EVALUATION OF A SEQUENCING BATCH REACTOR FOLLOWED BY MEDIA FILTRATION FOR ORGANIC AND NUTRIENT REMOVAL FROM PRODUCED WATER

by

Emily R. Nicholas

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Golden, Colorado

Date _____

Signed: _____
Emily R. Nicholas

Signed: _____
Dr. Tzahi Y. Cath
Thesis Advisor

Golden, Colorado

Date _____

Signed: _____
Dr. John McCray
Professor and Head
Department of Civil and Environmental Engineering

ABSTRACT

With technological advances such as hydraulic fracturing, the oil and gas industry now has access to petroleum reservoirs that were previously uneconomical to develop. Some of the reservoirs are located in areas that already have scarce water resources due to drought, climate change, or population. Oilfield operations introduce additional water stress and create a highly complex and variable waste stream called produced water. Produced water contains high concentrations of total dissolved solids (TDS), metals, organic matter, and in some cases naturally occurring radioactive material. In areas of high water stress, beneficial reuse of produced water needs to be considered.

Sequencing batch reactors (SBR) have been used to facilitate biological organic and nutrient removal from domestic waste streams. Although the bacteria responsible for the treatment of domestic sources cannot tolerate the high TDS concentrations in produced water, the microorganisms native to produced water have the functional potential to treat produced water. In a bench scale bioreactor jar test using produced water from the Denver-Julesburg Basin, the produced water collected was determined to be nutrient limited with respect to phosphorus. By adding a phosphorus supplement, soluble chemical oxygen demand (COD) removal was increased by over 20% and ammonia removal increased by approximately 40%. Various supplements including KH_2PO_4, centrate from an anaerobic digester, and activated sludge from a municipal SBR were tested to see how treatment changed with phosphorous type.

A pilot scale SBR followed by media filtration was used to evaluate the effects of operating conditions on produced water treatment. The hydraulic residence time ranged from 1.67 to 8.3 days during various phases of operation, with no measured effect on treatment performance. Adding 7.5 mg-P/L of KH_2PO_4 as a phosphorus supplement had the most significant effect on treatment performance on the system. The majority of COD removal switched locations from the filter columns to the bioreactors. Comparing total organic carbon (TOC) to COD, the biologically available portion of COD appears to be treated in the SBR treatment train while recalcitrant carbon and inorganic material may need to be removed via physical or chemical methods.

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CHAPTER 1
INTRODUCTION

Following the inception of hydraulic fracturing of oil and gas (O&G) wells, the O&G industry has been able to economically enhance petroleum production. Hydraulic fracturing is conducted after drilling the well and before O&G production begins. In the fracturing process fluid is injected into the target rock formation at extremely high pressures to create highly permeable pathways for oil or gas to flow more rapidly to the wellbore. Initially, the fluid produced from the well is dominantly flowback water from the hydraulic fracturing operation, and changes over time to dominantly fluid that naturally exists in the rock formation. The fluid native to petroleum reservoirs is usually a mixture of oil, gas, and water. Often, all water produced from a well is classified as produced water and has traditionally been treated as a wastewater stream.

1.1 Significance of oilfield waste

O&G operations take place in a variety of locations with respect to geography, climate, population density, and availability of water. According to the 2014 Ceres report, over half of all O&G wells are in areas experiencing drought.[1] Throughout the lifecycle of a well, the most water-intensive stage is hydraulic fracturing, with some areas consuming over 8 million gallons (~30,000 m^3) of water per well[2]. In arid regions or areas affected by drought, where hydraulic fracturing increases water demand on limited water resources, beneficial reuse of wastewater needs to be considered.

There are many drivers for beneficial water reuse, which include climate change, drought, increasing population, and environmental concerns. These factors may induce more stringent regulations focused on public and environmental health, and ultimately make water sourcing or disposal more expensive. Thus, regulations may be a dominant influential factor in making beneficial reuse of produced water a more favorable water management option.

1.2 Oil and gas waste streams

Although all water collected from an O&G well is typically classified as produced water, it can be separated into two categories. The first category is fracturing flowback fluid (FFB), which has water quality dependent upon the injection fluid used during hydraulic fracturing. Often, FFB has a relatively low concentration of total dissolved solids (TDS), and contaminants in this stream include surfactants, gelling agents, and biocides from the chemical additives used during hydraulic fracturing. Fluids used during hydraulic fracturing contain less than 1% chemical additives, and the exact mixture varies between wells. The second category is formation water, which is naturally present in the petroleum reservoir and has characteristics unique to each formation. Formation water typically contains relatively high concentrations of TDS, organic matter, volatile compounds, metals, and may contain naturally occurring radioactive material. The chemistry of produced water changes over time because of the difference in composition between FFB and formation water. Additionally, the volume of fluid produced from each well is dependent

upon the hydraulic fracturing operation and the permeability of the fractured formation. Examples of the spatial, temporal, and volumetric variability of produced water are summarized in Table 1.1 In the Marcellus Shale, TDS concentration in a well can change over time by an order of magnitude. When comparing shale plays in Texas and Alabama, TDS concentrations vary from 10,000 mg/L to 140,000 mg/L. TDS concentrations of produced water in Oklahoma can reach well over 200,000 mg/L.[2] Due to the variability in water quantity and quality, as well as geography, environmental conditions, and water management, potential treatment of produced water will be site specific.

