

DISSERTATION

SOIL DEGRADATION AND WATER SCARCITY: THE IMPORTANCE OF SOIL
ORGANIC MATTER AND REUSE OF NON-TRADITIONAL WATER SOURCES WITHIN
AGRICULTURAL SYSTEMS

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ABSTRACT

SOIL DEGRADATION AND WATER SCARCITY: THE IMPORTANCE OF SOIL ORGANIC MATTER AND REUSE OF NON-TRADITIONAL WATER SOURCES WITHIN AGRICULTURAL SYSTEMS

Our exponentially growing world will demand approximately 70% more agriculture production by 2050, yet according to the Food & Agriculture Organization of the UN, ~33% of land worldwide is experiencing soil degradation and by 2050, over 90% of soils could be degraded. Exacerbating problems with soil degradation are droughts that are becoming more common with a warming climate. According to the National Oceanic and Atmospheric Administration, ~60% of the USA experienced drought in 2022 and over 90% of the Western US is under drought conditions, including one of the largest agricultural regions in the world, California. Therefore, in order to address these urgent issues of soil degradation and water scarcity, agriculture needs to adapt to more sustainable management practices that emphasize the importance of maintaining soil health, specifically, soil organic matter (SOM), and implement treatment processes to utilize non-traditional water sources (i.e., wastewater from various sectors). This dissertation is a combination of two different research projects that focus on these topics. Two chapters are focused on soil degradation in agriculture in collaboration with an industry partner, Cutrale Citrus, and two chapters are focused on the reuse/treatment of non-traditional water sources in collaboration with the Department of Energy's National Alliance for Water Innovation (NAWI).

Our scope within the NAWI project was to develop a baseline paper (i.e., a review) for this concept within agriculture, specifically the reuse of agricultural wastewater and the treatment of

produced water (PW) for use as irrigation water. Since agricultural water quality has large regional variability, we focused on two agricultural regions, the Midwest and California. The Midwest has runoff primarily contaminated with nutrients that lead to eutrophication in the major water bodies of this region, while California has saline runoff that in some cases is too toxic to be released to the environment. California's agricultural runoff requires advanced treatment techniques while the Midwest could use existing tile drainage systems to capture runoff and re-apply it to cropland since the main contaminants are nutrients. The reuse of PW is more complicated since its often highly saline and contains other toxic organic compounds or metals. Kern County, CA has been reusing PW for over 20 years but only because their PW has low salinity, this allows them to implement low-cost treatments focused on dilution, but this reuse has been controversial. Our analysis showed there are many unknowns related to the toxicity of PW, so we also develop a path forward through the implementation of an "Adverse Outcomes Pathway" approach that could be utilized to minimize any risks associated with the reuse of this water for irrigation.

The research focused on soil health utilizes soil from a citrus grove in SW Florida managed by Cutrale Citrus. The first study focused on why tree size varied between areas of the grove with identical management practices and trees of the same age. Based on these observations it was clear that soil health varied between these areas, so we endeavored to understand what components of the soil, including both physiochemical parameters and biological indicators, were showing significant differences between the productivity regions. The results showed that SOM concentrations, enzyme activity, and microbial diversity were the components of the soil that were significantly different between these areas. Additionally, these trees were all infected with Citrus Greening disease, so we developed a hypothesis based on how this phloem-limiting infection could also be impacting soil health or conversely, how soil health could impact the progression of this

disease. Based on these results, the second study focused on how we could regenerate the SOM in this soil and improve soil health through the addition of different organic amendments (biochar and compost). A 400-day greenhouse study was conducted to look at changes to the SOM; we combined typical soil science analysis of SOM such as concentration and mineralization rate with molecular level analysis using high-resolution mass spectrometry (FT-ICR MS). Analysis of microbial diversity was also conducted but those results will not be finished in time to be included in the dissertation and will be included only in the published paper. The soils showed clear differences in molecular composition at both the start and finish of the study depending on which amendment was added. Overall, the compost soil showed an initial spike in activity followed by degradation and loss from the system while the biochar showed slower increases in activity and more stability in the soil. The molecular analysis clearly showed the shift of compost towards more oxygenated molecules and a decrease in the number of different chemical formula present, while the biochar soils had transformation occurring without much loss and contained molecules that were more reduced. Overall, this study showed how biochar is an effective amendment when considering the long-term impacts that one application could have compared to compost which has greater stimulation of the soil in the short term but quickly degrades and needs to be reapplied frequently.

When considering the issues facing agriculture in the 21st century it is important to take an all-inclusive approach because agriculture is comprised of interconnected systems. For example, if soil health and SOM are not properly considered then that soil might have less ability to store and absorb water so more erosion or nutrient leaching might occur. Or conversely, if water of poor quality is applied to a field, then salts could build up and degrade the soil. However, if we continue to have devastating droughts in the Western US then we might need to consider reusing alternative

water sources to irrigate our fields and we should begin to prepare for that possibility as our high-quality freshwater supplies dwindle.

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CHAPTER 1: INTRODUCTION

Agricultural soil degradation and increasing scarcity of freshwater are urgent global issues since an exponentially growing world population will demand approximately 70% more agriculture production by 2050 [1]. Yet at the same time ~33% of land worldwide is experiencing soil degradation and by 2050, over 90% of soils could be degraded [3] while simultaneously three quarters of the world population may be impacted by droughts [4]. Currently, 2.3 billion people are experiencing water scarcity and since 2000, the number and length of droughts has increased by 29% and caused economic losses over \$100 billion [4]. To help address these problems, this dissertation will investigate the potential of using alternative water sources for irrigation in anticipation of a warming world leading to less freshwater availability. In addition, this dissertation will discuss why soil organic matter (SOM) is an important aspect of an agricultural soil system and explore high-resolution analytical techniques that can elucidate molecular differences in how SOM changes over time. Understanding these aspects of SOM will highlight the importance in maintaining adequate SOM concentrations in these systems and explore the potential of using different management practices that can minimize soil degradation by understanding the molecular changes that SOM can undergo in response to the addition of different types of organic amendments.

Every year arable lands lose 75 billion tonnes of soil to erosion, which is an estimated financial loss of over \$400 billion [5]. However, erosion is only one type of physical soil degradation (other examples include compaction or desertification) and soils can also degrade via chemical (acidification or salinization), biological (soil organic carbon (SOC) depletion or biodiversity loss), or ecological changes (a combination of the aforementioned degradation processes) [1]. Unfortunately, the intensification of agriculture to meet the world's growing food

demand is also increasing soil degradation because existing agricultural practices are unsustainable. Historical management practices such as intensive tillage, heavy pesticide application, and over application of inorganic fertilizers have led to loss of SOC/soil organic matter (SOM), reduced soil biodiversity, and acidification [6]. To ensure the viability of agricultural soil with the growing demand for food, changes to these management practices are essential. This can be accomplished through a variety of sustainable practices such as reduced tillage [7] or use of cover crops [8], but if sustainable management practices were to focus on improving one component of a degraded soil it would be SOM concentrations because of its influence on many aspects of soil health [9, 10].

When comparing soils with different levels of erosion/degradation, SOM concentration is the strongest indicator of soil health while other predictors of soil quality such as available soil water, microaggregates, or enzyme activity are also heavily influenced by SOM concentrations [11]. Maintaining adequate levels of SOM is essential because of its influence on physical properties such as soil structure (i.e., soil aggregation), water retention, or cation exchange capacity (CEC), while also influencing soil biodiversity and related factors such as enzyme activity. SOM affects the physical properties of soil primarily through its impact on the stability of the soil aggregates which then influences other aspects of the soil such as increased water holding capacity or porosity [9]. Aggregate stability is highly influenced by SOM, especially when SOM concentration is low (2%) compared to soils with higher concentrations of SOM [12]. This stability is important because there is a positive correlation between aggregate stability and microbial biomass, plus the increased stability also has a positive impact on soil carbon cycling [13]. SOM affects the chemical properties of the soil through improved CEC since many of the organic compounds found in SOM contain numerous phenolic and carboxyl functional groups,

anionic groups that can bind the various cations in the soil and act as a buffer to minimize pH shifts [14]. Despite the significant impact that SOM has on the physical, chemical, and biotic properties of the soil, causalities between the concentration of SOM and crop yield are difficult to elucidate [15]. Correlations between these factors exist, but they are more prominent in soils with less than 2% soil organic carbon (SOC), or approximately 3.5% SOM. This was highlighted in a global meta-analysis that found increases in crop yield occurred with increases in SOC but this effect leveled off at around 2% SOC [16]. Others have proposed that 2% SOM (1.15% SOC) is a critical value at which significant impairments occur in the soil system but altogether there is contradictory evidence rebutting a specific threshold value since every soil system has unique characteristics and ecosystem services that would impact this value [17]. Overall, SOM is a vital part of the larger concept of soil health and understanding the impact that SOM has on soil health, and more specifically crop productivity, is the objective of Chapter 2.

In this first dissertation chapter we discuss how soil health is an important aspect for maintaining adequate crop production in agricultural systems, but the specifics of what entails a healthy soil can vary from region to region and crop to crop. In highly managed agricultural systems, unhealthy soil can be masked by intensive management practices, yet there must be detrimental cutoff points in various characteristics, such as soil organic matter (SOM) concentrations, where even highly managed systems start to lose productivity. This negative impact was observed in a Florida citrus grove containing Valencia orange trees with observable differences in tree size yet were otherwise managed identically. A soil health index demonstrated that the areas with smaller trees had a significantly lower index score and those soils contained significantly less SOM (average SOM = 0.57%) compared to areas with larger trees (average SOM = 0.94%). The areas of lower crop productivity also had less enzymatic activity of common carbon-

cycling enzymes and different microbial populations, which all together negatively affected soil health and corresponding plant productivity (Figure 1.1). This agricultural region is also known to have a Citrus Greening disease (HLB) infection rate of close to 100%, hence we developed a hypothesis that could explain how progression of this infection could be impacted by SOM concentrations and differences in microbial diversity. We posit that areas of this grove with healthier soil could have more resistance to the onset of fatal HLB symptoms. Consequently, soil organic matter distribution and concentration should be considered when establishing new groves in order to optimize soil and crop productivity. This paper was published in Soil and Environmental Health [2].



Figure 1.1 - Graphical abstract from Chapter 2 demonstrating the impact that differences in soil health can have on crop productivity [2]

Based on the results from Chapter 2, we endeavor in Chapter 3 to elucidate a more molecular level understanding of SOM stability in these soil systems because maintaining as much SOM as possible is vital for proper soil health and regenerating SOM in the depleted areas of this grove is essential. The use of organic amendments (i.e., compost, biochar, or cover crops) to

increase SOM concentrations is common practice in agriculture because of their potential to supply organic compounds and nutrients to the soil that can stimulate microbial activity and improve plant productivity [18].

The use of compost, organic material partially degraded in an aerobic environment, is a common management practice because of the many benefits it provides to the soil. The increased organic matter concentrations from compost helps maintain the soil pore structure of these amended soils, this is vital since this pore system is important to water movement/solute transport and can be reduced in compacted/degraded soils thus leading to increased erosion rates due to reduced percolation through the soil [19]. Compost does have some compositional variability since it can have varying proportions of labile and recalcitrant organic molecules depending on the feed material (labile fraction = 25 - 65%) [20]. This is important in regard to its mean residence time in the soil since over the course of the growing season the labile portion is completely mineralized and utilized by the microbiome for energy, while the more recalcitrant fraction is sequestered into the soil during that growing season [20], consequently compost is typically applied on a yearly basis if economically feasible.

Biochar as a soil amendment is different than compost because of the larger proportion of recalcitrant carbon structures that are created during pyrolysis of the organic feedstock used in biochar synthesis. The majority of the organic carbon in biochar is considered resistant to degradation in the soil environment and can remain in soil for hundreds of years [21]. However, the physiochemical properties of biochar that impact degradation rate, nutrient retention/availability, porosity, pH, lability, or CEC depend heavily on the feedstock choice, pyrolysis temperature, and pyrolysis speed [22]. Consequently, information on the method of

biochar synthesis or conducting physiochemical analysis is essential when using biochar as a soil amendment..

Biochar has also been shown to interact with the native SOM or other soil amendments through an effect termed “priming.” In positive priming, biochar addition increase the mineralization of the native SOM, in contrast to negative priming, which decreases the mineralization of the native SOM, and sometimes the biochar has no priming effect at all [23]. The negative priming effect can be beneficial since these synergistic interactions decrease the mineralization rate and can increase the residence time of other organic compounds added concurrently with the biochar or already present in the soil [24]. The relationship between biochar and other forms of organic matter present in the soil is important and it could be postulated that a mixed treatment of biochar and compost could offset the quick degradation rate of compost and extend the effects of that amendment. A study by Laird et al. (2017) showed an example of this result with a multi-year and multi-location study that showed biochar + manure treatments resulted in a 47% SOC increase in the top 15 cm when compared to a non-amended control. This result was also consistent over a variety of different soil types [25] and other studies have shown similar increases to SOC (39%) [26].

All together the cryptic nature of long-term SOM stability and the innate variability the soil has on this process is a research area that requires more clarity because of the impact more refined management methods could have on both agricultural soil health and atmospheric carbon sequestration. A recent review paper examining the permanence of carbon sequestration into soil concluded with the following quote in support of the impact that research in this field could have. “Integrating new scientific findings regarding soil carbon longevity into data-based C policies is critical for broader adoption of agricultural soil C sequestration projects that could expand the

contribution of soils to climate change mitigation on a global scale.” [18] The soil health research presented in this dissertation will contribute much needed data to this field by furthering our understanding of what soil parameters impact soil health the most while also utilizing high-resolution analytical techniques to further elucidate the relationship between the molecular composition of SOM with microbial diversity and other measures of soil health. This intricate web of interactions is the focus of the first two chapters presented in this dissertation with a primary hypothesis that SOM is the most important aspect of soil health and is the main focus of both chapters. When trying to replenish SOM in the system it will also be shown that different soil amendments will contribute distinct types of organic molecules to the soil system that could result in significantly different microbial populations and show differences in degradation kinetics. A basic overview of this concept and the objective of Chapter 3 can be seen in the conceptual diagram below, Figure 1.2. However, a properly functioning agricultural system depends on more than just healthy soil, and water quality and quantity are also a fundamental part of these systems that impacts both soil health and plant productivity.

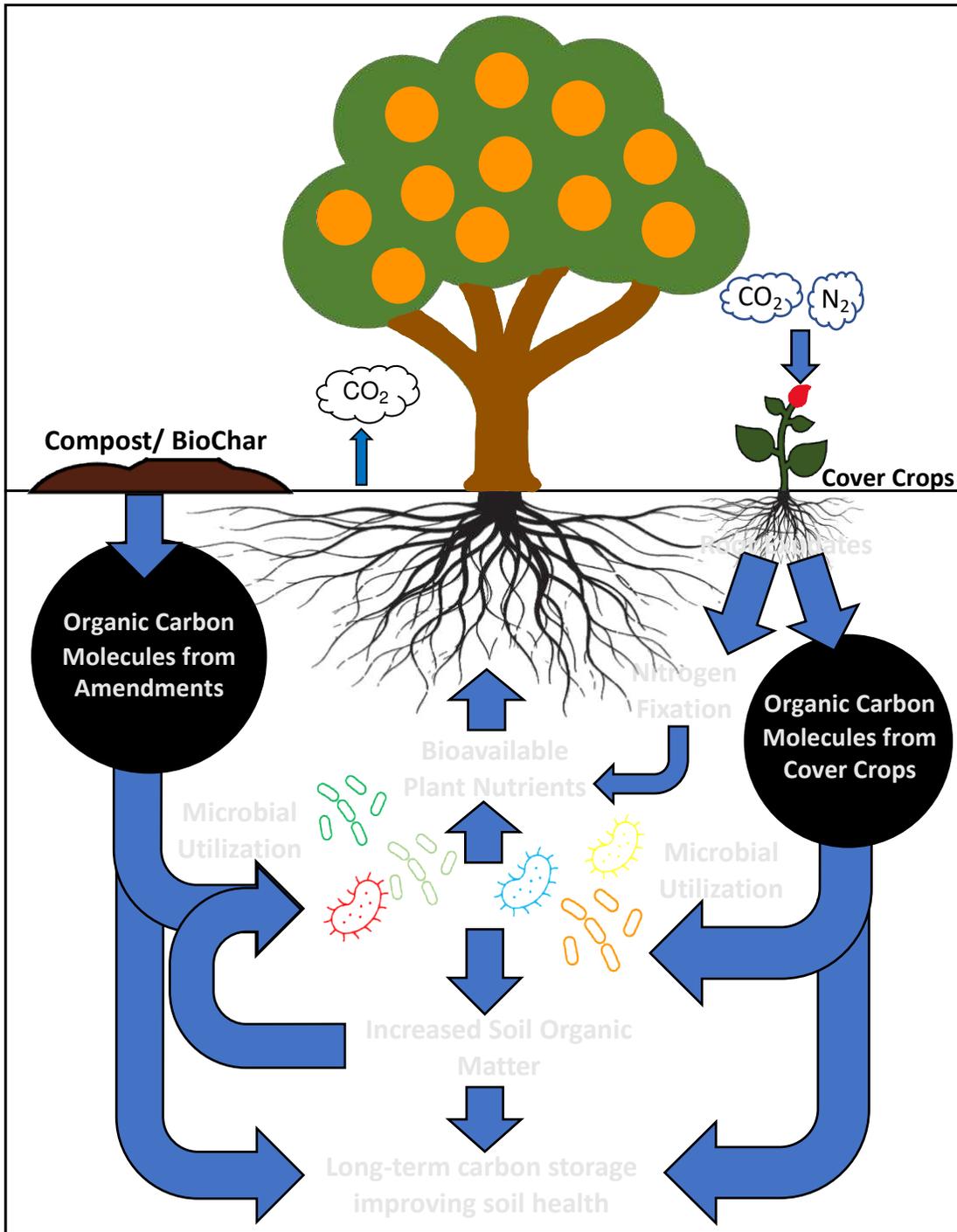


Figure 1.2 - overview of carbon cycling in the soil and the focus of Chapter 3

The final two chapters of this dissertation relate to another vital component of a properly functioning agricultural system, water quality, and when considering agricultural systems holistically, one can also understand water quality as an important factor demonstrating adequate soil health. These two chapters focus specifically on a project funded by the US Department of Energy, the National Alliance for Water Innovation (NAWI). The primary goal of this project was to transform our linear water system that has minimal reuse into a more resilient “circular water economy” [27]. Or in other words, the NAWI project focuses on understanding how we can properly treat and reuse a variety of wastewaters from different industries, specifically, the power, resource extraction, industrial, municipal, and agriculture sectors. The papers comprising these two dissertation chapters and the corresponding “[Technology Roadmap](#)” represent the first step for this project, with an end goal of developing appropriate technologies to reduce the cost of treating these non-traditional water sources.

The two papers presented here (Chapter 4 and 5) are review papers that establish “baseline metrics” for the reuse/treatment of these various water sources. Each chapter explores a variety of case studies in these sectors to utilize available “real world” data and then extrapolate this information into an estimated “Levelized Cost of Water” (LCOW) through the use of the Water Technoeconomic Assessment Pipe-Parity Platform (Water-TAP3) model developed by the National Renewable Energy Lab (NREL). Once these baselines were established, researchers from various universities and national labs could then benchmark their proposed desalination and treatment technologies against this LCOW to determine how effective the treatment technology was and if establishing these treatment technologies is economically viable. The two baseline papers published in this dissertation focus on the current state of technology for reusing wastewater

from agricultural sources for agriculture and the potential for reusing oil and gas produced water (PW), with a primary focus of reusing PW for agricultural use.

According to a USGS report from 2015, the United States withdraws 322 billion gallons of water per day (B gal/d) for use across all sectors. The majority of this water is withdrawn for use in either the agriculture sector (42%) or the power sector (41%), however in the power sector, only 3% of this water is for consumptive use (water removed from the available supply) [28]. Conversely in agriculture, 62% of water applied as irrigation is considered consumptive use, so every day in the USA, 73 billion gallons of water is withdrawn from the available supply and applied to crops as irrigation [28]. Other industries within the agricultural sector such as livestock production or aquaculture also consume fresh water and although the water use is relatively high (9.5 B gal/d) [28], compared to the amount of water applied as irrigation, this amount is simply a drop in the bucket. Therefore, this agricultural baseline focused specifically on wastewater from agricultural irrigation (runoff from fields) and the potential for reusing this wastewater for crop irrigation. The baseline is structured in a manner that accounts for the regionality of this wastewater, for example, the 17 Western states account for over 80% of the water applied as irrigation but altogether this sector was one of the most important baselines because irrigation accounts for 42% of the total freshwater withdrawals in the United States. Climate change, the pressure of a growing population, degrading water quality, and increased competition from other sectors could constrain continuous supply to meet future agricultural water demand. This study presents an evaluation framework to assess the potential reuse of agricultural drainage water for crop irrigation. Using a regional approach, we review the current state of agricultural drainage treatment and reuse and the institutional, economic, and other barriers that can influence the reuse decision. In the 31 eastern states, agricultural drainage contains valuable nutrients that can be

reused for irrigation with minimal treatment, while the 17 western states struggle with large volumes of saline drainage that can contain constituents of concern (e.g., selenium), preventing reuse without treatment (Figure 1.3). Using a new decision-support tool called WaterTAP3, a potential treatment train for saline agricultural drainage was analyzed to identify treatment challenges, research needs, and the potential implementation at a larger scale. As demonstrated by our case study, desalination of agricultural drainage is costly and energy intensive and will require sizable investments to fully develop and optimize technologies as well as manage the generated waste and brine. This chapter was published as part of the NAWI special edition in ACS ES&T Engineering [29].

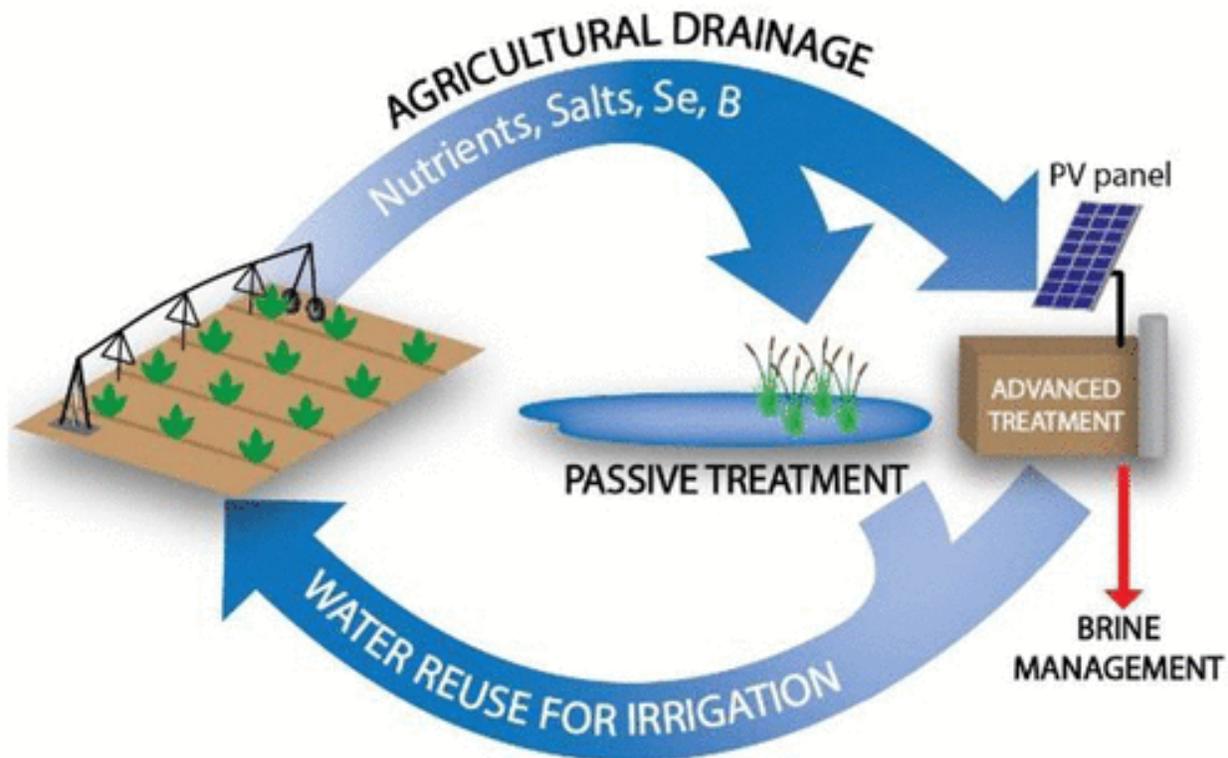


Figure 1.3 - Graphical abstract for Chapter 4 demonstrating the two pathways for treating agricultural drainage that depend on the constituents present in the runoff [29]

The last chapter from the NAWI project (Chapter 5) relates to the reuse/treatment of PW from oil and gas extraction. Every year, about 600 billion liters (160 billion gallons) of PW are produced by oil and gas extraction and the PW is subsequently disposed of in a variety of ways depending on the geographical location. Most commonly this water is reused within the sector for hydraulic fracturing but if it cannot be reused within the oil and gas sector, it is often times disposed of through deep well injection [30]. However, this method of disposal is controversial because of the increased prevalence of earthquakes that have occurred in areas that have undergone deep-well injections of wastewater. An overview of the seismic activity related to these injections suggested that the best predictors of seismic activity in these areas is both total injection volume and injection rate [31]. This implies that if this wastewater is given time to percolate through the subsurface after injection, the resulting seismic activity could be minimized but given the volumes of PW that are produced in some locations, a slower injection rate might not be feasible. Therefore, alternative disposal options need to be pursued for this saline wastewater and since a large amount of PW is accumulated in the arid west, beneficial reuse for agriculture seems like a win-win situation. However, this reuse situation is not straight forward due to the toxicity of PW and the societal hesitancy to use oil and gas extracted water for consumption, even in-direct consumption via application to crops.

This baseline paper explores a variety of reuse options utilizing the LCOW generated by the WaterTAP3 modeling program to determine the economic feasibility of these different treatment trains. Additionally, this paper investigates the toxicity of this water through a review of the current literature and proposes a process by which PW could be reused safely no matter the end-user (Figure 1.4). Determining the risk of adverse outcomes by reusing this water is vital

because not only does PW contain known carcinogens such as benzene, but the general public is skeptical of reusing this water for consumption, agriculture, or even to augment streams in arid environments. Altogether, advances in water treatment technologies paired with potential restrictions on oil and gas (O&G) produced water disposal could incentivize the beneficial reuse of treated produced water in the O&G industry. However, the remote nature of O&G operations limits the applicability of many of these solutions, which may be spatially inefficient, require operator supervision, or are ill-suited for the complex nature of produced water. Furthermore, the responsible, sustainable reuse of produced water as an alternative water source requires standardized analytical techniques for characterizing and determining the toxicity of treated produced water and improving our understanding of the fate and transport of various constituents. In the past decade, we made little progress in economically treating produced water for beneficial reuse outside of oilfield operations; the sole major breakthrough has been in the development of salt-tolerant fracturing chemicals that allow for reuse of produced water for fracking operations. Guided research should assist in the development of fit-for-purpose solutions to maximize the reuse of treated produced water. This is exemplified by the case studies presented here that detail

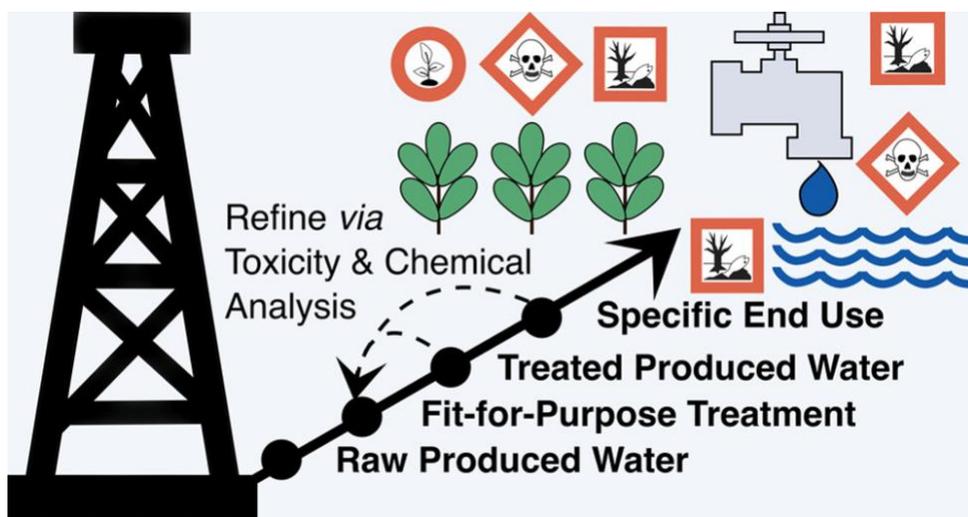


Figure 1.4 - Graphical abstract from the PW baseline (Chapter 5) demonstrating the proposed pathways for reuse that also consider toxicological assessment [32]

currently operating treatment facilities for reclamation and reuse of produced water. This chapter was published as part of the NAWI special edition in ACS ES&T Engineering [32].

Overall, this dissertation is a discussion on soil health, Chapter 2 explores the importance of maintaining soil health while Chapter 3 examines molecular changes in response to management practices that improve soil health. Chapter 4 and 5 are focused on water quality but this is also related to soil health. The reuse of saline water can be detrimental to soil health but concurrently a healthy soil can improve nutrient retention and improve water quality in areas where nutrient leaching can occur. These different topics have been presented at various conferences to highlight this work. Chapter 2 (Stokes et al. 2023) was presented at the 2021 Soil Science Society of America conference, Chapter 3 (Stokes et al. *in preparation*) was presented at the 2022 Soil Science Society of America conference, and Chapters 4 and 5 were presented at the NAWI 2021 annual meeting. Chapter 4 was also presented as a poster in 2022 at the Sustainable Agriculture Workshop.

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CHAPTER 2: DETERMINING SOIL HEALTH PARAMETERS CONTROLLING CROP PRODUCTIVITY IN A CITRUS GREENING DISEASE AFFECTED ORANGE GROVE

1. INTRODUCTION

Soil health is currently a major research focus for making agriculture more productive and sustainable. However, despite the increased focus on this concept, there still are not standardized means by which soil health is quantified and many indices lack biological parameters, such as microbial diversity, that are essential to a healthy soil [1]. The US Department of Agriculture defines soil health as “the continued capacity of soil to function as a vital living ecosystem that sustains plants, animals, and humans” but in many ways, soil health is a value judgement and a metaphor for how effectively a soil supports a specific function within a specific context [2]. However, soil functions are diverse, and desired ecosystem services could include site-specific impacts such as crop production or flood/landslide mitigation and downstream impacts such as water quality. But altogether, soil health influences plant production, water quality, human health, and climate [1]. Therefore, soil health is more generalizable when understood through identification of the four major functions a healthy soil performs: carbon transformation, nutrient cycling, maintenance of physical soil structure, and regulation of pathogens/pests [3]. Thus, it is apparent with these four functions of a healthy soil why if one surrogate were to represent soil health, soil organic matter (SOM) would be this proxy because it impacts the physical, chemical, and biological components comprising soil health [4, 5]. SOM composition and carbon cycling is also heavily influenced by the microbial community and its corresponding enzymatic activity, so an inclusive analysis of soil health should consider all of these components [6]. Altogether, SOM

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concentrations and microbial diversity in agricultural soil, plus corresponding plant productivity, are influenced by multiple factors including site-specific management practices and climate [7].

Global meta-analyses comparing crop yield to total soil organic carbon (SOC) concentrations found that in fields with less than 2% SOC (~3.5% SOM) increases in yield were positively correlated with increases in SOC/SOM, but above 3.5-4% SOM, this effect was not present [8, 9]. However, these studies also highlighted the large variability this relationship can have since every agricultural system has intrinsic differences such as local climates, soils, or management practices. For example, a tropical climate with significant rainfall and higher temperatures can increase SOM degradation rates by four fold when compared to temperate climates [10]. Our research sought to minimize these between system variations by focusing on one specific farm that had differences in crop productivity despite uniform management practices.

The agricultural system we investigated was a citrus grove located in south-central Florida, a region where it is also assumed that close to 100% of citrus trees are currently infected with Citrus Greening disease (HLB) [11], a problem that has been well studied within this specific citrus grove [12, 13]. HLB is a bacterial infection originating in the leaf, after transfer from the insect vector, eventually causing blockage of the phloem that restricts the movement of sugars and nutrients in the tree [14]. Subsequent progression of the disease leads to changes to the diversity of the soil microbiome [15], loss of fibrous root mass, and eventual death of the tree [16]. These symptoms in the root system and phloem could potentially impact soil health or conversely, soil health could impact the progression of HLB symptoms, but within HLB infected groves, soil health has not been well studied.

The objective of this research was to examine soil health by sampling certain locations within the grove based solely on one pillar of soil health, plant productivity, specifically the

differences in observable tree size. Since most of the trees studied were not of a fruit producing age (<5 years old), observable differences in tree size were used as a proxy for future crop productivity. Importantly, the varying tree sizes occurred in large, distinct areas, despite the trees being planted at the same time. These pre-existing differences in tree size within the grove created an ideal setting to elucidate mechanistic differences in soil health within an unmanipulated system since tree growth varied despite identical inputs of water, fertilizer, and pesticides within the blocks of identical trees. We hypothesized that these differences in plant productivity were caused by variability in soil health. However, since this is an all-encompassing term with indices that typically focus on physical and chemical parameters, we sought to discern differences in not just the physiochemical characteristics, but also biological indicators, specifically microbial diversity and extracellular enzyme activity.

2. MATERIALS AND METHODS

2.1 Field site

The field site was located at a citrus grove in Venus, Florida, USA; a region consisting of a sub-tropical climate with an average annual high temperature of 23°C and an average annual precipitation of 134 cm. The grove was approximately 4,050 ha in size and contained over a million Valencia orange trees (*Citrus sinensis* Valencia). The grove was divided into ~60 sub-sections called “blocks” that contained trees planted at the same time, from the same root stock (Swingle citrumelo), and receiving identical management practices. Distinct areas of contrasting tree size were identified by the producer within these identically managed blocks, with the most extreme areas containing trees that were twice the size of their neighboring trees (Figure S2.1). Importantly, in all of the blocks analyzed, one section of trees was always noticeably larger. These distinct

regions of tree size were likely the result of construction techniques used when building the grove. Dredged sediment from ponds added to adjacent regions of the grove in combination with soil leveling and transport to other areas could have caused these large differences of soil quality.

Management practices in the blocks included consistent rotations of varying insecticides, herbicides, and fungicides throughout the year [12], and fertigation applied through a drip/mist irrigation system that provided the trees with all necessary macro and micronutrients. The farm applied the maximum amount of various systemic and contact pesticides allowed to minimize the spread of the HLB-insect vector, the Asian citrus psyllid. The various blocks throughout the grove were managed generally the same way, and any variation between blocks was primarily based on the age of the trees in that specific block. None of the trees studied were fully mature and 4 out of the 6 blocks contained young trees that had not yet produced fruit (<5 years old), while the other two blocks of trees had started to produce fruit and were approximately 7 years old. Throughout the grove there was spatial variability in the specific soil type, but primarily a mixture of soils with fine sandy textures in Spodosol soil order [17].

2.2 Productivity differences and soil sampling

Samples were collected within specific blocks containing observable differences in tree size, with the low-productivity (LP) areas containing thousands of trees encompassing dozens of rows and up to ~25% of the area in some affected blocks (~15-25,000 trees/block). The observable differences in tree size varied from block to block, but the trees in the high productivity (HP) areas were always bigger and, in some places, were nearly twice the size of their identically managed neighbors. Follow up sampling trips to quantify tree size in relation to soil conditions were delayed due to the onset of the COVID-19 pandemic and eventually cancelled after multiple summers with

hurricane damage to the grove. Therefore, tree size was estimated based on pictures taken of the trees sampled and observational notes from the first field campaign. Within the six different blocks, three trees were randomly selected from each high and low productivity area, for a total of 18 composite soil samples in each productivity group (Figure S2.2). The order in which the blocks were sampled over the course of a week depended on recent pesticide applications, as some areas had active restricted entry intervals (REIs).

To minimize the natural soil heterogeneity within each tree's root zone, a composite sampling technique was utilized comprising ten individual soil cores based on a set pattern (Figure S2.3). In order to prevent any microbial contamination between sampling locations, all tools were thoroughly sanitized with 90% isopropyl alcohol before sampling each new location and the soil core was hammered into the ground in the new location to clean out the plastic liner and remove residual soil. Specifically, the soil cores were extracted with a 3.2-cm diameter stainless steel coring tool containing a PETG plastic insert to minimize metal contamination from the stainless steel. In order to reduce impurities from surface residues or recent fertilizer applications, the surface litter was removed from a wide area around the core and a 5 cm deep hole was dug before a 40 cm deep core was extracted. Each soil core was added to a plastic 5-gallon bucket then thoroughly mixed. The composite was then transferred into a quart-sized Ziploc bag, and immediately placed in a cooler filled with ice. Soils were then stored in a -18°C freezer until shipment in Styrofoam coolers filled with ice to Colorado State University. Upon receiving, soils were stored at 4°C while soil analysis was conducted or stored for the long-term in a -80°C freezer.

2.3 Sample preparation

Prior to analysis, sub-samples were removed from plastic storage bags and allowed to air-dry completely, approximately 4 days. These sub-samples were subsequently passed through a 2-mm sieve and stored in plastic bags at 4°C until further chemical analysis was conducted. Following chemical analyses, air-dried, 2-mm sieved soils were stored long-term in a -80°C freezer.

2.4 Soil health index

The soil health index from Amacher et al. [18] was selected because of its comparable use by the US Forest Service to measure soil health in forests. Although there are many different indexes that can be used that are more generalizable, our goal was not to generalize soil health. Instead, we sought to use this index as a tool that integrated 16 different variables into one metric by assigning values to each variable based on how beneficial a particular variable was to the tree, thus this index might be more aptly described as a “soil productivity index.” The variables comprising the index were coarse fragments (> 2-mm), soil pH, total organic C (estimated using [SOM]/1.75), total N, potassium (K), magnesium (Mg), calcium (Ca), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb), sulfur (S), and phosphorus (P). This index has limitations because it focused primarily on nutrients and only one physical parameter (coarse fragments) was included, but the objective was to only compare soil health within this specific system.

2.5 SOM, SOC, total N

SOM was analyzed via the loss on ignition method [19]. Briefly, ~5 g of air-dried, < 2-mm soil was first ground and sieved through a 355- μ m mesh, then put into a drying oven at 105°C for 24 h to remove water. Finally, it was combusted at 400°C for 16 h in a muffle furnace and allowed to cool in a CaSO₄ desiccator. The before/after mass difference was calculated as total organic matter. Subsamples of some blocks were replicated six times to examine soil heterogeneity.

For SOC and total nitrogen (N), air-dried, < 2-mm soil samples were first pulverized on a roller table overnight, then analyzed for carbonate content through the addition of dilute hydrochloric acid to the samples, but in this moderately acidic soil, no carbonates were detected. Subsequently, total carbon (C) and total N was determined via combustion analysis [19] (LECO Elemental Analyzer series CN928, St. Joseph, MI). However, because the concentration of SOC was below the instrument's carbon detection limit (SOC < 0.5 %), these data were not utilized.

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2.6 Soil physiochemical analyses

For soil nitrate concentration determination, 100 mL of a 0.01M KCl solution was added to 10 g of oven-dried, < 2-mm soil, and then shaken at 200 rpm for 1 h [20]. Afterwards, the mixture was centrifuged at 5000 g for 10 min and then filtered through a 0.2- μ m nylon syringe filter produced by VWR. The filtrates were briefly stored in polypropylene (PP) tubes (with minimal headspace) in a 4°C refrigerator until analysis via ion chromatography (IC; Dionex ICS-2100 series and an AS-DV autosampler). The IC mobile phase was potassium hydroxide (KOH) produced by a Dionex Eluent Generator Cartridge (ThermoScientific, Waltham, MA). The KOH was mixed with ultrapure water that had been degassed with N₂ for two hours prior to use. Quantification of sample concentrations were performed using a DS6 Heated Conductivity Cell (ThermoScientific, Waltham, MA) and compared to a set of 5 known calibration standards.

For soil ammonium concentration determination, 10 mL of 2M KCl extract was added to 1.0 g of air dried, < 2-mm soil [20]. The mixture was shaken on a reciprocating shaker at 200 rpm for 1 h before being filtered through a Whatman 0.45- μ m nylon syringe filter. The filtrate was then frozen until quantification via flow injection autoanalysis (3700 Automated Chemistry Analyzer, OI Analytical, College Station, TX).

Soil pH was measured using a pH probe as described by Thomas [21]. A ratio of 10 g soil:10 mL ultrapure water was shaken vigorously and let to stand for 10 min. Soil pH was then determined in the 1:1 mixture.

Electrical conductivity was determined utilizing a standard method [22]. Briefly, 40 mL of ultrapure water and 8 g of soil were added to a PP centrifuge tube and shaken vigorously, then the 5:1 mixture was analyzed using a conductivity probe.

Soil phosphorus (P) and all metals/metalloids were extracted from the soil using the Mehlich III extraction method, the recommended method for the fine sandy soils of Florida [23]

as described by Zhang et al. [24]. Elements within the extract were then quantified using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) that utilized a NexION 350D mass spectrometer (PerkinElmer, Waltham, MA). Samples were injected into the MS using a PFA-ST (Elemental Scientific, Omaha, Nebraska) nebulizer and a peltier controlled (PC3x, Elemental Scientific) quartz cyclonic spray chamber (Elemental Scientific) utilizing argon gas as the carrier phase. All chemicals used in this extraction were of trace metal grade quality and all materials were acid-washed prior to use to minimize contamination. For accurate quantification, six calibration standards were used, internal standards were injected with every sample, and a method blank was quantified and subtracted from the extract concentrations.

Analysis of soil texture was conducted using a standardized hydrometer method utilizing particle density to determine the percentage of sand, silt, and clay [25].

2.7 DNA extraction, amplicon sequencing, and bioinformatic analyses

Soils were stored in a -80°C freezer for 3 months until DNA was extracted from soils using the DNeasy Powersoil Kit (MO BIO Laboratories, Carlsbad, CA, USA) as per the manufacturer's instructions. Extracted DNA was quality checked using a NanoDrop 2000 (Thermo Fisher Scientific, Waltham, Massachusetts, USA), and quantity checked using a Qubit Fluorometer (Thermo Fisher Scientific), and then stored at -80 °C.

The diversity and community structure of soil bacteria was determined by amplicon sequencing using an Illumina MiSeq platform. We used the primer sets 515F/806R [26] to amplify a portion of the bacterial 16S rRNA gene. Bioinformatics processing was performed using a combination of USEARCH [27] and UNOISE3 [28]. Amplicon sequence variant (ASV) tables based on 97% sequence similarity were generated using the USEARCH pipeline. Sequencing run

quality was assessed using fastQC [29]. The raw sequences were discarded if they contained ambiguous nucleotides, had a low ($Q < 20$) quality score, or were short in length (< 100 bp). Adapters and primers were removed using cutadapt [30] and the samples were then demultiplexed. Paired-end reads were merged, and quality was assessed with an initial quality check test. The representative set database was created using the UCLUST and UPARSE algorithm [31]. Unique sequences were located and sorted into unique ASVs. ASVs were clustered using DADA2 and DeNoised using uNoise3 [32] as described [33]. ASV tables were generated by mapping reads to the representative set database. ASVs were counted at the sample level. Taxonomic identification of bacteria was obtained against the Silva database [34]. Bacterial sequences that match host mitochondria and chloroplast were removed.

2.8 Soil enzyme analysis

β -Glucosidase (BG), β -D-cellubiosidase (CB), β -Xylosidase (XYL), α -Glucosidase (AG) and N-acetyl- β -Glucosaminidase (NAG) activities were measured using 4-methylumbelliferyl (MUB) substrate yielding the highly fluorescent cleavage products MUB upon hydrolysis. All the enzyme assays were set up in 96-well microplates as described by [35] and [6]. Twelve replicate wells were set up for each sample and each standard concentration. The assay plate was incubated in the dark at 25 °C for 3 h to mimic the average soil temperature. Enzyme activities were corrected using a quench control. Fluorescence was measured using a microplate fluorometer (EnSpire 2300 Multilabel Reader, Perkin Elmer, Waltham, MA, USA) with 365-nm excitation and 460-nm emission filters. The activities were expressed as $\mu\text{mol activity h}^{-1} \text{g}^{-1}$ dry soil.

2.9 Statistical analysis

Microbiome samples were rarified to the lowest occupancy of 12,800 reads. We used the

R package ‘mctools’ to analyze microbial community structure [36]. To examine beta diversity, Bray–Curtis dissimilarity distances between the samples based on the operational taxonomic units (OTUs) were calculated and then ordinated in multidimensional scaling using a constrained redundancy analysis (RDA). Permutational multivariate analysis of variance (PERMANOVA) models were generated to determine significant beta-diversity differences between treatments. To examine alpha diversity, Shannon diversity indexes were calculated and evaluated through general linear models (GLMs). Tukey HSD tests were used to determine influence of treatments on alpha-diversity. Random forest (RF) analysis was used to investigate the indicator taxa at the phylum level involved in the differences between treatments [6]. RF analysis was conducted using the Microbiome analyst pipeline [37]. All other statistical analysis utilizing t-tests and linear regression were conducted in Microsoft Excel

3. RESULTS AND DISCUSSION

3.1 Soil health

A soil health index, emphasizing macro- and micronutrient concentrations [18], was applied to quantify soil health and compare the productivity regions within this specific system. The HP area had an average soil health index score of 53% of maximum (n = 18), while the LP area scored 44% (n = 18) (Figure 2.1), with differences between HP and LP areas significant at $p < 0.01$. It is important to note that this index did not consider any biological factors such as

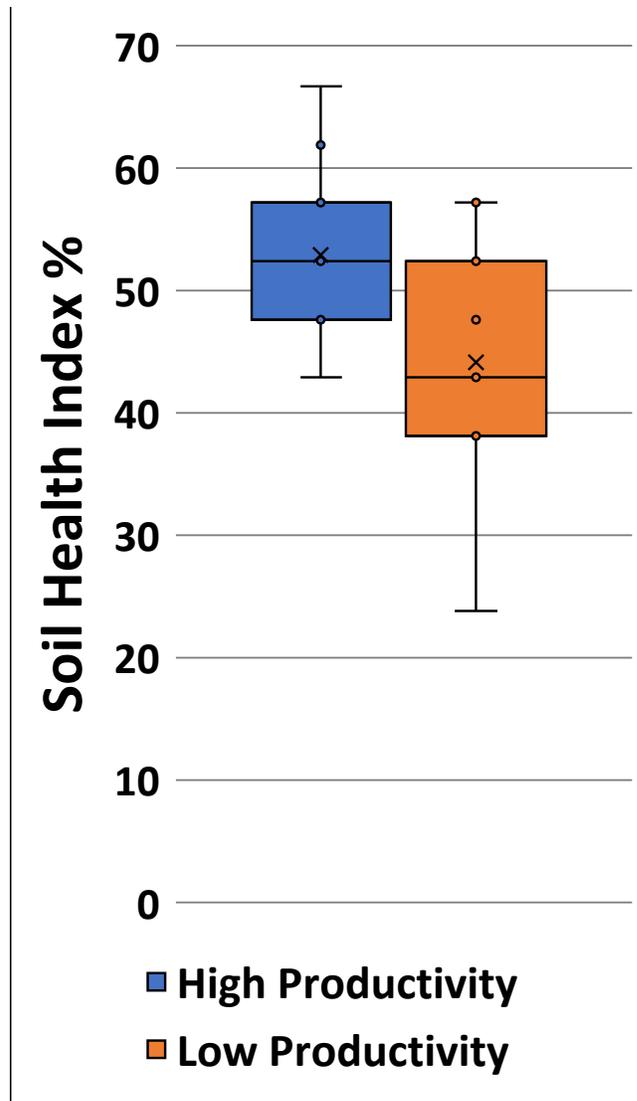


Figure 2.1 - Significant differences ($p < 0.01$) in soil health index scores between productivity areas, shown as a percentage of maximum possible score. X represents the mean index score.

enzymatic activity or microbial diversity, and only one physical characteristic, so is not generalizable to other systems. For example, if the values of these measured soil parameters were found in other soil systems, the soil would be considered “unhealthy” because of the low SOM concentrations (<1%) and acidity (average pH = 5.3). These characteristics influence the diminished physical soil structure present in this system, such as a lack of observable aggregates, and it would not support many of the desired ecosystem services that would be expected in other

regions. Therefore, it is important to consider this index as an estimate of healthy soil solely within this citrus grove.

