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Remediation of Risks in Natural Gas Storage Produced Waters: The Potential Use of Constructed Wetland Treatment Systems

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REMEDICATION OF RISKS IN NATURAL GAS STORAGE PRODUCED
WATERS: THE POTENTIAL USE OF CONSTRUCTED
WETLAND TREATMENT SYSTEMS

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Environmental Toxicology

by
Brenda Marie Johnson
December 2006

Accepted by:
Dr. John H. Rodgers, Jr., Committee Chair
Dr. James W. Castle
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ABSTRACT

Natural gas storage produced waters (NGSPWs) are generated in large volumes, vary in composition, and often contain constituents in concentrations and forms that are toxic to receiving system biota. This research had three major objectives: 1) Characterize NGSPWs to discern the constituents of concern present in these waters; 2) Design and measure performance of a pilot-scale hybrid constructed wetland treatments system (CWTS) for treating NGSPWs, and; 3) Discern the reliability of the Turner Designs TD500 handheld fluorometer for measurement of oil-in-water in produced waters containing algae. Produced waters contained chlorides, metals, and organics as constituents of concern. Using simulated produced waters, specifically designed hybrid pilot-scale CWTS decreased cadmium, copper, lead, and zinc concentrations below NPDES permit concentrations and decreased aqueous toxicity to *Ceriodaphnia dubia*. The handheld fluorometer was unable to produce reliable measurements of oil-in-water, requiring further research for a simple method for field measurement of oil-in-water.

DEDICATION

I dedicate this and all of my success to my father who has always encouraged me to make my time on this planet valuable and also my mother for offering endless encouragement in my times of doubt.

AKNOWLEDGEMENTS

I would like to extend a special thank you to my advisor, Dr. John Rodgers Jr. your continued patients and guidance will always be valued and appreciated. Thank you to my committee: Dr. Castle and Dr. Huddleston. To my little sister, anything is possible. To all of my lab-mates whom shared these past few years with me Derek, Chris, Maurice, O’Niell, the Lauras, Basma, and Evan your support made this possible, Thank you.

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CHAPTER 1

INTRODUCTION

Natural gas storage produced waters (NGSPWs) are waters brought to the surface when natural gas is reclaimed from underground storage facilities. As the demand for natural gas increases, there is concurrent increased production of NGSPW. At each storage site, NGSPWs assume unique characteristics based on the initial elements in the water, the storage formations, and contact with natural gas.

NGSPWs provide several environmental challenges. These waters are produced in large volumes, vary widely in composition, and often contain constituents in concentrations and forms that are toxic to receiving system biota (Collins, 1975; Ray and Engelhardt, 1992; Veil et al., 2004). The waters are produced at remote sites and are transferred to collection facilities where they are temporarily stored until treatment. Current treatment approaches for these waters are expensive as well as restricted by the Clean Water Act (CWA) through the National Pollutant Discharge Elimination System (NPDES) and the Safe Drinking Water Act through Underground Injection Control (UIC) (Fillo et al., 1992). In 2004, the United States consumed approximately 22 trillion cubic feet of natural gas; 77% of which was produced in the US (EIA, 2005). For one cubic foot of gas, from one to eight cubic feet of produced water is generated (Ray and Engelhardt, 1992). Typically, the character of the produced water is a combined result of the geologic formation water, extraction procedures, and the handling or processing of the water on the surface (Ray and Engelhardt, 1992). Currently, there are two

predominant approaches for treatment of NGSPW: reinjection to deep wells and transport to specialized treatment facilities (Nakels et al., 1992). These approaches are costly and becoming more complex as transport and reinjection are restricted by regulatory agencies.

Thorough characterization of NGSPW is essential for identifying problems associated with these waters. Produced waters typically contain a range of concentrations of many environmental constituents of concern such as chlorides, hydrocarbons, and inorganics (e.g. Cd, Cu, Pb, and Zn). A flexible and robust treatment approach is needed to manage these constituents of concern.

Constructed wetland treatment systems (CWTS) have been utilized to treat organics and inorganics independently, but this technology has not been used for NGSPW (Cronk, 1996; Hawkins et al. 1997; Lin and Mendelsohn, 1998; Knight et al. 1999; Gillespie et al. 2000; Murray-Gulde et al. 2003a; Murray-Gulde et al. 2003b). One defining characteristic of most produced waters is the high chloride content (which may exceed 3×10^6 mg/L chloride) (Collins, 1975; Ray and Engelhardt, 1992). Chloride concentrations can overpower other constituents of concern, and CWTS are not efficient or effective for treating conservative elements such as chlorides. Thus, there is a need for a hybrid system that includes constructed wetlands as well as a process or device for removing chlorides. Furthermore, a robust and flexibly designed CWTS is required to deal with the range of other constituents of concern such as organics and inorganics. These elements and compounds will likely be transferred and transformed in a CWTS through different pathways (Hawkins et al., 1997; Gillespie et al., 2000; Murray-Gulde et al., 2003a).

This research utilized a pilot-scale CWTS. A pilot-scale study serves to decrease uncertainties and confirm design features for future, field-scale constructed wetland treatment systems. To evaluate the potential use of CWTS to mitigate risks of NGSPW, performance parameters must be identified and measured. In this case, NGSPWs would ideally be renovated to the extent that they could be discharged to receiving aquatic systems. After constituents of concern have been identified and discharge limitations have been established, performance criteria can be developed.

In a complex matrix such as NGSPW, it is possible that some component could confound the measurement of targeted constituents. Measurements of concentrations of salts and metals have been accomplished in complex matrices such as produced waters (Murray-Gulde et al., 2003b). As NGSPWs are treated and phytotoxicity is no longer a problem, algae may become prevalent in the water column. Measurement of organics in produced water may be confounded by the presence of algae in the water column if a fluorometric technique is used.

This research addressed questions regarding performance of constructed wetland treatments systems as well as measures of that performance. This research had three major objectives:

1. Characterize natural gas storage produced waters to discern the constituents of concern present in these waters;
2. Design and measure the performance of a pilot-scale constructed wetland treatment system (CWTS) for treating NGSPW, and
3. Discern the reliability of the Turner Designs TD500 oil-in-water handheld fluorometer for measurement of produced waters containing algae.

Overall, this research contributed to the knowledge of NGSPW composition, provided a possible remediation approach for these waters, and identified potential difficulties for measurement of oil-in-water in samples containing algae.

Characterize natural gas storage produced waters to discern
the constituents of concern present in these waters

The purpose of this research was to characterize produced waters, to discern the constituents of concern present in these waters, and to determine the composition of water for use in the pilot-scale CWTS. Characterization was accomplished by: 1) reviewing published literature, 2) analysis of produced water composition records, and 3) analysis of produced water samples provided by natural gas storage companies. A comprehensive literature search specifically targeting NGSPWs was performed to provide additional composition data. Approximately 4,000 records of NGSPWs were provided by several natural gas storage companies. These records were managed utilizing the Statistical Analysis System (SAS Institute, 2002). NGSPW samples received from natural gas storage companies were chemically analyzed for composition. The compilation of these three sources of information provided a summary characterization of NGSPWs.

The aforementioned characterization of NGSPW was utilized to formulate simulated NGSPWs. The simulated natural gas storage produced waters were formulated to emulate the composition of actual produced waters illustrated through statistical analysis of data from various natural gas storage companies and were similar to published data (Pope and Pope, 1999; Ray and Engelhardt, 2003; Veil et al., 2004). Simulated

produced waters were composed of select constituents of concern that are frequently present in actual produced waters. A risk based approach was taken in the selection of specific constituents of concern. Compounds that were present in multiple produced water samples and that were in concentrations that posed eminent risks to *Ceriodaphnia dubia* were chosen as constituents of concern (oil-in-water, Cd, Cl, Cu, Pb, and Zn). Simulated NGSPWs were utilized in CWTS experiments because simulated waters allow for more complete knowledge of system input, which in turn allows for a better comparison with system output. They are also more cost effective for preliminary, pilot-scale experiments.

Design and measure the performance of a hybrid pilot-scale constructed wetland treatment system (CWTS) for NGSPW

The purpose of this research was to assess the treatability of NGSPW utilizing a pilot-scale hybrid CWTS. The approach is applicable to a wide range of waters produced from gas storage, as the composition and volumes of waters generated vary greatly among storage fields. Specific objectives of this pilot-scale study were: 1) to design and construct modular pilot-scale hybrid CWTS to remove specific constituents of NGSPW; and 2) to measure performance of the pilot-scale hybrid CWTS in terms of decrease of targeted constituents from inflow to outflow with concomitant decreases in toxicity. Because of the diverse composition of NGSPW, the treatment system needed to be flexible in design and incorporate different treatment mechanisms.

The treatment effectiveness and performance were evaluated based upon a decrease in concentrations of constituents of concern in inflow and outflow samples.

Discern the reliability of the Turner Designs TD500 oil-in-water handheld fluorometer for measurement of produced waters containing algae

Efficient and accurate oil-in-water measurements were necessary for effective evaluation of the system. Interferences from various constituents contained in mixtures such as produced waters often make accurate analytical measurements difficult. Because oil is a mixture of various organic compounds, gravimetric techniques and fluorometry are often used to quantify oil-in-water concentrations (i.e. as a bulk measurement). The purpose of this research was to discern the contribution of algae to oil-in-water measurements using a Turner Designs TD500 oil-in-water handheld fluorometer. The specific objectives were to: 1) measure oil-in-water unconfounded by algae, 2) measure the independent contribution of algae to fluorescence in the portion of the spectrum also used for oil-in-water measurements, and 3) discern the potential contribution of algae to false positive fluorometric measurements of oil-in-water.

New approaches are emerging utilizing fluorometry for measuring oil in water. Oil-in-water is a generic parameter; the fluorometer detects certain ‘indicator’ chemicals (fluorophores) contained within oil that fluoresce at specific wavelengths or bands of wavelengths. Algae present in the sample introduce chlorophyll and/or phaeophytin to the sample which fluoresce at the same wavelengths as oil and grease (APHA, 1998; Ryder, 2004). When this arises, a positive interference could occur, leading to false readings for oil in water.

Crude oils and other petroleum products contained in produced water are complex mixtures of hydrocarbon compounds. Ryder (2004) found that the 18 crude oils studied had excitation wavelengths scaling from 250-700 nm. Oils found in produced waters

may vary from heavy oils to light oils. Typically lighter oils tend to have narrow, intense fluorescence emission bands, while the heavy oils typically have broad bands with weaker emission (Ryder, 2004).

Spectrophotometry and fluorometry utilizing a 90% acetone extraction is the most commonly used method of chlorophyll *a* and phaeophytin determination in aqueous samples (APHA, 1998; Arar, 1997). Peak excitation and emission wavelengths for chlorophyll *a* are 430 nm and 663 nm, respectively (APHA, 1998). As noted above, hydrocarbons found in oils fluoresce at excitation and emission wavelengths spanning the full range of 250-700 nm (Ryder, 2004). This broad scan includes the wavelengths used for chlorophyll *a* and phaeophytin analysis, leading to the suggestion that there could be some interference when both oil and algae are present in the same sample.

Summary

This thesis is organized into chapters intended for publication in peer-reviewed journals. Therefore, some of the introductory material and methods are repeated, and some chapters have different citation and reference formats. Chapter 1 introduces some of the problems with NGSPWs and potential productive solutions for these problems. Chapter 2 contains a comprehensive review of produced water composition. Chapter 3 focuses on performance of a hybrid CWTS. Chapter 4 identifies difficulties in using fluorometry for measuring oil-in-water. Chapter 5 summarizes the results from this research.

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CHAPTER 2
CHEMICAL, PHYSICAL, AND RISK CHARACTERIZATION
OF NATURAL GAS STORAGE PRODUCED WATERS

Introduction

Natural gas storage produced waters (NGSPWs) are brought to the surface when natural gas is reclaimed from underground storage (Veil et al., 2004). These waters may contain elements and compounds that pose risks to aquatic biota if directly discharged to receiving systems. Currently, treatment and disposal of these waters is costly, which limits expansion of natural gas storage and threaten continued use of some storage facilities. Data are needed regarding the chemical and physical characteristics of these waters and the constituents of concern. Thorough characterization of these waters will facilitate development of efficient and effective treatment strategies.

As the demand for natural gas increases, there is concomitant increased production of NGSPW. According to the Energy Information Administration (EIA) of the United States (U.S.) Department of Energy, the U.S. consumed approximately 22 trillion cubic feet of natural gas in 2005 (EIA, 2005). At any given time, 8.2 trillion cubic feet of natural gas is stored in underground storage facilities (EIA, 2005). For each cubic foot of natural gas harvested from storage, one to eight cubic feet of water is produced (Ray and Engelhardt, 1992). At each storage site, NGSPWs assume unique characteristics based on the initial constituents in the water, the storage formations,

contact with the natural gas, and surface handling or processing of the water (Ray and Engelhardt, 1992).

NGSPWs provide several environmental challenges. These waters are produced in large volumes, vary widely in composition, and often contain constituents in concentrations and forms that are toxic to receiving system biota (Ray and Engelhardt, 1992; Veil et al., 2004). These waters are usually produced at remote sites and are often transferred to collection facilities where they are treated. Currently, the two predominant approaches for handling of NGSPWs are transport to specialized treatment facilities and disposal by injection into deep wells (Nakels et al., 1992). These approaches are expensive and regulated by the Clean Water Act (CWA) through National Pollutant Discharge Elimination System (NPDES) permits, and the Safe Drinking Water Act through Underground Injection Control (UIC) (Nakels et al., 1992). To develop viable and innovative approaches for treating these waters, a thorough understanding of their composition is essential.

This paper investigates the composition of NGSPWs and potential risks these waters pose for receiving aquatic systems. Produced waters typically contain a range of concentrations of many environmental constituents of concern such as chlorides, hydrocarbons, metals, and metalloids. The overall objective of this research was to characterize produced waters to discern potential constituents of concern that may limit surface discharge or reuse of these waters. The risk based approach used to identify constituents of concern involved: 1) review of published literature, 2) analysis of produced water composition records, and 3) analysis of produced water samples provided by natural gas storage companies.

Materials and Methods

Review of literature

A strategic review of literature provided an initial understanding of produced water composition. References utilized in this review originated from peer reviewed journals, grey literature, and internet sources. Grey literature refers to publications issued by government, academia, business, and industry, in both electronic formats and print, that may or may not have been peer reviewed. Internet sources were limited to government and organization websites (i.e. .gov and .org websites).

Produced water composition data assembled for this review included publications containing information specific for both natural gas storage and production. Water composition data from natural gas production were included because a majority of storage facilities are depleted natural gas reservoirs and may have geologic characteristics similar to currently producing reservoirs (Ostroff, 1965; Collins, 1975; Hunt, 1979). Composition data for produced water from offshore petroleum reservoirs were not included in this review because those waters differ fundamentally from NGSPWs from onshore reservoirs due to differences in initial constituents in the water, geologic formations, water handling, water processing, and water disposal (Ostroff, 1965; Collins, 1975; Hunt, 1979; Ray and Engelhardt, 1992; Reed and Johnsen eds., 1996). Composition data for oil production and refinery produced waters were omitted because the composition, volumes, handling, processing, and disposal of those waters differ significantly from natural gas storage produced waters (Ray and Engelhardt, 1992; Trefry et al., 1995; Reed and Johnsen eds., 1996; Utvik, 1999; Murray-Gulde et al., 2003; Faksness, 2004; Sirivedhin and Dallbauman, 2004).

Analysis of produced water composition records

Composition records of approximately 4,000 NGSPWs were provided by natural gas storage companies. These records were sorted by site (A through X) and analyzed using Statistical Analysis System (SAS Institute, 2002). Statistical analysis included sample size, mean, standard deviation, minimum, and maximum values for each constituent listed in the records. It was assumed that the laboratories that generated these data utilized standard analytical methods.

Analysis of produced water samples provided by natural gas storage companies

Samples of natural gas storage produced waters were provided by several natural gas storage companies. Elemental analyses were performed according to EPA Method 200.8 using a Sciex Elan 9000 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) (Perkin-Elmer, Norwalk, CT). Measurement parameters also included: temperature, pH, conductivity, alkalinity, hardness, dissolved oxygen (DO), chemical oxygen demand (COD), biochemical oxygen demand (BOD), chloride concentration, sulfate, total dissolved solids (TDS), total suspended solids (TSS), and oil/grease (Table 1). Analyses were performed in the Ecotoxicology Analytical Laboratory at Clemson University.

Table 1: Analytical methods for parameters measured for produced water samples received from natural gas storage companies.