Table 1.1. Average water use, range of water volume produced, and range of TDS concentrations by location. Produced water TDS concentration is one example of compositional changes in produced water that vary spatially and temporally. Adopted from Chesapeake Energy.[3]

	(PA) Marcellus Shale	(TX) Barnett Shale	(AL) Fayetteville Shale
Average water use per well (10^6 gallons)	5.6	4.0	4.9
"Initial" water produced per well during first 10 days of production (10^3 gallons)	500 – 600	500 – 600	500 – 600
TDS concentration range per well (ppm)	40,000 – >120,000	50,000 – 140,000	10,000 – 20,000

1.3 Produced water management

Current produced water management strategies vary by region; however, deep well injection is often the preferred disposal method due to its low cost. The most common beneficial reuse of produced water in 2012 was enhanced oil recovery, accounting for 45.1% of all produced water.[4] Enhanced oil recovery is a method of improving petroleum production by injecting fluid into a nearby non-producing well to essentially push hydrocarbons towards a producing well. Enhanced oil recovery is a water management option only while operators are still producing from wells. Less than 1% of produced water in the U.S. was used for an alternate beneficial reuse purpose.[4]

A study conducted by CH2M shows that the most cost effective reuse option for produced water is in oilfield activities (e.g., hydraulic fracturing, dust control).[2] Reuse in the O&G industry is a viable option while operations are still ongoing; however, when economic conditions result in decreased drilling, hydraulic fracturing, or production, other beneficial reuse options will need to be considered. Additionally, regulatory pressure may increase due to induced seismicity from disposal injection wells and may enforce and incentivize reuse of produced water. Reuse alternatives outside the O&G industry include livestock watering, irrigation, and streamflow augmentation. For example, water for livestock watering is recommended to have a TDS concentration of less than 7,000 mg/L, with some animals able to handle up to 10,000 mg/L TDS for a short duration.[5,6] The O&G industry has developed hydraulic fracturing technologies to accommodate reusing waters with high TDS concentration (e.g., produced water); however, TDS will need to be addressed when reusing produced water outside the oilfield. Other challenges associated with reusing produced water include suspended solids, scaling potential, and bacteria.

Advances in membrane technology have made desalination a more economically viable option; however, the membranes are expensive and sensitive to poor feed water quality (e.g., suspended solids, scaling potential, and microorganisms). Chemical damage of membranes occurs when incompatible chemicals impede membrane material performance. According to membrane companies, chemicals such as aromatic hydrocarbons are known to rapidly damage membranes[7], many of which are contained in produced water. To reduce water salinity through membrane desalination, a thorough pretreatment of produced water is needed for protection of the membranes and to make the process economically viable.

1.4 Challenges to reuse of produced water

An assessment of the Marcellus Shale in Pennsylvania revealed that the major cost factors of water management included quantity and quality of produced water, required level of treatment for reuse or disposal, and transportation method.[8] The Bureau of Reclamation conducted case studies of produced water management and estimated that the cost of produced water management ranges between $0.82 per barrel (1 barrel = bbl = 42 US gallons) and $18.25/bbl.[9] A breakdown of water management costs is summarized in Table 1.2 and shows that transportation and treatment are the two dominant factors influencing cost of produced water management. Treatment of produced water compared to underground injection for disposal can increase water management costs by over five times.

Table 1.2. Estimated cost range from produced water management,[9] indicating that treating produced water can be over five times more expensive than underground injection.

	Cost Range ($/bbl)	
	Low	*High*
Transportation	0.50	8.00
Water Sourcing	0.25	1.75
Underground Injection	0.07	1.60
Treatment	0.20	8.50
TOTAL (injection only)	**$0.82**	**$11.35**
TOTAL (treatment only)	**$0.95**	**$18.25**

1.5 Produced water treatment methods

Many technologies are capable of treating wastewater streams to a desired water quality. Various physical, chemical, and biological unit processes have been evaluated as potential technologies to treat produced water.[10] One prior method of produced water treatment was to discharge produced water to a publicly owned treatment works (POTW). Previous research indicates that between 6% and 20% by volume produced water from the Denver-Julesburg basin could be added to POTWs without significantly changing the quality of effluent produced;[11] however, the Environmental Protection Agency (EPA) has prohibited the treatment of produced water in POTWs.[12] Yet, biological treatment may be a viable method for pretreatment of produced water, specifically for removal of organic matter, before further treatment and desalination.

1.6 Sequencing batch reactors

Domestic wastewater treatment facilities use biological processes to remove organic matter and nutrients from municipal and some industrial wastewaters. The removal of organic matter and nutrients in these processes is referred to as biological nutrient removal (BNR). A typical treatment train starts with primary clarification to remove inert solids, followed by secondary treatment, which utilizes biomass (microorganisms), and ends with clarification via gravity or membrane separation. Centralized wastewater treatment facilities that treat large volumes of wastewater from a myriad of sources often use a sequence of basins to provide the changing conditions necessary for removal of organic matter and nutrients. Decentralized treatment facilities often have a smaller footprint and their wastewater may be from a single source and treated onsite. Sequencing batch reactors (SBR) have a smaller footprint because they utilize a single basin that cycles through aeration and settling stages to provide multiple environments for the microbial communities as shown in Figure 1. Multiple SBRs may be used in parallel to accommodate high flow rates.