3.2 Soil chemistry

Differences in SOM concentrations were consistent between productivity areas in every block analyzed. Altogether, the high productivity (HP) sites contained significantly greater ($p < 0.05$) SOM (average = 0.94% (9.4 g/kg), $n=18$ trees) than the low productivity (LP) areas (average SOM = 0.57% (5.7 g/kg), $n=18$ trees) (Figure 2.2). SOM is a vital part of a functioning soil system,

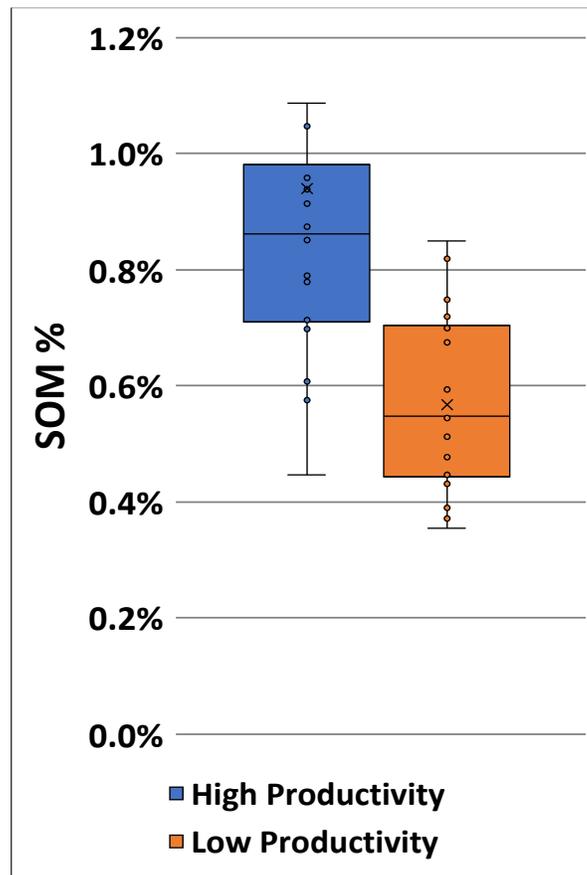


Figure 2.2 - Significant differences between high and low productivity areas ($p < 0.01$) for SOM concentrations. X represents the mean value. Outliers in these figures were removed for clarity but in the high productivity region, two SOM concentrations were measured at 2.4 % and 1.6%.

regardless of the desired function, because of its impact on the physical, chemical and biological functions of the soil [3]. In this agricultural system, the low SOM concentrations would impact both soil and plant health by decreasing nutrient retention, water holding capacity, and altering the soil microbiome [4, 5, 38]. These negative impacts are more pronounced in sandy soils [39], such as this system. These changes are apparent through decreased growth rates of the trees with critically low SOM concentrations. Research comparing SOM to crop yield in tropical soils estimates that a detrimental “cutoff point” exists around ~1.75% SOM [40], but our results demonstrate that in this highly managed tropical system, a relative cutoff point resides somewhere from 0.6% - 0.9% SOM. However, this could also demonstrate the potential for these trees to be even bigger for their given age if SOM concentrations were closer to 1.75%. Still, depending on the level of management a certain agricultural system receives (i.e., fertilizer inputs), a “cutoff point” is more likely a unique characteristic of each agricultural system and a highly managed system like this one could minimize the negative impact of a harmfully low SOM concentration. Additionally, SOM concentrations impact other aspects of soil health such as water quality and human health by influencing nutrient retention [41]. Consequently, in sandy soils with high hydraulic conductivity, lower levels of SOM can lead to more nutrient leaching from the soil into waterways, which increases the likelihood of eutrophication downstream. In this region, nutrient leaching from agriculture is a primary factor influencing the increased occurrence of red tide events on the Florida coast [42].

Analysis of plant macronutrients (i.e., N, P, and K) showed no significant differences between productivity areas for nitrate (Figure S2.4), ammonium, or potassium (Figure S2.5). This result is not surprising when considering the weekly fertigation applications (NPK and micronutrients), so any differences in soil concentrations would be difficult to elucidate. The

application rates of fertilizer may vary between the different blocks depending on the age of the trees, but within each block of trees, the rate is consistent.

The only macronutrient with significant differences between areas was extractable P, average in HP region = 45.6 mg/kg and LP region = 30.1 mg/kg ($p < 0.05$). SOM concentrations strongly affect the adsorption of phosphate to the soil [43]. Thus, the HP regions, with higher SOM concentrations, should have higher P concentrations, and regression analysis further supports the positive relationship between SOM and P ($R^2 = 0.51$, $p < 0.01$). Therefore, when considering that these areas have identical inputs of P, we can assume that the LP areas with smaller trees are utilizing less P for plant growth and have less P stored in the soil. Consequently, more P would be leaving the system and potentially entering the local system of canals adjacent to the field.

Additional regression analysis between various micronutrients and SOM was conducted and showed significant positive relationships ($p < 0.05$) between SOM and K ($R^2 = 0.40$), Zn ($R^2 = 0.33$), Ca ($R^2 = 0.35$), Cu ($R^2 = 0.30$), Mn ($R^2 = 0.29$), and Mg ($R^2 = 0.12$). For regression analysis, all samples were grouped together to highlight the impact of SOM on other variables within the soil system. Of the other nutrients demonstrating positive relationships with SOM concentration, Mg, Ca, Mn, and Zn also show significant differences ($p < 0.05$) between the HP and LP areas (Figure 2.3). Extensive research has shown the positive relationship between SOM and cation exchange capacity (CEC), especially in sandy soils [44]. This is one of the many factors explaining the importance of SOM when evaluating soil health and how differences in SOM can influence crop productivity. Other components of soil such as soil texture (Figure S2.6), EC (Figure S2.7), or pH (Figure S2.8) could also impact soil health, but analysis of these components did not find any significant differences between the productivity regions or any values that would be considered harmful to this specific agricultural system.

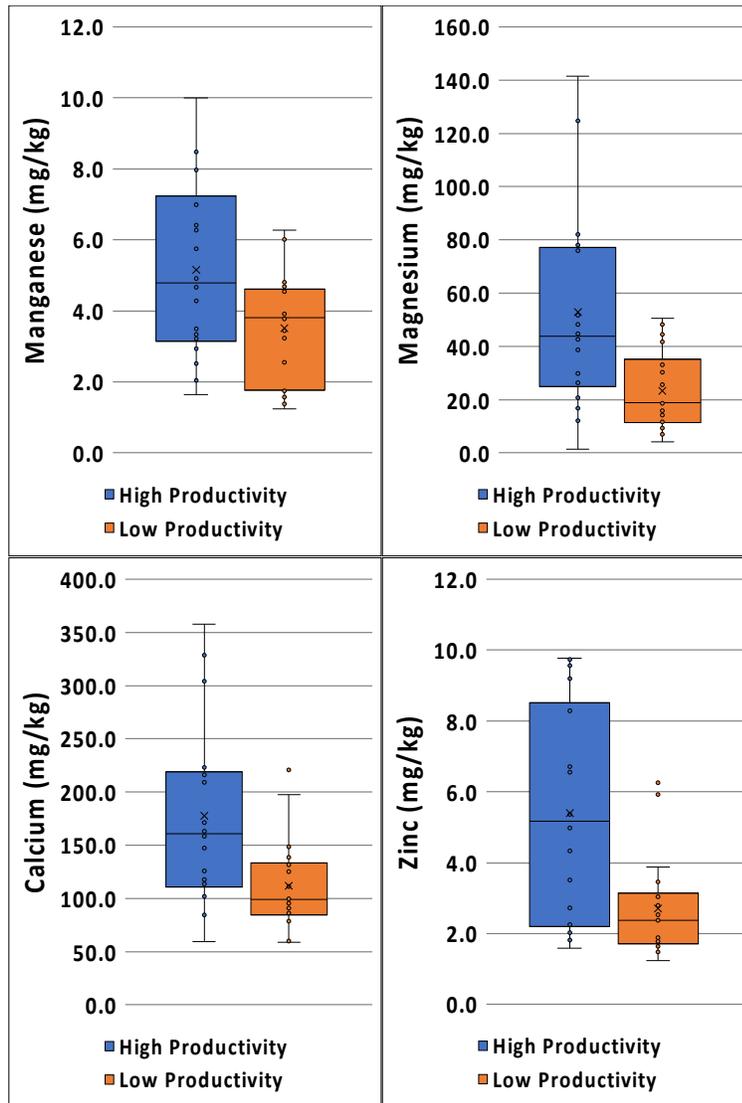


Figure 2.3 - Significant differences ($p < 0.05$) between productivity regions for common micronutrients. X represents the mean value.

3.3 Extracellular enzymes

Analysis of extracellular enzyme activity (EEA) was conducted since EEA has been closely linked to changes in soil health and carbon cycling [45]. Five different extracellular enzymes involved in carbon cycling were analyzed, including α -Glucosidase (AG), β -Glucosidase

(BG), β -D-cellubiosidase (CB), N-acetyl- β -Glucosaminidase (NAG), and β -Xylosidase (XYL). The difference in average enzymatic activity between the HP and LP areas was greatest when measuring CB activity ($p < 0.01$), HP = 247.1 $\mu\text{mol activity/g dry soil/ hour}$ and LP = 185.9 $\mu\text{mol activity/g dry soil/ hour}$. The difference in EEA between the HP and LP sites was also statistically significant ($p < 0.05$) for AG, BG, and NAG (Figure 2.4).

Enzyme activity is an effective indicator of the biological activity relating to soil health and the microbial community [46], but values can vary widely between studies so it is most reliable when utilized within a system and not between systems [47]. Nonetheless, when comparing the productivity regions, the HP areas have more enzyme activity than the LP areas which indicates a more robust microbial community [48]. Higher EEA also corresponds to areas of the grove that contain greater SOM concentrations, and typically SOM is correlated to enzyme activity in organic top soils. However, in mineral soils like this one, enzyme activity is primarily influenced by pH, water content, and microbial diversity [49]. Ultimately, HP areas have more cycling of carbon substrates, which should result in an increase in bioavailable plant nutrients leading to healthier soil and more productive plants.

3.4 Soil microbiome

16s-rRNA characterization of the soil microbiome showed significant differences between the soil microbiome populations in the two productivity regions through a variety of analysis methods. Redundancy analysis (RDA) utilized the productivity area of each soil sample to plot differences in beta diversity between samples (Figure 2.5a). A clear separation on axis 1 of the RDA and significant ($p < 0.05$) PERMANOVA results clearly demonstrated differences in the bacterial

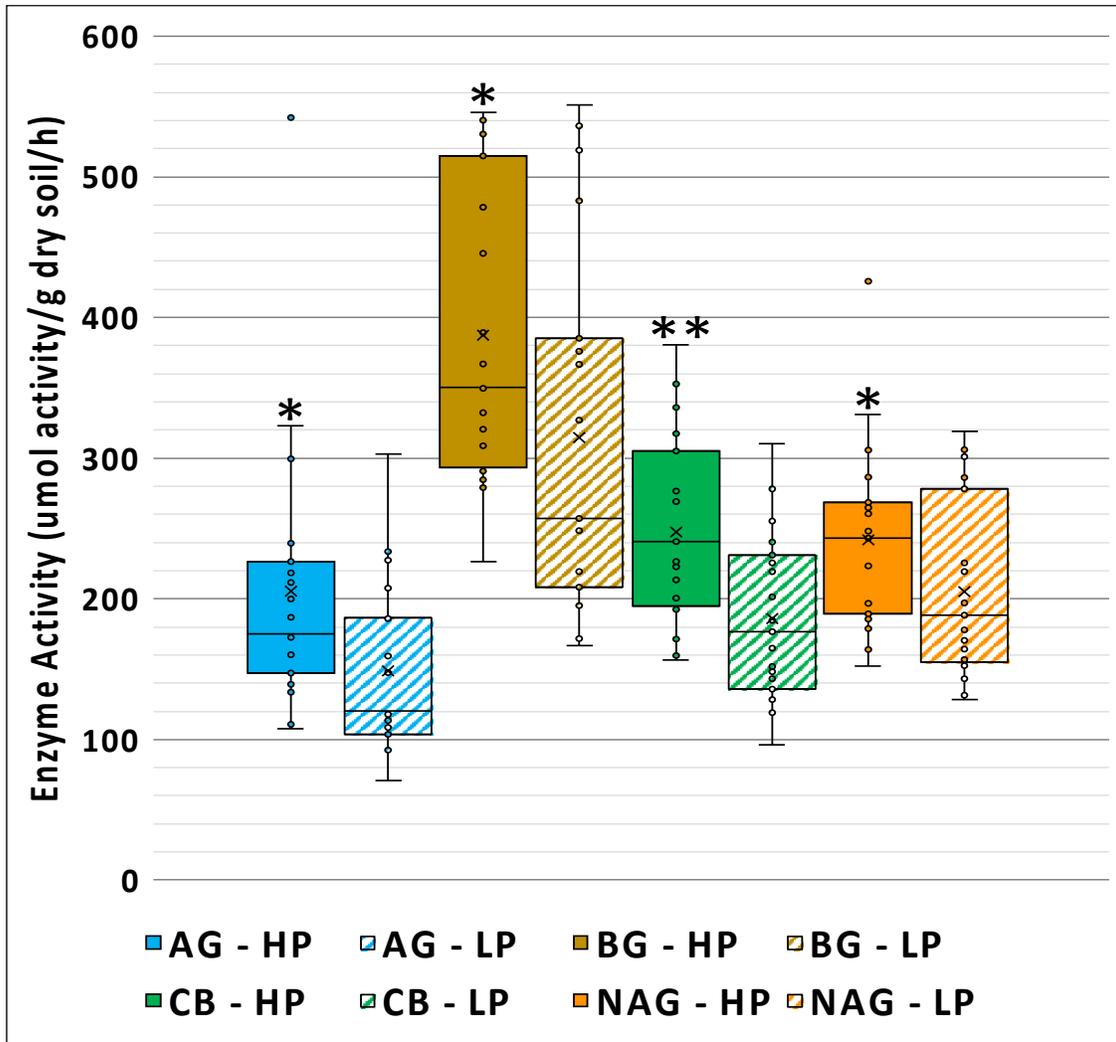


Figure 2.4 - Analysis of extracellular enzyme activity shows the 4 enzymes that had significantly different activities between the high productivity (HP) and low productivity (LP) areas. β -D-cellubiosidase (CB) activity was significant at $p < 0.01$ (shown as **), while α -Glucosidase (AG), β -Glucosidase (BG), and N-acetyl- β -Glucosaminidase (NAG) were significant at $p < 0.05$ (shown as *). X represents the mean activity value.

community structure between high and low productivity plots. However, no significant differences were observed when calculating the alpha diversity of these systems using the Shannon Index (Figure 2.5b). A random forest plot demonstrated that copiotrophic bacteria from the Firmicutes phylum were the strongest indicator of HP areas, while oligotrophic bacteria in the phylum

Thaumarchaeota and Verrucomicrobia were the two strongest indicators of lower quality soil in the LP areas (Figure 2.5c).

Typically, Thaumarchaeota are more abundant in soil with low SOM [50], while Verrucomicrobia abundance has an inverse relationship with soil fertility [51]. Whether low SOM concentrations led to shifts in microbial diversity or if microbial diversity changes led to lower SOM concentrations cannot be determined from these data, but typically the microbial population will determine the stability or decomposition rate of SOM [52]. However, in a citrus grove infected with HLB, the symptoms of this disease might also cause changes to soil health and corresponding microbial populations, a relationship that warrants additional research.

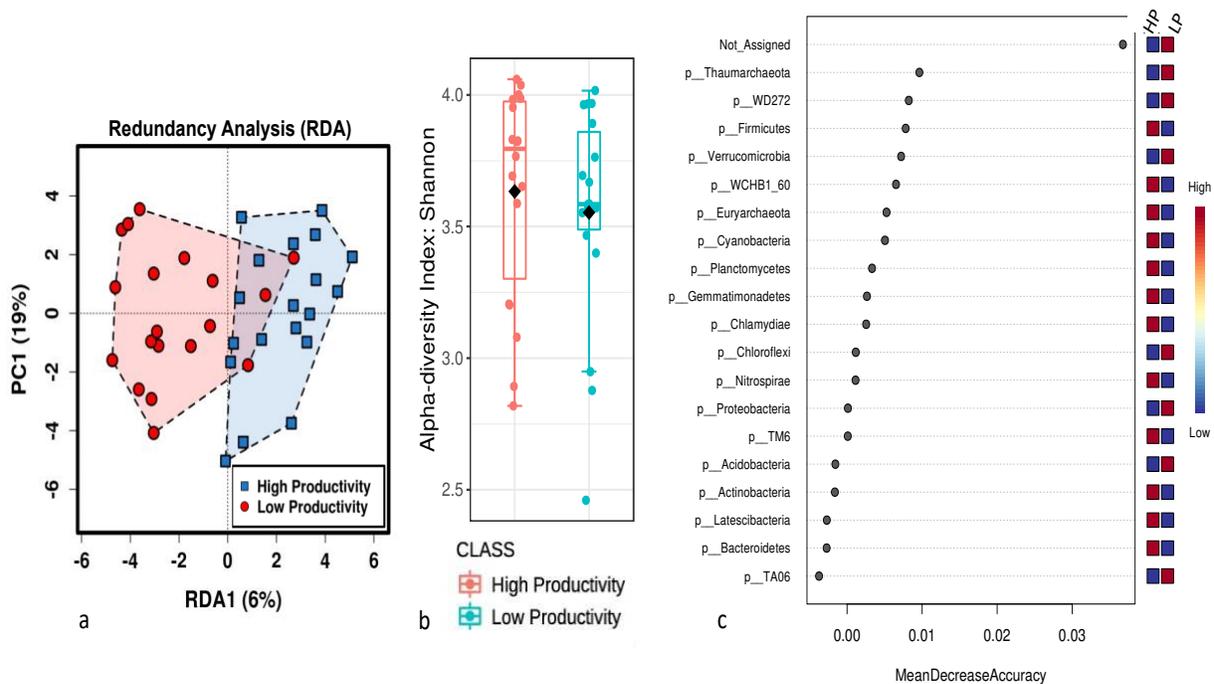


Figure 2.5 - (a) Significant differences in beta diversity ($p < 0.05$) between microbial populations in the high (HP) and low (LP) productivity areas using Redundancy analysis (RDA). (b) No significant differences in alpha diversity were found utilizing the Shannon Index. (c) Random forest analysis at the phylum level showing indicators for either HP or LP areas.

3.5 Implications of Citrus Greening Disease

An important aspect that was not directly studied but was impacting every tree in this grove is Citrus Greening disease (HLB). HLB is caused by the pathogen *Candidatus Liberibacter asiaticus*, with the infection causing an immune response that leads to blockage of the tree's phloem [53]. This blockage limits the movement of sugars [54] and changes the metabolic profile of the phloem [55], which ultimately impairs fruit quality and quantity [14]. This blockage could also impact soil health by altering the composition and quantity of metabolites transported through the phloem to the soil as root exudates, but to our knowledge any relationship between HLB infection and root exudates or soil health has not been studied. Alteration of root exudate composition or quantity could explain why HLB-infected trees have shifts in rhizosphere microbiome diversity and decreases in genes associated with carbohydrate and lipid metabolism [56]. This shift in microbial diversity also corresponds to an increase in microbes less beneficial to the plant and a proliferation of microbes ideally suited for degrading more recalcitrant forms of carbon [15]. Management practices that improve soil health, such as microbial inoculants or compost applications, have been shown to reduce the amount of pathogen in the roots [13], potentially leading to increased resistance of infected trees to the fatal consequences of HLB. Therefore, we hypothesize that soils with more SOM and a more robust microbial population would have additional resistance to the onset of detrimental HLB symptoms and could be a reason why this grove has large variations in tree size, a research topic that deserves further investigation.

4. CONCLUSION

SOM is an essential component of a healthy soil, but soil health cannot be quantified or properly assessed by solely using SOM concentrations. A comprehensive analysis of soil health

needs to consider soil function in addition to physical, chemical and biological metrics. This research demonstrates the impact SOM, EEA, and microbial diversity have on soil health and why biological indicators need to be considered when evaluating soil health. The complex relationships between these parameters can impact crop productivity through their influence on the bioavailability of plant nutrients. In tropical regions where soil carbon mineralization rates are relatively high, it is important to continuously monitor SOM concentrations to potentially avoid any detrimental impact on crop productivity or downstream impacts on water quality. Lastly, this study highlights the need for more research directed towards quantifying the relationship between HLB symptoms and soil health in an effort to reduce the impact of this fatal pathogen.

Author Contributions

According to the CRediT (Contributor Roles Taxonomy) criteria my contributions to this paper include conceptualization, methodology, validation, formal analysis, investigation, writing-original draft, and visualization. Contributions from T.B. include conceptualization, resources, writing – review & editing, supervision, project administration, and funding acquisition. The contribution from K. O. was investigation. Contributions from P.T. include conceptualization, methodology, resources, visualization, writing – review & editing, and funding acquisition. Contributions from J.I. include conceptualization and writing – review.

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CHAPTER 3: ELUCIDATING TEMPORAL CHANGES IN MOLECULAR SOM COMPOSITION IN SOILS AMENDED WITH BIOCHAR OR COMPOST

1. INTRODUCTION

In agricultural systems with SOM degradation, adding organic amendments such as compost or biochar can be an effective management practice to help restore SOM that has been lost. Historically, compost has been utilized in agricultural fields because it can supply bioavailable nutrients, sequester carbon, improve crop yield, limit soil erosion, improve soil moisture content, enhance crop nutritional content, and enrich soil biological properties and biodiversity [1-5]. However, these positive effects can be impacted by local environmental conditions, compost feed material, and the temporal scale in which the effects occur can vary based on these conditions [1-4]. Another organic amendment that can provide benefits to soil is biochar, an amendment formed through the pyrolysis of various types of organic feedstocks.

The long-term stability of biochar is one major advantage of using it as a soil conditioner because even if application of biochar ceases, the carbon sequestered will remain stable in the soil for the long-term, potentially for decades, in addition to the benefits to the physical properties of the soil [6]. This contrasts with other sustainable agricultural practices such as compost that decomposes and loses its beneficial properties on a much shorter timescale [1]. The economic feasibility of using biochar depends on the impact biochar has on crop yield [7] but meta-analysis of these types of studies has shown inconsistent results, with a range of yield changes fluctuating from -28% – +39% [8]. Another similar study integrated the results of 84 different biochar/crop yield studies and found that the positive relationship between biochar use and crop yield depended on innate soil conditions. Specifically, biochar had a larger positive effect on yield with crops

grown in soils possessing low CEC or SOC, one example being the highly weathered soil of the tropics [9]

Cover crops are another viable way to increase soil carbon, and the use of cover crops also provides additional benefits to the agricultural system. They add biodiversity to monoculture systems, minimize erosion, fix nitrogen, suppress weeds, scavenge nutrients [10], and increase the abundance of microbes in the rhizosphere [11]. This relationship to the microbial population could be considered the most important function of cover crops when the primary objective is to increase SOM concentrations and improve overall soil health. The low-molecular weight compounds that are exuded through the roots by cover crops are the compounds that have been shown to be the most prominent molecules affiliated with long-term stabilization of SOM [6, 12, 13]. These studies also highlight the complexity of carbon cycling within the soil system, so one approach is to utilize a framework to unravel these complex interactions based on substrate use efficiency (SUE) or the ratio of carbon substrate utilized for growth versus the amount of substrate respired [13]. The Microbial Efficiency Matrix Stabilization (MEMS) framework proposes that molecules with high SUE are more efficiently utilized by the microbes (SUE example: glucose = ~70% and lignin = ~20%), but overall the goal is to minimize the amount of carbon mineralized while transforming a majority of the substrate into microbial biomass or extracellular enzymes [13]. In the long-term, matrix stabilization of the SOM is favored by microbially transformed organic compounds and analysis has shown that a majority of SOM is of microbial origin. Thus, by enhancing the microbial biomass one could presume that SOM concentration in the long-term would be increased [6]. However, this stability is also affected by innate soil characteristics such as soil type, pH, or allophane presence so predictions are most relevant on a site by site basis [13].

Determining which organic amendment to add to a specific soil or cover crop to grow is complicated since the amendments have different effects on different soil types, or conversely, the soil type can modulate the impact of the amendment. Even the amendments themselves have large amounts of variability between batches depending on the conditions in which they were formed. In general, compost and biochar are fundamentally different since biochar is formed within hours through high temperature pyrolysis (no oxygen) while compost is formed over the course of months from aerobic degradation of organic waste products [14]. However, the composition of these soil amendments can vary significantly depending on the specific type of amendment used and even how that amendment was synthesized [14, 15].

Biochar is unique because of its synthesis via high temperature pyrolysis but within that process, there are multiple variables that can affect the composition of the biochar. Specifically, the pyrolysis speed, the feedstock type, and the pyrolysis temperature affect the total elemental composition and structure of the biochar. For example, a wood based biochar has higher carbon (C) content than other feedstocks and the higher the pyrolysis temperature, the larger the fraction of non-labile C [15]. In contrast, compost is formed slowly in aerobic environments, so the physiochemical properties of the final product are more consistent, and any variations are likely due to the choice of feedstock. Overall, the production of compost is more sustainable and economical because it is not energy intensive and does not require any specialized pyrolysis equipment [14]. The use of these organic soil amendments has been common for decades, thus the positive impact they have on restoring SOM and improving other properties of soil health has been studied extensively [14, 16-18]. Nonetheless, few studies have examined the molecular changes involved in SOM degradation in response to the addition of these different amendments because researchers lacked effective analytical techniques. One of the few studies that has taken a

molecular level view demonstrated that the presence of biochar in a soil can alter the composition and degradation of SOM [19]. Consequently, with recent advances in ultrahigh-resolution mass spectrometry conducted with Fourier Transformed-Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS), this type of molecular analysis of SOM is now feasible [20, 21].

FT-ICR MS analysis has been utilized to analyze the molecular composition of composts derived from different feedstocks [22], biochar [23], and agricultural soil after cover crop addition or corn stover decomposition [24]. Thus, we sought to utilize this type of characterization to analyze molecular level changes to SOM in an agricultural soil after application of either biochar or compost. Additionally, due to the lack of quantitative data from the FT-ICR MS, our goal was to compare changes to the molecular composition of the SOM to analysis of microbial diversity and quantitative measures of soil health utilizing common soil health methods such as SOM concentration, CO₂ mineralization rate, extracellular enzyme activity, and bioavailable nutrient concentrations [25]. We hypothesized that the soils amended with either compost or biochar would have unique molecular formulas in each sample that would correspond to their different degradation kinetics and these differences would correspond to variations in the analysis of the soil chemistry and biology.

2. METHODS

2.1 Experimental Setup

Soil was shipped in 5-gallon buckets (18.9 L) from a citrus grove in Venus, FL to Fort Collins, CO (with approval from USDA-APHIS) for a greenhouse study at CSU's Plant Growth Facility greenhouse. The soil was taken from an area of a citrus grove that had been identified by the producer as having poor soil health and was removed with a shovel from a 1 m x 1m square

that was no deeper than 0.5 m deep. To minimize soil heterogeneity within each triplicate of the different soil amendments, the soil was taken from the 5-gallon plastic buckets and thoroughly mixed together with the amendment in a large plastic container. Following complete mixing, the soil was added to a 2-gallon (7.6 L) plastic pot and packed down lightly to allow for 5 cm of space at the top of the pot.

The application rate for each amendment was calculated based on the surface area of the pot, by using the diameter of at the top of the pot, 26 cm (10 1/8 in). Each amendment had two different application rates based on typical agricultural management practices, identified as “low” and “high”. The application rate of each amendment was as follows: compost-low = 5 tons/acre (57 g/pot), compost-high = 10 tons/acre (114 g/pot), biochar-low = 2.5 tons/acre (28.5 g/pot), biochar-high (57 g/pot), biochar and compost mix = 28.5 g of each amendment for a total of 57 g of amendment in each pot. A nitrogen fixing cover crop, perennial pinto peanut, was grown in some of the pots either in combination with one of the aforementioned amendments or in unamended soils. The pinto peanut was selected because of its propensity as a cover crop in tropical environments and its ability to thrive in acidic, sandy soil. Two pinto peanut plugs were planted in each pot and there was a 100% transplant success rate. Another cover crop was also grown, bahiagrass, in an attempt to draw comparisons between the amended soils with two types of cover crops being grown (monocot vs dicot). However, due to considerably different root densities between the two plants that occurred over the course of the study, any temporal comparisons between samples were deemed invalid because of the effect that the root densities would have on both the SOM metrics and the nutrient concentrations. Comparisons between these samples at the Day 0 time point have been utilized since these samples were taken before any seeds/plugs were planted.

Over the course of the 13-month long greenhouse study, every pot was watered twice a week with ~500 mL of water and liquid fertilizer was applied to every pot once a month. The liquid fertilizer contained 200 ppm nitrogen (15-5-5 NPK) and all other necessary micronutrients, it was mixed with one of the weekly applications of water for a total volume of 500 ml. Any weeds that germinated in the soil that were remaining from the citrus grove, were immediately removed, and disposed of outside of the pot. The greenhouse maintained an average annual temperature of 22°C (72°F), 25% percent humidity, and had supplemental artificial light in the winter, with an average photoperiod of 12-13 hours.

2.2 Soil Amendments

The compost utilized for this study was sourced from the Colorado State University (CSU) industrial composting facility. The feedstock for this compost was a combination of food and paper towel waste from the CSU campus in addition to straw and horse manure from the CSU equestrian center. After thorough mixing and sieving, this compost was formed in large piles stored outside that were periodically mixed until completion of the composting process. The biochar was obtained from a commercial producer, High Plains Biochar (Laramie, WY), and was synthesized using 100% pine wood. The pyrolysis was conducted at 815 °C (1500°F) for fifteen minutes with essentially no oxygen present to maximize carbon content (~84% total organic C) and minimize ash (~8%). Comprehensive elemental analysis of the biochar provided by the manufacturer showed that the final biochar product had a pH of 9.5, total potassium (K) = 8932 mg/kg, total phosphorus (P) = 843 mg/kg, ammonia = 8.4 mg/kg, nitrate = 3.0 mg/kg, and organic nitrogen (N) = 6679 mg/kg. The distribution of biochar particle sizes was as follows, < 0.5 mm = 6%, 0.5 – 1 mm = 8%, 1-2 mm = 53%, 2-4 mm = 32%, and 4-8 mmm <1%.

2.3 Soil Sampling and Analysis Prep

Soil was sampled at three different time points in this study to analyze temporal changes within the soil system. For the baseline soil sample, soil was removed immediately following the mixture of the amendment into the soil, before the soil was placed into the three separate pots. This soil sub-sample was stored in a plastic bag and stored in a -80°C freezer until analysis was conducted. Subsequent rounds of soil sampling were conducted at the 6-month and 13-month time points; however, we focus specifically on the 13-month time point (Day 400) for the research presented here. When sampling the soil already established in the pot, a 2.5 cm diameter stainless steel soil corer was used to extract 4 separate soil cores dispersed around the pot that extended the entire depth of the pot, approximately 20 cm. These four cores were immediately placed in a plastic bag, mixed together, and then placed on ice in a cooler until long-term storage in a -80°C freezer.

Prior to any soil analysis, a subsample from each bag of soil was air dried for 3-4 days until completely dry. This air-dried soil was subsequently passed through a 2 mm sieve to remove larger soil aggregates, rocks, or roots. For any analysis method that required a finer soil, a subsample was placed in a small glass container with two ceramic rods and placed on a roller table for 24 hours to pulverize the soil.

2.4 FT-ICR MS

Extraction of DOM from the soil was done with the following method for analysis utilizing FT-ICR MS. There are multiple methods that can be used to extract different fractions of SOM/DOM which can be then analyzed via different ionization modes in the MS, the advantages and limitations of each can be found in a review by Bahureksa et al. [20]. All materials were acid

washed prior to use and precaution was taken on every step of the method to minimize any contamination from surfactants that could interfere with the results.

DOM was extracted from an unground soil sample by first weighing out 10.0 g of soil and placing it in a 50 mL Polypropylene Falcon tube. This tube was filled with 40 mL of ultrapure water and the mixture was shaken for 60 minutes at 150 rpm on a reciprocating shaker, followed by 15 minutes of centrifuging at 4600 g. The supernatant was filtered through a 0.45 μm cellulose acetate syringe filter, acidified to pH 2 using concentrated HCl, and refrigerated at 4°C overnight until solid phase extraction (SPE).

For SPE, Bond Elute PPL cartridges were used in combination with a vacuum manifold to allow for multiple extractions at once. Extracted DOM samples were removed from the refrigerator and allowed to warm up to room temperature before SPE began. SPE cartridges were attached to the manifold, and each was rinsed with 15 mL methanol (3 mL capacity conducted 5 times) that was collected below the cartridge and disposed of accordingly. Subsequently, each cartridge was rinsed with 15 mL of pH 2 water (using HCl) which was collected below the cartridge and disposed of accordingly. The DOM extract was then added to each labelled cartridge to collect the DOM and once all samples were cartridged, each was rinsed with 10 mL of pH 2 water to rinse salts into a plastic collector then disposed of appropriately. All SPE cartridges were removed from manifold and allowed to dry completely before eluting the DOM within hours. DOM on the SPE cartridges was eluted using 6 mL of methanol and collected using glass test tubes. These tubes were then dried down using N₂ gas until ~1.5 mL of eluent remained before being transferred to a 2 mL glass HPLC vial. These vials were wrapped in foil and stored at -20 °C until shipment to the National High Magnetic Field lab in Tallahassee, FL.

FT-ICR MS analysis was performed using a custom-built mass spectrometer, equipped with a 21T superconducting solenoid magnet and a modular software package for data acquisition (Predator). Samples were ionized via negative electrospray ionization and observed mass spectra were internally calibrated using the “walking” calibration method. Molecular formula were assigned to the MS spectra by utilizing the custom PetroOrg software and assigned formula were part of ≥ 3 peak carbon series and had less than ± 0.1 ppm mass error [26]. A LOD of 6σ was used to minimize ionization differences between samples and reduce biasing by large amounts of low abundance peaks that are most affected by ionization matrix effects. To further elucidate differences in sample comparison, formula that were identified in both samples were removed allowing the unique formula in each sample to be compared. All data processing after formula assignment was performed using RStudio (version 2023.03.0+386) utilizing R (4.3.2).

2.5 SOM, SOC, TN

Total soil organic matter was analyzed using the standard Loss on Ignition method [27]. Briefly, a ~10 g ground and sieved (355 μm mesh) soil sample was used to minimize any heterogeneity within the soil samples. This soil was placed in a pre-weighed ceramic crucible and then dried at 105 °C in an oven to ensure all soil water was evaporated. This oven dried sample was then moved to a desiccator to cool before a pre-combustion weight was quantified to the 0.01 mg decimal place. Following this measurement, the crucibles were placed in a muffle furnace at 400°C to combust for 16 hours. Once completed, these samples cooled in the desiccator before a post-combustion weight was obtained and the difference in mass was used to quantify the total SOM.

To analyze total carbon (TC) and total nitrogen (TN) approximately 100 mg of air dried and ground soil was placed in a tin foil sheet and rolled into a small ball. This sample was then weighed to the 0.01 mg decimal point (subtracting out the tared tin foil sheet) and placed in a VELP Elemental Analyzer. The sample was heated to over 800°C to release the carbon as CO₂ and the nitrogen as N₂. However, because a significant proportion of these samples had TC concentrations that were less than the detection limit of this instrument (< ~0.5% TOC), this data was not used.

2.6 Micronutrients, P, K, and Heavy Metals

The Mehlich III method was used to extract bioavailable nutrients. This method has been shown to be highly effective for quantifying the bioavailable fraction of soil nutrients in the sandy, acidic soil of Florida [28] and described in detail here [29]. Briefly, a mixture of trace metal grade nitric and glacial acetic acid was combined with trace metal grade ammonium nitrate, EDTA, and ammonium fluoride for a solution with a pH of 2.5. Composite samples of each triplicate were used and 1 g of air dried, 2 mm sieved soil was extracted with 10 mL of Mehlich III solution. This extract was filtered with a 0.45 µm PTFE syringe filter and 1 mL extract was combined with 9 mL of 2% nitric acid in preparation for analysis in the Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). The ICP-MS had a NexION 350D mass spectrometer (PerkinElmer, Waltham, MA) and samples were injected into the MS with a PFA-ST (Elemental Scientific, Omaha, Nebraska) nebulizer and a peltier controlled (PC3x, Elemental Scientific) quartz cyclonic spray chamber (Elemental Scientific), argon gas was the carrier phase. Analytes were measured accurately down to 1 ppb and a method blank was subtracted from every concentration before solution

concentrations were converted into mg analyte/kg soil values. To minimize any outside metal contamination, all previously cleaned materials were also acid washed prior to use.

2.7 Physiochemical Analysis

96-hour soil incubations were conducted with 20.0 g of air-dried soil from each sample triplicate rewetted with water calculated to be 50% water filled pore space, 3 mL of water in each sample. These rewetted soils were in a plastic container placed inside a larger glass jar (970 mL volume) with 9 mL of water placed in the glass jar to maintain a humid environment and prevent drying of the soil. These jars were sealed with lids containing rubber septa and placed in a 25 °C constant temperature room for 4 days. After this time, a calibrated infrared gas analyzer was used to quantify the concentration of CO₂ gas in the headspace of the glass jar using the ideal gas law to calculate the number of moles of CO₂, this number was further converted to μmol CO₂ mineralized per hour.

Soil pH was measured using the standard method with a pH probe as described in [30]. A 1:1 ratio of air-dried soil and ultrapure water was shaken vigorously and let stand for 10 minutes. Soil pH was then determined by measuring the acidity in the 1:1 mixture.

Inorganic nitrogen species were quantified from air dried soil by using the standard extraction method with a 2M KCl solution [31]. By mixing 10 mL of 2M KCl and 1 g of soil then shaking for one hour on a reciprocating shaker table an extraction was completed. After settling for 30 minutes, this mixture was filtered using 0.45 μm nylon syringe filters and then stored in a freezer until analysis. Quantification of ammonium and nitrate was determined by using Flow Injection Analysis (FIA).

2.8 Enzymes

β -Glucosidase (BG), β -D-cellubiosidase (CB), β -Xylosidase (XYL), α -Glucosidase (AG) N-acetyl- β -Glucosaminidase (NAG) and Phosphatase (PHOS) activities were measured using 4-methylumbelliferyl (MUB) as a substrate to yield highly fluorescent hydrolysis products. All the enzyme assays were conducted in 96-well microplates as described by [32] and [33]. Twelve replicate wells were set up for each sample and each standard concentration. The assay plate was incubated and shaken in the dark at 25 °C for 3 h before analysis was conducted. Fluorescence was measured using a microplate fluorometer (EnSpire 2300 Multilabel Reader, Perkin Elmer, Waltham, MA, USA) with 365-nm excitation and 460-nm emission filters. The activities were expressed as nmol activity h⁻¹ g⁻¹ dry soil.

3. RESULTS AND DISCUSSION

3.1 FT ICR-MS Molecular Composition

When analyzing results from FT ICR-MS it is important to first consider the extraction protocol that the data represent because the extraction method and certain instrument protocols (such as electrospray ionization positive mode (ESI +) or ESI - mode) can determine which molecules are detected by the MS [20, 34]. Therefore, because these samples were extracted with water and injected into the MS with ESI- mode, this analysis focuses on the fraction of SOM molecules that are water soluble and easily deprotonated. For example, this would include organic molecules with chemical structures such as carbonyl groups or cross-linked phenolics (i.e., carboxylic acids, lignin, or cellulose) but altogether these molecules can be characterized as dissolved organic matter (DOM). After acquiring this data and assigning molecular formula to as many datapoints as possible, the results are plotted on a Van Krevelen diagram (VKD). These

figures utilize the ratios of hydrogen : carbon (H:C) on the y-axis and the ratio of oxygen : carbon (O:C) on the x-axis, the combination of these ratios can then be used to approximate the most likely structural class most for each molecular formula (Figure 3.1). The primary focus of this molecular level analysis will be on soil samples containing the same mass of amendment applied (5 tons/acre), which represent the “high rate” of biochar (BH) and the “low rate” of compost (CL).

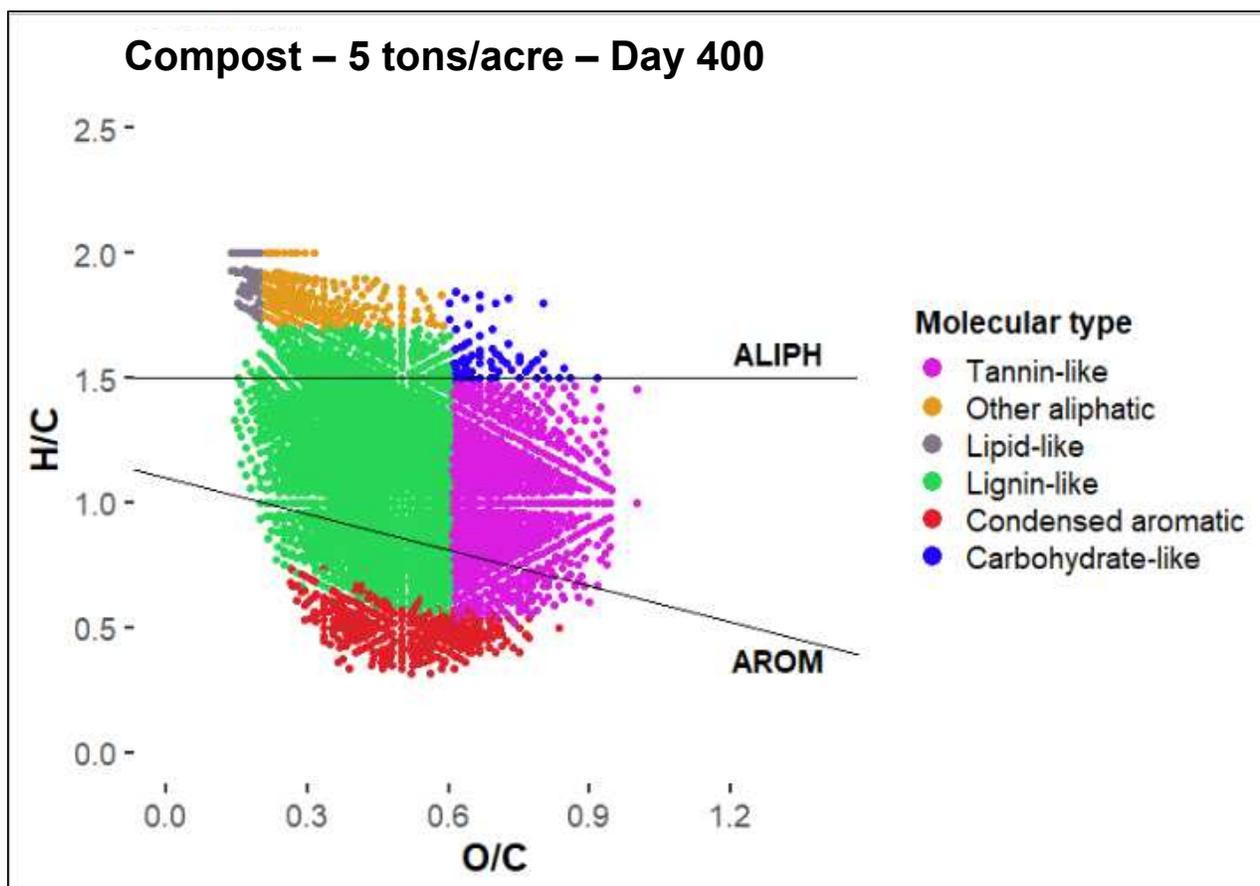


Figure 3.1 - molecular formula present in the low amendment rate of compost at Day 400. This specific Van Krevelen plot has color coding based on the most likely structural formula present in that region to give an example of the possible differences in structure that could be seen in the VKD with the subsequent figures.

Comparisons of these soil samples focus on two specific disparities between the amendments, the different molecular formula present in the soil immediately following application of the amendment and the temporal changes of molecular composition that occur over the course

of the study. Analysis of data from FT-ICR MS can be visualized by a VKD in a variety of ways, the most basic being a VKD showing every possible formula for the extracted DOM (Figure 3.2). This figure shows the relative similarities between the soils with the majority of the most abundant formula (relative to other formula within that specific soil) in the center of the plot where the “lignin-like” molecules reside, or in structural terms, the cross-linked phenolic compounds.

Altogether, the total molecular formula plotted for Day 0 of the compost sample was 16,402 and for the biochar was 9,308 formulae. However, when the VKDs are plotted with every identified formula, differences within these figures can be masked by the sheer volume of total formulas, so comparisons between samples can be more effectively elucidated by removing all formula that are in common between the samples. There were 7,788 molecular formulae in common between the samples and it can be assumed this would primarily include the molecular

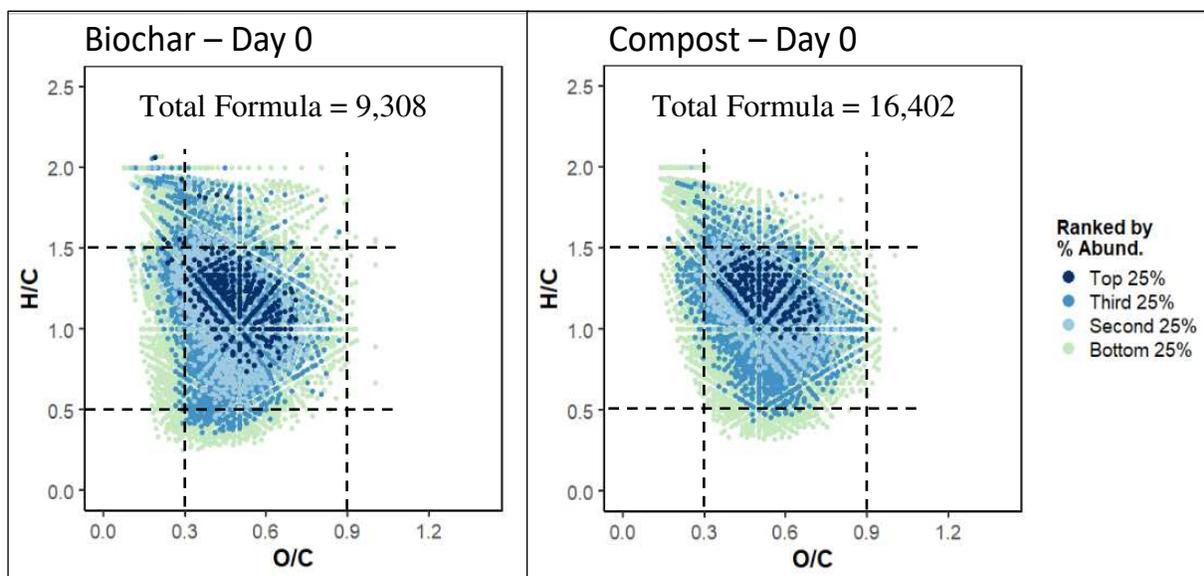


Figure 3.2 - Total formula identified by FT-ICR MS at Day 0 for soils amended with 5 tons/acre of biochar (left) and compost (right). The Van Krevelen diagrams are plotted with the ratio of hydrogen: carbon on the y-axis and the ratio of oxygen: carbon on the x-axis. Formula above an H/C = 1.5 would likely be aliphatic molecules.

formula extracted from the soil (not the amendment) since the soil composition/texture was nearly identical between the samples. To further support this assumption, quantification of the total molecular formula in the soil sample that did not have any amendment added showed it composed of 8,430 total formula and had a minimal amount of unique formula when compared to the compost amended soil (SI Figure 3.1). Consequently, we can assume that a majority of the unique formula in these VKD are from the amendment itself and not the soil.

