=median, na.rm=TRUE)
volume.sum=tapply(spill$volume, spill$Company, FUN=sum, na.rm=TRUE)
volume.mean=tapply(spill$volume, spill$Company, FUN=mean, na.rm=TRUE)
volume.sum
write.csv(volume.med,"C:/Users/arshores/Desktop/volume.med.csv")
write.csv(volume.sum,"C:/Users/arshores/Desktop/volume.sum.csv")
write.csv(volume.mean,"C:/Users/arshores/Desktop/volume.mean.csv")
kerr = spill[spill$Company == "KERR MCGEE OIL & GAS ONSHORE LP ", ]
kerr1 = spill[spill$Company == "KERR MCGEE GATHERING LLC ", ]
kerr2=kerr$volume
write.csv(kerr1,"C:/Users/arshores/Desktop/kerr1.csv")
write.csv(kerr,"C:/Users/arshores/Desktop/kerr.csv")
str(company.freq)
cor = cor(company.freq, method = "pearson", use = "complete.obs")
tapply(spill$volume, spill$Company, sum, na.rm=TRUE)
tapply(spill$volume, spill$Company, mean, na.rm=TRUE)
count
spill <- read.csv("C:/Users/arshores/Desktop/Hydrus paper/cogcc spills from about 2009 and
on/lm spills.csv", na.strings = " ")

```

```

spill$ranked.production = factor(spill$ranked.production,
levels=c("1","2","3","4","5","6","7","8","9","10","11","12","13","14","15","16","17","18","19","20
"),labels=c("KERR MCGEE OIL & GAS ONSHORE LP","NOBLE ENERGY INC","ENCANA OIL & GAS
(USA) INC","PDC ENERGY INC","BONANZA CREEK ENERGY OPERATING COMPANY LLC",
"EXTRACTION OIL & GAS LLC","WHITING OIL & GAS CORPORATION","BARRETT CORPORATION*
BILL","SYNERGY RESOURCES CORPORATION","GREAT WESTERN OPERATING COMPANY LLC",
"BAYSWATER EXPLORATION AND PRODUCTION LLC","K P KAUFFMAN COMPANY INC","EOG
RESOURCES INC","FOUNDATION ENERGY MANAGEMENT LLC",
"MONAHAN GAS & OIL INC","CARRIZO NIOBRARA LLC","WARD PETROLEUM
CORPORATION","SMITH OIL PROPERTIES INC","DCP MIDSTREAM LP","NGL WATER SOLUTIONS DJ
LLC"))
#business entity abbreviations removed
spill$ranked.production = factor(spill$ranked.production,
levels=c("1","2","3","4","5","6","7","8","9","10","11","12","13","14","15","16","17","18","19","20
"),labels=c("KERR MCGEE OIL & GAS ONSHORE (83)","NOBLE ENERGY (82)","ENCANA OIL & GAS
(8)","PDC ENERGY (27)","BONANZA CREEK ENERGY OPERATING (10)",
"EXTRACTION OIL & GAS (5)","WHITING OIL & GAS (15)","BILL BARRETT (9)","SYNERGY
RESOURCES (7)","GREAT WESTERN OPERATING (3)",
"BAYSWATER EXPLORATION AND PRODUCTION (9)","K P KAUFFMAN (6)","EOG RESOURCES
(4)","FOUNDATION ENERGY MANAGEMENT (10)","CARRIZO NIOBRARA (4)",
"MONAHAN GAS & OIL (1)","WARD PETROLEUM (1)","SMITH OIL PROPERTIES (1)","DCP
MIDSTREAM (27)","NGL WATER SOLUTIONS (2)"))
dist.operator= ggplot((na.omit(spill[!rowSums(spill[5] >500),])), aes(factor(ranked.production),
volume))+
geom_boxplot()+
theme(axis.text.x = element_text(angle = 90, hjust = 1))+
coord_flip() +
theme_bw()+
ylab("Volume spilled per site (bbl)") +
xlab("Operator (number of spills in 2015)")
dist.operator
write.csv(count , "C:/Users/arshores/Desktop/company.csv")
company.freq.median.removed <- read.csv("C:/Users/arshores/Desktop/Hydrus paper/cogcc
spills from about 2009 and on/company.workingdoc.medianoutlier.removed.csv", na.strings = "
")
str(company.freq)
#Median volume of water spilled
median.vol.energy= lm(median.spilled~total.production.9 + freq.ln,
data=company.freq.median.removed)
median.vol.energy1= lm(median.spilled.ln~total.production.9.ln + freq.ln,
data=company.freq.median.removed)
median.vol.energy2= lm(median.spilled.ln~total.production.9.ln ,
data=company.freq.median.removed)
median.vol.energy3= lm(median.spilled.ln~ + freq.ln, data=company.freq.median.removed)

```

```

AIC(median.vol.energy)
AIC(median.vol.energy1) #better model
AIC(median.vol.energy2)
AIC(median.vol.energy3)
anova(median.vol.energy2)
median.freq= lm(median.spilled~freq, data=company.freq)
median.freq1= lm(median.spilled.ln~freq.ln, data=company.freq)
AIC(median.freq)
AIC(median.freq1)
anova(median.freq1)
library(ggplot2)
intercept2 <- coef(median.vol.energy1)[1]
slope2 <- coef(median.vol.energy1)[2]
summary(median.vol.energy1)
# using the model, generate points for trendline
x_hat2 <-
seq(min(company.freq.median.removed$total.production.9),max(company.freq.median.remove
d$total.production.9),length=500) # generate a bunch of points between your min and max x
values
y_hat2 <- exp(intercept2) * x_hat2^slope2 # backtransform trendline
# Plot raw data and back-transformed trendline
trendline2 <- data.frame(x_hat2=x_hat2, y_hat2=y_hat2)
companybad=ggplot(company.freq.median.removed,aes(total.production.9, median.spilled,
na.rm=TRUE)) +
theme_bw()+
geom_line(data=trendline2, aes(x=x_hat2, y=y_hat2), col="dodgerblue")+
geom_point()+
#scale_y_continuous(limits = c(0, 85))+
xlab("Energy Production by a Operator in 2015") +
ylab("Median volume spilled at a site (brl)") +
theme(
panel.grid = element_blank(),
legend.background = element_rect(colour = "grey"))
companybad
#frequency versus average volume
companybad=ggplot(company.freq,aes(freq.add, volume.ave.add, na.rm=TRUE)) +
theme_bw()+
geom_line(data=trendline2, aes(x=x_hat2, y=y_hat2), col="dodgerblue")+
geom_point()+
scale_y_continuous(limits = c(0, 85))+
xlab("Number of spills by an operator in 2015") +
ylab("Average volume spilled at a site (brl)") +theme(
panel.grid = element_blank(),
legend.background = element_rect(colour = "grey"))

```

```

companybad
volume.freq= lm(ave.spilled^0.343434343~freq, data=company.freq)
anova(volume.freq2)
volume.freq1=lm(ave.spilled~freq, data=company.freq)
volume.freq2=lm(ave.spilled.ln~freq.ln+total.production.9.ln, data=company.freq) #Best model
anova(volume.freq)
AIC(volume.freq)
AIC(volume.freq1)
AIC(volume.freq2) #Best model
hist(residuals(volume.freq))
bc <- boxcox(volume.ave.add+.00001 ~ freq.add, data=company.freq)
bc
lamda=bc$x
lik=bc$y
bccom=cbind(lamda, lik)
bccom[order(-lik),]
plot(company.freq$freq.add.ln, company.freq$volume.ave.add.ln)
library(ggplot2)
#frequency versus total volume spilled
total13 <- lm(total.spilled ~ freq , data=company.freq)
wts.3 <- 1/fitted(lm(abs(residuals(total13)) ~ company.freq$freq))^2
total13.weight <- lm(total.spilled ~ freq , data=company.freq, weights=wts.3)
summary(total13.weight)
intercept2 <- coef(total13.weight)[1]
slope2 <- coef(total13.weight)[2]
x_hat2 <- seq(min(company.freq$freq),max(company.freq$freq),length=500) # generate a bunch
of points between your min and max x values
y_hat2 <- intercept2 + (x_hat2*slope2) # backtransform trendline
trendline2 <- data.frame(x_hat2=x_hat2, y_hat2=y_hat2)
companybad=ggplot(company.freq,aes(freq, total.spilled, na.rm=TRUE)) +
theme_bw()+
geom_line(data=trendline2, aes(x=x_hat2, y=y_hat2), col="dodgerblue")+
geom_point()+
xlab("Number of spills by an operator in 2015") +
ylab("Total volume spilled by an operator in 2015 (brl)") +
theme(
panel.grid = element_blank(),
legend.background = element_rect(colour = "grey"))
companybad
intercept2 <- coef(totalvol)[1]
slope2 <- coef(totalvol)[2]
# using the model, generate points for trendline
x_hat2 <- seq(min(company.freq.1$freq.add),max(company.freq.1$freq.add),length=500) #
generate a bunch of points between your min and max x values

```

