# THESIS

# PRODUCED WATER QUALITY CHARACTERIZATION AND PREDICTION FOR WATTENBERG FIELD

Submitted by

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### ABSTRACT

# PRODUCED WATER QUALITY CHARACTERIZATION AND PREDICTION FOR WATTENBERG FIELD

Produced water is the major Exploration &Production waste in oil and gas production operations on most onshore and offshore platforms. There are some concerns about the environmental impacts of produced water, because of the potential danger of large volume of water disposal by shale plays. Produced water is a complex mixture of dissolved and particulate inorganic and organic matters ranging from near freshwater quality to concentrated saline brine. The most abundant inorganic chemicals are calcium, magnesium, sodium and chloride. Other inorganic components, such as barium, strontium, boron, sulfate, carbonate and bicarbonate are also present in the produced water but at high concentrations. The dominant organic chemicals in most produced water are soluble low molecular weight organic acids and some aromatic hydrocarbons. Constituents of produced water vary a lot depending on a number of factors, including geographic locations, characteristics of formations (i.e. the depth of formation, porosity and permeability of formation rocks/sands, water content) and injected fracturing fluid. Since water is becoming a big issue in some arid areas and as regulations become more restrictive for disposal and reinjection, produced water reuse/recycle will be a solution to reduce the wastewater production and alleviate environmental effects. The main objective of this study was to statistically evaluate the produced water quality and to provide an assessment on the spatial distribution of specific groundwater quality parameters. Produced water samples were collected at 80 sample points (producing oil and gas wells) from May to August in 2012. pH,

conductivity, alkalinity, turbidity, total organic carbon, total nitrogen, and barium were tested at Colorado State University's Environmental Engineering lab; total dissolved solids (TDS), calcium, magnesium, sodium, potassium, strontium, boron, chloride and sulfate were measured in ACZ Laboratories Inc., Colorado. All the produced water samples were acidic with pH ranging from 5.1-6.8. TDS, cations, anions and organic carbons tested in our study varied a lot. Maps showing the spatial distributions of these parameters were made using ArcGIS. Linear correlations between chloride, conductivity/TDS, and cations (log) were shown, which made it possible to estimate unknown parameters. Spatial and temporal trends of pH, TDS and total organics together with inner relationships of ion concentrations could allow us to make predictions of produced water qualities. This project was the first phase of the development of a GIS application that will provide a tool that can benefit industry when making decisions regarding produced water recycling.

Keywords: produced water, Wattenberg filed, water quality, spatial interpolation, GIS application

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# **Chapter 1 Introduction**

Driven by new drilling technologies and hydraulic fracturing development, shale oil and gas is increasingly an unconventional natural gas source due to its abundant reserves and increasing fuel prices. One of the key challenges associated with shale oil and gas production is its environmental impact and the interplay between generated wastes and the environment. During the hydraulic fracturing process, a large amount of fluid, comprised of water and other added chemicals, is injected into the shale formations to extract shale gas, and as a result, a large amount of "wastewater", known as flowback and produced water will return to the surface together with the hydrocarbons. This released water, which usually contains formation water and fracture fluid, is high in dissolved solids, metals, and oil and grease, and can contaminate ground water or surface waters. Since environmental constraints have become stricter, adequate water treatment needs to be applied prior to surface disposal through underground reinjection or beneficial reuse to manage the excessive solids, metals and organic matter.

On the other hand, well drilling and completion require a large amount of water, and most of this fresh water comes from surface water, groundwater or municipal water. Since water is becoming an important issue, not only for water deficient regions, water reclamation is on the rise in the United States, and the techniques involved in this can be used in the shale oil and gas industry also.

Reusing produced water can reduce the demand for fresh water and change the waste into usable water resources. Appropriate treatment is a key factor to determine whether produced water recycling is economical or not, which will depend on the produced water quality and quantity. Water quality analysis is necessary to choose the "best" treatment processes for

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recycling. Since the chemical constituents of produced water, such as organic matter and total dissolved solids (TDS) vary with different formations and geological locations, it is impossible to implement the same treatment design at different locations. Therefore, treatment technologies would need to be customized for each area according to the water quality and quantity.

Meanwhile, to ensure that the reused water performs well as a fracture fluid and to prevent side effects, all the key water quality parameters involved should be determined and tested.

It is important to know the spatial and temporal behavior of produced water. Even though there are quite a few studies which investigate treatment methods for produced water, only a few papers have researched water quality characteristics and their spatial distribution and temporal variation. There is no research which combines the ArcGIS tools with water quality to predict the water quality for a specific point in order to study the water quality changes with time. Only a few shale gas plays are reusing flowback and produced water as fracture fluid or have a clear water quality standard.

This research aims to establish both a spatial and temporal water quality analysis, and to develop GIS tools to present the water quality distribution in order to recommend the best practical method of produced water recycling treatment. In this study, we focus on the flowback and produced water quality generated in the northern part of Wattenberg field in northern Colorado. Some chemical and physical tests will be conducted to examine the common constituents in the produced water. Also, we will study the differences in water quality over time, which may be attributed to the characteristics of the formations where the produced water originated.

A thorough overview of shale oil and gas (especially shale gas) development and applications of horizontal drilling and hydraulic fracture on the shale gas industry will be presented in

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Chapter 2. Water issues associated with shale oil/gas production, such as water demand for drilling and hydraulic fracture, produced water generation, produced water characteristics, and wastewater management, are summarized in chapter 2 as well as a brief geological introduction of Wattenberg field and the shale formation in Wattenberg field. The sampling plan, sample method, water sample measurement and analysis will be discussed in Chapter 3. Chapter 4 includes the results of many of the tests, and discusses the results of produced water quality, spatial distribution and temporal changes of major water components present in the produced water. Further GIS applications needed to establish a user-friendly interface web-based tool for water quality inquiries are also described.

#### **Chapter 2 Literature Review**

### 2.1 Unconventional natural oil and gas – Shale oil and gas development

Exploration and development of new resources of oil and gas has become a hot topic in recent years. Also, horizontal drilling and multi-stage fracturing technologies have made the production of oil and gas from unconventional resources possible, with very low permeability and low porosity.<sup>1</sup>

Among many unconventional natural oil and gas sources, shale and tight sands are considered to be the best newly developed oil and gas sources because of significant successes in extraction and production. (Figure 2.1) One kind of unconventional development that has gained attention and contributed to this increase is natural gas from shale formations which extend across the continental United States. Many gas companies are diverting their attention from the relatively easily accessible conventional reservoirs in order to gain access to the large volumes available the in shale formations even though they are difficult to develop.<sup>2</sup>

U.S. dry gas production trillion cubic feet per year



Fig 2.1, U.S. natural gas production, 1990-2035 (trillion cubic feet)<sup>3</sup>

Additions to natural gas production associated with shale gas activity have been instrumental in boosting overall wet gas proved reserves. Shale gas accounted for more than 90 percent of total net additions. Key shale states in 2009 include Arkansas (the Fayetteville Shale), Louisiana (the Haynesville), Oklahoma (the Woodford), Pennsylvania (the Marcellus), and Texas (the Barnett and Haynesville/Bossier).<sup>4</sup> The 11 percent increase in U.S. proved natural gas reserves took place during a low-price environment that resulted in negative revisions to existing reserves. This underscores the major improvements in shale gas exploration and production technologies (horizontal drilling coupled with hydraulic fracturing) and efficiency. Natural gas from shale represented 21 percent of U.S. gas reserves in 2009, with the majority coming from five major shale areas (see Figure 2.2).<sup>5</sup>



Fig 2.2, Estimated recoverable natural gas for major shale basins (TCF) in 2006 and 20086

North America has a large amount of shale gas, totaling about 5,146 Tcf (146 trillion cubic meters).<sup>7</sup> In the five major shale gas basins, Barnett basin, Fayetteville basin, Woodford basin, Haynesville basin and Marcellus basin, up to 3,760 trillion cubic feet of shale gas is stored underground and over 12% of the total shale gas is a recoverable resource.

Gas Shale Basins	Reso	urce	Recov	verable
	Tcf	Tcm	Tcf	Tcm
U.S. (5 Basins)	3,760	107	475	13
Canada (2 Basins)	1,380	39	240	7

Table 2.1, Shale gas endowments of North America

Table 2.1 makes a summary of shale gas endowments of North America. This table includes the total shale gas of 5 basins (Barnett, Fayetteville, Woodford, Haynesville and Marcellus) in the United States and 2 basins in Canada. Even though North America has an abundant endowment of shale gas, only a very small percentage of the available shale gas in the five major basins in the United States is being used. Detailed information of shale gas resources for five major shale plays in the United States is listed in table 2.2.

	Resource Endowment	Produced/Proved	Undeveloped Recoverable
Barnett	250	19	39
Fayetteville	320	3	50
Woodford	300	2	34
Haynesville	790	1	130
Marcellus	2,100	-	200
Total	3,760	25	453

Table 2.2, Shale gas resources within the United States

China is estimated to hold 15-30 trillion cubic meters of shale gas reserves, equal to or greater than those in the United States, <sup>8</sup> and the reserve of shale oil is about 31,567 billion tons.<sup>9</sup> Worldwide, the estimate of shale gas endowment is 16,110 Tcf (456 Tcm), about 40% of which would become recoverable, that is 6,350 Tcf.<sup>10</sup>

radio 210, resol tes or shale on monantae	Table 2.3,	Reserves	of shale	oil	worldwide <sup>11</sup>
-------------------------------------------	------------	----------	----------	-----	-------------------------

Continents		Known reserves (10 <sup>9</sup> bbl)			Total reserves $(10^9 \text{ bbl})$		
Rate of recovery		25-100	10-25	5-10	25-100	10-25	5-10
African		100	Little	Little	4000	80,000	450,000
Asia		90	14	-	5500	110,000	590,000
Australia and	New	Little	1	-	1000	20,000	100,000
Europe		70	6	-	1400	26,000	140,000
North America		600	1600	2200	3000	50,000	260,000
South America		50	750	-	2000	40,000	210,000
Total		910	2400	2200	17,000	325,000	1,750,000

Worldwide, although only a few shale oil reserves are known currently, North America, Africa and Asia have the biggest shale oil extraction potentials.

# 2.2 Current drilling and fracturing technology

Commercially productive gas shale reservoirs in the United States are found at altitudes between 500 and 11,000 feet, with poor porosity and permeability. Owing to the applications of new technology and field practices, shale gas production has experienced a great expansion. Though it has long been known that natural gas was embedded in shale rocks, it was only in 2002 and 2003 that the combination of two technologies working together – hydraulic fracturing and horizontal drilling –made recovering shale gas economically feasible and desirable.<sup>12</sup>

Hydraulic fracturing has proven to be the technology key to facilitating economic recovery of natural gas from shale. Hydraulic fracturing is a formation stimulation practice used to create additional permeability in a producing formation to allow natural gas to flow more easily toward the wellbore for purposes of production. Hydraulic fracturing can be used to overcome natural barriers to the flow of fluids. Barriers may include naturally low permeability common in shale formations or reduced permeability resulting from near wellbore damage caused by drilling activities. While methods of hydraulic fracturing continually change (mostly changes in the design process and updates to additives and propping agents), this technology is utilized by the natural gas industry to increase production and to support an ever increasing demand for energy.<sup>13</sup>

Water required for drilling and fracturing depends largely upon the type of wells being drilled. Usually, horizontal wells need much more water than vertical and directional wells due to the long distance. For each stage of a hydraulic fracture, an average of 5,000 gallons (119 bbl; diluted acid stage) up to 50,000 gallons (1190 bbl; prop stages) of frac fluid is needed, which means that the entire fracture operation would require approximately 2-4 million gallons of water, 3 million gallons (71,428 bbl) being most common. <sup>14</sup> A typical horizontal shale well requires a maximum of approximately 600,000 gallons (14,000 bbl) for drilling and 2-4 million gallons of water for hydraulic fracturing. For vertical and directional wells, water needed for fracturing is between 100,000 and 1,000,000 gallons (2,300 – 23,000 bbl). Also, substantial amounts of water are needed for hydraulic fracturing, usually several times more than for drilling.<sup>15</sup> Table 2.4 shows the estimated water needs for drilling and fracturing in four major shale gas plays.<sup>16</sup>

Shale gas play	Volume	of	drilling	Volume of fracturing	Total	volumes	of
	water per	well	(gal)	water per well (gal)	water	per well (g	al)
Barnett shale	400,000			2,300,000	2,700,	000	
Fayetteville shale	60,000			2,900,000	3,060,	000	
Haynesville shale	1,000,000	)		2,700,000	3,700,	000	
Marcellus shale	80,000			3,800,000	3,880,	000	

Table 2.4, Estimated water needs for drilling and fracturing wells in four major shale gas plays

\*volume data are approximate and may vary between wells

One of the challenges of the hydraulic fracturing process is the fact that it relies on the use of chemical additives to ensure that the fracturing functions well. Water consumed by hydraulic fracturing contains more than 99% water and sand, with extremely low probability of fracture fluid migration from the shale up to fresh water zones. Although the percentage of chemical additives in typical hydraulic fracture fluid is usually less than 0.5 percent by volume, the quantity of fluid used in these hydro-fractures is so large that the additives in a three million gallon hydro-fracture operation will be considerable.

## 2.3 Produced Water

Produced water is the largest wastewater stream in the oil exploration and production process. During well drilling and completion, some water will return to the surface, known as the fracturing flowback or produced water (a water based solution that flows back to the surface during and after the completion of hydraulic fracturing). There is no established way to define flowback and produced water. Sometimes they are identified according to the time of occurrence, the rate of return or the chemical composition.<sup>17</sup> Most of the flowback occurs quickly in the first seven to ten days, sometimes even shorter, while the rest can occur over a three to four week time period. Having a murky appearance from high levels of suspended particles (see figure 2.3), produced water often appears weeks after production and can last for years, with high TDS levels.



Horizontal Shale Flowback Rates

Fig 2.3, Flowback rate for Marcellus shale gas play

Both flowback and produced water are comprised of fracture fluid and formation water, but they have different concentrations of chemical components.

## 2.3.1 Water Volume

In 2007, onshore production in the United States generated an estimated 3.3 million  $m^3$  of PWs.<sup>18</sup> In the shale oil and gas plays, almost 2-30 barrels per day per well of produced water is co-generated with oil and gas, and this continues throughout the lifetime of a well.

Khatib and Verbeek <sup>19</sup> estimated that in 1999, about 77 billion barrels of produced water were generated worldwide for the whole year, which represents more than 200 million barrels per day for the entire world. Produced water volume annual estimates for onshore oil and gas wells in the United States for the years 1985, 1995, and 2001 were 21 billion bbl, 18 billion bbl, and 14 billion bbl, respectively.<sup>20</sup> Annual produced water volumes generated from the oil and gas industry are in the range of 15 to 20 billion barrels (1 bbl = 42 U.S. gallons), equivalent to a volume of 1.7 to 2.3 billion gallons generated daily.<sup>21</sup> In 1995, about 18 billion barrels of produced water was generated by U.S. onshore oil and gas operations.<sup>22</sup>

<b>`</b>				
	1985	1995	2002	2007
Total PW, 1000 bbl	20,608,505	17,922,200	14,160,325	20,995,174
Re-injection, 1000 bbl	-	16,488,424	-	19,945,416
Percent of re-injection, %	-	92%	-	95%
Discharge, 1000 bbl	-	1,433,776	-	1,049,758
Percent of discharge, %	-	8%	-	5%

Table 2.5, Annual onshore produced water generated in the United States

Different shale plays in diverse basins have different geological characteristics and occur in areas with very different water resources and water demand. For instance, in the Eagle Ford basin, located in Texas, there is nearly no flowback water after hydraulic fracturing, while in the Marcellus shale play, the flowback water is between 20 to 40 percent of the initial injected water volume.<sup>23</sup>

Fifteen to twenty-five per cent of the total volume of injected frac fluid will return to the surface within 30 days after hydraulic fracture as "flowback", and produced water will be continuously generated and reclaimed to the surface over the lifetime of a shale oil/gas well, at the rate of 2-10 bbl/day. Total volume of flowback and produced water was estimated at about 25 million barrels in 2011.<sup>24</sup>

It is estimated that more than 2 million gallons of water per well is being used in fracturing operations, and most of the water then is re-injected for disposal. Over 50% of this produced brine can be reused in subsequent well fractures, and 24% can be recovered as fresh water for beneficial use.<sup>25</sup> The volume of recovery is between 20 to 40% of the volume that was initially injected into the well. The rest of the fluid remains absorbed in the shale gas formation. A typical flowback of drilling fluids might run 40,000 bbl. After the initial 3-4 week post-fracturing recovery of drilling fluids, an additional 10,000 to 30,000 bbl of produced water may flow for up to two years. <sup>26</sup> Typically, 500,000 to 600,000 gallons per well will be generated in the first 10 days in Barnett, Fayetteville and Marcellus shale plays, representing 10% to 15% of the total water used in fracturing and drilling; 250,000 gallons per well is usually produced in the first 10 days in Haynesville shale play, which is only 5% of the total water injected.

The volume of produced water from oil and gas wells will not remain constant, and it increases with the age of the crude oil and natural gas well. API had calculated a water-to-oil ratio of approximately 7.5 barrels of water for each barrel of oil produced for the conventional hydrocarbon productions. For the survey of 2002 production prepared for this white paper, the water-to-oil ratio was calculated to have increased to approximately 9.5. For crude oil wells reaching the end of their lives, Weideman<sup>27</sup> reports that water can comprise as much as 98% of

the material brought to the surface. In these stripper wells, the amount of water produced can be 10 to20 bbl (barrel) for each barrel of conventional crude oil produced.

# 2.3.2 Water Quality

Produced water is derived from seawater but with higher dissolved solids or other metal ions due to physical and chemical reactions with formation rocks. It is characterized as highly saline water which is comprised of formation water (water trapped within shale formations or reservoirs) (shown in table 2.6) and fracture fluid (a mixture of fresh water and some chemical compounds to create fractures and keep underground shale formations overpressured).

Table 2.6, Physical and chemical properties comparison between formation water (conventional) and lab water<sup>28</sup>

	Lab water	Formation water	Formation water
Temperature (F)	82	82	185
pН	4.43	6.10	9.34
TDS (mg/L)	51	120	430
EC	105	241	850
Color (PtCo)	0	10.0	3.0
Oil and grease (mg/L)	0	4.35	1.4
$PO_4^{3-}$ (mg/L)	0	0	0
$SO_4^{2-}$ (mg/L)	0	9.02	6.74
$Cl^{-}(mg/L)$	< 0.01	0.1	0.1
Iron (mg/L)	0.05	0.28	0.16
Zinc (mg/L)	0	0.9	0
Manganese (mg/L)	0	0.002	< 0.01

Chemical composition of produced water is complex, including dispersed oil, dissolved hydrocarbons, organic acids, phenols, metals, and traces of chemicals added in the separation and production line.<sup>29</sup> Several studies have been presented on the chemical and physical characteristics of produced water.



