Recycling Produced Water in the Permian Basin

by

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Executive Summary

The rapid increase of oil exploration through hydraulic fracturing in the Permian Basin in western Texas is associated with production of large volume of wastewater containing potentially hazard chemicals. The wastewater is derived from water that is co-extracted with oil called "produced water." The management and disposal of the wastewater generated from unconventional oil and gas exploration are the most challenging topics given their low quality and potential environmental and human health risks. Unconventional oil wastewater is even more critical in western Texas where the water availability is limited. Oil wastewater in Western Texas is injected through deep-injection wells to the subsurface as a common disposal practice. Yet local companies are seeking to find ways to recycle oil wastewater for reuse for hydraulic fracturing or possibly other beneficial use.

This Master Project investigates the water quality of produced waters generated from the unconventional oil exploration in the Permian Basin and the treated water generate from a treatment site. As part of this study 15 water samples were collected at the Chiltepin Recycling Plant in Pecos, Texas, prior and after treatment that involved temporary storage of the oil wastewater in open reservoir that is managed with a continuous treatment of aeration to the pit. Water samples were analyzed at Vengosh Lab in Duke University for major elements and dissolved organic carbon (DOC). The data show that the Permian produced water is highly saline (chloride up to 27,000 mg/L, 1.4 time the salinity of seawater) with high concentrations of ammonium (175 mg/L), boron (50 mg/L), and DOC (220 mg/L). This water quality infers that disposal or leaking of the Permian wastewater to the environment would cause major damage to the ecological system and contamination of water resources. The data show that the water quality

of the treated water is indistinguishable that untreated and thus the recycling process in the site does not reduce the salts and contaminants potential of the Permian produced water.

1. Introduction

Working with Select Energy Services (SES), a water service company operating in the oil and gas industry, this Master's Project collects and analyzes samples of produced water from the Permian Basin in west Texas. The Permian Basin is a large shale play located in west Texas and New Mexico that is home to a surge of recent activity in unconventional oil exploration through hydraulic fracturing (Scanlon *et al.*, 2017). The basin is one of the largest active shale plays in the U.S. and has numerous reservoirs that are now more easily accessible through advances in hydraulic fracturing (Norris *et al.*, 2016). However, there is limited public information about the composition of wastewater generated in the Permian Basin.

To fill this knowledge gap, samples of Permian Basin produced water were collected and analyzed with the objectives of: 1) characterizing Permian Basin produced water, and 2) to provide feedback to SES on the performance of the treatment process at their recycling project in Chiltepin Recycling Plant. The SES recycling plant was built at a private salt water disposal (SWD) site. This infrastructure contains, two gun-barrel tanks, a battery (collection of tanks) for treatment and an additional tank to support the disposal at a SWD. The plant, Chiltepin, was constructed on a set containment footprint in congruence with the existing infrastructure that provides the initial first step of physical separation. The plant was constructed to treat produced water for reuse for new hydraulically fractured wells, as it can be sold at a lower price than freshwater and save on disposal costs. It is with this intention that the technology is vetted, but not clear conclusion of treatment capability can be determined without testing samples with potential methods identified. In this project, the primary evaluation for treatment was to determine the change in composition of the treated produced water. Currently, the recycling plant is not operated.

Produced water samples were collected and analyzed before and after treatment at the plant in order to characterize the chemistry and determine the treatment effectiveness in the plant and the ability to remove chemical constituents from the produced water. The produced water samples from the plant come from six different wells in the region and proxy for composition of other produced waters in the region. The purpose of the Chiltepin plant is to alter the produced water to a composition that would be able to be used as an efficient replacement to fresh water applied for hydraulic fracturing.

The major treatment objective of SES in the Chiltepin site is to convert the anoxic produced water into oxic water. Therefore, the daily parameter required for satisfactory treatment was to have an oxidized produced water or an oxygen reduction potential (ORP) greater than one hundred mV.