```

y_hat2 <- exp(intercept2) * x_hat2^slope2 # backtransform trendline
# Plot raw data and back-transformed trendline
trendline2 <- data.frame(x_hat2=x_hat2, y_hat2=y_hat2)
#frequency versus total spilled. Ln transformation gives best histogram
totalvol=lm(total.spilled~freq, data=company.freq)
totalvol1=lm(total.spilled.ln~freq.ln, data=company.freq)
AIC(totalvol)
AIC(totalvol1)
anova(lm(totalvol1))
anova(totalvol1)
summary(totalvol)
hist(residuals(totalvol))
plot(totalvol)
bc <- boxcox(total.spilled +1 ~freq + 1, data=company.freq)
bc
lamda=bc$x
lik=bc$y
bccom=cbind(lamda, lik)
bccom[order(-lik),]
wts.3 <- 1/fitted(lm(abs(residuals(freq.volumespilledbycompany)) ~ company.freq$freq.add))^2
eff.3 <- lm(volume.ave.add ~ freq.add, data=company.freq, weights=wts.3)
summary(eff.3)
intercept2 <- coef(freq.volumespilledbycompany)[1]
slope2 <- coef(freq.volumespilledbycompany)[2]
# using the model, generate points for trendline
x_hat2 <- seq(min(company.freq.1$freq.add),max(company.freq.1$freq.add),length=500) #
generate a bunch of points between your min and max x values
y_hat2 <- exp(intercept2) * x_hat2^slope2 # backtransform trendline
# Plot raw data and back-transformed trendline
trendline2 <- data.frame(x_hat2=x_hat2, y_hat2=y_hat2)
plot(trendline2)
#efficiency of companies at different produced water levels and gas production
#produced water and total production is in *10^-9
company.freq <- read.csv("C:/Users/arshores/Desktop/Hydrus paper/cogcc spills from about
2009 and on/company.workingdoc.csv", na.strings = " ")
str(company.freq)
library(car)
total <- lm(total.spilled ~ total.production.6 + freq + water.produced.bbl, data=company.freq)
total1 <- lm(total.spilled ~ total.production.6.ln + freq.ln + water.produced.3.ln,
data=company.freq) #best model
total2 <- lm(total.spilled ~ total.production.6.ln, data=company.freq)
total3 <- lm(total.spilled ~ freq.ln , data=company.freq)
total4 <- lm(total.spilled ~ water.produced.3.ln, data=company.freq)
total5 <- lm(total.spilled ~ total.production.6.ln + freq.ln , data=company.freq) #best model

```

```

total6 <- lm(total.spilled ~ freq.ln + water.produced.3.ln, data=company.freq) #best model
total7 <- lm(total.spilled ~ total.production.6.ln+ water.produced.3.ln, data=company.freq) #best
model
total8 <- lm(total.spilled ~ total.production.6 + freq , data=company.freq)
total9 <- lm(total.spilled ~ total.production.6 + water.produced.bbl, data=company.freq)
total10 <- lm(total.spilled ~ freq + water.produced.bbl, data=company.freq)
total11 <- lm(total.spilled ~ total.production.6, data=company.freq)
total12 <- lm(total.spilled ~ freq + water.produced.3.ln, data=company.freq)
total13 <- lm(total.spilled ~ freq , data=company.freq)
summary(total)
summary(total1)
summary(total2)
summary(total3)
summary(total4)
summary(total13)
library(car)
hist(residuals(total))
hist(residuals(total1))
hist(residuals(total10))
AIC(total)
AIC(total1)
AIC(total2)
AIC(total3)
AIC(total4)
AIC(total5)
AIC(total6)
AIC(total7)
AIC(total8)
AIC(total9)
AIC(total10)
AIC(total11)
AIC(total12)
AIC(total13)
Anova(total10, type="II")
plot(total10)
anova(lm(total))
summary(total10)
hist(residuals(total1))
#oil and gas generated versus produced water generated
#linear model of natural log transformed energy production versus produced water production
company.freq <- read.csv("C:/Users/arshores/Desktop/Hydrus paper/cogcc spills from about
2009 and on/company.workingdoc.csv", na.strings = " ")
eff <- lm(water.produced.3.ln ~ total.production.6.ln, data=company.freq)
eff1 <- lm(water.produced.3.ln ~ total.production.9, data=company.freq)

```

```

AIC(eff)
AIC(eff1)
anova(lm(eff))
summary(eff)
summary(eff1)
hist(residuals(eff))
#linear model for better estimates using weighted least squares
eff <- lm(water.produced.3.ln ~ total.production.6.ln, data=company.freq)
wts <- 1/fitted(lm(abs(residuals(eff)) ~ company.freq$total.production.6.ln))^2
eff.2 <- lm(water.produced.3.ln ~ total.production.6.ln, data=company.freq, weights=wts)
summary(eff.2)
plot(eff.2)
anova(eff.2)
#backtransformation of fit line for energy production versus produced water production
intercept1 <- coef(eff.2)[1]
intercept1
slope1 <- coef(eff.2)[2]
slope1
x_hat1 <-
seq(min(company.freq$total.production.6),max(company.freq$total.production.6),length=500) #
generate a bunch of points between your min and max x values
y_hat1 <- exp(intercept1) * x_hat1^slope1 # backtransform trendline
trendline1 <- data.frame(x_hat1=x_hat1, y_hat1=y_hat1) # combine trendline data for ggplot
Production.generation=ggplot(company.freq, aes(total.production.6, water.produced.3))+
  theme_bw()+
  geom_line(data=trendline1, aes(x=x_hat1, y=y_hat1), col="dodgerblue")+
  geom_point()+
  scale_x_continuous(labels=comma)+
  ylab(bquote('Produced water generated by an operator (bbl x 10'^6*')))+
  xlab(bquote('Total energy produced by an operator (BOE x 10'^6*')))+
  theme(
    panel.grid = element_blank(),
    legend.background = element_rect(colour = "grey"))
Production.generation
#linear model for better estimates using weighted least squares
eff <- lm(total.spilled.ln ~ total.production.6.ln, data=company.freq)
wts <- 1/fitted(lm(abs(residuals(eff)) ~ company.freq$total.production.6.ln))^2
eff.2 <- lm(total.spilled.ln ~ total.production.6.ln, data=company.freq, weights=wts)
summary(eff.2)
plot(eff.2)
eff1 <- lm(total.spilled ~ total.production.9, data=company.freq)
summary(eff)
summary(eff1)
AIC(eff)

```