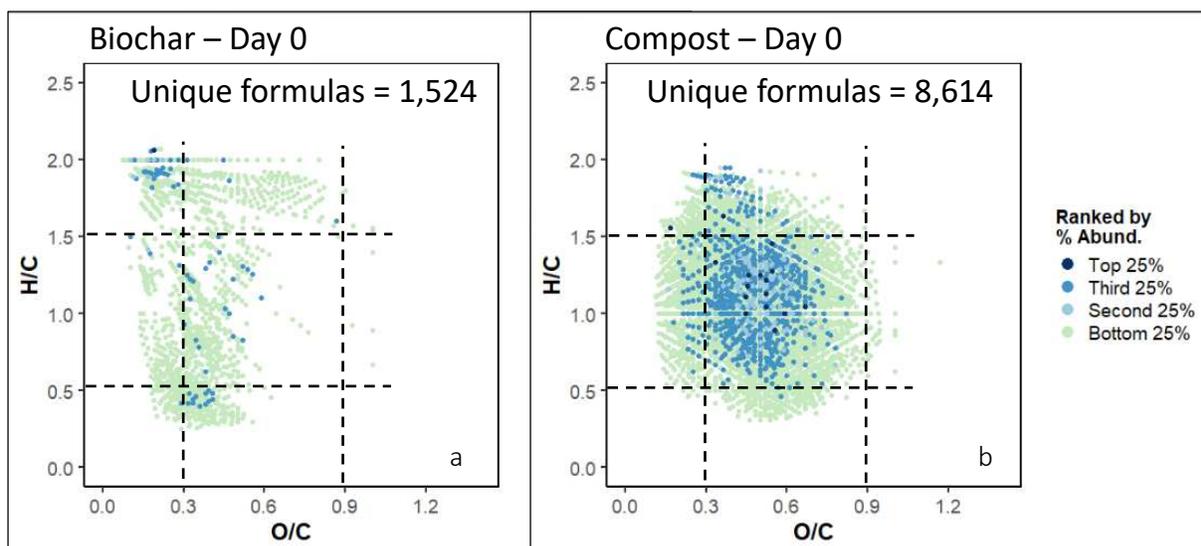


Figure 3.3 - Unique formula in each sample at Day 0 for soils amended with 5 tons/acre of biochar (left) and compost (right). The Van Krevelen diagrams are plotted with the ratio of hydrogen: carbon on the y-axis and the ratio of oxygen: carbon on the x-axis

The VKD showing unique formula within the BH sample (Figure 3.3a) shows that biochar has a majority of its unique formula at the extremes of the VKD. In general, the BH formula have a lower O/C than the CL and unique formula that represent condensed aromatic structures (H/C and $O/C < 0.5$), which would be expected when considering the known stability of biochar in the soil [35]. However, based on this, it is surprising to see a large cluster of unique biochar formula on the high end of the H/C axis in the aliphatic region of the VKD ($H/C > 1.5$), an area of the VKD where molecules that could potentially be more labile would be present. In the top left region of the VKD where $H/C = 2$ and $O/C < 0.3$, the BH samples had some relatively abundant formula,

and although this is in the aliphatic region, these formulae likely represent lipids which are less labile and can be more resistant to degradation. However, it is surprising to see that the BH soil contains some unique aliphatic molecules that are more oxidized and could be carbohydrates based on their location in the VKD. The CL soil also has some unique formula in the aliphatic region ($H/C > 1.5$) (Figure 3.3b), but generally it has formula that are more oxidized with a majority of its more abundant formula with an O/C greater than 0.3. The formula in the center of the CL VKD comprise a variety of cross-linked phenolic molecules and these are a common by-product of biomass degradation. The composition of the CL and BH confirms what would be expected of these two amendments based on what we know about their two different methods of synthesis. The CL sample is formed in an aerobic environment and is thus contains molecules with larger O/C ratios, while the BH sample is formed without oxygen so it's composition contains molecular formula with lower O/C ratios. The second objective of this analysis was to understand how these amendments change after aging in the soil over the course of 13 months.

After 400 days the primary takeaway from the analysis of the unique formula in the soils is that molecules show different rates of degradation and transformation. In the CL sample, a majority of the unique aliphatic molecules disappeared from the VKD (Figure 3.4b). This is in contrast to the BH sample that contained similar aliphatic molecules at Day 0, but after 400 days, these molecules are still present in the soil and the soils has even gained unique formula (likely from these disappearing the in the CL soil), thus demonstrating slower rates of degradation in the biochar amended soils (Figure 3.4a). Eventually these molecules would also be degraded in the BH soil and their presence after 400 days of aging is more a function of the temporal scale of this study since other research has shown that it can take 3-4 years for the lipids/long-chain alkanes present in biochar to degrade in soil [35]. Another example of faster degradation rates in the CL

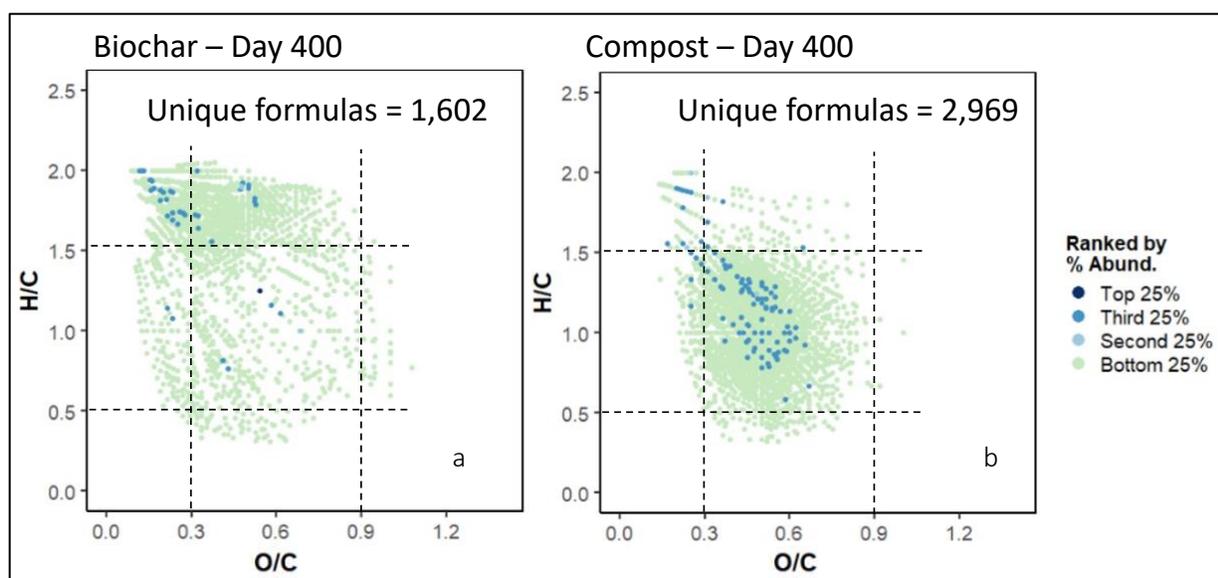


Figure 3.4 - Unique molecular formula in each soil after 400 days when comparing the different amended soils

sample is the loss of over 5,500 unique formulae from this soil, while the BH sample had an increase of a few hundred unique formula. And although we cannot conclude that these formula in the CL sample were completely mineralized and lost from the system, it does provide another piece of evidence supporting the mechanism of quicker degradation of SOM in compost amended soils compared to the BH sample that showed transformation of the SOM, but not loss of molecules.

Finally, when comparing the unique molecules in the soils at Day 0 and Day 400 within each amended soil, there is a comparable trend to the comparisons of the unique molecules present between samples. Essentially, the CL soils appear to be undergoing molecular transformation and loss of molecules from the system (Figure 3.6) while BH soils have molecules undergoing transformation but not complete mineralization (Figure 3.5). This is supported by quantifying the total molecules in each soil, the biochar amended soil starts with 9,308 formula and after 400 days, the total formula decreases slightly to 9,131. Conversely, the compost soil starts with 16,402 formulae but after 400 days, the soil only has 10,398 formulae remaining. Visually, the VKD

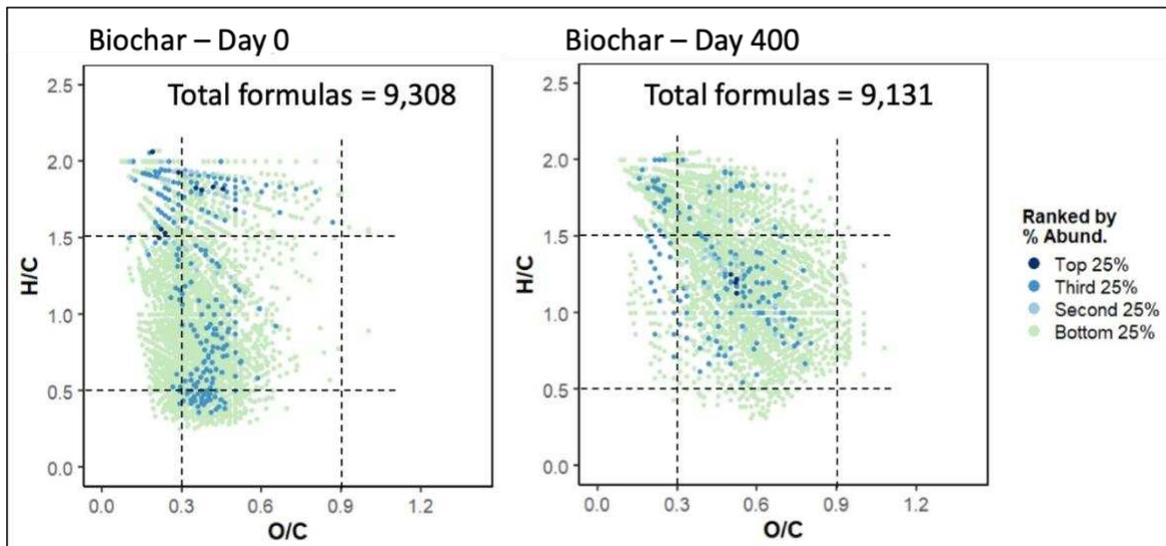


Figure 3.5 - unique molecules within the biochar amended soils when comparing Day 0 to Day 400. Day 0 has 2,596 unique formula and that increases to 2,773 unique formulae at Day 400

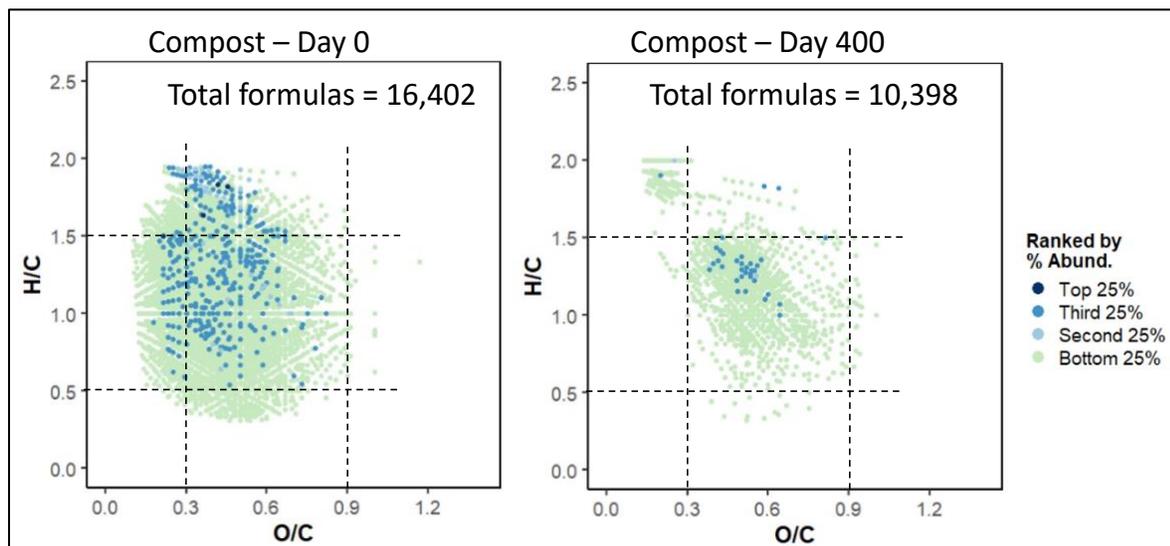


Figure 3.6 - unique molecules within the compost amended soils when comparing Day 0 to Day 400. Day 0 has 7,309 unique formula and that decreases to 1,275 unique formulae at Day 400.

comparing Day 0 to Day 400 highlights the difference in degradation kinetics of these two soils because although both samples have a variety of molecules with a $H/C > 1.5$, only the CL soil shows a loss of these unique molecules from the system over time. And conversely, the BH soil

actually shows an increase in the amount of unique aliphatic formula in the soil, which could be a function of SOM transformation, or more likely, a loss of these molecules from the CL soil and not from the BH soil. To further support these conclusions of degradation kinetics and molecular lability, the Nominal Oxidation State of Carbon (NOSC) was calculated, a value based on the molecular formula assigned from the FT ICR-MS.

3.2 Nominal Oxidation State of Carbon (NOSC)

One technique to analyze the balance between “energy availability” and “energy density” for the different molecules identified by FT ICR-MS is the calculation of NOSC. An example of the end-members of NOSC would be the most reduced species of carbon, methane (CH₄) with a NOSC = -4, while the most oxidized species of carbon would be carbon dioxide (CO₂) with a NOSC = +4.

$$\text{NOSC} = - \left(\frac{-Z + 4C + H - 3N - 2O + 5P - 2S}{C} \right) + 4$$

By calculating the average NOSC for every formula identified in the DOM from each soil, we can further highlight the differences in lability and available energy of the SOM in these two amended soils. The average NOSC calculated from the molecular formula in the CL-Day 0 sample was found to be 0.126 (primarily oxidized molecules) but when focusing solely on the formula unique to CL-Day 0, compared to BH-Day 0, the average NOSC value is 0.242. Conversely, when calculating the average NOSC for every formula in the BH-Day 0 samples, the value was -0.049 and the average NOSC for the formula unique to BH-Day 0, when compared to the CL-Day 0

sample, was -0.375 (Figure 3.7a). Therefore, it is clear from these unique formula that the biochar amendment is comprised of organic molecules that are more reduced, including some alkanes/lipids that have NOSC values close to -2, these are shown on the VKDs in Figure 2 and 3 as the points at $H/C = 2$ and $O/C < 0.3$. Accordingly, the DOM in biochar is more energy dense but the microbes are also required to utilize energy to degrade these molecules which is going to alter the degradation mechanisms the microbes utilize [36].

These NOSC results demonstrate that the native SOM is in more of an equilibrium state with a NOSC closer to zero but the addition of either biochar (reduced molecules) or compost (oxidized molecules) shifts that average SOM NOSC either positive or negative depending on the amendment. This difference in NOSC has a substantial impact on the fate of the carbon molecules and whether they will be mineralized and released to the atmosphere as CO_2 or preserved in the soil and added to the pool of native SOM. The compounds with larger (more positive) NOSC values found in the CL soil are decomposed faster (preferentially) and mineralized by the microbes for energy whereas the biochar soil with reduced compounds results in an opposite effect. When microbes utilize reduced compounds, such as the ones found in the BH soil, they are more likely to incorporate these molecules into cellular components such as their cell wall or other biopolymers [36]. This is an important distinction because when these SOM molecules are incorporated into the cell, instead of being utilized as an electron acceptor during microbial metabolism, they are likely to remain incorporated in the structure until the microbe dies. Subsequently these molecules become microbial necromass, one of the most persistent components of SOM and by some estimates, a majority of the SOM is composed of microbial necromass [37]. Thus, a reduced soil amendment such as biochar encourages the microbiome to incorporate the organic molecules into the cell and eventually be added to the soil in a persistent

form that increases SOM concentrations, while conversely when using an oxidized amendment such as compost the microbes are stimulated to mineralize these molecules into CO₂ and less SOM is preserved.

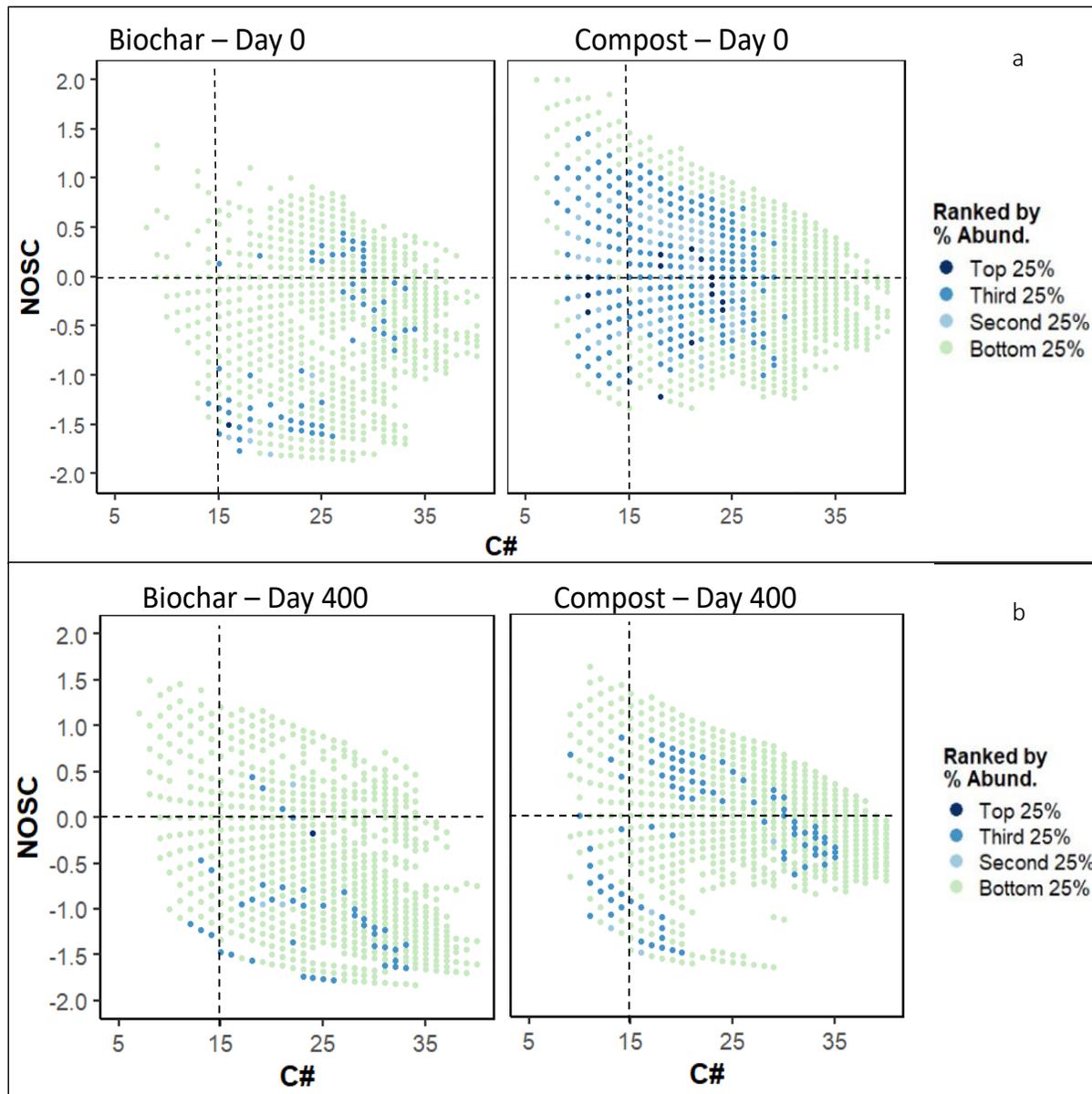


Figure 3.7 - NOSC values for every unique molecular formula (when comparing the amendments to each other) in the samples at Day 0 (top) on Day 400 (bottom), The number of carbons associated with these NOSC values are on the x-axis. Average NOSC for biochar is -0.375 while average NOSC for compost samples = 0.242 at Day 0 while average NOSC for unique formula at Day 400 is -0.449 for biochar and 0.198 for the compost soil.

Over the course of 400 days there are shifts in the average NOSC values of these soils that support the previous conclusions about SOM persistence and varying degradation rates between the soils. First, when calculating the NOSC of every formula in these soils at Day 400, the NOSC for the CL sample decreases by about 0.04 to a total NOSC of 0.088. While the average NOSC of the BH sample only decreased by 0.001 to a final NOSC of -0.048, or essentially remained constant (Figure 3.7b). This figure also demonstrates a loss of unique formula in the same manner as other VKDs, the CL soil is losing unique formula and concurrently the BH soil is gaining unique formula. This demonstrates that not only are these molecules disappearing from the CL soil, but the BH soil is also undergoing some molecular transformation and these molecules are appearing over 400 days. Most interesting is that some of the unique molecules in the BH sample that are appearing at Day 400, are molecules with a NOSC over 1, molecules that should have been degraded over the course of the study. However, when considering only the unique molecules in each sample, the average NOSC of these formula in each soil show that both soils became more reduced. The BH soil decreased by .07 to -0.449 while the CL soil decreased by 0.044 to 0.198.

3.3 Quantifying SOM Transformation

Analysis of three common soil health parameters was conducted to overcome the limitations of the FT-ICR MS analysis, specifically the inability of the instrument to have quantifiable results, and support the trends seen in the VKD. Specifically, these results support the evidence from the VKD that the biochar soils were undergoing molecular transformation without significant loss of carbon while the compost soils were not only undergoing molecular transformation, but the organic matter was also getting oxidized at a higher rate and lost from the

system. Quantifying changes in SOM concentration, CO₂ mineralization rate via 96-hour soil incubations, and extracellular enzyme activity was utilized as complementary data since these are effective methods to quantify soil health [25] and can support the hypothesis derived from the molecular analysis in the VKD. These quantifiable soil health metrics are also analogous to each other since changes in SOM concentration would be directly related to the CO₂ mineralization rate of the soil which would also be correlated to the activity of the carbon cycling enzymes present.

One of the limitations of this study's design was the sample size since each unique amendment/application rate only had a sample size of $n = 3$. This was because the primary focus of this study was to utilize high-resolution analytical techniques like FT ICR-MS, ICP-MS, and 16s-rRNA extractions to make comparisons between the samples but this analysis is expensive and time-consuming, so the number of samples analyzed had to be limited. For example, when analyzing trace metals in the ICP-MS, organic molecules in the FT ICR-MS, microbial populations via 16s-rRNA extractions, and EEA using fluorometric techniques we had to utilize composite samples (each triplicate combined in equal proportions into one sample) to maximize our resources for this wide variety of analysis. So, while this was necessary for those analysis, other analytical methods such as SOM concentrations or CO₂ mineralization were conducted with the individual samples, but that sample size was the minimum value needed for statistical analysis ($n=3$). Thus, due to these limitations the following results measuring SOM, mineralization rate, and EEA do not have any statistics associated with them and the figures emphasize the percent change. These figures should be viewed as complementary to the high-resolution analysis that was conducted on these samples instead of statistically significant values.

The following figures focus specifically on percent change over 400 days since the soils for each triplicate were only homogenized within the samples, so the starting SOM concentrations

of these soils were all slightly different. Over the duration of the study the soil with a low rate of biochar (BL) had an increase in SOM of 4.6% while the soil with a high rate of biochar (BH) had

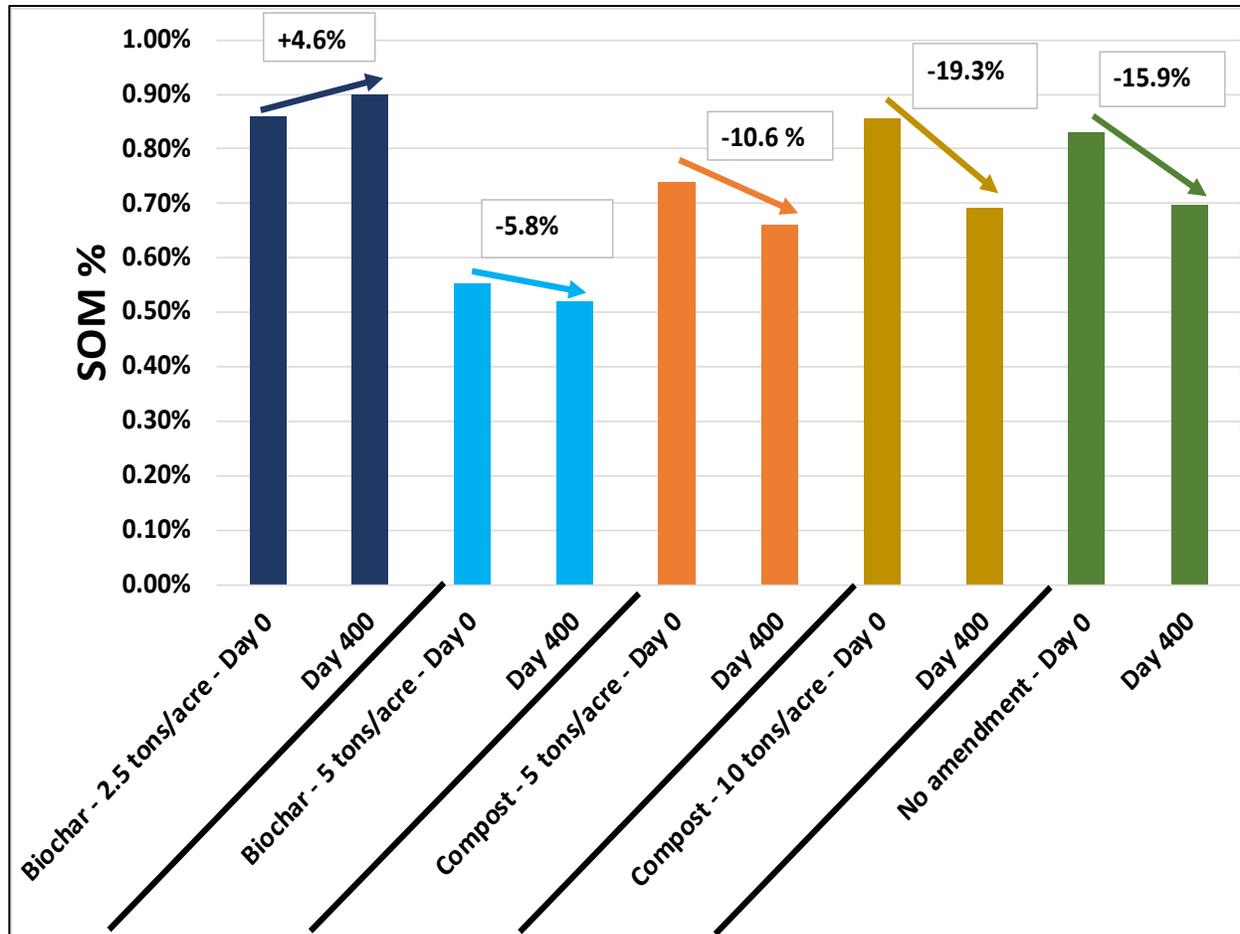


Figure 3.9 - changes in SOM concentrations for 5 different groups of samples over the course of 400 days. Molecular level analysis focused on the samples with application rates of 5 tons/acre

a decrease of 5.8%. Conversely, the soil with a low rate of compost (CL) had a decrease of 10.6% and the soil with a high rate of compost (CH) had a decrease of 19.3% (Figure 3.9). Some soils were analyzed that did not have any amendment added, only a cover crop grown, and this soil showed a ~16% decrease over the course of 400 days. Concurrently, the CO₂ mineralization rate analysis showed similar trends as the SOM data.

The compost soil, which had decreases in SOM concentration, also showed the largest rates of mineralization (Figure 3.10). Consistent with previous results, both compost samples showed opposite trends from the biochar amended soils. First, the compost soils had mineralization rates at Day 0 that were twice as high as the biochar amended soils, CL = 0.67 $\mu\text{mol C day}^{-1} \text{g soil}^{-1}$ and CH = 0.60 $\mu\text{mol C day}^{-1} \text{g soil}^{-1}$. And second, over the course of 400 days, this mineralization rate decreased by 35.3% and 16.4% to a final rate of 0.43 $\mu\text{mol C day}^{-1} \text{g soil}^{-1}$ and 0.50 $\mu\text{mol C day}^{-1} \text{g soil}^{-1}$ respectively. Conversely, the biochar amended soils had an initial mineralization rate about half of the compost soils starting rate and then this rate increased over time. The BL sample started at 0.32 $\mu\text{mol C day}^{-1} \text{g soil}^{-1}$ then increased 21% to 0.39 $\mu\text{mol C day}^{-1} \text{g soil}^{-1}$ while

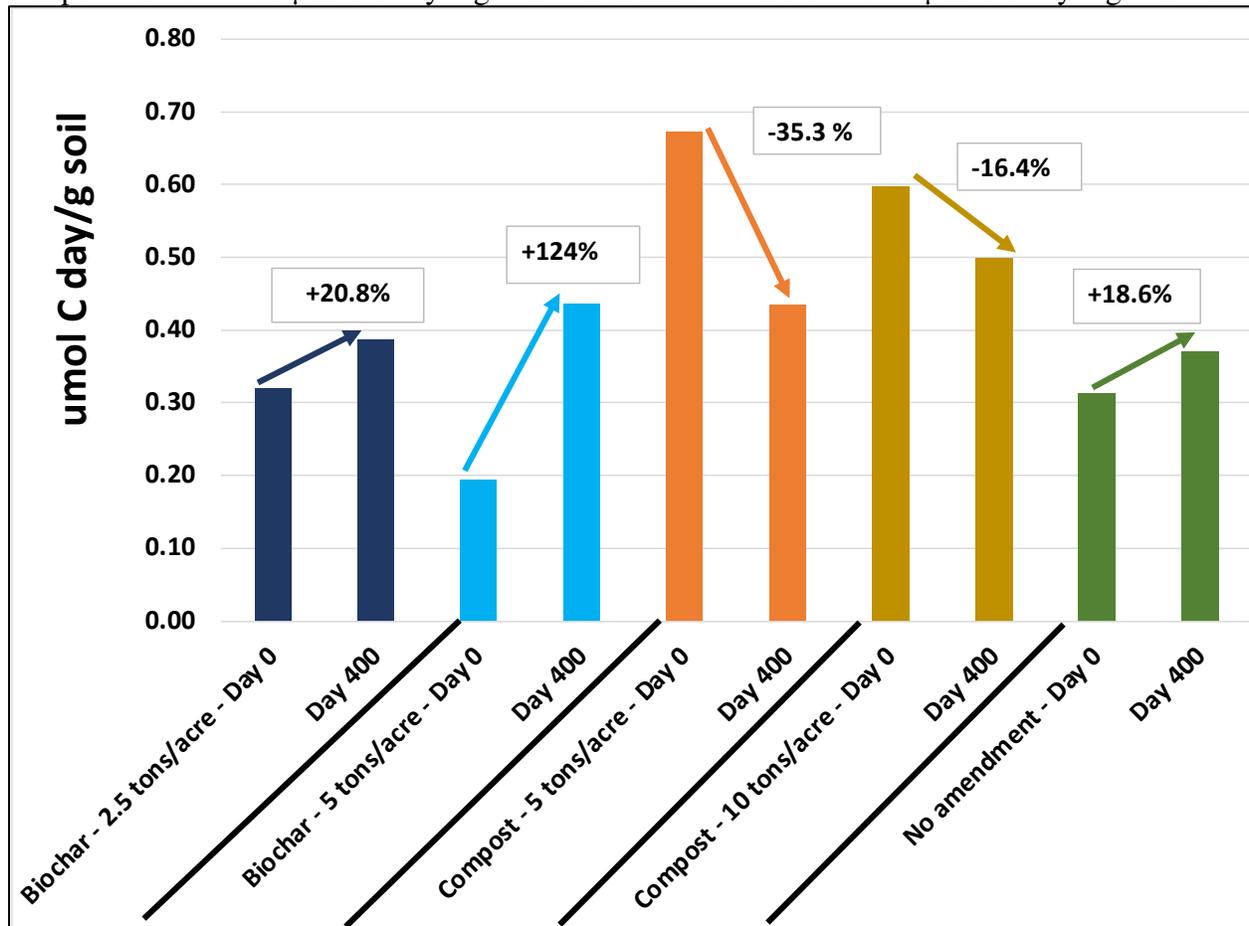


Figure 3.10 – carbon mineralization rate of biochar and compost at two different application rates as well as a soil with no amendment added

the BH sample started at $0.19 \mu\text{mol C day}^{-1} \text{ g soil}^{-1}$ then increased 124% to $0.44 \mu\text{mol C day}^{-1} \text{ g soil}^{-1}$. This supports the conclusions from the FT ICR-MS results that demonstrated that the compost amended soil had SOM that was composed of more labile molecules with higher NOSC values that would be mineralized more readily than the biochar amended soils.

Activity of extracellular enzymes are also closely related to changes in SOM concentration and mineralization rate since the activity of these enzymes is stimulated by the microbial population that is utilizing these various organic compounds for energy and microbial respiration. The mechanisms impacting EEA vary widely between soil systems and any changes can depend on texture, pH, SOM, and the microbial community but in a mineral soil like this one, microbial diversity and pH are would have the biggest influence on EEA [38]. Soil amendments also influence EEA in different ways, for example when biochar is added to an acidic soil it can increase the activity of certain enzymes and it typically increases microbial biomass as well [39]. Since the pH of these soils was relatively consistent between samples, it is likely that the microbial diversity would be different between these soils and is why this analysis will be included before this research is submitted for publication in a scientific journal.

Five different carbon cycling enzymes (β -Glucosidase (BG), β -D-cellubiosidase (CB), β -Xylosidase (XYL), α -Glucosidase (AG) and N-acetyl- β -Glucosaminidase (NAG)) plus one enzyme relating to phosphate cycling (Phosphatase (PHOS)) were analyzed. Activity of the AG and BG enzymes increased over the course of the study for BL, CH, and CL but for the BH sample, the activity of AG decreased from 2.71 to 2.27 nmol activity/g soil/hour, a decrease of 16%. Conversely, the AG activity of the BL sample had an increase from 1.84 to 2.58 nmol activity/g soil/hour (40%) (Figure 3.11). These two enzymes are synthesized specifically for degradation of low-molecular weight sugars (molecules with weight below the FT ICR-MS limit of detection

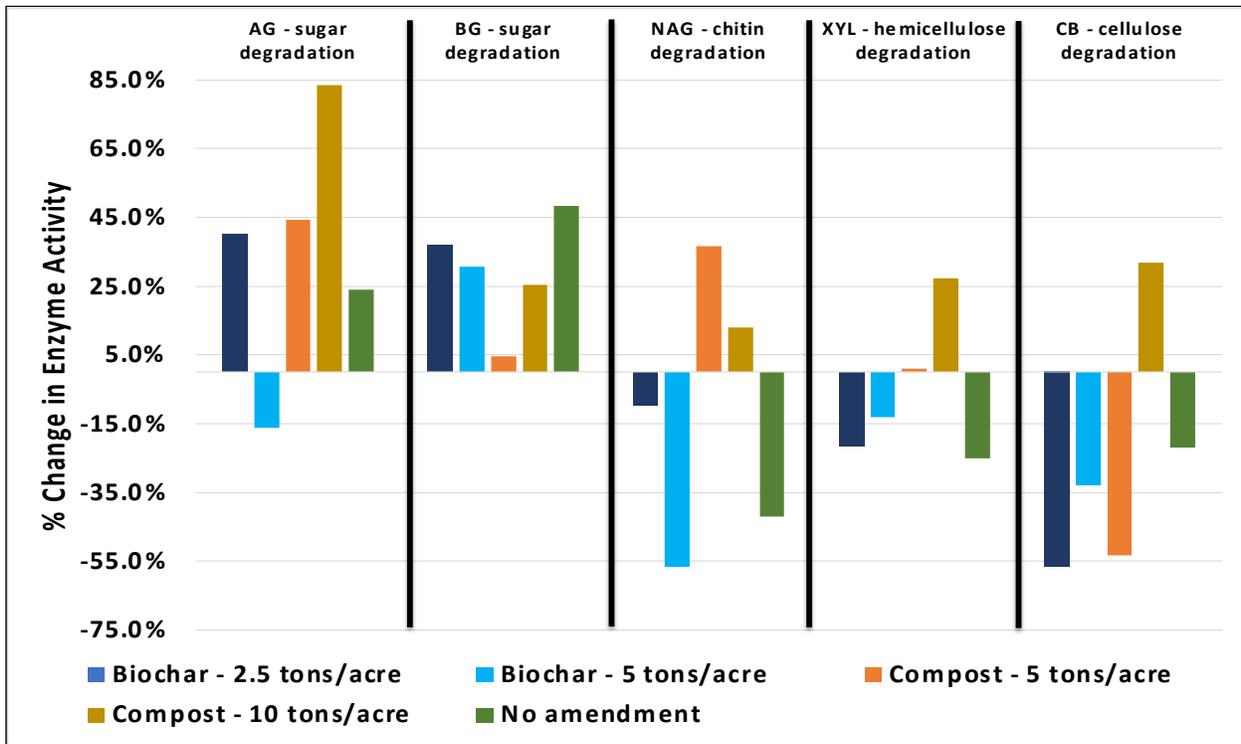


Figure 3.11 – changes in extracellular enzyme activity for five different carbon-cycling enzymes: β -Glucosidase (BG), β -D-cellubiosidase (CB), β -Xylosidase (XYL), α -Glucosidase (AG) and N-acetyl- β -Glucosaminidase (NAG). The substrates for enzymes AG and BG are primarily derived from root exudates while substrates for the three enzymes on the right are primarily derived from plant litter, or in this case the substrates from the organic amendments

(~200 Da)) and are likely added to the soil system as root exudates from the cover crop. The influence of the cover crop on EEA is highlighted in Figure 3.12, this figure displays EEA for the soils with no plants grown and shows how important the influence of root exudates are in stimulating EEA and influencing the corresponding soil microbiome. Because when there are no root exudates, there is a decrease in EEA regardless of what amendment is added to the soil but when there is only a cover crop and no amendment, there is still an increase in EEA for those soils.

Activity of NAG, XYL, and CB had decreases in EEA for both BH and BL samples that ranged from 9% to 56%, while the compost amended soils had increases in EEA for all but one of these samples. The CL sample had a decrease in enzyme activity from 2.37 to 1.11 nmol activity/g soil/hour (53%) for the CB enzyme while the CH soil had a 32% increase from 1.107 to 1.41 nmol

activity/g soil/hour. Both compost soils had increases in XYL and NAG activity with the CH sample having a larger increase over time for the XYL enzyme (27%) while the CL sample had a larger increase over time for the NAG enzyme (37%). Lastly, the changes in EEA for the phosphatase enzyme were similar for every sample and likely an effect of adding fertilizer containing P since every sample showed increases in this EEA. Overall, the changes in EEA over time support the results of both the changes in SOM and mineralization rate as well as the molecular level analysis conducted with FT ICR-MS. It is clear that the compost amended soils have quicker degradation of the soil amendment while the biochar is adding DOM to the soil that will likely become a more persistent form of SOM.

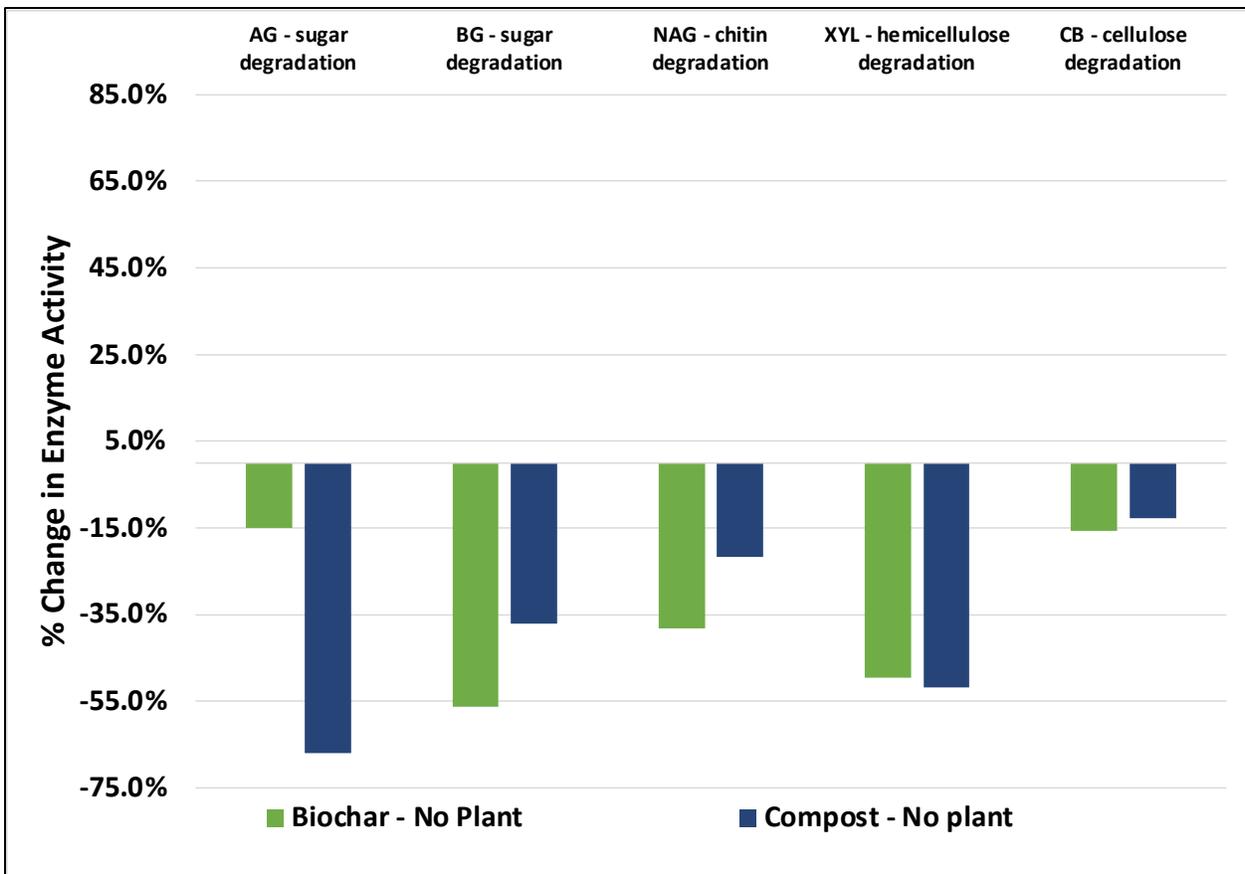


Figure 3.12 - changes in enzyme activity over 400 days for soils with no plants grown and only compost or biochar added at a rate of 5 tons/acre

3.4 *Physiochemical Analysis*

Nitrate and ammonium extractions showed that all samples had a consistent trend of both nitrogen forms being depleted from the soil over the course of the study and a majority of these Day 400 concentrations were below the limit of detection of 0.1 ppm. This was expected since these soils are inherently low in nutrients and the soils were only fertilized once per month. However, the Day 0 samples for soils amended with equal masses of compost and biochar ($n = 3$, this includes the soils that no amendment and both types of cover crop) had significantly different amounts of either ammonium or nitrate, depending on what amendment was added. The soils amended with compost at 5 tons/acre (CL) had an average initial soil nitrate concentration of 7.0 mg/kg while the soils containing biochar applied at 5 tons/acre (BH) had 0.56 mg/kg of soil nitrate, values that were significantly different ($p < 0.05$). Conversely, the CL samples started with 1.78 mg/kg of soil ammonium, and this was significantly lower ($p < 0.05$) than the BH samples which had 5.25 mg/kg. Compositional analysis of the biochar amendment did show it had some inorganic nitrogen remaining after pyrolysis, ammonium = 8.4 mg/kg and nitrate = 3.0 mg/kg, and that correlates to these results. Assuming minimal soil nitrogen to begin with, these results show that a large proportion of biochar's inorganic nitrogen is extractable, and each amendment supplies a significantly larger amount of each form of nitrogen to the system. Typically in compost, only a small proportion of the nitrogen remains for plant uptake after synthesis since a majority of it is utilized by microbes during the composting process but compost is rich in other micronutrients and can be used to partially replace inorganic fertilizers, but it only provides a small percentage of the required nitrogen [14].

Analysis of other bioavailable soil nutrients (i.e., P, K, and micronutrients) was conducted in the ICP-MS with composite samples, so, the following values represent the average

concentration of each triplicate. Similar to the analysis of inorganic nitrogen, all samples generally showed depletion of nutrients over time since they were all fertilizer limited. Some nutrients did show differences between initial soil concentrations in the various samples but due to the composite analysis technique, the following differences between samples cannot be verified statistically. The two composite samples of BH had an average P concentration of 32.2 mg/kg and this was similar to the two composite samples of CL that had a value of 37.3 mg/kg. Most micronutrients had similar values between samples that would require larger sample sizes to confirm any statistical differences, but the concentrations of Ca and K had large differences between amended soils so if each triplicate had been analyzed, this difference would have likely been significant. The BH soils had an average Ca concentration of 66.4 mg/kg and an average K concentration of 15.0 mg/kg, compared to the CL soils that had an average Ca concentration of 205.2 mg/kg and an average K concentration of 43.6 mg/kg.

These results show that not only is compost a nutrient rich material but some nutrients in the compost are bioavailable since these differences occurred before any inorganic fertilizer was added to these soil systems. Compositional analysis of the biochar showed that the biochar also contained substantial levels of some nutrients like P and K. (K) = 8932 mg/kg, total phosphorus (P) = 843 mg/kg, but based on the analysis of the bioavailable nutrients, less than 1% of K is extractable and less than 5% of total P is extractable. These calculations also assume no extractable P or K was present in the soil before addition of the amendment, which is unlikely, so these percent extractable values are likely even lower.

Soil from this specific citrus grove in Florida has previously been analyzed for texture and that analysis showed that this soil is 95+% sand and was from the soil class Spodosol [40]. Consequently, due to the texture and sub-tropical climate, this soil is mildly acidic but still ideal

for growing citrus trees. The pH of this soil immediately following addition of the amendment showed that all soils had a pH ranging from 5-6. Over the course of the study, most soils either stayed relatively consistent in acidity or became slightly more alkaline, but none had any changes greater than 1 pH unit. The CL and BH soils both had slight increases in pH over 400 days and finished at 6.44 and 6.06 respectively.