Fig 2.4, Constituents of produced water

As shown in figure 2.4, produced water is primarily comprised of soluble organic carbon and dissolved inorganic ions. Soluble organic carbons mainly exist as carboxylic acids and phenol, etc. Inorganic matter can be classified into two groups, cations and anions. Cations in produced water include monovalent ions such as sodium and potassium, divalent cations such as calcium, magnesium, strontium, barium and iron, and multivalent cations such as boron. Chloride, carbonate/bicarbonate, sulfate and phosphate are the major anions in produced water.

The chemical composition and physical properties of produced water vary considerably depending on the geographic location of the field, the geological formation from which the oil or gas is produced (i.e. the depth of formation, porosity and permeability of formation rocks/sands, water content and different formations such as shale, tight sands or coal-bed), the chemical additives added during fracturing, and the type of hydrocarbon production (such as petroleum and methane).<sup>30</sup> Concentrations of TDS, ions, and even organic matter can vary by multiple orders of magnitude for different basins and fields. For example, in Barnett shale plays, TDS will increase from 50,000 ppm initially to 140,000 ppm, and chlorides will begin increasing from 25,000 ppm up to 80,000 ppm after a period of production, but with a low concentration of total suspended solids (TSS). The same produced water quality situation happens in Marcellus, where TDS could reach a high level (more than 120,000 ppm) after long term production but with low TSS and moderate scaling tendency. In the Fayetteville shale play, on the other hand, concentrations of TDS and chloride of produced water are much less than in Barnett, with only up to 10,000 ppm of chloride and 15,000 ppm of TDS, with low calcium and magnesium as well. Different from these two shale plays, produced water from Haynesville shale has high TSS (up to 350 ppm), TDS, chloride and a high potential of scaling (high in calcium and magnesium).<sup>31</sup>

As an extended explanation of water quality variation, table 2.7 compares water qualities of 5day flowback generated in Marcellus and Barnett shale plays. All of the parameters listed in this table range widely. Averages of alkalinity, TDS, TOC (total organic carbon) and BOD (biological oxygen demand) are significantly different in the 5-day flowback produced by Marcellus and Barnett shale plays.

	1 2 1				
5 day flawkaal	Marcellus shale	play	Barnett shale play		
J-day Howback –	range	median	range	median	
pH	5.8-7.2	6.6	6.6-8.0	7.1	
alkalinity	48.8-327	138	238-1630	610	
TDS	38,500-238,000	67300	23,600-98,900	36100	
TSS	10.8-3,220	99	36.8-253	133	
TOC	3.7-388	62.8	9.5-99.1	18.1	
BOD	0-794	2.8	92.6-1480	319	
Oil and grease	0	<5	<4.8-1720	<5	

Table 2.7, 5-day flowback quality comparison between Marcellus shale and Barnett shale

Additionally, organic carbons also vary in different shale plays (table 2.8). Six major organic compounds (BTEX, phenol and pyridine) are discussed and compared in this table. Organic concentrations are varied in the six shale plays and even in the same play but at a different period of time.

	Bar	mett	Fayette	eville	
	first 30 days	first 30 days long term		long term	
	< 1-97	4.37-1,600	< 1-140	< 1-1.05	
Ethyl benzene	< 1-249	< 1-102	< 1-11	ND	
Toluene	1-578	8.8-3,250	< 1-117	ND	
Xylene	<3-2,480	< 3-2,630	< 3-60.1	< 3-4.86	
Phenol	ND-1,160	12-31	ND	ND-32	
Pyridine	ND-264	12-758	ND-534	ND-92	
	Haynesville		Marcellus		
	first 30 days	long term	first 30 days	long term	
Benzene	< 1-3,460	76-3,140	< 1-1,950	< 1-513	
Ethyl benzene	< 1-1,470	2.5-839	< 1-164	< 1-51.6	
Toluene	2.6-11,400	84-11,300	<1-3,190	< 1-918	
Xylene	12-10,700	31-14,500	< 2-1,970	< 3-439	
Phenol	ND-971	250-3,720	ND-459	ND-34	
Pvridine	ND-971	ND-15.5	ND-459	ND-56	

Table 2.8, Volatile and semi-volatile concentrations for major shale plays

In addition, produced water quality will change over time for one well due to the change of pressure, temperature or physical/chemical reactions during the extraction of oil and gas.



Fig 2.5, TDS, chloride and sodium change over time in Wattenberg field, 2012



Fig 2.6, Conductivity change with produced flow volume at Marcellus shale (20,000 intervals)<sup>32</sup>

Conductivity is a reflection of TDS, and both figures (figure 2.5 and figure 2.6) showed increasing trends either with the increasing of well production time or the water production volume.

#### Salts

Salinity is one of the most concerning aqueous constituents of either conventional or unconventional oil and gas produced water. Dissolved solid concentration of produced water, which can represent the salinity, may range from a few parts per thousand to the saturated level, and most produced water, especially shale gas produced water, has greater salinity than seawater, probably as a result of the water flowing through semipermeable shale units. Similar to seawater, produced water is usually dominated by sodium and chloride but at much greater levels than seawater, due to the evaporation of seawater in the formation reservoir. The other major ions present in produced water are calcium, magnesium, potassium and bicarbonate. In most cases of produced water quality studies, there is much more calcium than magnesium because of the exchange of calcium and magnesium during the process of dolomitization,

$$2C_a CO_3 + M_g^{2+} = C_a M_g (CO_3)_2 + C_a^{2+}$$

and the activity ratio of magnesium to calcium decreases with the increase of reservoir temperature.

The concentration of sulfate and carbonate are low in most produced water, which allows the presence of a relatively high concentration of barium and strontium. Barium and strontium originate from the interaction of formation water with different types of rocks. For example, the typical mass concentration of strontium is 600 mg/kg in limestone, 20mg/kg in sandstone and 300 mg/kg in shale; while average barium mass concentration is 10 mg/kg in limestone and 580 mg/kg in shale.<sup>33</sup> Other ions such as phosphate, nitrite, ammonium and sulfide concentrations are usually low, but in some produced waters are at elevated concentrations.<sup>34</sup>

#### Metals

Metals present in produced water are in the form of dissolved ions or particles. Some studies have found that produced waters tend to contain zinc (Zn), lead (Pb), manganese (Mn), iron (Fe) and barium (Ba) at concentrations widely exceeding the norms specified in regulations. Other well-known heavy metal pollutants like cadmium, chromium, nickel, vanadium and copper exhibit only low amounts, which are less than the defined standards.<sup>35</sup> The metal contents reported vary, but they are often dominated by barium and iron.

#### Organics

Some studies show that the dissolved hydrocarbons are dominated by the volatile aromatic fraction of the oil, namely benzene, toluene, ethyl-benzene and xylene (BTEX). The polynuclear aromatic hydrocarbons (PAHs) are dominated by naphthalene, phenanthrene and dibenzothiophene (NPD) and their  $C_1$ - $C_3$  alkyl homologues, but also compounds with higher molecular weight are reported, such as chrysene and benzo(a)pyrene. The phenols reported may be alkylated up to  $C_7$ . For most fields, the organic acids are reported to be dominated by  $C_1$ - $C_6$  acids.

To determine the effect that various drilling conditions might have on water-soluble organic (WSO) content in produced water, Bostick<sup>37</sup> used a simulated brine containing the major inorganic compounds found in the Gulf of Mexico and contacted this water with crude oil to investigate the effects of aqueous physical parameters, such as water cut, pH of produced water,

salinity, pressure, temperature, the type of crude oil sources and content of the water soluble organics in produced water.<sup>36</sup> They characterized the quantitative properties of the soluble organics and some inorganics present in the produced water generated by offshore oil wells in the Gulf of Mexico. Low molecular-weight acids, such as formic, acetic, and propionic were the most commonly found organic acids. Results showed that pH was the physical parameter that had the most influence on the concentration of soluble organics, while other parameters such as salinity, temperature and pressure had little effect on the soluble organics present in the produced water.

#### Produced water from conventional oil and gas plays

The U.S. Geological Survey (U.S.G.S.) published an extensive database containing an analysis of the major ions and total dissolved solids in produced water from conventional oil and gas wells in mainland U.S.A. They measured TDS, inorganic ions including sodium chloride (76% of the produced water), sodium bicarbonate, sodium sulfate, magnesium sulfate, magnesium chloride, arsenic, boron, silica, strontium, and calcium. They also measured total organic contents, including low molecular-weight aromatic hydrocarbons, such as benzene, ethyl benzene, toluene, phenol, and xylene, as well as total volatile organics and semi-volatile organics. TSS was also measured, including total polar compounds, volatile fatty acids, total recoverable oil and grease, 2-butanone, benzoic acid, bis (2-chlorethyl) ether, hexanoic acid, methylene chloride, m-xylene, naphthalene, N-decane, N-dodecan, N-hexadecane, N-tetradecane, p-cresol, phenol.<sup>37</sup> (Table 2.9 and Table 2.10)

Constituent	Units	Low	High	Median	Number of data points considered
TDS	mg/L	1000	400,000	32,300	33,189
Sodium	mg/L	ND	150,000	9,400	33,189
Chloride	mg/L	ND	250,000	29,000	33,189
Barium	mg/L	ND	850	Unknown	Unknown
Strontium	mg/L	ND	6,250	Unknown	Unknown
Sulfate	mg/L	ND	15,000	500	33,189
Bicarbonate	mg/L	ND	15,000	400	33,189
Calcium	mg/L	ND	74,000	1,500	33,189

Table 2.9, Common inorganic compounds in produced water

\*ND: non-detected (below detection limit); unknown, information was not provided by reference.

Constituent	Low	High	Medium	Technique (method)
TOC (mg/L)	ND	1,700	unknown	UV Oxidation/IR (EPA 415.1)
TSS (mg/L)	1.2	1,000	unknown	Gravimetric (EPA 160.2)
Total volatile organics (mg/L)	0.39	35	unknown	GC/MS (EPA 1624 Rev B and EPA 24&
Total polar compounds (mg/L)	9.7	600	unknown	Florisil column/IR
Volatile fatty acids (mg/L)	2	4,900	unknown	Direct GC/FID of water
Total recoverable oil and grease	6.90	210.0	39.8	Unknown
Benzene (mg/L)	ND	27	10	EPA Method 1624 and 624
Ethyl Benzene (mg/L)	ND	19	1.8	EPA Method 1624 and 624
Toluene (mg/L)	ND	37	9.7	EPA Method 1624 and 624
m-xylene (mg/L)	0.015	0.611	0.137	Unknown
Methylene chloride (mg/L)	1.41	1.71	0.179	Unknown

Table 2.10, Organic matters in produced water from conventional oil and gas

\*ND: non-detected (below detection limit); unknown, information was not provided by reference.

Produced water from gas production has higher concentrations of TDS, low molecular-weight aromatic hydrocarbons (such as benzene, toluene, ethylbenzene and xylene) and heavy metal (such as iron, magnesium and barium) components than produced water from oil sites. <sup>38</sup>

			1	2	U					
Analytes	pН	Conduc	tivity	TDS		Total hard	lness		Alkalinit	y
Conc.	$8.45 \pm 0.22$	10,551	-934	5,520±	718	124±23	mg/L	as	$235 \pm 20$	mg/L
Cations	Al	В	Ba	Ca	Κ	Mg	Na		Si	Sr
Conc.	$0.11 \pm 0.21$	$3.8 \pm 0.3$	$2.0\pm0.5$	$29.5 \pm 5.3$	6.9±1.1	11.1±1.	9 2250	0±327	7 2.7±0.	6
Anions	Cl		Br			Ι				
Conc.	3,306±854		51±17			50±8				
Organics	DOC	U	VA-254	Oi	l and grea	ase		Spec	ific UVA	
Conc.	1.75±0.20 r	ng/L 10	0.0±4.3 mg	g/L 0.7	70±0.41 n	ng/L		4.0±0	0.45 L /(n	n mg)

Table 2.11, Conventional produced water quality from a natural gas well

Concentration of total dissolved solids (TDS) of natural gas produced water is almost 400 times greater than the oil produced water. TDS in produced water is mainly attributed to the solids in the formation water. The possible reason could be that gas can be dissolved in water much faster and more easily than oil can, so more solids, most of which are metals in the form of cations, combine with the gas and dissolve in the natural gas produced water than in the oil produced water, thus causing a high level of TDS. Meanwhile, since the formation process and extraction of natural gas is usually associated with water, and interplays between natural gas, formations, and water would be more notable than those between oil and water, gas produced water may dissolve more solids than oil produced water. Additionally, formations with high temperature will result in formation water with high concentrations of dissolved solids because increased temperature leads to increased solubility, thereby causing more solids to be dissolved in the produced water.

## Produced water from unconventional oil and gas

In contrast to conventional oil and gas wells, the produced water from unconventional oil and gas wells comes in large volumes in the early stages of production. Water quality varies by formation types, such as tight sand, coal-bed methane or shale.

Table 2.12, Typical produced water qualities for conventional natural gas produced water (	NGPWs),
conventional oil PWs (OPWs) and shale gas PWs (SGPWs) <sup>39</sup>	

Constituents	NGPW	/s (mg/L)	OPW	OPWs (mg/L)		's (mg/L)
	Min	Max	Min	Max	Min	Max
pН	3.1	7	5.18	8.9	1.21	8.36
Conductivity (µS/cm)	4,200	586,000	838	1469	3,000	350,000
Alkalinity	0	285	300	380	160	188
Nitrate			1	2	ND	2,670
Phosphate					ND	5.3
Sulfate	1.0	47	8	13,686	ND	3,663
Oil and Grease	2.3	60		92		
$\operatorname{Ra}^{226}(\mathrm{pCi/g})$			0.1	9.7	0.65	1.031
HCO <sub>3</sub>			15	3501	ND	4,000
Al	0.4	83		0.06	ND	5,290
В	ND	58			0.12	24
Ba	0.091	17	0.07	7.4	ND	4370
Br	0.038	349			ND	10600
Ca	ND	51,300	4	52,920	0.65	83,950
Cl	1400	190,000	36	238,534	48.9	212,700
Cu	0.02	5	0.33	2.68	ND	15
F					ND	33
Fe	ND	1,100	0.1	0.5	ND	2,838
Κ	0.458	669.9	1.6	42.6	0.21	5,490
Li	0.038	64			ND	611
Mg	0.9	4300	2	5.96	1.08	25,340
Mn	0.45	6.5	1.4	8.1	ND	96.5
Na	520	120,000	405	126755	10.04	204,302
Sr	0.084	917	0.05	2.2	0.03	1,310
Zn	0.02	5	6.3	17.4	ND	20

\*ND: non-detected (below detect limit)

Shale gas produced water has a wide range of pH from 1 to 9, while typical produced water from conventional gas production is acid. Gas produced brine has greater TDS than oil produced water, and produced water from shale plays has even higher TDS than conventional gas

produced water. Low concentrations of sulfate in the shale gas produced water compared with oil produced water and conventional gas produced water allow for relatively high concentrations of dissolved barium, magnesium, strontium and iron. High total alkalinity as well as minimal precipitation can mostly be attributed to the high concentration of bicarbonate present in shale gas produced water, and due to the pH, a low concentration of carbonate ions appear in shale gas produced water.

#### **2.4 Produced Water Impact**

As the development of drilling and fracturing in areas which are not traditional oil or gas production fields increases, companies involved in the development of shale gas exploration are being required to use environmentally friendly drilling and hydraulic fracturing, which involves reusing a larger amount of produced water, reducing methane emissions, and using green fracture fluids.

The American Petroleum Institute (API) estimated that 149 million barrels of drilling wastes, 17.9 billion barrels of produced water and 20.6 million barrels of other associated wastes were generated in 1995 from exploration and production (E&P) operations. Almost 99% of the U.S. E&P waste volume is produced water.<sup>40</sup>

In the process of hydraulic fracturing, treatments which are used to stimulate gas production from shale have raised environmental concerns over excessive water consumption, drinking water well contamination, and surface water contamination from both drilling activities and fracture fluid disposal.<sup>41</sup>
One of the major issues associated with hydraulic fracturing is the "returning water" containing clays, chemical additives, dissolved metal ions and total dissolved solids (TDS). Along with the introduced chemicals, hydro-frac water is in close contact with the rock during the course of the stimulation treatment, and when recovered may contain a variety of formation material, including brines, heavy metals, radio nuclides, and organics that can make wastewater treatment difficult and expensive. The formation brines often contain relatively high concentrations of sodium, chloride, bromide, and other inorganic constituents, such as arsenic, barium, other heavy metals, and radio nuclides that significantly exceed drinking water standards. Meanwhile, produced water from gas production has higher contents of low molecular-weight aromatic hydrocarbons, such as benzene, toluene, ethylbenzene, and xylene (BTEX), and they are more toxic than those from oil operations.<sup>42</sup>

A drop in temperature and pressure would release these dissolved gases into the atmosphere as water is flowing to the wellhead with the extraction of oil and gas. BTEX are a group of more "toxic" gases than carbon dioxide, and they contribute to the greenhouse effect. Therefore, releasing them would become one of the more serious environmental concerns of the shale gas industry.

### 2.5 Water Management

The management of produced water presents many challenges and can pose significant costs to operators. Current techniques for produced water management include several methods such as underground injection either for increasing recovery or disposal, produced water treatment and discharge, evaporation, reuse and beneficial use. Especially for water-parched areas, the large quantities of water consumed during hydraulic fracturing could make shale gas production economically unsustainable as injected water during hydraulic fracturing containing lots of chemicals would contaminate the underground water. The large volumes of flowback water and produced water which are released with shale gas production can pollute the groundwater and surface water if not treated properly (see figure 2.7).



Fig 2.7, Image of water injection <sup>43</sup>

Water is injected into target formations through injection wells and spread throughout the nearby areas.

Produced water is currently trucked from wells to central treatment facilities and injection wells, and this transportation cost will be a significant part of the entire disposal cost. Hence, optimizing water management to reduce the environmental and economic impacts of produced

and flowback water and finding the best practical strategies for water is essential if shale gas production is to remain economical and sustainable.