```

AIC(eff1)
#energy produced versus spilled
company.freq <- read.csv("C:/Users/arshores/Desktop/Hydrus paper/cogcc spills from about
2009 and on/company.workingdoc.csv", na.strings = "")
spilled.energy <- lm(total.spilled ~ total.production.6, data=company.freq) #best model
spilled.energy1 <- lm(total.spilled ~ total.production.6.ln, data=company.freq) #best model
AIC(spilled.energy)
AIC(spilled.energy1)
wts <- 1/fitted(lm(abs(residuals(spilled.energy)) ~ company.freq$total.production.6))^2
spilled.energy.2 <- lm(total.spilled ~ total.production.6, data=company.freq, weights=wts)
summary(spilled.energy.2)
spilled=ggplot(company.freq, aes(total.production.6, total.spilled))+
theme_bw()+
geom_point()+
scale_x_continuous(labels=comma)+
ylab("Total produced water spilled by an operator in Weld County (bbl)")+
xlab(bquote('Total energy produced by an operator (bbl x 10'^9*')'))+
theme(
panel.grid = element_blank(),
legend.background = element_rect(colour = "grey"))
spilled+geom_smooth(method="lm", se=FALSE)
require(scales)
library(ggplot2)
#frequency of spill versus total produced water spilled by a company
#probably won't use this graph.
frequency.spillvolume=ggplot(company.freq, aes(freq, total.spilled))+
theme_bw()+
geom_point(size=3)+
xlab("Number of PW spills by an operator in 2015")+ylab(bquote('Produced-Water Volume (bbl x
10'^6*')'))+
scale_y_continuous(limits = c(0, 2000))+
theme(
panel.grid = element_blank(),
legend.background = element_rect(colour = "grey"))
frequency.spillvolume
frequency.spillvolume + stat_smooth(method = "lm", se=FALSE)
company.freq <- read.csv("C:/Users/arshores/Desktop/Hydrus paper/cogcc spills from about
2009 and on/company.workingdoc.csv", na.strings = "")
#total produced versus total spilled
total.spilled.produced <- lm(total.spilled.ln ~ water.produced.9.ln, data=company.freq)
total.spilled.produced1 <- lm(total.spilled ~ water.produced.9, data=company.freq)
AIC(total.spilled.produced)
AIC(total.spilled.produced1)
anova(total.spilled.produced)

```



```

summary(total.spilled.produced)
intercept1 <- coef(total.spilled.produced)[1]
slope1 <- coef(total.spilled.produced)[2]
x_hat1 <-
seq(min(company.freq$water.produced.9),max(company.freq$water.produced.9),length=500) #
generate a bunch of points between your min and max x values
y_hat1 <- exp(intercept1) * x_hat1^slope1 # backtransform trendline
trendline1 <- data.frame(x_hat1=x_hat1, y_hat1=y_hat1) # combine trendline data for ggplot
total1 <- lm(total.spilled.ln ~ total.production.9.ln + freq.ln + water.produced.9.ln,
data=company.freq) #best model
summary(total1)
intercept1 <- coef(total1)[1]
slope1 <- coef(total1)[4]
slope1
x_hat1 <-
seq(min(company.freq$water.produced.9),max(company.freq$water.produced.9),length=500) #
generate a bunch of points between your min and max x values
y_hat1 <- exp(intercept1) + x_hat1^slope1 # backtransform trendline
trendline1 <- data.frame(x_hat1=x_hat1, y_hat1=y_hat1) # combine trendline data for ggplot
produced.spilled=ggplot(company.freq, aes(water.produced.bbl, total.spilled))+
theme_bw()+
# geom_line(data=trendline1, aes(x=x_hat1, y=y_hat1), col="dodgerblue")+
geom_point()+
xlab(bquote('Produced-Water generated by an operator (bbl x 10'^9*')))+
ylab("Produced-water spilled in Weld County (bbl)")+
#scale_y_continuous(limits = c(0, 2000))+
theme(
panel.grid = element_blank(),
legend.background = element_rect(colour = "grey"))
produced.spilled
company.freq <- read.csv("C:/Users/arshores/Desktop/Hydrus paper/cogcc spills from about
2009 and on/company.workingdoc.csv", na.strings = "")
produced.spilled=ggplot(company.freq, aes(water.produced.bbl, total.spilled))+
theme_bw()+
geom_point(size=3)+
xlab("Volume of produced water spilled by an operator")+
ylab(bquote('Volume of produced water generated by an operator (bbl x 10'^9*')))+
scale_y_continuous(limits = c(0, 2000))+
theme(
panel.grid = element_blank(),
legend.background = element_rect(colour = "grey"))
produced.spilled
require(scales)
benefit <- lm(total.ave.add.ln ~ total.production.ln, data=company.freq)

```

```

plot(benefit)
anova(lm(benefit))
summary(benefit)
#Water produced vs water spilled
str(company.freq)
require(scales)
company.freq <- read.csv("C:/Users/arshores/Desktop/Hydrus paper/cogcc spills from about
2009 and on/company.csv", na.strings = " ")
freq.anova <- lm(freq ~ total.production, data=company.freq)
anova(lm(freq.anova))
summary(freq.anova)
plot(freq.anova)
hist(residuals(freq.anova))
library(MASS)
bc <- boxcox(freq.add ~ total.production, data=company.freq)
bc
lamda=bc$x
lik=bc$y
bccom=cbind(lamda, lik)
bccom[order(-lik),]
intercept3<- coef(freq.anova)[1]
slope3 <- coef(freq.anova)[2]
x_hat3 <-
seq(min(company.freq$total.production),max(company.freq$total.production),length=500) #
generate a bunch of points between your min and max x values
y_hat3 <- x_hat1^0.303 # backtransform trendline
trendline3 <- data.frame(x_hat3=x_hat3, y_hat3=y_hat3) # combine trendline data for ggplot
companybad=ggplot(company.freq,aes(total.production, freq, na.rm=TRUE)) +
theme_bw()+
#geom_line(data=trendline3, aes(x=x_hat3, y=y_hat3), col="dodgerblue")+
geom_point()+
scale_x_continuous(labels=comma)+
xlab("Total energy production by an operator in 2015") +
ylab("Number of spills by an operator") +
theme(panel.grid = element_blank(),legend.background = element_rect(colour = "grey"))
companybad
str(company.freq)
totalvolume <- lm(total.add ~ water.produced.dec.ln+total.production.ln, data=company.freq)
Anova(totalvolume, type="II")
summary(totalvolume)

```

## 12.22 PRODUCED-WATER SURFACE SPILLS AND THE RISK FOR BTEX-AND-NAPHTHALENE

### GROUNDWATER CONTAMINATION

```
hydrus <- read.csv("C:/Users/arshores/Desktop/Hydrus paper/hydrus_data_single_column.csv")
sims <- read.csv("C:/Users/arshores/Desktop/Hydrus paper/Hydrus Data/hydrus_mixing
zone.csv")
sims$depth<-as.factor(sims$depth)
sims$dimension<-as.factor(sims$dimension)
sims1= sims[sims$dimension == "1", ]
sims1ben= sims1[sims1$contaminant == "benzene", ]
sims1tol= sims1[sims1$contaminant == "toluene", ]
clayloam1ben = sims1ben[sims1ben$soil.type == "clayloam", ]
sandyloam1ben = sims1ben[sims1ben$soil.type == "sandyloam", ]
library(ggplot2)
#clay loam facet graph all intensities and depths
clayloam1$intensity <- factor(clayloam1$intensity, levels = c("high", "medium",
"low"),labels=c("High","Medium","Low"))
clayloamfacet=ggplot(clayloam1,aes(time,concentration,group=depth.watertable, na.rm=TRUE))
+xlabs("Time(days)") +
ylab(bquote('Concentration ('*mu*'g' / cm^3*')))+
#annotate("text", x = 51, y = 0.1, label = "EPA Limit")+
facet_grid(~intensity)+
scale_x_continuous(limits = c(44,60), expand = c(.1,.1), breaks=seq(44,60,2))+
theme_bw()+ #background is white bw
geom_line(aes(linetype=depth.watertable, color=depth.watertable), size=1)+
scale_linetype_manual(values=c("twodash", "dotted","dashed"))+
scale_color_manual(values=c('red','green','blue'))+
geom_hline(yintercept = 0.005, linetype="solid", color="grey")+
theme( #working in the theme function. Functions are specified by () get rid of gridlines
panel.grid = element_blank(), #1, completely gets rid of the grid lines to it is just white
background, which is what you want
legend.position=c(0.7, 0.7),
legend.background = element_rect(colour = "grey"),
axis.title.y=element_text(size=15),
axis.title.x=element_text(size=15))
clayloamfacet + labs(fill = "Watertable Depth (ft)", linetype="Watertable Depth (ft)",
color="Watertable Depth (ft)")
#clayloam1$annotations = c("EPA Drinking Water Limit",rep("",10),"EPA Drinking Water Limit")
#clayloamfacet = clayloamfacet + geom_text(aes(x=2.5,y=2.5,label=annotations))
#ann_text<- data.frame(time =50, concentration= 0.01,lab = "Limit", #intensity = factor("Low",
levels = c("Low","Medium","High")))
#clayloamfacet + geom_text(data = ann_text,label = "text")
library(ggplot2)
```