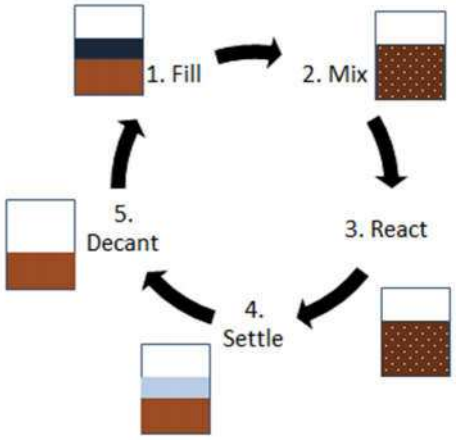

Figure 1.1. Stages in a sequencing batch reactor, starting with fill where raw influent enters the bioreactor followed by a mix stage, where activated sludge is dispersed throughout the bioreactor. The react stage allows the microbial communities in the mixed liquor to consume contaminants such as organics and nutrients. After the react stage, the bioreactor proceeds to settle before decanting off the clarified supernatant. During the decant stage activated sludge is left in the bioreactor to introduce microorganisms into the next batch of raw wastewater.

Organic matter is biologically removed from wastewater primarily through new cellular growth as microorganisms derive carbon from the organic matter to synthesize new cellular material.[13] During the microbial growth process, microorganisms also need inorganic nutrients (e.g., nitrogen and phosphorus) and an energy source, which may be organic carbon for some microorganisms.[13]Produced water is typically rich in organic matter, with total organic carbon (TOC) concentrations ranging from 1.2 to more than 5800 mg/L; however, the types of organic compounds present vary greatly and may include polycyclic aromatic hydrocarbons, heterocyclic compounds, aliphatic alcohols, aromatic amines, phenols, phthalates, fatty acids, and nonaromatic compounds.[14]

In municipal and some industrial wastewaters such as produced water, ammonium (NH_4^+) is the dominant form of nitrogen.[15] The pH of the water dictates the equilibrium concentration of ammonium and ammonia (NH_3). The BNR process begins with nitrification, when bacteria and archaea convert ammonia to nitrite (NO_2^-) and nitrite to nitrate (NO_3^-).[15] When ammonia is oxidized, the ammonium-ammonia equilibrium shifts towards ammonia, allowing ammonia oxidizing bacteria (AOB) to continue nitrification.[15] After nitrification, the BNR process stream enters an anoxic phase, where another group of bacteria begin the denitrification process, converting the nitrate to nitrogen gas (N_2). Industrial wastewater treatment facilities designed for denitrification are thought to have *Azoarcus, Thauera,* and *Zoogloea* as the primary denitrifying bacteria; however, it is likely that the microbial communities differ between each treatment facility.[15] The presence of salt in a municipal SBR environment has shown to greatly inhibit the treatment in the system. In one study the salt concentration in a membrane bioreactor system was increased from 0 to 35 g/L NaCl, resulting in approximately 90% reduction in dissolved organic carbon removal and cessation of the nitrification process.[16] The treatment potential of produced water by native microorganisms is further discussed in Section 1.8.

1.7 Media filtration

Media filtration is a common gravity driven separation process used to remove suspended solids from pretreated water or wastewater. Traditional media filters tend to be a low cost alternative to modern membrane filtration techniques due to lower capital and operating costs. Media in a filter can consist of a single material or multiple layers of different materials such as sand, anthracite, or garnet. The dominant removal mechanism in rapid media filtration is depth filtration.[17] Trickling filters or slow sand filters are two types of slow sand filtration, which facilitate attached biological growth to remove soluble organic matter as well as suspended solids. Previous studies have used attached growth systems such as biologically active filters and trickling filters to remove organic matter from waste streams of various industrial processes such as tanneries and plastics production.[18,19] Studies have shown significant removal of organic matter in a biologically active filter treating produced water.[20–22]

1.8 Treatment potential of microorganisms native to produced waters

Microbial communities from both hydraulic fracturing fluid and the hydrocarbon formation are brought to the surface in produced water.[23,24] It has been found that some microorganisms present in the source water survive the addition of biocides in the fracturing fluid.[25] The relative distribution of bacterial classes in the source water compared to microbial communities in the flowback and produced water over time is shown in Figure 1.2 for a well in Pennsylvania.[26] The class of bacteria and relative population density of each community changed over time, signifying that there is a distinct difference between the microbial communities being introduced by the hydraulic fracturing source water and the communities living in the rock formation.[25] Additionally, the abundance of the 16S rRNA genes decreases over time,[25] indicating that the microbial population in the formation is less dense than populations typical in surface waters. Another

study that looked at the type of microorganisms in produced water found that over 97% of all microbial communities were bacteria, less than 0.5% were Archaea, less than 1% were viruses, and less than 1.5% of Eukaryota.[26]