Shale play	Class II UIC	Water treatment	Reuse
Barnett	Local	No	Yes
Fayetteville	Distant	Evaluating	Evaluating
Haynesville	Local	No	No
Marcellus	Limited/exploring	Yes	Evaluating

Table 2.13, Water disposal options by gas basin

Produced water reuse is taking place in Barnett shale play while this process is under evaluation for Fayetteville and Marcellus. Currently, approximately 230,000 gallons of produced water is reused in the Barnett shale play, which makes up to 6% of total water needed to hydraulically fracture a new well, and therefore less water (concentrated brine) is injected into the injection well onsite.<sup>44</sup>

Typically, the primary water management practice is to re-inject produced water. This process uses saltwater disposal wells to return the water underground into porous rock formations similar to those from which it came. These formations are separated from treatable groundwater by thousands of feet of multiple layers of impermeable rock. However, underground injection of produced water is not always possible, as suitable injection zones may not be available. In those cases, produced water can be managed through reuse (filtration and blending), advanced process recycling (chemical treatment followed by distillation), and waste reduction (via evaporation) or processed through water treatment facilities. Most of the produced water is re-injected for disposal; more than 50% of this produced brine can be reused in subsequent well fractures. As much as 24% can be recovered as fresh water for beneficial use.

According to API's 1995 study, approximately 92% of all produced water generated was being re-injected underground. 71% of this produced water was injected for enhanced recovery,

and 21% was injected for disposal. The remaining 5% of produced water volume was either treated and discharged or beneficially used. For the last 3% of the produced water, percolation and evaporation ponds were the identified method of disposal. <sup>45</sup>

In 2007, on the other hand, nearly 95.2% - 98%, or more of produced water was re-injected, with about 55% injected to maintain formation pressure and increase the output of production wells, and the other 40% injected for disposal. The remaining 2-4.4% of the produced water was managed through evaporation ponds, offsite commercial disposal, beneficial reclamation and other methods. <sup>46</sup>

Class II UIC wells are the primary means for management of produced water from shale gas. In areas new to O&G development, commercial UIC wells may not yet be available. Some areas (e.g. Marcellus Shale play) are geologically challenged with limited available injection zones.

Beneficial reuse of produced water is to use this renovated water for irrigation, livestock water and industry water use (i.e. well drilling, hydraulic fracturing, pressure sustaining and secondary oil recovery). Table 2.14 lists the water quality criteria for drinking, irrigation and livestock.

parameter	End use cr	End use criteria (ppm)			Non-CBM	
	Drinking Irrigation		Livestock	-	(conventional gas well) Water	
pН	6.5-8	-	6.5-8	7-8	6.5-8	
TDS, mg/L	500	2,000	5,000	4,000-20,000*	20,000-100,000	
Benzene, ppb	5	5	5	<100	1,000-4,000	
SAR*	1.5-5	6	5-8	Highly varied	Highly varied	
Na <sup>+</sup> , mg/L	200	See SAR	2,000	500-2000	6,000-35,000	
Barium, mg/L				0.01-0.1	0.1-40	
Cl <sup>-</sup> , mg/L	250	-	1,500	1,000-2,000	13,000-65,000	
HCO <sub>3</sub> <sup>-</sup> , mg/L	-	-	-	150-2000	2,000-10,000	

Table 2.14, Typical values for produced water quality compared to some criteria<sup>47</sup>

\*total dissolved solid (TDS) range estimated for the lower 50 percentile

\*\*SAR=sodium absorption ration – a function of a ratio of Na to Ca and Mg level

Beneficial reuse for drinking has the most critical standard of water quality followed by use for irrigation, livestock and CBM (coal-bed methane) water, while for conventional gas wells, standards of water quality are much lower compared with livestock and other produced water reuse methods. Taking cost into consideration, reuse produced water for gas (or oil) well water would be both economically beneficial and feasible.

Well head generation makes the resource available on site, lowering transportation and trucking costs. Therefore, the market for treating produced water on site to meet water quality standards for use makes economic sense.



Fig 2.8, Range of applicability vs. cost

Capital cost of treatment for reuse of produced water will depend largely upon water quality (mainly TDS) (shown in figure 2.8). For produced water with high TDS, more than 260,000 mg/L, treatment for reuse will not be recommended due to its elevated cost (also shown in table 2.17).

Water used for fracturing (frac water) is usually fresh water containing low salt concentrations and low concentrations of soluble salt products such as barium and silica. Lower concentrations of soluble salts is an important consideration because precipitation of these salts in the formation would block fractures and lower formation permeability. Treated produced water used to supplement water quantities for hydraulic fracturing lowers the use of fresh water sources for well development and creates a more sustainable water use cycle within the well drilling operation.

## **2.6 Produced Water Treatment**

Produced water always contains high concentrations of TDS, metal ions as well as oil and grease. To ensure the injected produced water is confined in the injection zone in a manner that does not contaminate the water bearing geologic formation, produced water needs to be treated before injection. Therefore, to meet the UIC and RCRA (Resource Conservation and Recovery Act) regulations, removal of TDS, TOC, oil/grease, hardness, and metal ions (including ammonia and boron) are the main treatment goals. Table 2.15 shows the unit processes and their application to produced water treatment.

Treatment method	De- oilin g	Suspend solids removal	Iron removal	Ca & Mg removal softening	Soluble organic removal	Trace organics removal	Desalination & Brine volume red	Adjustment of SAR	Silicate & Boron removal
APT separator	✓	$\checkmark$							
Deep bed filter	$\checkmark$	$\checkmark$							
Hydroclone	$\checkmark$	$\checkmark$							
Induced gas flotation	$\checkmark$	$\checkmark$							
Ultra-filtration	$\checkmark$	$\checkmark$							
Sand filtration		$\checkmark$							
Aeration & sedimentation		$\checkmark$	$\checkmark$						
Precipitation Softening				$\checkmark$					$\checkmark$
Ion exchange			$\checkmark$	$\checkmark$					$\checkmark$
Biological treatment					$\checkmark$				
Activated carbon						$\checkmark$			
Reverse osmosis							$\checkmark$		
Distillation							$\checkmark$		
Freeze thaw evaporation Electrodialysis Chemical addition					$\checkmark$		$\checkmark$	~	

Table 2.15, Unit processes and their application to produced water treatment

 $\checkmark$  = indicates that the technology is applicable as a potential remedy as indicated by data collected from pilot or commercial scale units.

In addition to reinjection, some shale gas plays are trying to reuse the produced water. In the Barnett shale play, along with some traditional water sources (ground water, surface water and public water supplies), some new sources of water are being applied, like the treated waste water from municipal treatment plants and recycled water from hydraulic fracturing processes. (Figure 2.9)

To increase the number and types of water sources, it was planned that at least 30% of the total Chesapeake Barnett Shale water would come from treated waste water from water treatment facilities, totally 1.25 million gallons per day, and that up to 80% of the used water recovered over the life of the well could be recycled through municipal water treatment facilities.



Fig 2.9, Barnett Shale play brine desalination process

To meet water reuse requirements, the produced brine water will go through serial treatment facilities, hydrocyclones, filters, reverse osmosis (RO) membranes and the RO post treatment.

Constituent	Raw feed	RO filter	Removal Rate
Alkalinity, as CaCO <sub>3</sub>	188	34	82%
Bicarbonate	230	41	81%
Carbonate	<1.2	1	n/d
Hydroxide	<1	1	n/d
Conductivity	33000	2270	93%
Magnesium	73	1	99%
Silicon	78	2	97%
Calcium	1055	23	98%
Potassium	124	5	96%
Sodium	11570	416	96%
Boron	87	34	61%
Silica	1664	4	99%
pН	6.1	7	
Total Dissolved Solids	38300	1291	97%

Table 2.16, Treatment efficiency and characteristics of the raw water

RO treatment cost of Barnett Shale play is less than the cost of oil field produced water, which

indicates the feasibility of RO membrane treatment to treat gas well produced water.

Salinity of feed brine,	Power costs Kw Hr per 1,000 gal. Permeate						
TDS (mg/L)	Pre-treatment	RO desalination	Operating cost,	Operating cost,			
			\$ per 1,000 gal	\$ per bbl			
Contaminated surface water,	\$0.65	\$1.25	\$1.90	\$0.08			
1,500 TDS							
Gas well produced water,	\$2.5	\$2.00	\$4.5	\$0.19			
3,600 TDS							
Oil well produced brine,	\$2.20	\$6.00	\$8.20	\$0.34			
50,000 TDS							
Gas well produced brine,	\$2.00 (est.)	\$4.2 (est.)	\$6.20 (est.)	\$0.26			
35,000 TDS							

Table 2.17, Representative power costs of desalination of oil field brine

The cost of produced water reuse is much higher than treating contaminated surface water, because the high TDS present in the produced water makes the membrane treatment procedure cost more. Pre-treatment costs are almost the same for produced waters with different TDS concentrations, while RO desalination costs and operation costs are positively related to TDS concentration. Therefore, the higher the TDS concentration in the produced water, the higher the cost of produced water reuse will be.

# 2.7 Oil and gas production history in Wattenberg Field

Wattenberg field, located in northeast Colorado, is one of the largest natural gas deposits in the United States. (Figure 2.10)<sup>48</sup> It has been the site of conventional petroleum production for over forty years (since 1970), but recently it has become known for natural gas extraction and production.



Fig 2.10, Top U.S. gas fields by 2009 gas production<sup>49</sup>

In Wattenberg basin, which is located in the Denver DJ basin, the average depth of wells is between 7,000 and 8,000 feet.  $^{50}$ 

Wattenberg field has a long history of producing oil and gas, beginning four decades ago in 1970. At first, petroleum companies started producing oil from the D-J sandstone formation mainly in Weld County, located northeast of Denver, but recently more and more wells have been drilled to extract natural gas. It was estimated that 1.6-2.4 trillion cubic feet of natural gas could be extracted from Wattenberg field at a time when energy companies could only use conventional approaches from relatively high permeability formations. However, due to the development of horizontal drilling and hydraulic fracturing technologies, unconventional natural gas is becoming the major form of gas production in Wattenberg field, including shale gas and tight sandstone. Approximately 5.2 trillion cubic feet of natural gas are stored in the deep formations in Wattenberg field, which is equivalent to one year of America's homes gas supply.<sup>51</sup> Production of oil and gas has been increasing in the Wattenberg area (see figure 2.11).



# **Greater Wattenberg Area Annual Production**

Fig 2.11, Oil and gas production for greater Wattenberg field from 1999 to 2010

We applied the Public Land Survey System (PLSS) to subdivide and describe the land in Wattenberg field. Wattenberg field was subdivided by this rectangular system of survey, named "townships", each of which is approximately a 6-square mile rectangle containing 36 sections<sup>52</sup> (shown in figure 2.12). Each township is identified with a township and range designation.

Township designations indicate the location north or south of the baseline, and range designations indicate the location east or west of the Principal Meridian.



Fig 2.12, Wattenberg field divided by townships

Wattenberg field takes up an area of about 50 square miles from townships 2S to 7N, ranges 61W to 59W. However, in this study, the wells in Wattenberg field belonging to Noble Energy are located mainly within the "rectangular area" from townships 7N to 2S and range from 62W to 69W.





Fig 2.13, Productive Areas-Great Wattenberg Area, 2005

Fig 2.14, Noble well density in Wattenberg

Production activities in greater Wattenberg field in 2005 are shown in Figure 2.13<sup>53</sup> and Noble producing oil/gas wells are shown in Figure 2.14. Previous oil and natural gas production from Wattenberg field has come from the J-Sand, a 1.3-Tcf reservoir with some 30 million bbl of condensate in reserves. Typically, operators have produced from the Codell and Niobrara formations together using bridge plugs to separate fracture treatments. Because payout often was questionable from these zones, they got a late start.

## 2.8 Research Objectives

Water produced during oil and gas extraction comprises the most important part of the "waste" with respect to volume, and this produced water can be considered a potential benefit stream for the industry. Well drilling and completion operations require a large amount of fresh water, and this demand can be satisfied by reusing/recycling produced water. Since limited water is available in most of Colorado, supply and management of this resource is an essential issue for

the Wattenberg field located in the northeast part of the state. Reclaimed water can be used for agriculture, hydraulic fracturing or surface water augmentation, but the treatment processing required will vary widely depending on the quality of the water. Also, since geological characteristics of the formations have a range of spatially diverse characteristics, produced water properties can vary significantly throughout the field. To assure appropriate treatment plant design throughout the region of interest, it is necessary to understand the spatial distribution of produced water characteristics. In our study, produced water will be sampled and tested, and water chemical data will be collected at individual wellheads. Geographic Information Systems (GIS) modeling will be utilized to make spatial analyses of produced water quality and create several data layers, such as the key water parameter layer and the scaling potential index. The primary objectives of the study are:

1. Design data and sample collection plan to effectively model water quality in the Wattenberg field.

2. Collect water samples from oil and gas wells in the Wattenberg field and analyze samples for determined set of quality parameters.

3. Determine spatial variability of key water quality parameters using GIS tools.

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### **Chapter 3 Methods and materials**

The assessment of produced water quality for the Wattenberg field was conducted in four phases:

- (1) field work and sampling
- (2) water sample analysis
- (3) statistical and spatial analysis overview of produced water data
- (4) development of spatial prediction methods

# 3.1 Water Sampling

### **Sampling Sites**

The Colorado Oil and Gas Conservation Commission (COGCC) has posted yearly and monthly production reports with the first production dates for oil and gas wells from 1999 to 2011 on its official website, and the following analysis is based on these reports. Also, Noble Energy Company provided significant amounts of data.

Wells are identified mainly by their first production year, but information about each well is combined with oil/gas/water production data. If there is no production data of oil or gas before the first production date for a well, this well is defined as new in this year. On the other hand, if there is production data before the first production date, then we consider this well as a refracturing well of this year.



Fig 3.1, Number of new drilled wells by year

The number of wells drilled in the year from 1999 to 2011 is shown in figure 3.1. In the period from 1999 to 2004, newly drilled wells were less than 120 per each year. A great expansion of drilling occurred in 2005. Only 123 wells were drilled in 2004, but 3,306 were drilled in 2005, and the number of wells drilled continued to increase from 2005 till 2011. All the wells drilled before 2011 are vertical wells and in 2011, Noble Energy Inc. began to drill horizontal wells.

There is little information available about wells drilled or produced before the year 1999, such as produced water volume and production formation. Since most of these wells are no longer producing oil and gas, our target shale oil and gas wells are the producing wells drilled after 1999, or the wells drilled from 2000 to 2011. Figure 3.1 shows the number of wells drilled from 1999 to 2011 and total number of wells drilled by Noble Energy Inc., for each year. The number of newly drilled shale oil and gas wells has increased over time (from 1999 to 2011), which is

due to the development of shale oil and gas production. There was a huge jump in 2005, when over 3000 wells were drilled as compared with the 123 wells drilled in 2004. According to the drilling and fracture information offered by Noble Energy Inc. and COGCC (Colorado Oil and Gas Conservation Commission, <u>http://cogcc.state.co.us/</u>), the major wells drilled before 2011 were vertical wells, but in the year 2011, a total of 115 horizontal wells (green column in figure 3.1) were drilled, and this number is projected to increase in future years. With more shale oil and gas wells being drilled, especially horizontal wells which produce a great amount of produced water, more produced water will be generated and therefore, it is of great importance to investigate the water quality characteristics and find the "best-practice method" to treat these produced waters.

Since limited water quality data is available for previous years and even no water quality data for some old wells, it is hard to use existing data to make a statistical analysis. Compared with the wells drilled before 2000, wells drilled after 2000 have more valid information about produced water. For this reason, we decided to collect water samples from wells drilled during the 12-year period from 2000 to 2011.

An equal number of water samples were taken for each year from 2000 to 2011 to make a temporal trend analysis of produced water qualities. For example, if a total of 120 samples were taken, we would have randomly selected 10 wells for the year 2000, 10 wells for 2001, and so forth.

Another factor which impacts the water qualities and characteristics is the production formation characteristic. According to the production data from COGCC, Niobrara chalk formation, Codell formation, J Sandstone, D Sandstone and Sussex formation are the top five active producing formations in the Wattenberg field of Denver Bain (shown in figure  $3.2^{54}$ ).

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Fig 3.2, Accumulative production activity of major formations, 2005

Due to the different characteristics of formations (e.g. organic content, permeability), the constituents of produced water will be different. J sandstone formation covers 600,000 acres at depths from 7,600 feet to 8,400 feet (2,318 m to 2,562 m). The tight sand has porosity between 8% and 12% with permeability between 0.05 mD and 0.005 mD. The Codell-Niobrara combination is about 400 feet (122 m) shallower.

Depths of producing wells in Wattenberg field of Noble Energy Inc. until 2011 were between 6800-8500 feet. Hence, most wells produced oil, gas and water coming from multiple intervals, so produced waters were a mixture of formation water from multiple intervals (see figure 3.3). Though it is impossible to take produced water samples from only one particular formation, since all the Noble wells studied were producing oil and gas from both Niobrara-Codell interval and J Sandstone, we assumed that the formation geological characteristics had similar effects on all the produced waters to be sampled.



Fig 3.3, Typical depth of major oil/gas producing formations

It is well known that some water exists in the dissolved phase in gas in the reservoirs. The pressure and temperature of the formation along with the geological properties of formation rocks determine water volume as well as water quality. Table 3.1 shows the average depth, temperature and pressure of the Niobrara-Codell interval and typical water content in this reservoir. Also, water dissolved in gas will increase with the increasing of temperature and pressure.

wattenberg neid						
Reservoir	Average	Temperat	Pressure	Solubility of	Water	Water released
	depth	ure (F)	(psi)	water in gas	retained	at seperator
	(ft)			(1b/mmcf)	(1b/mmcf)	bbl/mmcf
Niobrara-	<b>7</b> 001	2.10	1051	100	22	1.05
Codell	7,091	240	4,254	480	33	1.25

Table 3.1, Depth, pressure and temperature of Niobrara-Codell interval and estimates of water released in Wattenberg field

\*1b/mmcf=pounds of water/million cubic feet of gas

# Sampled Wells



Huishu Li, Colorado State University, 2012

### Fig 3.4, Map of sampled wells

Wells were selected randomly by ArcGIS 10.0. Geographic information of the sampled wells is shown in figure 3.4 with three-dimension images and a two-dimension map. Both the boundary in the 2D map and the light pink area in the 3D image represent Wattenberg field as defined by COGCC.

All the producing wells are classified by the first production year regardless of whether they are new or re-fracturing wells, and the produced water quality, in terms of TDS, pH or calcium is

presented for each year. Therefore, any changes in produced water quality for different years will be available. Wells selected for sampling are listed in <u>Appendix 1</u>.