4. CONCLUSION

Soils support a wide variety of functions which will dictate how a soil is managed but typically, maintaining adequate levels of SOM is an essential part of every soil system. Therefore, when adding an organic amendment to the soil, it is important to consider the persistence a specific amendment might have in the soil in order to help maintain the concentration of SOM. The results of this study demonstrate on a molecular level why biochar is more persistent than compost because biochar is composed of a larger portion of reduced molecules with lower NOSC values. These molecules are still able to be utilized by the microbial community but instead of being mineralized as terminal electron acceptors, they are incorporated into the cellular components of the microbe eventually ending up as microbial necromass, a persistent portion that comprises the majority of SOM. Nutrient analysis demonstrated why compost can be used to replace some of the fertilizer needs of different crops since our results showed the compost amended soils contained larger concentrations of nitrate, P, and K. Consequently, compost stimulated the soils it was added to, but one could argue that the compost overstimulated the soil and provides the microbes with more of a short-term “sugar rush.” On the other hand, the biochar amendment also stimulated the soils since there were increases in mineralization rate and EEA over time, but it also demonstrated why it can be persistent in the soils for decades with its large proportion of reduced, “slow-release,”

organic molecules. Lastly, it is important to understand that the generalizability of these results is limited because every organic amendment can be different depending on how they were formed, and each reacts differently in different soil types. For example, this biochar is a wood-based biochar formed at high-temperature, so it is likely to have more carbon and less lability than a biochar formed from a different feedstock and synthesized at a lower temperature. Overall, our results demonstrated on a molecular level the different compositions of these common soil amendments and showed why an amendment such as biochar, with molecules that are more reduced, is a better option when considering the persistence of SOM in the soil.

Author Contributions

According to the CRediT (Contributor Roles Taxonomy) criteria my contributions to this paper include conceptualization, methodology, validation, formal analysis, investigation, writing-original draft, and visualization. Contributions from T.B. include conceptualization, resources, writing – review & editing, supervision, project administration, and funding acquisition. Contribution from M.L. include visualization, formal analysis, and data curation. Contributions from P.T. include conceptualization, methodology, resources, visualization, writing – review & editing, and funding acquisition. Contributions from A.M. include investigation and data curation.

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CHAPTER 4: OPPORTUNITIES FOR TREATMENT AND REUSE OF AGRICULTURAL DRAINAGE IN THE UNITED STATES

1. INTRODUCTION

Irrigation withdrawals including urban irrigation (i.e., golf courses, parks, nurseries) account for approximately 42% of the total freshwater withdrawals in the United States (U.S.) (Supporting Information (SI), Figure S4.1).¹ The next three highest freshwater users in the U.S. are thermoelectric power (33.8%), public supply (13.8%), and industrial (5.0%). In addition, agriculture reportedly accounts for more than 85% of human water consumption worldwide.³ The 2018 Irrigation and Water Management Survey reported that 102.9 billion m³ (83.4 million acre-feet) of irrigation water were applied at an average of 4,572 m³ per ha (1.5 acre-feet per acre).⁴

In addition to crop and horticultural production, agricultural water use includes freshwater withdrawals for livestock. However, water withdrawals for livestock are defined as a separate category by the United States Geological Survey (USGS) and include water used for watering, feedlots, dairies, and other on-farm uses.¹ Livestock accounts for 0.7% of the total freshwater withdrawals in the U.S, which equates to 7.57 million m³ (2.0 billion gallons) per day (Figure S1). In addition, meat and dairy processing are estimated to consume more than 1 billion m³ (266 billion gallons) of water each year.¹

According to the 2017 Census of Agriculture, there were more than \$388.5 billion in agricultural product sales, where crops accounted for more than \$193.5 billion.² In 2018, the average off-farm water cost across the U.S., which includes the cost of water from off-farm water

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suppliers (e.g., U.S. Bureau of Reclamation, irrigation districts, ditches, commercial companies, or community systems) and reclaimed water from off-farm facilities (e.g., municipal, livestock, industrial), was \$0.03 per m³.⁴ Depending on the state, the off-farm water cost ranged from \$0.01 per m³ (Wyoming) to \$2.94 per m³ (Rhode Island).⁴ Because human population and global food demand will increase for at least the next 30 years, agricultural demand for water is also likely to grow.⁵

Complicating the challenge of meeting this enormous demand, agricultural water demand is heterogeneous, varying regionally and seasonally. For crops, the required water volume varies with crop type, growth stage, precipitation, and climate, which affects the amount of water consumed through soil evaporation and plant transpiration (i.e., evapotranspiration demand).⁶ Crop yields are reduced when evapotranspiration demand is not met, especially during crop-dependent critical growth stages.⁷ However, agricultural water demand is not limited to evapotranspiration demand. Salt accumulation in the root zone also adversely affects crop yields, inhibiting seed germination, altering water uptake, and causing ion-specific toxicities or imbalances.⁸ As a result, additional water may be needed to leach salts from the root zone and for other crop-related purposes such as field preparation, chemical application, or frost protection.¹

The 17 western-most contiguous states (Western States) typically have more arid climates with appreciably less precipitation than the eastern U.S.⁹ According to the U.S. Department of Agriculture (USDA), the Western States, which contain 46% of the harvested cropland, accounted for 72% of the irrigated acres and 84% of the irrigation volume in 2018.⁴ Similarly, the USGS reported that these states accounted for 81% of all freshwater withdrawals for irrigation in 2015 (Figure 4.1).¹ According to the USGS report, Arkansas, Mississippi, and Florida are the most

intensive irrigators in the eastern U.S. The top five states in irrigated acres and irrigation volumes in 2018 are shown in Table 4.1.

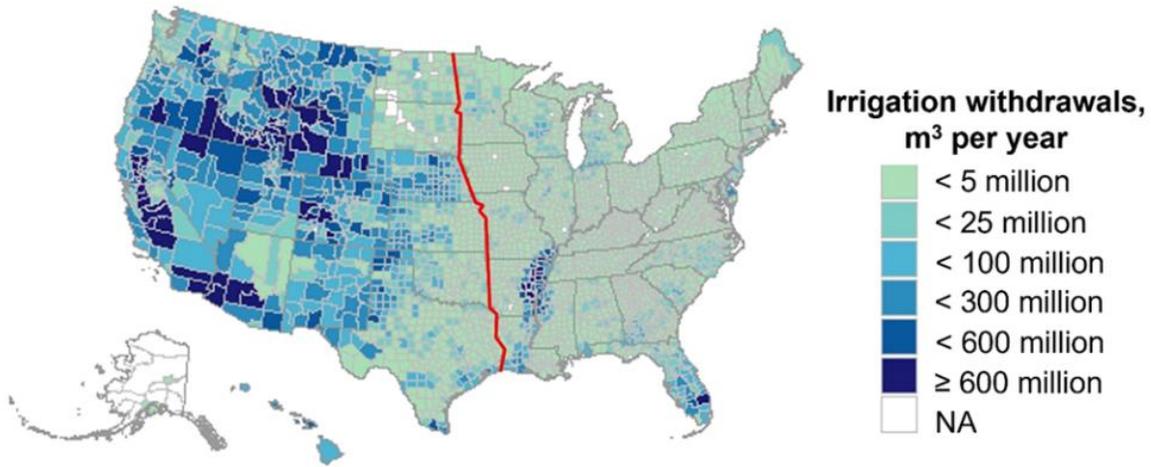


Figure 4.1 – Irrigation withdrawals based on USGS estimated use of water by county in the U.S. in 2015¹. The red line divides the U.S. into two regions: 17 western states (left) and 31 eastern states (right).

Table 4.1 - Top Five States in Irrigated Acres and Irrigation Volume⁴

State	Irrigated land		State	Irrigation volumes	
	hectares	acres		m ³	acre-feet
California	3.4 million	8.4 million	California	30.2 billion	24.5 million
Nebraska	3.1 million	7.7 million	Idaho	8.1 billion	6.6 million
Arkansas	1.7 million	4.2 million	Texas	6.5 billion	5.3 million
Texas	1.6 million	4.1 million	Arkansas	6.3 billion	5.1 million
Idaho	1.4 million	3.4 million	Nebraska	6 billion	4.9 million

1.1 Water Supplied to Agriculture.

1.1.1. Traditional Sources: Surface and Groundwater.

Fresh groundwater and surface water are the primary sources used across the U.S. to meet the nation’s agricultural irrigation water demand. In 2015, 48.4% of the total freshwater withdrawals for irrigation were attributed to groundwater, compared to surface water, which accounted for 51.6% of these withdrawals.¹ The substantial reliance on groundwater and surface

water for irrigation is due to several factors, including proximity and accessibility to traditional sources, minimal infrastructure requirements, and the relatively high water quality compared to nontraditional source waters (e.g., municipal wastewater, brackish water, produced water, and agricultural wastewater). However, the changing precipitation patterns (i.e., global warming and climate change), the pressure of the growing population, and the increase in competition among sectors (e.g., municipal, industrial) are driving the agricultural sector to explore additional and more sustainable water sources to meet the future agricultural water demand.

1.1.2. Nontraditional Sources: Municipal Wastewater, Seawater, and Brackish Groundwater.

The use of nontraditional water sources for irrigation is not a new concept and has been practiced in many countries to irrigate crops, golf courses, forests, and open-space landscapes.¹⁰ For example, more than 85% of treated wastewater is reused for agricultural irrigation in Israel, accounting for 50% of the total agricultural water use.¹¹ Desalinated seawater accounts for 40% of Israel's freshwater irrigation consumption.¹² However, in the U.S., there is a tremendous potential for expanding the use of alternative water sources for irrigation. For example, only 3.8% of the daily municipal wastewater volume is reused for agricultural and urban irrigation.¹³ Similarly, brackish ground- water (i.e., groundwater having total dissolved solids (TDS) levels ranging from 1,000 to 10,000 mg/L) accounts for 20% of groundwater in the U.S. and remains largely untapped for agriculture.¹⁴ Finally, the reuse of low-salinity produced water from oil and gas extraction for agricultural irrigation has been limited. The one prominent example is in Kern County, California, where low-salinity produced water (i.e., <1,000 mg/ L) has been treated and blended with freshwater for over 20 years.^{15,16} This complex reuse scenario has been investigated previously

and was further explored through road mapping and baselining efforts at the National Alliance for Water Innovation (NAWI) hub.¹⁷⁻²¹

Using nontraditional source waters for irrigation brings new challenges related to water quality as the chemical and microbial composition of these sources is profoundly different from freshwater sources. In general, good quality irrigation water is colorless, odorless, and foamless with circumneutral pH, minimum turbidity, TDS below 1,000 mg/L, and specific conductance below 150 mS/cm.²² Therefore, when considering nontraditional water sources for agricultural purposes, it is essential to identify the critical constituents affecting plant and soil conditions during long-term application. For example, reusing municipal wastewater for the irrigation of crops may result in the continuous exposure of the agricultural environment to contaminants of emerging concern (CECs), such as antibiotics, antibiotic-resistant bacteria (ARB) and antibiotic resistance genes (ARGs), engineered nanoparticles, pharmaceuticals and personal care products (PPCPs), endocrine-disrupting chemicals (EDCs), per- and polyfluoroalkyl substances (PFAS), microplastics, and pathogens.²³⁻²⁷ In addition to persistent organic pollutants and pathogens, elements (e.g., arsenic (As), boron (B), chloride (Cl), and selenium (Se)) present in excess amounts in nontraditional water sources can accumulate in soils and be taken up by crops.¹⁸

1.2. Water Discharged from Agriculture

Agricultural wastewater is produced from various farm activities, including commercial grain farming, produce processing (vegetables, fruits, etc.), cattle feedlots, dairy operations, and animal product processing (beef, poultry, pork, milk, cheese, etc.). The largest volume of agricultural wastewater is attributed to agricultural drainage, where it has been estimated that 170 million m³ (45 billion gallons) of excess irrigation water, containing valuable nutrients (i.e., nitrate

and phosphate), drains off agricultural fields every day in the U.S. (Figure S4.2).²⁸ Agricultural drainage volumes across the country have high spatial and temporal variability that depend on climate (primarily precipitation), soil type, crop type, topography, applied irrigation, and groundwater level.⁶

The large volumes of agricultural drainage in the 31 eastern-most contiguous states (Eastern States) compared to the Western States, are mainly due to the higher precipitation levels in these areas.⁹ In contrast, the low precipitation levels in the Western States necessitate higher irrigation volumes to support crops in these arid environments, with California being the largest consumer in the U.S. (Figure 4.1).¹ Agricultural drainage contains valuable nutrients that can be recycled back onto the fields. Like the previously mentioned nontraditional water sources, the use of agricultural drainage poses new challenges when using it as an irrigation water source because agricultural drainage can potentially include other constituents such as pesticides, microbes, salts, metals, or CECs (e.g., PFAS). Additionally, in the Western States, the high TDS concentrations and the presence of toxicants can hamper its direct reuse.²⁹ For example, in California's San Joaquin Valley, one of the most productive farming regions in the U.S., drainage can have TDS concentrations ranging from 5,000 to 20,000 mg/L.^{30,31}

In addition to agricultural drainage, it is important to acknowledge that the meat and dairy industries within the agricultural sector contribute significantly to wastewater volumes. In fact, wastewater generated by the agricultural meat and dairy processing facilities can reach up to 6.8 million m³ (1.8 billion gallons) per day. The meat and dairy processing industries are responsible for 36% of the water consumption in the food and beverage processing industry.³² However, wastewater flows from meat and dairy processing represent an even higher share of the food and beverage industry due to the large volumes of wastewater produced by cheese processing facilities

when removing whey from milk solids.²¹ The wastewater produced in these operations is typically treated and discharged to surface waters or blended with municipal wastewater for further treatment.³³ However, additional treatment of this nontraditional source to meet irrigation water quality requirements could provide a nutrient- rich water product that could meet up to 1.5% of the total demand for irrigation.^{2,34-40} Further details on the challenges and the research needs for reuse of beef processing wastewater can be found in the NAWI Technology Roadmap for the Agriculture Sector.²¹

1.3. Scope

This study evaluates the largest subset of agricultural wastewater, agricultural drainage water, for reuse in agricultural operations. We first review the characteristics of this new source water, its current reuse strategies, and potential reuse opportunities for agricultural applications. Due to the high temporal and spatial variability of individual farms (unique management practices, crop types, climate, and soil types), a regional approach was taken to evaluate the current and potential opportunities for reusing agricultural drainage for irrigation. Furthermore, we employ a new decision-support tool called WaterTAP3, developed by NAWI, to evaluate the treatment train for a selected case study to estimate the levelized cost of water (LCOW) and electricity requirements.⁴¹ A more detailed description of the WaterTAP3 methodology and assumptions can be found in the SI (see Text S1). In the final section, based on the literature review and case study analysis, we further discuss the challenges, opportunities, and future research needs to expand the reuse of agricultural drainage for irrigation in the U.S.

2. AGRICULTURAL DRAINAGE WATER

Agricultural drainage water is commonly used for irrigation by downstream agricultural producers but can also potentially be reused in the same region as supplemental irrigation water if applicable water laws permit. It is also important to note that treatment and reuse of agricultural drainage is not limited to providing irrigation water, but it is also essential to prevent freshwater salinization, eutrophication, and other environmental pollution (e.g., Se contamination). In the Midwest region, defined as the Mississippi River watershed, of the USGS SPATIally Referenced Regressions on Watershed attributes (SPARROW) model, agricultural drainage can contain up to 8 kg N fertilizer per hectare per year (3.24 kg N fertilizer per acre per year),⁴² which intensifies eutrophication events downstream and has annually caused over billion dollars in economic damage to freshwater/coastal areas in the Midwest and Gulf Coast.⁴³ For reference, the typical corn field in the Midwest receives about 60–80 kg N/acre/year, but this is subject to spatial variability as fertilizer application and discharge in some areas is minimal and depends on preceding crop rotations.⁴⁴ The main constituents of drainage in this region are nutrients, making direct reuse on-site with minimal treatment feasible.⁴⁵ In the Western States, agricultural drainage can contain high levels of salts and other constituents including nitrates, arsenic, boron, cadmium, lead, mercury, molybdenum, nickel, selenium, silver, uranium, vanadium, and traces of other constituents, depending on the location.⁴⁶

The right to divert, capture, and reuse drainage water is governed by water laws.⁴⁷ These laws vary from state to state, but two primary allocation systems have been followed: (1) The riparian doctrine governs the eastern U.S. (water-abundant areas); (2) The prior appropriation doctrine governs most of the western U.S. (water-scarce areas). Under the prior appropriation doctrine, prior established water uses are given greater seniority than later, compared to the riparian doctrine, where use is based on the property's proximity to the water source.⁴⁸ However, a few

states, including California, have adopted a hybrid system that incorporates elements of both systems.⁴⁹ Prior appropriation-based water laws in some Western States combined with the unique constituents of agricultural drainage in this region pose challenges to drainage water reuse for agricultural activities. However, the need for irrigation water, the abundance of agricultural activities, and the toxicity of agricultural drainage have driven regions in California to start assessing potential management strategies for saline drainage.

Figure 4.2 portrays common pathways for agricultural drainage and the potential pathways for treatment and reuse. The reuse of drainage water in the midwestern and southeastern regions is more common (but still not prevalent) and typically consists of capturing and storing water in a reservoir, then irrigating crops during dry periods.⁵⁰ In some western regions, advanced treatment technologies such as reverse osmosis (RO) may be required to reuse saline agriculture drainage for irrigation (e.g., California). However, such technologies are not widely adopted for agricultural drainage treatment due to the high costs associated with the technology infrastructure, energy requirements and brine disposal.⁵¹

3. REUSE OF AGRICULTURAL DRAINAGE WATER FOR IRRIGATION

Engineered drainage systems, including subsurface (i.e., tile drainage) and artificial surface drainage, are heterogeneously dispersed throughout the U.S. to remove excess irrigation water and precipitation from agricultural fields (Figure S3) and do not always coincide with places where irrigation demand is high. For example, the Western States, which account for more than 80% of irrigation withdrawals,¹ account for only 7% of the acres drained by tile drainage² and 29% of the acres drained by artificial surface drainage.² Nevertheless, where irrigation demand and engineered

drainage systems intersect, drainage water could be reused for irrigation, subject to applicable water laws.

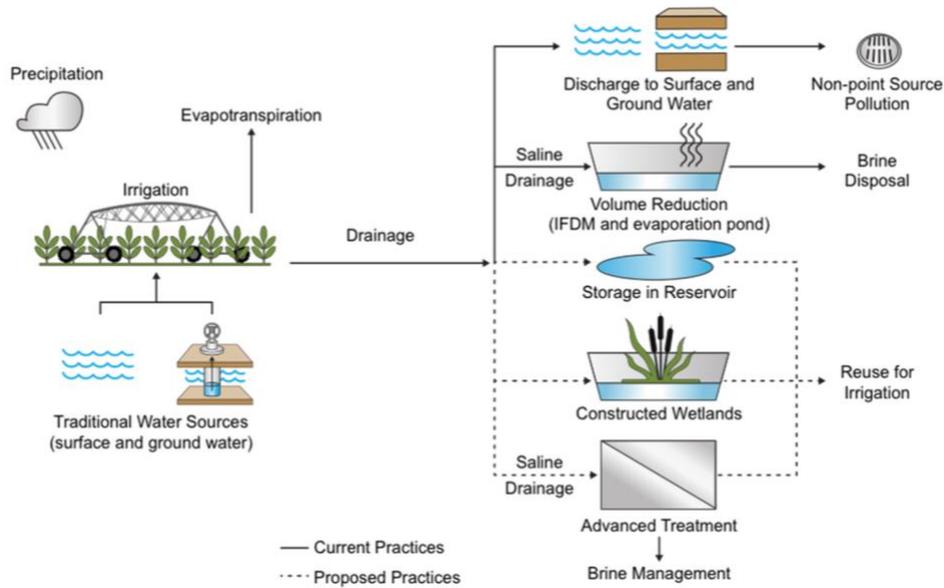


Figure 4.2 - Typical pathways for agricultural drainage (solid lines) and potential pathways (dashed lines) for drainage reuse to develop a circular water economy

Figure 4.3 estimates tile drainage reuse potential across the country by multiplying the irrigation withdrawals in Figure 4.1 by the fraction of farmland in each county that is drained by tile.² In effect, it links irrigation amounts to tile drainage capacity but fails to account for precipitation, which increases return flows, or consumptive use/evapotranspiration, decreasing return flows. The tile drainage reuse potential in the Western States may be optimistic as consumptive use is high with current irrigation methods, and precipitation is generally limited. Using these assumptions, it is estimated that 833 million m³ (220 billion gallons) per year are potentially available for reuse, with the Western States accounting for 65% of the total tile drainage reuse potential. This calculated reuse potential is considered the “low-hanging fruit” for tile

drainage reuse as these regions already have efficient collection systems (i.e., tile drains) installed in their fields, so the reuse systems are already partially constructed. These fields would require the installation of storage ponds and pumping systems to directly reuse this water. However, the construction of storage ponds on farms could require farmers to transfer land from crop production to water storage.

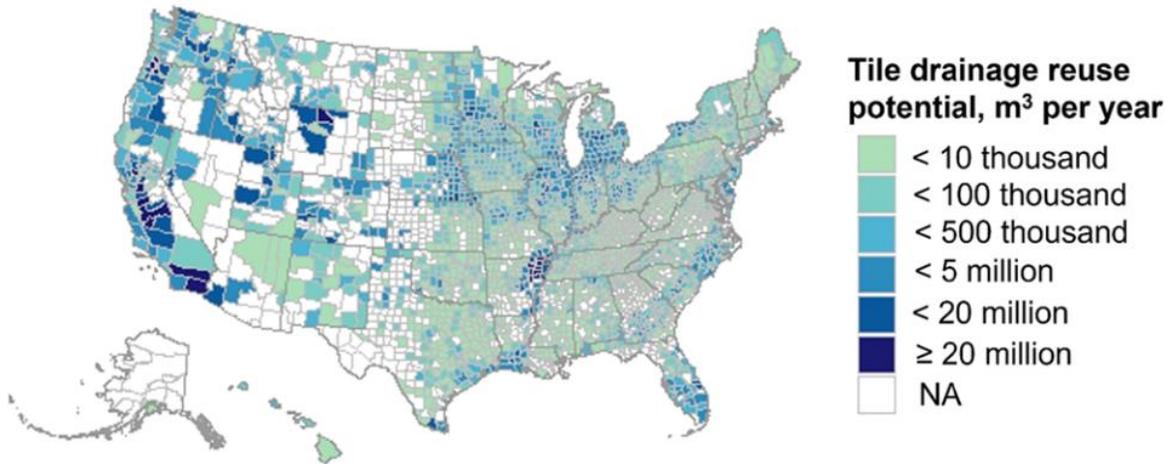


Figure 4.3 - Tile drainage reuse potential in counties across the U.S. based on irrigation withdrawals and percent farmland drained by tile. ^{1,2}

3.1. Reuse of Tile Drainage for Irrigation in the Mississippi River Watershed

The implementation of subsurface tile drainage systems in agricultural fields is a common practice in the poorly drained soils of the upper Midwest.² This type of drainage system lowers the water table and prevents saturation of the root zone by increasing the water drainage rate through the soil.⁵² A typical tile drainage system consists of perforated pipes (e.g., high-density polyethylene (HDPE), polyvinyl chloride (PVC), concrete, or clay) in the subsurface that direct water away from plant roots into surface water or canal systems adjacent to the field.⁵³ Henceforth, the term “tile drainage” is used to characterize water drained through a typical subsurface tile drainage system. Tile drainage combined with surface and subsurface runoff is referred to as “agricultural

drainage” or one subset of “agricultural wastewater”. Additionally, the sources of agricultural drainage include both natural precipitation (the primary source in this region) and supplemental irrigation from groundwater and surface water.

Tile drainage systems are extensively used in the Corn Belt States (primarily Illinois, Indiana, Iowa, Minnesota, and Ohio), accounting for approximately 50% of the fields in this region (Figure S4.3).⁵⁴ However, the increased drainage rate from the field (with seasonal variations) enhances the transport of nitrates and phosphates to nearby surface water, causing environmental problems and posing a risk to anyone directly consuming this water.⁵⁵ Furthermore, the application of fertilizers to optimize crop yield has caused millions of kilograms of nutrients to enter freshwater systems every year.⁵⁶ For example, based on the USGS SPARROW model, it is estimated that in the Corn Belt States of Indiana, Illinois, and Iowa, more than 6 kg of total nitrogen from farm fertilizer per hectare of cropland is annually discharged into surface water. In addition, total nitrogen loads can reach 10 kg per hectare in some areas within these states.⁴² For the same cropland in these states, the annual average of total phosphorus loads in the agricultural drainage ranges between 0.7 and 0.9 kg per hectare.⁴²

A recent report by the National Oceanic and Atmospheric Administration (NOAA) estimated that 65% of the total nitrogen in the Mississippi River system originates from agricultural fertilizer application.⁵⁷ According to this report, a 20%–30% reduction of nutrient loads would result in a 10% reduction of chlorophyll and a 30% increase in dissolved oxygen concentrations in coastal waters.⁵⁷ Thus, implementing a nutrient reduction strategy at the field level can significantly improve the annual hypoxic dead zone in the Gulf of Mexico and reduce the occurrence of toxic algal blooms.^{43,57}

Due to the high temporal and spatial variability of individual farms (unique management practices, crop type, weather, and soil),⁵⁸ a regional approach was taken to evaluate the current state of reusing agricultural drainage for irrigation. The Midwest and parts of the Southeast were grouped into one category due to similarities in drainage water composition (primarily nutrients), climate (amount of precipitation), soil conditions, and local water laws that allow for direct reuse of agricultural drainage.^{9,49} Nebraska and Kansas (i.e., major irrigation consumers in the Midwest) were excluded from this section as these two states are subject to hybrid prior appropriation water laws similar to California complicating the direct reuse of agricultural drainage.

The composition of tile drainage in the Midwest is different from the other major agricultural region of the country (i.e., California). Therefore, since the tile drainage in the Midwest consists primarily of a value product to the farmer (inorganic fertilizers), advanced treatment technologies (e.g., RO) are not required. Consequently, optimizing direct reuse storage and pumping systems is necessary to achieve a more economically feasible path to implementation while still creating a “sustainable circular water economy”.⁵⁹

3.1.1. Current Tile Drainage Reuse Systems

Managing tile drainage outflow consists of two main types of “controlled drainage” systems. The first system controls the outflow of tile drainage by raising the water table through the addition of a physical barrier to the drainage pipes/canal. This allows the irrigation water to have a longer residence time in the root zone and can slightly reduce nutrient loads.^{52,60} The other system consists of a series of units, where the drainage is first collected in holding ponds or wetlands; then, the water is subsequently recycled to be reapplied as irrigation water to the fields.⁶¹ Controlled drainage connected to holding ponds (i.e., passive treatment systems) and pumping

networks are often referred to as “tailwater recovery” or “drainage water recycling” systems. These direct reuse systems reduce fertilizer loads from croplands by both recycling the nutrients onto the field through irrigation water and via natural processes in the reservoir such as denitrification or sedimentation (Figure 4.4).

In general, drainage water management systems have shown large variability in fertilizer load reductions from cropland, with ranges from 24% to 79% for nitrogen⁶¹⁻⁶⁴ and 12% to 32% for phosphorus.^{61,63,65} Additionally, for farms with an average annual precipitation of at least 500 mm (20 in.), these storage/ direct reuse systems can potentially provide water for the entire

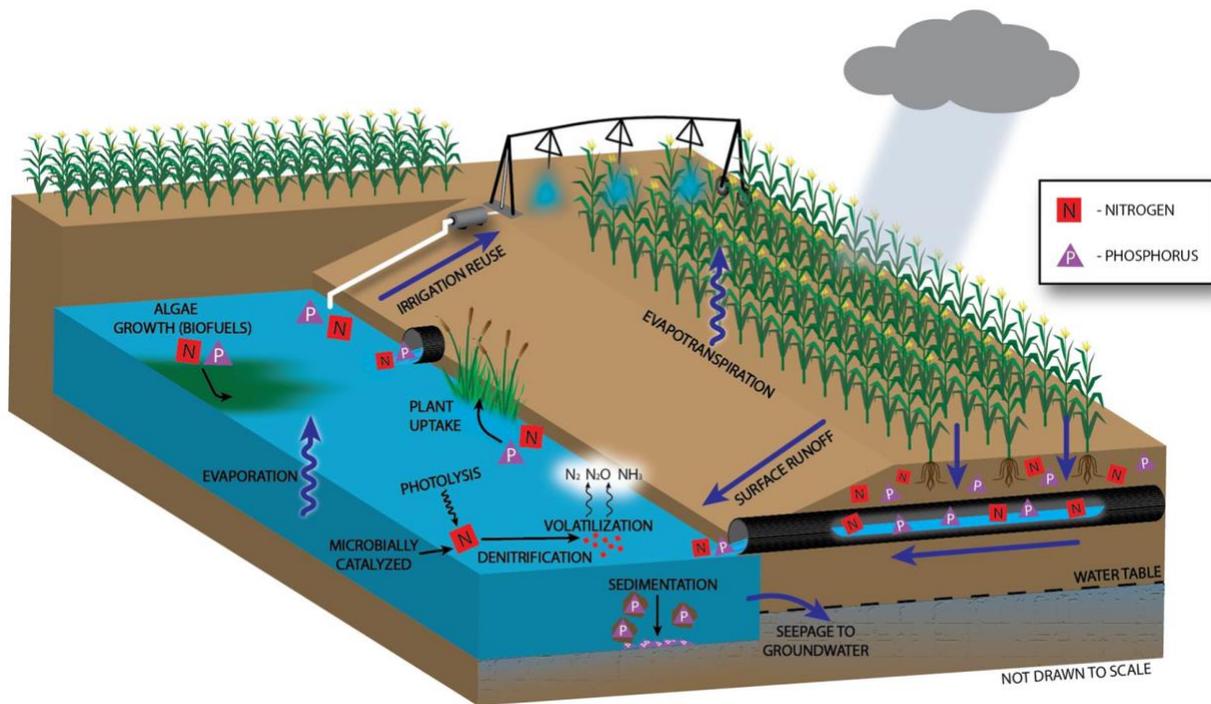


Figure 4.4 - “Tailwater recovery systems” or “drainage water recycling” schematic. Natural treatment processes such as denitrification, photolysis, and sedimentation of organic matter and associated nutrients are shown in the reservoir.

growing season’s irrigation demand, eliminating the need for supplemental irrigation in near- or above-average precipitation years (~50% of the years).⁶⁶ Consequently, if direct reuse systems

were extensively implemented across the Mississippi River drainage system, groundwater withdrawals for irrigation could be potentially reduced by 48% as irrigation withdrawals in this region are over 24.7 billion m³ (6.5 trillion gallons) every year.^{1,54} This irrigation reduction estimate reflects a best-case scenario for agricultural drainage reuse, but reducing groundwater withdrawals will be an important benefit of reusing agricultural drainage in the near future as many aquifers in the Midwest (e.g., Ogallala, Cambrian–Ordovician, and Mississippi River Valley alluvial) are depleting at unsustainable rates.^{67,68} Furthermore, the impending consequences of this water deficit may eventually reduce corn production in the region due to climate change-induced decreases in precipitation that will increase the reliance on ever-depleting groundwater stores.⁶⁹

3.1.2. Potential Treatment and Reuse of Tile Drainage

Reusing tile drainage in the Midwest is the most feasible option among all agricultural systems since the nutrient-rich water of this region does not require advanced treatment, and storage/pumping systems can be installed in line with existing tile drainage systems, thus minimizing capital costs and the topographical challenges associated with collecting runoff. As of 2017, tile drainage systems had been implemented in approximately 40%–50% of croplands across the upper midwestern states, including Iowa (53%), Indiana (49%), Ohio (49%), Illinois (39%), and Minnesota (37%).² However, most of these tile-drained fields do not include a reuse/storage system since these systems are solely focused on increasing soil drainage rates to reduce root zone saturation.⁵² Cost remains the largest barrier for implementing such reuse systems since initial capital investments range between \$200,000 and \$400,000, depending on the existing infrastructure, and would require transforming 5%–10% of the cropland into either a reservoir or canal.^{67,70} However, a cost–benefit analysis of “tailwater recovery systems” in Arkansas that

incorporated environmental costs/benefits and government subsidy/payback programs found that even with the large initial capital costs of construction, the benefits of these systems consistently outweighed the costs over a 40 year period.⁶⁷ Thus, when solely considering farms in the Midwest with existing tile drainage systems, installation of storage and pumping reuse systems in these fields could reduce effluent fertilizer loads by about 50% and 20% for N and P, respectively,⁶¹⁻⁶⁴ and supplemental irrigation demands would be met in about 50% of years.⁶⁶ Consequently, the reuse systems could potentially eliminate the discharge of about 56 million kg of nitrogen fertilizer and 3 million kg of phosphorus every year, while also reducing freshwater irrigation withdrawals by approximately 21% (235 million m³ (62 billion gallons) per year).⁴²

3.2. REUSE OF SALINE TILE DRAINAGE FOR IRRIGATION IN CALIFORNIA

In contrast to the Midwest, tile drainage in the western U.S. can have high levels of constituents of concern, including salt, Se, and B, that prevent the direct reuse of drainage. It is estimated that there are 77 million ha (190.3 million acres) of salt-affected land in the U.S., with a large percentage occurring in the Western States.⁷¹ In addition, a USGS study in 2003 identified that 11 of the 17 Western States are susceptible to Se issues from irrigation water, and further site testing found that regions in nine of the Western States were considered contaminated with Se (surface water samples with Se concentrations greater than 0.005 mg/L and/ or sampled bird eggs containing embryotoxic concentrations of Se).⁷² While many Western States face similar agricultural drainage problems, the focus of the research community has been on saline drainage management specifically in California. The aggregate effects of the high number of agricultural activities, water shortages, and increasing concern for salt and Se in the environment make California a focus area for drainage reuse and a potential region for implementing advanced

treatment technologies. million ha (8.4 million acres) of land.⁴ Due to years of irrigation, the salinity of irrigation waters, large volumes of agricultural drainage, and shallow water tables, California has an immediate need for managing and treating saline agricultural drainage.⁷³ The amount of irrigation needed in this area and increasing water stress due to droughts, paired with the large volumes of saline drainage, provide an opportunity to treat and reuse the drainage as supplemental irrigation water reducing the environmental strain of saline drainage.

Using irrigation volumes,¹ irrigation consumptive use volumes,¹ and area of farmland drained by tile,² it was estimated that 1.6 million m³ per day (419 million gallons per day (MGD)) of tile drainage could be potentially reused in the state of California, with about 8% of the estimated tile drainage in the San Joaquin Valley and almost 90% in the Imperial Valley. A large amount of agricultural drainage in the Imperial Valley drains to the Salton Sea, a landlocked lake with concerns of salts, pesticides, and toxic metals in the water and sediment and poor air quality caused by these toxic residues.^{75,76} In the past, agricultural drainage from the west side of the San Joaquin Valley was stored in the Kesterson Reservoir, now part of the San Luis National Wildlife Refuge. However, the toxic levels of Se in the drainage water caused embryotic deformities in aquatic birds and environmental harm, so the reservoir was closed to incoming drainage waters.^{51,77,78} The main constituents of concern for reuse for irrigation in this region are TDS, salts, Se, B, and Cl, which can be present in excess amounts affecting crop health and safety.⁴⁶

3.2.1. Current Tile Drainage Reuse and Management Systems

Currently, the reuse of saline drainage is very limited due to the presence of potentially toxic salts and the relatively low cost of fresh irrigation water (average off-farm irrigation water

cost in the U.S. is \$0.034/m³ or \$42.37/acre-ft).⁴ Agricultural drainage produced in the San Joaquin Valley can have TDS levels ranging from 5,000 to 20,000 mg/L.⁷⁹ For reference, waters with a TDS range of 1,000 to 10,000 mg/L are categorized as brackish, and waters with a TDS range of 10,000 to 100,000 mg/L are denoted as highly saline.⁸⁰ Saline drainage water can be discharged into the ocean in coastal areas, but this can lower water quality and cause eutrophication.⁴⁶ In addition, ocean disposal of saline drainage water is not a feasible option for inland locations. In the California region, salinity restricts the direct reuse of tile drainage as studies have shown that irrigating crops with saline water can lower crop yields and reduce soil microbial diversity.^{81,82}

Current practices of reusing saline drainage include blending, cyclic, and sequential reuse. Blending involves mixing high-quality water with saline drainage, requiring a large amount of freshwater. Depending on the salinity of the drainage water, blending to a level that would not affect crop yield or soil health may not be economically feasible.⁸² Alternatively, the cyclic strategy uses two water sources that can be rotated or used separately over the seasons for different crops. With this practice, high-quality water is used to irrigate crops until germination, and the source water is switched to saline drainage when crops have a higher salt tolerance.⁸³ Finally, sequential reuse entails reducing drainage volumes by applying it in series to increasingly salt-tolerant crops (e.g., salt-tolerant grasses, trees, and halophytic plants). Integrated on-farm drainage management (IFDM) includes the practice of sequential reuse and captures the final concentrated drainage for disposal into an evaporation basin or solar evaporator.^{84,85} In 1995, Red Rock Ranch, on the west side of the San Joaquin Valley, implemented an IFDM system that proved to be an effective, although temporary, disposal method until a more sustainable solution is developed.⁸⁴ Figure 4.5 shows an example of an IFDM system layout.⁸⁶

Evaporation basins are commonly implemented for saline drainage disposal. However, the construction of these basins comes at the expense of reducing growing areas. It has previously been suggested that in the Central Valley (consisting of the Sacramento Valley and the San Joaquin Valley), approximately 10% of the total drainage area would need to be dedicated to evaporation ponds to effectively manage tile drainage on a farm, but this suggestion can change based on irrigation practices and farm management.⁸⁴ In Central California, more than 2,900 ha (7,166 acres) of land is devoted for evaporation basins for the disposal of agricultural drainage waters.⁸⁷

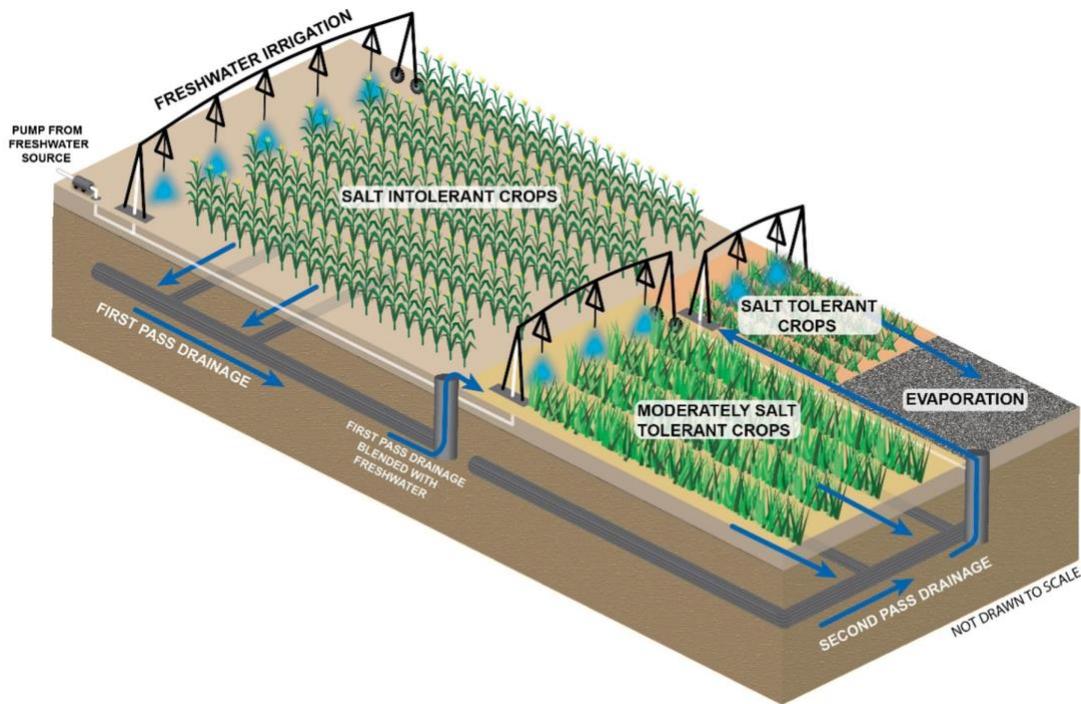


Figure 4.5 - Integrated on-farm drainage management (IFDM) combines sequential reuse with the disposal of concentrated tile drainage into an evaporation pond or solar evaporator.

This approach raises concerns related to Se toxicity to waterfowl and other species attracted to water bodies.^{87,88} Although the management price may be higher than evaporation basins, solar evaporators can reduce the risk to wildlife as the concentrated saline drainage water is distributed

on the surface of the evaporator at a rate that prevents ponding.⁵¹ For example, at the Red Rock Ranch, using more efficient irrigation strategies and IFDM led to only 6% (reduced from the recommended 10% without IFDM) of the project area to be employed for reuse and evaporation.⁸⁴ Implementing IFDM on farms using tile drainage systems could reduce the amount of land currently being used for saline drainage disposal, resulting in more land for high-value, salt-sensitive crops.

In addition to strategies related to the reuse and disposal of saline drainage, passive treatment (i.e., constructed wetlands) is another option to remove nutrients, Se, B, salts, and other constituents of concern from agricultural drainage. The performance of constructed wetlands depends on plant type, microorganisms, geometry, hydraulics, substrate, and water temperature and quality.⁸⁹ The primary challenge with using constructed wetlands to treat Se-laden water is the Se bioaccumulation in sediments and plant materials, enhancing its transfer into the food chain.⁹⁰ Agricultural water discharged from the western San Joaquin Valley can contain toxic Se amounts, with concentrations frequently ranging from 0.14 to 1.4 mg/L of Se in some regions.⁹¹ However, there is limited data on constructed wetlands that can consistently reduce the Se levels in agricultural drainage to below the U.S. Environmental Protection Agency (EPA) water quality criteria of 0.005 mg/L.⁹² Salt-tolerant plants in constructed wetlands have the potential to remove various constituents of agricultural drainage (e.g., Se, B, and sodium)⁹³ but may not be able to achieve concentrations that are suitable for long-term use for irrigation (e.g., 0.02 mg/L Se; 0.75 mg/L B).^{92,94} Future research will need to focus on improving the efficiency of constructed wetlands and other passive treatment options for the treatment of saline drainage.

3.2.2. Potential Treatment and Reuse of Agricultural Drainage Water

The potential use of agricultural drainage as a water source for irrigation throughout the California Central Valley is currently constrained due to the presence of toxic constituents in the tile drainage, which requires blending with high-quality water or treatment.⁸⁴ The current management strategies for the disposal of saline drainage (e.g., evaporation ponds, sequential reuse) are becoming unsustainable due to the accumulation of toxic constituents, including Se, B, and salt.⁹⁰ There are concerns that as receiving water quality decreases, discharge standards will become more restrictive, resulting in the need for more widespread reuse strategies and treatment technologies.⁸⁶ Membrane desalination processes can be employed to reduce salinity of tile drainage, but these technologies have high costs associated with the energy requirements and the additional need for the disposal of large volumes of brine. Concerning nutrient and Se removal, potential treatment options include ion exchange, distillation, chemical reduction, algal–bacterial selenium removal (ABSR), volatilization, electrochemical processes, adsorption, and biological precipitation.^{95,96} Identifying and optimizing the best available technologies to treat saline agricultural drainage can help supplement traditional irrigation water sources and reduce environmental impacts.

3.2.3. Advanced Treatment Case Study: San Luis Demonstration Plant, California

The San Luis Demonstration Treatment Plant (SLDTP), located in the Panoche Drainage District in California’s Central Valley (Fresno County), was designed to demonstrate the large-scale treatment of saline agricultural drainage.⁹⁷ Due to the demonstration nature and pilot scale of this treatment plant, the treated water was not directly reused for irrigation purposes. The

SLDTP was operated by the U.S. Bureau of Reclamation for three years (from January 2016 to December 2018) to test the feasibility of removing toxic constituents (i.e., salts and Se) present in this region's agricultural drainage. This case study does not represent the current common, widespread practices for the reuse of saline agricultural drainage, but it was selected to demonstrate one option of advanced treatment technologies to desalinate agricultural drainage in California. The SLDTP treated 1090 m³/d (288,000 gallons per day) of second-pass agricultural drainage, a lower quality, higher salinity raw water than first-pass agricultural drainage.⁹⁸ To our knowledge, in addition to the SLDTP, there are only two other large-scale established agricultural drainage water treatment facilities: the Yuma Desalting Plant (YDP)99,100 in Arizona and the Al Mahsamma Agricultural Drainage Treatment, Recycling, and Reuse Plant in Egypt.¹⁰¹

3.2.3.1. Treatment Technologies

The SLDTP main treatment train includes a two-stage anoxic bioreactor process (i.e., the ABMet bioreactor that consists of a biofilm, an activated carbon bed filter, and a nutrient feed, i.e., carbon source, to maintain the biomass)¹⁰² for the removal of nutrients and Se, ultrafiltration (UF), and reverse osmosis (RO).¹⁰³ In this treatment train, seawater reverse osmosis (SWRO) and brackish water reverse osmosis (BWRO) processes were placed in parallel as shown in Figure 4.6. The Se-laden waste from the ABMet bioreactor was treated further in a clarifier and filter press. The dewatered Se solids were sent for disposal, and the filtrate from the filter press was sent back to the feed tanks. The RO brine (i.e., concentrate) was not treated, but it was blended with the treated effluent (i.e., permeate) and discharged into a trench drain.

3.2.3.2. Water Quality

The water qualities of the raw influent tile drainage, permeate from the BWRO and SWRO processes in the SLDTP, and end-use requirements for long- and short-term irrigation are

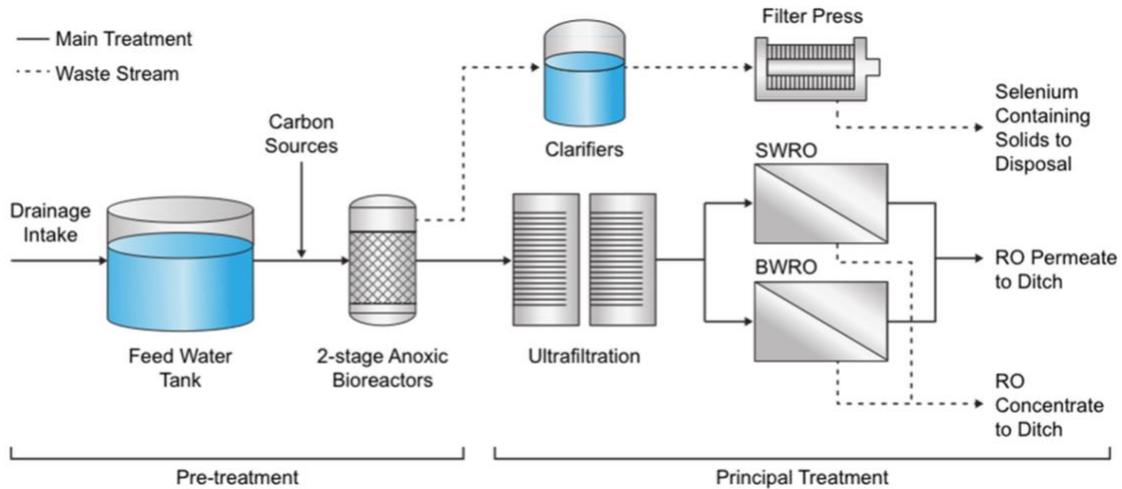


Figure 4.6 - Simplified process flow diagram for the San Luis Demonstration Plant (SLDTP). Pretreatment focuses on the removal of Se, whereas principal treatment is focused on salt removal. SWRO, seawater reverse osmosis; BWRO, brackish water reverse osmosis

summarized in Table S1. Se, B, and TDS concentrations in the raw tile drainage are at toxic levels for plants and animals, reinforcing the need for treatment before reuse for irrigation. Even after treatment, boron levels were higher than the recommended levels for irrigation water. While some crops have high salt tolerance, the TDS levels in the untreated drainage water ranged between 9,400 and 15,400 mg/L, which makes the water severely hazardous necessitating treatment before reuse for irrigation.¹⁰⁴

3.2.3.3. Case Study Results

The SLDTP was analyzed in WaterTAP3⁴¹ using parameters and data from the pilot runs (treatment capacity of 45 m³/h, average influent TDS of 12,400 mg/L, and water recovery of 61%).¹⁰³ Assumptions used for this analysis are described in the Supporting Information (see Text S4.2). Table S4.2 summarizes the financial and operational data modeled within WaterTAP3.⁴¹ On the basis of the WaterTAP3 model, the estimated LCOW using the treatment train in the SLDTP is \$1.73/m³ (Figure 4.7). The small scale of this case study, the location, and the land cost can affect capital cost estimations within the WaterTAP3 model.⁴¹ As a result, the cost of treated water is significantly higher than the average off-farm water cost in California, \$0.06/m³ (\$67.97/acre-ft),⁴ but during periods of drought, bids for freshwater may be significantly higher.¹⁰⁵ At full-scale, the direct cost of treating the water is expected to be lower, but the overall cost of transportation and treatment might negate the cost savings due to higher conveyance costs.⁵⁹ In addition, it is important to note that the LCOW estimated using the WaterTAP3 simulation does not consider the costs associated with the transportation of the treated water and brine treatment or disposal.