```

#graphing all contaminants for sandyloam and clayloam at 1 ft high intensity
sims_allcont <- read.csv("C:/Users/arshores/Desktop/Hydrus
paper/btexn_clayandsandy_1ft_high.csv")
str(sims_allcont)
sims_allcont$Contaminant <- factor(sims_allcont$Contaminant, levels = c("benzene", "toluene",
"ethylbenzene","xylene","naphthalene"))
sims_allcont$soil.type <- factor(sims_allcont$soil.type, levels = c("clayloam",
"sandyloam"),labels=c("Clay Loam","Sandy Loam"))
sims_allcont[!rowSums(sims_allcont[3] <40),]
#comparing 3D and 1D benzene sandyloam
allsims <- read.csv("C:/Users/arshores/Desktop/Hydrus paper/Hydrus data/hydrus_mixing
zone.zero.csv")
str(allsims)
allsims$dimension<-as.factor(allsims$dimension)
allsims$depth.m<-as.factor(allsims$depth.m)
allsims1 = allsims[allsims$intensity == "high", ]
allsims2 = allsims1[allsims1$soil.type == "sandyloam", ]
allsims3 = allsims2[allsims2$contaminant == "benzene", ]
#allsims = allsims[allsims$depth.watertable == "10", ]
allsims3$dimension <- factor(allsims3$dimension, levels = c("1", "3"),labels=c("1D","3D"))
dimensionbenzene=ggplot(allsims3,aes(time.zero,concentration,group=depth.m, na.rm=TRUE))
+xlabs("Time(days)") +
ylab(bquote('Concentration ('*mu*'g' / cm^3*')))+
facet_grid(~dimension)+
scale_x_continuous(limits = c(38,60), expand = c(.1,.1), breaks=seq(38,120,4))+
theme_bw()+ #background is white bw
geom_line(aes(linetype=depth.m, color=depth.m), size=1)+
geom_hline(yintercept = 0.005, linetype="twodash", color="grey")+
theme(
legend.position=c(0.5, 0.28),
legend.background = element_rect(colour = "grey"))
dimensionbenzene
dimensionbenzene + labs(linetype="Water table Depth (cm)", color="Water table Depth (cm)")
#comparing toluene in sandyloam in 1D and 3D at all depths to water table
allsimstoluene <- read.csv("C:/Users/arshores/Desktop/Hydrus
paper/hydrus_data_1_24_17.csv")
str(allsims)
allsimstoluene = allsimstoluene[allsimstoluene$intensity == "high", ]
allsimstoluene = allsimstoluene[allsimstoluene$soil.type == "sandyloam", ]
allsimstoluene = allsimstoluene[allsimstoluene$contaminant == "toluene", ]
#allsims = allsims[allsims$depth.watertable == "10", ]
allsimstoluene$dimension<-as.factor(allsimstoluene$dimension)
allsimstoluene$depth.watertable<-as.factor(allsimstoluene$depth.watertable)

```

```

allsimstoluene$dimension <- factor(allsimstoluene$dimension, levels = c("1",
"3"),labels=c("1D","3D"))
dimensiontoluene=ggplot((allsimstoluene[!rowSums(allsimstoluene[1]
<45),]),aes(time,concentration,group=depth.watertable, na.rm=TRUE)) +
xlab("Time(days)") +
ylab(bquote('Toluene Concentration ('*mu*'g' / cm^3*')))+
facet_grid(~dimension)+
scale_x_continuous(limits = c(38,60), expand = c(.1,.1), breaks=seq(38,120,4))+
theme_bw()+ #background is white bw
geom_line(aes(linetype=depth.watertable, color=depth.watertable), size=1)+
geom_hline(yintercept = 1, linetype="twodash", color="grey")+
#scale_linetype_manual(values=c("twodash", "twodash", "twodash", "dotted", "dashed"))+
#scale_color_manual(values=c('red','green','blue','purple','orange'))+
theme( #working in the theme function. Functions are specified by () get rid of gridlines
# panel.grid = element_blank(), #1, completely gets rid of the grid lines to it is just white
background, which is what you want
legend.position=c(0.5, 0.28),
legend.background = element_rect(colour = "grey"))
dimensiontoluene
dimensiontoluene + labs(linetype="Watertable Depth (ft)", color="Watertable Depth (ft)")
(allsimstoluene[!rowSums(allsimstoluene[1] <45),])
# facet graph of sandy loam ben and tol using 3D for 5 ft and 10 ft and 1D for 1 ft
allsims1D3D <- read.csv("C:/Users/arshores/Desktop/Hydrus paper/hydrus data/hydrus_mixing
zone.zero.csv")
allsims1D3D = allsims1D3D[allsims1D3D$soil.type == "sandyloam", ]
allsims3D = allsims1D3D[allsims1D3D$dimension == "3", ]
allsims1D = allsims1D3D[allsims1D3D$dimension == "1", ]
allsims1Dlow = allsims1D[allsims1D$intensity == "low", ]
allsims1D1ft = allsims1D[allsims1D$depth == "1", ]
allsims1Dmed = allsims1D1ft[allsims1D1ft$intensity == "medium", ]
allsims1Dhigh = allsims1D1ft[allsims1D1ft$intensity == "high", ]
allsims3D5 = allsims3D[allsims3D$depth == "5", ]
allsims3D10 = allsims3D[allsims3D$depth == "10", ]
allsims3D5med = allsims3D5[allsims3D5$intensity == "medium", ]
allsims3D5high = allsims3D5[allsims3D5$intensity == "high", ]
allsims3D10med = allsims3D10[allsims3D10$intensity == "medium", ]
allsims3D10high = allsims3D10[allsims3D10$intensity == "high", ]
allsims1D1 = allsims1D[allsims1D$depth == "1", ]
allsims1Dlow = allsims1D[allsims1D$intensity == "low", ]
D3Dsandy =
rbind(allsims1Dlow,allsims1Dmed,allsims1Dhigh,allsims3D5med,allsims3D5high,allsims3D10med
,allsims3D10high)
D3Dsandy$intensity <- factor(D3Dsandy$intensity, levels = c("high", "medium",
"low"),labels=c("High Intensity","Medium Intensity","Low Intensity"))

```