### **Field Sampling Schedule**

According to <u>Appendix 2</u>, for the analyses test, including anions (carbonate/bicarbonate, sulfate and chloride), alkalinity, TDS and TOC, the minimum size of sample will be 500 mL; for the analyses of the Tier 3 test, including cations (calcium, magnesium, barium, iron, potassium and sodium), the minimum size of sample will also be 500 mL.

As recommended by US EPA sample collection and preservation, two 500 mL plastic (HDPE) bottles of produced water were collected at each well site. One 500 mL bottle of sample water was shipped to the certified lab to measure trace metals (Tier 3), and the other 500 mL bottle of produced water was used for tests of anions, organic, and other water parameters (Tier 2) at the CSU Environmental Engineering labs. Samples were refrigerated until the analysis and filtered through a 0.45-µm filter before the test (Standard Method 3005).

Sample well sites can be located via GPS by longitude and latitude. The water test worksheet format is shown in <u>Appendix 3</u> and <u>Appendix 4</u>.

All the produced water samples were collected from separator tanks. (Figure 3.5) Oil, gas and water were separated in these separators due to their different density. Water and oil present in the liquid phase, and water settles at the bottom of the separator tank, with oil on top of the water. Gas exists in the gas phase, and it is transported to the central collection site by pipelines.



Fig 3.5, Separator tank (separator) and field water sampling

But in the field, some separators were hard to find because they were not located at the well heads and we lacked the actual locations of the separators. In addition, water side valves on some separators were corroded and therefore very difficult to open, so finally we collected 66 samples rather than the 90 samples we had planned. The following results and discussions will be based on these 66 samples.

### **3.2 Water sample analyses**

# 3.2.1 Water quality test parameters

The objectives for reuse treatment include: petroleum hydrocarbons removal, friction reducers and other polymer additives removal, inorganic scale forming compounds removal, and bacteria disinfection. In reusing produced water and fracturing flowback, one of the most critical issues is the potential of decreasing or failure of well performance caused by excessive amounts of some chemicals and bacteria.

Heavy metal compounds could adhere to well holes, producing pipes, or other surface facilities causing scaling. Oil and gas scales are hard mineral compounds that precipitate from brine solution and may adhere to solid surfaces in the reservoir, production tubing, or surface facilities. Scale accumulation will constrict fluid flow, limit production, and possibly cause damage to downhole equipment, such as electrical submersible pumps (ESPs). Safety may be compromised by scale deposition in subsea safety valves, and some scales constitute a health hazard, because they are naturally occurring radioactive materials (NORM) that may be expensive and dangerous to remove and dispose of.

Table 3.2.	Water	aualitv v	s fracturing	performance
1 4010 5.2,	,, acci	quanty	5 mactaring	periormanee

Concern	Water Parameter	Impact
Friction reducer	Multivalent Ions	Can impair effectiveness and drive up horsepower
Scaling	CaCO <sub>3</sub> , CaSO <sub>4</sub> , BaSO <sub>4</sub> , SrSO <sub>4</sub> , FeSO <sub>4</sub>	Equipment and line fouling, loss of formation
Bacteria	Sulfate reducing bacteria	Sour formation $(H_2S)$ safety
Metals	Iron (Fe)	Formation plugging (Iron oxides)
Suspended solids	Sand, silts, clays, scale particles	Formation damage, loss of permeability

Table 3.2 shows the various dangerous impacts of chemicals. Scaling, oxidized metal compounds and solids cause plugging and fouling. Among these actors, metal ions and scale anions (sulfate and carbonate) are the primary chemicals which can have side effects on well performance. Wellbores or pipes can be plugged by sediments due to the precipitation taking place when barium sulfate, calcium sulfate, or calcium carbonate is present.<sup>55</sup>

The chemical conditions of different types of brine cause the various precipitations. Table 3.3 lists some common scale-forming compounds and reasons which cause these scales in the oil and gas plays.<sup>56</sup> The top three common kinds of well scaling in the oil and gas industry are calcite (CaCO<sub>3</sub>), calcium sulfate (CaSO<sub>4</sub>) and barite (BaSO<sub>4</sub>).<sup>57</sup>

Name	Chemical formula	Primary variables
Calcium carbonate	CaCO <sub>3</sub>	Partial pressure of CO <sub>2</sub> , temperature, total dissolved salts,
		рН
Calcium sulfate:		Temperature, total dissolved salts, pressure
Gypsum	$CaSO_4 \cdot 2H_2O$	
Hemihydrate	$CaSO_4 \cdot \frac{1}{2}H_2O$	
Anhydrite	CaSO <sub>4</sub>	
Barium sulfate	$BaSO_4$	Temperature, pressure
Strontium sulfate	$SrSO_4$	Temperature, pressure, total dissolved salts
Iron compounds:		Corrosion, dissolved gases, pH
Ferrous carbonate	FeCO <sub>3</sub>	
Ferrous sulfide	FeS	
Ferrous hydroxide	$Fe(OH)_2$	
	$Fe(OH)_3$	

Table 3.3, Common oilfield scales

Scale and precipitation occur not only in the equipment and facilities, such as pumps, tubing, flow lines and pipes, but also in the formation. Impairment of permeability of oil and gas bearing formations is also due to scale formation.

The premise of scaling is that water must be supersaturated, which means ions dissolved in water have exceeded what is thermodynamically possible; as a result, salts begin to precipitate. Super saturation can occur in many ways either by changes in environmental conditions (pH, temperature and pressure), or a mixture of two incompatible waters. pH, temperature and pressure are the main factors affecting solubility, and super saturation levels are different under various pH, temperature and pressure conditions, up to orders of magnitude differences. For instance, blending of injected seawater, which is rich in sulfate ions, and reservoir water, which contains a lot of divalent cations, such as calcium, barium and strontium, would lead to metal-sulfate precipitation. Scale potentials are reported as saturation level (degree of super saturation). Table 3.4 describes the ratio of the observed water chemistry to the water chemistry at equilibrium, for the reactants involved.

Table 3.4, Scale forming salts list

Salt	Saturation concentration, mg/L
Calcium carbonate (CaCO <sub>3</sub> )	8
Calcium fluoride (CaF <sub>2</sub> )	29
Calcium orthophosphate (CaHPO <sub>4</sub> )	68
Calcium sulfate (CaSO <sub>4</sub> )	680
Strontium sulfate (SrO <sub>4</sub> )	146
Barium sulfate (BaSO <sub>4</sub> )	3
Silica, amorphous (SiO <sub>2</sub> )	120

During the drilling process, high pressure is applied to create fractures, but this pressure increase will also drive the immigration of solids towards the wellbore causing some nearby areas to get clogged by those mud solids. In addition, temperature and pressure changes occurring during oil and gas production leads to a large gradient of pressure and temperature near the wellbore and surface, under which conditions precipitation will take place.

Two types of scaling occurring during oil and gas operations are carbonate scale and sulfate scale. Typical carbonate scale is carbonate calcium, and it is sometimes accompanied by iron carbonate.

$$C_a^{2+} + CO_3^{2-} \rightarrow C_a CO_3$$
$$Fe^{2+} + CO_2^{2-} \rightarrow FeCO_3$$

Carbon dioxide dissolved in water will be present as three terms, dissolved CO<sub>2</sub> gas, carbonate, and bicarbonate. Carbonate combined with calcium, iron or other metal ions will form scales. Usually carbonate scale is influenced largely by pH, temperature and pressure. For example, calcite scale formation (CaCO<sub>3</sub>) is usually a result of the pressure drop during gas and oil production. Because this pressure drop removes the carbon dioxide from the solution, the pH of the solution will increase and cause calcite precipitation. Also, a secondary consequence of the pressure drop is that the solubility of the calcite goes down with the decrease in pressure.<sup>58</sup> Deposition of calcium carbonate could also be the result of the combination of calcium and bicarbonate, which is one major cause of scale in oilfield operations.<sup>59</sup>

$$Ca(HCO_3)_2 \leftrightarrow CaCO_3 + CO_2 + H_2O_3$$

Also, an increase of pH and temperature results in less calcium carbonate dissolved in water, which means that more calcite will precipitate under high pH and high temperature.

Another major scale-forming compound is sulfate salt, including  $CaSO_4$ ,  $BaSO_4$  and  $SrSO_4$ . These sulfate salts tend to precipitate under high temperature, with the exception of barium sulfate, which shows the opposite trend. High pressure will dissolve more salts than a low pressure solution.<sup>60</sup> Solubility of sulfate salts and calcium carbonate can be estimated and scale potential can also be predicted. Calcium carbonate scale potential indices calculated are based upon the most accurate estimate of the carbonate species distribution. The results are reliable even in the presence of free hydroxide alkalinity and high silica levels.



Fig 3.6, Scale deposition locations in offshore injection well <sup>61</sup>

Figure 3.6 gives the possible locations in which precipitation could be taking place in an offshore injection well. It is an illustration of which places are the most likely to have scaling issues throughout the whole operation system and the probable reasons for the scale. Usually, precipitations happen in places where two distinct waters meet (locations a, c, d, e, f, g, h, I, j, and k) or temperature/pressure changes (locations b, e, h and k). The locations in an onshore oil and gas well and production system which are at highest risk for having the most scaling potential will be the same as those shown in figure 3.6.

Hence, in order to prevent well scaling and plugging and to ensure that the reused water performs well during the hydraulic fracturing, metal cations (scaling-form metals) should be measured before treatment, including calcium, magnesium, barium, iron and strontium. In addition, anions, such as sulfate and carbonate/bicarbonate, which would combine with these cations to create scale, also need to be analyzed. Integrated information about metal ions and scale anions will provide basic knowledge of the scale potential of certain produced water.

High TDS increases friction in the hydraulic fracturing process, and high solids can plug wells and decrease biocide effectiveness. Iron oxide will also cause plugging.

Boron is another water parameter of concern for produced water reuse. Since boron is added into the fracturing fluid as a cross-link chemical in the hydraulic fracturing process, the concentration of boron present in the reclaimed water would affect the fracturing crosslinker's performance. Therefore, boron has also been put into the key parameters' list. All the parameters listed in table 3.5 were the major concerns in this study, and it is important that those water parameters be measured.

Table 3.5, Water quality test parameters for produced water reusing

Inorganic compounds		Organic compounds	Others
Na	Ba	Total Organic Carbon	pH
Ca	Sr	Total Carbon	Electric Conductivity (EC)
Mg	$HCO_{3}^{-}/CO_{3}^{-2}$		COD
Fe	$SO_4^{2-}$		TDS
В	$PO_4^{3-}$		Total Nitrogen

#### **3.2.2** Water quality measurements

Calcium, magnesium, sodium, chloride, alkalinity as  $CaCO_3$  (quality insurance and ion balance requirement) and total dissolved solids (TDS) were measured by a certified laboratory.

Lab	Metals	TDS	Anions	Volatil e organi cs	Metals, only	Metals and Anions	Metals & Anions &TDS	Metals & Anions &TDS &Volatile organics
City of Fort Collins, Lab	\$235			\$135	\$235	\$235	\$235	\$370
ACZ Laboratories, Inc.	\$43.2	\$8.8	\$36.8	\$123	\$43.2	\$80	\$88.8	\$211.8
Accutest Mountain States	\$70	\$12	\$67	\$125	\$70	\$137	\$149	\$274
CO Department of Public Health and Envir Lab	\$114	\$15	\$80	\$100	\$114	\$194	\$209	\$309

Table 3.6, Costs of certified labs in CO

\*Metals include calcium, magnesium, barium, iron, sodium and potassium

\*Anions include carbonate/bicarbonate, sulfate, phosphate and chloride

Table 3.6 shows the capital costs charged by four certified labs in state of Colorado having the certifications to test metals, TDS, anions and organics. Finally, we choose ACZ laboratories Inc. to do the analysis of calcium, magnesium, barium, strontium, sodium, potassium, chloride, alkalinity and TDS (shown in table 3.7).

Table 3.7, Water parameters tested in the certified lab, CSU Environmental Engineering lab and on-site

	Analysis
ACZ	Na, Ca, Mg, Sr, Ba, B, $Cl^{-}$ , $SO_4^{2-}$ , $PO_4^{3-}$ , TDS, $HCO_3^{}$
CSU lab	pH, Electric Conductivity, TC, TN, TOC,
On site	Temperature

Tier 1: produced water temperature was read from thermometers on the separate tanks (figure 3.7) and documented on the worksheet (<u>Appendix 2</u>).



Fig 3.7, A thermometer on a separator

Tier 2: all the water samples were brought to Environmental Engineering lab of Colorado State University and the pH was tested immediately by EPA 150.1 using Fisher Scientific Accumet AB15 Basic and Bio-Basic pH/mV/°C Meter. For the determination of the dissolved elements, water samples were filtered following standard method 200.7 section 8.2. They were filtered through a 0.45 µm pore diameter membrane filter after the pH test, because filtration should be tested at the time of collection or as soon thereafter as practically possible. For dissolved wet chemistry methods (Chloride, Phosphorus, TDS and Sulfate) samples were filtered through Whatman Glass Microfibre Filters 934-AH.

Dissolved ferrous was tested using HACH method 8146, adapted from standard methods for the examination of water and wastewater,  $15^{\text{th}}$  edition 201 (1980). The 1-10 phenanthroline indicator in the Ferrous Iron Reagent reacts with ferrous iron (Fe<sup>2+</sup>) in the sample to form an orange color in proportion to the iron concentration. Ferric iron (Fe<sup>3+</sup>) does not react. The ferric iron concentration can be determined by subtracting the ferrous iron concentration from the results of a total iron test. Test results are measured at 510 nm by a Model DR/2500 Laboratory

Spectrophotometer. The detective range of  $Fe^{2+}$  is 0.02 to 3.00 mg/L with 95% confidence limits of distribution from 1.98 to 2.02 mg/L.

Total carbon (TC), inorganic carbon (IC), total organic carbon (TOC) and total nitrogen (TN) was measured by SHIMADZU TOC-VWS/TOC-VWP. TC is first converted to carbon dioxide heated under UV illumination by adding phosphoric acid and the oxidant (persulfate). The area of carbon dioxide signal is measured and converted to total carbon concentration using a pre-prepared calibration curve. Inorganic carbon is first acidified with phosphoric acid and then heated to carbon dioxide. This carbon dioxide is detected by the NDIR and the sample IC concentration is measured in the same way as TC. The total organic carbon concentration is the difference between total carbon and inorganic carbon.

COD was tested using HACH method 8000 (high range plus), adapted from standard methods 5220D. The results in mg/L COD are defined as the milligrams of O<sub>2</sub> consumed per liter of sample under the conditions of this procedure. The sample is heated for two hours with sulfuric acid and a strong oxidizing agent, potassium dichromate. Oxidizable organic compounds react, reducing the dichromate ion  $(Cr_2O_7^{2-})$  to a green chromic ion  $(Cr^{3+})$ . When 200–15,000 mg/L colorimetric method is used, the amount of  $Cr^{3+}$  produced is determined using Model DR/2500 Laboratory Spectrophotometer with a wavelength of 620 nm. The detective range of COD is 200 to 15,000 mg/L with 95% confidence limits of distribution from 7850 to 8150 mg/L.

As EPA suggested, inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used to determine metals and some nonmetals in the solution, following *Method 200.7*. Chloride was tested by EPA *Method 300.1*. Total hardness as CaCO3 was calculated by following equation

*Total Hardness*  $(as CaCO_3) = 2.497 \times [Ca^{2+}] + 4.118 \times [Mg^{2+}]$ 

TDS can be measured using EPA 160.1 or Standard Method 2540B. Titration is used to measure bicarbonate and carbonate concentration, following Standard Method 2320B.

The following table 3.8 and table 3.9 present the analyses that were performed on each produced water sample and the respective laboratory method suggested by USEPA and Standard Methods:

Table 3.8, Laboratory analyses and analytical methods suggested by EPA
------------------------------------------------------------------------

Analyst	USEPA Methods	Standard	Method	
		Methods	detection limit	
Major cations:	EPA Method			
Dissolved sodium, calcium, magnesium,	6010			
potassium, iron				
Major anion:	EPA			
Chloride, sulfate, carbonate, bicarbonate,	300/SM2320B			
nitrate, nitrite	EPA 353			
Dissolved metals:	EPA Method			
Arsenic, barium, cadmium, chromium, lead,	6010			
selenium, manganese				
Fluoride	EPA 300			
Bromide	EPA 300			
Chloride		4500- Cl <sup>-</sup> -B;	10-10,000 mg/L	
		HACH titration	500-100,000	
		method	mg/L	
Ammonia		4500-NH <sub>3</sub> D	0.03 mg/L	
Sulfate		$4500-SO_4^{-2}$	0.1 mg/L	
pH	EPA 150.1	4500-H* B	0.01 SU	
Total dissolved solids (TDS)	EPA 160.1	2540 B	0.1 mg/L	
Total suspended solids (TSS)		2540 B	0.1 mg/L	
Alkalinity		2320 B	2 mg/L as	
			CaCO3	
Dissolved methane	RSK 175			
Benzene, toluene, ethybenzene, xylenens	SW846 8260B			
(BTEX)				
Conductivity	SM2510B	2510 B	0.1 µS/cm	
Oil and Grease	1664 A		-5 mg/L	

Parameter	Methods and Method detection limit (mg/L)						
Metals and metalloids	Inductively coupled plasma-atomic emissions spectrometry (ICP-AES):						
(mg/L)	200.7						
-	Cu	0.005	Fe	0.006			
	Mg	0.001	Cd	0.003			
	Zn	0.02					

Table 3.9, Extended laboratory analytical methods

### 3.3 Produced water quality by U.S.G.S survey

### **3.3.1 Produced water quality for the United States**

To address the environmental concerns caused by produced water, the U.S. Geological Survey initiated an investigation on produced water quality, which was sampled from the 1960s to the 1980s. Unfortunately, this data does not reflect current water quality.

Although much of the information in this database cannot be examined and checked, and the sample analysis would not be standardized compared with modern standard water tests, this database can still provide some tendencies in water constituent differences from different geological areas. Because of the lack of detailed produced water quality information, this database with specific ion concentrations (calcium, magnesium, sodium, potassium, chloride, bicarbonate and sulfate) and water quality parameters such as TDS and pH in almost every major oil and gas basin in the United States, can be used as a background tool to understand how produced water varies in major components and in different geological areas on a large scale.

Also, after real field data of produced water quality for Wattenberg field or maybe for an even larger area can be acquired, we can make comparisons between this U.S.G.S produced water database and the new database to find out how the chemical and physical attributes of produced water have changed.