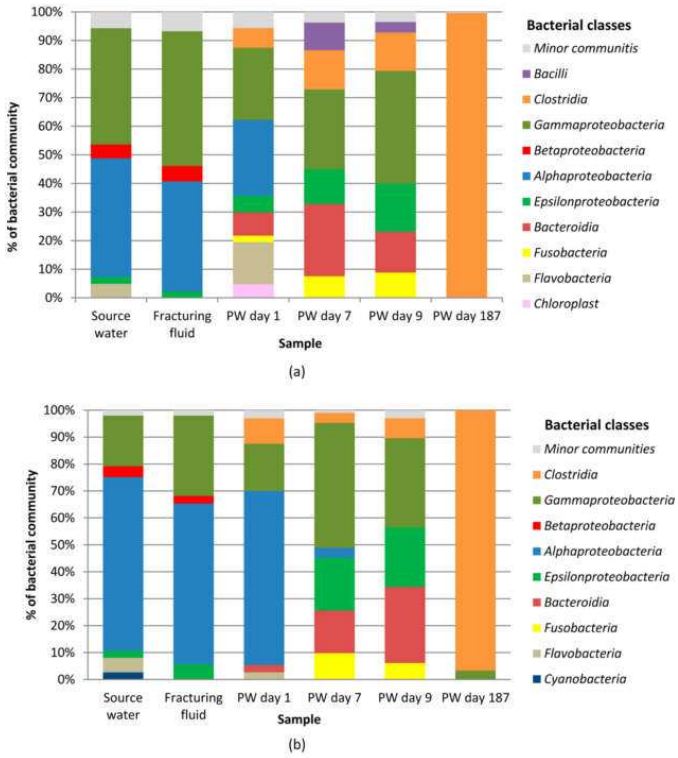

Figure 1.2. Relative distribution of 16S rRNA gene sequences for bacteria in a Pennsylvania well using (a) tag-encoded pyrosequencing and (b) clone libraries.[27] Microbial communities changed over time, indicating that the produced water has native microbial communities, which were not introduced by the source water used for hydraulic fracturing.

Studies have shown a significant shift over time towards microbial communities that are facultative aerobic/anaerobic and halophilic as the fluid shifts from flowback to produced water.[23,26,27] On day 187 in Figure 1.2, pyrosequencing revealed that over 99% of the bacterial community was found to be of the *Clostridia* class in the *Halanaerobiales* order.[25] *Halanaeobiales* are in the genera *Haloanerobium*, which comes from the Greek words *hals, an, aer,* and *bios*, or in other words: salt life with no air.[28] Other halotolerant and facultative anaerobic orders present in produced water include *Bacteroidales, Fusbacteriales, Campylobacterales, Alteromonadales,* and *Vibrionales.*[25] Members of the order Haloanaerobiales and family Haloanaerobiacaea have been identified in various saline environments such as the marine salterns, the Dead Sea, and produced water.[29] *Haloanaerobium salsugo* is one such microorganism that was found in oilfield brine and was proposed as a new strain of species in 1994.[30] Upon further study, the *Haloanaerobium salsugo* was found to have a salt tolerance between 6 and 24% NaCl.[30] Without NaCl present, the *Haloanaerobium salsugo* cells would lyse, even when other salt ions such as potassium and magnesium were substituted for sodium in NaCl.[30] Similar salt tolerances were found in the

species *Haloanaerobium congolense*, another moderately halophilic bacterium discovered in oil wells.[29] The *Haloanaerobium congolense* microorganism was first found in an African oil well, and is related to members of the *Haloanaerobium* genus.[29] Similar to its fellow genus members, *Haloanaerobium congolense* can use either thiosulfate or elemental sulfur as electron acceptors, while producing acetate, hydrogen, and carbon dioxide as waste products during glucose fermentation.[29] Growth of *Haloanaerobium congolense* is inhibited by its hydrogen byproduct when sulfur is used as an electron acceptor.[29] When thiosulfate is used as the electron acceptor, the hydrogen does not seem to inhibit growth.[29] Many of the *Haloanerobium* were found to have optimal growing conditions above 20 °C, at neutral pH, and approximately 10% NaCl.[29–31]

Many different types of halophilic anaerobic bacteria are found in produced water, with slightly varying preferential environmental growth conditions as summarized in Table 1.3.[30] The preferences of each microorganism demonstrate that although the varying water characteristics of produced water may make treatment difficult, some microbial communities may be able to survive the fluctuating conditions. Shotgun metagenomic surveys can give some indication of functional potential these microbial communities possess. In a study of a natural gas well located in the Marcellus Shale in Pennsylvania, the general microbial class distribution was similar to previous studies and indicate an overall increase in functional potential from the microbial communities as water produced from a well changes from flowback to produced water.[26] Additionally, between 10 and 20% of the DNA sequences had an unknown function,[26] indicating that further research is needed to fully understand the functional potential of microorganisms native to hydrocarbon formations. The sequences with known functional classification were separated into Level 1 functional categories shown in Figure 1.3. The miscellaneous, or unknown category, appears to contain a significant amount of sequences (8-9%).[26] Overall, the study shows and increase in the stress response functions in the produced water compared to the source water.[26] Level 1 metabolic capabilities such as aromatic compound metabolism, nitrogen metabolism, and sulfur metabolism suggest that the microorganisms natural in produced water, if in significant biomass, may have the capability of treating the produced water to some level.