```

D3Dsandy$depth.m <- as.factor(D3Dsandy$depth.m)
D3Dsandy$dimension<-as.factor(D3Dsandy$dimension)
D3Dsandy$contaminant <- factor(D3Dsandy$contaminant, levels = c("benzene",
"toluene"),labels=c("Benzene","Toluene"))
str(D3Dsandy)
bensand = D3Dsandy[D3Dsandy$contaminant == "Benzene", ]
tolsand = D3Dsandy[D3Dsandy$contaminant == "Toluene", ]
#sim of sandy loam with benzene and toluene faceted
#Partially 3D and 1D sims
#only benzene sandy loam 1D and 3D
allsim_no3D1ft=ggplot(bensand,aes(time.zero,concentration,group=depth.m, na.rm=TRUE)) +
xlab("Time(days)") +ylab(bquote('Concentration ('*mu*'g' / cm^3*')))+
facet_wrap(~intensity, scales="free")+
scale_x_continuous(limits = c(0,40), expand = c(.1,.1), breaks=seq(0,40,5))+
theme_bw()+
geom_line(aes(linetype=depth.m, color=depth.m), size=1)+
geom_hline(yintercept = 0.005)+
theme(
panel.grid = element_blank(),
legend.background = element_blank())
allsim_no3D1ft
allsim_no3D1ft + labs(linetype="Depth to Water Table (cm)", color="Depth to Water Table (cm)")
ggsave("Fig3.tiff", units="in", width=10, height=4, dpi=150)
#only toluene sandy loam 1D and 3D
allsim_no3D1ft=ggplot(tolsand,aes(time.zero,concentration,group=depth.m, na.rm=TRUE)) +
xlab("Time(days)") +
ylab(bquote('Concentration ('*mu*'g' / cm^3*')))+
facet_wrap(~intensity, scales="free")+
scale_x_continuous(limits = c(0,40), expand = c(.1,.1), breaks=seq(0,40,5))+
theme_bw()+
geom_line(aes(linetype=depth.m, color=depth.m), size=1)+
geom_hline(yintercept = 1)+
theme(
panel.grid = element_blank(),
legend.background = element_blank())
allsim_no3D1ft
allsim_no3D1ft + labs(linetype="Depth to Water Table (cm)", color="Depth to Water Table (cm)")
ggsave("Fig4.tiff", units="in", width=10, height=4, dpi=150)
#clay loam benzene and toluene
allsims1D3D <- read.csv("C:/Users/arshores/Desktop/Hydrus paper/hydrus data/hydrus_mixing
zone.zero.csv")
sim_clay = allsims1D3D[allsims1D3D$soil.type == "clayloam", ]
sim_clay$depth.m<-as.factor(sim_clay$depth.m)
sim_clay$dimension<-as.factor(sim_clay$dimension)

```

```

sim_clay$intensity <- factor(sim_clay$intensity, levels = c("high", "medium",
"low"),labels=c("High Intensity","Medium Intensity","Low Intensity"))
sim_clay$contaminant <- factor(sim_clay$contaminant, levels = c("benzene",
"toluene"),labels=c("Benzene","Toluene"))
benclay = sim_clay[sim_clay$contaminant == "Benzene", ]
tolclay = sim_clay[sim_clay$contaminant == "Toluene", ]
clay=ggplot(benclay,aes(time.zero,concentration,group=depth.m, na.rm=TRUE)) +
xlab("Time(days)") +
ylab(bquote('Concentration ('*mu*'g' / cm^3*')))+
facet_wrap(~intensity, scales="free")+
scale_x_continuous(limits = c(0,40), expand = c(.1,.1), breaks=seq(0,40,5))+
theme_bw()+
labs(linetype="Depth to Water Table (cm)", color="Depth to Water Table (cm)")+
geom_line(aes(linetype=depth.m, color=depth.m), size=1)+
geom_hline(yintercept = 0.005)+ theme(
panel.grid = element_blank(),
legend.background = element_blank())
clay
ggsave("Fig5.tiff", units="in", width=10, height=4, dpi=150)
dev.off()
claytol=ggplot(tolclay,aes(time.zero,concentration,group=depth.m, na.rm=TRUE)) +
xlab("Time(days)") +
ylab(bquote('Concentration ('*mu*'g' / cm^3*')))+
facet_wrap(~intensity, scales="free")+
scale_x_continuous(limits = c(0,40), expand = c(.1,.1), breaks=seq(0,40,5))+
theme_bw()+
geom_line(aes(linetype=depth.m, color=depth.m), size=1)+
#geom_hline(yintercept = 1)+
theme(
panel.grid = element_blank(),
legend.background = element_blank())
claytol
claytol + labs(linetype="Depth to Water Table (cm)", color="Depth to Water Table (cm)")
ggsave("Fig6.tiff", units="in", width=10, height=4, dpi=150)
#all containants clay and sandy loam high intensity 1 ft
shallow <- read.csv("C:/Users/arshores/Desktop/Hydrus paper/hydrus data/all contaminants
sandy clay 1 ft high intensity.csv")
shallow$contaminant<-as.factor(shallow$contaminant)
shallow$contaminant <- factor(shallow$contaminant, levels = c("benzene", "toluene",
"ethylbenzene", "xylene", "naphthalene"))
shallow$soil <- factor(shallow$soil, levels = c("sandyloam", "clayloam"),labels=c("Sandy
Loam","Clay Loam"))
str(shallow)
#both soil types and all contaminants at 30 cm below the ground

```

```

#shallow groundwater all contaminants in both soil ---with only the peak
shallow <- read.csv("C:/Users/arshores/Desktop/Hydrus paper/hydrus data/all contaminants
sandy clay 1 ft high intensity.onlypeak.csv")
shallow$contaminant<-as.factor(shallow$contaminant)
shallow$contaminant <- factor(shallow$contaminant, levels = c("benzene", "toluene",
"ethylbenzene", "xylene", "naphthalene"))
shallow$soil <- factor(shallow$soil, levels = c("sandyloam", "clayloam"),labels=c("Sandy
Loam","Clay Loam"))
str(shallow)
#shallow groundwater all contaminants in both soil ---with only the peak
shallowgw=ggplot(shallow,aes(time.zero,concentration,color=contaminant, na.rm=TRUE)) +
geom_line(aes(linetype=contaminant, color=contaminant), size=1)+
xlab("Time(days)") +
ylab(bquote('Concentration ('*mu*'g' / cm^3*')))+
facet_wrap(~soil, scales="free")+
#scale_x_continuous(limits = c(0,4), expand = c(.1,.1), breaks=seq(0,4,0.5))+
theme_bw()+geom_hline(yintercept = 0.005, linetype="solid", color="black")+
theme(
panel.grid = element_blank(),
legend.background = element_rect(colour = "grey"))
shallowgw
shallowgw + labs(linetype="Contaminant", color="Contaminant")
ggsave("Fig1.tiff", units="in", width=7, height=3, dpi=300)
allcont=ggplot((shallow[!rowSums(shallow[3]
<40),]),aes(time,concentration,group=contaminant, na.rm=TRUE)) +
xlab("Time(days)") +
ylab(bquote('Concentration ('*mu*'g' / cm^3*')))+
#annotate("text", x = 51, y = 0.1, label = "EPA Limit")+
facet_grid(~soil)+
scale_x_continuous(limits = c(38,60), expand = c(.1,.1), breaks=seq(38,60,2))+
theme_bw()+ #background is white bw
geom_line(aes(linetype=Contaminant, color=Contaminant), size=1)+
scale_linetype_manual(values=c("twodash", "twodash", "twodash", "dotted", "dashed"))+
scale_color_manual(values=c('red','green','blue','purple','orange'))+
#scale_fill_manual(legend_title) +
geom_hline(yintercept = 0.005, linetype="twodash", color="grey")+
geom_hline(yintercept = 1, linetype="twodash", color="grey")+
theme( #working in the theme function. Functions are specified by () get rid of gridlines
panel.grid = element_blank(), #1, completely gets rid of the grid lines to it is just white
background, which is what you want
legend.position=c(0.25, 0.7),
legend.background = element_rect(colour = "grey"))
allcont
#profile of clay loam 10ft benzene high intensity

```