Throughout 34 states in the United States, a total of 58,706 produced water samples from 1921 to 1980 were collected and measured. Water samples without TDS values were eliminated since TDS is one of the major parameters which impacts produced water quality, choice of treatment technology, and estimation of operation cost. Finally, a statistical analysis was made based on the remaining 58,654 pieces of valid data. Ordinary Kriging was used to predict the major water parameters of concern based on the 53,336 data points provided by the U.S.G.S.

Correlations between individual water quality parameters were tested by the SPSS Pearson Correlation Method, and correlation coefficients are listed in Table 3.10.

	pН	TDS	Ca	Mg	Κ	Na	Cl	$SO_4^{2-}$	HCO <sub>3</sub> <sup>-</sup>
pН	1.000	-0.635	-0.559	-0.456	-0.110	-0.570	-0.642	0.126	0.446
TDS		1.000	0.783	0.662	0.201	0.866	0.999	-0.090	-0.403
Ca			1.000	0.668	0.192	0.584	0.792	-0.185	-0.319
Mg				1.000	0.109	0.445	0.672	-0.047	-0.270
Κ					1.000	0.193	0.197	0.001	-0.032
Na						1.000	0.864	-0.109	-0.358
Cl							1.000	-0.120	-0.412
$SO_4^{2-}$								1.000	0.030
HCO <sub>3</sub> <sup>-</sup>									1.000

Table 3.10, Pearson correlation coefficients (58,654 valid data)

The fact that the correlation coefficient between TDS and chloride is very significant (0.999) indicates that there is a positive correlation. Concentrations of sodium, calcium, magnesium and chloride might have negative effects on pH, but bicarbonate has a positive effect on pH.



Fig 3.8, Correlations between major cations, chloride and TDS

There is an exceptionally close correlation between chloride and total dissolved solids (TDS) (i.e.,  $R^2 = 0.999$ ). This is as expected since chlorides are the predominant anion in produced water. TDS levels range from approximately 1002 mg/L to nearly 400,000 mg/L. Regional distribution of the TDS levels appears to vary significantly, with differences of several magnitudes. A Kriging interpolation can only use data values greater than 0, so our statistical analysis of water quality only included those data having values more than 0.

	TDS	pН	Ca	Mg	Na	K	Cl-	HCO <sub>3</sub> <sup>-</sup>	$SO_4^{2-}$
Count	23,904	16,323	23,809	23431	23,909	8,104	23,396	23,344	22,030
Min	1,002	5.00	1	1	0.44	0.74	2	1	1
Max	399,290	8.98	74,185	33056	146,770	28,022	249,490	14,000	15,000
Mean	88,343	7.18	4936.4	1090.9	24,218	2424	53,003	739.1	1,291
Std. Dev.	86,680	0.88	7,368	1,651	26,126	3,956	54,062	993	1,691
1-st quartile	11858	6.57	312.5	75.0	2906.9	49	5098	159	140
2-rd quartile	144400	7.90	6946.9	1608.8	42624	3291.9	88003	965.7	1839

Table 3.11, Statistical analysis

Ordinary Kriging, Universal Kriging, CoKriging and other Kriging methods are available in ArcGIS 10.0. Distribution pattern is a key factor affecting which one of the Kriging methods to use. We tested all the water parameters distributions by using ArcGIS 10.0 QQplot (a plotting method that evaluates whether the tested data follow normal distribution) and got Normal QQplot curves. (Figure 3.9) pH and TDS followed normal distribution with no transformation, and other tested parameters in the U.S.G.S. database, mainly inorganic ions (cations and anions included), fit normal distribution after log transformation. Therefore, it is feasible to use the Ordinary Kriging interpolation since all data followed normal distribution with or without transformations.
## Concentration distributions of major produced water parameters



Fig 3.9, Distributions of produced water parameters

Trend analysis is the second step of the two preparations necessary for Kriging interpolation. ArcGIS 10.0 has a trend analysis tool to help us decide the order of trend to remove before Kriging and trend of curves of each water parameter. This is shown in Figure 3.10.



Fig 3.10, Trend analysis

Produced water components vary a lot with geological locations in our maps. Cations and TDS concentrations show a declining trend from east to west and a slightly increasing trend from north to south. All the anions except chloride show the opposite trend, increasing from east to west and decreasing from north to south with pH showing the same trends as anions (except chloride). The chloride changing trend is similar to the cations, indicating that chloride is the major anion present in the produced water.

After completion of the distribution analysis and trend analysis, the U.S.G.S. data then can be added into ArcGIS Map 10.0 and Ordinary Kriging, the geo-statistical analysis program we chose, can proceed.

U.S.G.S. Produced Water Survey



Fig 3.11, Estimated metal concentrations using U.S.G.S database

All the prediction maps (pH excluded) were clipped to the U.S lower 48 states boundary. From the prediction maps, we can see that the concentrations of calcium, magnesium, potassium, bicarbonate and sulfate are less than 10,000 mg/L in most produced waters, but the sodium concentration for most areas is more than 10,000 mg/L. Sodium, calcium and chloride are the prevailing ions in produced water, making it "Na-Ca-Cl" based water. TDS is mainly determined by sodium and chloride. Usually membranes are used to remove TDS, especially RO membrane, and the membrane treatment cost largely depends on the TDS level in the influent stream. Since desalination costs are a function of water salinity, produced water with less than 10,000 TDS (total dissolved solids) will be the best candidate for membrane treatment.<sup>62</sup> High TDS will cause membrane scale and shorten the lifetime of the membranes.

In the areas having lots of cations, such as calcium, magnesium and sodium, chloride is the dominant anion; while in those areas with high concentrations of sulfate and bicarbonate, sodium is the major cation.



Fig 3.12, Average pH and TDS value changes with sampled depth

Well upper depth was defined as the depth of the top of the sampled interval (Number, Long integer; Null entries: 10,853); lower depth was the depth of the bottom of the sampled interval.<sup>63</sup> Wells were divided into different strata groups, such as 0-1000, 1000-2000 feet etc., according to the upper and lower depth. Next, average pH values were calculated within each group to represent the pH of this stratum. (Fig 3.12) For example, a well, having upper depth of more than 1000 feet and lower depth of less than 2000 feet was classified in the stratum "1000-2000". We can see from figure 3.12 that pH decreased as the sampled depth increased, which indicates that produced water becomes more acidic as depth increases. With the transmission of produced water from deeper reservoirs to shallower reservoirs or to the surface, pH will increase as a result of the change in the carbonate equilibrium:

$$H^{+} + HCO_{3}^{-} = CO_{2}(aq) + H_{2}O(liq) = CO_{2}(g) + H_{2}O(liq)$$

The loss of ambient pressure during this transport will cause dissolved carbon dioxide to release from water systems, driving this reaction to the right. Therefore, more acidic produced water will appear in the deep formations.

## 3.3.2 Produced water quality for the state of Colorado

We extracted produced water quality data of Colorado from the U.S.G.S survey database and analyzed the water quality characteristics.

Table 3.12, TD	OS ranges of	produced w	ater in Colorado
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TDS, mg/L	Number of Wells	Percentage
<5,000	534	26.73%
5,000-10,000	370	18.52%
10,000-20,000	477	23.87%
20,000-30,000	204	10.21%
30,000-40,000	99	4.95%
40,000-50,000	53	2.65%
50,000-60,000	45	2.25%
60,000-70,000	50	2.50%
70,000-80,000	17	0.85%
80,000-100,000	29	1.45%
>100,000	120	6.01%
Average TDS	25376	

In approximately 45% of the produced water in Colorado, TDS is less than 10,000 mg/L, which is treatable by membranes. Most produced water with TDS less than 30,000 mg/L has the potential to be reused as fracturing fluid by blending it with fresh water.



# Water Quality Interpolations, CO (Data source: U.S.G.S)

Fig 3.13, Water quality prediction State of Colorado (database: U.S.G.S)

We used the ordinary Kriging prediction method to predict pH values for Colorado, based on the U.S.G.S. data. Since some wells have been sampled at different times and have multiple pH values, we take the average of all the pH values and use the mean for each well. Also, we have eliminated some data points without pH, and as a result, we worked with 856 total valid data points. The prediction map indicates that pH is between 7 and 8 for most parts of Colorado,



Fig 3.14, Values of TDS and pH of produced water at different sample well depths (database: U.S.G.S)

The TDS level went up as the sampled depth increased, which was the opposite trend of pH values. With the increase in depth, temperature and pressure increased (geothermal gradient 25<sup>0</sup>C/km), causing more solids to dissolve in the water. Produced water samples were collected from different formations, such as Niobrara formation, Dakota formation, Codell sandstone formation, etc.

## **3.4 Spatial Interpolation**

The characteristics of produced water quality closely relate to the geographic locations and formation properties. Assessing the performance of some spatial interpolation methods to estimate the contents of produced water components, therefore, is one way to understand the change of produced waters by location.

Spatial interpolation is defined as the procedure of estimating the values of some target properties at unobserved locations based on the set of observed values at known locations. The value of using a geo-statistical analysis tool such as Kriging and Vonoroi involves the estimation of physical and chemical characteristics for locations within the target area that are not sampled.<sup>64</sup> The inferred values are estimates of what the values should be at a particular location; therefore, the accuracy of spatial analysis relying on the interpolation of known data is subject to a degree of uncertainty. <sup>65</sup> Most spatial interpolation methods (geo-statistical analysis) can be achieved in ArcGIS 10.0. Different interpolation methods can generate different predictions at the same locations. For example, two TDS level maps of produced water (Figure 3.14) resulted from two different interpolations performed on the same dataset (U.S.G.S produced water database): Thiessen polygon and Kriging.



#### Thiessen Polygon and Kriging TDS prediction Models

Fig 3.15, TDS prediction by Thiessen polygon and Kriging Models

## 3.4.1 Kriging

Kriging is a technique of making optimal, unbiased estimates of regionalized variables at unsampled locations using the structural properties of the semivariogram and the initial set of data values (David 1977), allowing the differentiation between water quality spatial variability to be presented in illustrations. It has been used in soil science, atmospheric science and groundwater studies (Ahmed 2003). For each estimated point, the adjacent points provide a weighted contribution to the estimate, depending upon the semi-variogram function.<sup>66</sup>

$$Z_{v}^{*} = \sum_{i=1}^{n} \theta_{i} Z_{v_{i}}$$

Where  $Z_{v}^{*}$  is the predicted amount of the variable in the desired point,  $\theta_{i}$  is the weight of the dependent quantity to *i*th sample and  $Z_{v_{i}}$  is the amount of variable in point *i*.

The ordinary kriging interpolation method was applied to estimate the value of each un-sampled point. Variables with different sampling events were averaged and used.

#### **3.4.2** Thiessen polygons

Thiessen polygons, also known as the Voronoi Diagrams, are an exact method of interpolation that assumes that the values of unsampled locations are equal to the value of the nearest sampled points. This method is commonly used in the analysis of climatic data when the local observations are not available, and so the data from the nearest weather stations are used. Thiessen polygons define the individual 'regions of influence' around each of a set of points such that any location within a particular polygon is nearer to that polygon's point than to any other point, and therefore, has the same value.<sup>67</sup> A major difficulty with the Thiessen-polygon approach is that the measures are assumed to be more homogenous within units (polygons) and to change values only at the boundaries. Since there is only one observation per polygon, no within-area variation can be estimated.<sup>68</sup>

#### **Chapter 4 Results and Discussions**

#### 4.1 Produced water characteristics in Wattenberg field

#### 4.1.1 Chemical and physical characterization

Produced water contains similar inorganic components as seawater, rich in sodium and chloride ions. Dresel and Rose <sup>69</sup> explained the origin of the produced brines were a mixture of seawater and fresh water after some physical (evaporation, mixing or filtration) and chemical reactions (such as precipitation, mineralogical exchanges in rocks and etc.). When considering the chemical concentrations of the brine, electro-neutrality must be maintained and charge balances were used in this study to assure adherence to this principle. The charge balance can be described as:

$$Charge \ Balance = \frac{\sum c_{iM_i}}{\sum |c_{iM_i}|}$$
$$milliequivalents = \frac{c_i}{molecular \ weight} \times valence$$

 $C_i$  is molality of ion *i*, and  $M_i$  is charge of ion *i*. Charge balance within 5% is acceptable. Meq is the abbreviation of milliequivalents to represent the amount of substance in the water. The charge balance table is shown in <u>Appendix 5</u>. All of the produced water samples having the charge balance agree within 10%. 54 samples out of total 66 samples have the charge balance no greater than 5% and 12 samples have the charge balance exceeding 5% but less than 10%. Samples having charge balance greater than 5% are the diluted water samples with excessive

anions. This pattern might indicate unaccounted-for cations that need to be included in our future study.



Fig 4.1, Detected frequencies

Major cations contained in produced water were sodium, calcium, magnesium, strontium, barium and boron, and minor cations were iron and potassium (detected frequencies shown in figure 4.1). Most of the cations, except boron originally came from formation water and the reaction with formation rocks. Usually, boron was added in the fracture fluid as the crosslinker  $(B(OH)_4)$  to maintain fracture fluid viscosity when ambient temperature increased. Therefore, with the mixture of formation water and fracture fluid, some boron ions will dissolve in this water and return to the surface as produced water. Chloride and bicarbonate are the primary

anions in produced water in Wattenberg field. Very low concentrations of phosphate and sulfate are present in the reclaimed brine. In our test, only 8 samples out of 65 water samples had sulfate concentrations above the detectable limit. Since pH for all the produced water samples was below 7, carbonate was nearly zero and most inorganic carbon existed as bicarbonate and carbonic acid. A summary of the produced water quality measured in our study is shown below.

Table 4.1, Produced water characteristics of shale gas produced water in Wattenberg field

Analyte	pН		TD	S				
Mean (mg/L)	5.91		1828	18285				
Standard Error	0.0485		1535					
Median	5.93		1790	00				
Standard Deviation	0.391		12376	5.83				
Minimum (mg/L)	5.1		790	)				
Maximum (mg/L)	6.8		5120	00				
Range	1.7		5041	10				
Confidence Level	0.097		306	7				
Analyst	Ca	Mg	Ba	Fe	Sr	В	Na	K
Mean (mg/L)	381.00	43.00	18.00	81.00	55.00	14.00	5755.00	116.00
Standard Error	35.00	4.24	2.09	11.24	5.46	0.99	470.49	15.18
Median	301	34	13.9	47.5	44.8	14.8	5790	82
Standard Deviation	282.21	34.18	16.84	90.65	44.01	7.96	3793.24	122.37
Minimum (mg/L)	13.3	0.5	0.277	0.55	1	1.1	239	3.2
Maximum (mg/L)	1170	140	60	424	183	41.2	15200	700
Range	1156.7	139.5	59.723	423.45	182	40.1	14961	696.8
Confidence Level	69.93	8.47	4.17	22.46	10.91	1.97	939.92	30.32
Analyst	C	l <sup>-</sup>	H	ICO <sub>3</sub> <sup>-</sup>	SC	$D_4^{2-}$		
Mean (mg/L)	1079	9.00	1	96.00	4.00			
Standard Error	897	.93		13.57	1.37			
Median	100	00		169	0			
Standard Deviation	7239	9.35	1	09.38	11.01			
Minimum (mg/L)	37	0		0		0		
Maximum (mg/L)	290	00		631	60			
Range	286	30		631	60			
Confidence Level	1793	3.82	27.10		2.	.73		
Analyst	Total carbo	on	Inorganic Total		al organic carbon		Total	COD
Mean (mg/L)	519.00		15.00		504.00		36.00	2711
Standard Error	75.978		1.952		75.455		2.906	290
Median	319.2		9.823		312.231		33.1	1980
Standard Deviation	612.556		15.741		608.338		23.426	2340
Minimum (mg/L)	108.3		0		89.6		0.88	480

Maximum (mg/L)	4383.6	58.98	4357.332	179.98	13946
Range	4275.3	58.98	4267.732	179.1	13466
Confidence Level	151.78	3.90	150.74	5.80	580

All the produced waters in this study came from vertical wells in Wattenberg field and water qualities varied significantly. The average TDS of produced water in Wattenberg was 18,285 mg/L with an average pH of 5.9. Ion concentrations were in various ranges as were the organics.

Table 4.2 Produced water characteristics from three other shale plays and Wattenberg field

Parameter	Unit	Fayetteville	Marcellus	Barnett	North Wattenberg
Sodium	mg/L	5362.6	24445.0	12453.0	5754.8
Magnesium	mg/L	77.3	263.1	253.0	42.9
Calcium	mg/L	256.3	2921.0	2242.0	380.6
Strontium	mg/L	21.0	347.0	357.0	55.4
Barium	mg/L	0.8	679.0	42.0	18.2
Iron	mg/L	27.6	25.5	33.0	80.7
$SO_4$ <sup>2-</sup>	mg/L	149.4	9.1	60.0	3.5
HCO <sub>3</sub> <sup>-</sup>	mg/L	1281.4	261.4	289.0	196.0
Cl	mg/L	8042.3	43578.4	23797.5	10798.6
TDS	mg/L	15,219	72,533	39,570	18,285

\* Water quality data source for Fayetteville, Marcellus and Barnett was from Fountain Quail Water Management Inc.<sup>70</sup>

\* Water quality in north Wattenberg field is from this study.

\* Water quality varies:

Brackish TDS: 5,000 – 35,000 ppm

Saline TDS: 35,000-50,000 ppm

Brine TDS: 50,000-150,000 (or plus 150,000) ppm

Produced water from Fayetteville and Wattenberg shale plays, known as "brackish water" with TDS between 5,000 ppm to 35,000 ppm, had less salinity (TDS) compared with PWs from Marcellus and Barnett. Cations such as magnesium, calcium, barium and strontium increased dramatically with increasing TDS, while sulfate showed a decreasing trend as TDS went up. Fayetteville produced water had an abundance of bicarbonate and sulfate, indicating a high scale potential. A high concentration of bicarbonate suggested acid water produced by Barnett shale

and compared with Fayetteville, sulfate scale would not pose much of a problem in reusing their produced water.

Table 4.3, Shale plays comparisons

	Fayetteville	Marcellus	Barnett	Niobrara	
Age	Mississippian	Devonian	Mississippian	Cretaceous	
Depth (feet)	4,000-6,500	5,000-8,500	6,000-9,000	6,000-10,000	
Thickness (feet)	50-300	50-300	200-500	150-500	
TOC (%)	2-4	4-6	3-8	1-8	
					-

Table 4.3 shows a comparison of the geologic characteristics of the four shale plays discussed above. The depth of the Barnett shale formation is 6,000 to 9,000 feet, Marcellus is similar and the Fayetteville is somewhat shallower. The Niobrara shale formation is found between 6,000 and 10,000 feet deep. The Wattenberg field is part of the Niobrara shale play. Deep shale formations in Marcellus and Barnett might be a reason that caused a high concentration of total dissolved solids.<sup>71</sup>

#### 4.1.2 Correlations of Ions

#### TDS vs. ions

Origin 8.6 (a computer program for data analysis and graphing) was applied in our study to make correlations and curve fittings. As the primary quality parameter, TDS is closely related to ion concentrations, including all the cations and anions measured in this study. Figures 4.2 to 4.4 show the correlations between TDS and other ions.