Parameter	Method	Method Detection Limit
pH	Instrumentation: Orion Model 420A	0.01
Conductivity	Instrumentation: YSI 30	0.1 μ S/cm to 1 mS/cm
Alkalinity	Standard Methods: 2320 B	2 mg/L as CaCO ₃
Hardness	Standard Methods: 2340 C	2 mg/L to 10 mg/L as CaCO ₃
Chloride	High: HACH titration method	500 mg/L
	Low: HACH colorimetric method 8207	25 mg/L
COD ¹	HACH- modified from Standard Methods: 5220 D	3 mg/L
Sulfate	Standard Methods: 4500 E	1 mg/L
TDS ²	Standard Methods: 2540 C	0.1 mg/L
TSS ³	Standard Methods: 2540 D	0.1 mg/L
Oil/Grease	Fluorometer	1 mg/L

¹ Chemical Oxygen Demand

² Total Dissolved Solids

³ Total Suspended Solids

Identify constituents of concern

A risk based approach was used for selection of specific constituents of concern. Constituents of concern (COC) were identified as elements or compounds in NGSPWs at sufficient concentrations to pose risks to receiving system biota. As an initial effort to identify constituents of concern in NGSPWs, NPDES permits were obtained from a variety of sources including industry and government websites (USEPA, 2004), the United States Environmental Protection Agency (USEPA), and natural gas storage companies. Several USEPA offices were contacted, including those in Ohio, Pennsylvania, New York, and West Virginia, to obtain sample permits. This information

was used to create a “model” NPDES permit for the NGSPWs to summarize the constituents of concern from the perspective of the NPDES permitting process.

In addition, constituents of concern that may pose risks for sensitive, sentinel aquatic species such as microcrustaceans were identified based upon published toxicity. *Ceriodaphnia dubia* were chosen as the assessment species for this study because they are sensitive to many constituents commonly found in NGSPWs and are routinely used in toxicity testing required by NPDES permits (USEPA, 1995; Sauer, 1997). *C. dubia*, commonly named ‘water fleas’, are freshwater arthropods that occur in littoral areas of lakes, ponds, and marshes throughout the world. Any constituent present in concentrations known to adversely affect the survival or reproduction of *C. dubia* was identified as a constituent of concern.

Results

Review of literature

A limited number of peer reviewed journal articles were found with data specific to natural gas storage or production (Fillo et al., 1992; Shepherd et al., 1992). The literature review yielded the list of constituents contained in Table 2 (Fillo and Evans, 1990; Shepard et al., 1992; and USEPA, 2000). Constituents of concern in these waters include chloride concentration (salinity), inorganics (metals, transition metals, non-metals, metalloids), and organics (oil and grease). Chloride values from these sources indicate that these NGSPWs range from nearly fresh to hyper-saline with chloride concentrations ranging from 1,400 to 380,000 mg/L: seawater contains approximately 19,000 mg/L chloride (Stumm and Morgan, 1996). Other potential inorganics of concern (maximum concentration) include aluminum (83 mg/L), arsenic (1.51 mg/L), barium

(1740 mg/L), boron (56 mg/L), bromide (1149 mg/L), cadmium (1.21 mg/L), copper (5 mg/L), iron (1100 mg/L), lead (10.2 mg/L), lithium (235 mg/L), nickel (9.2 mg/L), and zinc (5 mg/L). Organic components such as surfactants (0.08 to 1200 mg/L) and oil and grease (2.3 to 60 mg/L) are also potentially problematic in these waters. Parameters such as pH (3.1 to 7.0) and total dissolved solids (2.6 to 360 g/L) or total suspended solids (8 to 5484 mg/L) are also of concern in these NGSPWs.

Table 2: Constituents (mg/L) in natural gas produced waters.

Constituent	Min	Max	Constituent	Min	Max
pH ¹	4.4	7.0	Iron ¹	ND	1100
pH ²	3.1	6.47	Iron ²	39	680
Conductivity (umhos/cm)	4200	180000	Lead ²	<0.2	10.2
Alkalinity ²	136000	586000	Lithium ²	18.6	235
TDS ¹	0	285	Magnesium ¹	0.9	4300
TDS ²	2600	310000	Magnesium ²	1300	3900
TSS ¹	139000	360000	Manganese ¹	0.045	6.5
TSS ²	14	800	Manganese ²	3.59	65
BOD ₅ ¹	8	5484	Nickel ¹	ND	0.02
COD ¹	75	2870	Nickel ²	<0.08	9.2
Aluminum ¹	2600	120000	Potassium ²	149	3870
Aluminum ²	ND	0.4	Silver ²	0.047	7
Arsenic ¹	<0.50	83	Sodium ¹	520	45000
Arsenic ²	0.004	1	Sodium ²	37500	120000
Barium ¹	<0.005	1.51	Strontium ¹		6200
Barium ²	ND	26	Sulfate ²	<1.0	47
Boron ¹	9.65	1740	Sulfide ¹	ND	19
Bromide ²	ND	56	Tin ¹	ND	1.1
Cadmium ¹	150	1149	Zinc ¹	ND	0.022
Cadmium ²	ND	0.015	Zinc ²	<0.02	5
Calcium ¹	<0.02	1.21	TOC ¹	67	38000
Calcium ²	ND	25000	Surfactants ²	0.08	1200
Chloride ¹	9400	51300	Benzene ¹	1.8	6.9
Chloride ²	1400	190000	Benzene ³	<0.010	10.3
Chromium ¹	81500	167448	Toluene ¹	0.857	3.37
Copper ¹	ND	0.03	Toluene ³	<0.010	18
Copper ²	ND	0.02	Oil/Grease ¹	6	60
	<0.02	5	Oil/Grease ²	2.3	38.8

Reference: ¹(Fillo & Evans 1990), ²(USEPA, 2000), ³(Shepard et al., 1992)

Analysis of produced water composition records

Composition records for natural gas storage produced waters were provided by three natural gas storage companies. These records contained data on pH values, density, and concentrations of chloride, sodium, calcium, manganese, barium, magnesium, iron, carbon dioxide, hydrogen sulfide, sulfate, sulfide, bicarbonate, and total dissolved solids (Table 3). Chloride concentrations in these waters ranged from essentially fresh (1 mg/L) to hyper-saline (384,000 mg/L). Other constituents of concern included barium (non-detect to 5,481 mg/L), iron (0.1 to 135,000 mg/L), hydrogen sulfide (non-detect to 1,290 mg/L), sulfate (non-detect to 102,912 mg/L), and sulfide (0.034 to 1,400 mg/L). Parameters such as pH (3 to 11) and total dissolved solids (up to 494,000 mg/L) are also of concern in these waters.

Table 3: Results from natural gas storage produced water composition records (concentration in mg/L unless specified).

Site	pH					Chloride					Sodium				
	N	Min	Med	Max	sd	N	Min	Med	Max	sd	N	Min	Med	Max	sd
A	106	4.5	6	7.47	0.57	100	14.7	37500	2E+05	65577	32	98.1	13885	72955	26749
B	35	4.4	6.1	7.1	-	5	16	20	230	104.3	-	-	-	-	-
C	5	6.4	6.7	6.8	0.16	5	373	518	629	105.8	-	-	-	-	-
D	29	4.5	5.7	6.8	0.6	24	49	2030	1E+05	36468	8	119	2908	38136	16131
E	5	5.15	5.59	6	0.35	5	82.9	40600	82000	33722	3	7852	15770	29697	11059
F	8	4.9	5.95	6.7	0.5	7	-	94.9	2E+05	74876	1	-	124	-	-
G	159	3.4	6	8.7	0.77	123	20	1514	2E+05	40027	10	36.8	721	16477	5030
H	41	5.06	6.67	7.45	0.51	41	4.45	17300	1E+05	28767	41	0.015	3000	65200	14331
I	329	3.4	6.5	11	0.68	252	4.9	29800	3E+05	30683	-	-	-	-	-
J	185	4.3	6.38	8.7	0.8	183	12.1	8000	2E+05	52373	36	27	3388	67697	17059
K	174	4.09	6.045	8.6	0.88	173	2.4	27000	3E+05	20162	17	125	29061	46678	15421
L	524	3.6	6.5	9.3	0.817	457	1.1	2516	4E+05	60519	55	15.1	891	76824	25375
M	85	5.53	6.67	7.62	0.37	83	19.8	24900	1E+05	32957	83	14.6	13540	2E+05	28174
N	13	5.1	6	7.47	0.64	13	14.7	256	2E+05	54879	4	98.1	6110	61247	28710
O	78	4	5.48	7.65	0.65	77	1700	2E+05	3E+05	63428	7	30.6	15842	56732	23414
P	856	3	6.44	10.3	1.02	766	1	1000	3E+05	27811	95	0.64	98.7	16477	2605
Q	96	4.5	6.435	4.89	0.55	95	3.03	433	1E+05	12680	42	1	11.3	2099	353
R	24	5	6	7	0.5	24	1450	2E+05	2E+05	73545	9	4694	64595	72955	21204
S	163	4.87	6.3	10.7	0.7	160	13	3000	2E+05	21277	24	16.9	101.8	17733	4401
T	10	4.95	6.12	7.1	0.67	10	300	1015	1E+05	42436	3	33.9	55.7	41133	23722
U	11	5.41	6.44	7	0.48	11	180	36000	1E+05	34855	2	11559	-	25192	-
V	40	4.56	6.22	8	0.71	111	20	3000	2E+05	49691	14	7.54	726	22058	8494
W	17	5.3	6	7	0.43	17	5000	1E+05	2E+05	60385	5	1477	29861	53030	23450
X	127	4.34	6.26	9.5	0.9	127	20	3000	2E+05	55256	17	6.93	1813	63029	16414

Table 3: Results from natural gas storage produced water composition records (concentration in mg/L unless specified) (Continued).

Site	Calcium					Manganese					Barium				
	N	Min	Med	Max	sd	N	Min	Med	Max	sd	N	Min	Med	Max	sd
A	35	40	10800	64000	17082	100	0	8.9	2830	338.5	-	-	-	-	-
B	16	4	210	880	357	30	0.5	14	580	150.9	-	-	-	-	-
C	-	-	-	-	-	5	1.65	2.2	3.3	0.69	-	-	-	-	-
D	10	40	440	12000	4886	24	0.61	3.27	790	160.4	3	13	21	209	110.9
E	3	10800	16000	25600	7508	5	5.85	12.3	399	171.4	-	-	-	-	-
F	1	-	50	-	-	7	1	11.8	885	325.8	7	-	0	-	-
G	51	50	1600	31600	9192	109	0.4	6.6	32.8	7.1	33	5	303	3824	1088
H	34	0.01	1510	7590	2086	41	0.5	8.47	91.2	17.1	4	0.9	17.9	38.3	20.7
I	-	-	-	-	-	284	0.4	6.295	790	53.5	-	-	-	-	-
J	68	50.8	3800	76000	18089	131	0.1	8.7	276	27.7	26	0.092	0.423	347	78.1
K	61	80	12000	65200	20134	138	0.39	8.7	91.4	14.1	35	0.271	203	4255	1032
L	104	8	665	89200	19693	331	0.01	4.29	203	21.9	55	0.187	22.5	5481	860.9
M	83	13	1230	10700	2853	1	6.32	6.32	64.2	11.6	5	1.2	2	7.22	2.5
N	5	40	400	54000	24043	13	0.42	2.02	57.1	16	-	-	-	-	-
O	21	9200	23600	65280	14241	78	0.6	6	56	7.8	21	14	48	2417	701.3
P	189	0.24	53	24000	2472	651	0.01	2.2	2321	102.5	61	0.1	1.69	324	54.9
Q	39	1	7.26	524	129	92	0.1	4.95	27.83	5.8	1	-	0.79	-	-
R	9	4800	26400	33600	8780	24	0.71	80	2830	609.7	-	-	-	-	-
S	68	2	360	8400	2049	138	1.4	9.956	127.7	15.3	19	0.092	8	474	127
T	8	80	320	36800	12894	10	0.7	9.3	26.8	7.7	2	8.6	-	8.9	-
U	2	7200	-	12000	-	11	2.24	17.4	618	211	-	-	-	-	-
V	40	18	840	78000	16587	90	0.1	6	367	48.8	3	3	4	14	6.1
W	5	800	22800	45600	18930	17	2.1	9.98	98.5	22	5	-	2440	-	-
X	49	0.66	1600	86000	19043	101	0.4	6.97	102	17.4	4	3	7	22	9

Table 3: Results from natural gas storage produced water composition records (concentration in mg/L unless specified) (Continued).

Site	Magnesium					Iron					CO ₂				
	N	Min	Med	Max	sd	N	Min	Med	Max	sd	N	Min	Med	Max	sd
A	35	2.4	1220	25192	4193	100	1.4	331	99000	12665	34	10	119	440	120.6
B	19	0.009	110	450	130.8	17	11	140	960	298.7	-	-	-	-	-
C	-	-	-	-	-	5	64	111	136	27.7	5	31.7	99	156	44.1
D	10	2.44	24.4	2440	846.4	24	30	434	98500	19970	9	61.6	91	158.6	31.8
E	3	2440	3440	2440	0	5	4.51	980	62400	27496	3	374	396	409	17.69
F	1	-	2.4	-	-	7	56.5	779	99000	36677	1	-	287.1	-	-
G	51	2.44	244	1244	2729	136	20	304	16200	1512	122	123	700	4930	794
H	41	0.15	352	2470	529.7	40	15.4	164	5310	1293	40	1	134.5	1007	211
I	-	-	-	-	-	338	2.1	107.5	5400	587.2	257	8.8	190	11583	804.8
J	68	2.4	336	16494	3550	180	5	424	4710	742.6	173	1.2	554.4	6000	756
K	61	24.4	1220	16348	3930	164	1.2	496	4948	884	146	100	1000	7871	1293
L	99	1.2	244	37210	4409	470	1	229	9760	1192	377	1	614	9454	927.4
M	83	2.9	323	1740	475.7	78	0.8	45.65	1640	271.3	83	7	135	1090	142.2
N	5	2.44	24.4	2440	1066	13	23.9	300	3620	1110	5	10	91	286	101.7
O	21	244	244	2440	991	78	50	275	2720	425	76	17.6	564	1208	178
P	163	0.01	12.2	2440	291.1	834	0.1	170	26234	420.3	566	0.1	217.8	0.067	945
Q	42	0.08	1.335	86.4	16.9	94	1.24	329	3506	645.9	95	1	273	3360	729.7
R	9	244	2440	2440	466.2	24	1.4	7.85	1260	266.7	9	10	127	440	120.7
S	67	0.24	24.4	732	154	162	27.8	444.5	6820	1151	156	10	673	10840	1062
T	8	2.44	61	2440	838.8	10	22	451.5	1898	548	10	297	539	1139	245
U	2	1220	-	1464	-	11	126	896	44400	13132	2	286	-	352	-
V	38	0.244	244	4880	1241	111	5	487	23700	2385	107	110	600	16434	1828
W	6	244	2196	2440	1163	17	135	659	1E+05	3553	5	79	115	127	20.98
X	47	0.2	244	4880	1151	124	20	455	17000	2214	119	0.7	614	10395	1338

Table 3: Results from natural gas storage produced water composition records (concentration in mg/L unless specified) (Continued).

Site	H ₂ S					Sulfate					Sulfide				
	N	Min	Med	Max	sd	N	Min	Med	Max	sd	N	Min	Med	Max	sd
A	35	0	0	286	48.2	35	0	17	1E+05	17383	-	-	-	-	-
B	-	-	-	-	-	34	1	84.5	440	98	37	0.034	6.1	620	112
C	1	-	3	-	-	4	12	21	84	34.1	1	-	1.28	-	-
D	3	0.1	0.1	0.6	0.29	1	-	98	-	-	-	-	-	-	-
E	3	0	0	1.5	0.86	3	107	380	399	163.4	-	-	-	-	-
F	1	-	0.3	-	-	1	-	164	-	-	1	-	2.99	-	-
G	23	0.1	0.8	192	39.8	69	2	74	4440	642.1	2	5	-	181	124.4
H	26	0.22	1.86	201	211.6	40	1	269	1150	338.2	40	0.25	2.15	366	90.5
I	78	0.1	0.5	17.4	3.7	211	0.5	140	2050	268.2	26	0.12	0.885	18.6	4.6
J	21	0.02	0.1	8	1.7	72	0.141	36	2730	391	-	-	-	-	-
K	22	0.1	0.4	2.2	0.6	77	0.145	42	3874	506.5	2	25	-	160	-
L	60	0.01	0.5	163	31.4	248	0.204	101.5	3612	503.9	2	30.08	-	30.5	-
M	59	0.06	0.36	73	9.9	83	3	283	3250	463	75	0.1	0.6	73	9.03
N	2	0.3	-	8	-	1	-	23	-	-	-	-	-	-	-
O	5	0.1	0.3	2.5	1.006	16	2	4.9	90	21.9	-	-	-	-	-
P	214	0.005	0.3	750	52	513	0.1	14	7050	643	25	0.09	0.15	1187	237
Q	52	0.1	28.99	1290	258	65	1	75	3900	596.5	64	0.79	31	1400	296
R	2	-	0.5	-	-	8	9	37	110	37.5	-	-	-	-	-
S	20	1	0.1	1	0.25	90	0.099	56.5	1366	220.9	1	-	0.1	-	-
T	-	-	-	-	-	8	3.09	29.23	109.3	44.7	-	-	-	-	-
U	-	-	-	-	-	2	70	-	394	-	1	-	10.8	-	-
V	11	0.1	0.1	1	0.35	69	4	151	2830	519.9	-	-	-	-	-
W	5	0	4.5	8	3.17	5	10	44	248	117	-	-	-	-	-
X	18	0.1	0.3	2.5	0.57	65	4	82	1005	286.5	1	-	0.2	-	-

Table 3: Results from natural gas storage produced water composition records (concentration in mg/L unless specified) (Continued).