```

profile <- read.csv("C:/Users/arshores/Desktop/Hydrus paper/hydrus
data/profile_highintensity_clayloam_10ft_format.csv")
profile$day <- factor(profile$day, levels = c("60", "100",
"150", "200"), labels=c("15", "85", "135", "185"))
profile$day<-as.factor(profile$day)
str(profile)
profileben=ggplot(profile,aes(depth,concentration,color=day, na.rm=TRUE)) +
coord_flip()+
ylab(bquote('Concentration ('*mu*'g' / cm^3*')))+
xlab("Depth Below Surface (cm)") +
#facet_wrap(~intensity, scales="free")+
#scale_x_continuous(limits = c(38,100), expand = c(.1,.1), breaks=seq(38,120,10))+
theme_bw()+
geom_line()+
geom_line(aes(linetype=day, color=day), size=1)+
geom_hline(yintercept=0.005, linetype="twodash", color="blue")+
scale_colour_grey()+
theme(
panel.grid = element_blank(),
legend.background = element_rect(colour = "grey"))
profileben
profileben + labs(linetype="Time after Spill", color="Time after Spill")
ggsave("Fig8.tiff", units="in", width=4, height=3, dpi=150)
profiles1 <- read.csv("C:/Users/arshores/Desktop/Hydrus paper/hydrus
data/sandyloam_profile.csv")
profiles1$day<-as.factor(profiles1$day)
str(profile)
profilebens1=ggplot(profiles1,aes(depth,concentration,color=day, na.rm=TRUE)) +
coord_flip()+
ylab(bquote('Concentration ('*mu*'g' / cm^3*')))+
xlab("Depth Below Surface (cm)") +
#facet_wrap(~intensity, scales="free")+
#scale_x_continuous(limits = c(38,100), expand = c(.1,.1), breaks=seq(38,120,10))+theme_bw()+
geom_line()+
geom_line(aes(linetype=day, color=day), size=1)+
geom_hline(yintercept=0.005, linetype="twodash", color="blue")+
scale_colour_grey()+
theme(
panel.grid = element_blank(),
legend.background = element_rect(colour = "grey"))
profilebens1
profilebens1 + labs(linetype="Time after Spill", color="Time after Spill")
ggsave("Fig9.tiff", units="in", width=4, height=3, dpi=150)
dimensioncompare <- read.csv("C:/Users/arshores/Desktop/Hydrus paper/3d.1d.ben.csv")

```

```

dimensioncompare$intensity <- factor(dimensioncompare$intensity, levels = c("high",
"medium","low"),labels=c("High Intensity","Medium Intensity", "Low Intensity"))
dimensioncompare$depth <-as.factor(dimensioncompare$depth)
str(dimensioncompare)
dimensioncompare$D<-as.factor(dimensioncompare$D)
dim=ggplot(dimensioncompare,aes(depth,conc, fill=contaminant)) +
facet_wrap(~intensity, scales="free")+
ylab(bquote('Peak Concentration ('*mu*'g' / cm^3*')'))+
xlab("Depth Below Surface (cm)") +
theme_bw()+
geom_point(aes(shape=contaminant), size=3.5)+
# geom_hline(yintercept=0.005)+
#geom_hline(yintercept=1)+
scale_shape_manual(values=c(17, 16, 2, 1))+
theme(
panel.grid = element_blank(),
legend.background = element_blank())
dim+labs( color="Contaminant and Dimension", fill="Contaminant and Dimension",
shape="Contaminant and Dimension")
ggsave("Fig2.tiff", units="in", width=10, height=4, dpi=600)

```

## 8.23 PHYTOREMEDIATION OF BTEX AND NAPHTHALENE FROM PRODUCED-WATER SPILL SITES

### USING POACEAE

```

#Comparing soil control with soil from foxtail barley and perennial ryegrass treatments at days 7
and 14 after the surface produced water spill
soil=read.table("C:/Users/arshores/Desktop/phytodata/longformat_soil_difference.csv",header=
T,sep=";",quote="", stringsAsFactors = FALSE)
#Create separate files for each contaminant in the control and treatment soils
bensoil=soil_diff[soil_diff$contaminant == "benzene", ]
tolsoil=soil_diff[soil_diff$contaminant == "toluene", ]
ethsoil=soil_diff[soil_diff$contaminant == "ethylbenzene", ]
xylsoil=soil_diff[soil_diff$contaminant == "xylene", ]
napsoil=soil_diff[soil_diff$contaminant == "naphthalene", ]
library(lsmmeans)
#ANCOVA comparing benzene in treatment and control soil at day 7 and 14
soilcompareben <- lm(log10(control.diff+1000) ~ day.after.exposure*species+siblings,
data=bensoil)
anova(lm(soilcompareben))
summary(soilcompareben)
lsmmeans(soilcompareben, pairwise ~day.after.exposure|species)
lsmmeans(soilcompareben, pairwise ~species|day.after.exposure)

```

*#ANCOVA model evaluating and determining if assumptions are met: Comparing the effect of treatment soil and control soil over time to see how benzene is affected.*

```
plot(soilcompareben)
qqPlot(residuals(soilcompareben))
hist(residuals(soilcompareben))
range(residuals(soilcompareben))
p <- qqplot(siblings, control.diff, shape = species, color = day.after.exposure, data = bensoil)
p + geom_smooth(method = "lm", se = FALSE, fullrange = T)
```

*#ANCOVA comparing toluene in treatment and control soil at day 7 and 14*

```
soilcomparetol <- lm(log10(control.diff+1000) ~ day.after.exposure*species+siblings,
data=tolsoil)
anova(lm(soilcomparetol))
summary(soilcomparetol)
```

```
lsmeans(soilcomparetol, pairwise ~ species | day.after.exposure)
```

```
lsmeans(soilcomparetol, pairwise ~ day.after.exposure | species)
```

```
p <- qqplot(siblings, control.diff, shape = species, color = day.after.exposure, data = tolsoil)
p + geom_smooth(method = "lm", se = FALSE, fullrange = T)
```

*#ANCOVA model evaluating and determining if assumptions are met: Comparing the effect of treatment soil and control soil over time to see how toluene is affected.*

```
plot(soilcomparetol)
qqPlot(residuals(soilcomparetol))
hist(residuals(soilcomparetol))
range(residuals(soilcomparetol))
```

*#ANCOVA comparing ethylbenzene in treatment and control soil at day 7 and 14*

```
soilcompareeth <- lm(log10(control.diff+1000) ~ day.after.exposure*species+siblings,
data=ethsoil)
anova(lm(soilcompareeth))
summary(soilcompareeth)
```

```
lsmeans(soilcompareeth, pairwise ~ species | day.after.exposure)
```

```
lsmeans(soilcompareeth, pairwise ~ day.after.exposure | species)
```

```
p <- qqplot(siblings, control.diff, shape = species, color = day.after.exposure, data = ethsoil)
p + geom_smooth(method = "lm", se = FALSE, fullrange = T)
```

*#ANCOVA model evaluating and determining if assumptions are met: Comparing the effect of treatment soil and control soil over time to see how ethylbenzene is affected.*

```
plot(soilcompareeth)
qqPlot(residuals(soilcompareeth))
hist(residuals(soilcompareeth))
range(residuals(soilcompareeth))
```

*#ANCOVA comparing xylene in treatment and control soil at day 7 and 14*

```
soilcomparexyl <- lm(log10(control.diff+1000) ~ day.after.exposure*species+siblings,
data=xylsoil)
```