Fig 4.2, plot of TDS vs.sodium and chloride



Fig 4.3, plot of TDS vs. calcium, magnesium, strontium and potassium



Fig 4.4, plot of TDS vs. calcium, magnesium, strontium and potassium

Chloride and sodium had the closest correlations with TDS with  $R^2$  of linear fittings of both parameters greater than 0.95, followed by strontium, magnesium, calcium, barium and boron with  $R^2$ >0.70, which also indicated good linear correlations. Potassium, iron and bicarbonate had the lowest linear correlations with TDS,  $R^2$ <0.10.

Meanwhile, "TDS" was calculated by alkalinity, cations and anions by the following equation:

Calculated TDS =  $0.6 \times Alkalinity + Na + K + Ca + Mg + Cl^{-} + SO_{4}^{2-}$ 

For quality assurance, the acceptable range of ratio of measured TDS divided by calculated TDS should be between 1.0 and 1.2, and majority of our data were in the acceptable range.

Table 4.4, Ratios of measured TDS over calculated TDS

Residue TDS @180C	Calculated TDS	Ratio- measured/cal culated	WELLS	Residue TDS @180C	Calculate d TDS	Ratio- measured/c alculated
13900	13700	1.01	LUNDVALL 30-111-1Z	2570	2310	1.11
29400	28100	1.05	GOLDBERG N24-(2-7-8)	18000	16000	1.13
21500	21500	1.00	OLSON USX 0 29-25	22500	22300	1.01
35200	33200	1.06	EDWARDS 15-11-15-14	8400	7870	1.07
23500	23300	1.01	EDWARDS 31-15-32-15	17500	15400	1.14
24100	23900	1.01	GOLDBERG N 14-20D	25700	26600	0.97
38600	37000	1.04	COULSON 19-(32-34)	34100	31700	1.08
51200	45100	1.14	SMITH 1 & 9-5	12100	11400	1.06
4470	4270	1.05	LEY 1 & DEITRICH 6-10	6450	5950	1.08
45900	40600	1.13	COLEMAN 23-29D	3310	2990	1.11
17300	15300	1.13	STINAR 13-32	1160	1120	1.04
6070	5810	1.04	ELLIOT USX 31-(9-10)	35700	34800	1.03
36300	36000	1.01	BERNHARDT 0 13-7	7380	6820	1.08
48200	45300	1.06	MORFORT 4-10	5340	5050	1.06
15700	15700	1.00	JERKE G 7-28	17900	17200	1.04
19100	18500	1.03	CONNELL C 4-11	1710	750	1.13
39100	19000	2.06	NIKOLORIC N5-5/W20	17400	1570	1.09
31400	29300	1.07	COX PMC 8-6	20100	16000	1.09
21800	21400	1.02	RUDOLPH 2-(31 32)	13900	20000	1.01
18100	16100	1 12	GOLDBERG N 11-(12 25)	15000	12400	1 12
5130	/970	1.12	KAMMERZELI 4-14 13-4	850	1/100	1.12
12200	11700	1.03	SATER C 23-28D	25100	24100	1.00
2010	1010	1.04	THOUTT #1	12800	12300	1.04
	Residue TDS @180C         13900         29400         21500         35200         23500         24100         38600         51200         4470         45900         17300         6070         36300         48200         15700         19100         39100         31400         21800         18100         5130         12200         2010	Residue TDS @180C         Calculated TDS           13900         13700           29400         28100           21500         21500           35200         33200           23500         23300           24100         23900           38600         37000           51200         45100           4470         4270           45900         40600           17300         15300           6070         5810           36300         36000           48200         45300           15700         15700           19100         18500           39100         19000           31400         29300           21800         21400           5130         4970           12200         11700	Residue TDS @180CCalculated TDSRatio- measured/cal culated13900137001.0129400281001.0521500215001.0035200332001.0623500233001.0124100239001.0138600370001.0451200451001.14447042701.0545900406001.1317300153001.0136300360001.0148200453001.0615700157001.0019100185001.0339100293001.0721800214001.0218100161001.12513049701.0312200117001.04201019101.05	Residue TDS @180C         Calculated TDS         Ratio- measured/cal culated         WELLS           13900         13700         1.01         LUNDVALL 30-111-1Z           29400         28100         1.05         GOLDBERG N24-(2-7-8)           21500         21500         1.00         OLSON USX 0 29-25           35200         33200         1.06         EDWARDS 15-11-15-14           23500         23300         1.01         GOLDBERG N 14-20D           38600         37000         1.04         COULSON 19-(32-34)           51200         45100         1.14         SMITH 1 & 9-5           4470         4270         1.05         LEY 1 & DEITRICH 6-10           45900         40600         1.13         COLEMAN 23-29D           17300         15300         1.13         STINAR 13-32           6070         5810         1.04         ELLIOT USX 31-(9-10)           36300         36000         1.01         BERNHARDT 0 13-7           48200         45300         1.06         MORFORT 4-10           15700         15700         1.00         JERKE G 7-28           19100         18500         1.02         RUDOLPH 2-(31 32)           18100         16100         1.12 </td <td>Residue TDS @180C         Calculated TDS         Ratio- measured/cal culated         WELLS         Residue TDS @180C           13900         13700         1.01         LUNDVALL 30-111-12         2570           29400         28100         1.05         GOLDBERG N24-(2-7-8)         18000           21500         21500         1.00         OLSON USX 0 29-25         22500           35200         33200         1.06         EDWARDS 15-11-15-14         8400           23500         23300         1.01         EDWARDS 31-15-32-15         17500           24100         23900         1.01         GOLDBERG N 14-20D         25700           38600         37000         1.04         COULSON 19-(32-34)         34100           51200         45100         1.14         SMITH 1 &amp; 9-5         12100           4470         4270         1.05         LEY 1 &amp; DEITRICH 6-10         6450           45900         40600         1.13         COLEMAN 23-29D         3310           17300         15300         1.04         ELLIOT USX 31-(9-10)         35700           36300         36000         1.01         BERNHARDT 0 13-7         7380           48200         45300         1.06         MORFORT 4-10</td> <td>Residue TDS @180C         Calculated TDS         Ratio- measured/cal culated         WELLS         Residue TDS @180C         Calculate d TDS           13900         13700         1.01         LUNDVALL 30-111-12         2570         2310           29400         28100         1.05         GOLDBERG N24-(2-7-8)         18000         16000           21500         21500         1.00         OLSON USX 0 29-25         22500         22300           35200         33200         1.01         EDWARDS 15-11-15-14         8400         7870           23500         23300         1.01         EDWARDS 31-15-32-15         17500         15400           24100         23900         1.01         GOLBERG N 14-20D         25700         26600           38600         37000         1.04         COULSON 19-(32-34)         34100         31700           51200         45100         1.14         SMITH 1 &amp; 9-5         12100         11400           4470         4270         1.05         LEY 1 &amp; DEITRICH 6-10         6450         5950           45900         40600         1.13         STINAR 13-32         1160         1120           6070         5810         1.04         ELLIOT USX 31-(9-10)         35700         3</td>	Residue TDS @180C         Calculated TDS         Ratio- measured/cal culated         WELLS         Residue TDS @180C           13900         13700         1.01         LUNDVALL 30-111-12         2570           29400         28100         1.05         GOLDBERG N24-(2-7-8)         18000           21500         21500         1.00         OLSON USX 0 29-25         22500           35200         33200         1.06         EDWARDS 15-11-15-14         8400           23500         23300         1.01         EDWARDS 31-15-32-15         17500           24100         23900         1.01         GOLDBERG N 14-20D         25700           38600         37000         1.04         COULSON 19-(32-34)         34100           51200         45100         1.14         SMITH 1 & 9-5         12100           4470         4270         1.05         LEY 1 & DEITRICH 6-10         6450           45900         40600         1.13         COLEMAN 23-29D         3310           17300         15300         1.04         ELLIOT USX 31-(9-10)         35700           36300         36000         1.01         BERNHARDT 0 13-7         7380           48200         45300         1.06         MORFORT 4-10	Residue TDS @180C         Calculated TDS         Ratio- measured/cal culated         WELLS         Residue TDS @180C         Calculate d TDS           13900         13700         1.01         LUNDVALL 30-111-12         2570         2310           29400         28100         1.05         GOLDBERG N24-(2-7-8)         18000         16000           21500         21500         1.00         OLSON USX 0 29-25         22500         22300           35200         33200         1.01         EDWARDS 15-11-15-14         8400         7870           23500         23300         1.01         EDWARDS 31-15-32-15         17500         15400           24100         23900         1.01         GOLBERG N 14-20D         25700         26600           38600         37000         1.04         COULSON 19-(32-34)         34100         31700           51200         45100         1.14         SMITH 1 & 9-5         12100         11400           4470         4270         1.05         LEY 1 & DEITRICH 6-10         6450         5950           45900         40600         1.13         STINAR 13-32         1160         1120           6070         5810         1.04         ELLIOT USX 31-(9-10)         35700         3

UPRC 31-14/31- 116/BERNHARDT J	12500	11900	1.05	SAMUEL J 7-9 7-15	12500	12100	1.03
SCHANK 2J 35-21	790	706	1.12	CONNELL C 4-29	10100	9450	1.07
SCHMIER B 32-30D	17600	18100	0.97	AURORA USX AB 25-(11/25)	32800	32200	1.02
WELLS 34-3/43-3	23300	23700	0.98	HOWARD USX A 9-13	19600	20100	0.98
WR USX AA 25-(9/10/15/16)	23900	22700	1.05	HOWARD USX A9-(9/14/15/23)	24800	24700	1.00
RYANN STATE 16-23	3890	3830	1.02	COOPER 23-1-20	22500	22400	1.00
FERGUSON B 24-30	5030	4900	1.03	COOPER 23-15	18500	18600	0.99
PATRIOT B 16-(9-16)	9310	9250	1.01	MCDANIEL 32-15/42-15	22700	22000	1.03
ALLES F 33-29 D	1450	1390	1.04	DINNER 15-(42/43)	23000	22400	1.03
HAMILTON 25-(13/14/15)	9730	9640	1.01	WR USX AA 23-(1/2/7/8)	28100	28400	0.99
WEBSTER B 6-(1/2/8)	12500	13000	0.96				



Fig 4.5, Plot of chloride, total dissolved solids and sodium

Level of total dissolved solids (residual) of produced water was mainly determined by concentration of sodium chloride (figure 4.5).



Fig 4.6, Plot of calcium versus magnesium & strontium

Calcium, magnesium, barium and strontium were classified as belonging to a group of "alkaline earth metals" but varied a lot in their abundance. Being abundant in rocks and soil, particularly limestone and dolomites, calcium and magnesium were the most common soluble metal ions in produced water. Although the concentrations of strontium and barium were one to two orders of magnitude lower than those of calcium and magnesium in water and rocks and are less soluble, they are still found in sandstone and igneous rocks in appreciable concentrations. Compared with calcium, magnesium and strontium, the concentration of barium was low.



Fig 4.7, Plot of calcium and barium

Figure 4.6 and 4.7 show the relationships between the "alkaline earth metals". Magnesium, strontium and barium increased with increasing calcium, and among these three metals, magnesium and strontium had closer relationships with calcium, shown in figure 4.3,  $R^2$ >0.95 than barium,  $R^2$ =0.64. The linear correlations of calcium, magnesium and strontium can be used to estimate metal ions concentrations by using one of the three parameters.



Fig 4.8, Sr:Ca and Mg:Ca molar ratio (mg/L) in water versus TDS

Sr:Ca and Mg:Ca ratios increased as TDS increased following an exponential trend line, rising rapidly as TDS increased from several hundred to 20,000 ppm and gradually increasing after TDS reached 20,000 ppm. This trend could be applied to explain the water quality differences from Fayetteville, Marcellus, Barnett and Wattenberg. Although TDS for PWs generated from Marcellus and Barnett, varied a lot with TDS of Marcellus at almost 2 times that of Barnett PW, concentrations of calcium, magnesium and strontium either varied very little or were at almost the same level. According to our trend lines, TDS of both Marcellus and Barnett exceeded 20,000 ppm and therefore Sr:Ca and Mg:Ca ratios did not change a lot as TDS increased. But a

comparison between Fayetteville and Marcellus shows that the calcium, magnesium and strontium of Marcellus were nearly ten times greater than they were in Fayetteville, while TDS was only 4.7 times greater.

Produced water has an origin that is related to seawater. After certain chemical (precipitation, oxidation) and physical (evaporation, filtration and etc.) interactions with formation rocks over a long period, seawater becomes formation water, and when combined with fracturing fluid during the hydraulic fracturing process, it is returned to the surface as produced water. Even though this water has been through a series of reactions, some chemicals originating from seawater or formation rocks will present in the produced water.<sup>72</sup>

Carpenter <sup>73</sup> used "MCl<sub>2</sub>" to represent the conservative compounds during the evaporation of seawater to the point of precipitation of carnallite (KMgCl<sub>3</sub>.6H<sub>2</sub>O).MCl<sub>2</sub>. MCl<sub>2</sub> is primarily the amount of alkaline earth charge balanced by chloride (except for barium) but barium is added for its abundance in our water samples.

$$MCl_2 = Ca^{2+} + Mg^{2+} + Sr^{2+} + Ba^{2+} - SO_4^{2-} - CO_3^{2-}$$

In the process of seawater evaporation, concentration of chloride does not change a lot and therefore can indicate the degree of evaporation. MCl<sub>2</sub> here represent these dissolved species which would form some different mineral species or precipitate during the process of evaporation. Hence, plots of MCl<sub>2</sub> versus Cl are plots of concentrations versus the level of evaporation and the comparison of plots of MCl<sub>2</sub> versus Cl and the evaporation plot of seawater could indicate the relationship of produced water to seawater.



Fig 4.9, Plot of log Cl<sup>-</sup> (meq) versus log MCl<sub>2</sub> (meq)

Here, we use this  $MCl_2$  to represent the total concentration of divalent cations, including calcium, magnesium, barium, strontium and iron, since concentrations of sulfate and carbonate are negligible based on our observations and hence these ions will not affect  $MCl_2$  as much as these divalent cations do. The linear correlation ( $R^2$ =0.9089) between chloride and the sum of divalent cations is very high and the deduced equation could be used to estimate total concentration of divalent cations by known chloride concentration.

Given a value for chloride, sodium, calcium, magnesium, strontium, or total dissolved solids, the remainder of these parameters can be estimated using figures 4.5 through 4.7 and figure 4.9.

Besides the inorganic ions, total organic carbon (TOC), total nitrogen (TN) and chemical oxygen demand (COD) were also measured to investigate the dissolved organic compounds in produced water. Concentrations of total carbon (TC), inorganic carbon (IC), total organic carbon (TOC), total nitrogen (TN) and COD are presented in figure 4.10 shown as columns with different colors and plot of TC and TOC is also included in this figure.



Fig 4.10, Organic compounds present in produced water

Table 4.5, Organics

	TC	IC	TOC	TN	COD
average	519.4	14.88	504.493	36.24	2711
min	108.3	0	89.6	0.88	480
max	4383.6	58.98	4357.332	179.98	13946

Overview of organic concentrations is shown in table 4.5.

Total carbon varies a lot for different produced water samples, with the minimum concentration of 108.3 mg/L and the maximum of 4383 mg/L, and organic carbon represents almost 99% of the total carbon. This indicates that the produced water contains a far greater amount of dissolved oil and gas contents than the combination of inorganic carbon, including bicarbonate, carbonate and dissolved carbon dioxide.



Fig 4.11, Plot of TOC and COD

COD/TOC ratio varied for different pollutants, ranging from 175%-665%. There was 1.2 to 8 times more carbon that can be oxidized by the strong oxidizing agent potassium permanganate (KMnO4) than there was carbon bound in organic compounds. The average COD/TOC ratio in our study was 656% with a minimum ratio of 238% and maximum of 2465%. The plot of TOC and COD is shown in figure 4.11, with linear tendency  $R^2$ =0.7437.

Dispersed oil, BTEX (benzene, toluene, ethylbenzene and xylene), NPD (napthalene, phenanthrene, dibenzothiophene, and C1-C3 substituted homologues), and PAH (polyaromatic hydrocarbons), organic acids, phenol and substituted phenols are the main soluble organic compounds which contribute to the total organic carbon concentration in produced water. McFarlane's (2002) water characterization study showed that among all of the aqueous physical

parameters, pH had the greatest effect on the solubility of organics derived from oil and organic compounds. The soluble organic concentration will go up if pH increases.<sup>73</sup>



Fig4.12, Plot of pH and TOC

Fig 4.12 shows the increasing trend of organic carbons as pH increases, which is the same as McFarlane's observation but with different correlation patterns. Both studies indicate that more organic carbon tends to dissolve in the produced water if the pH value is high and a small change in pH will result in a relatively obvious change in the amount of organics.

## **4.1.3** Water chemistry vs. formation geology

Geological properties of formations are another influential factor leading to the differences in produced water quality. Although there are numerous complicated geological characteristics, well depth was studied for its impact on produced water quality (e.g. pH and TDS). Well depth is also an indicator of temperature, deeper wells generally have a higher temperature.

 $Temperature = surface \ temperature + geothermal \ gradient \ \times \ depth$ 

We use MTD, measured total depth, to represent well depth, and MTDs were accessed from ESER (<u>http://www.eser.org/</u>) and COGCC (<u>http://cogcc.state.co.us/</u>) websites. MTD is plotted versus pH and TDS in Figure 4.13.