Site	Bicarbonate					TDS					Density g/cm ³				
	N	Min	Med	Max	sd	N	Min	Med	Max	sd	N	Min	Med	Max	sd
A	35	0	85	366	112.8	36	0	43518	3E+05	1E+05	35	1	1.047	3	0.33
B	21	1	370	920	302.9	1	-	700	-	-	-	-	-	-	-
C	5	1.83	164.7	317	113.1	-	-	-	-	-	-	-	-	-	-
D	8	61	137	153	33.3	10	491.7	10093	1E+05	55035	10	1	1.007	1.111	0.044
E	3	183	336	336	88.3	3	61271	1E+05	1E+05	39037	3	1.047	1.093	1.099	0.029
F	1	-	293	-	-	1	-	2417	-	-	1	-	1	-	-
G	93	1	561.2	11468	2036	-	-	-	-	-	51	1	1.007	1.19	0.052
H	40	8	374.5	1690	365.4	41	124	42000	4E+05	79531	41	1.005	1.05	1.16	0.03
I	243	1	439	23424	2023	-	-	-	-	-	-	-	-	-	-
J	120	36.6	414.8	2930	386.4	-	-	-	-	-	68	1	1.119	1.242	0.072
K	119	1	720	22963	2941	-	-	-	-	-	61	1	1.056	1.256	0.086
L	283	1.2	671	22570	3474	-	-	-	-	-	104	1	1.003	1.252	0.083
M	83	18	293	6060	934.8	83	476	66470	5E+05	95582	81	1.015	1.035	1.175	0.044
N	4	73.1	183	244	81.7	5	583.4	1788	3E+05	1E+05	5	1	1.01	1.253	0.11
O	57	2.44	109.8	830	145.2	-	-	-	-	-	21	1.074	1.202	1.236	0.06
P	532	0.5	207	81984	532	45	95	1024	61397	11404	186	1	1	1.113	1.003
Q	95	1.22	237	1159	242	44	110	1637	9860	2061	43	1.005	1.015	1.06	0.013
R	3	0.5	1	201	115.6	9	28750	2E+05	3E+05	80787	9	1.021	1.204	1.21	0.06
S	137	12.2	463	4514	567.9	-	-	-	-	-	68	1	1.004	1.049	0.008
T	10	24.4	134.2	1391	414	-	-	-	-	-	8	1	1.001	1.175	0.06
U	2	73.2	-	366	307	2	58287	1E+05	-	-	2	1.044	-	1.078	-
V	88	24.4	476	1434	273.9	-	-	-	-	-	40	1	1.046	1.224	0.06
W	5	0	85	244	99.1	5	8267	2E+05	3E+05	1E+05	5	1.006	1.125	1.204	0.09
X	87	2.44	244	1952	309	-	-	-	-	-	49	1	1.008	1.252	0.082

Samples

Samples of NGSPWs were obtained from several gas storage facilities in New York, Pennsylvania, and West Virginia and analyzed for constituent concentrations (Tables 4 and 5). COD analysis for samples with elevated chloride levels was omitted because chlorides interfered with this analysis. Some sulfate values were omitted because of interferences caused by turbidity in the sample, and other values were below detection limits. Chloride concentrations in these samples range from essentially fresh (57 mg/L) to hyper-saline (220,000 mg/L). Other inorganics of concern (at their maximum concentrations) include aluminum (11 mg/L), arsenic (51 mg/L), barium (17.4 mg/L), boron (24 mg/L), bromide (348.7 mg/L), iron (768 mg/L), and mercury (0.087 mg/L). Parameters such as pH (4.3 to 9.65) and total dissolved solids (up to 404,253 mg/L) or total suspended solids (up to 3,337 mg/L) may also be of concern in these waters.

Table 4: General water characteristics of natural gas storage produced waters from samples provided by natural gas storage companies.

Sample	pH	Conductivity (mS/cm)	Alkalinity mg/L	Hardness mg/L	Cl mg/L	COD mg/L	Sulfates mg/L	TDS mg/L	TSS mg/L	Oil/Grease mg/L
1	5.13	1180	110	164	275	NA	NA	888	511.4	78
2	7.5	56.5	362	18	25 000	NA	NA	40 011	62.6	8
3	5.27	33.87	52	16	20 000	NA	NA	26 121	841.0	NA
4	4.22	26.53	NA	14	20 000	NA	NA	29 373	535.3	268
5	4.78	26.6	104	120	1 500	NA	NA	12 475	691.6	8
6	5.68	43.9	684	12	25 000	NA	NA	30 373	945.3	500
7	6.33	144.4	190	140	75 000	NA	NA	131 648	463.4	30
8	4.46	32.59	NA	12	20 000	NA	NA	23 827	1 096.3	NA
9	6.55	107.1	352	58	50 000	NA	NA	82 489	264.5	7
10	5.58	86	28	440	4 000	NA	NA	5 991	271.9	NA
11	5.86	58.3	140	26	30 000	NA	NA	44 082	655.4	296
12	7.07	132.1	244	76	60 000	NA	NA	104 669	152.4	8
13	6.12	185.35	43	3700	120 000	NA	NA	197 551	60.6	114
14	5.6	NA	124	2800	57	NA	NA	282	419.6	NA
15	4.14	>200	NA	>150 000	220 000	NA	NA	404 253	132.0	181
16	4.3	199.3	NA	106	125 000	NA	NA	225 302	1 028.8	NA
17	5.26	>200	30	152	165 000	NA	NA	317 796	1 337.4	NA
18	NA	NA	NA	NA	115 000	NA	NA	NA	NA	NA
19	NA	NA	NA	NA	165 000	NA	NA	NA	NA	NA
20	4.3	>200	NA	112	120 000	NA	NA	230 013	1 028.8	NA
21	NA	NA	NA	NA	120 000	NA	NA	NA	NA	NA
22	9.65	0.999	108	10	102	12.94	ND	38 938	43.5	NA
23	7.85	1.142	90	22	171	11.18	ND	731	41.8	NA
24	8.58	3.228	130	16	770	14.12	ND	1 831	ND	NA
25	7.84	1.115	388	6	155	18.82	ND	668	101.9	NA
26	8.11	1.13	428	2	144	11.18	ND	763	24.5	NA
27	9	2.904	176	28	1 500	45.88	ND	1 676	92.4	NA

NA-not available

ND-non detect

Table 5: Inorganic analysis by ICP-MS (ug/L) of NGSPWs from samples provided by natural gas storage companies.

Sample	Cl	Na	K	Li	Mg	Ca	Mn	Fe	B	C
1	195 470	39 969	2 631	336	4 747	3 926	12 494	255 384	42	15 806
2	29 736 190	184 755	79 081	6 508	268 101	87 211	7 536	3 997	226	46 773
3	16 639 694	1 288 357	34 161	3 288	151 595	66 892	6 086	347 681	57	166 492
4	17 331 424	1 444 653	37 709	4 280	138 221	71 847	15 410	725 846	125	166 231
5	924 714	114 391	3 332	470	6 558	3 567	5 826	374 342	40	27 160
6	21 251 349	2 006 084	43 968	4 773	150 481	56 817	9 456	655 829	172	47 314
7	54 019 955	214 876	96 876	6 277	501 804	531 355	13 855	35 882	23	158 120
8	15 739 942	1 260 390	27 678	2 878	106 331	58 091	10 135	768 588	52	142 432
9	58 603 197	194 176	107 041	7 837	414 426	231 585	9 409	27 247	94	37 638
10	4 473 659	366 684	9 405	980	25 662	10 335	1 737	139 239	35	59 140
11	29 737 174	368 605	57 918	5 255	264 062	107 086	11 577	245 048	116	160 162
12	71 717 190	206 617	109 504	9 007	437 749	276 937	13 183	1 645	70	48 691
13	108 968 477	850 780	302 463	64 108	3 671 739	818 199	8 333	6 328	6 816	1 077 742
14	133 399	7 432	673	47	634	1 021	691	41 024	19	30 047
15	6 579 351	10 888 157	174 578	27 220	535 229	228 598	345	10 161	2 217	18 505
16	26 772 067	170 499	357 171	3 295	167 284	318 230	1 139	41 488	1 098	12 047
17	22 162 977	160 375	365 023	3 777	156 953	312 440	372	11 615	1 134	6 518
18	15 569 079	10 065 250	241 856	3 320	105 613	211 707	932	85 351	1 044	13 040
19	12 282 468	13 704 257	262 654	3 892	110 525	210 037	258	16 705	1 119	3 894
20	33 292 369	11 512 012	669 900	17 702	551 470	493 491	632	24 586	9 451	78 326
21	25 196 216	282 299	583 644	26 047	598 417	431 836	715	27 087	24 506	222 954
22	N/A	>13 800 000	458	38	421	1 559	21	477	42	N/A
23	N/A	>13 800 000	594	53	448	4 563	31	1 131	50	N/A
24	N/A	>13 800 000	1 099	83	1 449	1 652	2	8	49	N/A
25	N/A	>13 800 000	550	38	478	1 397	34	812	43	N/A
26	N/A	>13 800 000	486	46	423	1 063	29	1 529	40	N/A
27	N/A	>13 800 000	1 354	99	2 955	3 832	22	1 216	49	N/A

Table 5: Inorganic analysis by ICP-MS (ug/L) of NGSPWs from samples provided by natural gas storage companies (Continued).

Sample	Cd	Cu	Pb	Zn	As	Se	Hg	S	Al	Si	P
1	0.53	3.33	2.16	205.03	11.91	17.48	0.27	13 769	58.89	2 333.40	ND
2	1.54	7.48	0.45	131.80	2 168.17	36.29	1.32	294 904	95.21	2 406.85	ND
3	0.43	6.84	0.39	57.77	9 348.43	25.01	0.33	101 296	29.94	1 423.28	0.40
4	12.40	10.20	0.68	291.81	51 484.52	23.88	0.41	106 672	473.24	1 474.76	15.72
5	0.13	1.13	0.10	499.92	614.60	43.78	0.15	17 170	13.83	1 896.86	222.01
6	0.30	5.89	0.39	66.79	329.87	23.18	0.34	45 304	15.07	2 388.14	763.60
7	1.73	47.04	21.17	247.69	3 182.22	ND	86.77	ND	126.80	2 369.56	ND
8	0.34	7.01	0.54	318.77	10 295.24	33.54	8.08	59 919	29.29	1 621.28	21.80
9	0.21	20.96	0.11	75.13	1 935.56	57.76	5.99	163 671	7.70	1 654.96	ND
10	0.78	5.30	0.42	239.42	3 612.34	18.39	0.99	41 676	10.96	526.97	ND
11	0.93	14.39	0.62	100.64	8 944.42	56.91	4.50	202 718	30.42	1 484.37	5.58
12	0.63	27.31	0.23	98.75	975.99	69.00	2.48	188 065	8.46	876.58	ND
13	2.20	55.70	1.53	269.85	7 819.47	74.95	2.35	1 556 326	29.28	2 928.23	268.54
14	5.46	8.61	0.37	151.98	157.62	73.43	0.08	59 991	2.61	401.80	0.37
15	0.39	26.17	5.14	57.45	3 301.87	ND	ND	ND	4.26	49.17	ND
16	0.60	21.81	5.83	193.52	1 349.72	ND	0.26	ND	2.14	163.24	ND
17	0.78	21.42	8.03	200.66	1 737.97	ND	0.47	ND	1.54	91.14	ND
18	0.92	38.34	19.96	152.02	1 501.75	ND	0.22	ND	13.91	218.81	ND
19	0.57	22.41	4.69	145.60	2 053.16	ND	0.72	ND	11.87	98.29	ND
20	0.26	22.00	8.13	104.06	1 705.18	ND	0.48	ND	19.62	600.96	ND
21	0.54	21.82	10.29	184.06	1 846.41	ND	0.53	ND	29.42	751.46	ND
22	0.02	3.11	0.76	63.59	1.38	3.92	ND	N/A	2 785.48	2 675.63	54.90
23	0.03	9.02	0.65	229.59	10.75	7.30	ND	N/A	11 008.80	4 192.77	59.77
24	0.07	2.38	0.49	18.42	8.70	3.05	0.61	N/A	175.88	705.16	1.73
25	0.11	8.93	2.72	90.41	1.81	0.82	ND	N/A	147.64	2 636.28	82.31
26	0.08	7.03	0.81	82.10	2.40	ND	ND	N/A	60.93	3 007.36	81.82
27	0.31	26.42	2.37	485.53	9.55	4.43	0.25	N/A	215.02	2 865.48	50.04

Table 5: Inorganic analysis by ICP-MS (ug/L) of NGSPWs from samples provided by natural gas storage companies (Continued).

Sample	Ba	Ti	V	Cr	Co	Ni	Ga	Ge	Br	Rb	Sr
1	244.66	15 235	ND	ND	1.31	14.28	0.48	0.56	732.21	1.88	802.30
2	333.66	429 952	292.11	41.06	15.16	46.87	1.42	0.91	115 268.59	242.45	43 292.18
3	286.75	301 811	154.24	94.26	3.86	65.82	0.83	1.46	65 463.41	115.86	27 956.60
4	663.07	358 958	155.11	96.10	11.38	96.21	0.99	2.50	65 923.47	123.24	26 958.55
5	320.18	14 559	ND	ND	1.22	6.79	0.32	0.78	2 319.44	6.41	1 234.89
6	17 424.92	281 275	170.76	31.02	3.19	51.47	0.80	2.51	88 551.72	106.01	31 390.44
7	1 643.16	4 402 664	674.39	212.56	29.49	297.70	2.06	1.59	275 567.11	391.66	210 209.19
8	701.88	271 448	137.62	82.48	7.51	73.46	1.22	2.14	66 618.89	ND	26 779.23
9	1 868.65	2 060 542	562.36	47.64	12.73	206.00	2.30	1.29	238 704.41	393.20	103 559.30
10	1 365.80	41 265	33.31	29.56	1.23	14.26	0.27	0.58	12 739.68	24.78	4 423.59
11	1 037.93	522 931	275.04	105.08	12.77	111.28	0.89	1.72	133 663.86	225.03	58 533.99
12	1 531.68	2 668 168	708.65	61.55	21.31	64.94	3.16	1.46	285 095.72	390.14	136 466.31
13	1 468.06	9 080	1 133.94	63.49	57.51	140.13	1.75	2.70	348 719.76	1 018.00	384 675.32
14	234.55	1 259	10.54	33.41	0.94	17.86	0.48	0.47	752.50	1.92	657.92
15	11 578.35	ND	87.89	ND	19.98	67.82	ND	0.73	62 831.38	838.14	547 174.94
16	2 667.40	2 526 032	345.03	28.71	16.03	276.01	0.45	1.08	171 737.02	ND	787 284.93
17	2 580.78	2 530 108	346.37	13.39	16.87	98.67	0.35	1.05	150 261.06	ND	707 537.89
18	2 381.06	1 827 623	332.57	35.61	17.17	302.79	0.44	1.64	116 771.74	1 010.00	512 545.72
19	2 750.77	1 933 179	296.04	7.54	17.14	131.08	0.23	1.26	110 524.24	ND	578 236.83
20	4 911.65	661	315.97	20.48	17.25	183.51	0.21	1.30	137 789.60	1 589.65	917 947.42
21	4 491.84	407	260.82	21.05	18.98	106.47	0.11	1.03	116 743.73	1 545.15	844 515.04
22	91.25	63 810	0.37	1.96	0.23	2.35	0.59	1.95	379.08	2.25	83.83
23	173.31	191 453	2.41	103.55	0.23	3.96	1.49	0.98	509.96	2.31	114.84
24	151.27	52 904	13.78	22.38	0.06	2.21	0.18	ND	2 991.26	3.48	274.02
25	115.16	60 148	2.10	10.89	0.67	5.78	0.43	1.26	434.22	3.04	92.81
26	173.41	82 238	1.03	36.67	0.22	5.13	0.14	0.85	460.64	2.03	92.83
27	1 271.47	148 750	15.26	21.99	0.63	12.33	0.50	1.70	3 067.58	5.13	1 047.38

Table 5: Inorganic analysis by ICP-MS (ug/L) of NGSPWs from samples provided by natural gas storage companies (Continued).