The incentive in “recycling” for the operator is that excess treated produced water could be sold for reuse as well as the saved money from disposal costs. In this setting, larger scale recycling projects would ideally limit the amount of treatment needed for reuse. This is ideal as the region is already stressed for fresh water (Kondash *et al.*, 2018), driving up the price of both fresh water and its alternatives, for the increased water footprint for hydraulic fracturing (Kondash *et al.*, 2017). The other pricing incentive for operators is the saved cost in disposal of produced water. In order to facilitate recycling, we first characterize representative produced water then examine the efficacy of treatment of the water from the Chiltepin plant.

1.2. Background on the Permian Basin

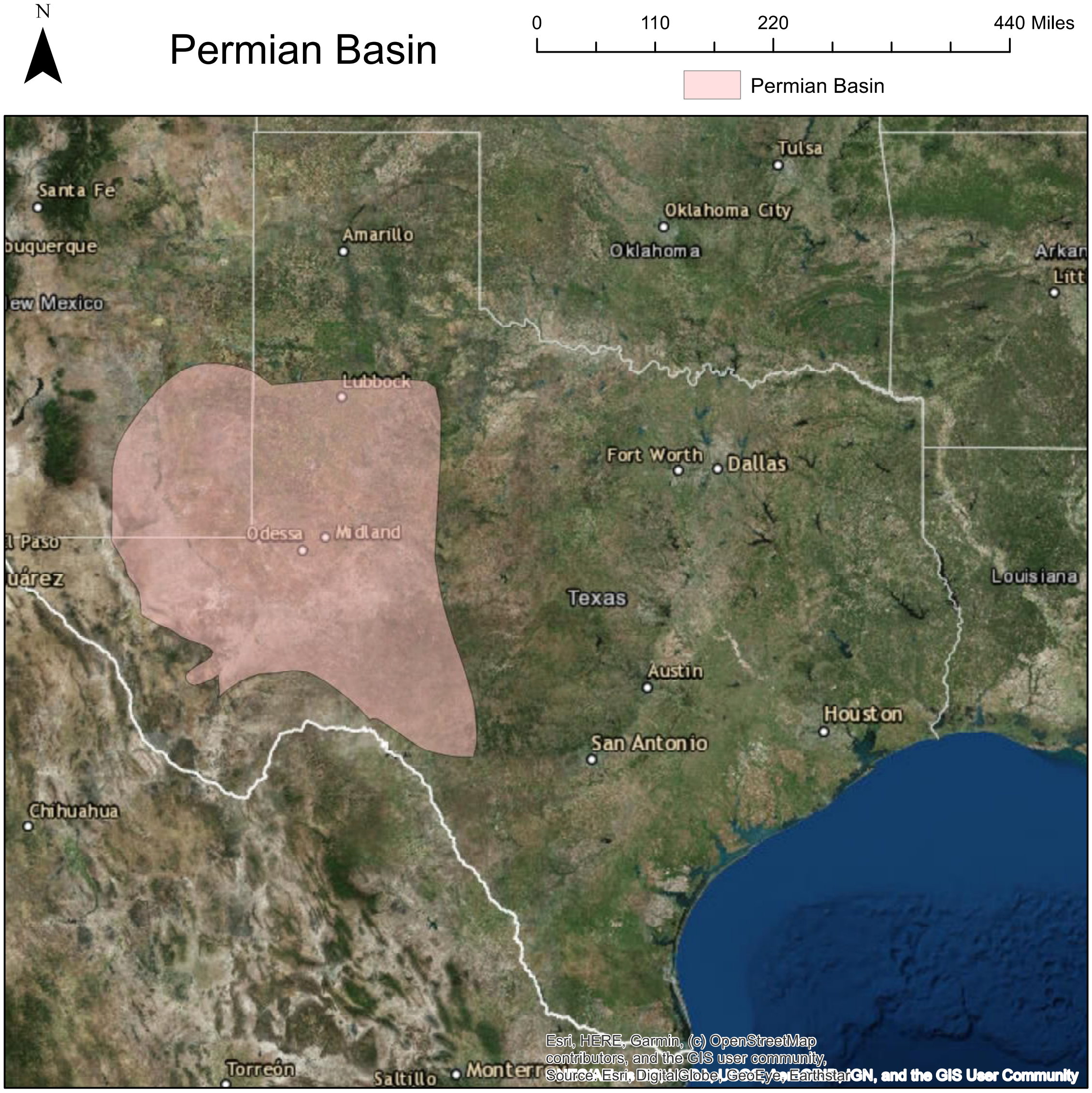

Figure 1. Map of Chiltepin and Nearest Roads and Cities to Site Location.