Table 1.3. Comparison of fermentative halophilic anaerobic bacteria[30] indicating that the halotolerant bacteria have similar preferential growth conditions, which vary enough to potentially be resilient to changing water quality.

Parameter	*H. salsugo*	*H. praevalens*	*S. lortetii*	*S. marismortui*	*H. chitinovorans*
Morphology	Rod	Rod	Rod	Rod	Rod
Size (μm)	0.3-0.4 x 2.6-4.0	0.5-1.5	0.5-0.6 x 2.5-10	0.6 x 3-13.0	0.5 x 2.5-8.0
Gram reaction	Negative	Negative	Negative	Negative	Negative
Temperature range (°C)	23-51	12-45	25-50	25-50	30-45
pH range	5.6-8.0	6.0-8.0	NR	NR	7.0
NaCl conc. (g/L)	60-240	50-250	60-120	30-180	30-290
Optimum NaCl conc. (g/L)	90	125	80-100	30-120	120
Generation time (h)	9	4	8	0.6	2.5
Sampling Source	Oil Brine	Great Salt Lake, UT	Dead Sea	Dead Sea	Solar Saltern

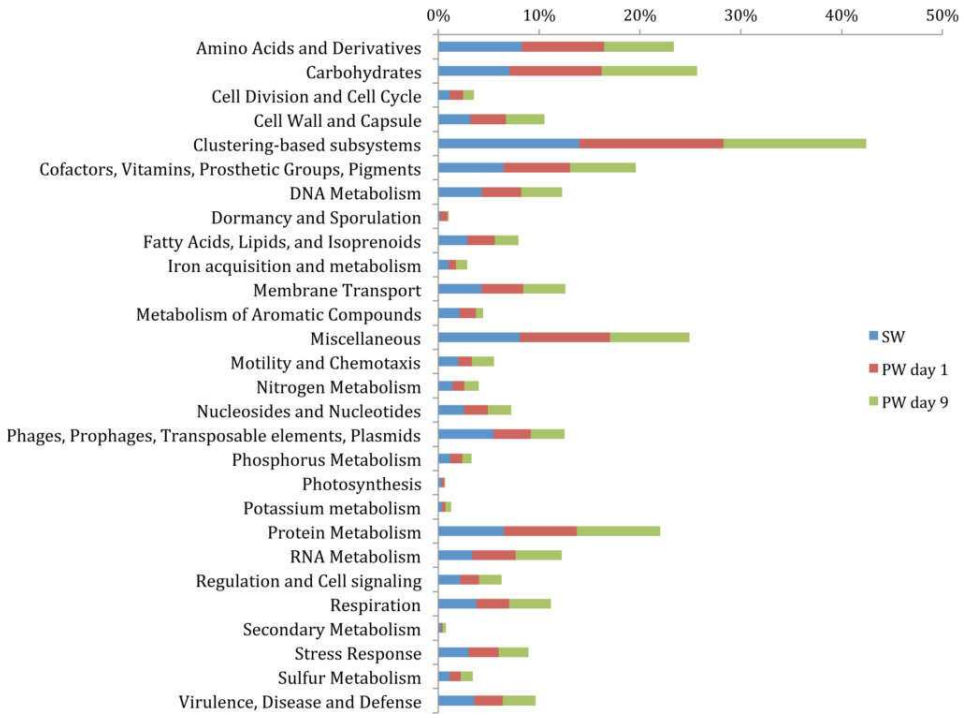

Figure 1.3. Level 1 functional categories found in DNA segments from source water (SW), and produced water (PW) from days one and nine in a Marcellus Shale natural gas well in Westmoreland County, Pennsylvania.[26]

1.9 Research objectives

The main objective of this study was to evaluate the treatment of produced water by microorganisms native to the produced water in conventional activated sludge treatment followed by media filtration. SBRs and media filters were used to facilitate the BNR process. Over the course of the study suspended growth of microorganisms were evaluated in both a bench scale setup and a pilot scale treatment train. The bench-scale study focused on bioreactor performance optimization, produced water chemistry, and chemical additives impact on microbial processes. The pilot-scale study focused on the effects of operating conditions such as cycle time and duration of aeration on biological treatment in the bioreactors and media filters. Due to the high salinity of produced water, this treatment process, once optimized, may serve as an effective pretreatment to membrane desalination.

CHAPTER 2
MATERIALS AND METHODS

The bench and pilot scale systems were designed, built, and tested at the Advanced Water Technology Center laboratory of the Colorado School of Mines. The bench system was used to determine optimal environment in the bioreactor for suspended growth. The pilot system was used to evaluate the treatment of produced water in a sequencing batch reactor followed by a media filter.

2.1 Produced water feed

Raw produced water from the Denver-Julesburg (D-J) basin was used for all experiments. The main stream of produced water was collected bi-weekly from a mature six-well pad in Weld County, Colorado and is referred to as PW1 in this manuscript. Additional produced water for limited bench scale testing was collected from a disposal well and is referred to as PW2 in this manuscript. PW1 was stored in 250 gallon totes at ambient temperature, and PW2 was stored in 5 gallon carboys at room temperature. The average water quality of PW1 and PW2 is summarized in Table 2.1.