Sample	I	Be	Sc	Zr	Nb	Mo	Ru	Pd	Ag	In	Sn	Sb
1	ND	0.07	0.01	0.04	0.03	ND	ND	ND	ND	ND	0.07	0.47
2	824.95	0.19	0.02	3.48	0.15	1.58	0.17	0.20	ND	0.00	0.49	2.17
3	477.82	ND	0.02	0.12	0.11	0.25	0.72	0.15	0.91	0.05	0.73	0.80
4	586.11	0.16	0.02	0.11	0.22	0.11	0.65	ND	0.36	0.15	0.53	3.94
5	8.12	0.04	0.00	0.10	0.04	ND	0.11	0.00	ND	0.00	0.05	0.26
6	610.78	0.24	0.01	0.30	0.19	1.26	0.09	0.09	0.09	0.00	0.08	0.74
7	3 156.33	ND	0.08	0.49	1.79	0.46	1.69	0.13	0.62	0.02	1.05	4.96
8	588.97	0.04	0.02	0.40	0.23	0.17	0.48	0.11	0.07	0.03	0.25	1.36
9	2 188.21	0.24	0.04	0.40	0.61	0.27	1.29	0.06	0.28	0.04	0.35	1.86
10	143.17	0.07	0.00	0.14	0.03	0.03	0.05	ND	ND	0.02	0.17	0.28
11	1 002.83	0.07	0.03	0.74	0.19	1.04	1.00	0.19	0.00	0.06	0.35	2.24
12	2 595.86	0.34	0.04	0.33	0.80	0.31	1.86	0.09	0.44	0.02	0.31	2.72
13	3 913.53	0.37	0.10	0.19	1.41	2.68	0.44	0.13	0.86	0.30	0.46	14.94
14	38.59	0.08	0.03	0.01	0.01	ND	0.07	0.01	ND	0.00	0.09	0.09
15	129.92	0.03	ND	0.03	0.53	0.01	0.32	0.04	ND	0.02	0.27	40.53
16	948.43	0.06	ND	0.02	1.37	ND	18.96	0.03	0.36	0.08	0.29	15.88
17	778.12	ND	ND	ND	1.95	ND	6.01	0.03	0.29	0.06	0.24	21.33
18	376.78	ND	ND	0.36	1.24	0.62	3.40	0.05	0.34	0.03	0.91	18.43
19	357.94	ND	ND	0.15	1.27	0.32	3.76	0.03	0.25	0.03	0.41	26.95
20	952.85	0.27	ND	0.09	0.62	ND	0.96	0.09	0.34	0.02	0.62	24.20
21	802.15	0.02	0.01	0.11	0.61	ND	0.75	ND	0.21	0.02	0.25	24.05
22	21.20	ND	0.36	0.27	0.01	0.53	ND	0.03	0.02	0.00	0.07	0.18
23	16.25	ND	1.38	0.20	0.01	0.26	ND	0.03	ND	0.00	0.50	0.26
24	37.45	ND	0.37	0.12	0.00	0.58	ND	0.02	0.02	ND	0.09	1.50
25	14.67	ND	0.40	1.49	0.01	0.58	ND	0.04	0.01	ND	ND	0.23
26	36.42	0.01	0.69	0.70	0.04	0.26	ND	ND	ND	ND	0.12	0.29
27	43.30	0.03	0.46	1.34	0.03	0.98	0.05	0.08	0.03	ND	0.68	0.39

Table 5: Inorganic analysis by ICP-MS (ug/L) of NGSPWs from samples provided by natural gas storage companies (Continued).

Sample	Te	Cs	Eu	La	Ce	Pr	Nd	Sm	Gd	Tb	Dy	Ho	Er	Tm
1	ND	0.03	0.06	0.02	0.09	0.01	0.03	ND	0.00	0.00	ND	ND	0.01	0.00
2	0.52	8.03	0.06	0.13	0.18	0.01	0.04	0.10	ND	0.01	0.01	0.00	0.01	0.01
3	0.31	5.28	0.07	0.01	0.06	0.01	0.03	ND	0.01	0.01	0.00	0.01	ND	0.00
4	0.36	4.34	0.17	1.86	0.14	0.03	0.19	0.16	0.10	0.03	0.05	0.00	0.01	0.00
5	ND	0.08	0.08	ND	0.03	0.00	0.01	ND	ND	ND	ND	0.00	ND	0.00
6	0.15	0.17	3.25	0.17	0.05	0.02	0.14	0.27	0.10	0.02	0.10	0.03	0.06	0.01
7	1.17	18.53	0.45	0.29	ND	0.10	0.08	0.02	ND	0.01	ND	0.01	0.03	0.01
8	0.28	3.34	0.18	ND	0.03	0.00	0.01	ND	ND	ND	0.00	0.01	ND	0.01
9	0.58	16.13	0.46	0.11	0.07	0.02	0.04	0.08	0.01	ND	0.03	0.01	0.02	0.01
10	ND	0.92	0.27	0.11	0.24	0.02	0.08	0.00	0.01	0.00	ND	0.00	0.00	0.00
11	0.87	11.18	0.26	0.05	0.04	0.11	0.21	0.04	0.01	0.00	0.01	0.00	0.01	0.01
12	1.69	22.60	0.39	0.22	0.06	0.05	0.09	0.02	0.02	0.01	0.04	0.02	0.03	0.01
13	4.43	104.94	1.15	0.58	ND	0.16	0.41	0.34	0.24	0.06	0.12	0.05	0.05	0.13
14	ND	ND	0.21	0.02	0.03	0.00	ND	ND	ND	0.00	ND	0.00	ND	0.00
15	2.27	196.40	9.85	0.89	0.13	0.18	0.67	0.17	0.06	0.01	0.02	0.03	0.05	0.15
16	1.80	163.14	0.67	1.40	ND	0.32	0.20	0.03	0.04	0.01	0.01	0.01	0.02	0.03
17	1.73	174.19	0.79	1.66	ND	0.43	0.16	0.04	ND	0.01	0.01	0.01	0.03	0.06
18	1.12	124.19	0.73	1.38	0.09	0.33	0.56	0.09	0.07	0.01	0.06	0.01	0.03	0.04
19	1.41	156.18	1.05	1.66	0.21	0.37	0.48	0.06	0.05	0.01	0.04	0.02	0.04	0.05
20	2.16	239.09	2.25	1.50	0.40	0.28	0.33	0.10	0.09	0.01	0.05	0.02	0.05	0.07
21	2.35	222.17	2.83	1.03	ND	0.26	0.35	0.11	0.14	0.01	0.06	0.01	0.06	0.09
22	0.03	0.13	0.02	0.08	0.22	0.04	0.13	0.00	0.02	0.01	0.05	0.01	0.02	0.01
23	ND	0.07	0.03	0.04	0.11	0.01	0.01	0.01	ND	ND	ND	0.01	ND	0.00
24	ND	0.05	0.02	0.02	0.06	0.00	0.01	ND	ND	0.01	ND	0.00	ND	0.01
25	ND	0.26	0.02	0.26	1.33	0.09	0.47	0.10	0.14	0.01	0.08	0.02	ND	0.01
26	ND	0.05	0.02	0.07	0.22	0.03	0.11	0.02	ND	0.00	0.01	0.00	ND	0.00
27	ND	0.17	0.11	0.27	1.19	0.10	0.44	0.12	0.10	0.02	0.07	0.02	0.01	0.01

Table 5: Inorganic analysis by ICP-MS (ug/L) of NGSPWs from samples provided by natural gas storage companies (Continued).

Sample	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Tl	Bi	Th	U
1	0.00	0.00	0.00	ND	ND	0.00	0.00	ND	ND	95.75	ND	0.01	0.00	0.02
2	0.01	0.01	0.02	0.00	0.04	0.01	0.00	ND	ND	95.75	0.04	0.06	0.01	18.79
3	ND	0.00	ND	0.00	0.04	0.01	ND	ND	ND	ND	0.02	0.08	0.01	0.25
4	ND	0.01	ND	0.00	0.03	0.01	ND	ND	ND	ND	0.01	0.05	0.00	0.28
5	ND	0.00	ND	ND	0.00	0.00	0.00	ND	ND	ND	ND	0.02	0.00	0.01
6	0.09	0.08	0.02	0.00	0.00	0.01	0.01	ND	ND	ND	0.01	0.01	0.02	2.64
7	0.03	0.04	0.00	0.01	0.02	0.01	0.01	ND	ND	ND	0.07	0.06	0.01	0.24
8	ND	0.01	0.03	0.03	0.02	0.01	0.00	0.00	ND	ND	ND	0.04	ND	0.03
9	0.02	0.03	0.01	0.01	ND	0.01	0.01	0.02	ND	ND	0.00	0.04	0.01	2.93
10	0.00	0.00	0.00	ND	ND	0.00	0.00	ND	ND	ND	0.01	0.04	ND	0.01
11	0.01	0.01	0.01	0.00	0.12	0.01	0.01	ND	ND	67.77	0.02	0.04	0.01	5.03
12	0.05	0.01	0.02	0.00	0.01	0.01	ND	ND	ND	ND	0.06	0.03	ND	4.80
13	0.26	0.11	0.12	0.08	0.11	0.06	0.09	0.14	0.02	ND	2.02	0.17	0.16	7.05
14	ND	0.00	ND	0.00	ND	ND	0.01	ND	ND	ND	ND	0.01	ND	0.01
15	0.04	0.60	0.01	0.01	ND	0.01	0.05	ND	ND	ND	0.02	0.01	ND	ND
16	ND	0.06	0.01	0.01	ND	0.01	0.01	ND	ND	ND	0.18	0.01	ND	0.04
17	0.04	0.08	0.02	0.01	ND	0.01	0.02	ND	ND	ND	0.17	0.00	ND	0.02
18	0.02	0.07	0.01	0.01	0.17	0.02	0.00	ND	ND	ND	0.10	0.01	0.06	0.11
19	0.04	0.10	ND	0.01	ND	0.00	0.03	ND	ND	ND	0.01	0.00	0.03	0.05
20	0.08	0.14	0.00	0.01	ND	0.03	0.02	ND	ND	ND	0.21	0.04	0.02	0.06
21	0.06	0.09	0.05	0.05	ND	0.01	0.01	ND	0.03	ND	0.11	0.02	0.00	0.11
22	ND	ND	ND	ND	0.14	ND	ND	0.01	0.01	ND	0.02	0.15	0.01	0.05
23	ND	ND	ND	ND	0.14	ND	ND	ND	ND	ND	0.01	0.07	0.00	0.04
24	ND	ND	ND	ND	0.23	ND	ND	ND	ND	ND	ND	0.04	0.00	0.02
25	ND	0.01	ND	0.00	0.14	ND	ND	ND	ND	ND	0.00	0.33	0.11	0.14
26	ND	ND	ND	0.00	0.20	ND	ND	ND	ND	ND	ND	0.01	0.02	0.03
27	ND	0.01	ND	0.00	0.42	ND	ND	ND	ND	ND	0.04	0.04	0.02	0.11

Compare and Contrast Data Sources

Constituents of concern in NGSPWs include chlorides (salinity), inorganics (metals, transition metals, non-metals, metalloids), and organics (oil and grease). Chloride concentrations from all three data sources indicate NGSPWs range from essentially fresh (1 mg/L) to hyper-saline (384,000 mg/L). Barium and iron that were identified as of concern by data from literature, records and samples we analyzed. Aluminum, arsenic, and bromide were identified as constituents of concern from both literature sources and NGSPW samples that we analyzed, but values for these elements were not present in the records provided by gas storage companies. Concentrations of cadmium, copper, lead, lithium, nickel, and zinc reported in the literature were sufficient to identify these elements as potential constituents of concern. Hydrogen sulfide, sulfate, and total sulfide were potential constituents of concern identified from records provided by natural gas storage companies. Samples of NGSPW that we analyzed contained boron and mercury in concentrations that may pose risk to receiving system biota. Organics (e.g. oil and grease) were potentially of concern for NGSPW samples reported in the literature and for samples that we analyzed, but these parameters were not included in the records provided by natural gas storage companies. For comprehensive evaluation, all information sources were useful due to the additional analyses of parameters provided by each. The comprehensive data help to ensure that any constituent that should be considered is included in identification of constituents of concern.

Constituents of Concern

Constituents of concern were identified by comparing the composition (concentration) data in Tables 2-5 with NPDES discharge limits (Table 6) and toxicity data obtained from the USEPA ECOTOX database (USEPA, 2005). The “model” NPDES permit is compiled from constituents of concern or interest in actual permits for petroleum or hydrocarbon related industries operating in New York, Ohio, Pennsylvania and West Virginia. Constituents of concern based upon this analysis are listed in Table 7.

Table 6: Model (comprehensive) NPDES Permit for discharge of natural gas storage produced waters. Limits based on New York, Ohio, Pennsylvania, and West Virginia NPDES permits for petroleum or hydrocarbon related industry. Limit ranges illustrate the minimum and maximum values found in NPDES permits.

Constituent	Limits	Units	Constituent	Limits	Units
pH	6-9	SU	Barium	154	mg/L
BOD5(20°C)	29-57	mg/L	Chloride	5,000	mg/L
CBOD5	25	mg/L	Total Residual Chlorine	0.038	mg/L
COD	170-292	mg/L	Chromium, Total	0.0001-0.1	mg/L
TDS	500	mg/L	Copper, Total	0.37-1.0	mg/L
TDS	30-70	mg/L	Cyanide, Total	0.4	mg/L
			Fluoride, Total	30	mg/L
Oil and Grease	15	mg/L	Iron, Total	0.6-9.4	mg/L
Total Organic Carbon (TOC)	5	mg/L	Lead, Total	0.4	mg/L
PAH	2.8-12.2	mg/L	Manganese, Total	1-4.4	mg/L
Benzene	0.06-2.88	µg/L	Mercury, Total	0.004	mg/L
Toluene	0.028-5.0	µg/L	Nickel, Total	2	mg/L
Ethyl benzene	0.142-5.0	µg/L	Nitrogen, Ammonia Total (as N)	1.5-6.6	mg/L
Ortho-Xylene	5	µg/L	Phosphorous, Total	1	mg/L
Xylene, Meta & Para	0.01-100	µg/L	Sulfide, Total	0.21-1.0	mg/L
BTEX	< 5.0	µg/L	Tin, Total	0.05	mg/L
			Zinc, Total	0.4-5.0	mg/L
Toxicity					
Zero discharge of water containing toxic substances in concentrations that are toxic to human, animal or aquatic life					

Table 7: Constituents of concern in NGSPWs as determined from the literature review, analysis of records, and analysis of samples and based on NPDES permit limits as well as toxicity to *C. dubia*.

Constituent	Concentration (mg/L)		NPDES limit	
	min	max	min	max
pH	3	11	6	9
COD	11.18	45.88	170	292
Total Dissolved Solids	ND	494000		500
Total Suspended Solids	8	5484	30	70
Barium	ND	5481	154	154
Chloride	1	384000		5000
Chromium, Total	0.002	0.213	0.0001	0.1
Copper, Total	0.001	5	0.37	1
Iron, Total	0.008	135000	0.6	9.4
Lead, Total	ND	10.2		0.4
Manganese, Total	ND	2830	1	4.4
Mercury, total	ND	0.087		0.004
Nickel, Total	0.002	9.2		2
Sulfide, Total	0.034	1400	0.21	1
Zinc, Total	ND	5	0.4	5
Oil and Grease	ND	38.8		15
Concentration (mg/L)			Toxicity Data	
Aluminum	0.002	83	1.6 LOEC ^R	
Arsenic	ND	51	1.14 NOEC ^M	
Cadmium	ND	1.21	0.001 NOEC ^R	
Calcium	0.01	89200	1830 48h LC ₅₀ ^M	
Lithium	18.6	235	0.92 LC ₅₀ ^M	
Magnesium	ND	3900	880 48h LC ₅₀ ^M	
Silver	0.047	7	1.93 96h LC ₅₀ ^M	
Sodium	0.015	200000	1740 LC ₅₀ ^M	
^M mortality ^R reproduction				
*Toxicity data from USEPA ECOTOX Database 7-day <i>Ceriodaphnia dubia</i> Static-Renewal Toxicity Tests (unless noted)				

Discussion

Characteristics of NGSPWs are controlled primarily by the geology of rock formations in which the gas is stored. Water characteristics may be influenced to a varying extent by fluids used for well completion and production stimulation and by chemical additives such as corrosion inhibitors, scale inhibitors, and biocides. Natural gas is stored underground in predominantly sedimentary porous and permeable formations, such as aquifers and depleted oil and gas reservoirs, and in caverns dissolved in salt formations. Naturally occurring groundwater is brought to the surface as gas is recovered from storage, particularly from permeable formations such as sandstones and limestones.

Water from aquifer storage facilities is typically fresh, with the water originating by infiltration of meteoric water into the ground. Natural gas storage in aquifers tends to be at shallower depth than storage in depleted oil and gas reservoirs, which occur over a wide range of depth (from a few hundred to thousands of feet) and vary greatly in their geologic characteristics. Much of the water produced from depleted reservoir storage is “formation water,” sometimes called “connate water,” which was trapped in the formation for millions of years. The characteristics of this water result from the combined influence of water trapped in the sediment at the time of initial burial, water that migrated through the formation during diagenesis, and reactions between pore water and solid matrix of the formation. Because of the various, complex factors that influence composition of formation waters, the characteristics of produced waters can vary greatly among nearby gas storage fields, particularly if the specific formation used for storage differs among the fields.