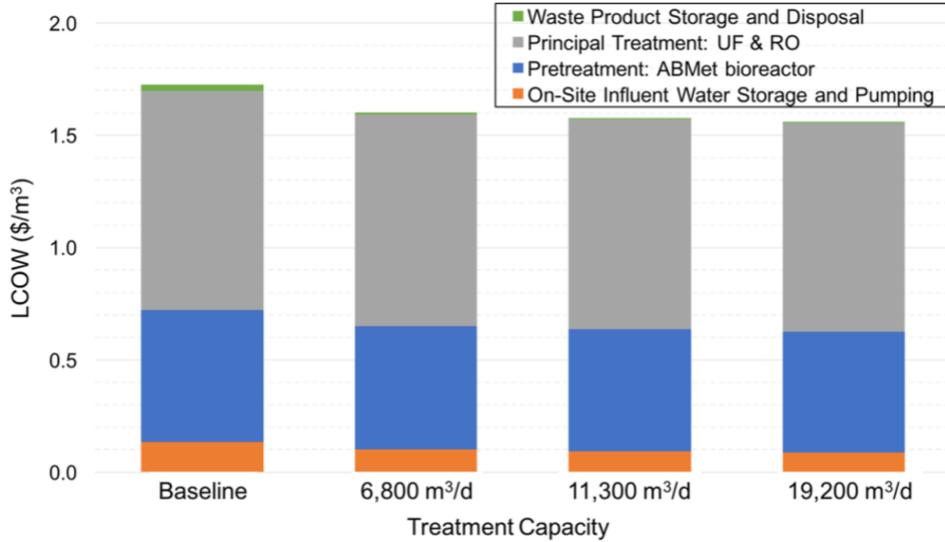


Figure 4.5 - Levelized cost of water (LCOW) for the San Luis Demonstration Treatment Plant (SLDTP) treatment train at different capacities.

The main cost driver is capital costs, accounting for about 58% of the total water costs (Figure S4a). A cost breakdown of the LCOW contribution by process area is shown in Figure S4a. Based on the WaterTAP3 estimates, the principal treatment process (consisting of UF and RO) account for 57% of the LCOW and 76.7% of the energy intensity (Figure S4.5). Due to the significant contribution to the LCOW, advancements that lower the cost of the principal treatment processes are needed (i.e., use of renewable energy, optimization of treatment processes, and valorization of treatment byproducts) (Section 4.2).

3.2.3.4. Scenario Analysis

Based on the literature review and WaterTAP3 analysis, the cost of treating saline drainage is highly impacted by the salinity of the inlet water and the scale of the treatment facility. An

analysis was done to estimate the LCOW and water recovery for a range of TDS concentrations common in the second-pass agricultural drainage entering the SLDTP (Figure S4.6). As expected, agricultural drainage salinity is a key cost driver for principal treatment. For lower salinity agricultural drainage (e.g., minimum SLDTP influent TDS of 9,400 mg/L), a higher water recovery can be achieved, producing a larger volume of treated water available for reuse as irrigation water. Alternatively, implementing sequential reuse before treating the drainage would increase the inlet salinity but reduce the volume of drainage requiring treatment.

To determine the impact of treatment capacity on the LCOW, WaterTAP3 was used to analyze a scenario for agricultural drainage treatment in Fresno County. On the basis of irrigation volumes, area of tile-drained farmland, and irrigation consumptive use volumes, it is estimated that 22,600 m³/d (5.9 MGD) of tile drainage are potentially available for capture and treatment in Fresno County.^{1,2} Scaling up the SLDTP treatment train to treat 6800 m³/d (1.5 MGD) (treatment of about 30% of available tile drainage) would reduce the average LCOW to \$1.60/m³. Increasing the treatment capacity to 11,300 m³/d (3 MGD) (treatment of about 50% of available tile drainage) and 19,200 m³/d (5 MGD) (treatment of about 85% of available tile drainage) would result in very similar estimated LCOW of \$1.58/m³ and \$1.56/m³, respectively (Figure 4.7). The LCOW only considered the cost of treatment without accounting for the conveyance cost. Larger scale systems would require large distribution systems (i.e., piping and pumping), potentially offsetting some of the treatment cost savings. While the high LCOW can seem like a barrier to prevent the implementation of treatment of saline drainage water, it is important to also consider how treatment could reduce the environmental damage caused by untreated highly saline wastewater. To determine the exact cost savings, a comprehensive life cycle analysis (LCA) would need to be conducted. However, the benefits of producing additional irrigation water, slowing the salinization

of productive agricultural land, and meeting increasingly stringent water discharge requirements could outweigh the high LCOW of treating saline agricultural drainage, especially if government incentives are implemented.

4. IMPLICATIONS AND PERSPECTIVES

4.1. Limitations

The wider implementation of the SLDTP treatment train, or a similar treatment approach for saline tile drainage, is limited by its high cost and lack of safe and cost-effective brine disposal options. Although brine treatment and disposal are not included in this case study, brine management would be necessary if this treatment train was implemented at full-scale. Brine disposal options may include evaporation ponds or deep well injection. If the concentrate salinity is too high, or the concentrate cannot be blended with other water sources, brine treatment may be required. However, despite recent developments in zero liquid discharge (ZLD) technologies, there is still a need for low-cost, high-performance brine treatment systems that can potentially be integrated with renewable energy sources.^{106,107} In addition, to offset the costs associated with brine treatment and disposal, salts in agricultural drainage (e.g., sodium sulfate, sodium chloride, and calcium sulfate) may be recovered via selective valorization and reused in agricultural operations (e.g., meat and dairy processing facilities) or sold to other industries. For example, sodium sulfate can be recovered using electrochemical processes and used to produce sodium hydroxide and sulfuric acid, but this may not be cost effective with current technology.⁵¹

Conveyance of the treated water is an important consideration that will increase the LCOW for the SLDTP, but it was excluded from this analysis as it is highly site specific. Future analysis

is needed to assess and compare the overall cost of localized systems, similar to the SLDTP with high water treatment cost and shorter conveyance distance, to district-scale systems with lower treatment cost, but longer conveyance distance. However, it is important to note that the conveyance cost of treated agricultural drainage could potentially be lower than other nonagricultural alternative water sources if topological conditions are optimal (i.e., low elevation). Given the high LCOW of treatment, managing agricultural drainage on a drainage district/county scale may be more feasible than on an individual farm scale. In a large-scale reuse scenario, the treated drainage water could be discharged into the existing network of canals, ditches, and other water bodies to transport the irrigation water to the farms. Suppose that 50% of the tile drainage available in the San Joaquin Valley (i.e., 64,000 m³/d or 17 MGD) is treated to remove salts and toxic constituents and assuming similar water quality to the drainage water at the SLDTP and a water recovery of 61%, this could result in 14 million m³ of irrigation water per year (3.7 billion gallons per year), while consequently producing a large volume of brine that would require management.

4.2. Research Needs and Outlook

While the SLDTP case study demonstrated that the treatment of agricultural drainage can be costly compared to current freshwater prices, it is important to examine the environmental damage that untreated or poorly managed agriculture drainage can cause to sensitive ecosystems. In this scenario, treating agricultural drainage is essential to prevent further environmental deterioration (e.g., soil salinization, harmful algal blooms), and the treatment byproduct (i.e., water) can potentially serve as irrigation water. However, it remains a challenge to determine the

widespread impact of discharging untreated tile drainage due to spatial and temporal variations across the U.S. and the lack of data and monitoring. Over the years, a few localized drainage impact studies have been conducted and determined that the lack of drainage treatment can have high costs. For example, Welle and Mauter estimated that in 2014 soil salinization in California reduced agricultural revenues and crop yield by 8% and 12%, respectively, resulting in an estimated loss of \$3.7 billion.¹⁰⁸ In a different study, Bouldin et al. conducted a cost–benefit analysis on the implementation of tailwater recovery systems in Arkansas. These researchers found that by incorporating various societal benefits and government subsidies, the overall value of these reuse systems considerably outweighed the capital expenses.⁶⁷

Eutrophication, soil salinization, and other environmental damages (e.g., Se contamination) are costly consequences of current agricultural drainage management. Future technoeconomic analysis (TEA) needs to be holistic, incorporating ecological benefits associated with drainage treatment. For example, the cost of drainage treatment may be comparable or cheaper when compared to the cost associated with environmental remediation due to salts, nutrients, or other toxicants (e.g., Se and B). Ideally, the TEA would need to consider metrics beyond the LCOW such as the impact on receiving water quality (e.g., toxicity), potential resource recovery (e.g., water, salts, and nutrients), possible environmental impacts (e.g., carbon footprint and eutrophication), conveyance (e.g., proximity and accessibility to supplies and disposal sites), and agroecosystem impacts (e.g., crop and soil health).

Regarding the treatment of saline drainage, our analysis of the SLDTP case study showed that the LCOW was mainly driven by RO and UF costs, as both are energy-intensive processes. This calls for innovation and the need to optimize these processes for implementation in agriculture. Advances in sensors and automated digital networks may allow us to better optimize

treatment by adjusting the recovery of the system depending on the inlet water quality. In addition, developing membrane materials that are robust and resilient to variations in agricultural drainage water quality may prolong the lifetime of membranes and reduce operating and maintenance costs (e.g., membrane replacement and cleaning processes). Another potential improvement opportunity is the implementation of different pretreatment technologies that can remove constituents that can cause fouling and scaling downstream (e.g., nanofiltration and electro dialysis). Finally, the economic feasibility of the evaluated water treatment train can be enhanced by integrating low-cost renewable energy sources (e.g., solar energy or waste heat) to provide the required electricity of the system. While technological advancements can potentially reduce the LCOW for the treatment of saline drainage water, a cradle to grave analysis is needed to accurately estimate the economic value of agricultural water.

5. CONCLUSIONS

In the U.S., there are approximately 833 million m³ (220 billion gallons) per year of tile drainage that is potentially available for reuse in agricultural operations. The opportunities for reusing agricultural drainage for irrigation vary regionally across the U.S. due to heterogeneous demand, water quantity and quality variability, and proximity and accessibility to traditional and other nontraditional water sources (e.g., seawater, municipal wastewater, brackish water). In water-stressed regions of the U.S. (e.g., southern California), farmers have been using blended nontraditional source waters (e.g., low salinity produced water blended with freshwater in Kern County) to irrigate high-value crops such as almonds and citrus.²¹ As demonstrated by the SLDTP case study, desalination of saline agricultural drainage is costly, energy intensive, and presents

many treatment challenges. Full-scale implementation will require sizable investments in research to fully develop technologies as well as better manage the waste and concentrate. However, if these barriers could be overcome, the treatment and reuse of agricultural drainage water would not only address the water-scarcity problem farmers face in many western regions, but it could also address compounding challenges associated with salt accumulation and toxicity concerns related to B, Se, and As. In other regions where water scarcity is not widespread, like the Midwest U.S., this approach could reduce nutrient discharges and associated eutrophication as well as alleviate stress in over drafted aquifers.

In practice, the decision to treat and reuse agricultural drainage water may also depend on the value of the crops being irrigated. For example, advanced treatment may be more economically feasible in California as high-value crops (e.g., tomatoes, grapes, strawberries, citrus, or nuts) are typically grown in this region. In contrast, in the Midwest, direct reuse and storage systems may only be feasible in the Corn Belt States, where crop value is higher than other areas of the Midwest.²

Finally, the WaterTAP3 analysis of the SLDTP facility in California showed that the LCOW, including both capital and operating costs over the facility's life, of treating saline tile drainage is about \$1.73/m³. This is significantly higher than the current average cost of freshwater in the state (\$0.06/m³).⁴ However, treating saline tile drainage may be increasingly feasible in the future with changing regulations, increasing freshwater scarcity, decreasing water quality, advancements in low-cost efficient treatment technologies, and utilization of alternative energy sources.

Author Contributions

According to the CRediT (Contributor Roles Taxonomy) criteria my contributions to this paper include validation, investigation, writing-original draft, and visualization. Contributions from C.H., K.W., R.Y. M.K., and B.G. validation, investigation, writing-original draft, and visualization. Contribution from T.B. and D.D. include conceptualization, resources, writing - review & editing, supervision, project administration, and funding acquisition. Contributions from T.M.B., T.T., J.M., J.S-D., and D.H. include conceptualization, investigation, and writing-review & editing. Contributions from M.A-P., S.S., A.K. include conceptualization. Contributions from A.M., Z.H., A.E., and P.K. include formal analysis, data curation, and visualization.

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CHAPTER 5: OIL AND GAS PRODUCED WATER REUSE: OPPORTUNITIES, TREATMENT NEEDS, AND CHALLENGES

1. INTRODUCTION

Use, disposal, and reuse of water associated with oil and gas (O&G) production has been a topic of interest to O&G operators, regulators, water users, and researchers for decades, but over the past decade, this interest has peaked due to the increase in hydraulic fracturing operations, water scarcity, and environmental and toxicological concerns. Recent analyses have highlighted the extensive volumes of produced water associated with different O&G production basins, as well as the potential management options for produced water across the basins.¹⁻³ These studies suggest that the recycling and beneficial reuse of produced water (e.g., reuse for irrigation, livestock watering, streamflow augmentation, municipal water supplementation, cooling water, dust suppression, ice control on roadways) must be viewed in terms of both regional availability and end user demand. Drivers for recycling and beneficial reuse of produced water often include reducing the freshwater intensity of O&G production,⁴ minimizing seismicity associated with deep well disposal,⁵ providing source water for other sectors,^{6,7} and enhancing potential resource recovery from these waters.⁸⁻¹⁰ Yet, despite a desire to increase produced water reuse, techno-economic, regulatory, and social challenges complicate beneficial reuse of produced water.¹¹ The confluence of these factors has resulted in the reinjection of ~92% of the 24.4 billion barrels (1.025 trillion gallons/508 million m³) of produced water generated in the United States (US) in 2017 into the subsurface and minimal beneficial reuse.¹

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This dearth of reuse has not been the result of an absence of support for fundamental and applied research among the various stakeholders. However, due to widespread regional variability in produced water quality, generation, and management regulations, produced water research over the past several decades has involved predominantly a single or limited number of investigators or business-driven development of intellectual property, research papers, and field trials of technologies. In most cases, these studies addressed the characterization and treatment of specific waters and did not propose universally applicable produced water characterization or treatment technologies. This has led to a myriad of papers and literatures that often stymies stakeholder's search for relevant information, as highlighted in Tables S5.1 and S5.22 in the Supporting Information (SI), which categorize the range and breadth of topics covered. These tables identify select literatures that address water quantity, water quality, water treatment technologies, and water management issues.

Widespread regional variability in water availability and produced water quantity have been highlighted in several recent studies,¹⁻³ including Scanlon et al., who not only identified the regionality of water use but also connected it to potential reuse options.³ The literature identified in Table S5.1 also highlights that produced water generation also differs both by basin and by well within the same basin due to the type of well (conventional or unconventional), drilling method, completion type, and age of well, resulting in water-to-oil ratios that range nationally from 3:1 to more than 10:1.^{2,3,12,13} For example, in 2017, the Permian Basin, a relatively wet tight oil basin, produced upward of 1.66 billion barrels (69.7 billion gallons/264 million m³) of produced water, while the Marcellus Basin, a relatively dry shale gas basin, only produced 0.033 billion barrels (1.34 billion gallons/5.25 million m³) of produced water.² Conventional O&G wells are drilled into geological formations where oil and natural gas readily flow to the wellbore, while

unconventional O&G wells tap into previously unconventional geological sources such as shale gas, coalbed methane (CBM), shale oil, tight oil, and oil sands. While conventional produced water is often reinjected into medium-to-high permeability reservoirs for pressure maintenance or enhanced oil recovery (EOR), unconventional produced water often cannot be reinjected into the low- permeability reservoirs associated with unconventional production.¹⁴ For context, between 2009 and 2016, O&G operations in the Permian used 27 billion barrels (1.134 trillion gallons/4.29 billion m³) of conventional produced water for EOR and disposed of 6.6 billion barrels (277 billion gallons/1.05 billion m³) of conventional and 5.5 billion barrels (231 billion gallons/0.87 billion m³) of unconventional produced water via saltwater disposal wells.¹⁴ Recycling or beneficial reuse of unconventional produced water is further impeded by the temporally mismatched supply and demand for water within the hydraulic fracturing processes that can inhibit recycling within O&G without the presence of extensive storage, water handling, and conveyance infrastructures.¹¹

Management of these spatially and temporally variable quantities of produced water is further confounded by the inconsistency of produced water quality and the resulting treatment challenges. Produced water contains variable concentrations of inorganics, organics, microorganisms, suspended solids, radioisotopes, and dissolved gases which vary by factors including the well's natural geologic formation, type of well, type of hydrocarbon being produced, and well production time.^{1,12,15-22} Literatures revealing the variability in water quality are also presented in Table S5.1. In particular, total dissolved solids (TDS) concentrations, ranging from <1000 to >250,000 mg/L, can present substantial challenges for both treatment and residual management.^{12,15,23} While organic matter in raw or pretreated produced water (total organic carbon (TOC) < 1500 mg/L) is generally not a limiting factor in disposal or recycle, sustainable beneficial

reuse may be limited by concerns surrounding characterization, fate, and toxicity of constituents identified in produced water.^{1,12,15–22,24,25}

A Google Scholar search of publications and patents illustrates the growing interest in produced water treatment (from 25 in the 1960s to 5780 in the 2010s) using commercially available technologies like reverse osmosis (RO) desalination, nanofiltration (NF), and membrane bioreactor (MBR) and such novel technologies as forward osmosis, osmotically assisted RO, membrane distillation, and eutectic freezing for removal of bulk TDS and/or organics, along with a range of technologies for precision separation of trace constituents. In addition to the numerous papers focused on individual technologies, since the 1970s more than 80 review papers, including several recent reviews, have discussed the generation, characterization, and treatment of produced water (Table S5.2).^{26–32} For example, Conrad et al. specifically addresses the need for fit-for-purpose treatment to meet the varying end use water quality requirements.¹³ Nevertheless, there are only a few examples in which novel technologies or treatment trains have been deployed for beneficial reuse of produced water.^{33–35}

Moreover, no technological solution is complete without considering the disposal of residuals, regulatory constraints associated with disposal and reuse, and the environmental and health impacts of disposal and reuse. Regional, federal, and state regulations further influence the feasibility of various produced water management options. The U.S. Environmental Protection Agency (EPA) enacts national environmental regulations and grants primacy to state agencies to enact state-specific regulations that meet or exceed the stringency of the national regulations.³⁶ Title 40 of the Code of Federal Regulations Part 435 (40 CFR 435) Subchapter C does not allow onshore upstream O&G facilities east of the 98th meridian to discharge pollutants from produced water or other O&G fluids to surface waters.³⁷ In contrast, for onshore O&G facilities west of the

98th meridian, 40 CFR 435 Subchapter E allows for the discharge of produced water to surface water if the facility has a state and/or federally issued National Pollutant Discharge Elimination System (NPDES) permit, assuming that the effluent limitations of 40 CFR 437 are met. State-level produced water regulations depend on factors including the state's political and environmental climate, the state's water rights laws, the type of O&G resources, and the associated produced water quantity and quality. For more information on the produced water quantity, quality, and regulations surrounding produced water management, please refer to Table S5.1 in the Supporting Information.

While the treatment costs, residual management, and regulatory constraints remain significant barriers for produced water recycling, a secondary concern is the potential for toxicity associated with the beneficial reuse of produced water. As such, the design and operation of these treatment trains must mitigate risk associated with ecotoxicity, human toxicity, and soil and crop health relevant to specific end uses. Past work has highlighted common treatment technologies utilized by O&G companies that emphasizes the varying levels of treatment required for different end uses (Figure 5.1), but typically these technologies are selected based on the removal of target species rather than toxicity-relevant metrics for a specific beneficial use.

To this end, there is a need to understand and address the current limitations associated with quantifying toxicity and environmental impacts to develop end use specific water quality criteria that can guide fit-for-purpose treatment strategies. This perspective utilizes several case studies to review current management practices for produced water and examines potential scenarios for expanding recycle and beneficial reuse; however, scientific advancements are needed for the better characterization and assessment of produced water being considered for beneficial reuse. Thus, a second integral component of this perspective is a discussion of both the challenges

of characterizing the chemical composition and toxicity of produced water for specific end uses as well as a proposed strategy for assessing produced water toxicity to enable sustainable, beneficial reuse of produced water for specific end uses.

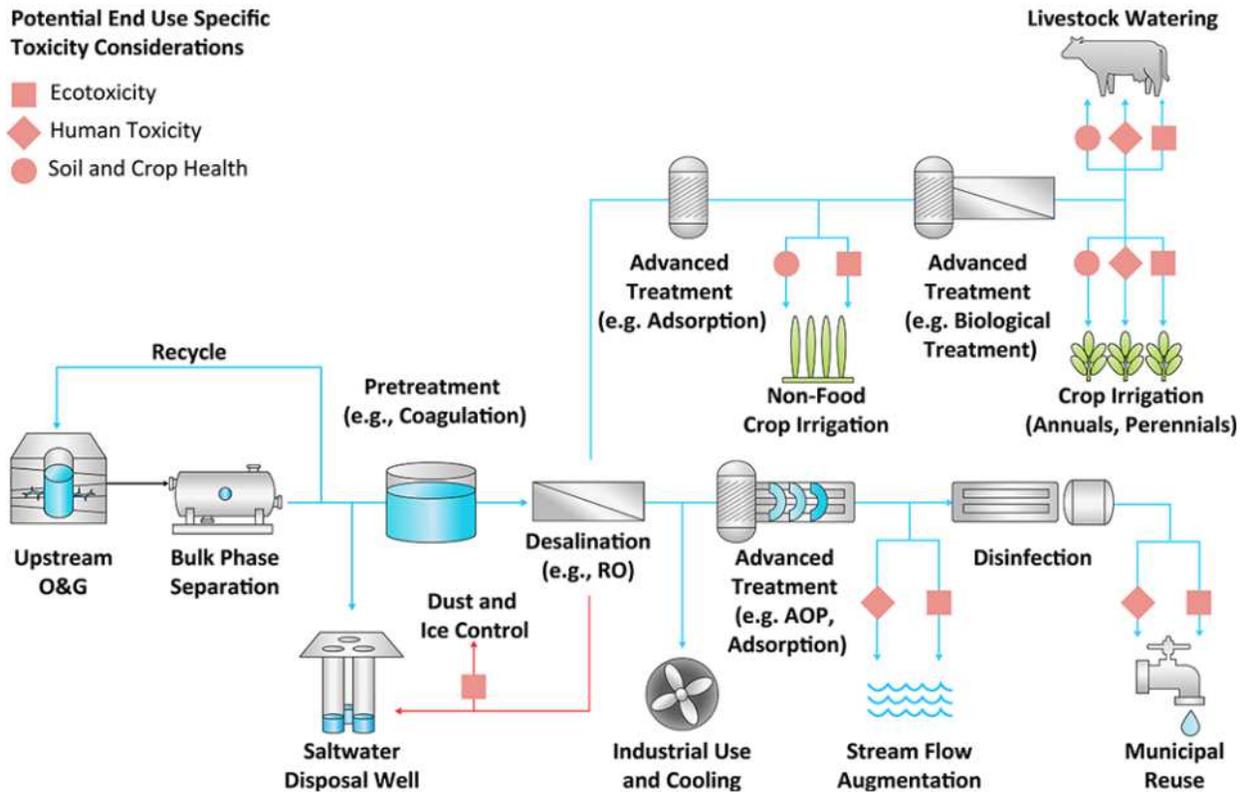


Figure 5.1 - Common proposed produced water management options and corresponding potential toxicity concerns associated with specific end uses. Appropriate water treatment trains depend on both initial water quality and desired end use. Depending on these factors, water treatment could include the separation of oil, grease, and suspended solids (e.g., API gravity separator, dissolved air flotation, coagulation/flocculation, sedimentation), removal of bulk organics and target constituents (e.g., biological treatment, adsorption), desalination (e.g., electro dialysis, reverse osmosis), and post-treatment (e.g., advanced oxidation processes, ion exchange, disinfection). Red arrows indicate concentrate/brine streams.

2. METHODS

Recycling or beneficial reuse of produced water has been implemented successfully in several cases. Analyses of these cases can be used to set the stage for identifying potential additional management options, as well as the current limitations and concerns surrounding expanded beneficial reuse. From disposal to recycling, treatment needs increase minimally in complexity, but as we expand from recycling to beneficial reuse applications, variable regulatory policies, treatment complexity, and public perception play more significant roles in realizing produced water reuse potential.

In this perspective, we utilize a literature-based analysis of current and potential management scenarios to assess the current potential for expanding both recycling and beneficial reuse. As highlighted earlier, most produced water is reinjected into the subsurface for either disposal or EOR. We chose six different case studies that highlight current common practices to represent possible produced water management approaches. The cases selected are (1) treatment and disposal of produced water via saltwater waste disposal (SWD) wells in the Permian Basin in Texas, (2) collection, treatment, and recycling of produced water in the Anadarko Basin in Oklahoma, (3) treatment, recycling, and beneficial reuse of produced water in the Marcellus Basin in Pennsylvania, (4) treatment and beneficial reuse of produced water for streamflow augmentation in the Denver–Julesburg (DJ) Basin in Colorado and in the Powder River Basin in Wyoming, (5) treatment and beneficial reuse of produced water for agricultural irrigation in the San Joaquin Basin in California, and (6) proposed treatment and beneficial reuse of produced water for municipal reuse in the Powder River Basin in Wyoming. These case studies were chosen to

represent a wide geographic area, various commonly implemented or proposed end uses for produced water, and where data were readily available to model the treatment train.

For case studies where enough data were available, we modeled the treatment train using the Water Techno Economic Assessment Pipe-Parity Platform (WaterTAP3). Specifically, three fit-for-purpose treatment approaches were evaluated based on previously reported literatures and assumptions in WaterTAP3 data to assess the levelized cost of water (LCOW, \$/m³), energy intensity (kWh/m³), and water recovery (%) using WaterTAP3. WaterTAP3 simulates a steady state water treatment train and unit performance as well as capital and operating costs based on source water conditions, unit-level configurations for water treatment technologies, and system-level techno-economic assumptions. All unit processes achieve both flow and constituent mass balances.

WaterTAP3 estimates total installed costs for unit processes within the treatment train (e.g., capital cost of equipment and installation), fixed operating costs (e.g., employee salaries, plant maintenance), and variable operating costs (e.g., chemical addition, electricity) at the unit level. LCOW is then calculated from the total installed costs, operating costs, and a financial capital recovery factor with respect to the total volume of treated water stream. The following analysis presents an adjusted LCOW (\$/m³) with respect to the total volume of influent produced water. WaterTAP3 calculates the system-level electricity intensity based on the electricity consumption of each unit within the treatment train and the volume of treated water by the system. The cost of energy (\$/kWh) is based on the state-level cost of electricity for industrial purposes as reported by the U.S. Energy Information Administration. Facility locations are noted in the SI.

Analysis in WaterTAP3 is analogous to a Class 4 Feasibility Study as defined by the Association for the Advancement of Cost Engineering International Recommended Practice No.

18R-97.38 As such, the uncertainty is –30% to +50% and is based on the availability of data, technology readiness level of the modeled technology, and the analysis approach. Additional details regarding the WaterTAP3 are available in Miara et al. and in the SI.³⁹

Cases were evaluated for current economic and technological feasibility, and multiple scenarios with differing water qualities were generated and analyzed based on previously reported literature data. Alternate treatment scenarios endeavored to assess the applicability and potential of produced water management approaches in the context of increasing both recycling and beneficial reuse of produced water. Techno-economic modeling was performed to determine what research and development advances are needed to address cost trade-offs of produced water treatment trains. Also, while we compare the costs of water treatment to current water prices and disposal options, changing water availability trends and increasing prices for water may mean that some options for treating produced water for different end uses will become more economically competitive over time.

3. PRODUCED WATER TRENDS AND CASE STUDIES ANALYSES

3.1. Recycling

The upstream O&G industry uses billions of barrels of water per year to extract resources from underground geologic formations.^{40,41} While water withdrawals for O&G constitute less than 1% of the total withdrawals in the US, O&G operations use of nearby surface and groundwater may exacerbate problems associated with water scarcity in semiarid and arid regions.^{2,3,41–43} Furthermore, water use for unconventional O&G production nearly doubled between 2011 and 2018, and is anticipated to continue to increase.⁴ Consequently, there is both industry and public interest in reducing the freshwater footprint of the upstream O&G industry.

Recycling of produced water within the upstream O&G sector is preferable when economically viable as it minimizes the use of external water sources, reduces produced water management liability concerns, and limits the management of produced water (e.g., treatment, conveyance, and disposal).^{11,35} Before recycling, insoluble oil, microorganisms, iron, and boron are traditionally removed via fit-for-purpose treatment trains with oil–water separations, solids separation, disinfection, and iron removal.^{11,44} Desalination is often not necessary for recycling as recent advances in hydraulic fracturing chemicals have enabled the recycling of produced water with TDS of nearly 300,000 mg/L.^{45,46} However, this level of treatment may not be adequate to reduce public concerns surrounding spills and the potential resulting contamination of surface waters, groundwater, and soil.^{47–49} In particular, in basins with relatively high salinity produced water, like the Permian and Bakken (often greater than 200,000 mg/L TDS), there are additional concerns related to scaling and potential for spills that may increase the costs of both treatment and conveyance.¹¹

Expansion of recycling may alleviate the potential for the competition for water by O&G exploration and production with other end uses (e.g., agricultural, municipal);⁴² nonetheless, recycling is frequently limited by logistics and economics instead of treatment capabilities. Within relatively dry basins (e.g., Marcellus, Eagle Ford, Niobrara, and Haynesville), recycling varies from more than 90% within the Pennsylvania region of the Marcellus to approximately 1% within the Haynesville and Eagle Ford Basins, respectively.^{2,11,50} The wide variability in recycling has been attributed to factors such as regulatory limitations on SWD in the Marcellus leading to high produced water management costs for conveyance, the logistics of handling a relatively limited quantity of water within a large basin in the Eagle Ford, spatial and temporal changes of water demand and production over the life of the field in the Permian, and unfavorable economics for

recycling within the Haynesville due to poor initial water quality and quantity.¹¹ While midstream water infrastructure (e.g., storage, conveyance, and treatment) may help to mitigate some of these challenges, widespread development of midstream water infrastructure within a basin often requires both substantial capital investment and time.¹¹ Thus, recycling is highly dependent on regional and local conditions. As such, widespread changes in industrial practices will likely require prioritized research in characterization, adaptable treatment trains, logistics, and regulations rather than broad improvements in treatment technologies. For example, if technology goals were guided by innovative, cost-effective toxicity removal approaches that are end use specific, this would be a disruptive change that fundamentally alters existing practice and revolutionizes treatment process engineering for complex waters. The following two case studies highlight limitations and state-of-the-art management practices to expand water recycling within the Permian and Anadarko Basins.

3.1.1. Disposal and Recycling: Permian Basin, Texas.

Texas has cultivated a logistical and regulatory environment where recycling of produced water may be technically but not economically feasible.⁵¹ Texas has a plethora of SWD (~8000 wells) with an estimated average pressure utilization of ~65% within the Permian Basin.⁵²⁻⁵⁴ Consequently, approximately 54% of the 9.9 billion barrels of produced water generated in 2017 were disposed of via SWD wells.¹ In contrast, Texas has fewer facilities for the treatment and recycling of produced water, which can exacerbate economic and logistic challenges and lead to potential competition in water scarce years.⁵⁵ As such, the recycling of produced water (excluding EOR) within the Permian Basin in Texas is estimated at 10%–15%, albeit exact numbers are unknown.^{11,51,56} Meanwhile, water use for O&G within the Permian Basin is currently estimated

to be near 1.2 billion barrels (50 billion gallons/0.2 billion m³) per year, with a potential to increase to an estimated 8.8 billion barrels (370 billion gallons/1.4 billion m³) by 2030.⁵¹ Thus, increasing the recycling of produced water within the Permian could provide an important avenue for meeting future water demand within the industry. However, over the life of the field, produced water volumes may overtake hydraulic fracturing water demand and limit the overall effectiveness of recycling operations, leading to planning and logistics concerns for operators.

The minimal treatment requirements, availability of SWD facilities, and associated reduced liability frequently enable SWD wells to be the most economic management option, in part due to the limited consideration of externalities. Traditional integrated treatment processes for injection include the separation of both suspended solids and oil and grease (e.g., gun barrel tanks, filtration) followed by chemical addition (e.g., antiscalants, corrosion inhibitors, biocides) to protect the well, formation, and related equipment.^{2,12,57} A generalized flow diagram of this process is shown in Figure 5.2A.

WaterTAP3 analysis of SWD facilities in the Permian indicated an adjusted LCOW of \$1.11/m³ (\$0.18/bbl) with an energy intensity of 0.41 kWh/m³ (0.07 kWh/bbl), as shown in Figure 5.2B and C, respectively. These results are near those of actual SWD cost previously reported in the literature in the Permian that range from approximately \$2.50 to 12.50/m³ (\$0.40–1.99/bbl).^{43,58} Yet, conveyance, particularly trucking distances, is often a substantial portion of the cost for both SWD wells and recycling. Including conveyance, disposal fees are reported to range from approximately \$12.60 to 25.20/m³ (\$2.00–4.01/bbl) within the Permian Basin.^{43,58,59} Analysis in WaterTAP3 supports the idea that conveyance costs may be a significant driver for increasing recycling of produced water. For example, WaterTAP3 estimates a 9-fold

increase in the adjusted LCOW if produced water is conveyed 50 miles via truck. While this effect may be mitigated in

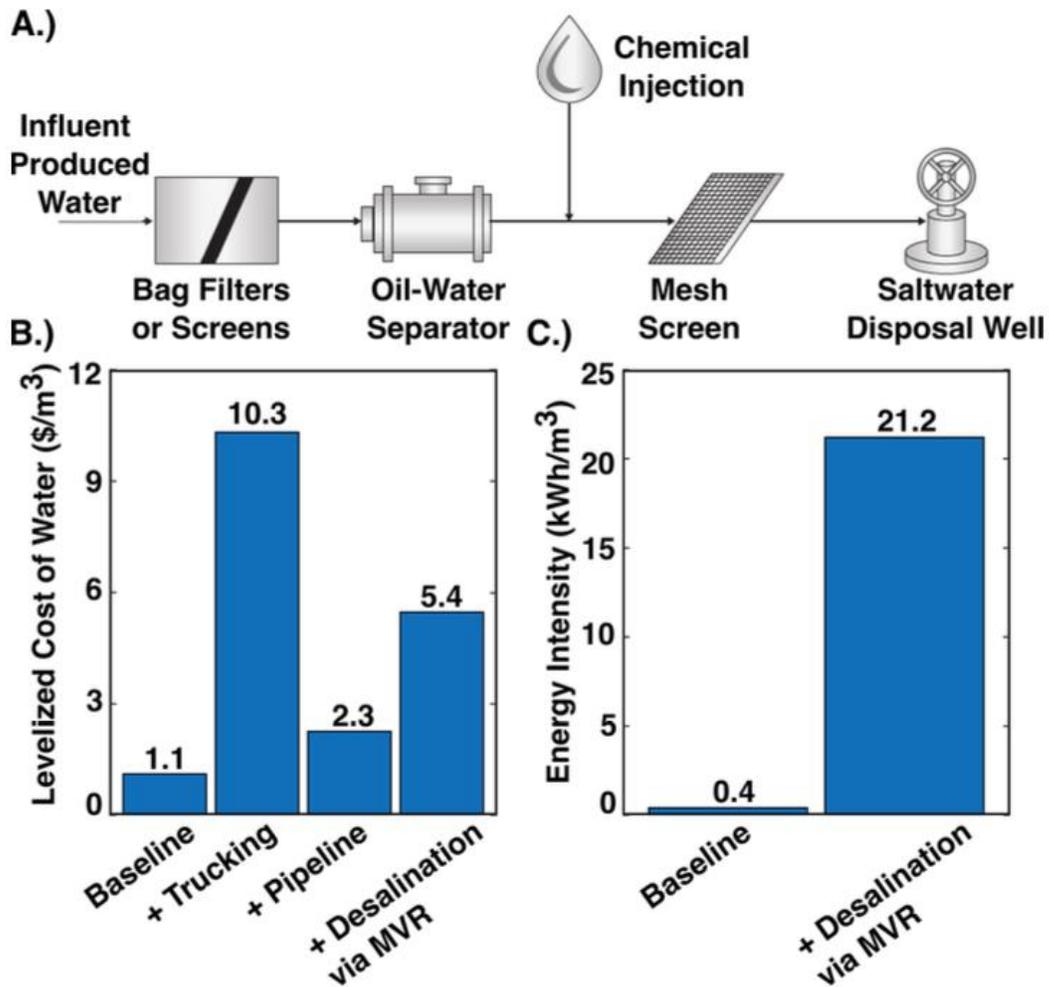


Figure 5.2 - (A) Generalized process flow diagram of baseline treatment train for the disposal of produced water at an SWD facility. Variation in the (B) adjusted LCOW and (C) adjusted energy intensity of the baseline, baseline with 50 miles of conveyance via trucking, baseline with 50 miles of conveyance via pipeline, and baseline with intensified brine management. Additional details on the case study and Water TAP3 inputs are available in the SI. Abbreviations are as follows: mechanical vapor recompression (MVR), levelized cost of water (LCOW), and energy intensity (EI).

part through conveyance via pipeline, WaterTAP3 still estimates conveyance via 50 miles of pipeline more than doubles the adjusted LCOW. Thus, there is interest in both shortening required

conveyance distances and in developing and expanding oilfield water midstream operations (e.g., hydrovascular networks, storage, and centralized treatment facilities) within the Permian and other Texas basins.^{60,61}

Recent changes (Texas House Bill 2771) have reduced permitting requirements for the discharge of produced water to only an NPDES permit from the Texas Commission on Environmental Quality (TCEQ).^{62,63} The TCEQ permits still follow the federal effluent limitations of 40 CFR 435 as well as the state discharge effluent limitations laid out in 30 TAC 307. By easing this permitting process, the Texas legislature hopes to incentivize discharge of produced water for beneficial environmental purposes in the drought-stricken western portion of the state and potentially begin the process of assessing produced water for aquifer recharge.

Thus, intensification of treatment at either SWD facilities or centralized treatment facilities could enable water recovery from produced waters destined for disposal. In particular, pretreatment and desalination utilizing MVR to recover water has been evaluated and field tested in the Barnett Shale Play in Texas.^{64,65} In this approach, produced water-precipitated iron, organics, and suspended solids are removed via coagulation and sedimentation. A set of modular MVR units then desalinates the produced water to generate a stream that can be recycled.⁶⁵ Yet, WaterTAP3 modeling indicates a nearly 5- fold increase in the adjusted LCOW of the process, with the MVR accounting for 83% of the adjusted LCOW and ~90% of the electricity intensity. The contributions of each unit process to the adjusted LCOW and electricity intensity are shown in Figures S5.5 and S5.6 in the Supporting Information. Thus, while recovering water and decreasing disposal volumes may be useful in semiarid and arid regions, the high cost may inhibit economic feasibility. Furthermore, there may still be toxicity concerns and additional treatment requirements for sustainable, beneficial reuse of the treated water recovered from produced water.

3.1.2. Recycling: Anadarko Basin, Oklahoma.

Oklahoma, like Texas, does not explicitly quantify the recycled volume of produced water. Of the approximately 2.8 billion barrels (118 billion gallons/0.445 billion m³) of water produced in 2017, the Oklahoma Corporation Commission (OCC) reported that approximately 45% and 55% were reinjected for EOR and SWD, respectively.¹ An increase in seismic events linked to hydraulic fracturing operations and SWD injection volumes, specifically within the Oklahoma Area of Interest (AOI), heightened interest in limiting disposal and promoting other produced water management techniques. Induced seismicity, particularly in the context of injection and seismicity in Oklahoma, has been a focus of past studies and is outside the scope of this perspective.^{5,66-68} However, future regulations that limit SWD to mitigate induced seismicity concerns may lead to recycling of produced water or other management techniques.

The OCC's O&G Conservation Division has endeavored to reduce disposal volumes via SWD wells within the Oklahoma AOI to 40% below 2014 injection volumes to mitigate the risk of induced earthquakes.⁶⁹ To accomplish this objective, Oklahoma has begun to incentivize the development of centralized produced water treatment facilities and conveyance systems through regulatory measures (OK SB 1875), like those clarifying issues of ownership and liability of produced water while being transported to centralized treatment facilities and back to wells for recycling.⁷⁰ Clearly defining the ownership of and responsibility for produced water during conveyance allows O&G companies to better assess and manage the risks of conveying and treating produced water at centralized facilities that could be owned by a third-party company. However, logistics and costs for the conveyance of produced water could hinder recycling and beneficial reuse of Oklahoma produced water. Thus, the Oklahoma Produced Water Working

Group (PWWG) anticipates that cooperative expansion of water distribution systems would likely facilitate increased recycling of produced water within (and potentially between) Oklahoma's STACK and Mississippi Lime plays.⁷⁰

Newfield Exploration Company, an operator in the STACK play, installed an extensive network of storage, conveyance, disposal, and treatment systems to enable recycling of produced water.¹¹ This network includes approximately 150 miles of HDPE pipe, 10 million barrels (420 million gallons/ 1.6 million m³) of freshwater storage, and 5 million barrels (210 million gallons/0.8 million m³) of treated produced water storage. Newfield's extensive pipeline infrastructure has reduced truck traffic by approximately 60,000 round trips per year.¹¹ Along with reduced truck traffic, pipeline conveyance may reduce the chance of spills and labor costs.^{49,71}

Newfield's Barton Water Recycle Facility provides sufficient treatment of produced water for recycling within the upstream O&G industry. The facility is capable of processing approximately 30,000 barrels per day (1.26 million gpd/4800 m³/day) from approximately 40 well sites.^{11,72} A simplified process flow diagram is shown in Figure 5.3. Influent wastewater is pumped into a series of tanks, where both insoluble organics and solids are removed. Effluent water from the pretreatment process is then transferred to aerated biological treatment holding ponds to oxidize contaminants; the hydraulic residence time in these ponds is approximately 21 days. Following biological treatment, the water reaches a quality suitable for recycling.⁷² Water that is not recycled is disposed of via SWD wells.⁷³ The capital cost of the entire piping and treatment network was approximately \$90 million, and Newfield incurs roughly \$1.26/m³ (\$0.20/bbl) to treat the water. Chemical costs are constant across the process.¹¹

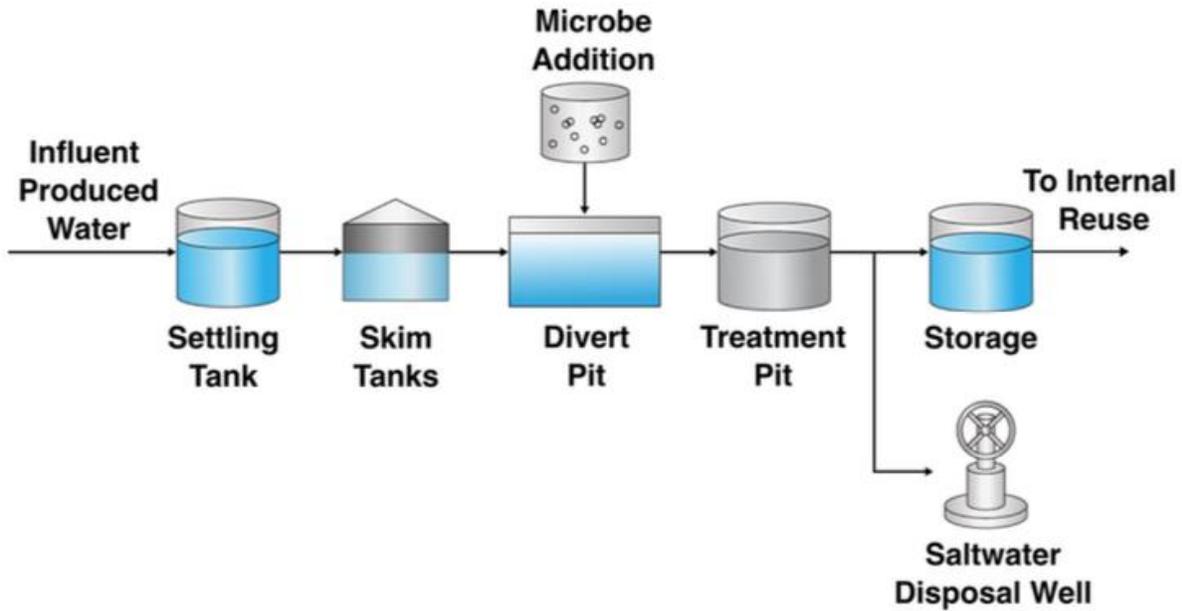


Figure 5.3 - Simplified process flow diagram of Newfield Exploration Company's Barton Water Recycle Facility

The OCC's continued effort to divert produced water management from SWD wells to centralized treatment facilities may help to increase the recycling of produced water. While the expansion of both recycling and beneficial reuse could aid in the economics of centralized treatment facilities, the Oklahoma PWWG identified that beneficial reuse is limited in part by a lack of toxicological understanding of risk to both the environment and public health for many commonly proposed beneficial reuse options.⁷⁰ These environmental and human health concerns must be addressed to expand the beneficial reuse of produced water responsibly and sustainably.

3.2. External Beneficial Reuse

The responsible beneficial reuse of produced water often necessitates extensive fit-for-purpose treatment and management practices. Beneficial reuse of produced water often raises

concerns associated with the contamination of surface and groundwater,⁴⁹ plant health,^{74,75} soil contamination,⁷⁶⁻⁷⁸ and human toxicity that limit industry and public acceptance.⁷⁹⁻⁸² Frameworks and regulations are needed to address toxicology risks and public acceptance issues for beneficial reuse (discussed in Section 4).