The United States is the first country to widely exploit shale-plays for economic production of unconventional oil and natural gas. Of particular importance is the Permian Basin due to its vast size of available reservoirs in the form of oil and gas. The basin has been producing oil and gas conventionally since 1925, but due to advances in hydraulic fracturing and horizontal drilling this has allowed for a significant increase in drilling activity (Kondash *et al.,* 2017). The Permian Basin spans both New Mexico and western Texas and consists of 3 smaller basins (Val Verde, Midland, and Delaware), arches, and other trapping structures (Baumgardner *et al,* 2016). The basin spans from two-hundred fifty miles three-hundred-mile (Figure 1). Although named for its more productive conventional geologic layer, Permian, the regions interbedded silt and clay units known as shale plays, have the largest unconventional resource, estimated to produce 3.4 x 10^9 barrels of oil (Baumgardner *et al.,* 2016).

This unconventional activity is primarily located in the Midland Basin and the Delaware Basin, where the Chiltepin site is located. The larger geologic structures made conventional oil and gas attainable in the area and limited primarily by structure amongst the geologic unit, while these shale plays, which are significantly larger in thickness are located in the Midland and Delaware Basins. The separation between the two basins is a tectonically uplifted platform of basement rock, Central Basin Platform, that was unique in its ability to trap oil for conventional purposes. Surrounding this uplifted basin are significant shale plays that in one formation in the Midland Basin, east of the Delaware Basin, the Wolfcamp Shale is estimated to produce roughly 75 x 10 barrels of oil equivalent (Scanlon *et al.,* 2017).

This unconventional extraction of hydraulic fracturing uses high amounts of pressure and liquid to exploit weaknesses between the interstitial sediments comprising the unit, such as silt, shale. The liquid used in this process is typically a water with some combination of sand or chemicals or both to further assist at expanding existing cracks, creating new connectivity to reserves or improving the overall production of an existing well. In order to achieve greater production and permeability the water footprint associated with unconventional extraction has also increased (Kondash *et al.,* 2017).

The wells providing produced water for Chiltepin are located within the western lobe of the Permian basin, with the closest town being Pecos, Texas to the north (20 miles), and larger cities of Midland/Odessa, Texas to the east-northeast and Carlsbad, New Mexico to the west-northwest directions. Delaware Basin and the Central Basin Platform. Both contain oil and natural gas reserves and share a similar depositional history of marine deposition leaving siltstone, sandstone as well an evaporite formations serve as an excellent sealant for conventional extraction (Scanlon *et al.*, 2017).

The Chiltepin recycling plant site is located in the Delaware Basin overall extraction and production of crude oil is increasing as seen by the yearly rate in Reeves County, Texas (Figure 2). This is also indicative of the rise in unconventional extraction, as this corresponds with the advances in hydraulic fracturing and horizontal drilling (Scanlon *et al.*, 2017; Kondash *et al.*, 2017). This increase in activity is echoed by a 19% production increase from January 2018 compared to the following year. Reeves County ranks fourth in oil production out of two hundred and fifty-four