In the Appalachian basin, where numerous gas-storage fields have been developed in depleted oil and gas fields, our analysis of produced water data confirms that water composition varies among different geologic formations. In waters produced from gas storage fields in the Lower Devonian Oriskany sandstone of West Virginia and Pennsylvania, chloride concentration varies widely but is commonly hyper-saline (exceeding 200,000 mg/L in some samples). This high salinity is consistent with published values of formation water resistivities for the Oriskany Sandstone (Roen and Walker, 1996), which when converted to salinity yield values similar to those from our investigation of gas storage produced waters. High salinity waters of the Oriskany Sandstone and other deeply buried sedimentary formations of the Appalachian basin are interpreted as basinal brines, consistent with accumulation of thousands of feet of sedimentary strata in a tectonically active basin. As the waters remained buried deeply for a vast expanse of geologic time, ionic concentrations increased beyond the normal salinity of seawater trapped in the formation at the time of sediment deposition.

In contrast to the Oriskany Sandstone and other older formations of the Appalachian basin, salinity of waters produced from gas storage in depleted oil and gas reservoirs of the younger (Upper Devonian to Pennsylvanian age) formations is generally less, which is consistent with published values of formation water resistivity (Roen and Walker, 1996). Salinity in many of these younger formations is in the range of 4,000 to 50,000 mg/L, reflecting shallower burial depth in comparison with the older formations.

Characteristics and concentrations of elements and compounds in NGSPWs were determined from data from published literature, company records, and analyses of samples from storage facilities. NGSPWs range from essentially fresh water (≤ 400

mg/L chloride) requiring little or no treatment prior to discharge or reuse to hyper-saline waters ($\geq 40,000$ mg/L chloride) that require extensive treatment. The primary constituent limiting treatment and reuse of these waters is chlorides. NGSPWs may contain transition metals that may or may not be included on NPDES permits, but require treatment. In addition, levels of organic carbon (e.g. oil and grease, chemical oxygen demand, biochemical oxygen demand, etc.) may require treatment to mitigate risks to receiving systems. The metals and organics can likely be treated with conventional or innovative biologically based approaches.

Mitigation of the risks presented by NGSPWs is a challenge. Figure 1 provides a flow-diagram used to determine a risk mitigation strategy. Given the conservative nature of chlorides and their resistance to conventional treatment strategies, only two possibilities for risk mitigation are apparent: removal or comanagement with lower chloride waters. NGSPWs containing chloride concentrations from essentially non-detect to about 5,000 mg/L can be readily treated for surface water discharge or reuse. Comanagement of NGSPWs with surface waters such as stormwater or shallow subsurface waters may yield waters that can be readily treated by onsite systems. For natural gas storage sites located near high saline waters (e.g. oceans, estuaries) or large volumes of flowing waters with low chloride contents (e.g. major rivers), surface water discharge may be possible. For other sites, deep subsurface injection of the high chloride waters may be the best alternative.

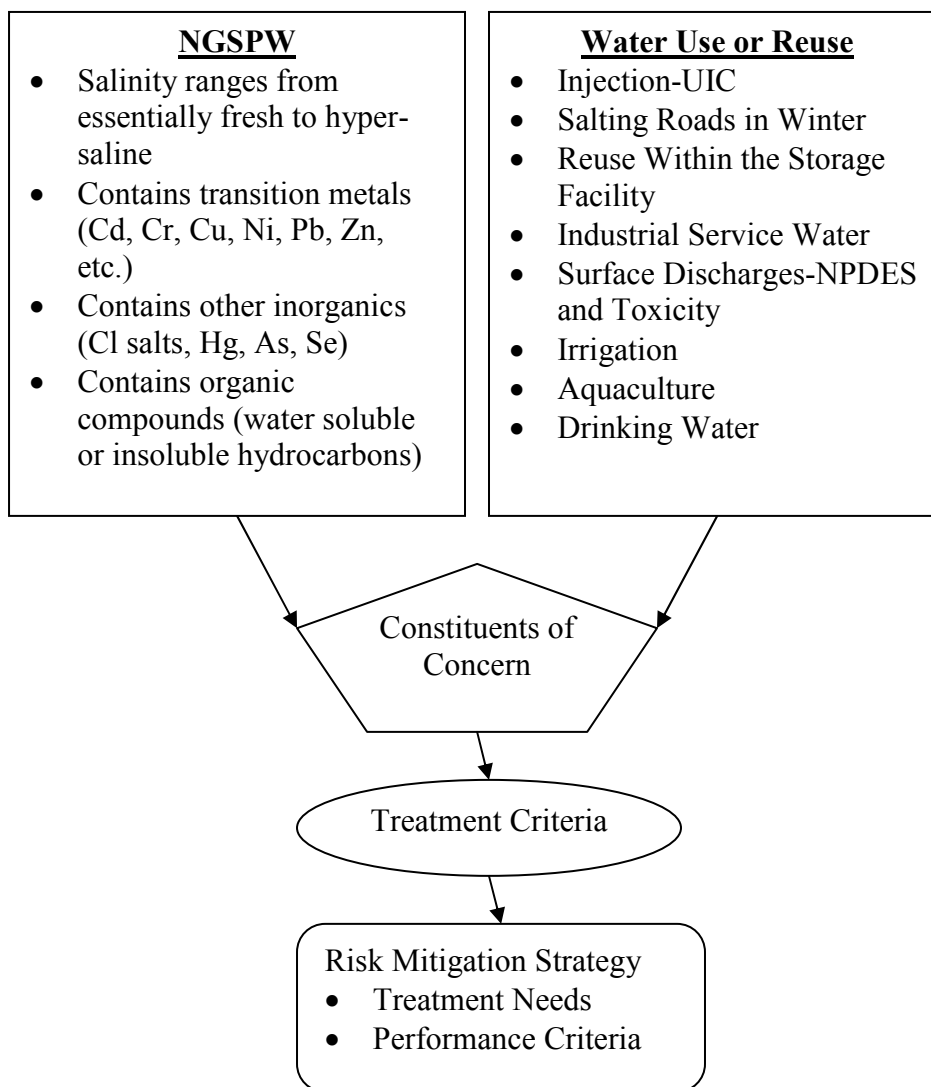


Figure 1: Flow-diagram to determine risk mitigation strategy.

NGSPWs categorized as freshwater (<2,500 mg Cl/L) should be readily treated onsite for reuse or for discharge to fresh surface waters. As chloride concentrations increase (brackish, saline, hyper-saline), the intensity of treatment and cost required for treatment should rise concomitantly. The practicality of onsite treatment of NGSPWs categorized as brackish (2,500 to 15,000 mg Cl/L) will depend on the availability of low chloride water at the site as well as the location of the storage facility. Finally, saline

(15,000-40,000 mg Cl/L) and hyper-saline (>40,000 mg Cl/L) NGSPWs will be the most problematic requiring removal of chlorides or comanagement with low chloride waters or wastestreams. Removal of chlorides will probably require a significant energy and resource investment. Comanagement with low chloride streams may be an efficacious initial approach for risk mitigation where possible. Options for reuse are related to the water quality achieved through treatment. The degree of treatment required is a function of the degree and form of contamination and the reuse criteria or requirements.

Summary

The composition of NGSPWs varies widely in terms of both constituents and concentrations. The composition of NGSPWs controls the potential for discharge to surface waters or reuse as well as requirements for treatment to mitigate risks. Comparisons of NGSPW composition with NPDES discharge limits, toxicity profiles for sensitive aquatic organisms and reuse criteria permitted identification of potential constituents of concern requiring risk mitigation. NGSPWs range in salinity from fresh water to hyper-saline. Importantly, chlorides are the predominant constituent of concern in most NGSPWs. Published records, analyses of NGSPWs provided by companies, and independent analyses of NGSPW samples indicated that most of these waters also contain constituents of concern that include transition metals and a variety of water soluble and insoluble organics. With chlorides as the initial parameter primarily influencing decisions and strategies, risk mitigation may range from simple onsite treatment to more complicated and costly approaches. Risk mitigation strategies for NGSPWs will have to be robust or site specific to deal with the diverse compositions.

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CHAPTER 3
PERFORMANCE OF A PILOT-SCALE HYBRID
CONSTRUCTED WETLAND TREATMENT
SYSTEM FOR SIMULATED NATURAL
GAS STORAGE PRODUCED WATERS

Introduction

Natural gas storage produced waters (NGSPWs) are brought to the surface when natural gas is reclaimed from underground storage facilities (Veil et al., 2004). NGSPWs are generated in relatively large volumes and contain a variety of constituents that limit disposal or reuse of the water (Chapter 2). The United States produces 20 billion barrels of produced water each year (Veil et al., 2004). Produced waters pose a challenge for treatment because they vary widely in composition. Materials such as chlorides, metals, metalloids, and hydrocarbons are of concern in these waters.

Expansion of existing gas storage fields and development of new fields are limited by the high costs associated with wastewater treatment and disposal. Currently, there are two common methods for handling produced water. One method is to transport the produced water to specialized treatment facilities followed by surface discharge of the treated water and the other is to reinject the water to the subsurface (Nakels et al., 1992). Volumes of produced water are increasing and conventional treatment methods are becoming exponentially more costly as surface discharge and re-injection regulations under the Clean Water Act (CWA), National Pollutant Discharge Elimination System

(NPDES), and Underground Injection Control (UIC) grow more stringent (Fillo et al., 1992). Finding new approaches for handling produced waters is essential for continued operation of many existing storage fields and for development of new storage capacities.

Although the salinity of some produced waters may be low enough to meet NPDES discharge limits, concentrations of other constituents in these waters may preclude discharge, resulting in a need for treatment or disposal. Specifically designed constructed wetland treatment systems (CWTS) have been used to treat many constituents of concern found in NGSPWs independently, but this concept or technology has not been tested for produced waters from gas storage fields (Cronk, 1996; Hawkins et al. 1997; Lin and Mendelsohn, 1998; Knight et al. 1999; Gillespie et al. 2000; Barton and Karathanasis, 2001;; Murray-Gulde et al. 2003a; Murray-Gulde et al. 2003b). Because of the diverse composition of NGSPW, a treatment system needs to be flexible in design and contain different treatment methods. This is accomplished by utilizing reactors or wetland cells that are specifically designed to treat constituents of concern. Utilizing a modular system with specifically designed reactors provides for removal of chlorides, hydrocarbons, and metals. Constructed wetland treatment systems are relatively inefficient for removal of conservative elements such as chlorides from the water column. Produced waters can have chloride concentrations ranging from non-detect to greater than 300 g/L. For this reason a treatment process or device, such as reverse osmosis, must be utilized; thus the system is a hybrid CWTS.

Testing the system at pilot-scale provides a physical model of the theory used to specifically design the hybrid treatment system. Pilot-scale systems provide removal rate coefficients, can be manipulated to improve performance, and provide proof-of-concept

data to increase support of regulatory agencies. Utilization of a pilot-scale study serves to decrease uncertainties and confirm design features for future, field-scale constructed wetland treatment systems.

Just as shipping and treatment of actual NGSPWs are costly, shipping of these waters for research purposes is also costly and prohibitive for a comprehensive pilot-scale study. In this case, simulated waters can be formulated to mimic NGSPWs with a wide range of constituents. Utilization of simulated waters has many benefits. Simulated waters allow for a complete knowledge of system input, which in turn allows for a better comparison with system output. Simulated waters are also more cost effective for preliminary, pilot-scale experiments. The simulated natural gas storage produced waters are designed to closely replicate the composition of actual waters as shown by statistical analysis of data from various natural gas storage companies and are in agreement with published data (Collins, 1975; Hunt, 1979; Ray and Engelhardt, 1992; Reed and Johnsen, 1996; Pope and Pope, 1999; USEPA, 2000; USEPA, 2004; Veil et al., 2004).

The purpose of this research is to assess the treatability of NGSPWs utilizing a pilot-scale hybrid CWTS. The approach should be applicable to a wide range of waters produced from gas storage, as the composition and volumes of waters generated vary greatly among storage fields. Specific objectives of this pilot-scale study were: (1) to characterize natural gas storage produced waters; (2) to design and construct modular pilot-scale hybrid CWTS to remove specific constituents of NGSPW; and (3) to measure performance of the pilot-scale hybrid CWTS in terms of decrease of targeted constituents from inflow to outflow with concomitant decreases in toxicity.

Materials and Methods

Characterization of produced waters

Produced waters were characterized in order to develop an understanding of the concentrations of constituents of concern in NGSPWs and to determine the composition of simulated water for use in the pilot-scale CWTS. Composition of NGSPWs was determined through a literature review, analysis of approximately 4,000 records of produced waters provided by several natural gas storage companies, and analysis of samples provided by several natural gas storage companies. NGSPW composition records were analyzed using the Statistical Analysis System (SAS Institute, 2002). Statistical analysis included mean, standard deviation, minimum, and maximum values for each constituent listed in the records. It was assumed that the laboratories that generated these data utilized standard methods to obtain values. Samples of natural gas storage produced waters were provided by several natural gas storage companies and elemental analyses were performed according to U.S. EPA Method 200.8 using a Sciex Elan 9000 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) (Perkin-Elmer, Norwalk, CT). Other parameters measured included: temperature, pH, conductivity, alkalinity, hardness, dissolved oxygen (DO), chemical oxygen demand (COD), biochemical oxygen demand (BOD), chloride concentration, sulfate, total dissolved solids (TDS), total suspended solids (TSS), and oil/grease (APHA, 1998).

The compilation of data obtained from literature sources, records, and sample analysis was used to formulate simulated NGSPWs. Simulated NGSPWs were utilized in CWTS experiments because shipping of these waters for research purposes is costly and

simulated waters allow for more complete knowledge of system input, which in turn allows for efficient comparison with system output

Design and Construction

Because the composition of NGSPW varies, a CWTS that utilizes a modular design offers flexibility for treatment of different waters. Each module is designed to treat specific constituents of concern. Removal of oil from water is accomplished through physical separation in an oil/water separator or by biodegradation in the constructed wetland modules. Chloride, a conservative element, requires energy driven physical removal from the water column which is accomplished in this case through reverse osmosis. Metals may be removed through various biogeochemical processes including; organic complexation with detritus, hydrolysis, sorption to biotic and abiotic exchange sites, and precipitation of metal complexes (i.e. metal sulfides and metal oxyhydroxides). The modular approach allows for a flexible and robust system that can be arranged utilizing different modules based upon the composition of NGSPWs. Specific design and construction considerations for each of the modules in the pilot-scale hybrid CWTS are discussed below.

Detention Basins

Detention basins were utilized in this system for formulation and storage of simulated produced waters at various stages in treatment. The primary detention basin, where the simulated water was mixed and stored, was a 3780 L polypropylene carboy. The other two detention basins were 2070 L polypropylene carboys. These basins were

utilized to store sufficient volumes of wastewater to efficiently operate the reverse osmosis system.

Oil/Water Separator

An oil/water separator served to remove water-insoluble and water-soluble organics. The oil/water separator was based on an American Petroleum Institute (API) design; the modified separator was 121.9 cm long by 61.0 cm wide by 33.0 cm deep. The modified separator implemented several oil removal techniques including; skimmers, baffles, dissolved air floatation, and filtration (Luthy et al. 1978; Wilkinson, 2000).

Saltwater Wetland

A saltwater module was designed to remove residual water soluble organics from water after the oil/water separator to avoid fouling of the reverse osmosis (RO) membranes by organics. The saltwater module consisted of two saltwater wetland cells in series connected by PVC pipe fittings and approximately 30 cm long segments of 1.9 cm diameter poly-tubing placed 6 cm below the top of each Rubbermaid® container. Each cell was contained in a 121.9 cm long by 77.5 cm wide by 63.5 cm deep, 378 L Rubbermaid® container with approximately 215 L of surface water. The hydroperiod or hydraulic retention time (HRT) of the CWTS was maintained at 24 hours per cell or 48 hours for the entire saltwater module (flow rate of 149 mL/min). The cells contained quartz sand hydrosol and were planted with a mixture of both the tall and short forms of *Spartina alterniflora* Loisel (smooth cordgrass).

Reverse Osmosis

The reverse osmosis (RO) system was required to remove chlorides from produced waters. The Aquapura[®] TESERO-600-SW (Tempest Environmental Systems, Inc. Durham, NC) system utilizes a 25.4 cm 5 micron prefilter and two 6.35 cm by 101.6 cm membranes. This RO system has a concentrate pressure of 774 psi and requires a flow rate of 8.7 L/min.