Table 2.1. Water quality parameters for the produced water used in this study. PW1 had relatively consistent characteristics (see Table A-1 for statistics), as it was collected from a single multi-well pad. The phosphorus concentration of PW1 was consistently less than one, and was often below detection limit. Batches of PW2 was collected from an injection well, which had continuously changing water characteristics.

	PW1	**PW2 Batch 1**	**PW2 Batch 2**	**PW2 Batch 3**	**PW2 Batch 4**	**PW2 Batch 5**
pH	6.66	5.83	6.52	6.34	5.81	6.65
Conductivity (mS/cm)	28	55.5	38	36	35	40.2
COD (mg/L)	1562	1580	1843	1854	6283	-
sCOD (mg/L)	1509	1100	1852	1456	5740	1110
NH_3 (mg-N/L)	25	32	31	26	20	33
TDS (g/L)	13.6	27.4	30	39	17.8	19.8
TSS (mg/L)	109	-	30	22	67	53
VSS (mg/L)	106	-	30	21.2	43	35
Chloride (mg/L)	10384	16990	16868	15089	11034	11698
Phosphorus (mg/L)	< 1	1.06	-	1	3.6	n.a.*
Sum Cations (mg/L)	5289	10232	13372	23819	6652	7997
Sum Anions (mg/L)	8359	17203	17066	15270	11150	11837

*non-detect

2.2 Bench scale experimental setup

A bench scale jar tester (Figure 2.1) was used to optimize bioreactor performance. The six 2-L jars were operated at room temperature under unique bioreactor conditions. A small air pump was connected to a timer to automatically control the intermittent aeration of all jars using a 1” air diffuser stone. All jar reactors were operated in identical 24-hour cycles. Every morning, before the manual decant-stage, pH and conductivity were measured in each jar using handheld probes (Thermo Fisher Scientific Inc., Waltham, MA). After the measurements were recorded, the mixing and aeration were stopped to allow for 20 minutes

of settling before 600 ml of supernatant was decanted from each jar. Following the decant, 600 ml of feed water was added in addition to a unique treatment step in each jar, as summarized in Table 2.2. Subsequently, the automatic mixing and aeration were resumed. Initially, the system was programmed to cycle through 30 minutes of mixing with aeration followed by 30 minutes of settling until the daily settling/decant/fill. After day 45 the programming was modified to have continuous mixing and intermittent aeration in alternating 30-minute intervals until the daily settling/decant/fill procedure. Due to evaporation, deionized water was added to each jar every 3-4 days to maintain 2 L of liquid in the bioreactors.

Figure 2.1. The bench scale system consisting of a standard jar tester and six 2-L jars. An air pump was used to intermittently aerate the content of all the jars.

Samples were collected twice a week from PW1, PW2, the mixed liquor in each jar, and the supernatant of each jar. 50 ml of mixed liquor was collected from each jar during mixing immediately before settling and decant. During sampling events in which mixed liquor was collected, only 550 ml of decant was collected to maintain a 600 ml of fill. Bi-weekly analysis of total suspended solids (TSS), volatile suspended solids (VSS), and turbidity was conducted on the mixed liquor in each jar. Ammonia, nitrate, chemical oxygen demand (COD), and soluble COD (sCOD) analyses were conducted weekly on the feed and supernatant of each jar. The procedures are described in section 2.4 below.

Table 2.2. Feed water source and treatment for each 2 L jar bioreactor in the bench testing experiment. All jars except jar A used the same produced water for feed, while jar A used water from a disposal well.

Jar Name	Feed Water Source	Treatment (dosed daily with feed water)
PW2	PW2	None
Baseline	PW1	None (Baseline)
AS Jar	PW1	200 mg solids from return activated sludge (AS) of municipal SB-MBR
Probiotic Jar	PW1	10 mg/L Biogenesis probiotics (Probiotic Solutions, Gilbert, AZ)
H_2O_2 Jar	PW1	300 mg/L H_2O_2 pretreatment to feedwater with 24 hr settling before addition
KH_2PO_4 Jar	PW1	7.5 mg - P/L KH_2PO_4
Centrate Jar	PW1	7.5 mg-P/L of mesophilic phase digester effluent (Metro WW, Denver, CO)
Attached Growth Jar	PW1	Mesh filter (Orenco, Sutherlin, OR) in jar to promote attached growth

2.3 Pilot scale experimental setup

The pilot scale experiments were conducted on a modified system that was previously used to study an SB-MBR treatment designed to co-treat municipal wastewater and produced water.[11] In this study, the bioreactors were not inoculated with biomass from another treatment system, but grew only from biomass entering with the feedwater. Two treatment trains were operated in parallel and are hereby referred to as treatment trains 1 and 2. Both treatment trains contain an SBR followed by a media filter, as shown in Figure 2.2.