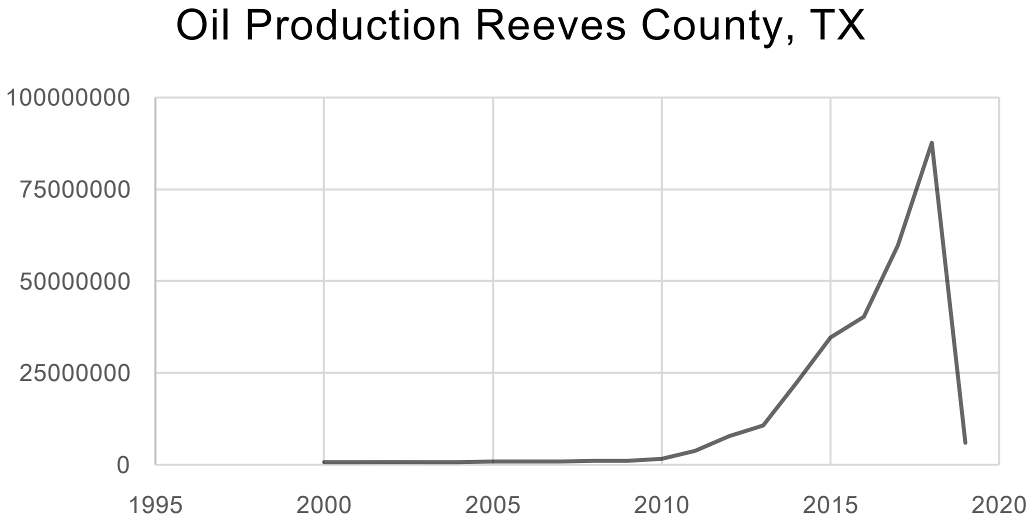

Figure 2. Oil Production in Barrels of Crude Oil from Reeves County, Texas (Texas Drilling, WWW)

counties in the entire state of Texas, at over 5,940,407 barrels (or 16% of the Monthly total for all of Texas occurring from this county within the Permian) (Railroad Commission of Texas, WWW).

1.3. Advances in Horizontal Drilling and Increase Demand on Water

Advances in both methods of access to reservoirs, what is considered accessible and viable as well as advances in horizontal drilling efforts allow for previously un-accessible oil and gas reservoirs in shale formations. These advances have had a significant impact on the amount of product being produced for each well. However, with these advances comes an increase in water demand associated with the production of each well (Kondash *et al.,* 2017).

This is a difficult problem in areas of water-stress, such as the Permian Basin (Freyman, 2014; Scanlon *et al.*, 2017; Wilson, 2015), as the amount of water needed for one well is estimated between 10,693 and 92,460 barrels of water, or 449,106 – 3,883,320 gallons of water needed per well (Kondash *et al.,* 2017). The water is often supplied utilizing pre-exisiting geographic features such as running rivers or lakes and ponds. However, in regions of water-stress that is not an option and it is more common to utilize temporary structures such as above ground storage tank (AST) or mobile water trucks, often filled externally by buying treated water directly from water treatment plants in the region. All of these variations can greatly impact the operating and disposal expenses associated with a new well. This further justifies the investment into recycling projects as a way to reduce the amount of freshwater needed for new wells, while reducing the volume of produced water needing to be managed.

2. Select Energy Services and Chiltepin Recycling Plant

Select Energy Services

Select Energy Services (SES) is a service company in the oil and gas industry that specializes in Water Solutions. The name reflects the varying services SES can provide for water in its' various forms from production to disposal, this include but is not limited to, water sourcing, water transport (permanent or temporary), containment of fluids (on or offsite), well testing, handling of flowback and produced formation water, transportation and recycling or disposal of drilling, and completion and production fluids (Select Energy Services, WWW). The newly formed engineered water solutions group is responsible for creating the Chiltepin site. The plant was designed with the intent of utilizing the pre-existing infrastructure associated with the clients SWD. The entire plant from conception, bid, to construction and launch occurred in approximately one-month time. This is a contributing factor as to why SES was willing to have a third party collect and evaluate samples from the Chiltepin site. As a product of this master's project SES hopes to gain better understanding of how to evolve their known treatment methods into appropriate methods of "recycling" produced water, based on the samples captured at Chiltepin.

Chiltepin Recycling Plant

The path of water as it pertains to this project, begins when produced water is distributed by the operator owned mid-stream facility to the plant (Figure 3). Produced water arrives at the Chiltepin site (Figure 4). Before beginning the "recycling" process, untreated produced water samples are captured. Once produced water enters the tank infrastructure. It undergoes physical separation through operator provided infrastructure. This is the initial step of treatment taken to provide systematic physical separation from flowing through the two gun-barrel tanks and subsequent series of six tanks referred to as a battery. After exiting the battery, Select Energy Services treatment interventions begin. The second step is to add an oxidizing chemical, hydrogen peroxide, to the produced water.