```
anova(lm(soilcomparexyl))
```

```
summary(soilcomparexyl)
```

```
plot(soilcomparexyl)
```

```

hist(residuals(soilcomparexyl))
lsmeans(soilcomparexyl, pairwise ~ species | day.after.exposure)
lsmeans(soilcomparexyl, pairwise ~ day.after.exposure | species)
p <- qplot(siblings, control.diff, shape = species, color = day.after.exposure, data = xylsoil)
p + geom_smooth(method = "lm", se = FALSE, fullrange = T)
#ANCOVA model evaluating and determining if assumptions are met: Comparing the effect of
treatment soil and control soil over time to see how xylene is affected.
plot(soilcomparexyl)
qqPlot(residuals(soilcomparexyl))
hist(residuals(soilcomparexyl))
range(residuals(soilcomparexyl))
#ANCOVA comparing naphthalene in treatment and control soil at day 7 and 14
soilcomparenap <- lm(log10(control.diff+10000) ~ day.after.exposure*species+siblings,
data=napsoil)
anova(lm(soilcomparenap))
summary(soilcomparenap)
lsmeans(soilcomparenap, pairwise ~ day.after.exposure | species)
#ANCOVA model evaluating and determining if assumptions are met: Comparing the effect of
treatment soil and control soil over time to see how naphthalene is affected.
plot(soilcomparenap)
qqPlot(residuals(soilcomparenap))
hist(residuals(soilcomparenap))
range(residuals(soilcomparenap))
p <- qplot(siblings, control.diff, shape = species, color = day.after.exposure, data = napsoil)
p + geom_smooth(method = "lm", se = FALSE, fullrange = T)
#Creating files separate files for each contaminant to evaluate a particular contaminants'
differences between root and shoot tissue over time in each species
long_format_bt看_tissue <-
read.table("C:/Users/arshores/Desktop/phytodata/long_format_bt看_tissue.csv",header=T,sep=
",",quote="", stringsAsFactors = FALSE)
long_format_bt看_tissue$day.after.exposure<-
as.factor(long_format_bt看_tissue$day.after.exposure)
bentiss=long_format_bt看_tissue[long_format_bt看_tissue$contaminant == "benzene", ]
toltiss=long_format_bt看_tissue[long_format_bt看_tissue$contaminant == "toluene", ]
ethtiss=long_format_bt看_tissue[long_format_bt看_tissue$contaminant == "ethylbenzene", ]
xyltiss=long_format_bt看_tissue[long_format_bt看_tissue$contaminant == "xylene", ]
naptiss=long_format_bt看_tissue[long_format_bt看_tissue$contaminant == "naphthalene", ]
#ANCOVA comparing differences in benzene between root and shoot tissue over time in both
species. Checking assumptions of model are satisfied.
bentisscompare<-lm(total.mass ~ day.after.exposure*fraction.tested*species*siblings,
data=bentiss)
plot(bentisscompare)
anova(lm(bentisscompare))
lsmeans(bentisscompare, pairwise~day.after.exposure*fraction.tested*species*siblings)

```

```

lsmeans(bentisscompare, pairwise ~ fraction.tested | species | day.after.exposure)
#ANCOVA comparing differences in toluene between root and shoot tissue over time in both
species. Checking assumptions of model are satisfied.
toltisscompare<-lm(log10(total.mass) ~ day.after.exposure*fraction.tested*species*siblings,
data=toltiss)
plot(toltisscompare)
anova(lm(toltisscompare))
lsmeans(toltisscompare, pairwise~day.after.exposure*fraction.tested*species*siblings)
lsmeans(toltisscompare, pairwise ~ species | fraction.tested | day.after.exposure)
#ANCOVA comparing differences in ethylbenzene between root and shoot tissue over time in both
species. Checking assumptions of model are satisfied.
ethtisscompare<-lm(log10(total.mass) ~ day.after.exposure*fraction.tested*species,
data=ethtiss)
plot(ethtisscompare)
qqPlot(residuals(ethtisscompare))
hist(residuals(ethtisscompare))
range(residuals(ethtisscompare))
anova(lm(ethtisscompare))
lsmeans(ethtisscompare, pairwise~day.after.exposure*fraction.tested*species)
lsmeans(ethtisscompare, pairwise ~ fraction.tested | species | day.after.exposure)
#ANCOVA comparing differences in xylene between root and shoot tissue over time in both
species. Checking assumptions of model are satisfied.
xyltisscompare<-lm(log10(total.mass) ~ day.after.exposure*fraction.tested*species*siblings,
data=xyltiss)
str(xyltiss)
anova(lm(xyltisscompare))
qqPlot(residuals(xyltisscompare))
hist(residuals(xyltisscompare))
range(residuals(xyltisscompare))
plot(xyltisscompare)
lsmeans(xyltisscompare, pairwise~day.after.exposure*fraction.tested*species*siblings)
lsmeans(xyltisscompare, pairwise ~ day.after.exposure | fraction.tested | species)
#ANCOVA comparing differences in naphthalene between root and shoot tissue over time in both
species. Checking assumptions of model are satisfied.
naptisscompare<-lm(log10(total.mass) ~ day.after.exposure*fraction.tested*species*siblings,
data=naptiss)
plot(naptisscompare)
hist(residuals(naptisscompare))
lsmeans(naptisscompare, pairwise~day.after.exposure*fraction.tested*species*siblings)
nap=lsmeans(naptisscompare, pairwise ~ fraction.tested | day.after.exposure | species)
#Creating files to analyze root/shoot contaminant differences
library(lme4)
library(lmerTest)
library(lsmeans)

```

```

library(plyr)
master_doc_GC_MS_BTEXN <-
read.table("C:/Users/Amanda/Desktop/phytodata/master_doc_GC_MS_BTEXN.csv",header=T,se
p=";",quote="", stringsAsFactors = FALSE)
master_doc_GC_MS_BTEXN$day.after.exposure<-
as.factor(master_doc_GC_MS_BTEXN$day.after.exposure)
tissue=master_doc_GC_MS_BTEXN[master_doc_GC_MS_BTEXN$fraction == "tissue", ]
# Checking interaction plots. Looking to see if the number of siblings in a plot differentially
effects the amount of contaminant found in each tissue type at different days.
p <- qplot(siblings, benzene.total.fraction, color = day.after.exposure, data = tissue)
p +geom_smooth(method = "lm", se = FALSE, fullrange =
T)+facet_grid(benzene.total.fraction~fraction.tested)+facet_grid(benzene.total.fraction~species)
p <- qplot(siblings, toluene.total.fraction, shape = fraction.tested, color = day.after.exposure,
fill=species, data = tissue)
p + geom_smooth(method = "lm", se = FALSE, fullrange = T)
p <- qplot(siblings, ethylbenzene.total.fraction, shape = fraction.tested, color =
day.after.exposure, fill=species, data = tissue)
p + geom_smooth(method = "lm", se = FALSE, fullrange = T)
p <- qplot(siblings, xylene.total.fraction, shape = fraction.tested, color = day.after.exposure,
fill=species, data = tissue)
p + geom_smooth(method = "lm", se = FALSE, fullrange = T)
p <- qplot(siblings, naphthalene.total.fraction, shape = fraction.tested, color = species,
fill=day.after.exposure, data = tissue)
p + geom_smooth(method = "lm", se = FALSE, fullrange = T)
#repeated measures-alternative to ANCOVAs for plant tissue contaminant concentrations. Tissue
type over time is treated as a repeated measure
root.shoot.ben=lmer(log10(benzene.total.fraction) ~species * day.after.exposure *
fraction.tested + (1|ID), data=tissue)
plot(root.shoot.ben)
root.shoot.tol=lmer(toluene.total.fraction ~species * day.after.exposure * fraction.tested +
(1|ID), data=tissue)
plot(root.shoot.tol)
root.shoot.eth=lmer(log10(ethylbenzene.total.fraction) ~species * day.after.exposure *
fraction.tested + (1|ID), data=tissue)
plot(root.shoot.eth)
root.shoot.xyl=lmer(xylene.total.fraction ~species * day.after.exposure * fraction.tested + (1|ID),
data=tissue)
plot(root.shoot.xyl)
root.shoot.nap=lmer(log10(naphthalene.total.fraction) ~species * day.after.exposure *
fraction.tested + (1|ID), data=tissue)
plot(root.shoot.nap)
anova(root.shoot.ben, ddf="Kenward-Roger")
lsmeans(root.shoot.ben, pairwise~ species|day.after.exposure*fraction.tested)
anova(root.shoot.tol, ddf="Kenward-Roger")

```