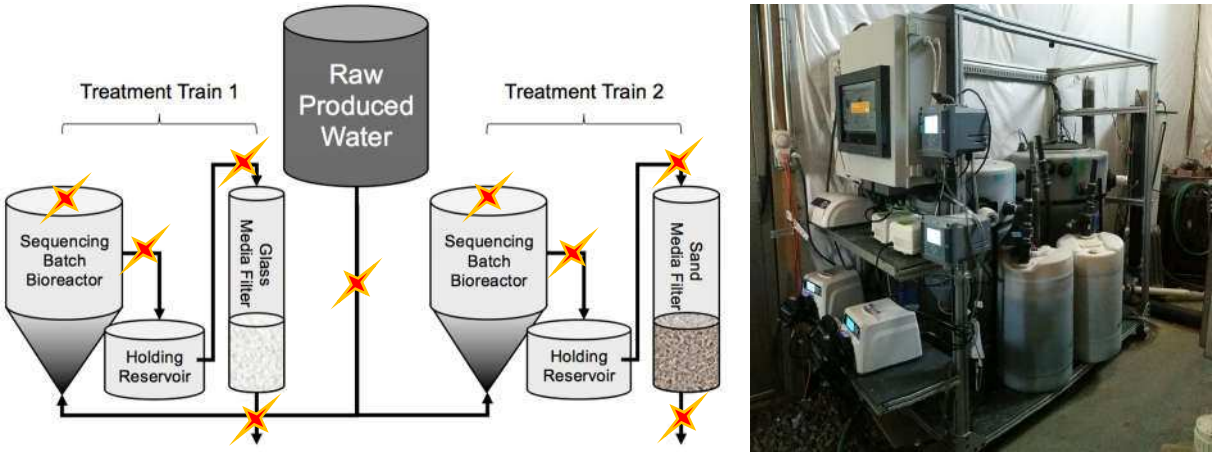

Figure 2.2. Picture of pilot system (right) and sketch of hydraulic flow through the pilot system (left). Raw produced water was introduced to the bioreactors through an actuated ball valve at the bottom of each conical-bottom tank. After each batch cycle was over, supernatant drained into a holding reservoir, until it was pumped continuously through media filter. Treatment trains 1 and 2 are identical except for the media types, with train 1 using recycled crushed glass, and train 2 using silica sand. Sampling points are indicated by stars.

A peristaltic pump was used to dose 5.7 L (1.5 gallons) of produced water through the bottom of each 30-gallon conical-bottom tank bioreactor at the beginning of each cycle. Each bioreactor contained 3125 g of spent granular activated carbon (GAC) and a 10 cm (4”) diameter aeration stone, which rested at the bottom of the bioreactor on a mesh plate. The aeration stones were supplied with air by a linear air pump (Alita Industries, Arcadia, CA). A 15 cm (6”) diameter 17.8 cm (7”) tall plastic cylinder was suspended from the center of the lid of each bioreactor to facilitate better mixing during aeration. Each bioreactor operating cycle began with a fill stage followed by an aeration with mixing stage that was followed by a settling stage. During the different phases of testing, the durations of aeration stages followed by settling stages varied as summarized in Table 2.3. After the last settling stage, the cycle ended with a decant stage, where supernatant was drained by gravity through an actuated ball valve (Ashai, Ryan Herco, Denver, CO) into a 15 gallon holding reservoir. From the holding reservoir, a peristaltic pump with two pump heads continuously delivered 20 ml/min of bioreactor supernatant to the top of the media filter column and pulls 10 ml/min of effluent from the bottom of each media filter. The extra 10 ml/min of supernatant drained by gravity through an overflow port in the filter column. The filter column of treatment train 1 contained 20/40

glass media (Glass Advantage Inc., Fargo, ND) and the filter column of treatment train 2 contained 20/40 silica sand media. Due to the low concentration of suspended solids in the bioreactors, no mixed liquor was wasted, and solids collected during backwash from each filter were returned to the respective bioreactor.

Samples were collected once a week from the influent (PW1), the mixed liquor from each bioreactor (approximately 25-30 minutes into each cycle), supernatant from each bioreactor (within 5 minutes of decant), influent into each filter column, and effluent out of each filter column. Sample analysis included TSS, VSS, turbidity, COD, sCOD, ammonia, iron, and nitrate, as described in section 2.4. The pilot system is equipped with multiple sensors that continuously measured the conditions in the system. These include pH, conductivity, oxidation-reduction potential, and dissolved oxygen. Data were logged by a data acquisition software (Labview, National Instruments Corp., Austin TX), a WebMasterONE series controller (WALCHEM, Holliston, MA), and an instrument control system (Labjack, UE9-Pro, Lakewood, CO). The software and control integration allowed the pilot scale system to be fully automated.

Table 2.3. Operating conditions during phases of treatment of the bioreactors in the pilot system. Total cycle time began at 2 hours and slowly increased to 5 hours. During phase 5, the 5 hour cycle time was held constant while phosphorus was added to each bioreactor at a concentration of 7.5 mg/L KH_2PO_4-P. During phase 6 the amount of aeration increased in the bioreactors while cycle time and phosphorus addition were held constant.