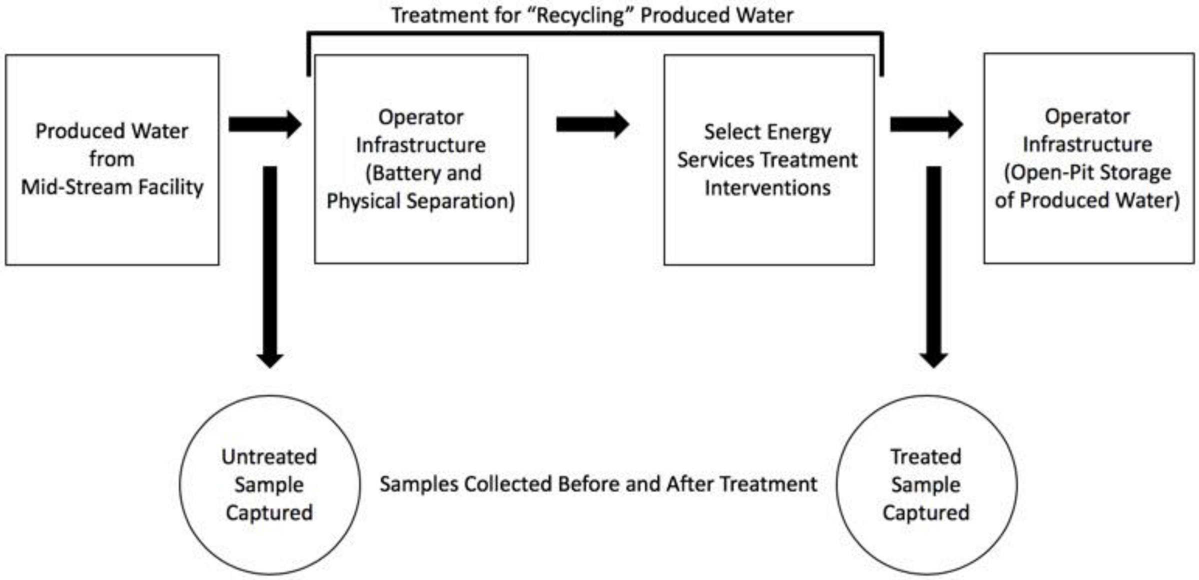

Figure 3. Flow-Diagram of Recycling Operation at Chiltepin -

In order to increase the residence time of step two a settling tank is provided. The third step in treatment for produced water is entering the gas flotation unit, (GFU). The GFU provides a three-weir series tank that provides compressed air in the form of bubbles to float out unwanted particulates from the produced water and be skimmed out. Particulates that are removed are re-entered into step two, while allowing the rest of produced water to continue to its final step of filtration. The filtration step is accomplished through a series of sock filters.

Figure 4. Chiltepin Recycling Plant, Pecos, Texas. Foreground is Select Energy Services Treatment Interventions from left to right, settling tanks, gas flotation unit, and filtration. Background from left to right tank battery, gun barrels and additional tank associated with disposal at SWD.

The initial step taken by SES was to add an oxidizer to the produced water. This was a common practice in many treatment projects that directly reused produced water for hydraulic fracturing as well as meeting the ORP parameter set by the company. Due to the pricing points of oxidizing chemicals SES tested and put forth in original bid, the oxidizer chosen by the client, was was hydrogen peroxide. The dosing of the hydrogen peroxide was set to match the produced water exiting the battery and for the purpose of this project that ratio is considered constant. In order to prolong residence and reaction time before the next step a settling tank with storage of 500 barrels is used. The tank is elevated to allow for gravity flow of produced water instead of utilizing additional pumps.

The secondary step taken was to incorporate the use of a GFU. This method is proven efficient by off-shore service companies, such as the one who aided with design of plant and provided the inaugural unit and has gained in popularity. This unit uses compressed air from atmosphere and adds bubbles to sequential weirs to float out contaminants (Environmental Protection Agency, 2013).