Freshwater Wetland

The freshwater module was designed to remove residual metals post-RO and can also function independently as a treatment system for waters with <4,000ppm chloride concentration. The freshwater wetland module consisted of series of two parallel reactors each containing four cells in series. The four cells in series provided sampling locations and prevented “short circuiting” of flow. Each cell was contained in a 121.9 cm long by 77.5 cm wide by 63.5 cm deep, 378 L Rubbermaid[®] container. The cells were connected by PVC pipe fittings and approximately 30 cm long segments of 1.9 cm diameter poly-tubing placed 6 cm below the top of each Rubbermaid[®] container. Each cell contained approximately 140 L of surface water. By maintaining a flow rate of 97 mL/min, the HRT of the CWTS was 24 hours per cell or 96 hours for the entire freshwater module. The first two cells in each series contained hydrosol consisting of river sediment amended with 3% pine mulch (by volume), and the top 10cm were amended with 1.5% gypsum (by volume). These cells were planted with *Schoenoplectus californicus* C.A. Meyer (California bulrush). The final two cells in each train contained quartz sand hydrosol and were planted with *Typha latifolia* L. (broadleaf cattail).

Performance

Simulated waters were formulated to represent categories of produced water: freshwater, brackish water, saline water, and hyper-saline water. Treatment effectiveness and performance were evaluated from the samples of inflow and outflow waters. Samples were collected from the initial detention basin and at intervals throughout the system (at the outflow of each module) with consideration of the hydraulic retention time. Sampling and analyzing the outflow from each module allowed us to discern the time and location of removal of constituents of concern from the water column.

Cadmium, copper, lead, zinc, oil and grease, and chloride concentrations represented the constituents of concern for these NGSPWs along with results from toxicity experiments. These parameters were used to make decisions regarding the efficacy of the performance of pilot-scale hybrid CWTS. Explanatory parameters were used to understand background conditions in the system and the potential for specific transfers and transformations of constituents of concern to occur (Table 1). Metal data include percent removal and rate coefficients which were calculated using Equations 1 and 2. Percent metal removal was calculated by:

$$\% \text{ removal} = \left(\frac{[I] - [O]}{[I]} \right) 100$$

Equation 1

where [O] is the final outflow metal concentration (mg/L), and [I] is the initial inflow metal concentration (mg/L).

Rate coefficients for removal of metals from the water column were estimated assuming a first-order reaction rate:

$$k = \frac{-\ln ([O]/[I])}{t} \quad \text{Equation 2}$$

where k is the rate coefficient (day^{-1}), $[O]$ is the final outflow metal concentration (mg/L), $[I]$ is the initial inflow metal concentration (mg/L), and t is hydraulic retention time (days) of the entire system.

Table 1: Analytical methods for parameters measured in samples from the pilot-scale hybrid constructed wetland treatment system.

Parameter	Method	Method Detection Limit
Temperature	Instrumentation: YSI Model 52	0.5°C
pH	Instrumentation: Orion Model 420A	0.01
Conductivity	Instrumentation: YSI 30	0.1 µS/cm
Alkalinity	Standard Methods: 2320 B	2 mg/L as CaCO ₃
Hardness	Standard Methods: 2340 C	2 mg/L as CaCO ₃
DO ¹	Instrumentation: YSI Model 52	0.1 mg/L
COD ²	Closed reflux colorimetry (HACH- modified from Standard Methods: 5220 D)	3 mg/L
BOD ³	Standard Methods: 5210 B	0.1 mg/L
Chloride	High: HACH Drop Count Titration Method	500 mg/L
	Low: HACH colorimetric method 8207	25 mg/L
Sulfate	Standard Methods: 4500 E	1 mg/L
Metals	Atomic Absorption Spectrometry (AA)	Cd-0.002 mg/L Cu-0.010 mg/L Pb-0.050 mg/L Zn-0.005 mg/L
	Inductively Coupled Plasma-Atomic Emissions Spectrometry (ICP-AES): USEPA 200.8	Cd-0.010 mg/L Cu-0.010 mg/L Pb-0.015 mg/L Zn-0.010 mg/L
TDS ⁴	Standard Methods: 2540 C	0.1 mg/L
TSS ⁵	Standard Methods: 2540 D	0.1 mg/L
Oil and Grease	Total Petroleum Hydrocarbon HACH Method 10050 Immunoassay method	1.0 mg/L
Bulk Redox	Standard Voltmeter, Accumet® calomel reference electrode, and <i>in situ</i> platinum-tipped electrodes (Faulkner et al., 1989).	±10mV

¹ Dissolved Oxygen

² Chemical Oxygen Demand

³ Biological Oxygen Demand

⁴ Total Dissolved Solids

⁵ Total Suspended Solid

As another measure of treatment performance, toxicity experiments were used to estimate decreases in potential risks for receiving system organisms. Organisms such as *C. dubia* respond to numerous constituents in the water and may respond even when analytical results suggest an absence of toxicity. *C. dubia* are sensitive to changing species of potentially toxic elements, decreases in elemental toxicity, and potential interactions between compounds or elements present in NGSPWs that chemical analyses may not detect. Toxicity of simulated produced waters was measured using *C. dubia* in a 7-day static renewal toxicity test (Lewis et al., 1994). *C. dubia* were exposed to both inflow and outflow waters that were diluted to eliminate toxicity from chlorides (<400mg/L Cl). Comparisons were made among treatment and control organisms using Statistical Analysis System (SAS Institute, 2002). Statistical differences for mortality were determined by chi-square analysis, and differences in reproduction were determined using analysis of variance (ANOVA) with Dunnett's mean separation.

Results and Discussion

Characterization of Produced Waters

Produced waters vary significantly in composition because of geologic formation of the source water, contact with hydrocarbons, and other production processes (Ray and Engelhardt, 1992; Veil et al., 2004). Produced waters were statistically grouped into four general categories (Fresh, Brackish, Saline, and Hyper-saline) using primarily the median and quartiles of chloride concentrations found in NGSPWs. Based on their presence in concentrations that pose potential risks for receiving aquatic system biota, six targeted constituents (chlorides, cadmium, copper, lead, zinc, and oil/grease) were chosen to represent produced water composition for the purpose of evaluating treatment

effectiveness. The constituents chosen (Cl, Cd, Cu, Pb, Zn, and oil/grease) were used to formulate simulated waters for treatment in this study. The target inflow concentrations for simulated NGSPWs are shown in Table 2.

Table 2: Composition of Fresh, Brackish, Saline, and Hyper-saline simulated NGSPWs.

Constituent	Chemical Source	Fresh Target Inflow (mg/L)	Brackish Target Inflow (mg/L)	Saline Target Inflow (mg/L)	Hyper-Saline Target Inflow (mg/L)
Chlorides	CaCl ₂ , NaCl, MgCl ₂ ·6H ₂ O	<400-2,500	2,500-15,000	15,000-40,000	>40,000
Cadmium	CdCl ₂	0.4	0.4	0.8	1.2
Copper	CuCl ₂ ·2H ₂ O	0.8	1.7	3.3	5.0
Lead	PbCl ₂	1.0	5.5	6.8	10.2
Zinc	ZnCl ₂	5.0	23.0	45.9	69.0
Oil/Grease	Motor Oil	20.0	19.0	49.0	78.0

Module Design and Construction

Individual modules were constructed to remove constituents present in natural gas storage produced water. These modules were arranged to create a flexible and robust treatment system that could be modified to treat constituents found in NGSPWs. Figure 1 is a schematic of the full system for treatment of high chloride (>4,000 mg/L Cl) produced waters that also contain metals and organics.

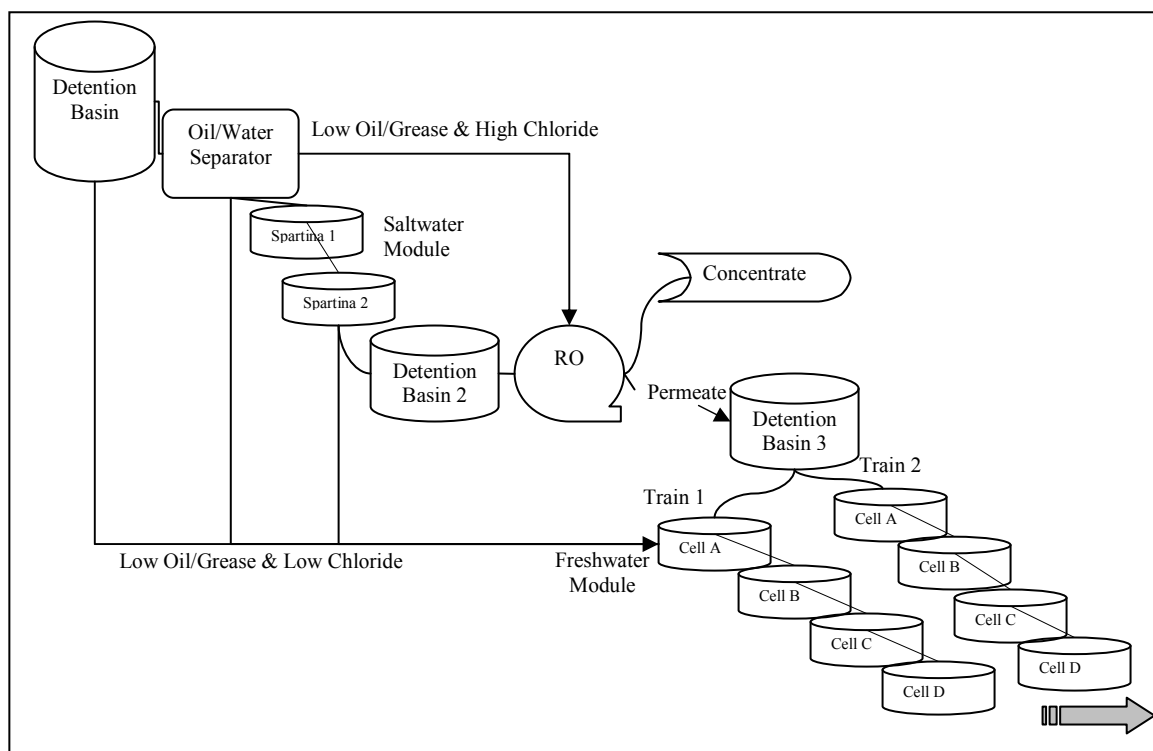


Figure 1: Schematic for the pilot-scale hybrid constructed wetland treatment system for treatment of constituents in natural gas storage produced waters.

Different modules were utilized for treatment of each of the simulated NGSPWs outlined in Table 2. Each water was formulated and mixed in the first detention basin for 24h prior to introduction to the system. For treatment of constituents in simulated Fresh and Brackish NGSPWs, the saltwater wetland and RO system were bypassed because chloride concentrations were $<4,000$ mg/L. The oil/water separator and the freshwater module were used for treatment of simulated Fresh NGSPW. The freshwater module was used independently to treat simulated Brackish NGSPW. Treatment of constituents in simulated Saline and simulated Hyper-saline waters utilized the entire pilot-scale hybrid CWTS: oil/water separator, saltwater module, RO, and freshwater module.

Performance

System performance was measured by decrease in concentrations of constituents of concern and toxicity from the inflow simulated NGSPWs to the outflow from the CWTS.

Constituents of Concern

Each constituent of concern (Cd, Cu, Pb, Zn and organics) was removed effectively from the water column by the pilot-scale hybrid CWTS. Percent removal and removal rate coefficients for Cd ranged from 38.4 to 99.6% and 0.121 to 0.745 days⁻¹ respectively, for these waters. Percent removal and removal rate coefficients for Cu ranged from 90.6 to greater than 99.8% and 0.555 to 0.953 days⁻¹, respectively. Results from this pilot-scale study show greater removal of Cu than results from the Hawkins et al. (1997) pilot-scale study with inflow and outflow concentrations of 22.4 and 12 ug/L, respectively, resulting in 33% removal. Murray-Gulde et al. (2003a) found comparable removal of copper in a full-scale CWTS with 78% removal of total-recoverable Cu, where average inflow and outflow Cu concentrations were 25 (±10) ug/L and 6 (±3) ug/L, respectively. Percent removal and removal rate coefficients for Pb ranged from 93.1 to greater than 99.3% and 0.474 to 0.964 days⁻¹, respectively. The removal of Pb in this pilot-scale study is greater than removal found by Hawkins et al. (1997) who found 79% removal of Pb with 10.5 ug/L inflow concentration and 2.2 ug/L outflow concentration. Percent removal and removal rate coefficients for Zn ranged from 40.0 to 99.8% and 0.128 to 0.758 days⁻¹, respectively. Removal of Zn from the simulated NGSPW was comparable to removal observed in microcosm and pilot-scale wetland studies performed by Gillespie et al. (1999, 2000) and Hawkins et al. (1997) who

reported removal percentages ranging from 38 to 85%. Performance of the CWTS was least for the metals in the treatment of simulated brackish water; however, 0.157 mg Cd/L, 0.953 mg Cu/L, 2.539 mg Pb/L, and 8.655 mg Zn/L were removed from the water column.

Table 3: System inflow concentration (mg/L), outflow concentration (mg/L), percent removal, and rate coefficients (days⁻¹) for cadmium, copper, lead and zinc in simulated NGSPWs. Detection limits for each element were: 0.002 mg Cd/L, 0.006 mg Cu/L, 0.006 Pb/L, and 0.005 mg Zn/L.

Water Category	Cadmium (as CdCl ₂)			
	Inflow	Final Outflow	% removal	k (days ⁻¹)
Fresh	0.312	0.008	97.6%	0.745
Brackish	0.409	0.252	38.4%	0.121
Saline	1.008	0.004	99.6%	0.705
Hypersaline	1.976	0.008	99.6%	0.686
	Copper (as CuCl ₂)			
	Inflow	Final Outflow	% removal	k (days ⁻¹)
Fresh	0.703	Non-Detect	>99.1%	0.953
Brackish	1.052	0.099	90.6%	0.592
Saline	5.314	0.063	98.8%	0.555
Hypersaline	3.498	Non-Detect	>99.8%	0.796
	Lead (as PbCl ₂)			
	Inflow	Final Outflow	% removal	k (days ⁻¹)
Fresh	0.744	Non-Detect	>99.1%	0.964
Brackish	2.557	0.176**	93.1%	0.669
Saline	6.012	0.136	97.7%	0.474
Hypersaline	13.170	0.095	99.3%	0.616
	Zinc (as ZnCl ₂)			
	Inflow	Final Outflow	% removal	k (days ⁻¹)
Fresh	5.180	0.367	92.9%	0.530
Brackish	21.630	12.985	40.0%	0.128
Saline	48.634	0.374	99.2%	0.608
Hypersaline	79.400	0.185	99.8%	0.758

k = rate coefficient

* indicates a non-detect value was present (ND values were not included in average calculations)

Figures 2-5 illustrate removal of Cd, Cu, Pb, and Zn from the water column by the pilot-scale CWTS. For the simulated Fresh and Brackish experiments, Cd, Pb, and Zn were primarily removed in the initial two cells of the freshwater CWTS. Figure 3 illustrates Cu removal from the simulated Saline NGSPW using the saltwater portion of the CWTS. Though the primary purpose of the saltwater wetland module was removal of residual organics post-oil/water separator treatment, the saltwater system was also effective in removal of metals from the water column.

Oil/grease was measured as total petroleum hydrocarbons (TPH) in the inflow and outflow for simulated Fresh NGSPW. The inflow water contained 1.5 mg/L TPH as diesel fuel. The oil/water separator outflow and final outflows were non-detect (<1 mg/LTPH as diesel fuel).

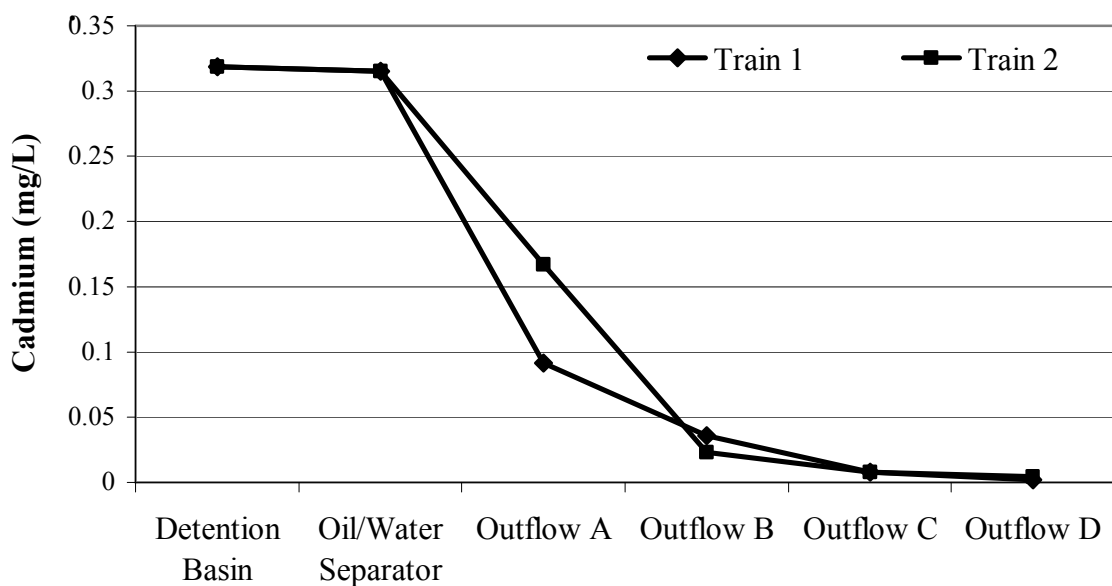


Figure 2: Cd removal from simulated fresh NGSPW by the pilot-scale CWTS.