Fig 4.13, pH and TDS changes with well depth

The highest TDS occurred from 7100 to 7400 feet below ground in figure 4.13. pH showed a slightly increasing trend as the depth increased but in general no significant correlations were found. Depth was a direct reflection of temperature and pressure. Being "Na-Cl-Ca" type water, the pH of shale produced water in our study was dominated by the following two reactions:

$$H^{+} + HCO_{3}^{-} = CO_{2}(aq) + H_{2}O(liq) = CO_{2}(g) + H_{2}O(liq)$$
(1)

$$Ca^{2+} + 2HCO_3^{-} = CaCO_3(s) + H_2O(liq) + CO_2(g)$$
<sup>(2)</sup>

The increase of pH occurring during the transport of produced water from reservoir to surface was a result of pressure change. Generally speaking, pressure goes up with the increase in depth. When produced water flows from a deep shale formation to the surface, the decreasing pressure will result in the reduction of carbon dioxide in the gas causing reaction (1) to go to the right. Therefore, as hydrogen decreases, the pH goes up. If the water is saturated with calcite (*CaCO*<sub>3</sub>), the loss of carbon dioxide will lead to calcium precipitation according to reaction (2).

$$CaCO_3 + 2H^+ = CO_2(g) + H_2O(liq) + Ca^{2+}$$
(3)

pH could be calculated by the known temperature and derived from reaction (3).<sup>74</sup>

Meanwhile, since reaction (1) is exothermic reaction, rising of temperature will stimulate this reactions go to the right. Increasing of depth results in the increasing of temperature, which motivate reaction (1) go to the right and leave less hydrogen in water, leading to the increasing of pH.

Overall, pressure and temperature affect pH simultaneously but do the opposite. The slightly increasing trend of pH shown in figure 4.13 indicates temperature is the dominant controlling factor of pH.
One impact of depth on TDS could be explained by "dissolution of materials". As water percolates downwards, it would dissolve ionic and non-ionic particles from minerals. Thus, water leaves the upper formation to the underlying formation will be rich in salts.

Temperature can also affect TDS due to evaporation process. Since evaporation rate is high under high temperature, water molecules evaporate rapidly under a high temperature and salts will remain in the produced water causing the increasing of salinity level.

pH is another factor influencing total dissolved solids in water. Usually, hydrogen ion is small and it is able to enter into mineral structure disrupting the boundaries within minerals. Those "broken" constituents will dissolve in water and contribute to a higher concentration of total dissolved solids. In addition, water with low pH, which is acidic, tends to dissolve solids in the rocks.

In the natural system, factors that influence water qualities are much more complicated than what we have discussed due to complex reactions between water and formation rocks.

#### 4.1.4 Water quality temporal trend

Produced water samples in our study were collected from oil-gas-water separator tanks, which usually had multiple pipelines connected to several wellheads. As a result, the water in these separator tanks was the mixture of reclaimed water from different wells and therefore it was hard to get the temporal information from these mixed water samples. So in order to investigate operation time effects on the produced water quality, we selected water samples coming from the separator tanks that were only connected to one well. Ultimately, 31 water samples were valid for this temporal analysis. "Age of well" was defined by the "operation year", which referred to the length of one well's production time, and we used operation years to represent the producing period by year. For example, wells having first production date in the year 2012 were defined to have one operation year, while wells having first production date in the year 1999, were defined as having 14 operation years.

 $operation \ years = 2013 - year \ of \ the \ first \ production \ date \ of \ produced \ water$ 

Also, we averaged the pH or TDS values for those samples having the same production years. For instance, if three wells began to generate produced water in the year 2000, water quality in this year would be the average of these three wells.



Fig 4.14, TDS and pH changes with time

There was no obvious trend of pH according to our data except a slightly decreasing trend with time. TDS increased for the first 3 years of operation and then decreased thereafter.

Being comprised with formation water and fracturing fluid, produced water quality can reflect the formation water components and concentrations. Also, formation water is somehow related to groundwater.



Fig 4.15, COD changes with time

Figure 4.14 and figure 4.15 show the declining trends of pH and COD with time. As previously discussed, a higher concentration of organic carbon correlates with increased pH

values and COD had a linear relation with TOC. Therefore, with the decline of pH, produced water will have less COD as well as TOC concentrations.

#### 4.2 Spatial distribution of major produced water qualities in Wattenberg field

Because of the lack of a useful database of produced water quality, U.S.G.S produced water quality database might be a source to predict produced water qualities in Wattenberg field. U.S.G.S database was added into ArcGIS 10.0 to create ArcGIS maps and then water quality predictions can be done using the Kriging method. Based on the geographic location (longitude and latitude) of a well, values of water quality can be calculated by Kriging. The difference between the estimated values based on the U.S.G.S database and the real tested results from this study will indicate the fitness of the prediction method (Kriging). TDS and pH are the essential parameters of produced water and so we compared predicted and tested values of TDS and pH, which are shown in figure 4.16.



Fig 4.16, Comparison between tested and prediction values

F tests and t-tests were applied to determine whether the variances and means of test values and prediction values are the same or not. Our tested pH values were 1-3 pH units less than the Ordinary Kriging estimated pH values by U.S.G.S. database (table 4.6).

F-test	real TDS	estimated TDS	real TDS	estimated TDS
Mean	16285	20664	5.99	7.60
Variance	220988818	8932041	0.079	0.007
Observations	26	26	30	30
F	24.74		10.64	
		<0.05, variances		<0.05, variances
P(F<=f) one-tail	4.05E-12	different	4.47E-09	different
F Critical one-tail	1.96		1.86	
T-test	Real TDS and	estimated TDS	Real pH and	l estimated pH
Hypothesized Mean				
Difference	0		0	
df	27		34	
t Stat	-1.47		-29.95	
			2.518E-	>0.05, means
P(T<=t) one-tail	0.076	>0.05, means same	26	different
			5.036E-	>0.05, means
P(T<=t) two-tail	0.152	>0.05, means same	26	different

Table 4.6, F-test and t test results between real test data and estimated values

This pH drop may have been due to the sampling time and methods between our study and the U.S.G.S. survey. Most of our produced water samples were from wells with the first production date later than 1999, while all the produced water data collected by U.S.G.S were before 1980. As shown above, pH will decrease along with well operational years, which could be the best possible explanation. Also, different sources of produced water may contribute to the differences in TDS. Produced water obtained in the U.S.G.S produced water survey were mainly from conventional oil and gas production sources with high permeability and large pore size, but produced water in our study came from shale formations which had low permeability and smaller pore size. A difference in the physical properties of the formations would impact the reactions between formation water and formation rocks, thereby resulting in different characterizations of PWs. Though our tested TDS values were slightly less than the estimated TDS values, they did not show the obvious differences as those shown by pH.

Because of the similar geological situation within Wattenberg field, we could make predictions of water qualities, such as pH and TDS, based on known data, using ArcGIS tools. As described in the previous chapter, Kriging can be applied for spatial interpolation allowing water quality predictions throughout a producing field. Since one water sample contained produced waters from different oil/gas wells, as a result, produced water quality results will be the same for those wells and this is a similar situation as one application of a Voronoi map. Therefore, a Voronoi map is useful to represent water quality distribution in Wattenberg field. For example, a separator tank is the data collection station and all the wells connected to this separator tank are the controlling points. The data collection station and all the controlling points comprise one region with same water qualities and will be colored the same in a Voronoi map.

Based on our chemistry analysis, pH and TDS were the most important parameters impacting other aqueous properties. pH and TDS distribution and prediction maps are shown in figure 4.17 and figure 4.18. Our produced water samples were collected from north Wattenberg field, with latitudes from 40.70° to 40.19° (north to south) and longitudes from 105.12° to 104.85° (west to east), which ranges from 62W to 68W and townships from 4N to 7N.









Fig 4.17, pH interpolation maps



Fig 4.18, TDS maps

pH gradually increased from north to south and most produced water from the northern part of Wattenberg field had pH less than 6, indicated by blue, green and light yellow areas in the pH prediction map. TDS of produced water on the northern edge of Wattenberg field was higher than TDS of the central part. If the geographic location of one well is given, we can get the water quality from TDS and pH Kriging prediction maps and future treatment design could be based on these predictions. More valid data is necessary to get better predictions with higher accuracy. These predictions can be used for the produced water reuse treatment design.

For one application, usually, there is the TDS limit for the wastewater treatment either for reuse or reinjection, high saline produced water could not be treated directly unless it is diluted. In this case, produced water with low TDS could be used as the dilution water to dilute the high TDS produced water to meet the treatment requirement. We can use this TDS prediction map to choose the nearest well with low estimated TDS.

For another possible application, if a treatment facility is designed to reuse produced waters from some nearby oil/gas wells, each individual produced water quality could be estimated using the pH and TDS prediction map and therefore the influent quality will be calculated by each segments' quality and quantity.

Additionally, both the prediction methods and prediction maps can be uploaded into ArcGIS online to create web-based GIS water quality predict tools. User can get the predicted produced water quality information by giving the latitude and longitude of one well, which could help the public monitor water qualities or oil and gas companies make decisions on water treatment design.



Fig 4.19, North-south and east-west cross section view map of shale reservoirs: (a) north-south cross section map; (b) east-west cross section map

Maps of depths of Niobrara, Codell and J Sandstone with a north-south cross section and an east-west cross section are shown in figure 4.19. Most of the produced water collected in our study came from Codell and the Codell-Niobrara interval with a few wells producing from the J sandstone. North of the township 4N, the depths of Niobrara, Codell and J Sand become greater. Depth impacts the level of solids dissolved in the produced water. The deeper the formation, the more TDS would be expected in the produced water within a certain range. In addition to the impact depth has on water quality, geological characteristics of formations will also affect produced water composition.

	Codell	Niobrara	J standstone
Depth (feet)	7,100-7,300	6000-7000	8000-10000
Thickness (feet)	14-16	20-30	25
Porosity (%)	8 to12	10-14	
Permeability (mD)	0.022	< 0.1	0.01-0.1
Other	Abundant pore-filling		Marine sandstone
	clay, calcite cements,		
	and iron oxide		

Table 4.7, Geological characters of major shale reservoirs in Wattenberg field

Produced water from shale gas wells producing oil, gas and water from Niobrara shale had more dissolved solids than did those from Codell sandstone and J sandstone. This result was in agreement with U.S.G.S produced water survey.

#### **Chapter 5 Conclusions**

Chemical components and physical properties of produced water from shale gas production wells in Wattenberg field were determined in this study. Results were compared with chemical compositions of produced water from Fayetteville, Marcellus and Barnett shale fields. Produced water from shale gas wells in Wattenberg field was "Na-Cl-Ca" type water. Dominant ions in the produced water were chloride, sodium and calcium and minor ions were magnesium, strontium, barium, iron, potassium and bicarbonate. The concentration of sulfate was low in the produced waters in this study. Plots of TDS, chloride and sodium, calcium, magnesium and strontium, chloride and MCl<sub>2</sub> indicated good correlations among these chemical parameters. Some of these linear relationships can be used to estimate unknown parameters. Among the aqueous parameters, TDS and pH used to relate the produced water quality and other water quality parameters. Based on observations in Wattenberg field, TDS will decrease with time after 1-2 years of operation. Depth is another factor causing different TDS and pH. Overall, TDS and pH showed an increasing trend with depth increasing while in this study, pH increased slightly with increasing depth; TDS increased with depth increasing but TDS would decrease when depth reached 7200 feet and became greater. Spatial distribution of TDS and pH also showed different trends in Wattenberg field which might relate to the formation depth and other geological characters of formations. ArcGIS 10.0 was used to interpolate pH and TDS of produced water in Wattenberg field, and the map showing produced water qualities was also published online. A future study will focus on the completion of produced water samples from shale gas wells in Wattenberg field and establish a more comprehensive database on temporal changes in produced water qualities.

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### Appendix 1

Well_name	Date	ΑΡΙ	latitude	longitude	year	Formatio n1	Formation 2	Formation 3	Formation 4
Lindblad 22-20	22-Jun	05-123-11341	40.475482	-104.803269	1983	CODL			
Lindblad 20-25X	22-Jun	05-123-26734	40.477139	-104.806445	2011	NB-CD			
KODAK 34-21	22-Jun	05-123-22082	40.448449	-104.882545	2004	NB-CD	NBRR	CODL	
KODAK 34-22	22-Jun	05-123-22202	40.449503	-104.886666	2004	NB-CD	NBRR	CODL	
KODAK 34-24	22-Jun	05-123-22080	40.445287	-104.881159	2004	NB-CD	NBRR	CODL	
KODAK 34-25	22-Jun	05-123-23959	40.446629	-104.885515	2008	CODL	NB-CD	NBRR	
Stromberger 13- 31	22-Jun	05-123-20316	40.485102	-104.844994	2001	CODL			
Stromberger 13- 32	22-Jun	05-123-26334	40.485219	-104.849149	2008	CODL			
Stromberger 13- 35	22-Jun	05-123-26235	40.482451	-104.847551	2008	CODL			
Stromberger 1-3	22-Jun	05-123-10110	40.480612	-104.842993	1997	NB-CD	SUSS	JSAND	
KODAK 34-15	22-Jun	05-123-23932	40.446550	-104.875470	2007	NB-CD	NBRR	CODL	
KODAK 34-11	22-Jun	05-123-22097	40.448366	-104.872542	2004	NB-CD	NBRR	CODL	
KODAK 34-12	22-Jun	05-123-22084	40.448361	-104.876330	2004	NB-CD	NBRR	CODL	
KODAK 34-32	22-Jun	05-123-21649	40.441696	-104.885887	2004	CODL			
KODAK 34-31	22-Jun	05-123-22096	40.441267	-104.880950	2004	CODL	NB-CD		
KODAK 34-23	22-Jun	05-123-22081	40.445339	-104.886821	2004	NB-CD	NBRR	CODL	
Schaeffer 17-31	22-Jun	05-123-24117	40.485670	-104.803740	2008	CODL			
Schaefer 17-32	22-Jun	05-123-25388	40.485502	-104.809114	2008	CODL			
Harrington 2-30	22-Jun	05-123-10610	40.464087	-104.823391	1999	CODL	JSAND	SUSS	
BOOTH USX EE 23-15P	28-Jun	05-123-30198	40.554832	-104.627767	2010	NB-CD	NBRR	CODL	
WALCKER 12-23	28-Jun	05-123-29579	40.589611	-104.504455	2011	NB-CD			
WALCKER USX AB 01-07P	28-Jun	05-123-31225	40.604654	-104.494022	2011	NB-CD			
WALCKER USX AB 01-08P	28-Jun	05-123-31301	40.604180	-104.489920	2011	NB-CD	LYNS		
STATE BOOTH 36-11	28-Jun	05-123-23126	40.535420	-104.604270	2005	NB-CD	NBRR	CODL	
KOHLHOFF USX AB 17-02P	28-Jun	05-123-31169	40.578300	-104.571270	2011	NB-CD			
KOHLHOFF USX AB 17-01P	28-Jun	05-123-31198	40.578210	-104.566460	2011	NB-CD			
FURROW USX AB15-99HZ	28-Jun	05-123-31249	40.568360	-104.527110	2010	NB			
AURORA USX AB 25-25	28-Jun	05-123-25954	40.540768	-104.503180	2007	NB-CD	NBRR	CODL	

AURORA USX AB 25-11P	28-Jun	05-123-30351	40.542888	-104.500382	2010	NB-CD	NBRR	CODL	
JOHNSON A 13- 15	29-Jun	05-123-26645	40.481240	-104.496580	2008	CODL			
JOHNSON A 13- 23	29-Jun	05-123-26611	40.482426	-104.493852	2008	NB-CD	NBRR	CODL	
HOWARD USX A 9-13	29-Jun	05-123-24494	40.495090	-104.562070	2007	NB-CD	NBRR	CODL	
HOWARD USX A 09-14D	29-Jun	05-123-33524	40.496960	-104.550060	2011	NB-CD			
HOWARD USX A 09-15D	29-Jun	05-123-33522	40.496950	-104.549970	2011	NB-CD			
HOWARD USX A 09-09D	29-Jun	05-123-33527	40.496960	-104.549900	2011	NB-CD			
HOWARD USX A 09-23	29-Jun	05-123-33526	40.496960	-104.549820	2011	NB-CD			
COOPER 23-1-20	29-Jun	05-123-30426	40.472140	-104.516710	2010	NB-CD	NBRR	CODL	
COOPER 23-15	29-Jun	05-123-25310	40.475300	-104.512640	2008	NB-CD	NBRR	CODL	
MCDANIEL 32-15	29-Jun	05-123-23547	40.487910	-104.533900	2006	CODL			
MCDANIEL 42-15	29-Jun	05-123-23538	40.488000	-104.529110	2006	CODL			
DINNER 15-42	29-Jun	05-123-21997	40.484882	-104.647788	2004	NB-CD	NBRR	CODL	
DINNER 15-43	29-Jun	05-123-20032	40.480665	-104.647709	2001	CODL			
ROUSE USX A 05- 05	29-Jun	05-123-29403	40.516405	-104.581845	2009	NB-CD	NBRR	CODL	
ROUSE USX A 05- 06	29-Jun	05-123-29405	40.516436	-104.575912	2009	NB-CD	NBRR	CODL	
WR USX AA 23-1	3-Jul	05-123-29493	40.477642	-104.396499	2009	NB-CD	NBRR	CODL	
WR USX AA 23-2	3-Jul	05-123-25803	40.477565	-104.401367	2008	NB-CD	NBRR	CODL	
WR USX AA 23-7	3-Jul	05-123-29491	40.473599	-104.401575	2009	NB-CD	NBRR	CODL	
WR USX AA 23-8	3-Jul	05-123-25808	40.473830	-104.396785	2008	NB-CD	NBRR	CODL	
NAT'L HOG FARMS 12-21	3-Jul	05-123-20809	40.386706	-104.447915	2002	CODL	DK-J	DKTA	JSND
NAT'L HOG FARMS 21-21	3-Jul	05-123-20815	40.390330	-104.444000	2002	JSND	NB-CD	DKTA	JNBCD
WELLS 34-3	3-Jul	05-123-21013	40.423064	-104.420673	2002	JSND	NB-CD	CODL	
WELLS 43-3	3-Jul	05-123-21157	40.426896	-104.415543	2003	JSND	NB-CD	CODL	
WR AE 32-03	3-Jul	05-123-30469	40.448623	-104.349084	2010	NB-CD	NBRR	CODL	
WR AE 32-04	3-Jul	05-123-30480	40.448625	-104.354246	2010	NB-CD	NBRR	CODL	
WR USX AA 25-9	3-Jul	05-123-29419	40.455679	-104.377943	2009	NB-CD	NBRR	CODL	
WR USX AA 25- 10	3-Jul	05-123-25738	40.455682	-104.382691	2008	NB-CD	NBRR	CODL	
WR USX AA 25- 15	3-Jul	05-123-29421	40.452000	-104.382760	2009	NB-CD	NBRR	CODL	
WR USX AA 25- 16	3-Jul	05-123-25742	40.452058	-104.377973	2008	NB-CD	NBRR	CODL	
WR USX BB 1-1	3-Jul	05-123-30474	40.433773	-104.378192	2009	NB-CD	NBRR	CODL	
WR USX BB 1-2	3-Jul	05-123-26768	40.433863	-104.382860	2008	NB-CD	NBRR	CODL	
WR USX BB 1-7	3-Jul	05-123-26101	40.430561	-104.382805	2008	NB-CD	NBRR	CODL	
WR USX BB 1-8	3-Jul	05-123-26769	40.430368	-104.377510	2008	NB-CD	NBRR	CODL	