The final step at Chiltepin is to use a filtration system on the produced water. The filtration system utilized sock filters of varying micron sizes to filter out larger particulates in series (100 to 50).

Produced water that does not make it through the entirety of the plant is cycled back into the plant or is sent directly to a degradation tank for disposal. If produced water makes it through the entire plant, it is then stored in an open pit where it can be re-used for industrial applications or most likely for hydraulic fracturing.

2. Samples and Methodology

Samples

The samples from Chiltepin site were collected over a ten-day period time that provided six complete sets of untreated and treated produced water. Two additional samples (A and B) were collected from the mid-stream station in an attempt to capture any noticeable chemical difference between previously recycled produced water and initial produced water at Chiltepin. The first sample (A), captures produced water from the mid-stream facility and is compositionally no different than the six samples from Chiltepin. This same composition in water was re-used and the returning produced water is captured in sample B.

All eight samples were obtained following both site specific and U.S. Geological Survey (USGS) sampling protocols (USGS, 2011). Field measurements were taken when samples were taken for temperature, pH, and specific conductivity. Some samples required filtration for dissolved anions, and this was done in the field through 0.45μm. The samples were sent to Duke University for processing.

Methodology

The three machines utilized for compositional data were the, inductively coupled plasma mass spectrometry (ICP-MS), an ion chromatography (IC) and alkalinity measurements to determine the dissolved inorganic carbon (DIC) content through titrations. The ICP-MS was calibrated to the NIST 1643e standard and to determine element concentration based on the atomic mass. The IC, Dionex IC DX-2100, and determines the major cations within the compositions of the produced water. Nitrate was analyzed via QuickChem Method 10-107-04-2-D (Nitrate / Nitrite in Waters by Hydrazine Reduction) (Warner *et al.*, 2014; Coyte *et al.*, 2018).

3. Results

Table 1 presents the summarized t concentrations of the samples investigated in this MP including produced water entering the Chiltepin site (untreated) and after the site (treated).

Table 1. Comparison of Concentrations Present in Untreated and Treated Water from Chiltepin Recycling Plant. All concentrations are in ppm, with boron (B) in ppb.

	Untreated			Treated			Change (%)
	Average	min	max	Average	min	max	Average
Cl	26720	25343	28522	26679	25995	27319	-0.15
Br	166	148	193	172	162	199	3.43
SO4	734	668	799	733	681	772	-0.12
Ca	739	697	812	759	719	807	2.70
Na	15480	14105	16238	15143	10872	16385	-2.18
K	166	148	175	164	156	169	-1.58
Mg	141	107	174	136	111	173	-3.62
NH4	178	166	192	178	168	186	-0.06
B (ppb)	44755	41765	47489	44296	42658	47589	-1.03
DOC	221	171	356	260	220	318	17.80

The results show that the Permian produced water is highly saline (chloride is 1.4 times the salinity of seawater), with high concentrations of Na, B, ammonium, and DOC (Table 1). This type of water could pose environmental and human health risks and contaminatioin of water resources upon released to the environment. The high salinity, B, ammonium, and DOC prevents using this water for beneficial use (e.g., agriculture, dust suppression) without adaquate treatment and removal of these constituents.

Although this is a limited sample size of the produced water coming out of the Permian Basin, the results still provide a preliminary evaluation of the chemistry of the produced water from the Permian Basin before and after treatment. The indication that recycling is working is evident in a lower concentration in constitute from untreated to treated. This is indicated by the Change (%) column found in Table 1.

The differences between the average values of the treated versus untreated produced water for the different chemical constituents were typically below 5%, which represent the analytical error. The only exception is the DOC with higher values in the treated water, which could also reflect analytical noise. Therefore, the data show that the treatment through oxidation that is conducted at Chiltepin site has zero effect on the water chemistry and quality.

The distribution in fluctuating produced water composition can be exhibited by Figure 5, and indicates the information displayed in Table 1. The red line represents no effect between treated and untreated samples, with data that falls above this line represents enrichment of the constituents after treatment. Those constituents with data below the line indicate reduction in their concentrations.