Consequently, beneficial reuse of produced water generally requires the removal of constituents such as oil and grease, total suspended solids (TSS), TDS, biological oxygen demand, chemical oxygen demand, and pathogenic bacteria via conventional and advanced water and wastewater treatment processes.^{3,12} More highly regulated beneficial reuse of produced water may also require further treatment for removal of constituents such as selenium, boron, radionuclides, and low molecular weight organics via desalination, advanced oxidation, and adsorption processes. For beneficial reuse, treatment trains might require a process dedicated to reducing the toxicity of the treated produced water to ensure public and environmental safety. Recently, promising studies have shown that photocatalysis-driven advanced oxidation processes (ozonation, rare metal catalyst, Fenton processes) can greatly reduce produced water toxicity.⁸³⁻⁸⁸ Other technologies and processes have shown a potential for reducing toxicity, such as adsorption (granulated activated carbon, powder activated carbon, zeolite),^{89,90} ion exchange, and biological treatments (activated sludge, MBR)⁹¹⁻⁹⁴ but require more research to determine their applicability for produced water treatment.²⁷ Furthermore, if primary, secondary, and tertiary treatments are needed to meet effluent requirements, ensure sustainability, and address public concerns, the resulting treatment system may not be economically viable. Some states, such as New Mexico, have passed regulations that prioritize beneficial reuse and promote research to balance the protection of human health and the environment with increased beneficial reuse of produced water to limit reliance on freshwater resources.⁹⁵ New Mexico also established a research center to identify needed technology and

regulation research to address public health concerns and overcome the economic and safety challenges limiting produced water recycling.⁹⁶

In particular, beneficial reuse of high salinity produced water remains a major challenge due to the current limited options for cost-effective desalination treatments that generate water of adequate quality for potential beneficial reuse, paired with the large volume of residuals that must be managed. Beneficial reuse of produced water with TDS as low as 2000 mg/L may require desalination via membrane-based (NF and RO) or thermal-based (eutectic freezing and MVR) processes to meet effluent requirements. If treatment of high salinity produced waters (TDS > 75,000 mg/L) were extended to ZLD, the volume of solid salts generated would be overwhelming. For example, produced water in the Permian Basin routinely exceeds TDS concentrations of 95 g/L that are mostly NaCl, and the produced water in the basin is expected to exceed 13,000 billion gallons (49 billion m³) over the lifetime of the play (the next 50–100 years).² Assuming an average TDS of 100 g/L and a 100% water recovery, one O&G basin will generate nearly 4.92 billion metric tons of salt over the lifetime of the play, highlighting the potential salt management issues if ZLD was employed industry wide.^{2,97,98} The salt, naturally occurring radioactive material (NORM), and brine residuals management associated with desalination and advanced treatment is nontrivial, and the economics of managing these residuals, whether through ultimate disposal or solidification, need to be considered in assessing the overall economic feasibility of specific treatment operations.

Enhanced resource recovery of either water or valuable constituents (e.g., insoluble hydrocarbons, lithium, iodine) may help offset the cost of produced water treatment.^{8,9,11} For example, prior to disposal, recycling, or beneficial reuse of produced water, insoluble hydrocarbons may be recovered using conventional oil–water separation techniques^{99–101} or novel

higher-efficiency, modular methods.^{102,103} In contrast, recovering inorganic compounds from the concentrated brines generated by treatment processes is often more technically and economically viable. Yet, advances in solute-tailored functionalization of membranes for enhanced selectivity could enable resource recovery earlier in the treatment process.^{104–107} Further research must identify regions where saleable constituents are present in sufficient concentrations to have economic potential, as well as the fit-for-purpose solutions to best extract and refine these constituents.

While treating and adopting produced water for beneficial reuse poses greater challenges for achieving the desired water quality and pipe parity, some existing state-of-the-art management practices have already enabled the beneficial reuse of produced water. The following case studies discuss beneficial reuse scenarios with more stringent effluent standards and limitations: (1) recycling environmental surface discharge and resource recovery in the Marcellus Basin, (2) streamflow augmentation in the DJ and Powder River Basins, (3) agricultural irrigation in the San Joaquin Basin, and (4) municipal reuse in the Powder River Basin.

3.2.1. External Reuse, Recycling, and Surface Water Discharge: Marcellus Basin, Pennsylvania.

Treatment, recycling, and beneficial reuse of produced water within the Pennsylvania portion of the Marcellus Basin is incentivized due to water scarcity and regulatory limitations for underground injection. The combination of Pennsylvania's geology and state regulations (25 Pa Code § 78.18) has resulted in fewer than 15 permitted SWD facilities in the state, culminating in the recycle of approximately 90% of produced water generated in Pennsylvania.^{50,108} Pennsylvania has passed legislation that encourages the development of centralized treatment facilities and conveyance systems by streamlining permitting and reducing regulatory requirements for storage

and conveyance (25 Pa Code § 299). Residual brine streams and remaining produced water are often transported to Ohio, where SWD regulations are less stringent, for injection at a total cost of up to \$94–126/m³ (\$14.94–20.03/bbl).¹¹ Therefore, the O&G industry is financially motivated to pursue innovative options that enable both recycling and beneficial reuse of produced water within the Marcellus.¹⁰⁹

Eureka Resources operates multiple facilities that receive produced water from more than 200 wells and multiple operators in the Marcellus Basin.¹¹⁰ These centralized water treatment facilities include combinations of the treatment processes described in the following section to generate multiple qualities of effluent water, while, when possible, valorizing residuals.⁷³ The specific processes and extent of processing vary by facility based on multiple factors, including customer needs and influent water quality. A simplified, generic process flow diagram of the Eureka Resources process is shown in Figure 5.4.

In general, the treatment facilities have reported capacities of 4000–10,000 barrels (168,000–420,000 gallons/636–1590 m³) of produced water per day.¹⁰⁹ Influent produced water is screened for various water quality parameters (e.g., screened by pH and concentrations of TDS, methanol, and TSS) before entering the treatment train. While influent produced water quality can vary substantially, the TDS are typically 100,000 mg/L.^{111,112} Treatment costs may increase due to factors including increased chemical usage for produced waters with TDS in excess of 150,000 mg/L.^{111,112} Oil and solids are first separated in a primary clarifier. Recovered oil is reclaimed for

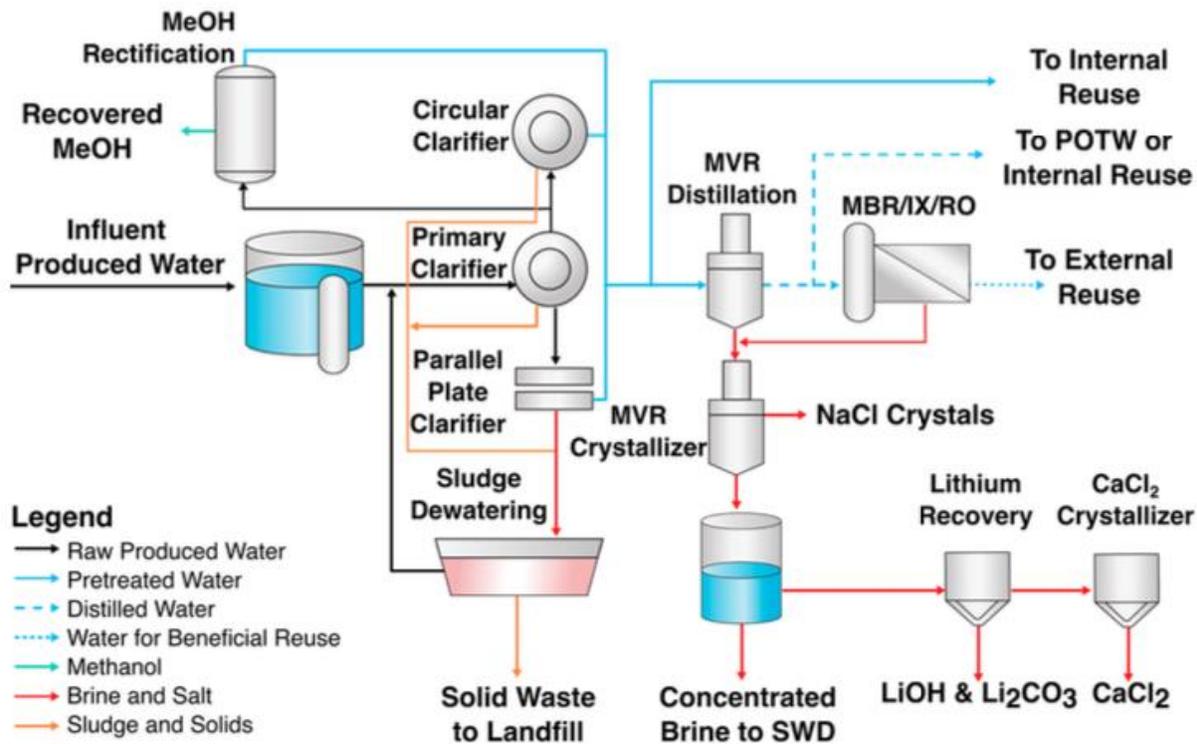


Figure 5.4 - Simplified process flow diagram of various processes employed at Eureka Resources' centralized produced water treatment facilities.^{110,111,114} Abbreviations are as follows: methanol (MeOH), mechanical vapor recompression (MVR), ion exchange (IX), membrane bioreactor (MBR), reverse osmosis (RO), publicly owned treatment works (POTW), and SWD well.

reuse, while the solid stream is dewatered prior to landfill disposal.^{110,113} Eureka Resources estimates that 10–30 tons of solid waste per day is generated for produced water treatment plant with a capacity of 4000 barrels (168,000 gallons/636 m³) per day.¹¹¹ At some facilities, water with elevated methanol concentrations (>500 mg/L) is pretreated using a rectification column to recover methanol for reuse within the O&G industry prior to further treatment.^{109,114} The resulting methanol purity is typically 97%, with trace contaminants (e.g., BTEX, acetone, zinc, calcium, aluminum, water).¹¹⁴ De-oiled produced water flows through the primary clarifier and then one of two parallel clarification treatment trains. While one treatment train is designed for higher TSS streams (e.g., drilling fluids), each train includes pH adjustment and chemical addition, a flash

mixer, a clarifier, and an equalization tank.^{73,109} Effluent water is classified as pretreated wastewater and may be used for internal purposes within the O&G industry.

Pretreated wastewater is desalinated via MVR to produce distilled water that may be recycled or discharged to publicly owned treatment works.¹⁰⁹ This distilled produced water may be further treated with an MBR followed by ion exchange and RO to generate water that meets Pennsylvania's de-wasting effluent standards (Pennsylvania Department of Environmental Protections' WMGR123 Appendix A General Permit Requirements) for direct discharge to surface waters.^{73,113} While high-purity MVR distillate traditionally does not require further polishing, the advanced treatments are necessary to meet the de-wasting standards due to more stringent requirements for the WMGR123 permit. To further evaluate this extended treatment train performance, Eureka Resources worked with the Center for Sustainable Shale Development to conduct additional toxicity and characterization testing with the goal of mitigating toxicity.¹⁰⁹

Eureka Resources endeavors to valorize residual streams from desalination and advanced treatment through resource recovery from the concentrated brine generated during desalination.^{73,109} Concentrated brine (either NaCl or 20% CaCl₂) generated during this process can be reused as a drilling fluid additive, treated via an advanced brine management train, or transported to an SWD facility for disposal.^{73,109,110} Eureka Resources' facilities may also produce NaCl crystals via crystallizer for reuse outside of O&G.^{109,113} Finally, Eureka Resources is currently in the process of developing lithium and CaCl₂ precision separation technology to further valorize the brine generated during this process.

Ultimately, this case study highlights the relevance of flexible, fit-for-purpose produced water treatment that includes resource recovery valorization and reductions in produced water disposal.^{73,109,114} Yet, the viability of this extensive treatment process is contingent on the elevated

cost of produced water management in Pennsylvania.¹¹ Eureka Resources has reported treatment costs for reuse of flowback and produced water of \$40.63–62.50/m³ (\$6.50–10.00/ bbl).^{111,112} For more extensive treatment, the reported crystallization costs are approximately \$68.75/m³ (\$11.00/ bbl), with the potential to reduce to approximately \$43.75/m³ (\$7.00/bbl) with integrated, commercially viable resource recovery.^{111,112} Thus, while this treatment and management approach is often viable within the Marcellus, the elevated cost of treatment and management far exceeds disposal or recycle costs within the Permian and Anadarko Basins. Further, relatively similar facilities, even within the Marcellus, have been idled, highlighting the often volatile economic viability of produced water reuse.¹¹⁵ In particular, shifts in the price of oil affect exploration, production, and consequently the generation of produced water. This instability in the produced water supply may undermine the profitability of these large, centralized treatment facilities. However, management approaches like this may become more common if concerns related to the adequate treatment of produced waters and our understanding of the risks associated with beneficial reuse alter regulatory requirements.

3.2.2. Streamflow Augmentation: Denver–Julesburg Basin, Colorado, and Powder River Basin, Wyoming.

To enable streamflow augmentation with produced water, operators need to meet and receive local and NPDES permits for specific contaminants and water qualities. An example is a permit that an operator has requested from the Colorado Department of Public Health and Environment for discharging treated/blended produced water from a tight shale formation into the South Platte River and St. Vrain Creek in the DJ Basin in northeastern Colorado (PEL230027). Water from a large network of pipelines in the basin that contains a mix of purchased surface and

groundwater and treated produced water (MBR or RO desalination with conventional and ion exchange pretreatment) (first dilution step) is discharged to streams (second dilution step). The discharge limit is based on an elaborate mass balance of various constituents in the pipeline produced water and the water flow rate in the two streams. For the DJ produced water considered in this evaluation, the ratio between discharge flow and streamflow ranges from 1:43 (St. Vrain Creek) and 1:114 (South Platte River) for chronic low flow that represents the 30-day average low flow recurrence in a three-year interval. No data regarding the presence or quantification of organics were submitted to the division with the Preliminary Effluent Limits (PEL) application; therefore, testing for organics would be submitted with the permit application to determine which specific organic compounds are present and need to be removed.

Another example of surface discharge for streamflow augmentation was described by Plumlee et al. in a study that presented a decision support tool that was developed as part of a new framework for produced water treatment and beneficial reuse.⁶ Average water quality was obtained from approximately 90 wells in the Powder River Basin in Wyoming, with an average TDS concentration of ~900 mg/L; this TDS concentration is less than the limit for irrigation (2000 mg/L) and for livestock watering (5000 mg/L) in Wyoming. With respect to streamflow augmentation, the average conductivity values met standards for the Powder River, but the average sodium adsorption ratio (SAR) exceeded the standard. Thus, the produced water would require post-treatment prior to any stream discharge. The decision support tool developed by Plumlee et al. proposed a short treatment train consisting of chemical disinfection, media filter, and potentially NF desalination for sensitive receiving streams. That said, considering the high quality of the raw produced water, the decision support tool gave higher priority to beneficial reuses that demand

higher water quality (e.g., aquifer recharge, fisheries, irrigation, livestock watering, and other industrial applications) than streamflow augmentation.

3.2.3. Agricultural Irrigation: San Joaquin Basin, California.

Treatment of produced water for irrigation could help alleviate the water demand of drought-stricken states with large agricultural practices, such as California and Texas. Currently, the beneficial reuse of conventional produced water for agricultural purposes is done on a small scale, and one operation within the San Joaquin Basin in Kern County, California, has been in operation for over 20 years. Federal regulations in 40 CFR 435 allow for the discharge of O&G produced water for environmental or agriculture use. In California, the Regional Water Quality Control Boards manage the NPDES program and require companies discharging produced water for agricultural uses to provide a list of chemicals added to the water before drilling, the volume of produced water being discharged, and evidence that the discharged produced water meets the effluent limits set by the board for irrigation use. However, the use of produced water for irrigation in Kern County should be viewed as an exception that may not be replicable on a national scale because the background TDS concentrations of produced water in parts of Kern County are very low (<1000 mg/L), and the produced water is co-located with elevated agricultural irrigation demand.^{2,116} For wider use of produced water for agriculture in other oilfield play, cost-effective treatment technologies are needed to reduce high TDS values in other regions to a level similar to Kern County.

The Cawelo Water District ponds, located in Kern County, California, receive treated produced water from neighboring O&G sites, blend it with irrigation water (up to 50% produced water), and then distribute the water for agricultural irrigation (e.g., citrus fruits, nuts). The ponds

have consistently provided reclaimed produced water for agricultural beneficial reuse (longer than any other facility) since the early 1990s and constitute one of the only such facilities in the US. Due to the age of this facility and the requirements of the water district, there is a large amount of historical data on the process and environmental impacts associated with this facility.^{116–119}

One treatment facility, Station 36, upstream of the Cawelo ponds can treat 900,000 barrels (38 million gallons/143,000 m³) per day of produced water from the Kern River oil field. The Cawelo ponds may also receive up to 175,000 barrels (7.4 million gallons/27,800 m³) per day of water from the Valley Water Management Company from the Kern Front oil field. Treatment of high-quality produced water for agricultural beneficial reuse in Kern County focuses on oil–water separations before blending with surface water and pumped groundwater to lower the concentration of dissolved constituents such as As, Na, B, Cl, and Se. As shown in Figure 5.5A, produced water entering the treatment facility first undergoes mechanical/gravity separation, followed by sedimentation, air flotation, and finally filtration through walnut shell filters. Most of the pretreated water is pumped to a series of reservoirs for polishing (evaporation of VOCs), blending, and eventual transfer to the agricultural irrigation systems.¹¹⁹

Beneficial reuse of produced water in Kern County is enabled by the proximity to agricultural needs, low salinity, and low concentrations of constituents like boron. These factors allow for the treatment train to focus on low-cost oil removal, while subsequently utilizing blending with freshwater to lower the concentration of toxic constituents. WaterTAP3 analysis indicates that the adjusted LCOW for the baseline Kern County scenario is \$0.09/m³ (\$0.01/bbl) with a corresponding energy intensity of 0.44 kWh/m³ (0.07 kWh/bbl) as shown in Figure 5.5B and C, respectively. The contributions of each unit process to the adjusted LCOW and electricity intensity for the Kern County baseline study can be seen in Figures S5.10 and S5.11 in the

Supporting Information, respectively. As with the SWD case studies, increasing the required conveyance distances reduces the economic viability of the produced water management option. WaterTAP3 analysis indicates that increasing either the piping or trucking distance to 50 miles will increase the adjusted LCOW to \$0.04/m³ (\$0.01/bbl) and \$0.07/m³ (\$0.01/bbl), respectively.

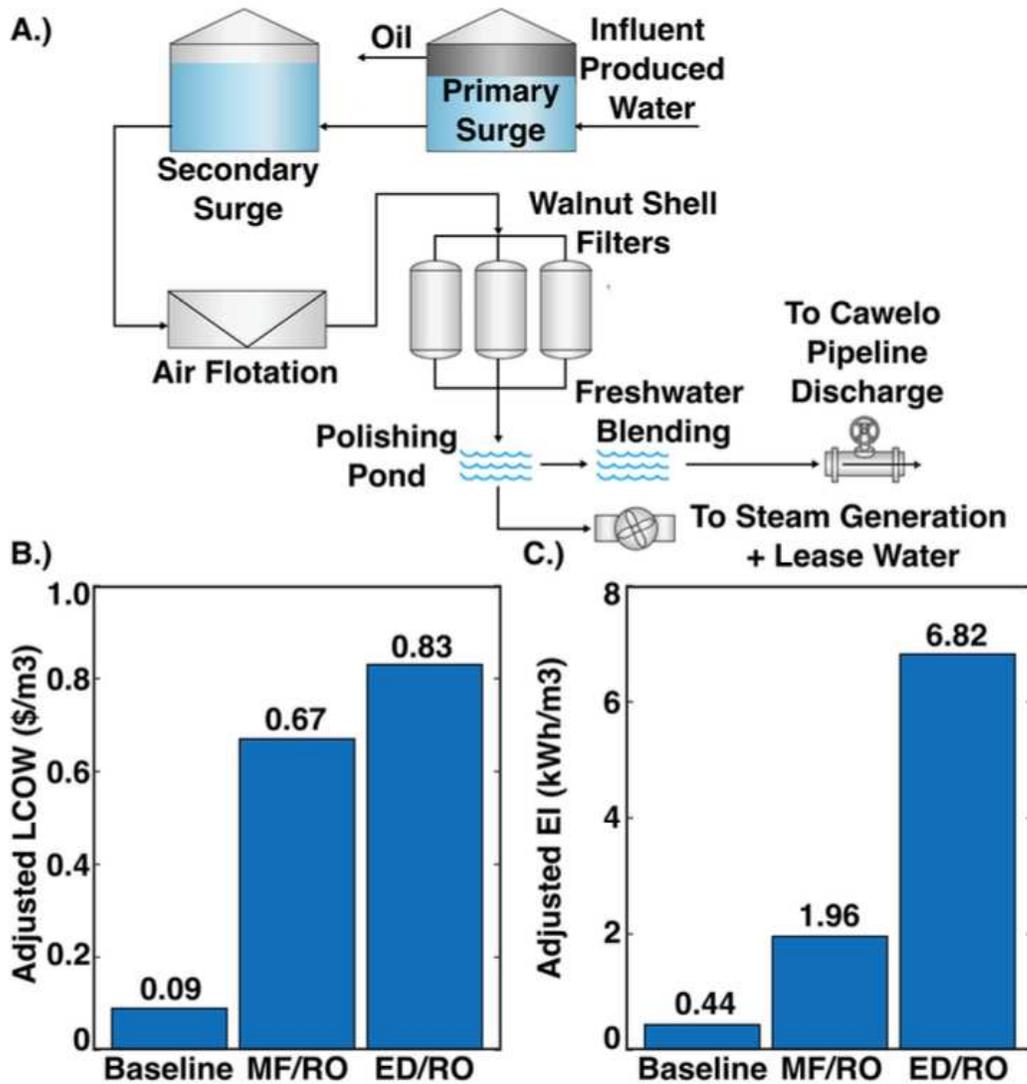


Figure 5.5 - (A) Simplified process flow diagram of the produced water treatment train for agricultural irrigation in Kern county.¹¹⁹ Variation in (B) adjusted LCOW and (C) adjusted energy intensity of the baseline, baseline with additional ED/RO treatment for elevated TDS. Additional details on the case study and Water Tap3 inputs are available in the SI. Abbreviations are as follows: levelized cost of water (LCOW) and energy intensity (EI).

Yet, blending may not be sufficient for sustainable soil and plant health when irrigating with lower quality produced water.^{74,75,120} When the background TDS concentrations are higher (as is typical in other O&G plays), the water will require further pretreatment and desalination to remove salts before use for irrigation, which will result in an overall higher cost of treatment in order to meet SAR guidelines to prevent soil sodicity. Due to these sensitivities, agriculture irrigation requires a much higher water quality than does SWD or recycling. For a brackish produced water with TDS of 10,000 mg/L, WaterTAP3 indicates that incorporating desalination approaches like microfiltration (MF) with RO increases the adjusted LCOW of the blended water stream to \$0.67/m³ (\$0.11/bbl) with a corresponding energy intensity of 1.96 kWh/m³ (0.31 kWh/bbl). The contributions of each unit process to the adjusted LCOW and electricity usage are shown in Figures S5.10 and S5.11 in the Supporting Information, respectively. Yet, as most produced waters have much higher salinities, these values and this approach would still likely have limited applicability.

Furthermore, for produced waters with elevated boron concentrations (>0.5 mg/L), treatment processes may be necessary to meet recommendations for protecting plant and soil health.^{74,121} Common methods for boron removal in produced waters include adsorption, ion exchange, and membranes (e.g., RO, electrodialysis (ED), electrodialysis reversal (EDR)).¹²² Efficient boron removal in RO membranes often requires operation at high pH, as nonionized boric acid is the dominant species in relevant pH ranges (i.e., 6–8) and may diffuse through the membrane.^{123–125} Yet, high pH may exacerbate the fouling of the membrane surface (e.g., calcite scaling).^{126–129} One novel approach utilizes a hybrid ED/RO membrane system to reduce the concentration of anions and cations via ED, increase the pH to alter boron speciation, and remove boron via RO.^{124,130} WaterTAP3 analysis of a hybrid ED/RO membrane system and baseline

pretreatment for enhanced boron removal produces an adjusted LCOW of \$0.83/m³ (\$0.13/bbl) with a corresponding energy intensity of 6.82 kWh/m³ (1.08 kWh/bbl). The WaterTAP3 simulation models ED performance; however, replacing the ED unit with an EDR unit could potentially reduce the LCOW and energy intensity of these treatment trains. The contributions of each unit process to the adjusted LCOW and electricity usage are shown in Figures S5.10 and S5.11 in the Supporting Information. While these case studies consider the presence of both elevated salinity and boron, the presence of other recalcitrant constituents could require additional treatment processes, further increasing both the adjusted LCOW and energy intensity of the treatment approach. Furthermore, with agricultural water costs in California generally ranging from \$0.014 to 0.89/m³ (\$0.002 to 0.14/bbl), these options may not be economically viable at the present time.¹³¹

While similar treatment processes for produced water beneficial reuse in agricultural irrigation may have the potential for adoption in other low salinity basins (e.g., San Juan Basin, Raton, Powder River Basin), expansion to basins with higher salinity produced water with trace contaminants and larger required conveyance distances are unlikely to be economically feasible. Prior assessments of minimally treated CBM from the Powder River Basin for use in agricultural irrigation has demonstrated that minimally treated CBM produced water allows for the short-term growth of crops, with negligible detrimental effects to the crops, but accelerates the long-term degradation of soil health.^{132–134} Furthermore, there has been some social backlash from consumers to the beneficial reuse of produced water for agricultural irrigation.¹³⁵ To combat these public concerns, regulatory agencies have performed sampling tests for the health of crops irrigated with produced water (e.g., almonds, garlic, mandarins) and tests on the soil health irrigated with the produced water.^{136–138} Additional research into human and ecological toxicity may be necessary

to confirm the safety or dictate additional treatment needs for widespread use of treated produced water for agriculture irrigation.

3.2.4. Municipal Reuse: Powder River Basin, Wyoming.

While beneficial reuse options like irrigation and streamflow augmentation are of interest in semiarid regions, water scarcity in severe drought-stricken regions may justify assessing the viability of municipal reuse or even direct potable reuse (DPR). In particular, many regions with significant CBM production experience water stress, which could be partially mitigated through the beneficial reuse of low salinity CBM produced water. For example, in the Damodar Valley Basin in eastern India, a techno-economic analysis indicated that RO-treated CBM produced water could provide high-quality water for an estimated 3.5 million people over 20 years.¹³⁹ Another techno-economic analysis by Meng et al. suggested that RO-treated unconventional and conventional produced waters in California could provide drinking water for one million residents per year.¹³¹

Singh and Colosi evaluated the feasibility of DPR of CBM produced water from the Damodar Valley Basin for both centralized and decentralized RO treatment systems.¹³⁹ In the centralized system, the RO-treated produced water is pumped through a pipe network into homes. In contrast, in the decentralized system, raw produced water is treated in homes for point-of-use RO treatment. For both cases, a non-commercial desalination technology, Wind-Aided Intensified eVaporation and Membrane Crystallization (WAIV-MCr), was modeled for brine management. WAIV-MCr is a process that concentrates the brine 10 times through evaporative processes, and a subsequent membrane process further intensifies the brine, resulting in solid salt byproducts, a clean water stream (50% recovery), and a membrane brine purge.¹⁴⁰ WAIV-MCr may have limited

applicability due to its ambient condition requirements (e.g., wind) and its inability to recover freshwater.¹⁴¹ While Singh and Colosi evaluated RO as the only treatment step in the centralized DPR treatment train, the WaterTAP3 results presented herein focus on the centralized treatment train and incorporate UV inactivation and addition of chlorine to comply with US drinking water regulations (e.g., disinfection credits, chlorine residual) (Figure 5.6). These additional treatment steps were added to inactivate pathogens and prevent microbial regrowth in the distribution system.

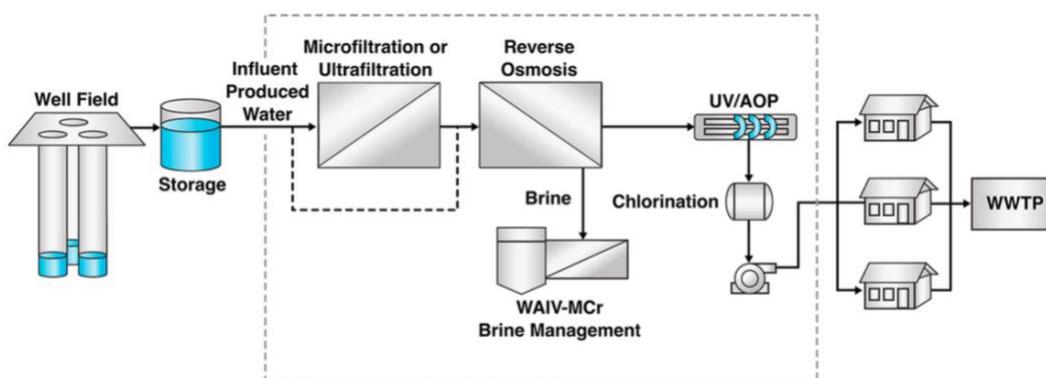


Figure 5.6 - Process flow diagrams for a proposed centralized treatment systems for municipal reuse. Abbreviations are as follows: Wind-Aided Intensified eVaporation and Membrane Crystallization (WAIV-MCr), ultraviolet (UV), and advanced oxidation process (AOP). Additional details on the case study and Water TAP3 inputs are available in the SI.

The potential for municipal reuse of produced water in the US was evaluated using CBM produced water from the Powder River Basin. WaterTAP3 analysis of the modified centralized treatment train indicates an adjusted LCOW of approximately \$2.20/m³ (\$0.35/bbl) with an energy intensity of 1.40 kWh/m³ (0.22 kWh/bbl) for a 4500 m³/day treatment facility. Similar to the original analysis, greater than 50% of the adjusted LCOW can be attributed to the WAIV-MCr (Figure S5.13), highlighting the importance of cost-effective brine and residual management approaches in achieving pipe parity.¹³⁹ Thus, improvements in either the brine management

technologies or co-location of the centralized treatment facilities with SWD could help to improve the economic viability of this produced water management approach. Yet, while the estimated LCOW is above the municipal water costs from freshwater sources ($\$0.30\text{--}0.80/\text{m}^3$ or $\$0.05\text{--}0.13/\text{bbl}$), they are relatively similar to those of brackish water or seawater desalination for municipal use ($\$0.90\text{--}1.70/\text{m}^3$ ($\$0.14\text{--}0.27/\text{bbl}$) and $\$1.80\text{--}4.20/\text{m}^3$ ($\$0.29\text{--}0.67/\text{bbl}$), respectively) and could provide a potential solution for rural homeowners rather than build out brand new municipal water treatment districts.¹⁴² In response to growing water scarcity, some municipalities have started to rely on brackish and seawater desalination facilities to provide municipal water, and thus, CBM produced water for municipal reuse may be financially feasible.

However, while it may be economically viable for these treatment trains to achieve potable drinking water standards, the lack of toxicological information on unregulated constituents in this water limits the ability to safely adopt low salinity produced water for potable use. The general lack of toxicological studies on produced water poses both a scientific and a social hurdle in the adoption and general public's acceptance of these waters for more sensitive uses (e.g., food crop irrigation and municipal usage). Furthermore, many states lack regulations concerning municipal wastewater DPR and those that do have complex regulations and limitations concerning DPR.¹⁴³ Given the social and regulatory hurdles encountered during the implementation of DPR with municipal wastewater, it is difficult to imagine the drivers that would enable DPR with produced water in the US. Ultimately, responsible, sustainable beneficial reuse of produced water may require holistic chemical characterization and toxicological assessment to inform treatment train development to appropriately mitigate risk to the public and the environment (as depicted in Figure 5.1).

4. CHEMICAL CHARACTERIZATION AND TOXICOLOGICAL CHALLENGES

The complex chemistry of produced water creates characterization challenges that, when coupled with the understudied nature of drilling/fracturing fluids and the transformation products that form in the well, leads to difficulties in evaluating the success or failure of produced water treatment trains. Current research is attempting to overcome some of these challenges in characterizing produced water^{31,144} and suggests that numerous unregulated or proprietary chemicals may be present in any particular untreated produced water stream^{25,145,146} and therefore potentially exist in treated produced water. The difficulty in characterizing constituents in produced waters, in addition to the lack of data, has likely hampered policymakers and regulatory agencies in developing policies that enable advanced treatment of produced water to facilitate alternative water reuse. This, coupled with the lack of data on completion and production chemicals, and with clear and defined treatment goals, likely creates concerns that the water may not be adequately characterized or treated for the desired end use. Therefore, future research efforts must identify analytical and bioanalytical methods for indicator/priority compounds or transformation products in produced water. These indicators, which would serve as metrics for the evaluation of treatment technologies for beneficial use of produced water, must capture the breadth of water quality concerns for the targeted end use.

There is a critical need for developing rigorous protocols that ensure sustainable management and beneficial reuse of treated produced water. Previous studies have identified these needs and suggested that such protocols should include components to address monitoring, process control, treatment effectiveness, and potential environmental and health risks. In addition, phased approaches for evaluating produced water management options have been developed (GWPC) that

incorporate both initial and beneficial reuse evaluations, legislative and regulatory assessment, logistics, economics, and benefits (Phase I).¹¹ Evaluation is followed by the identification of contaminants for treatment and risk analysis using pilot testing and effluent characterization (Phase II), traditional risk assessment methodologies (Phase III), and risk management (Phase IV).¹¹ While these recently developed approaches have significant potential for addressing produced water management at scale, they have failed to address the underlying gaps associated with assessing the suitability of produced water for particular end uses.

Untreated produced water matrix complexity (e.g., salts, organics, microorganisms) creates challenges for results in the application failure of traditional water and wastewater analytical methods, often due to interferences induced by specific constituents present at high concentrations in these waters and a dearth of analytical methods for analyzing unknown organic compounds present in these fluids and brines. Because an appropriate array of indicators and bioanalytical tools has yet to be identified or developed, these current methods fail to connect treatment process selection to chemical- or toxicity-based end points relevant for a specific use. Consequently, the systematic framework required to properly assess the chemical or toxicity end points of a waste product as complex as produced water has not yet been developed. Thus, while Figure 5.1 highlights the need to incorporate toxicity end points for particular end uses, an appropriate framework to link technology performance to end use specific toxicity measures is still lacking.

In terms of bioanalytical tools, several studies have allowed for a basic assessment of which particular fractions might contribute the most to certain toxicological end points, but they have rarely extended to whole organisms. This work has been performed on various model invertebrate and vertebrate systems and has been carried out almost exclusively with raw produced water. End points that have been studied include mortality (LC50),¹⁴⁷ developmental effects in early life

stages,¹⁴⁸ endocrine disruption,^{147,149} estrogenicity,¹⁵⁰ physical and behavioral impairment,^{78,150,151} cardiovascular effects,^{152–154} oxidative stress,^{155,156} ionoregulatory stress,¹⁵¹ metabolic stress,¹⁵⁷ and genotoxicity.¹⁵⁰ While these studies have contributed to our general knowledge of the toxicity associated with raw produced water, none have outlined approaches that could be followed to assess the toxicity of treated produced water.

Treated produced water matrices with, for example, lower salt and organics will be substantially different from the raw water matrix. A common practice of diluting water samples before analysis often results in the inability to detect compounds that were originally present at low concentrations. Not only does this practice create challenges in comparing pretreated and post-treated water, but it also may result in a gap in assessing synergistic chemical interactions during toxicity assessments. The analytical challenges are compounded by the multitude of unknown compounds present in produced water from either the subsurface,¹⁵⁸ proprietary fracturing fluid additives,¹⁵⁹ subsurface transformation products,¹⁶⁰ or the formation of chemicals during treatment.¹⁶¹ Thus, significant efforts are needed to either identify or find indicators to assess the toxicity of treated produced water for use outside the O&G industry.

4.1. Toxicological Considerations

Toxicity analysis, both acute and chronic, is the most reliable approach for determining the long-term suitability and safety of produced water for beneficial reuse. The use of toxicity assays for assessing treated effluent quality for surface discharges is often required. Whole effluent toxicity (WET) is employed within the NPDES permits program to evaluate the toxicity of the entire waste stream and should be considered as part of pretreatment compliance inspections of municipal wastewater treated effluent.¹⁶² While the selection of methodologies for toxicity testing

of treated produced water will likely vary depending on the desired end use, both short-term and long-term impacts need to be considered.

Acute toxicity, generally defined as an adverse outcome after short-term exposure, can be evaluated through classic toxicology methods such as LC50 assays¹⁶³ or focused on specific end points (e.g., estrogenicity to genotoxicity) using in vitro bioassays. The evaluation of chronic toxicity (an adverse outcome after long-term exposure) is challenging because it must consider the life cycle of an organism with respect to exposure duration and adverse effects.¹⁶⁴ This can make causal relationships difficult to determine because additional confounding factors can play a role concurrently during the exposure period (i.e., synergistic or antagonistic effects). Synergistic effects are adverse outcomes amplified by the presence of other compounds;¹⁶⁵ this is especially concerning because produced waters are complex heterogeneous mixtures with many compounds that have the potential to interact with other natural organic and inorganic matter. This brief review of treated produced water toxicity focuses on two of the alternative beneficial reuse pathways discussed above: beneficial reuse for crop irrigation and streamflow augmentation. While different end uses of treated produced water may have differing acceptable levels or optimal assessment tools for toxicity (i.e., cooling tower reuse vs irrigation for crops), the two examples selected represent beneficial reuse options of near-term interest that may have direct impacts on ecological systems and indirect impacts on human health.

4.1.1. Irrigation

The agricultural sector has the greatest potential for beneficial reuse of treated produced water² but also has potential for toxic exposures to a variety of end points/ biological systems. Beneficial reuse for irrigation involves indirect human exposure through consumption of food

products irrigated with treated produced water but also includes environmental exposure to animals, plants, freshwater, and soil systems. The long-term impact on soil health in cropland is an essential component of evaluating this beneficial reuse pathway and the potential accumulation of inorganic chemicals, such as simple salts, boron, arsenic, NORMs, or metals, that could prove detrimental to agricultural soil health. There has been little research to date in this area, with the only long-term use of treated produced water for irrigation occurring in the San Joaquin Basin, which was detailed in Section 3.2.3. This paucity is compounded since the water in that basin is not representative of produced waters found elsewhere in the US (primarily its low TDS values).

Recent greenhouse studies have investigated the irrigation of crops with diluted, untreated produced water to address several questions regarding the role of simple dilution when irrigating crops.^{74,75} These projects demonstrated that even when salinity concentrations meet local irrigation recommendations, diluted produced water (e.g., 5% produced water, 95% freshwater) can still adversely affect soil health by impacting the soil's physical properties, changing the soil microbiome, and overall decreasing crop yield.¹²⁰ Similar studies suggest that diluted produced water induces greater suppression of the plant's immune response⁷⁴ and promotes plant stressors (i.e., saline or oxidative stress) that lead to greater decreases in crop yield compared to controls containing the same concentration of salts but no other known contaminants.⁷⁵ Thus, current dilution targets that focus solely on salinity are not necessarily appropriate; targeted end points should address soil health and plant toxicity as depicted in Figure 5.1.

The studies described above complement the analysis of agricultural fields in Kern County, California, that demonstrates an accumulation of sodium and boron in fields irrigated with diluted produced water, even in cases when the water met local criteria for boron (less than 1 mg/L) or contained only 17% more sodium than local groundwater.¹¹⁶ In general, the effects of these

inorganic contaminants on soil health and plant physiology are well understood,^{166,167} so treatment approaches can be designed to reduce their impacts using existing knowledge. For example, the scenario options identified for the Kern County case studies include desalination and boron removal using membrane technology. Evaluation of the impact of these improvements on salt accumulation and soil and plant health is needed. However, even in this case, more work is also needed to determine if there are relevant synergistic effects involving inorganic contaminants within this complex mixture, and future toxicity analyses need to focus on the impacts of treated produced water on the soil fauna necessary for a healthy soil (i.e., bacteria, fungi, nematodes, or earthworms).

There is little to no research on how treated produced water impacts the surrounding environment and its many receptors (e.g., ecotoxicological risks to plants or wildlife). The only research to date is on spills or releases of untreated produced water that correlate O&G activity to increases in endocrine disrupting compounds (EDCs) in nearby surface water,¹⁶⁸⁻¹⁷⁰ compounds that can cause adverse reproductive effects in freshwater organisms.¹⁴⁷ Thus, thorough characterization of the TOC remaining in treated produced water will be necessary because excess irrigation water could drain from agricultural fields into nearby surface water systems, and the uptake and accumulation of organic compounds found in flowback and produced water have been demonstrated in wheat plants.⁷⁹ Uptake and accumulation of complex organic molecules such as PAHs,¹⁷¹ EDCs, personal care products, and pharmaceuticals have also been shown to occur in corn,¹⁷² leafy vegetables,¹⁷³ wheat,¹⁷⁴ and root vegetables¹⁷⁵ through irrigation with reclaimed wastewater. While flowback and produced water likely does not contain any pharmaceuticals or personal care products, the uptake of these compounds into plants shows the potential for crops to transport similar complex organic molecules into the plant biomass. Overall, our understanding of

plant uptake, the formation of toxic metabolites through plant metabolism,¹⁷⁶ and the potential for synergistic effects of these organic compounds with pesticides or inorganic compounds¹⁷⁷ remains limited. In the absence of rigorous research and analytical methods for assessing end use specific toxicity of treated produced water, it will be difficult to develop metrics to guide engineers and regulators and reassure the public.

4.1.2. Streamflow Augmentation

Streamflow augmentation is another method that O&G producers use to discharge their produced water. This practice is allowed in arid states west of the 98th meridian and is regulated under the NPDES permit system (Section 3.2.2). Requirements for obtaining these permits and effluent limits of specific parameters may be site specific and vary from state to state or by EPA region. For example, at a discharge site in Wyoming, the NPDES permit has specific effluent limits for oil and grease, TDS, specific conductance, chloride, sulfate, Ra²²⁶, and pH, while acute toxicity is also analyzed every 6 months.^{7,80} This is in contrast to the NPDES permitting in Colorado that also requires an assessment of chronic toxicity.⁸⁰ Produced water discharged for streamflow augmentation typically undergoes some type of treatment prior to release to meet NPDES regulations for oil and grease levels (<10 mg/L at this site). The treatment prior to discharge can be through separators (heat, gravity, or chemical), settling ponds, flotation, and/or skimming.⁷

Analysis of streamflow augmenting produced water effluent at one site in Wyoming showed that these treatment trains are effective at meeting NPDES requirements at the discharge point. However, downstream four of the six regulated parameters increased in concentration, and specific conductance increased above the permissible limit for NPDES regulated effluent (only regulated at the effluent discharge).^{7,178} At the discharge point, the produced water effluent

underwent comprehensive chemical characterization that showed the presence of over 20 unregulated volatile/ semi-volatile organic compounds and three different types of surfactants.^{7,179} Concurrent mutagenicity assessments of effluent at the discharge point showed increased mutation rates with four different mutation types when compared to a negative control, but these mutation rates decreased as the discharge flowed down the augmented stream.⁸⁰ This produced water discharge was eventually consumed by cattle downstream in an ephemeral lake, but consumption also occurred as close as ~100 m to the effluent discharge. Eventually, the augmented stream terminated upon entering a perennial river or at times even dried out before reaching the river.⁷ This example highlights the importance of linking treatment trains to end use toxicity measures as suggested in Figure 5.1. The presence of both salinity and organic compounds downstream of the discharge point suggest that more advanced treatment is needed. Both advanced oxidation and adsorption processes are capable of reducing toxicity. As a result, treatment trains such as that provided within the Eureka Resources case study may be necessary. More importantly, this work brings to question the use of the current NPDES permitting approach and highlights the need for thorough chemical characterization and toxicity assessments to fully understand the risks of discharging treated produced water to the environment. Within the context of discharge to natural water bodies, the presence of bioaccumulating contaminants in complex produced water discharges can represent another threat that must be considered.¹⁸⁰ These issues have added importance in the arid west, where produced water effluent might be the major water source of an ephemeral water body that is consumed by various animals/livestock; alternatively, if the effluent flows into a perennial river, it would eventually be utilized downstream for either agriculture or as a drinking water source.¹⁸¹ While the cost of treatment and toxicity testing may deter streamflow augmentation with produced water, treatment process advances and improved toxicity testing

approaches may prove to be cost effective in the future. Indeed, future toxicity testing may be less expensive and more informative than existing analytical tools such as high-resolution chromatography/mass spectrometry.

4.1.3. Bioanalytical Tools

Toxicological characterization of produced water to date has primarily focused on diluted raw produced water and on either organic or inorganic fractionated components of raw water. Chemical separation techniques (e.g., solid phase extraction) have been used to partition organic components from inorganics without dilution, allowing for bioassay testing of each fraction at a variety of dilutions. However, we currently lack the standard separation/dilution methods to facilitate comparisons among research studies and between raw and treated samples. Future methods must address this limitation to allow the development of generalizable insights and produced water toxicological databases.

4.2. Proposed Method for Assessing Toxicity in Treated Produced Water

The complexity of produced water makes it difficult to establish methods to determine biological toxicity. However, even more challenging is the fact that each produced water has a distinct composition, and when volatile organic compounds dissipate, the composition and toxicity of the water will change. This makes it exceedingly difficult to formulate thresholds for concentrations of constituents in either raw or treated produced water that might be expected to generate adverse environmental effects. One approach to solving this problem is the implementation of an adverse outcome pathway. The adverse outcome pathway concept uses existing toxicity testing methodologies at all levels of biological organization relevant to human

and ecological risk assessment.¹⁸² Adverse outcome pathways identify molecular and biochemical changes following exposure to a given chemical or effluent, and use of these as sublethal, early warning signs of eventual toxicity at the individual and/or population level provide a useful approach to follow in evaluating a treatment process that meets that water's specific end use (Figure 5.7).

Adverse outcome pathways could be integrated into an assessment of biological toxicity as follows. Preliminary "first tier" testing should initially establish links between mortality and exposure utilizing, for example, traditional toxicity tests such as LD/LC50 assays with early life stages, usually the most sensitive developmental stage. Ideally, such assessments would be performed chronically (the most realistic exposure scenario) and should involve a wide variety of different produced waters extracted from different geological formations that have gone through the same range of treatment steps. Chronic assessments would also allow samples to be taken over time for determination of sublethal changes, allowing linkage of these more subtle effects to mortality. The specific sublethal end points of interest should focus on pathways known to be impacted by salts (i.e., whole body ion homeostasis and associated enzymes, such as sodium/potassium ATPase), organic compounds (i.e., induction of biotransformation pathways, such as cytochrome P450 enzymes), and metals (e.g., metal handling pathways, such as metallothionein).

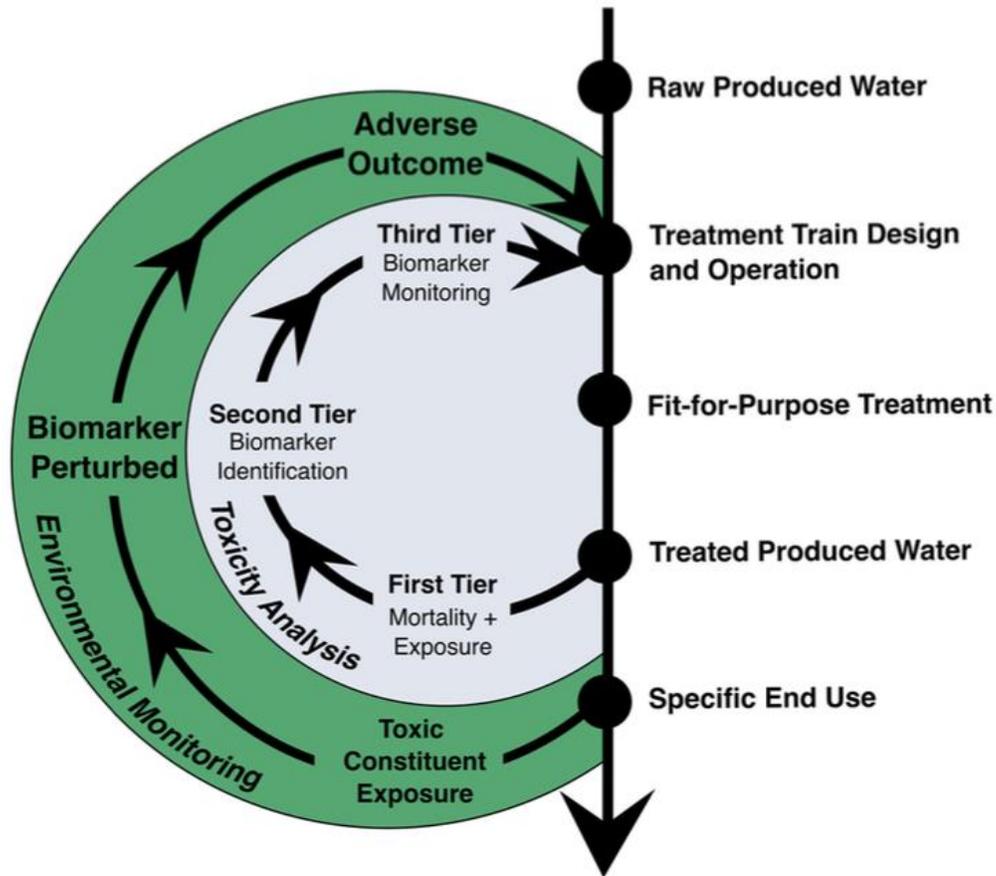


Figure 5.7 - Proposed method for incorporating adverse outcome pathways and toxicity analysis into the design and operation of fit-for-purpose treatment trains for specific end uses of produced water.