```

lsmeans(root.shoot.tol, pairwise~ species| day.after.exposure*fraction.tested)
anova(root.shoot.eth, ddf="Kenward-Roger")
lsmeans(root.shoot.eth, pairwise~ species| day.after.exposure*fraction.tested)
anova(root.shoot.xyl, ddf="Kenward-Roger")
lsmeans(root.shoot.xyl, pairwise~ species| day.after.exposure*fraction.tested)
anova(root.shoot.nap, ddf="Kenward-Roger")
lsmeans(root.shoot.nap, pairwise~ species| day.after.exposure*fraction.tested)
#Preparing file for biomass comparison with different treatments
wetbiomass <-
read.table("C:/Users/Amanda/Desktop/phytodata/wetbiomass.csv",header=T,sep=","quote="",
stringsAsFactors = FALSE)
wetbiomass$species<-as.factor(wetbiomass$species)
wetbiomass$treatment<-as.factor(wetbiomass$treatment)
wetbiomass$fraction<-as.factor(wetbiomass$fraction)
str(wetbiomass)
wetweightfb = wetbiomass[wetbiomass$species == "fb", ]
wetweightpr = wetbiomass[wetbiomass$species == "pr", ]
wetweightfbroot = wetweightfb[wetweightfb$fraction == "root", ]
wetweightfbshoot = wetweightfb[wetweightfb$fraction == "shoot", ]
wetweightprroot = wetweightpr[wetweightpr$fraction == "root", ]
wetweightprshoot = wetweightpr[wetweightpr$fraction == "shoot", ]
#statistically analyzing differences between biomass across treats in one species and one tissue
type
fbshoot<- lm(log10(mass) ~ treatment, data=wetweightfbshoot)
anova(lm(fbshoot))
lsmeans(fbshoot, pairwise ~ treatment)
plot(fbshoot)
fbroot<- lm(log10(mass) ~ treatment, data=wetweightfbroot)
anova(lm(fbroot))
lsmeans(fbroot, pairwise ~ treatment)
plot(fbroot)
prshoot<- lm(log10(mass) ~ treatment, data=wetweightprshoot)
anova(lm(prshoot))
lsmeans(prshoot, pairwise ~ treatment)
plot(prshoot)
prroot<- lm(log10(mass) ~ treatment, data=wetweightprroot)
anova(lm(prroot, type=3))
lsmeans(prroot, pairwise ~ treatment)
plot(prroot)
#graphing control soil data (all 5 contaminants on one graph)
library(plyr)
long_form_masterdoc <-
read.table("C:/Users/arshores/Desktop/phytodata/long_format_btex_data.csv",header=T,sep=","quote="", stringsAsFactors = FALSE)

```

```

str(long_form_masterdoc)
longformat_controlsoil = long_form_masterdoc[long_form_masterdoc$fraction.tested ==
"Control soil", ]
str(longformat_controlsoil)
longformat_controlsoil_summary<-ddply(longformat_controlsoil, c( "day.after.exposure",
"contaminant"), summarise, N= length(concentration), mean=mean(concentration), sd=
sd(concentration), se= sd/sqrt(N))
longformat_controlsoil_summary$contaminant<-
factor(longformat_controlsoil_summary$contaminant, levels=c("benzene", "toluene",
"ethylbenzene","xylene","naphthalene"))
library(ggplot2)
ggplot(longformat_controlsoil_summary, aes(x=day.after.exposure, y=log10(mean),
fill=contaminant, type="b")) +
geom_line(aes(linetype=contaminant))+
geom_point(size=0.3) +
theme_bw()+
xlab("Time after Exposure (days)") +
ylab("Log10 Concentration (ng/g soil)")+
geom_errorbar(aes(ymin=log10(mean-se), ymax=log10(mean+se)), width=.1)+
theme( #working in the theme function. Functions are specified by () get rid of gridlines
legend.key=element_blank(),
panel.grid.major = element_blank(), panel.grid.minor = element_blank())
#Graphing the change in soil total mass of each contaminant in treatment soil versus control soil
lsmeans <-
read.table("C:/Users/arshores/Desktop/phytodata/lsmeans_summary.csv",header=T,sep="," ,quote="" ,
stringsAsFactors = FALSE)
lsmeans$contaminant<-factor(lsmeans$contaminant, levels=c("benzene", "toluene",
"ethylbenzene","xylene","naphthalene"))
lsmeans$species <- factor(lsmeans$species, levels = c("fb", "pr"), labels=c("foxtail
barley","perennial ryegrass"))
lsmeans$day.after.exposure <- factor(lsmeans$day.after.exposure, levels = c("7", "14"),
labels=c("Day 7","Day 14"))
ggplot(data=lsmeans, aes(x=species, y= mean.1)) +
geom_bar(stat="identity", width=0.5) + facet_grid(contaminant~day.after.exposure,
scales="free") +
geom_hline(yintercept = 0, linetype="solid")+
xlab("Treatment") +
ylab("Change in Total Contaminant Mass (ng)")+
theme_bw() +
geom_errorbar(aes(ymin=mean.1-se, ymax=mean.1+se), width=.1, position=pd)
#Graphing root/shoot tissue contaminant concentrations over time for both species
tissue.siblings<-
read.table("C:/Users/arshores/Desktop/phytodata/tissue.siblings.1.csv",header=T,sep="," ,quote="" ,
stringsAsFactors = FALSE)

```



```

tissue.siblings$day.after.exposure<-as.factor(tissue.siblings$day.after.exposure)
tissue.siblings$contaminant<-factor(tissue.siblings$contaminant, levels=c("benzene", "toluene",
"ethylbenzene","xylene","naphthalene"))
tissue.siblings$fraction.tested<-factor(tissue.siblings$fraction.tested, levels=c("shoot", "root"))
tissue.siblings[tissue.siblings$fraction.tested == "shoot", ] =
transform(tissue.siblings[tissue.siblings$fraction.tested == "shoot", ],
ybegin = ybegin + tissue.siblings[tissue.siblings$fraction.tested == "root", "mean"],
yend = yend + tissue.siblings[tissue.siblings$fraction.tested == "root", "mean"])
library(ggplot2)
library(digest)
cols <- c("root" = "grey","shoot" = "black")
legend_title <- "Tissue Type"
pd <- position_dodge(0.3)
ggplot(data=tissue.siblings, aes(x=day.after.exposure, y= mean, fill=fraction.tested)) +
geom_bar(stat="identity", width=0.5) + facet_grid(contaminant~species, scales="free") +
xlab("Time after Exposure (days)") +
ylab("Total Mass of Contaminant in Each Tissue Fraction (ng)")+
theme_bw() +
scale_fill_manual(legend_title,values = cols) +
geom_errorbar(aes(ymin=ybegin , ymax= yend ),width=.3, position=pd)\
#Graphing biomass from no treatment, salt treatment and btex+salt
wetbiomass <-
read.table("C:/Users/arshores/Desktop/phytodata/wetbiomass.csv",header=T,sep="," ,quote="",
stringsAsFactors = FALSE)
str(wetbiomass)
wetbiomass$day.fraction<-as.factor(wetbiomass$fraction)
wetbiomass$species <- factor(wetbiomass$species, levels=c("fb", "pr"), labels=c("foxtail barley",
"perennial ryegrass"))
wetbiomass$treatment <- factor(wetbiomass$treatment, levels = c("control", "salt", "pw"),
labels=c("control","salt","salt + organics"))
wetbiosummary<-ddply(wetbiomass, c( "species", "fraction","treatment"), summarise, N=
length(mass), mean=mean(mass), sd= sd(mass), se= sd/sqrt(N))
wetbiosummary$fraction <- factor(wetbiosummary$fraction, levels = c("shoot", "root"))
library(ggplot2)
library(plyr)
ggplot(data=wetbiosummary, aes(x=treatment, y= mean)) +
geom_bar(stat="identity") + facet_grid(fraction~species)+
xlab("Treatment") +
ylab("Mass (g)/individual plant")+
theme_bw() +
geom_errorbar(aes(x = treatment,ymin = mean-se,ymax = mean+se),data=wetbiosummary,
width=0.25)

```