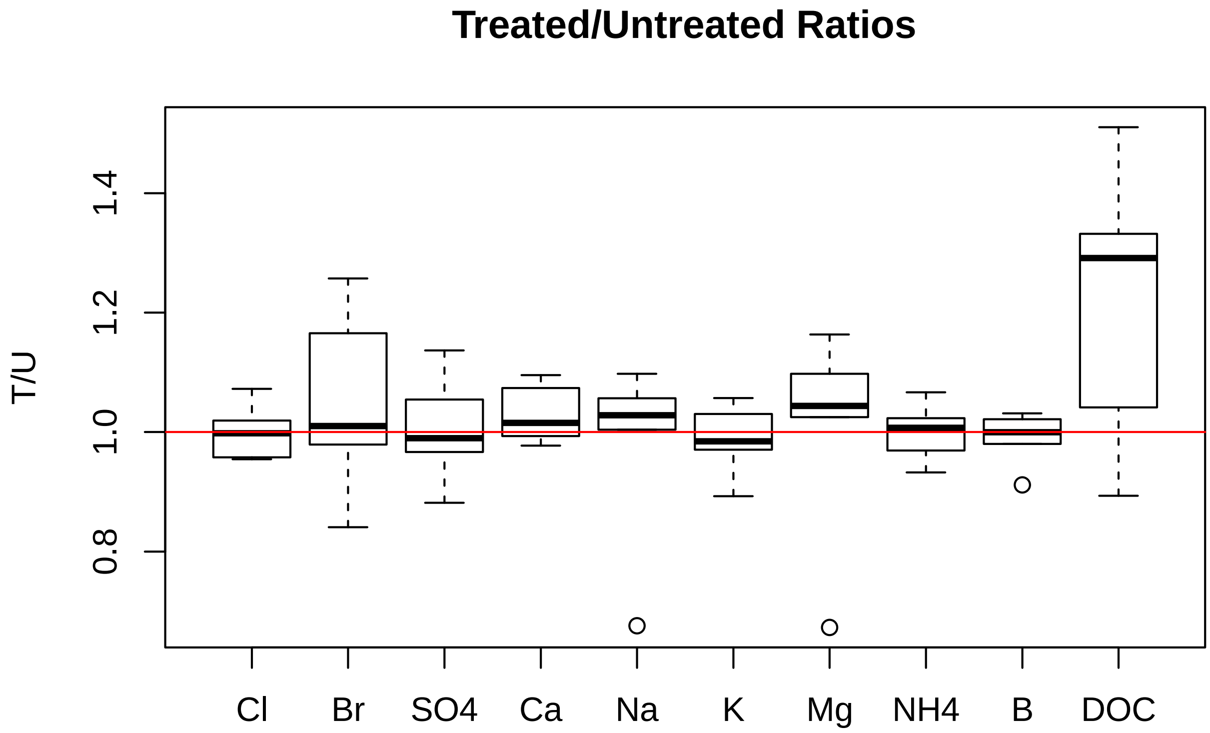

Figure 5. Treated vs. Untreated Ratios of Samples

3.1. *Additional Information from A to B*

The results between A, before Chiltepin, and B, round-trip back to Chiltepin are displayed. In most cases the differences were negligible and within the analytical error. The only exceptions are Ca and DOC (Table 2 & Figure 6). Given that this is based on only two samples, it is hard to evaluate if this is an analytical error or different water sources that were supplied to the plant.

	A	B	Difference %
Cl	26743	25526	-4.55
Br	161	155	-3.48
SO4	802	679	-15.31
Ca	129	635	393.48
Na	16376	14131	-13.71
K	166	160	-3.17
Mg	150	129	-13.95
NH4	178	173	-2.89
B (ppb)	48116	50021	3.96
DOC	194	218	12.49

Table 2. Comparison of Concentrations Present in Untreated and Treated Water from Chiltepin Recycling Plant.