This “first tier” approach would be conducted in combination with “second tier” methods, based on the end use of the water and its potential to impact broader receptors in the environment. These may include “omics” techniques (e.g., transcriptomics, proteomics, epigenomics, and metabolomics), which are wide-scale screening techniques that can be used to identify other end points that are consistently changed upon produced water exposure.¹⁸³ First and second tier approaches would be of greatest efficacy if performed in standard model organisms across multiple phyla. Standard model organisms offer a greater availability of genetic information along with the ease of culturing such animals in the laboratory, and the past use of standard organisms will

facilitate knowledge of exposure history. These studies will be critical to establish robust adverse outcome pathways and to establish the strongest linkages between sublethal change and eventual mortality. Once established, biomarkers that have been identified as early warning signals of future adverse effects will have to be verified in region-specific monitoring for the “third tier”. Ideally, field-collected biota (of greatest relevance to the specific region and end user) can be sampled and assessed for the sublethal changes. This may ultimately require lab-based verification that the relationship between exposure and effect holds for the species of interest. Following this multilevel adverse outcome pathways approach, treatment technologies could be evaluated for their ability to not just reduce toxicity but ideally eliminate it from these complex industrial waters.

Overall, the adverse outcome pathway method can be used to continuously monitor toxicity regardless of the effluent’s end use. Adverse outcome pathway analysis would be able to verify the effectiveness of any proposed treatment for produced water. If toxicity is appearing in vitro, then the specific biomarkers affected can help identify which class of chemicals is causing toxicity, and the treatment system can be modified accordingly. Once a certain treatment system has been established, the adverse outcome pathway method allows for a framework to establish credible regulations/policy because the targeted biomarkers are reliable indicators of toxicity that can be used to monitor the effectiveness of the treatment and beneficial reuse systems in situ. Therefore, if O&G producers want to beneficially reuse produced water at a specific location for a specific outcome, they could concentrate on the biomarkers that would be the focus of any regulatory requirements, then independently develop a treatment system and analyze the potential toxicity of the treated produced water in key model organisms (i.e., organisms defined by the end use and environmental restrictions). Lastly, long-term monitoring of the biological systems exposed to this treated produced water would be essential and should be conducted by testing different phyla of

animals in the field for these established bioindicators; this monitoring would act as an alarm system, indicating adverse outcomes that might be manifesting in the environment.

5. CONCLUSIONS AND RESEARCH NEEDS

This perspective presents a current baseline of treatment methods of produced water in the O&G industry. We first provided a baseline of current water treatment practices for different end uses of produced water and then provided context and analysis for six case studies. These six case studies were chosen to represent different water treatment and disposal methods, different geographic regions, and different end uses of treated produced water. Where data were available, we modeled these case studies in the WaterTAP3 model to assess the LCOW and energy use for different treatment trains and source waters. On the basis of these modeled case studies, we also examined sensitivities and scenarios to determine the implications of utilizing treatment in other regions and water qualities. Even though the LCOW of current treatment practices may not be competitive with current water and treatment costs, technology innovations, changing water availability, mutable regulations, and rising water costs over time are likely to cause these treatment trains to become competitive with other water sources, especially when examining opportunities in water scarce regions. In cases such as CBM for municipal reuse, the economics may appear to be competitive with similar nontraditional water sources such as brackish water, but water treatment economics may not be the sole driver for future increased beneficial reuse of produced water. Regulatory frameworks are needed to ensure that environmental and health risks of beneficial use are communicated and managed. Frameworks should address monitoring, process control, treatment effectiveness, and potential environmental and health risks and can build off past developed frameworks (GWPC).

This perspective attempts to provide a framework that (a) links such tools to treatment train selection and optimization to reduce the potential toxicity associated with the beneficial reuse of produced water and (b) can be applied to case studies of treated produced waters of varying composition and end use targets, with the goal of identifying appropriate chemical indicators, biomarkers, and bioanalytical assays that correctly assess the risk associated with each particular end use. Thus, research is needed that employs a comprehensive adverse outcome pathway methodology for a range of waters and uses. The resulting data can be used to develop monitoring tools or optimize treatment trains that are relevant to produced water beneficial reuse for a specific end point. This analysis should begin with a baseline case in which produced water beneficial reuse has been employed for a long period of time, such as Kern County agricultural beneficial reuse. Comprehensive adverse outcome pathway testing on treated water, plant species, and soil samples would provide a baseline for the study of more complex waters in Colorado, Wyoming, Texas, and New Mexico. While this approach is necessary for reducing the risks associated with the beneficial reuse of produced water, it can also be applied to other industrial reclaimed water reuse scenarios, as well as to other unconventional water sources.

Author Contributions

According to the CRediT (Contributor Roles Taxonomy) criteria my contributions to this paper include validation, investigation, writing-original draft, and visualization. Contributions from C.C., J.M., C.M., M.B., J.R., and T.B., include validation, investigation, writing-original draft, and visualization. Contribution from T.B., L.K., and T.C.. include conceptualization, resources, writing -review & editing, supervision, project administration, and funding acquisition. Contributions from J.S-D. and J.M. include conceptualization, investigation, and writing-review

& editing. Contributions from A.M., Z.H., A.E., K.S., and P.K. include formal analysis, data curation, and visualization.

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CHAPTER 6: SUMMARY

Altogether this dissertation is a culmination of work that is examining different aspects of soil health. Soil health is an all-encompassing term that describes more than just the “health” of soil and includes the impact soil has on other aspects of the ecosystem such as water quality and human health. However, this is one of the challenges when working with soil health because there are various definitions, some of which are inclusive of downstream effects of soil while some are narrower in scope and focused on site specific impacts. For example, the US Department of Agriculture defines soil health “as the continued capacity of soil to function as a vital living ecosystem that sustains plants, animals, and humans.” This definition prioritizes one of the primary functions of soil, plant productivity, and highlights that a healthy soil is needed to maximize the yield of crops that can sustain animals and people. Chapter 2 of this dissertation explores this definition of soil health by analyzing the soil in different areas of a citrus grove based on observable differences in plant growth. Because these citrus trees were of identical age and managed identically, differences in soil health were hypothesized as the reason behind these differences in crop productivity. Soil analysis demonstrated that SOM concentrations were significantly different between these areas, thus the impact that SOM has on other aspects of a healthy soil system was driving these differences in plant productivity.

The results from Chapter 2 are supported by other research that all generally agree SOM is the most important component of soil health and the component that impacts both the site-specific functions and the downstream effects on ecosystems. One of the broader definitions of soil health is presented in a recent perspective by Lehmann et al. [1] in which they argue that the four primary impacts of a healthy soil are plant production, water quality, human health, and climate. They

propose a variety of management practices that can improve these four functions and the first option for improving the soil health as it relates to these functions is adding organic matter to the soil [1]. Thus, based on the results of Chapter 2 and the need to improve the soil in that citrus grove, Chapter 3 investigates how adding different organic amendments to the soil can affect the composition of SOM.

This study utilized high-resolution analytical techniques to analyze how the organic components of the SOM change over time in response to the addition of either biochar or compost and a cover crop. High resolution mass spectrometry (FT ICR-MS) showed that biochar contains molecules that are more reduced and consequently more resistant to degradation while the compost contained organic molecules that were more oxidized and thus more easily degraded. Based on the residence times of these different amendments in the soil, these results show that when considering all functions of soil health, biochar is a better choice of amendment for this soil system. Biochar sequesters carbon into the soil for potentially decades, retains nutrients thus reducing nutrient leaching, and improves the physical structure of the sandy soil studied. The final portion of that research will analyze the microbial diversity to elucidate the impact these different amendments had on the microbiome to fully understand these molecular level impacts. Altogether, improving these organic soil components will increase the productivity of the orange trees grown which is the primary goal of the farmer, but improved water quality typically correlates with improved soil health as well.

Understanding water quality through the lens of water reuse/treatment is the primary objective of Chapters 4 and 5 but in these various reuse scenarios, soil health is always a factor. For Chapter 4, the focus was on reuse of agricultural wastewater within agriculture but one of the biggest challenges with this reuse process is the spatial variability across the USA and temporal

variations that limits generalizability of reusing irrigation runoff. The two regions this review paper focused on were California and the Midwest, two areas that have different constituents in the runoff and different water laws that dictate the legality of reuse. As this paper relates to soil health these two regions can be summarized in the following manner. In California, where irrigation runoff is saline, reuse of this water without prior treatment can harm soil health by concentrating salts in the soil. Salinity can collapse the soils physical structure resulting in compaction or erosion and can also be toxic to the soil microbiome. Conversely, in the Midwest, irrigation runoff contains high concentrations of fertilizer nutrients in the irrigation runoff and although at typical runoff concentrations these compounds are not toxic to organisms, they can enhance eutrophication downstream. These algal blooms can be toxic to humans and other organisms while also depleting the water of oxygen which kills fish and result in large economic losses to tourism and the fishing industry. By improving soil health in the Midwest, these soils could retain more nutrients, require less fertilizer application, and absorb more water leading to less erosion, all of which would result in improved water quality and human/animal health downstream.

Lastly, Chapter 5 focused on the reuse and treatment of produced water (PW) from oil and gas extraction. Two of the reuse case studies focuses on the feasibility of reusing this water for agriculture, either directly as crop irrigation or indirectly by augmenting ephemeral streams that livestock drink. PW has many toxic contaminants that limit its reuse, mainly salts, metals, and organic contaminants of emerging concern (CEC) that can all be toxic to the ecosystem in which it is reused. The salts cause similar problems to soil health as discussed above but in addition to those problems, this water can also damage soil health by concentrating metals such as boron, arsenic, or other heavy metals which are toxic to the soil fauna and the plants that are grown in the

soil. Plants can accumulate these metals or CECs in their biomass causing toxicity to the organisms that consume them and thus impacting the human health component of soil health. So, the reuse of PW for agriculture is a concern in regard to soil health because of the potential for damaging soil systems if the water is not properly treated.

In conclusion, maintaining soil health is one of the most important ecological issues on our planet right now because of the impact soil has on every system in the environment. By emphasizing the importance of soil health, understanding its impact across environmental systems, and properly managing the organic matter in the soil we can utilize soil to improve a variety of environmental issues. When maintaining soil health we can preserve adequate crop production, improve water quality, and utilize soil as a carbon sink. And although soil has many functions, by focusing on the management of SOM and minimizing soil degradation, we can support these various functions simultaneously because a healthy soil means healthy people and a healthy planet.

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APPENDICES

APPENDIX A: SUPPLEMENTARY INFORMATION FOR CHAPTER 2



Figure S2.1 - low productivity region in the foreground and high productivity region in background

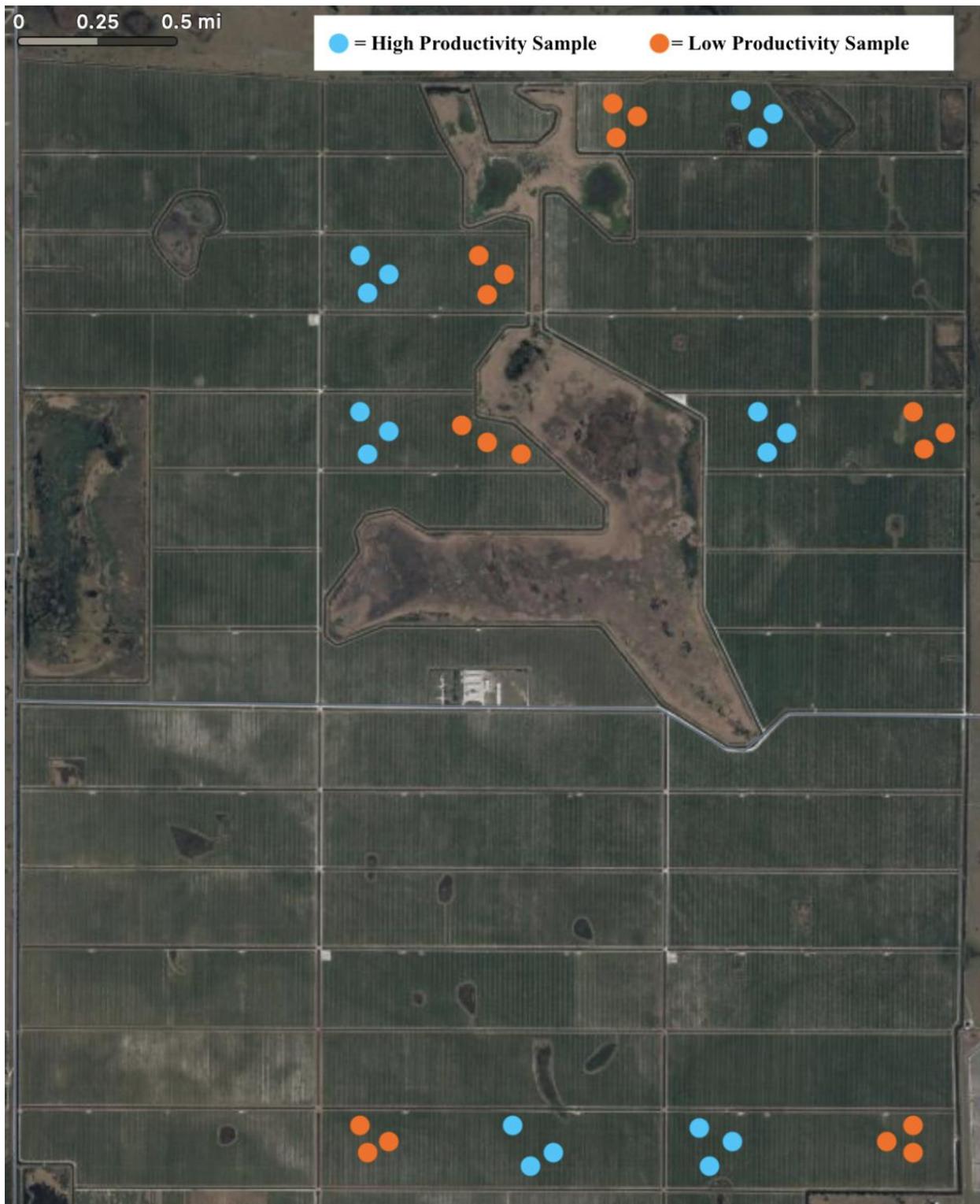


Figure S2.2 - sampling locations within the citrus grove

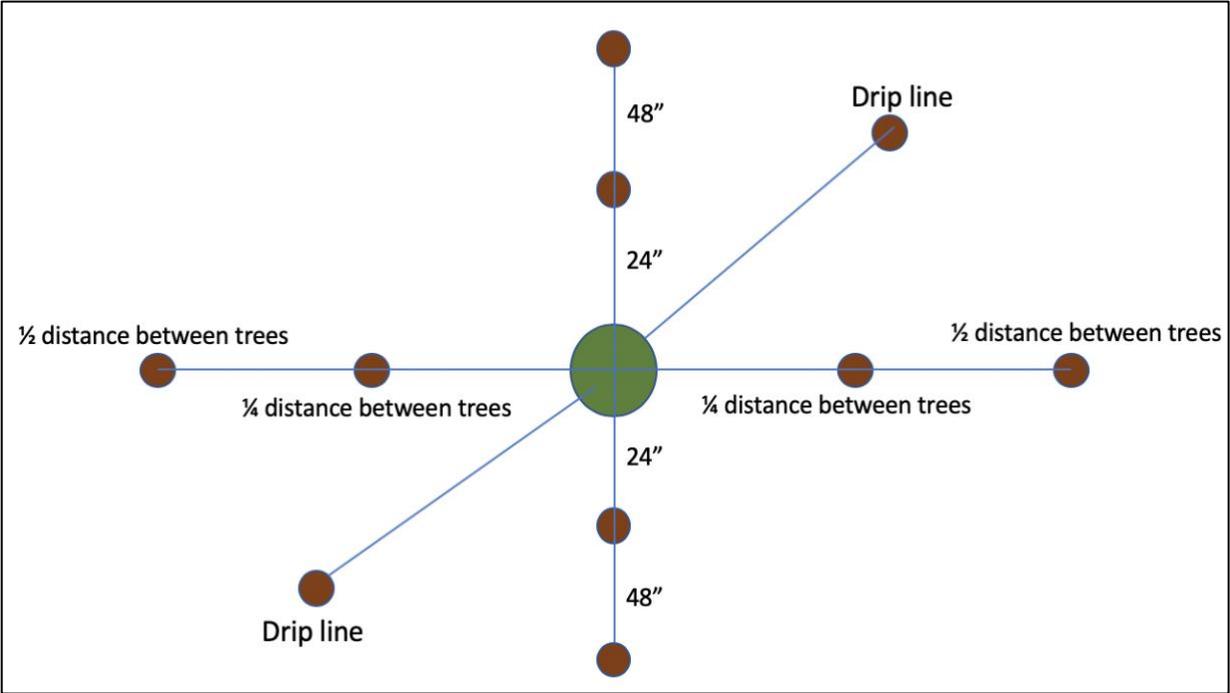


Figure S2.3 - composite sampling scheme

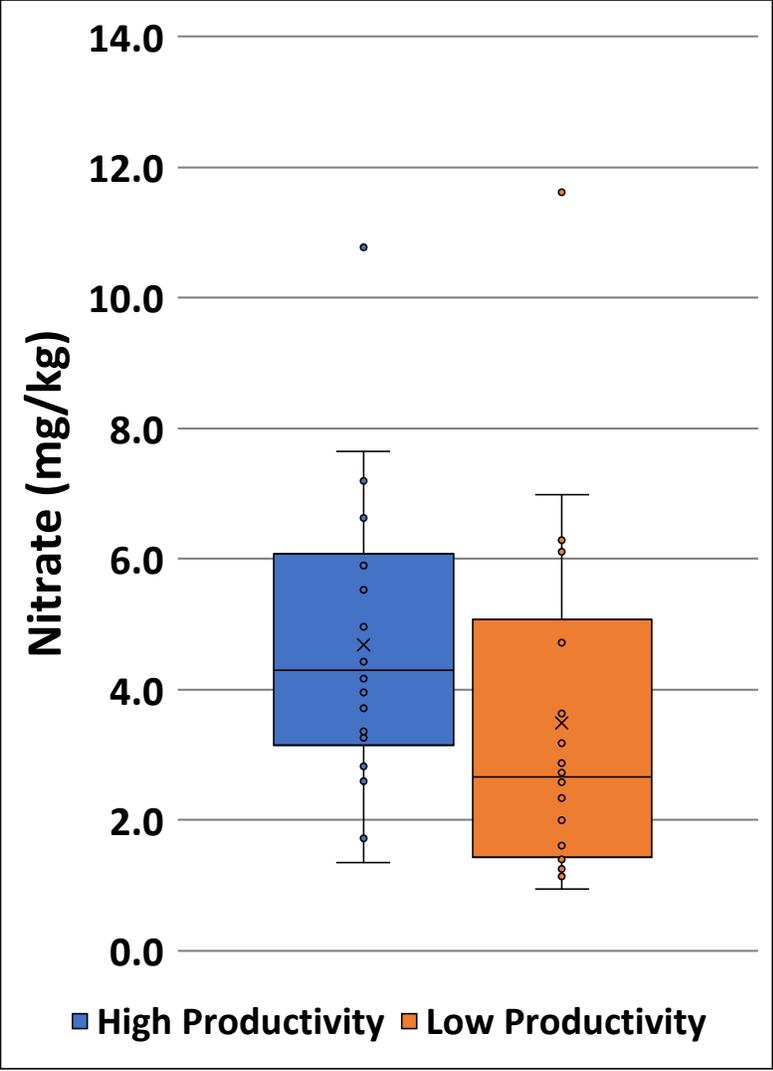


Figure S2.4 - non-significant differences in extractable soil nitrate

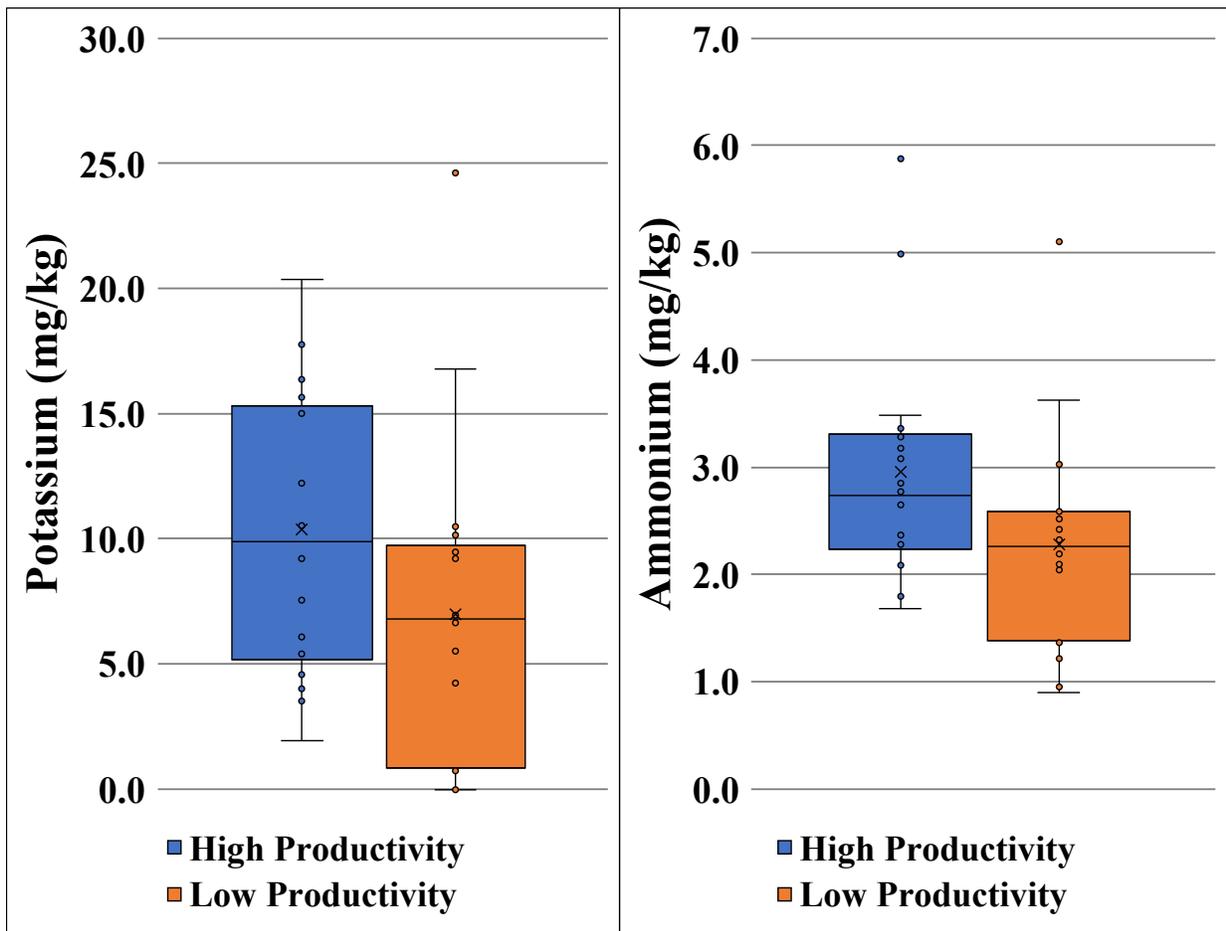


Figure S2.5 - non-significant differences in soil extractable K, $p=0.10$ (a) and ammonium, $p=0.06$ (b) showing similar trends between high productivity and low productivity regions of the grove

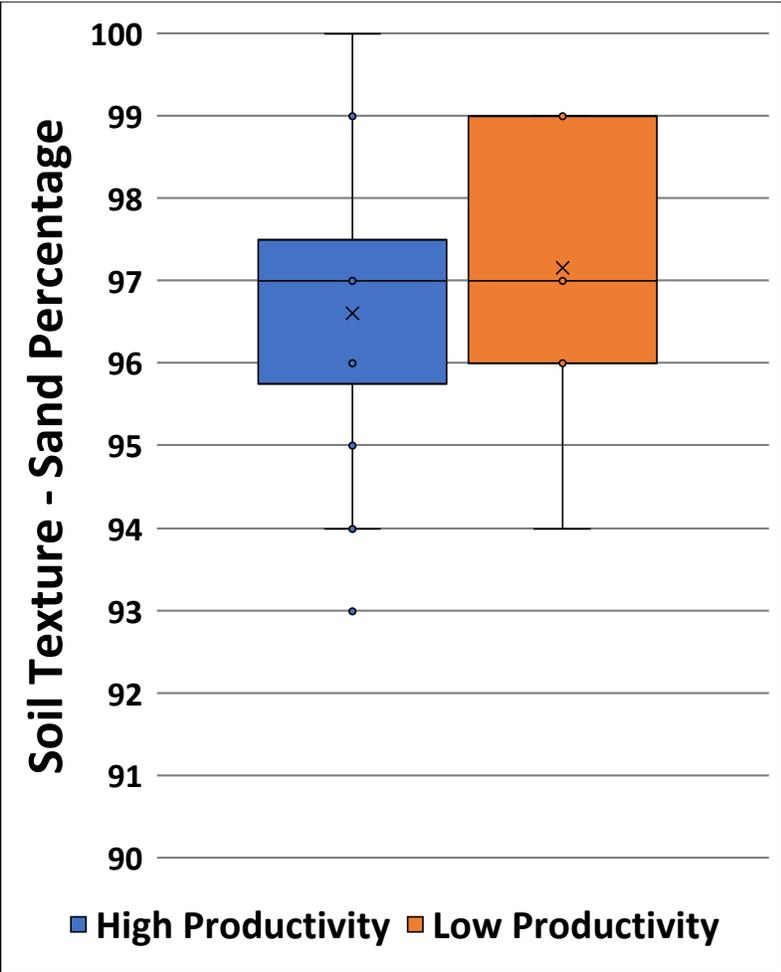


Figure S2.6 - non-significant differences in the percentage of sand comprising soil texture

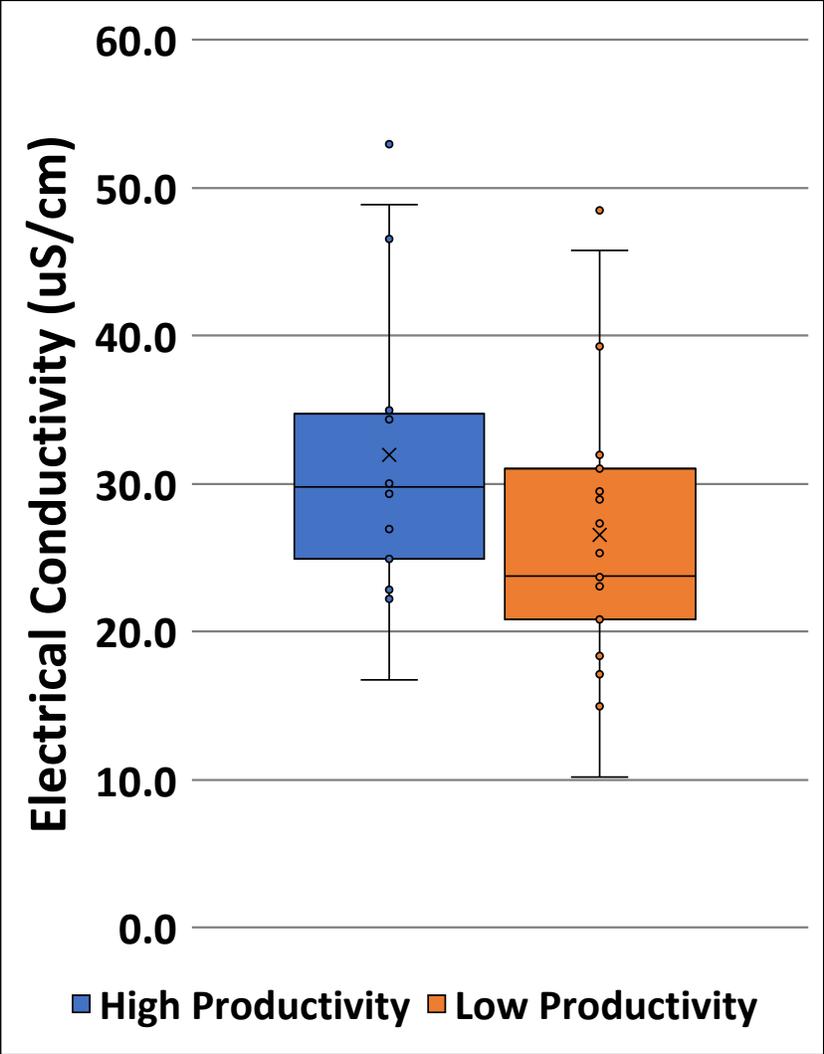


Figure S2.7 - non-significant differences in electrical conductivity

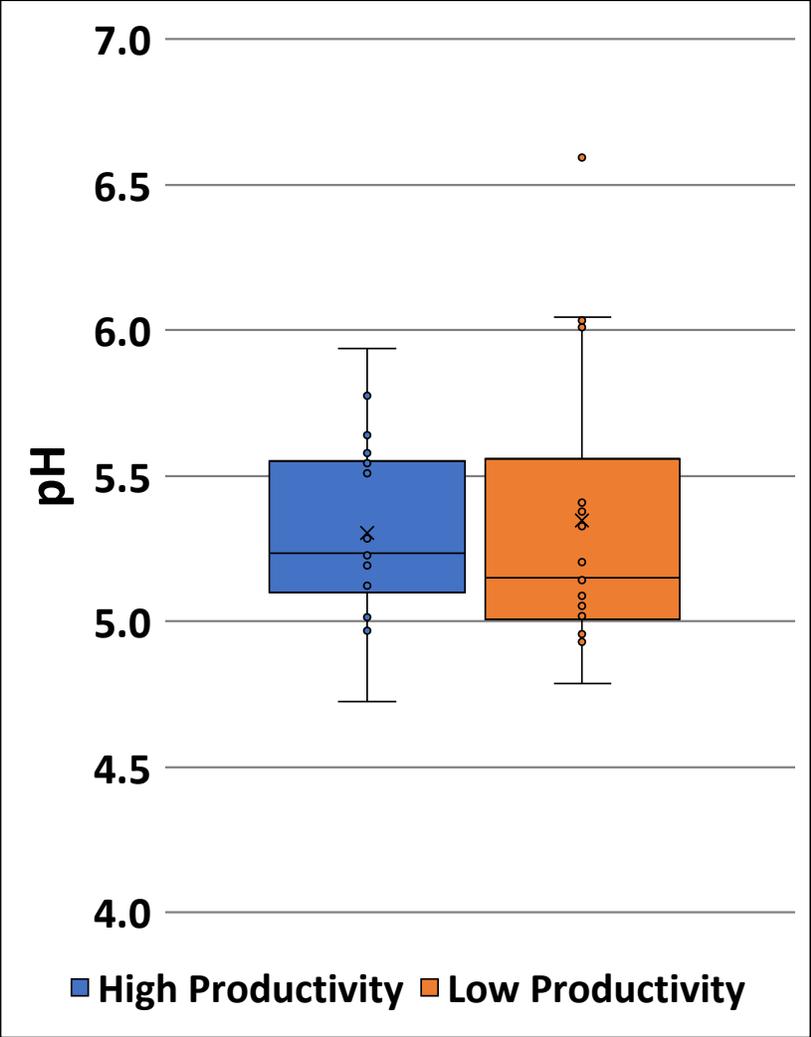


Figure S2.8 - non-significant differences in soil pH

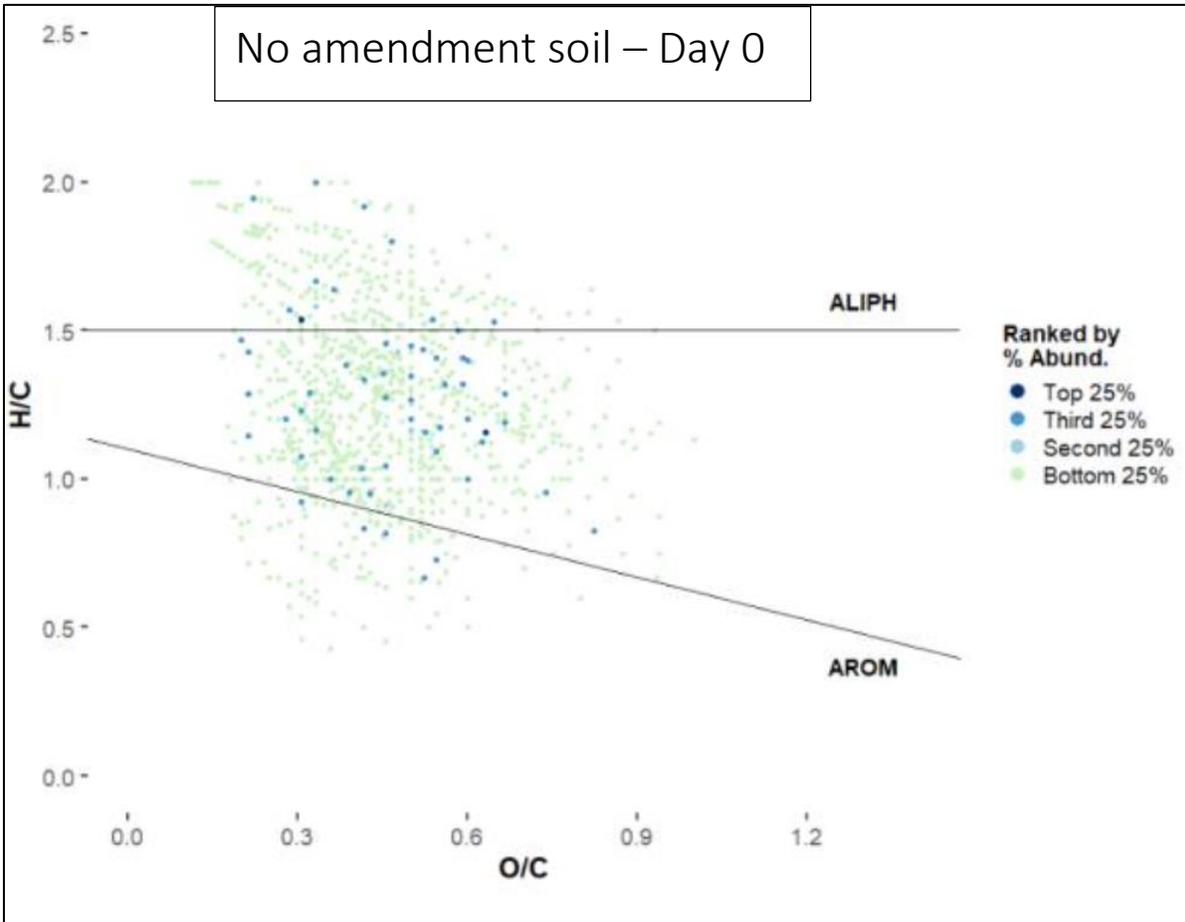


Figure S3.1 - soil with no amendment at Day 0 showing unique formula when compared to the compost amended soil

APPENDIX C: SUPPLEMENTARY INFORMATION FOR CHAPTER 4

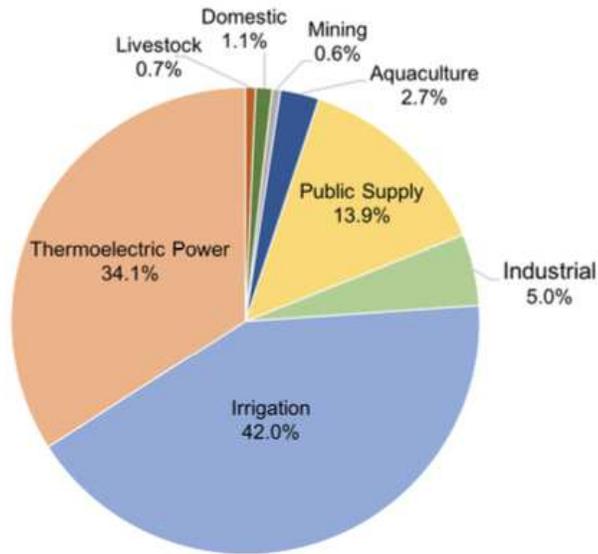


Figure S1. 2015 freshwater withdrawals by sector in the U.S.¹

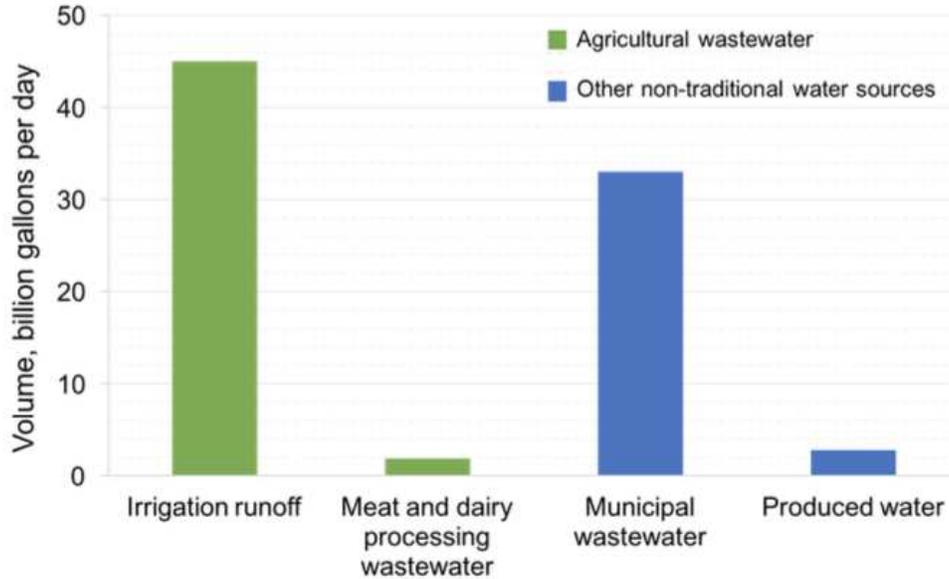


Figure S2. Volumes of selected non-traditional source waters including agricultural wastewater produced daily in the U.S.²⁻⁴

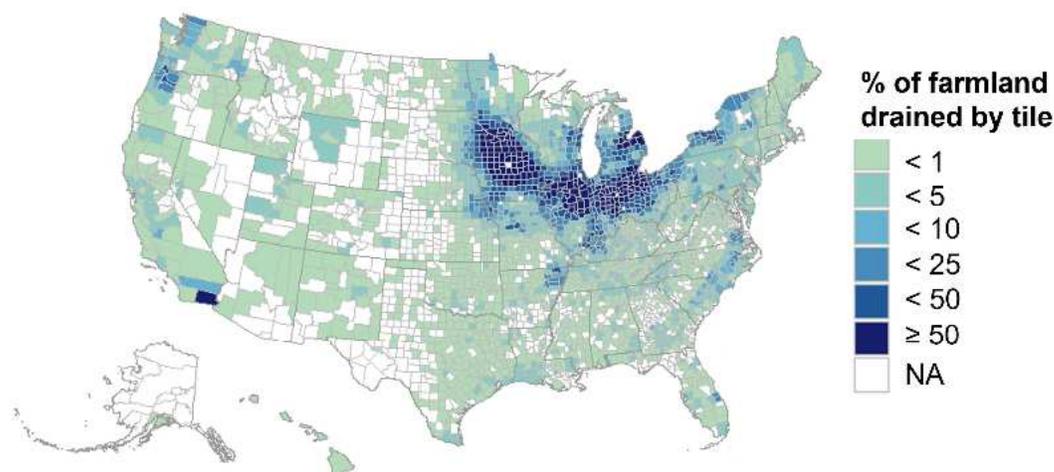


Figure S3. Distribution of tile drainage systems for each county in the U.S. based on the 2017 USDA Agricultural Census.⁵

Table S1. Water Qualities from SLDTP Influent and Effluent⁶ and Target Effluent for Irrigation Reuse⁷⁻⁸.

Parameter	Units	Influent (Average)	Effluent (BWRO)	Effluent (SWRO)	Target Effluent ^A (Long-term use)	Target Effluent ^A (Short-term use)
Selenium	µg/L	208.9	BDL	0.60	20 ⁸	20 ⁸
Arsenic	µg/L	13	-	-	100 ⁸	2,000 ⁸
Boron	µg/L	30,504	12,417	21,321	750 ⁸	2,000 ⁸
Calcium	µg/L	483,400	330,000	1,970,000	-	-
Chloride	µg/L	3,074,000	62,500	40,200	70,000	-
Chromium	µg/L	14.5	BDL	2.40	100 ⁸	1,000 ⁸
Iron	µg/L	963.8	BDL	BDL	5,000 ⁸	20,000 ⁸
Manganese	µg/L	28	BDL	BDL	200 ⁸	10,000 ⁸
Mercury	µg/L	1.5	-	-	-	-
Nitrate + Nitrite as N	µg/L	12,500	100	130	5,000 ⁷	30,000 ⁷
Total Phosphorus	µg/L	64.3	BDL	BDL	1,000 ⁷	5,000 ⁷
Sulfate	µg/L	7,225,500	80,800	28,800	-	-
Uranium	pCi/L	33.1	-	-	-	-
pH	SU	6.6	-	-	6.5 ⁷	8.4 ⁷
TDS	mg/L	12,408	94.5	147.2	-	-

^A Target water quality concentrations are general guidelines that might not be suitable for all crops.
BDL – below detectable limit

Text S1. WaterTAP3 methodology

Cost estimates within the WaterTAP3 model were calculated at the unit process level based on the specific case study. This was then aggregated to encompass the full treatment train to provide costs including capital investment, annual operation, and maintenance costs. The model contains a library of water quality data for non-traditional water sources and includes technical and cost parameters for a range of treatment technologies. WaterTAP3 is constrained such that the unit processes achieve mass balances for the existing or specified end-use parameters (i.e., water recovery, constituent removal requirements) and these parameters use factors and equations to represent limitations of each unit process. WaterTAP3 users can choose from parameters including technology, source water, and end-user water quality requirements to develop a technoeconomic analysis and proposed treatment train. Full documentation of inputs, assumptions, and equations can be found in a public-access cloud-based folder created by NAWI and the WaterTAP3 developers (<https://github.com/NREL/WaterTAP3>).

Text S2. WaterTAP3 case study assumptions

The capital cost, O&M costs, electricity consumption, TDS rejection, and water recovery of the RO unit model were based on a basic representation of the physical performance of the process. The feed water quality was defined according to the TDS concentration (12,408 mg/L). Membrane performance (i.e., permeate and salt fluxes) was determined based on pressure drop equations and mass transfer balance. The capital cost was estimated using the cost of membrane area (\$ per m²), capital cost of the pump required to deliver the transmembrane pressure, and the RO infrastructure. Using the transmembrane pressures reported in the SLDTP, the following pressures were used in the RO WaterTAP3 simulations: 36 bar (520 psi) and 25.5 bar (370 psi) for SWRO and BWRO, respectively. All other variables in the reverse osmosis model have default assumptions that can be found in Miara et al.⁹ To better match industry standards, the cost of electricity used in the WaterTAP3 model was assumed to be the average industrial cost of electricity in California, instead of using the government subsidized cost that was available to the SLDTP. Finally, cost data for other treatment units such as the ABMet bioreactor were estimated using standardized cost metrics built into WaterTAP3.⁹ A more detailed description of the WaterTAP3 methodology and assumptions can be found in Miara et al.⁹

Table S2. Summary of financial and operational data modeled within WaterTAP3.

Analyzed Parameters	WaterTAP3 Model
Total Capital Investment, million (MM) \$	3.73
Operating and Maintenance, MM\$/year	0.18
Levelized Cost of Water (LCOW), \$/m ³	1.73
Electricity Consumption, kWh/m ³	2.69
Inlet Water Recovery, %	61.14

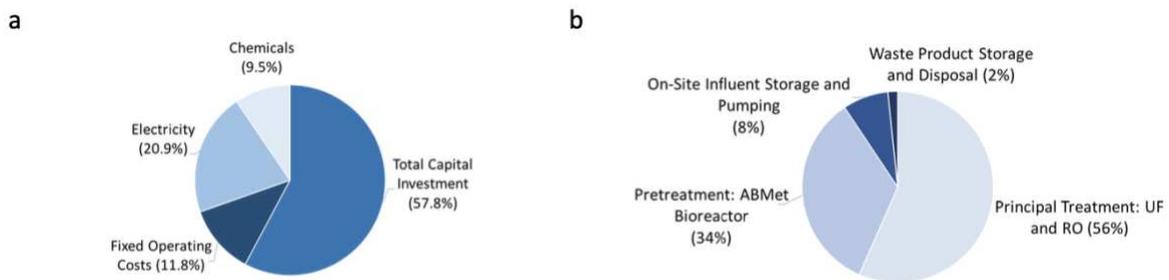


Figure S4. WaterTAP3 estimated cost breakdown by (a) major cost category and (b) treatment process area, respectively.

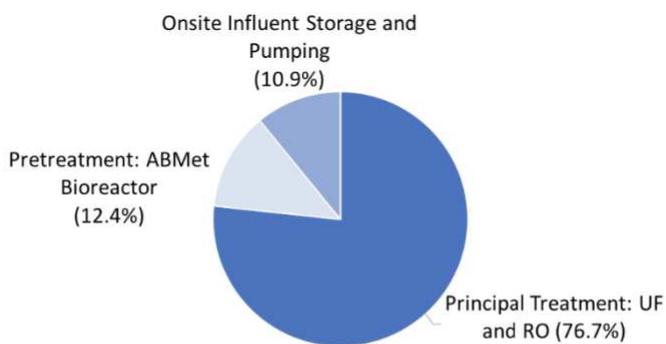


Figure S5. WaterTAP3 estimated electricity consumption breakdown by treatment process area.