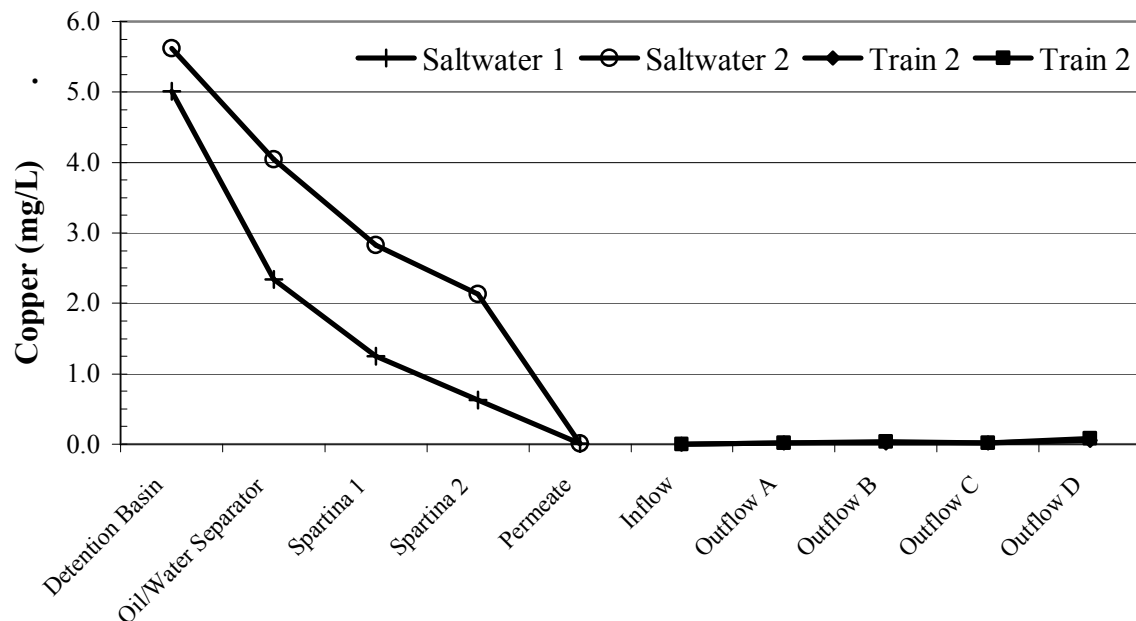


Figure 3: Cu removal from simulated saline NGSPW by the pilot-scale CWTS.

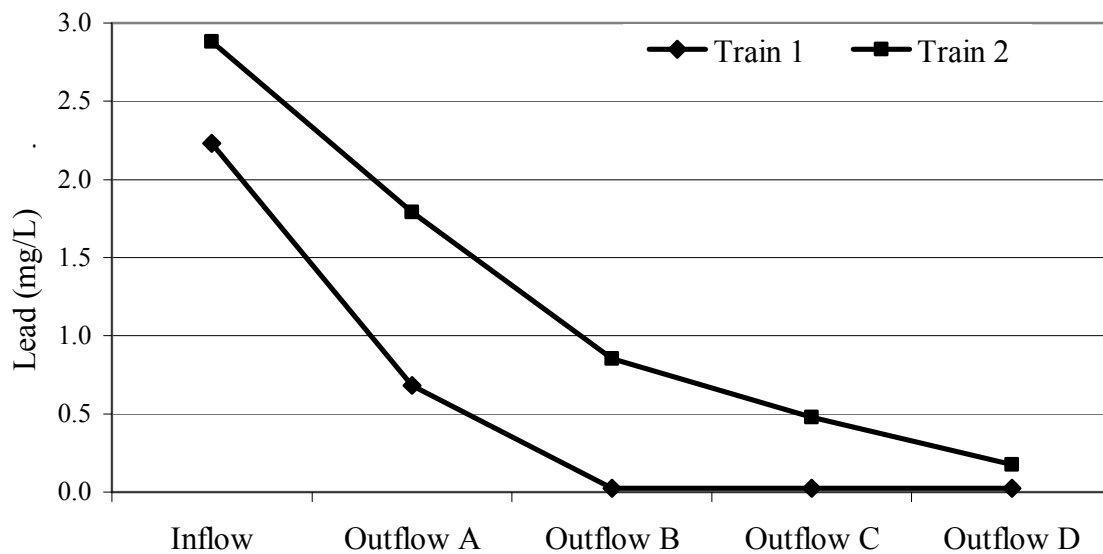


Figure 4: Pb removal from simulated brackish NGSPW by the pilot-scale CWTS.

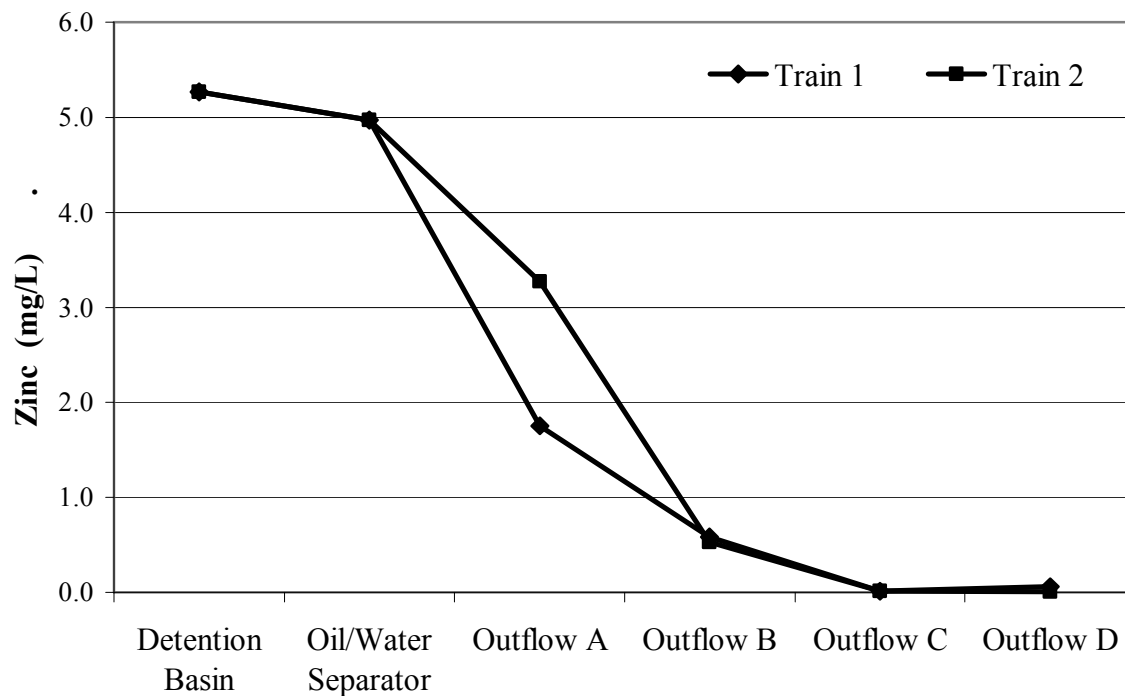


Figure 5: Zn removal from simulated fresh NGSPW by the pilot-scale CWTS.

Toxicity

Toxicity experiments were used to assess performance of the pilot-scale CWTS using *C. dubia* in 7-day static renewal toxicity tests for each simulated NGSPW. *C. dubia* were exposed to inflow and outflow waters from the pilot-scale CWTS. Chloride concentration for Brackish, Saline and Hyper-saline simulated produced waters would contribute directly to the toxicity of the sample, and thus conceal other potential toxicants (Sauer et al., 1997). Samples were diluted to chloride concentrations less than 400 mg Cl/L.

Fresh NGSPW inflow water to the CWTS was toxic; exposures of 5% resulted in 90% mortality of *C. dubia*. A 1% dilution of inflow water caused no mortality of *C. dubia*, however statistically decreased reproduction was observed. No mortality or

reproductive effects were observed for *C. dubia* exposed to undiluted (100%) outflow from the CWTS. These results indicate mitigation of risk (i.e. decrease in toxicity) to *C. dubia* from Fresh NGSPWs by the pilot-scale CWTS.

For the Brackish NGSPW, both the inflow and outflow waters were toxic; however, the outflow water was less toxic than the inflow water. Exposures of 2.5% Brackish NGSPW inflow water resulted in complete mortality of *C. dubia*. Inflow waters diluted to 1.2% caused no mortality but statistically decreased reproduction. Outflow waters diluted to 2.5% caused no mortality but reproduction impairment was observed. Outflow waters diluted to 1.2% caused no measured toxicological effects. Decreased performance in terms of removal of toxicity may be the result of the lack of maturity of the system and relatively high initial loading of constituents of concern. The Brackish NGSPW was the first water introduced to the system. Upon analysis of samples, noting that there was not efficient removal, the system was given more time to mature before continuing experiments with the simulated Fresh, Saline, and Hyper-saline NGSPWs.

For both Saline and Hyper-saline NGSPW inflow waters resulted in complete mortality of *C. dubia* while outflow waters resulted in no mortality or reproductive effects. Saline and Hyper-saline inflow waters were diluted to 3% and 1.2%, respectively, in order to eliminate toxicity from chlorides. Outflow waters were not diluted because the RO unit removed chlorides.

Toxicity to *C. dubia* was reduced from inflow to outflow for each of the four waters. Though the outflow brackish waters were still toxic, the toxicity was decreased from inflow to outflow. Toxicity was removed completely by the pilot-scale CWTS for Fresh, Saline, and Hyper-saline NGSPWs.

Conclusions

CWTS in this pilot-scale study were capable of removing constituents of concern and consequently toxicity from simulated NGSPWs. This pilot-scale system utilized a modular design, which allowed for flexibility in treatment of waters that varied widely in composition. Fresh and some brackish NGSPWs may be readily treated with freshwater CWTS. NGSPWs with chloride concentrations greater than the tolerance of *S. californicus* and *T. latifolia* require either comanagement with lower chloride waters or additional treatment. Chloride concentration is a dominating factor in choosing a risk mitigation strategy for treating NGSPWs. RO systems, as used in this study, provided adequate chloride removal. Further research is needed to investigate alternative and cost effective chloride removal processes. The use of hybrid CWTS for mitigation of risks posed by NGSPWs is a readily implemented approach with the potential to reduce the costs of handling water produced from gas storage fields.

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CHAPTER 4
THE RELIABILITY OF THE TURNER DESIGNS TD500
OIL-IN-WATER HANDHELD FLUOROMETER FOR
MEASUREMENT OF PRODUCED WATERS
CONTAINING ALGAE

Introduction

Oil contains various compounds that are usually measured as a generic parameter: oil-in-water or oil and grease. Oil enters surface and ground waters through a variety of sources including accidental, incidental, and purposeful introductions. Accidental inputs include spills, shipwrecks, structural failures, pipeline breaks and weather induced leakages (e.g. Hurricanes Katrina and Rita in 2005). Stormwater runoff from roads and parking lots is a major source of incidental introduction of oil into water. Oil is deliberately discharged, in the form of produced water, into surface and groundwater through permitted discharges (NPDES) and injection to designated wells (Nakels et al., 1992). For monitoring of mitigation activities and other situations requiring real time information on oil-in-water concentrations, rapid measurements are needed. Methods used for comprehensive monitoring of oil-in-water are both time consuming and costly. An accurate, rapid, and field portable method for measurement of oil-in-water would be useful for many situations encountered in daily activities.

For comprehensive measurement of oil-in-water, several methods have been developed including gas chromatography, infrared chromatography, solid phase and

liquid/liquid extraction, gravimetric measures, UV absorbance, total organic carbon (TOC), total petroleum hydrocarbon (TPH) immunoassay, and fluorometry (APHA 1998, Romero 1999, Lambert 2003, Ryder 2004). These methods produce results that are operationally defined, and thus the measurements are not readily comparable (Lambert, 2003). Since oil-in-water is a generic parameter and does not indicate the specific constituents contained in the oil, often a screening level measurement of oil-in-water would suffice (Maher 1982). Rapid screening measurements typically involve fluorometry because instrumentation can be field portable (Lambert et al. 2003). Both direct and extraction methods are used to measure oil-in-water using fluorometry (Lambert et al. 2003; MORE). Lambert et al. (2003) noted there was little correlation between the results of the extraction and direct reading methods of the oil-in-water samples, possibly due to unrepresentative sampling or unknown interferences. In field situations, such as produced water discharges, site waters may contain complicating or confounding factors such as algae. If algal pigments fluoresce in the portion of the spectrum that is included in oil-in-water measurements then a false positive result may be observed (Fuchs et al. 2002; Resch-Genger et al. 2005).

The purpose of this research was to discern the contribution of algae to the fluorescence measures of oil-in-water for produced water samples. Specific objectives were: 1) to measure oil-in-water unconfounded by algae, 2) to measure the independent contribution of algae to fluorescence in the portion of the spectrum also used for oil-in-water measurements, and 3) to discern the potential contribution of algae to false positive fluorometric measurements of oil-in-water.

Materials and Methods

The extraction procedure utilized for oil and grease analysis was derived from the Turner Designs *FastHex* Method for extraction (Turner, 2005). The extraction solvent for this method is UV Spectrophotometric Grade n-Hexane. Oil-containing water samples were prepared by decreasing the pH<2 with 6N hydrochloric acid (at this pH chlorophyll *a* is hydrolyzed into phaeophytin). One hundred mL of the acidified sample was transferred to a 125 mL Erlenmeyer flask where 10 mL of hexane was added. After capping the flask, the solution was mixed on a magnetic stirplate for one hour. The solution was allowed to separate for approximately 15-20 minutes; the hexane extract was removed and utilized for fluorometric analysis.

To measure oil-in-water concentrations by the extraction method, solutions were prepared at 0, 10, 20, 40, 80, and 100 mg/L based on specific gravity of the oil. Each solution was made in a one liter volumetric flask using Shell[®] Rotella[®] T SAE 15W-40 motor oil and nanno-pure water. These solutions were extracted with 10mL of UV Spectrophotometric Grade hexane.

To prepare a standard curve for extracted oil-in-water, standards were made at 0, 100, 200, 400, 800, and 1000 mg/L by adding Shell[®] Rotella[®] T SAE 15W-40 motor oil directly to hexane. A stock of 1000 mg/L was made and subsequent concentrations were obtained through serial dilutions.

Water samples containing algae were prepared using *Raphidocelis subcapitata* and a field site sample containing a mixture of *Chlorella*, *Chroococcus*, *Ulothrix*, *Scenedesmus*, *Staurastrum*, *Microcystis*, *Mallomonas*, and *Aphanizomenon* at various cell densities (ranging from 10^3 to 10^6 cells/mL). Each solution was made in a one liter

volumetric flask using different cell densities of algae. These solutions were extracted with 10mL of UV Spectrophotometric Grade hexane.

Experiments were conducted to measure oil in nano-pure water using the extraction procedure, to measure algae in water without the presence of algae, and to measure a series of concentrations of oil-in-water in the presence of algae.

A positively correlated standard curve was expected for both the oil-in-water and algae in water solutions. If algae interfere with oil-in-water experiments (as expected) the curve for oil-in-water in the presence of algae should parallel either above (positive interference) or below (negative interference) the oil-in-water curve.

Results and Discussion

The first objective of this study was to measure oil-in-water in samples unconfounded by algae. Figure 1 illustrates three separate extractions of solutions of 0, 10, 20, 40, 60, 80, 100 mg oil /L in water (predicted concentrations). The inconsistency in the data indicates that the extraction method is not reliable for measuring oil-in-water for this concentration range using this instrument since the standard curves for these measurements were unreliable (Figure 2). There are many potential sources of error in the extraction method: adsorption of organics to the glass (Maher, 1982), inadequate mixing, differences in mixing between flasks, emulsion formation as well as others.