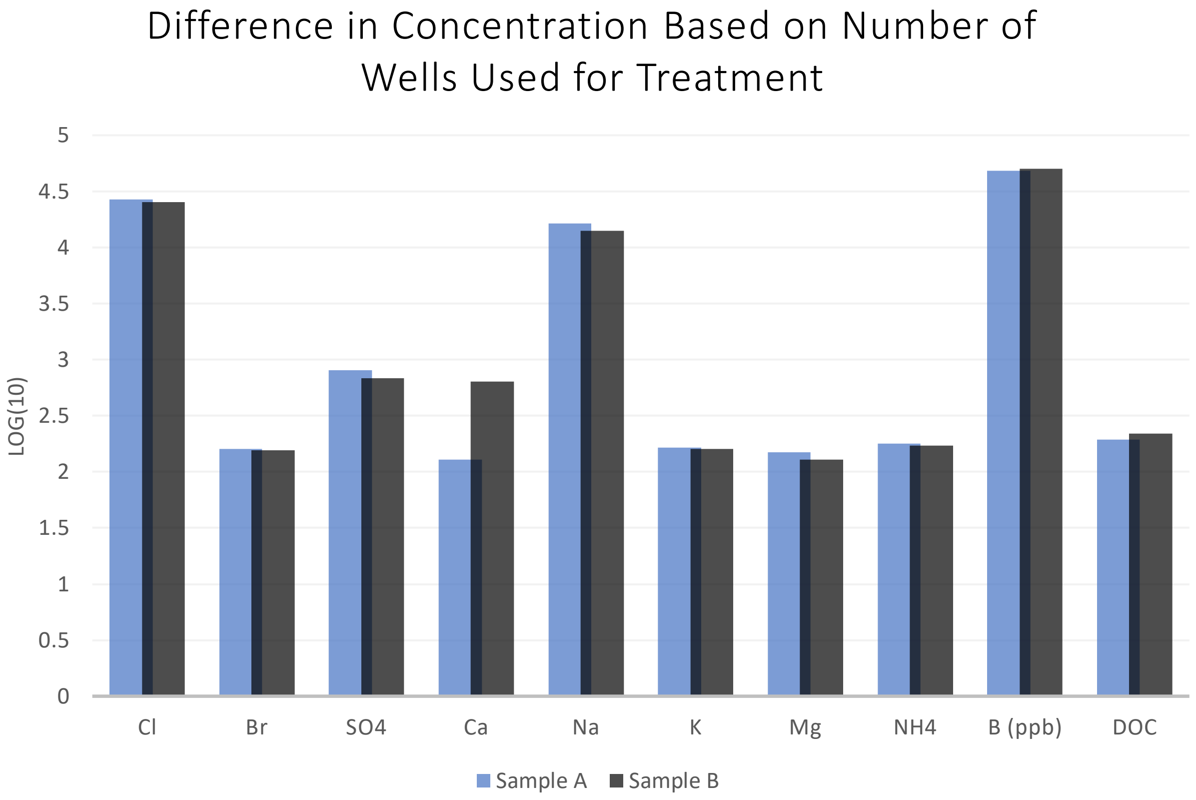

Figure 6. Comparison of Concentrations (Log Transformed) from Produced Water provided from A and B – Mid-Stream Facility; Sent back to Chiltepin.

4. Conclusion

Although limited in scope this change in concentrations of constituents across reuse life-span should be further explored with additional samples and analysis. This could provide a potential framework for what the largest concentrations would be for when additional wells are added and be factored into future treatment protocols. More samples must be collected for a larger study in order to prove larger overall trends and causation between the discrepancies in concentrations of constituents.

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Throughout the summer of 2018, I was able to utilize my background and current concentration in water resources management by assisting in water sourcing for drilling activity, water and produced water transfer, as well as treatment methods for a national oil and gas service company, Select Energy Services (SES). This required working knowledge of different shale and oil plays in Oklahoma, Texas, and New Mexico. In addition to the applications aforementioned a large component of this internship were assisting in the launch of a first-generation recycling plant, Chiltepin, that is owned and operated by SES and leased to a client, operator, at their private SWD location.

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Figure 6. Select Energy Services Chemist Cindy Peña and Intern Carly Osborne Standing on Gas Flotation Unit (GFU) at Chiltepin Recycling Plant. Photo taken May 26th 2018 0100.