WR USX BB 1-17	3-Jul	05-123-25108	40.431694	-104.379745	2007	NB-CD	NBRR	CODL	
WR USX AA 35- 09	3-Jul	05-123-29530	40.441415	-104.396483	2009	NB-CD	NBRR	CODL	
WR USX AA 35- 15	3-Jul	05-123-29528	40.437518	-104.401704	2009	NB-CD	NBRR	CODL	
WR USX AA 35- 16	3-Jul	05-123-25884	40.437410	-104.396641	2008	NB-CD	NBRR	CODL	
WR USX AA 35- 23	3-Jul	05-123-25051	40.439530	-104.399010	2007	NB-CD	NBRR	CODL	
SAMUEL J 7-9	2-Aug	05-123-25604	40.411950	-104.818590	2005	NB-CD	CODL	NBRR	JSAND
SAMUEL J 7-15	2-Aug	05-123-25605	40.411960	-104.818480	2005	CODL			
UPRC 31-1116	2-Aug	05-123-18024	40.340040	-104.767830	1999	NB-CD	CODL	NBRR	
UPRC J31-14	2-Aug	05-123-22425	40.350760	-104.825340	2004	CODL			
BERNHARDT J 31- 21	2-Aug	05-123-29252	40.355131	-104.824011	2009	NB-CD	CODL	NBRR	
BERNHARDT J 31- 22D	2-Aug	05-123-29102	40.355075	-104.823957	2009	NB-CD	CODL	NBRR	
GOLDBERG N 24- 2	2-Aug	05-123-18983	40.390201	-104.839146	1999	CODL			
GOLDBERG N 24- 7	2-Aug	05-123-18984	40.387350	-104.838550	1999	CODL			
GOLDBERG N 24- 8	2-Aug	05-123-21109	40.386284	-104.833841	2002	NB-CD	CODL	NBRR	
SCHANK J 35-21	2-Aug	05-123-26443	40.358183	-104.747850	2008	NB-CD	CODL	NBRR	
LUNDVALL J 30- 19	2-Aug	05-123-26533	40.376077	-104.824964	2007	CODL			
LUNDVALL 30- 11H6	2-Aug	05-123-18111	40.368312	-104.825642	2006	NB-CD	CODL		
GOLDBERG N 14- 20D	4-Aug	05-123-30115	40.397941	-104.866134	2010	NB-CD	CODL	NBRR	
EDWARDS 15-11	4-Aug	05-123-21339	40.405170	-104.872910	2004	CODL			
BERNHARDT O 13-7	4-Aug	05-123-20183	40.313270	-104.836920	2001	CODL			
EDWARDS 31-15	4-Aug	05-123-22324	40.405020	-104.876606	2004	NB-CD			
EDWARDS 32-15	4-Aug	05-123-22917	40.401990	-104.876162	2005	NB-CD			
Rudolph 2-31	4-Aug	05-123-21102	40.427697	-104.861065	2003	CODL			
Rudolph 2-32	4-Aug	05-123-21263	40.427685	-104.865815	2003	CODL			
Coulson 19-32	4-Aug	05-123-23444	40.383120	-104.943420	2006	CODL			
Coulson 19-34	4-Aug	05-123-29134	40.380240	-104.937620	2008	NB-CD	CODL	NBRR	
GOLDBERG N 14- 12	4-Aug	05-123-21165	40.397813	-104.866132	2006	CODL			
GOLDBERG N 14- 25	4-Aug	05-123-23795	40.396110	-104.865016	2006	CODL			
ELLIOT USX S 31- 09P	4-Aug	05-123-31240	40.267040	-105.039020	2010	NB-CD	CODL	NBRR	
ELLIOT USX S 31- 10	4-Aug	05-123-25148	40.266933	-105.043290	2007	NB-CD	CODL	NBRR	
OLSON USX O 29- 25	4-Aug	05-123-24414	40.280568	-104.918625	2009	CODL			
MONFORT 4-10	16-Aug	05-123-20250	40.332290	-104.770250	2001	NB-CD	CODL	NBRR	
KAMMERZELL 4- 14	16-Aug	05-123-20096	40.335960	-104.787470	2000	NB-CD	CODL	NBRR	

KAMMERZELL 13- 4	16-Aug	05-123-13584	40.335329	-104.791614	1999	NB-CD	CODL		
SMITH 1	16-Aug	05-123-11922	40.332290	-104.562670	1999	NB-CD	NBRR	CODL	
SMITH 9-5	16-Aug	05-123-17348	40.328196	-104.561960	1999	NB-CD	NBRR	CODL	
CONNELL C 4-11	16-Aug	05-123-21176	40.339913	-104.557673	2003	NB-CD	NBRR		
JERKE G 7-28	16-Aug	05-123-25212	40.334165	-104.701545	2007	NB-CD	CODL	NBRR	
COLEMAN C 23- 29D	17-Aug	05-123-30836	40.303459	-104.524935	2011	NB-CD			
SATER C 23-28D	17-Aug	05-123-30804	40.303100	-104.514670	2012	NB-CD			
THOUTT 1	17-Aug	05-123-11079	40.303200	-104.548620	1999	NB-CD	NBRR	CODL	
COX PM C 8-6	17-Aug	05-123-14174	40.329156	-104.576884	1999	NB-CD	CODL	NBRR	
LEY 1	17-Aug	05-123-11921	40.335840	-104.591110	2000	NB-CD	CODL	NBRR	
DEITRICH 6-10	17-Aug	05-123-17359	40.338918	-104.590856	2009	NB-CD	CODL	NBRR	
DEITRICH 6-23	17-Aug	05-123-24010	40.337653	-104.588561	2006	NB-CD	CODL	NBRR	
NIKOLORIC C 5-5 & 20	17-Aug	05-123-20235	40.343180	-104.581280	2002	JSAND			
STINAR C 13-32	17-Aug	05-123-30941	40.312978	-104.508936	2010	NB-CD	CODL	NBRR	
CONNELL C 4-29	17-Aug	05-123-24872	40.348040	-104.559760	2007	NB-CD	CODL	NBRR	
RYANN STATE 16- 23	17-Aug	05-123-25398	40.308660	-104.549629	2008	NB-CD	CODL	NBRR	
FERGUSON B 24- 30	25-Jul	05-123-25119	40.391613	-104.508652	2007	NB-CD	CODL	NBRR	
PATRIOT B 16-9	25-Jul	05-123-14928	40.397913	-104.547986	1999	CODL			
PATRIOT B 16-10	25-Jul	05-123-14929	40.397536	-104.552004	1999	CODL			
PATRIOT B 16-15	25-Jul	05-123-14930	40.393370	-104.552492	1999	CODL			
PATRIOT B 16-16	25-Jul	05-123-14931	40.393400	-104.547873	1999	CODL			
PATRIOT B 16-11	25-Jul	05-123-15244	40.397522	-104.556647	1999	CODL			
PATRIOT B 16-13	25-Jul	05-123-15245	40.393660	-104.562240	1999	CODL			
PATRIOT B 16-14	25-Jul	05-123-15246	40.393610	-104.557310	1999	CODL			
PATRIOT B 16-12	25-Jul	05-123-15564	40.397440	-104.562450	1999	CODL			
ALLES F 33-29D	25-Jul	05-123-30281	40.362560	-104.670680	2009	NB-CD	CODL	NBRR	
THISTLE DOWN B 31-24D	25-Jul	05-123-28057	40.351701	-104.592762	2009	NB-CD	CODL	NBRR	
HAMILTON 25-13	25-Jul	05-123-15393	40.364240	-104.618020	1999	CODL	NB-CD	NBRR	
HAMILTON 25-14	25-Jul	05-123-15394	40.364260	-104.613701	2002	NB-CD	CODL		
HAMILTON 25- 15B	25-Jul	05-123-16497	40.364210	-104.609950	1999	NB-CD	NBRR	CODL	
Webster B 6-1	25-Jul	05-123-13852	40.433427	-104.587268	1988	NB-CD	CODL	NBRR	
Webster B 6-2	25-Jul	05-123-13494	40.433626	-104.589919	1987	CODL	NBRR		
Webster B 6-8	25-Jul	05-123-18576	40.429080	-104.585000	1999	NB-CD- LYONS	NB-CD	CODL	
HAMILTON 25- 10B	25-Jul	05-123-15392	40.368350	-104.608550	2002	NB-CD	NBRR	CODL	
SCHMIER B 32- 30D	25-Jul	05-123-29003	40.360926	-104.580839	2009	NB-CD	CODL	NBRR	

Parameter	Volume (mL)	Container	Preservation	Holding time
рН	25	G, P	None	Immed. & on-
				site
Cations	250	Р	Field rinse, HNO <sub>3</sub>	180 days
(major cations, trace			pH<3	
elements)				
Anions	250	Р	Field rinse	
Chloride	100-200	G, P	Cool 4°C	28 days
Sulfate	50-100	G, P	Cool 4°C	28 days
Alkalinity (CaCO <sub>3</sub> )	200	G, P	Cool 4°C	14 days
BOD-5 day	500-1000	G, P	Cool 4°C	48 hrs
BOD- long term	500	G, P	Cool 4°C	24 hrs
COD	50-250	G, P	H <sub>2</sub> SO <sub>4</sub> pH<2	28 days
Total & total volatile	100	G, P	Cool 4°C	7 days
Turbidity	100-250	G, P	Cool 4°C	48 hrs
			Store in dark	
VOC	2 to 4	G vials/TLS	HCl pH<2	14 days
	40 ml vials		No headspace	
			Cool 4°C	
Total organic carbon (TOC)	125	G	≤6 °C	28 days
			Store in dark	
			HCl or H <sub>2</sub> SO <sub>4</sub> to	
			pH<2	
Total dissolved solids (TDS)			Cool 4°C±2 °C	7 days
Oil and Grease	1000	G only wide	H <sub>2</sub> SO <sub>4</sub> pH<2	28 days
		mouth		

# Sample Containers, preservation and holding time requirements

# Tier 1 On-Site Water Test Worksheet

Organiza	tion/tester na	me		Well ID#(1-12								
Well nam	ne											
Well location(Longitude)/(Latitude) (GPS)												
Sample Depthfeet												
Sample Formation:NiobraraCodellJ SandD Sand												
Date/ (MM/DD/YY)												
Sample Start Time (AM/PM) : End Time (AM/PM)												
Air temp	erature:	°F										
Well	Water	Conductivity	/ рН	Tu	irbidity, NTU		DO, mg/L %					
ID#	Temp, °F						saturation					
Sampling	volume:	mL										
Today's weather : sunny partly cloudy overcast light rain heavy rain												
Yesterda	y's weather:	sunny p	artly cloudy	overcast	light rain	heavy ra	ain					

COMMENTS:

Well ID #	Chemical Analysts	Level	Test Method or Test equipment
	TSS, mg/L		
	TDS, mg/L		
	TOC, mg/L		
	Sulfate (SO <sub>4</sub> ), mg/L		
	Carbonate (CO <sub>3</sub> ),		
	mg/L		
	Bicarbonate		
	(HCO₃), mg/L		
	Chloride (Cl), mg/L		
	Phosphate (PO <sub>4</sub> ),		
	mg/L		
	Oil and Grease		
	BETX(optional)		
	Alkalinity		

#### Tier 2 CSU Lab Water Test Sheet

Tester Name

Well ID# \_\_\_\_\_(1-120) Well API# \_\_\_\_\_(05-123-XXXX)

Test Date / / (M/D/Y)

 Test Start Time
 (AM/PM) ; Test End Time
 (AM/PM)

Air temperature \_\_\_\_\_ °F

Sampling volume \_\_\_\_\_ mL

Signature:

#### Charge Balance

Test_	Ca	Mg	Ва	Fe	Sr	В	Sr	К	Cl-	HC	$SO_4$	catio	anio	charge
1-10	389	37	9.8	79.	50.	9.9	441	52	870	122	0	223.	247.	5%
1-11	776	85	40.	38	11	16.	930	23	175	182	0	466.	496.	3%
1-12	669	73	19	44.	98.	13.	682	87	137	140	0	347.	388.	6%
1-13	941	10	52.	64.	13	21.	107	21	210	201	0	540.	595.	5%
1-14	450	57	38	18.	68.	14.	799	22	144	185	0	388.	409.	3%
1-15	697	76	21.	47.	99.	19.	779	15	150	98	0	395.	424.	4%
1-16	200	16	4.5	113	28.	4.4	180	35	360	85	0	96.8	102.	3%
1-17	783	94	56.	12.	11	25	124	77	233	346	0	601.	662.	5%
1-18	111	13	57.	30	16	29.	152	10	282	293	0	747.	800.	3%
1-19	604	69	9.1	135	89.	20.	117	12	230	504	50	562.	657.	8%
1-20	107	14	2.8	25	14.	4	145	41	251	230	0	73.3	74.5	1%
1-21	980	11	58.	25.	15	26.	136	10	255	224	0	667.	722.	4%
1-22	117	14	52.	45	18	25.	147	90	290	230	60	727.	822.	6%
1-23	567	73	46.	142	84.	22.	110	68	202	355	0	530.	575.	4%
1-24	293	31	20.	39.	43.	12.	517	48	100	165	0	250.	284.	6%
1-25	373	43	30.	43	57.	17.	686	42	126	169	0	331.	358.	4%
1-26	419	48	27.	20.	58.	21.	869	14	152	269	0	416.	433.	2%
1-27	434	42	23.	65	58.	20	737	99	143	179	0	359.	406.	6%
1-28	410	40	8.1	65.	53.	19.	605	12	118	216	0	301.	336.	6%
1-29	501	48	13.	300	68.	17.	726	93	140	119	0	366.	396.	4%
1-30	561	60	18.	249	85.	18.	718	11	143	87	0	366.	404.	5%
1-31	338	34	19.	94.	48.	15	631	50	116	174	0	305.	330.	4%
1-32	424	52	20.	184	62.	20.	954	81	181	308	0	458.	515.	6%
1-33	261	31	28.	280	38.	16.	645	18	116	328	0	318.	332.	2%
1-34	220	40	27.	424	47.	14.	775	13	155	0	0	376.	437.	7%
1-35	426	59	27.	294	73.	22.	983	62	185	294	0	476.	526.	5%
1-36	301	37	27.	151	85.	41.	740	18	145	334	0	367.	414.	6%
1-37	284	35	15.	122	42	20.	721	19	133	435	0	348.	382.	5%
1-38	188	21	4.2	107	26	17	564	69	970	631	20	268.	284.	3%
2-01	292	33	18.	1.2	44.	9.8	408	45	750	101	0	200.	213.	3%
2-02	259	24	12.	52.	36.	11.	408	52	740	159	0	200.	211.	3%
2-03	515	54.	15.	83	81.	14.	528	21	980	140	0	275.	278.	1%
2-04	13.	0.5	0.2	32.	1	1.6	248	7	370	110	0	13.4	12.2	5%
2-05	26.	2.5	0.7	50.	3.2	3.7	670	7.3	114	105	0	34.1	33.8	0%
2-06	82.	6.9	2.0	108	8.8	2.8	732	24.	138	128	0	42.2	41.0	2%
2-07	533	67.	60	93	84.	17.	936	58	164	217	0	453.	466.	1%
2-08	275	25.	6.2	37	37.	5.9	252	50	490	100	0	131.	139.	3%
2-09	244	22.	6.5	55.	29.	7	214	78	420	172	0	114.	121.	3%
2-10	412	59.	9.5	74	56.	13	481	57	940	180	0	258.	268.	2%

2-11	155	21	8.5	352	21	11.	432	14	750	334	0	218.	217.	0%
2-12	931	11	27.	14.	13	21.	997	70	197	217	0	519.	559.	4%
2-13	399	38	14.	114	56.	12.	470	89	870	123	0	239.	247.	2%
2-14	954	99.	39.	97	14	21.	114	73	220	184	0	568.	623.	5%
2-15	791	10	28.	198	12	14.	723	68	139	173	0	380.	394.	2%
2-16	127	11.	6.4	58.	14.	5.3	168	27	310	149	0	85.5	89.8	2%
2-17	21.	1.7	1.1	12.	2.4	1.1	239	11.	430	74	0	12.8	13.3	2%
2-18	200	29.	5.1	34.	25	19.	380	26	690	298	0	193.	199.	2%
2-19	43.	3.9	1.0	12.	5.1	2.4	533	17	930	68	0	27.6	27.3	0%
2-20	264	28.	1.3	125	37.	13.	599	10	107	160	0	289.	304.	3%
2-21	94.	5.2	0.8	113	6.5	4.5	100	11	180	125	0	54.8	52.8	2%
2-22	414	48	26.	1.2	60.	22.	852	21	146	350	0	410.	417.	1%
2-23	231	25	10.	45.	32.	13.	426	21	740	199	0	211.	211.	0%
2-24	421	43	32.	27.	53.	19.	692	13	122	331	0	339.	349.	2%
2-25	421	43	2.4	49.	16.	8.6	197	13	360	142	0	119.	103.	7%
2-26	377	28	4.9	112	41.	24.	579	75	960	187	0	288.	273.	3%
2-27	24.	1.8	0.3	18.	1.9	2.1	386	3.2	630	114	0	19.7	19.6	0%
2-28	226	22	13.	23.	32.	10.	317	35	590	105	0	157.	168.	3%
2-29	78	6	3.2	5.2	9.3	5.2	128	31	233	148	6	63.2	68.2	4%
2-30	82	8	5.6	2.0	11	5.5	172	11	299	124	0	82.2	86.3	2%
2-31	224	22	5.9	10.	32.	10.	303	82	580	102	0	152.	165.	4%
2-32	22	1	0.3	2.9	1.5	2.9	446	22	800	132	23	22.3	24.9	5%
2-33	212	22.	17.	26.	31.	10.	406	48	720	140	0	196.	205.	2%
2-34	170	19	5.6	13.	20.	9.9	288	44	600	158	10	151.	171.	6%
2-35	262	27	1.9	0.5	35.	10.	408	13	830	143	30	201.	236.	8%
2-36	92.	8.3	3.1	5.7	11.	6.1	169	77	300	123	20	83.5	86.8	2%
2-37	360	32	8.9	1.3	47.	17.	592	98	115	144	10	288.	326.	6%