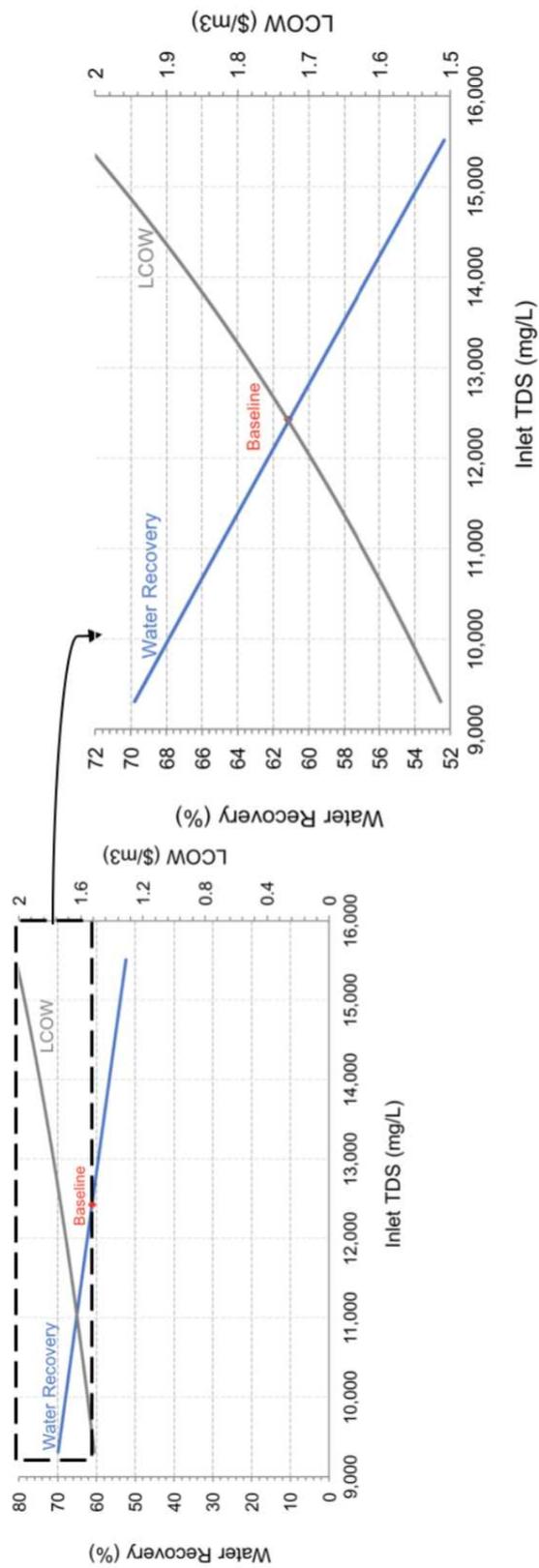


Figure S6. Tradeoff between water recovery and LCOW as a function of inlet salinity for applicable conditions in the SLDTP.

APPENDIX D: SUPPLEMENTARY INFORMATION FOR CHAPTER 5

Supporting Tables

Table S1: Summary of recent papers and resources for Produced Water Quality, Quantity, Regulations, Environmental Impacts, and Management.

Title	Authors	Year	DOI
Produced Water Quality			
Water quality assessment downstream of oil and gas produced water discharges intended for beneficial reuse in arid regions	M.C. McLaughlin, T. Borch, <i>et. al.</i>	2020	doi.org/10.1016/j.scitotenv.2020.136607
U.S. Geological Survey National Produced Waters Geochemical Database v2.3	Engle, M. A., Saraswathula, V., Thordsen, <i>et. al.</i>	2019	doi.org/10.5066/F7J964W8
Produced water characteristics, treatment, and reuse: A review	Al-Ghouti, Mohammad A.; Al-Kaabi, Maryam A.; <i>et. al.</i>	2019	doi.org/10.1016/j.jwpc.2019.02.001
A critical review of risks, characteristics, and treatment strategies for potentially toxic elements in wastewater from shale gas extraction	Y. Sun, D. Wang, <i>et. al.</i>	2019	doi.org/10.1016/j.envint.2019.02.019
Temporal characterization and statistical analysis of flowback and produced waters and their potential for reuse	K. Oetjen, K.E. Chan, <i>et. al.</i>	2018	doi.org/10.1016/j.scitotenv.2017.11.078
Organic compounds in hydraulic fracturing fluids and wastewaters: A review	Luek, Jenna L.; Gonsior, Michael	2017	doi.org/10.1016/j.watres.2017.07.012
A review of crosslinked fracturing fluids prepared with produced water	Li, Leiming; Al-Muntasheri, Ghaithan A.; Liang, Feng	2016	doi.org/10.1016/j.petlm.2016.10.001
Physical, chemical, and biological characteristics of compounds used in hydraulic fracturing	Stringfellow, William T.; Domen, Jeremy K.; <i>et. al.</i>	2014	doi.org/10.1016/j.jhazmat.2014.04.040
Organic substances in produced and formation water from unconventional natural gas extraction in coal and shale	W. Orem, C. Tatu, <i>et. al.</i>	2014	doi.org/10.1016/j.coal.2014.01.003
A review of fracturing fluid systems used for hydraulic fracturing of oil and gas wells	Barati, Reza; Liang, Jenn Tai	2014	doi.org/10.1002/app.40735
Spatial and temporal correlation of water quality parameters of produced waters from Devonian-age shale following hydraulic fracturing	E. Barbot, N.S. Vidic, <i>et. al.</i>	2013	doi.org/10.1021/es304638h
Produced water in the Western United States: Geographical distribution, occurrence, and composition	Benko, Katie L.; Drewes, Jorg E.	2008	doi.org/10.1089/ees.2007.0026
Produced Water Quality (Analytical Methods)			
A Critical Review of Analytical Methods for Comprehensive Characterization of Produced Water	W. Jiang, L. Lin, X. Xu, <i>et. al.</i>	2021	doi.org/10.3390/w13020183
Emerging analytical methods for the characterization and quantification of organic contaminants in flowback and produced water	Karl Oetjen, Cloelle G.S. Giddings, <i>et. al.</i>	2017	doi.org/10.1016/j.teac.2017.07.002

Title	Authors	Year	DOI
Produced Water Quantity			
U. S. Produced Water Volumes and Management Practices in 2017	J. Veil	2020	Web link
Can we beneficially reuse produced water from oil and gas extraction in the U.S.?	B.R. Scanlon, R.C. Reedy, <i>et. al.</i>	2020	doi.org/10.1016/j.scitotenv.2020.137085
Will Water Issues Constrain Oil and Gas Production in the United States?	B.R. Scanlon, S. Ikonnikova, <i>et. al.</i>	2020	doi.org/10.1021/acs.est.9b06390
Water Issues Related to Transitioning from Conventional to Unconventional Oil Production in the Permian Basin	B.R. Scanlon, R.C. Reedy, <i>et. al.</i>	2017	doi.org/10.1021/acs.est.7b02185
Produced Water Regulations and Management			
Produced water report: Regulations, current practices, and research needs	S.R. Chard, N. Saunders	2019	Web link
Special Focus on Produced Water in Oil and Gas Fields: Origin, Management, and Reinjection Practice	Y. Liang, Y. Ning, L. Liao, B. Yuan	2018	doi.org/10.1016/B978-0-12-813782-6.00014-2
Advances in acute toxicity testing: Strengths, weaknesses, and regulatory acceptance	E.O. Erhirhie, C.P. Ihekwereme, E.E. Ilodigwe	2018	doi.org/10.2478/intox-2018-0001
Produced Water Management and Environmental Impact			
Unconventional Oil and Gas Production: Waste Management and the Water Cycle	Liden, Tiffany; Clark, Billy G.; <i>et. al.</i>	2017	doi.org/10.1016/bs.ammp.2017.08.012
An overview on exploration and environmental impact of unconventional gas sources and treatment options for produced water	Silva, Tania L.S.; Morales-Torres, Sergio; <i>et. al.</i>	2017	doi.org/10.1016/j.jenvman.2017.06.002
Downhole Transformation of the Hydraulic Fracturing Fluid Biocide Glutaraldehyde: Implications for Flowback and PW Quality	G.A. Kahrilas, J. Blotevogel, E.R. Corrin, T. Borch	2016	doi.org/10.1021/acs.est.6b02881
Injection-Induced Earthquakes	W.L. Ellsworth	2013	doi.org/10.1126/science.1225942
The intensification of the water footprint of hydraulic fracturing	A.J. Kondash, N.E. Lauer, A. Vengosh, Erratum	2019	doi.org/10.1126/SCIENCE.AAX8764
Coalbed methane produced water screening tool for treatment technology and beneficial use	M.H. Plumlee, J.F. Debroux, <i>et. al.</i>	2014	doi.org/10.1016/j.jugr.2013.12.002
Ecological Effects of Produced Water Effluents from Offshore Oil and Gas-Production Platforms	Brian S.Middleditch	1984	doi.org/10.1016/0302-184X(84)90003-9

Table S2: Selected papers summarizing produced water treatment technologies.

Title	Authors	Year	DOI
Produced Water Treatment Reviews			
Fit-for-purpose treatment goals for produced waters in shale oil and gas fields	Coonrod, Christina L.; <i>et al.</i>	2020	doi.org/10.1016/j.watres.2020.115467
Produced water characteristics, treatment, and reuse: A review	Al-Ghouti, Mohammad A.; Al-Kaabi, Maryam A.; <i>et al.</i>	2019	doi.org/10.1016/j.jwpe.2019.02.001
State of the art of produced water treatment	Jimenez, S.; Mico, M.M.; Arnaldos, M.; Medina, F.; Contreras, S.	2018	doi.org/10.1016/j.chemosphere.2017.10.139
Treatment modalities for the reuse of produced waste from oil and gas development	Tiffany Liden, Inês C. Santos, <i>et al.</i>	2018	doi.org/10.1016/j.scitotenv.2018.05.386
Oil and Gas Produced Water Management: A Review of Treatment Technologies, Challenges, and Opportunities	Nasiri, Masoud; Jafari, Iman; Parmiankhoy, Behdad	2017	doi.org/10.1080/00986445.2017.1330747
A review of issues and treatment options for wastewater from shale gas extraction by hydraulic fracturing	Estrada, Jose M.; Bhamidimarri, Rao	2016	doi.org/10.1016/j.fuel.2016.05.051
Produced water treatment technologies	Igunnu, ET; Chen, G Z	2014	doi.org/10.1093/ijlct/cts049
Review technologies for oil and gas produced water treatment	Fakhru'l-Razi, Ahmadun; Penashteh, Alireza; <i>et al.</i>	2009	doi.org/10.1016/j.jhazmat.2009.05.044
Oil-Water Separation Treatment Processes			
Emulsions in porous media from the perspective of produced water re-injection – A Review	Ilgar Azizov, Marcin Dudek, Gisle Øye	2021	doi.org/10.1016/j.petrol.2021.109057
Gas Flotation of Petroleum Produced Water: A Review on Status, Fundamental Aspects, and Perspectives	Piccioli, Martina; Aanesen, Svein Viggo; <i>et al.</i>	2020	doi.org/10.1021/acs.energyfuels.0c03262
Materials and Technologies for the Tertiary Treatment of Produced Water Contaminated by Oil Impurities through Nonfibrous Deep-Bed Media: A Review	Sobolciak, Patrik; Popelka, Anton; <i>et al.</i>	2020	doi.org/10.3390/w12123419
Overview on petroleum emulsions, formation, influence, and demulsification treatment techniques	Murtada Mohammed Abdulredha; Siti Aslina, Hussain; Luqman, Chuah Abdullah	2020	doi.org/10.1016/j.arabj.2018.11.014
Coalescence processes to treat produced water: an updated overview and environmental outlook	Carlos Eduardo De Farias Silva, <i>et al.</i>	2019	doi.org/10.1007/s11356-019-06016-x
Biological Treatment Processes			
Adsorptive batch and biological treatments of produced water: Recent progresses, challenges, and potentials	Maryam A.Al-Kaabi, Nabil Zouari, <i>et al.</i>	2021	doi.org/10.1016/j.jenvman.2021.112527

Title	Authors	Year	DOI
A Review of Algae-Based Produced Water Treatment for Biomass and Biofuel Production	Rahman, Ashiqur; Agrawal, Saumya; <i>et. al.</i>	2020	doi.org/10.3390/w12092351
Biological Treatments of Oilfield Produced Water: A Comprehensive Review	Nicolas Lusnier; Isabelle Seyssiecq; <i>et. al.</i>	2019	doi.org/10.2118/195677-PA
Biological treatment of oil and gas produced water: a review and meta-analysis	Camarillo, Mary Kay; Stringfellow, William T.	2018	doi.org/10.1007/s10098-018-1564-9
Biocides in hydraulic fracturing fluids: A critical review of their usage, mobility, degradation, and toxicity	G.A. Kahrilas, J. Blotevogel, P.S. Stewart, T. Borch	2015	doi.org/10.1021/es503724k
Desalination Treatment Processes			
Zero Liquid Discharge of Ultrahigh-Salinity Brines with Temperature Swing Solvent Extraction	Chanhee Boo, Ian H. Billinge, <i>et. al.</i>	2020	doi.org/10.1021/acs.est.0c02555
Membrane-less and Non-Evaporative Desalination of Hypersaline Brines by Temperature Swing Solvent Extraction	Chanhee Boo, Robert K. Winton, <i>et. al.</i>	2019	doi.org/10.1021/acs.estlett.9b00182
Desalination of shale gas produced water: A rigorous design approach for zero-liquid discharge evaporation systems	Viviani C. Onishi, Alba Carrero-Parreño, <i>et. al.</i>	2017	doi.org/10.1016/j.jclepro.2016.10.012
Emerging desalination technologies for water treatment: a critical review	Arun Subramania, Joseph G. Jacangelo	2015	doi.org/10.1016/j.watres.2015.02.032
The sweet spot of forward osmosis: Treatment of produced water, drilling wastewater, and other complex and difficult liquid streams	B.D. Coday, P. Xu, <i>et. al.</i>	2014	doi.org/10.1016/j.desal.2013.11.014
Desalination and reuse of high-salinity shale gas produced water: Drivers, Technologies, and future directions	Devin L. Shaffer, Laura H. Arias Chavez, <i>et. al.</i>	2013	doi.org/10.1021/es401966e
Membrane Treatment Processes			
The Role of Membrane-Based Technologies in Environmental Treatment and Reuse of Produced Water	Ehsan Zolghadr, Mostafa Dadashi Firouzjaei, <i>et. al.</i>	2021	doi.org/10.3389/fenvs.2021.629767
Potential and implemented membrane-based technologies for the treatment and reuse of flowback and produced water from shale gas and oil plays: A review	Chang, Haiqing; Li, Tong; Liu, Baicang; <i>et. al.</i>	2019	doi.org/10.1016/j.desal.2019.01.001
New Developments in Membrane Technologies Use in the Treatment of Produced Water: A Review	Zoubeik, Mohamed, Ismail, Mohamed; <i>et. al.</i>	2018	doi.org/10.1007/s13369-017-2690-0
Membrane fouling for produced water treatment: A review study from a process control perspective	Jepsen, Kasper L.; Bram, Mads Valentin; <i>et. al.</i>	2018	doi.org/10.3390/w10070847
Produced water treatment by membranes: A review from a colloidal perspective	Dickhout, J.M.; Moreno, J.; <i>et. al.</i>	2017	doi.org/10.1016/j.jcis.2016.10.013

Title	Authors	Year	DOI
Use of membrane technology for oil field and refinery produced water treatment- A review	Munirasu, Selvaraj; Haija, Mohammad Abu; Banat, Fawzi	2016	doi.org/10.1016/j.psep.2016.01.010
Polymeric membranes for produced water treatment: an overview of fouling behavior and its control	Subrata Mondal	2016	doi.org/10.1515/revce-2015-0027
Challenges and trends in membrane technology implementation for produced water treatment: A review	Salem Alzahrana, Abdul Wahab Mohammad	2014	doi.org/10.1016/j.jwpe.2014.09.007
Challenges and trends in membrane technology implementation for produced water treatment: A review	Alahrani, Salem; Mohammad, Abdul Wahab	2014	doi.org/10.1016/j.jwpe.2014.09.007
Advanced performance evaluation of a reverse osmosis treatment for oilfield produced water aiming reuse	M. Melo, H. Schluter, et. al.	2010	doi.org/10.1016/j.desa.1.2009.09.095
Ceramic-Ultra- and Nanofiltration Membranes for Oilfield Produced Water Treatment: A mini review	Ashaghi, K. Shams; Ebrahimi, M.; Czermak, P.	2008	doi.org/10.2174/1876325100701010001
AOP, Photocatalysis, and Electrochemical Treatment			
Advanced oxidation processes in the removal of organic substances from produced water: Potential, configurations, and research needs	Marco Coxa, Giulio Farinella Alberto Tiraferria, et. al.	2021	doi.org/10.1016/j.cej.2021.128668
Treatment of produced water with photocatalysis: Recent advances, affecting factors and future research prospects	Lin, Lu; Jiang, Wenbin; et. al.	2020	doi.org/10.3390/catal10080924
Bioelectrochemical approaches for removal of sulfate, hydrocarbon, and salinity from produced water	Pratiksha Jain, Mohita Sharma, et. al.	2017	doi.org/10.1016/j.chemosphere.2016.09.081
Decontamination of produced water containing petroleum hydrocarbons by electrochemical methods: a minireview	Elisama Vieira dos Santos, Jessica Horacina Bezerra Rocha, et. al.	2014	doi.org/10.1007/s11356-014-2780-4
Adsorption Treatment			
Adsorption as a Process for Produced Water Treatment: A Review	Roghayeh Yousef, Hazim Qiblawey, Muftah H. El-Naas	2020	doi.org/10.3390/pr8121657
Use of carbon materials for produced water treatment: a review on adsorption process and performance	A. Faraji, M. Cuccarese, S. Masi, et. al.	2021	doi.org/10.1007/s13762-021-03395-y
Contaminant Specific Treatment Processes			
Lithium Recovery from Oil and Gas Produced Water: A Need for a Growing Energy Industry	A. Kumar, H. Fukuda, et. al.	2019	doi.org/10.1021/acsenergylett.9b00779
Resource Recovery and Reuse for Hydraulic Fracturing Wastewater in Unconventional Shale Gas and Oil Extraction	H. Chang, B. Liu, J.C. Crittenden, R.D. Vidic	2019	doi.org/10.1021/acsc.est.9b06240

Title	Authors	Year	DOI
Rare Earth Elements Occurrence and Economical Recovery Strategy from Shale Gas WW in the Sichuan Basin, China	L. Tian, H. Chang, P. Tang, et. al.	2020	doi.org/10.1021/acssuschemeng.0c04971
Boron in produced water: Challenges and improvements: A comprehensive review	Ezechi, Ezerie Henry; Isa, Mohamed Hasnain; et. al.	2012	doi.org/10.3923/jas.2012.402.415
Residuals Management			
Membrane distillation crystallization for brine mining and zero liquid discharge: opportunities, challenges, and recent progress	Youngkwon Choi, Gayathri Naidu Long D. Nghiem, et. al.	2019	doi.org/10.1039/C9EW00157C

Saltwater Disposal Case Study and What-If Analysis

The WaterTAP3 technoeconomic assumptions for the saltwater disposal baseline case study and what-if analysis are as follows

Table S3: Technoeconomic assumptions for treatment trains modeled in WaterTAP3 for the saltwater disposal baseline case study and what-if analysis.

Variable	Value	Variable	Value
Analysis Year	2020	Default Cap Scaling Exp.	0.7
Location Basis	Texas	Default Opex Scaling Exp.	0.7
Plant Life Years	15	Cap. by Equity	0.4
Land Cost Percent	0.0015	Debt Interest Rate	0.08
Working Capital Percent	0.05	Expected Return on Equity	0.1
Salaries Percent	0.001	Default TPEC Multiplier	3.4
Employee Benefits Percent	0.9	Default TIC Multiplier	1.65
Maintenance Cost Percent	0.008	Base Salary Per Fixed Cap Inv.	0.0005
Laboratory Fees Percent	0.002667	Plant Capacity Utilization	1
Insurance and Taxes Percent	0.001867	Capital Recovery Factor	0.1168

Baseline Saltwater Disposal Well Case Study

The baseline case study in WaterTAP3 was modeled with an influent flow rate of 25,000 barrels per day. The holding tank was assumed to have an average storage time of 2 hours with a surge capacity of 0.2.

Figure S1: Process flow diagram for baseline saltwater disposal well case study.

Table S4: WaterTAP3 analysis results in 2020 dollars for baseline saltwater disposal well case study.

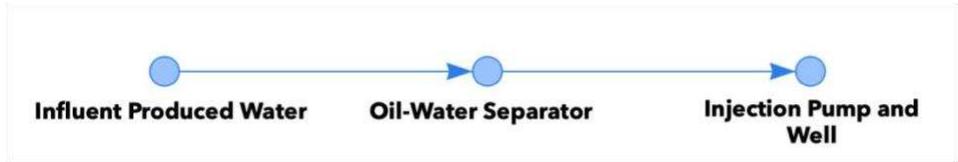
WaterTAP3 range is based on the expected uncertainty of the WaterTAP3 model (-30%/+50%).

Intensified Brine Management with Saltwater Disposal Well Case Study

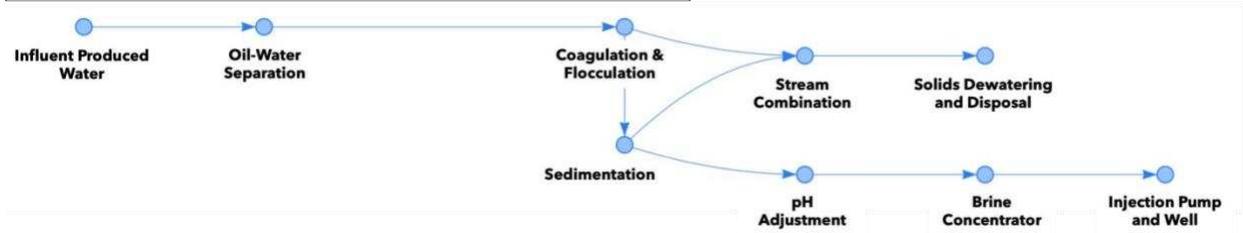
The intensified brine management with saltwater disposal well case study in WaterTAP3 utilized an influent flow rate of 25,000 barrels per day with an influent total dissolved solids concentration (TDS) of 50,000 mg/L. Treatment train is based on work by Veil et al., and Hayes et al., describing and evaluating a similar facility.^{1,2}

Figure S2: Process flow diagram for intensified brine management with saltwater disposal well case study. Mechanical vapor recompression modeled as a brine concentrator in WaterTAP3.

Table S5: WaterTAP3 analysis results in 2020 dollars for the intensified brine management prior to saltwater disposal case study. WaterTAP3 range is based on the expected uncertainty of the WaterTAP3 model (-30%/+50%).



WaterTAP3 Estimate	WaterTAP3 Range
Total Capital Investment (MM\$)	12.19 8.53 – 18.28
Operating and Maintenance (MM\$/Year)	0.19 0.13 – 0.28
Levelized Cost of Water (\$/m ³)	1.11 0.78 – 1.67
Adjusted Levelized Cost of Water (\$/m ³)	1.11 0.78 – 1.67
Energy Intensity (kWh/m ³)	0.41 0.29 – 0.61
Adjusted Energy Intensity (kWh/m ³)	0.41 0.29 – 0.61



WaterTAP3 Estimate	WaterTAP3 Range
Total Capital Investment (MM\$)	48.09 33.66 – 72.14
Operating and Maintenance (MM\$/Year)	2.31 1.62 – 3.47

Levelized Cost of Water (\$/m ³)	6.07	4.25 – 9.11
Adjusted Levelized Cost of Water (\$/m ³)	5.47	3.83 – 8.20
Energy Intensity (kWh/m ³)	23.61	16.53 – 35.41
Adjusted Energy Intensity (kWh/m ³)	21.24	14.87 – 31.87
Water Recovery (%)	89.96	-

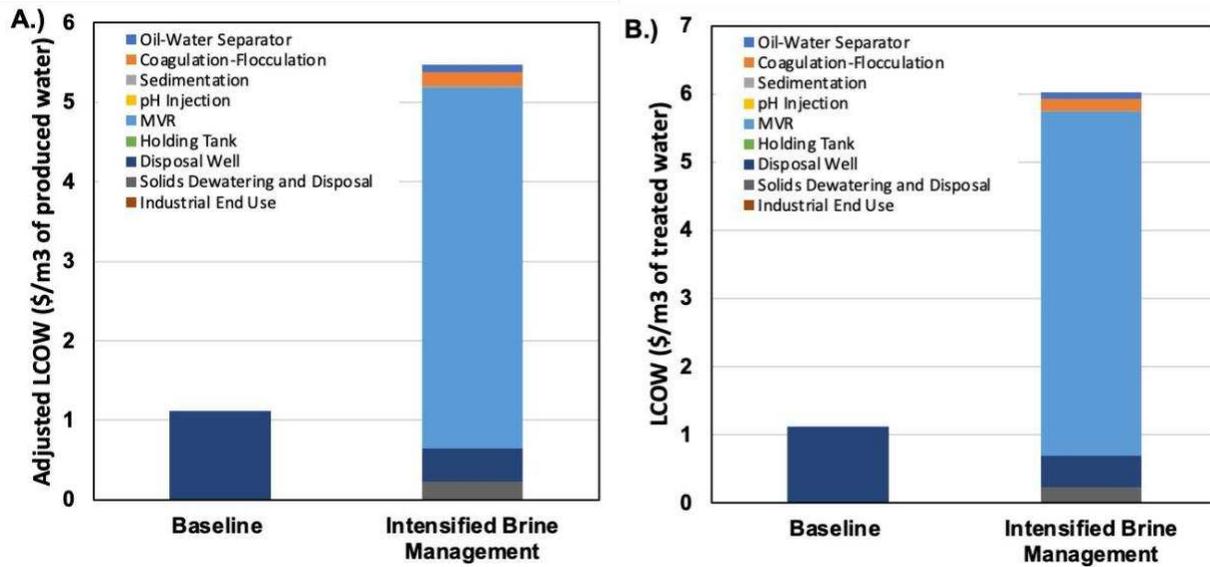


Figure S3: The contribution of each unit process to the (A) adjusted levelized cost of water (\$/m³) and the (B) levelized cost of water for the saltwater disposal baseline and intensified brine management case studies.

Figure S4: The contributions of each unit process to the (A) adjusted energy intensity (kWh/m³) and the (B) energy intensity for the saltwater disposal baseline and intensified brine management case study.

Agricultural Irrigation Case Study and What-If Analysis

The WaterTAP3 technoeconomic assumptions for the agricultural irrigation baseline case study and what-if analysis are as follows

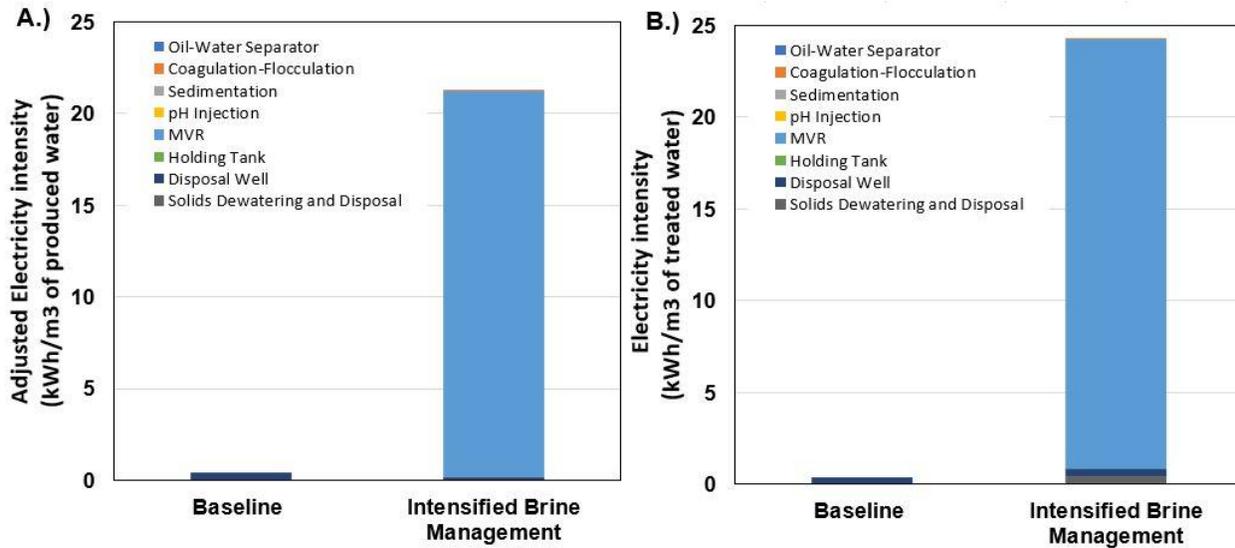


Table S6: Technoeconomic assumptions for treatment trains modeled in WaterTAP3 for the agricultural irrigation baseline case study and what-if analysis.

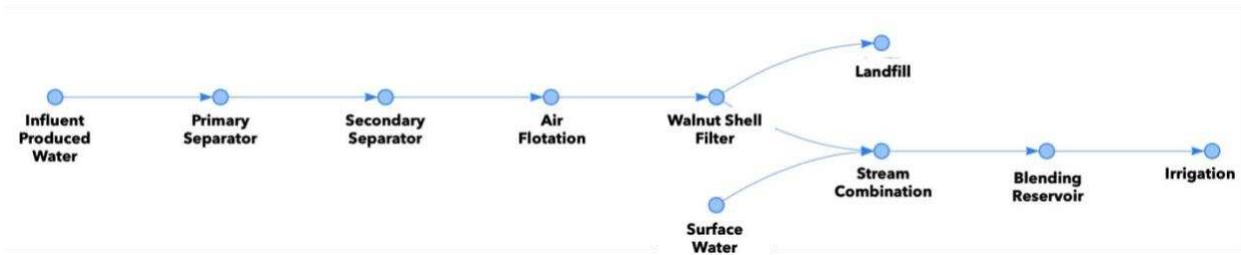
Variable	Value	Variable	Value
Analysis Year	2020	Default Cap Scaling Exp.	0.7
Location	Basis California	Default Opex Scaling Exp.	0.7
Plant Life	Years 30	Cap. by Equity	0.4
Land Cost	Percent 0.0015	Debt Interest Rate	0.04
Working Capital	Percent 0.05	Expected Return on Equity	0.1
Salaries	Percent 0.001	Default TPEC Multiplier	3.4
Employee Benefits	Percent 0.9	Default TIC Multiplier	1.65
Maintenance Cost	Percent 0.008	Base Salary Per Fixed Cap Inv.	0.0005
Laboratory Fees	Percent 0.003	Plant Capacity Utilization	1
Insurance and Taxes	Percent 0.002	Capital Recovery Factor	0.0578

Baseline Case Study

The process was modeled with an influent flow rate of 22.00 MGD and a total dissolved solids concentration of 500 mg/L. The treated produced water was blended with 40.0 MGD of surface water with a total dissolved solids concentration of 81 mg/L. The treatment train, volumes, and water quality information modeled in WaterTAP3 is based on the Chevron's NPDES self-monitoring permit for the Produced Water Reclamation Project Kern River Area Station 36 Kern River Oil Field and the Cawelo Water District Ponds Water Reclaimed Water Impoundment Sampling.^{3,4}

Figure S5: Process flow diagram for baseline agricultural reuse of high-quality produced water.

Table S7: WaterTAP3 analysis results in 2020 dollars for baseline agricultural reuse of high-quality produced water. WaterTAP3 range is based on the expected uncertainty of the WaterTAP3 model (-30%/+50%).



WaterTAP3 Estimate	WaterTAP3 Range
Total Capital Investment (MM\$)	14.21 9.95 – 21.33
Operating and Maintenance (MM\$/Year)	2.00 1.40 – 3.00
Levelized Cost of Water (\$/m ³)	0.03 0.02 – 0.05
Adjusted Levelized Cost of Water (\$/m ³)	0.09 0.06 – 0.14
Energy Intensity (kWh/m ³)	0.16 0.11 – 0.24
Adjusted Energy Intensity (kWh/m ³)	0.44 0.31 – 0.66
Water Recovery (%)	99.49 -

Elevated Salinity Case Study

The following process was modeled with an influent flow rate of 22.00 MGD, total dissolved solids concentration of 10,000 mg/L, and a boron concentration of 0.78 mg/L. The treated produced water was blended with 40.0 MGD of surface water with a total dissolved solids concentration of 81 mg/L.



Figure S6: Process flow diagram the elevated salinity case study.

Table S8: WaterTAP3 analysis results in 2020 dollars for baseline agricultural reuse of high-quality produced water. WaterTAP3 range is based on the expected uncertainty of the WaterTAP3 model (-30%/+50%).

WaterTAP3 Estimate	WaterTAP3 Range
Total Capital Investment (MM\$)	155.58 108.91 – 233.37
Operating and Maintenance (MM\$/Year)	11.24 7.87 – 16.86
Levelized Cost of Water (\$/m ³)	0.26 0.182 – 0.39
Adjusted Levelized Cost of Water (\$/m ³)	0.67 0.47 – 1.01
Energy Intensity (kWh/m ³)	0.78 0.55 – 1.17

Adjusted Energy Intensity (kWh/m ³)	1.96 1.37 – 2.94
Water Recovery (%)	89.754 -

Elevated Boron Case Study

The process was modeled with an influent flow rate of 22.00 MGD, total dissolved solids concentration of 10,000 mg/L, and a boron concentration of 30.0 mg/L. The treated produced water was blended with 40.0 MGD of surface water with a total dissolved solids concentration of 81 mg/L. The treatment train modeled in WaterTAP3 is based on work discussed in the Kern County baseline as well as work by Landsman et al., and Dydo et al., developing and evaluating hybrid ED/RO processes.^{5,6}



Figure S7: Process flow diagram for the elevated boron case study. Abbreviations are as follows: electro dialysis (ED).

Table S9: WaterTAP3 analysis results in 2020 dollars for baseline agricultural reuse of high-quality produced water. WaterTAP3 range is based on the expected uncertainty of the WaterTAP3 model (-30%/+50%).

WaterTAP3 Estimate	WaterTAP3 Range
Total Capital Investment (MM\$)	212.88 149.02 – 319.32
Operating and Maintenance (MM\$/Year)	31.83 22.28 – 47.75
Levelized Cost of Water (\$/m ³)	0.55 0.39 – 0.83
Adjusted Levelized Cost of Water (\$/m ³)	0.83 0.58 – 1.25
Energy Intensity (kWh/m ³)	2.57 1.80 – 3.86
Adjusted Energy Intensity (kWh/m ³)	6.82 4.77 – 10.23
Water Recovery (%)	94.322 -

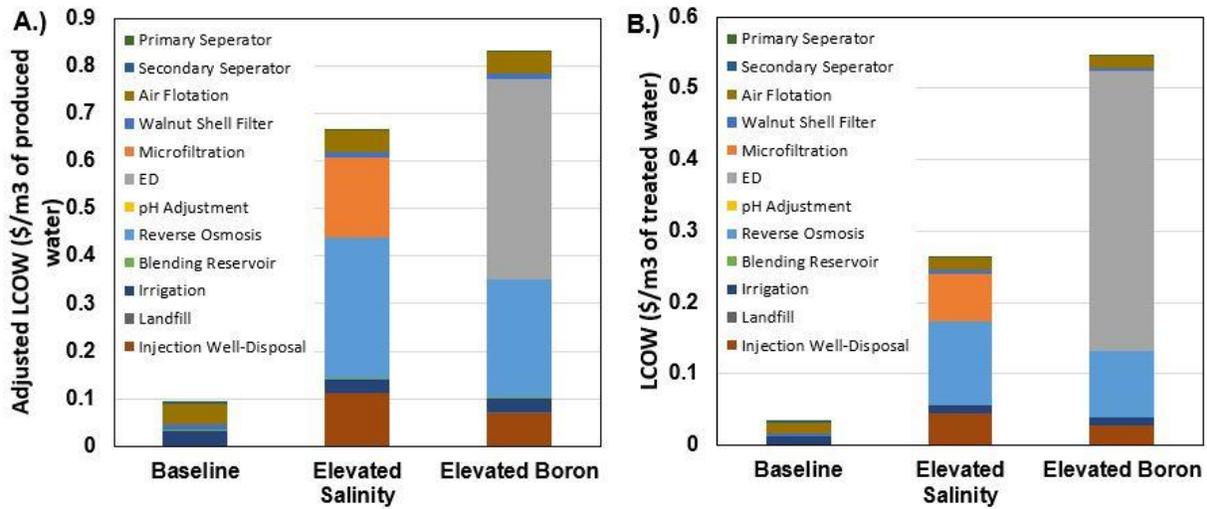
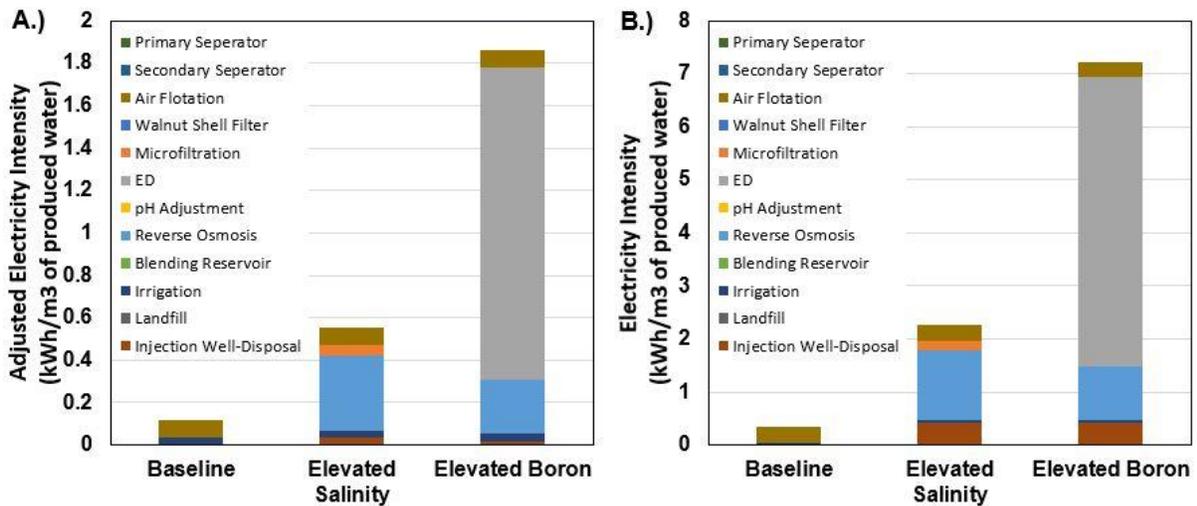


Figure S8: The contribution of each unit process to the (A) adjusted levelized cost of water ($\$/\text{m}^3$) and the (B) levelized cost of water for the agricultural irrigation baseline, elevated salinity, and elevated boron case studies.

Figure S9: The contributions of each unit process to the (A) adjusted energy intensity (kWh/m^3) and the (B) energy intensity for the agricultural irrigation baseline, elevated salinity, and elevated boron case studies.



Municipal Reuse Case Study

The WaterTAP3 techno-economic assumptions for the municipal baseline case study are as follows.

Table S10: Techno-economic assumptions for treatment trains modeled in WaterTAP3 for the agricultural irrigation baseline case study and what-if analysis.

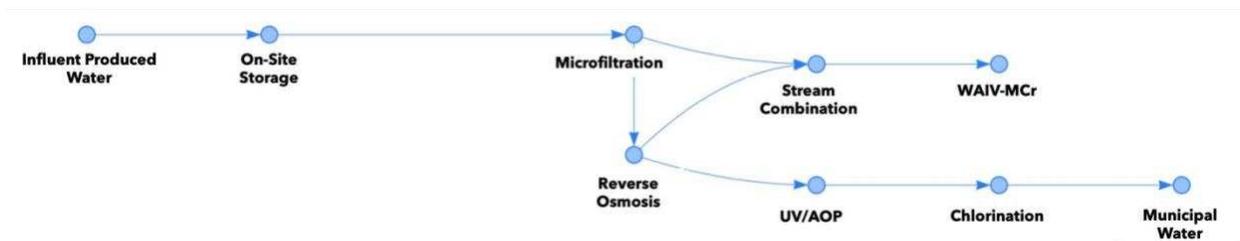
Variable	Value	Variable	Value
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Analysis Year 2020 Default Cap Scaling Exp. 0.7
Location Basis Wyoming Default Opex Scaling Exp. 0.7
Plant Life Years 30 Cap. by Equity 0.4
Land Cost Percent 0.0015 Debt Interest Rate 0.08
Working Capital Percent 0.05 Expected Return on Equity 0.1
Salaries Percent 0.001 Default TPEC Multiplier 3.4
Employee Benefits Percent 0.9 Default TIC Multiplier 1.65
Maintenance Cost Percent 0.008 Base Salary Per Fixed Cap Inv. 0.0005
Laboratory Fees Percent 0.003 Plant Capacity Utilization 1
Insurance and Taxes Percent 0.002 Capital Recovery Factor 0.0651

The following process was modeled with an influent flow rate of 1.19 MGD and a total dissolved solids concentration of 1,230 mg/L. Additional water quality parameters are shown in Table S8. The treatment train modeled in WaterTAP3 is based on work by Singh et al., conducting a technoeconomic analysis of a similar facility and the water quality modeled in WaterTAP3 is based on work by Plumlee et al., conducting a technoeconomic analysis on a similar CBM produced water source.^{7,8}

Figure S10: Process flow diagram for municipal reuse of coalbed methane produced water. Abbreviations are as follows: Wind-Aided Intensified eVaporation and Membrane Crystallization (WAIV-MCr), ultraviolet (UV), and Advanced Oxidation Process (AOP).

Table S11: Source water constituent levels of CBM from the Powder River Basin⁸



Constituent	Concentration (mg/L)
Alkalinity as CaCO3	800
Bicarbonate Alkalinity as CaCO3	800
Calcium	32
Chloride	13
Electrical Conductivity	199
Fluoride	1
Hardness	300
Magnesium	14
Potassium	36
Sodium	314

Constituent	Concentration (mg/L)
TDS	1230
TSS	9

Table S12: WaterTAP3 analysis results in 2020 dollars for baseline municipal reuse of coalbed methane produced water. WaterTAP3 range is based on the expected uncertainty of the WaterTAP3 model (-30%/+50%).

WaterTAP3 Estimate	WaterTAP3 Range
Total Capital Investment (MM\$)	41.45 29.02 – 62.18
Operating and Maintenance (MM\$/Year)	0.92 0.64 – 1.38
Levelized Cost of Water (\$/m ³)	2.37 1.66 – 3.56
Adjusted Levelized Cost of Water (\$/m ³)	2.19 1.53 – 3.29
Energy Intensity (kWh/m ³)	1.50 1.05 – 2.23
Adjusted Energy Intensity (kWh/m ³)	1.40 0.98 – 2.10
Water Recovery (%)	92.94

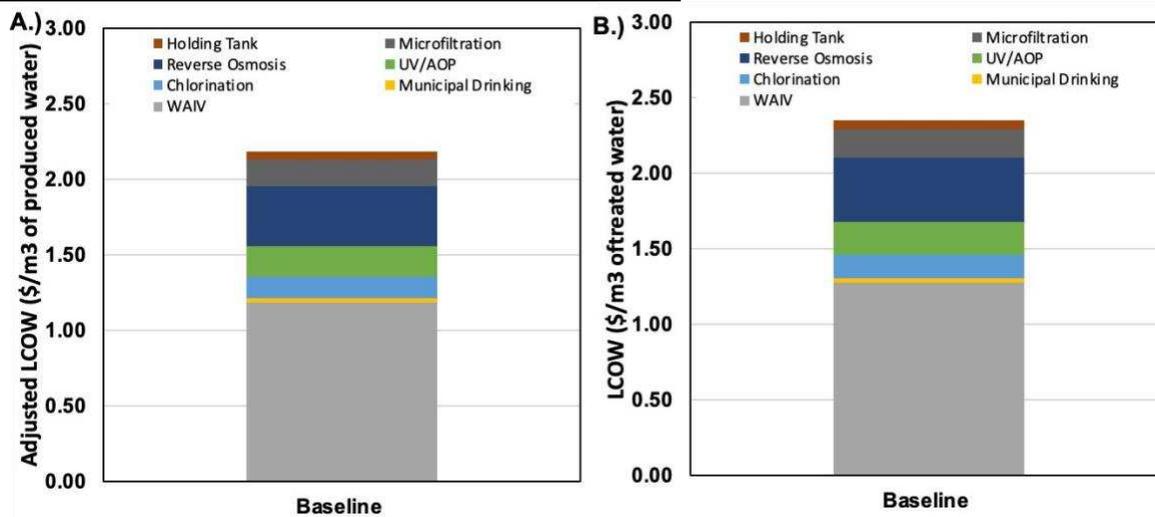


Figure S11: The contribution of each unit process to the (A) adjusted levelized cost of water (\$/m³ of influent produced water) and (B) the levelized cost of water (\$/m³ of treated water) for baseline municipal reuse case study.

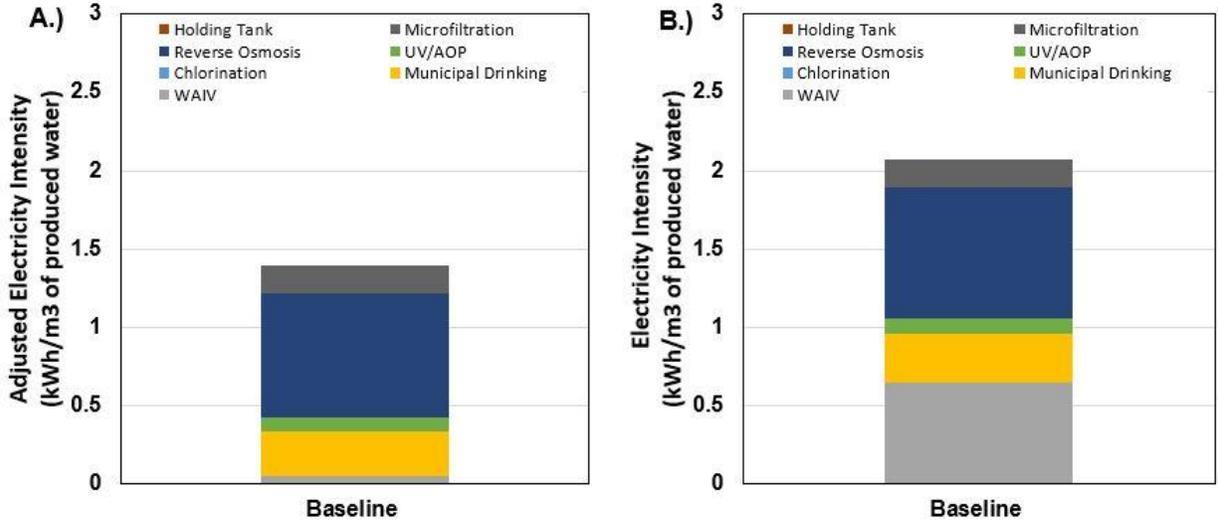


Figure S12: The contributions of each unit process to the (A) adjusted energy intensity (kWh/m³) and the (B) energy intensity for the baseline municipal reuse case study.

Water TAP3 Assumptions and Unit Level Performance Results

Table S13: System and unit level configuration assumptions

Case Study	Unit Process	Parameter
Saltwater Disposal	Passthrough	
	Oil-Water Separator	Avg. Storage Time: 2 (hours); Surge Capacity: 0.2
	Injection Well Disposal	
Agricultural Reuse	Primary Separator	
	Sedimentation	Settling Velocity: 0.005
	Air Flotation	
	Walnut Shell Filter	
	Blending Reservoir	Water Type: Surface Water
	Irrigation	
Municipal Reuse	Holding Tank	Avg. Storage Time: 24 (hours); Surge Capacity: 0.2; Water Type: Powder River Basin CBM
	Microfiltration	
	Reverse Osmosis	No Energy Recovery Device
	UV AOP	Chemical Name: Hydrogen Peroxide; Dose: 5; UV Dose: 300, UVT In: 0.95; AOP: True
	Chlorination	Chemical Name: Chlorine
	Municipal Drinking	
	WAIW	

UV AOP = Ultraviolet Advanced Oxidation Process; Dose is in mg/L

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