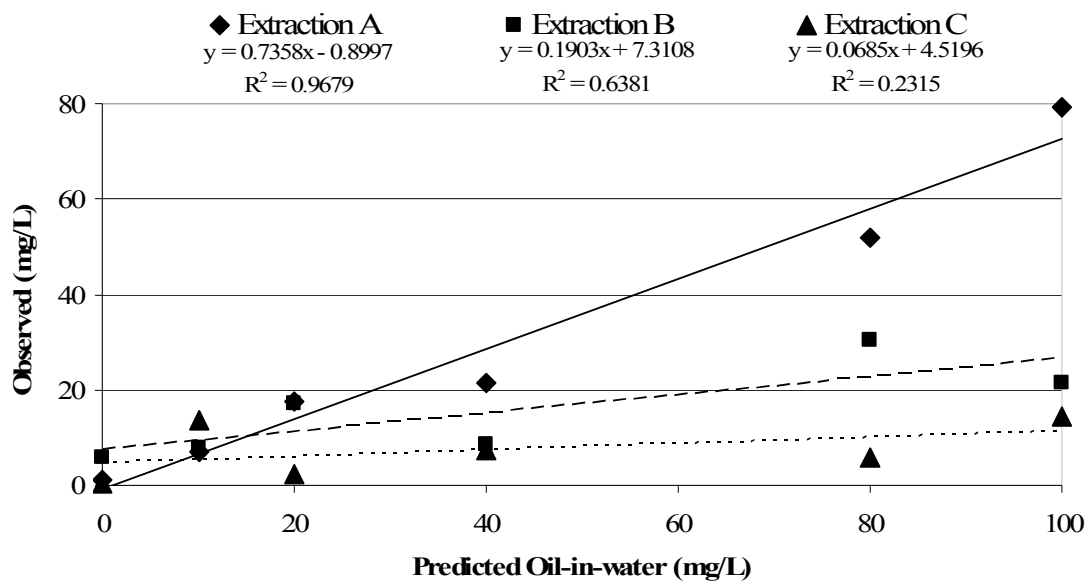


Figure 1: Hexane extraction of oil-in-water samples measured with the handheld fluorometer.

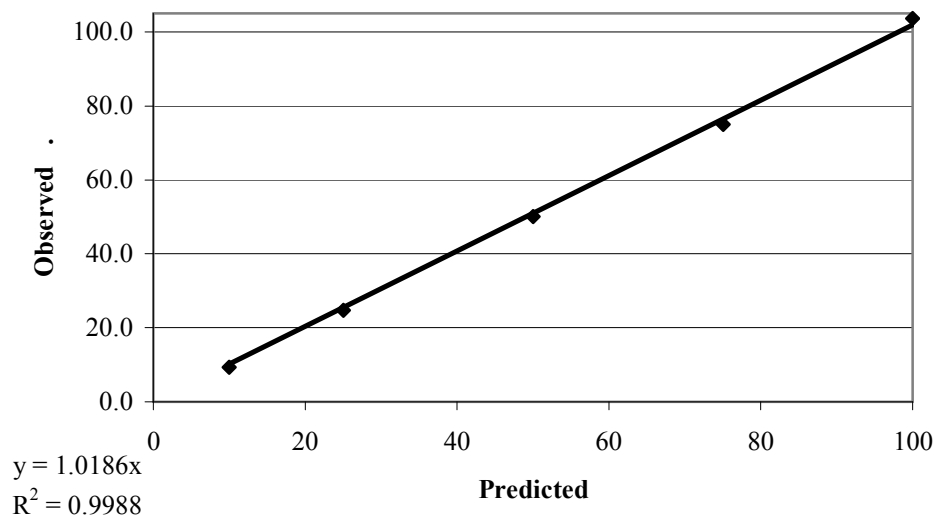


Figure 2: Standard curve for oil in hexane.

The second objective of this study was to measure the independent contribution of algae to fluorescence in the portion of the spectrum used for oil-in-water measurements. Two different sources of algae were used to evaluate the potential for algae to contribute “false positive” fluorescence to an oil-in-water measurement. Figure 3 illustrates the correlation between relative oil-in-water concentration and a series of cell densities of *R. subcapitata*. The potential for algae to contribute to relative fluorescence is apparent, especially at higher, but realistic cell densities. Figure 4 illustrates a field sample of algae containing *Chlorella*, *Chroococcus*, *Ulothrix*, *Scenedesmus*, *Staurastrum*, *Microcystis*, *Mallomonas*, and *Aphanizomenon* at a series of cell densities. The lack of a linear relationship between the relative oil-in-water concentration and cell densities for this algal sample is apparent. These results are indicative of other extractions and measurements of algal samples and the lack of a reliable relationship between observed algal fluorescence and cell density using this extraction procedure and this instrument.

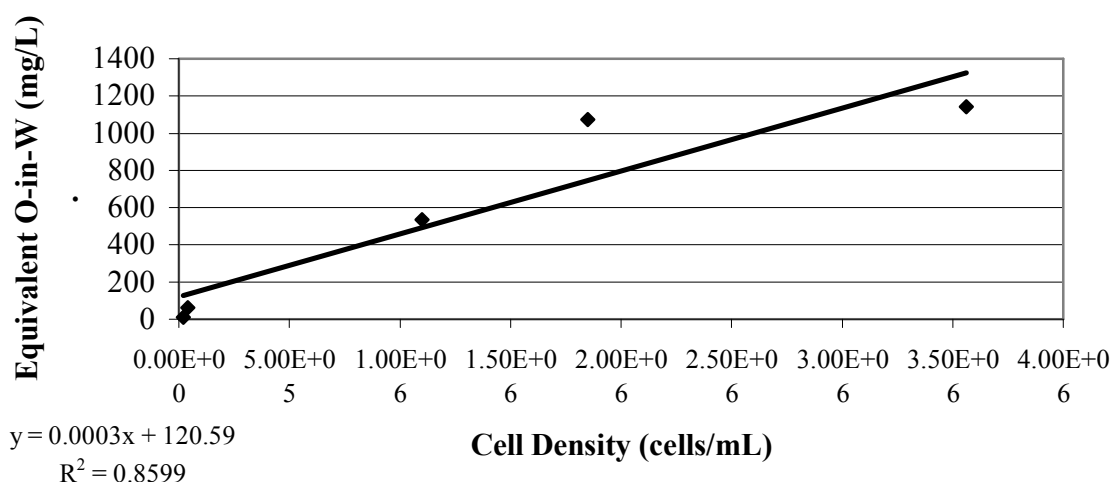


Figure 3: Hexane extraction of *R. subcapitata* at varying cell densities measured by the handheld fluorometer.

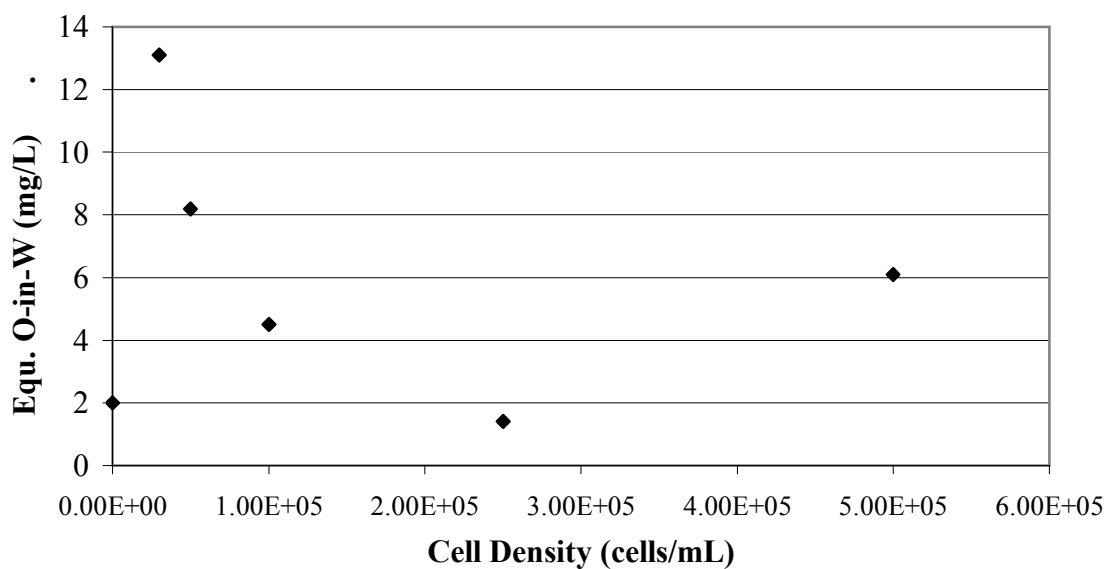


Figure 4: Hexane extraction of site water algae at varying cell densities measured by the handheld fluorometer.

Since the initial experiments to discern the reliability of the Turner Designs TD 500 for measuring oil-in-water and algae in water samples after hexane extraction did not produce predictive relationships, it was unlikely that this instrument would yield reliable results for water samples containing both oil and algae. The results from a comprehensive experiment with oil-in-water samples confounded by the presence of algae (Figure 5) illustrate that this instrument is unreliable for accurate or precise measurements of field collected samples. This is unfortunate since the “standard” method (USEPA. 1999) for analysis of oil-in- water is time and resource consuming. A rapid and simple method producing accurate and repeatable results is needed for field situations.

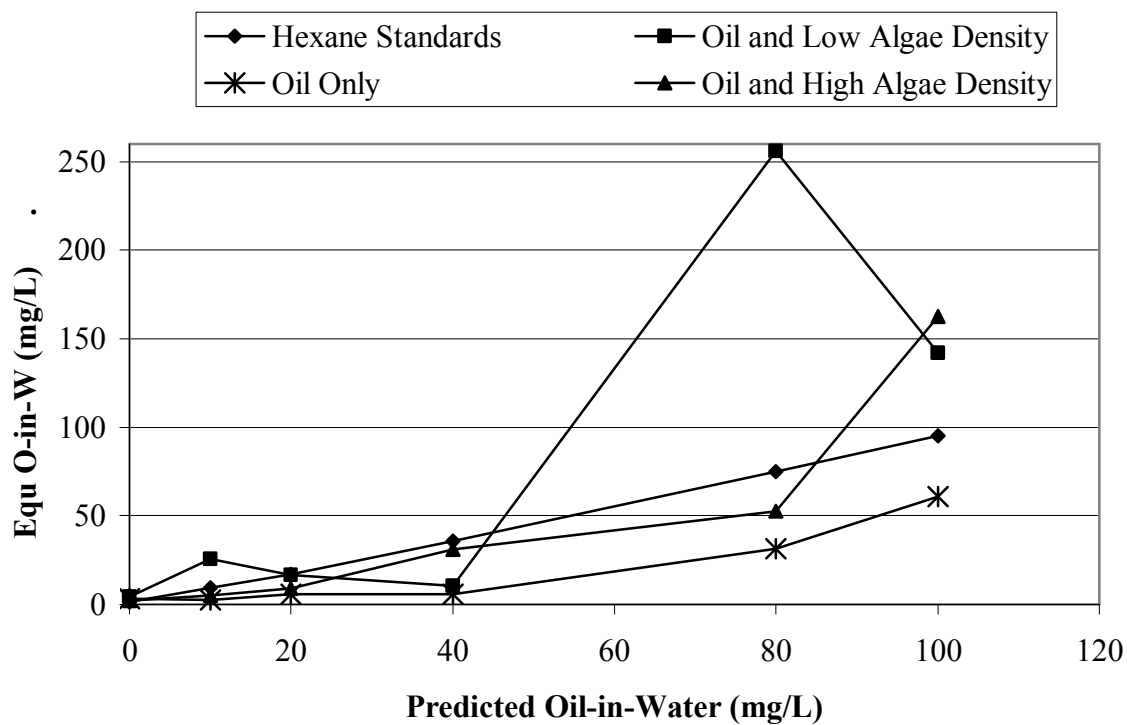


Figure 5: Standard curve (oil-in-hexane), oil-in-water extraction and extractions of two different mixtures of oil and algae in water. Oil concentrations were varied in samples containing *R. subcapitata* at a low algal density (2.8×10^5 cells/mL) and a high algal density (1.5×10^6 cells/mL).

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CHAPTER 5

SUMMARY AND CONCLUSIONS

Introduction

Natural gas storage produced waters (NGSPWs) provide several environmental challenges. These waters are produced in large volumes and vary widely in composition (Ray and Engelhardt, 1992; Veil et al., 2004). The two predominant approaches for treatment of NGSPW are costly and becoming more complex as transport and reinjection are scrutinized by regulatory agencies. A flexible and robust treatment approach is needed to manage these constituents of concern.

Constructed wetland treatment systems (CWTS) have been utilized to treat organics and inorganics independently, but this technology has not been used for NGSPW (Cronk, 1996; Hawkins et al. 1997; Lin and Mendelssohn, 1998; Knight et al. 1999; Gillespie et al. 2000; Murray-Gulde et al. 2003a; Murray-Gulde et al. 2003b).

This research addressed questions regarding performance of constructed wetland treatments systems for treatment of NGSPWs as well as measures of that performance. This research had three major objectives: (1) Thoroughly characterize natural gas storage produced waters to discern constituents of concern present in these waters; (2) Design and measure the performance of pilot-scale CWTS for treating NGSPW, and (3) Discern the contribution of algae to oil-in-water measurements using a Turner Designs TD500 oil-in-water handheld fluorometer.

This research was initiated to contribute to our knowledge of NGSPW composition, provide a possible remediation approach for these waters, and identify potential difficulties and possible solutions for measurement of oil-in-water in samples containing algae.

Chemical, physical, and risk characterization
of natural gas storage produced waters

. The purpose of this research was to thoroughly characterize produced waters to discern composition of NGSPWs and potential risks these waters may pose for receiving aquatic systems. Characterization was accomplished through: 1) reviewing published literature, 2) analysis of produced water composition records, and 3) analysis of produced water samples provided by natural gas storage companies. A risk based approach was used to identify specific constituents of concern. Constituents of concern were identified by comparing the composition (concentration) data with NPDES discharge limits and toxicity data obtained from the USEPA ECOTOX database (USEPA, 2005). Elements or compounds that were present in multiple produced water samples and that were in concentrations that posed eminent risks to *Ceriodaphnia dubia* were chosen as constituents of concern.

Performance of a pilot-scale hybrid constructed wetland treatment system for simulated natural gas storage produced waters

The purpose of this research was to assess the treatability of NGSPWs utilizing a pilot-scale hybrid CWTS. Specific objectives of this pilot-scale study were: (1) to design and construct modular pilot-scale hybrid CWTS to remove specific constituents of NGSPW and (2) to measure performance of the pilot-scale hybrid CWTS in terms of decrease of targeted constituents from inflow to outflow with concomitant decreases in toxicity.

The treatment effectiveness and performance were evaluated based upon a decrease in concentrations of constituents of concern in inflow and outflow samples as well as decline in toxicity from inflow to outflow from the pilot-scale CWTS. Concentrations of constituents of concern as well as toxicity were reduced from inflow to outflow for each of the simulated produced waters, illustrating effective removal of constituents of concern in simulated NGSPWS (Chapter 3).

The reliability of the Turner Designs TD500 oil-in-water handheld fluorometer for measurement of produced waters containing algae

Efficient and accurate oil-in-water measurements were necessary for effective evaluation of the system. Interferences from various constituents contained in mixtures such as produced waters often make accurate analytical measurements difficult. Because oil is a mixture of organic compounds, gravimetric techniques and fluorometry are often used to generically quantify oil-in-water concentrations (i.e. as a bulk measurement). The purpose of this research was to discern the contribution of algae to the fluorescence measures of oil-in-water for produced water samples. Specific objectives were: 1) to measure oil-in-water unconfounded by algae, 2) to measure the independent contribution

of algae to fluorescence in the portion of the spectrum also used for oil-in-water measurements, and 3) to discern the potential contribution of algae to false positive fluorometric measurements of oil-in-water.

Since the initial experiments to discern the reliability of the Turner Designs TD 500 for measuring oil-in-water and algae in water samples after hexane extraction did not produce predictive relationships, it was unlikely that this instrument would yield reliable results for water samples containing both oil and algae. The results from a comprehensive experiment with oil-in-water samples confounded by the presence of algae (Chapter 4: Figure 7) illustrate that this instrument is unreliable for accurate or precise measurements of field collected samples. This is unfortunate since the “standard” method, US EPA method 1664, for analysis of oil-in- water is time and resource consuming. A rapid and simple method producing accurate and repeatable results is needed for field situations.

Conclusions

Overall, this research contributed to current understanding regarding NGSPW composition, proposed CWTS as a possible remediation approach for these waters, and identified potential difficulties for measurement of oil-in-water in samples containing algae using a Turner Designs TD-500.

CWTS offer flexible and robust treatment for constituents of concern in NGSPWs. Pilot-scale studies show that constructed wetland treatment systems are effective in the mitigation of risks in simulated NGSPWs, in reducing concentrations of constituents of concern and reducing toxicity to *C. dubia*. Data obtained from this pilot-scale study can be used for design parameters for future demonstration and field-scale CWTS.

The results from a comprehensive experiment with oil-in-water samples confounded by the presence of algae illustrate that the Turner Designs TD-500 is unreliable for accurate or precise measurements of field collected samples. This is unfortunate since the “standard” method is time and resource consuming. A rapid and simple method producing accurate and repeatable results is needed for field situations.

Two chapters in this thesis will be submitted for publication in peer-reviewed journals. Chapter 2 contains a comprehensive review of gas storage produced water composition and potential constituents of concern for remediation and will be submitted to *Air, Water, and Soil Pollution*. Chapter 3 focuses on performance of pilot-scale hybrid CWTS for treating targeted constituents in simulated NGSPWs and will be submitted to *Environmental Geoscience*. Chapter 4 identifies difficulty in measurement of oil-in-water using a handheld fluorometer and may be submitted to the *Bulletin of Environmental Contamination and Toxicology*.

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