Phase	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Day	0-93	93-138	138-182	182- 236	236- 307	307- 427	427- 446
Stage Order				*mins*			
Fill	2	2	2	2	2	2	1
Aeration & Mix	27	27	27	27	27	43	43
Settling	27	27	27	27	27	15	15
Aeration & Mix	27	27	27	27	27	45	45
Settling	27	27	27	27	27	15	15
Aeration & Mix	0	30	30	30	30	45	45
Settling	0	30	30	30	30	15	15
Aeration & Mix	0	0	30	30	30	45	45
Settling	0	0	30	30	30	15	15
Aeration & Mix	0	0	0	30	30	30	30
Settling	0	0	0	30	30	20	20
Decant	10	10	10	10	10	10	10
Total Cycle Time (mins):	120	180	240	300	300	300	299
Hydraulic Residence Time (days):	1.67	2.50	3.33	4.17	4.17	4.17	8.31
Total Aeration Time (mins):	54	84	114	144	144	208	208
Additional BR Treatment:	n/a	n/a	n/a	n/a	7.5 mg - P/L *	7.5 mg - P/L *	7.5 mg - P/L *

* KH_2PO_4 added daily

2.4 Analytical procedures

Immediately upon sampling, the pH was measured and the sample was prepared for analysis. Preparations included diluting samples to account for chloride interference limits with specific analytical tests. Hach kits were used to measure several analytes as summarized in Table 2.4. Turbidity was measured on all samples collected from both the pilot and the bench scale systems using a digital turbidimeter (2100N; HACH, Loveland, CO).

Table 2.4. Analytes measured using Hach kits with respective sample preparation, procedure, and quantification range.

Analyte	Sample Preparation	Quantification Range *mg/L*	Hach TNT Number
COD, Low Range	None	3-150	821
COD, High Range	None	20-1500	822
sCOD, Low Range	Filtered*	3-150	821
sCOD, High Range	Filtered*	20-1500	822
NH_3-N, High Range	None	2.0-47.0	832
NO2-N, Low Range	None	0.001-0.60	839
NO_3-N, Low Range	None	0.23-13.5	835
Fe	None	0.2-6.0	858
PO_4-P, Low Range	Filtered*	0.05-1.50	843
PO_4, High Range	Filtered*	1.5-15.0	844

*0.45 µm polyethersulfone membrane filters (VWR International, Radnor, PA)

On a monthly basis, all samples from the bench and pilot scale systems were analyzed for concentration of cations/metals using inductively coupled plasma optical emission spectroscopy (ICP-OES; Optima 5300 DV, PerkinElmer, Fremont, CA) and anions using ion chromatography (IC; ICS-900, Dionex, Sunnyvale, CA). Organic carbon (total and dissolved) and total nitrogen (TN) were measured using a carbon analyzer (Shimadzu TOC-L, Columbia, MD). Alkalinity measurements were conducted by digitally titrating 1.6 N sulfuric acid into 100 ml of raw, unfiltered samples until the sample reached a pH of 4.5. Total suspended solids, fixed suspended solids, and volatile suspended solids were measured using Standard Method 2540.[32]

2.5 Microbial analysis

Samples of mixed liquor from the bench jar bioreactors and from all sampling points in the pilot system were collected in 50 mL falcon tubes for biological analysis. All samples were immediately stored in a freezer at -20 °C. Before processing, samples were allowed to thaw for approximately 30 minutes. 40 mL of each sample was then centrifuged at 7,000G for 45 minutes. The supernatant was removed and the solid pellet was frozen. Each pellet was thawed before a lysis solution was added to each sample vial. The vials were then vortexed until the pellet was solubilized. The solution was then added to bead beating tubes. DNA extraction from each tube was done with the ZymoBIOMICS DNA MiniKit according to manufacturer specifications. DNA samples were sent to Duke's Center for Genomic and Computational Biology and sequenced on an Illumina MiSeq (Illumina Inc., San Diego, CA). The returned 16S rRNA sequences were de-multiplexed via the Sabre package. Quality of data and taxonomy classification was determined using dada2 and managed with the phyloseq package. All data was rarefied to 6,018 sequences per sample before processing further. Unweighted NMDS ordinations were produced using the phyloseq package. Heat maps were produced with the ampvis package.

2.6 Statistical analysis

Confidence intervals were developed for percent removal of COD, sCOD, and ammonia for pilot and bench systems to determine if average percent removal was statistically different. Type of distribution was determined to be normal for each data set.[33] Distributions were unable to be determined for data sets with fewer than six data points; however, all other data sets were normally distributed and therefore all data sets were assumed to have a normal distribution. Jar bioreactor percent removals were compared with a 95% confidence interval and results are shown in Appendix A Tables A.2, A.3, and A.4.

CHAPTER 3

RESULTS AND DISCUSSION

Treatment performance of each system was primarily based upon the ability to remove organic carbon and ammonia from raw produced water. Results are presented first by system, then by constituents.

3.1 Bench scale jar testing

Various treatment methods to improve removal of organic matter and nutrients from produced water were evaluated in a bench-scale bioreactor jar setup (section 3.1). Results from the top performing jars (AS jar, KH_2PO_4 jar, and centrate jar) compared to the baseline are presented here and additional results are included in Appendix A.

3.1.1 pH and conductivity

The pH in all bioreactor jars ranged from 7.0 to 8.5 as shown in Figure 3.1. The pH in all jars was higher than the feed water, indicating that treatment in the bioreactors increases the pH; however, all jar bioreactors maintained a stable pH in the normal range of conventional activated sludge treatment.

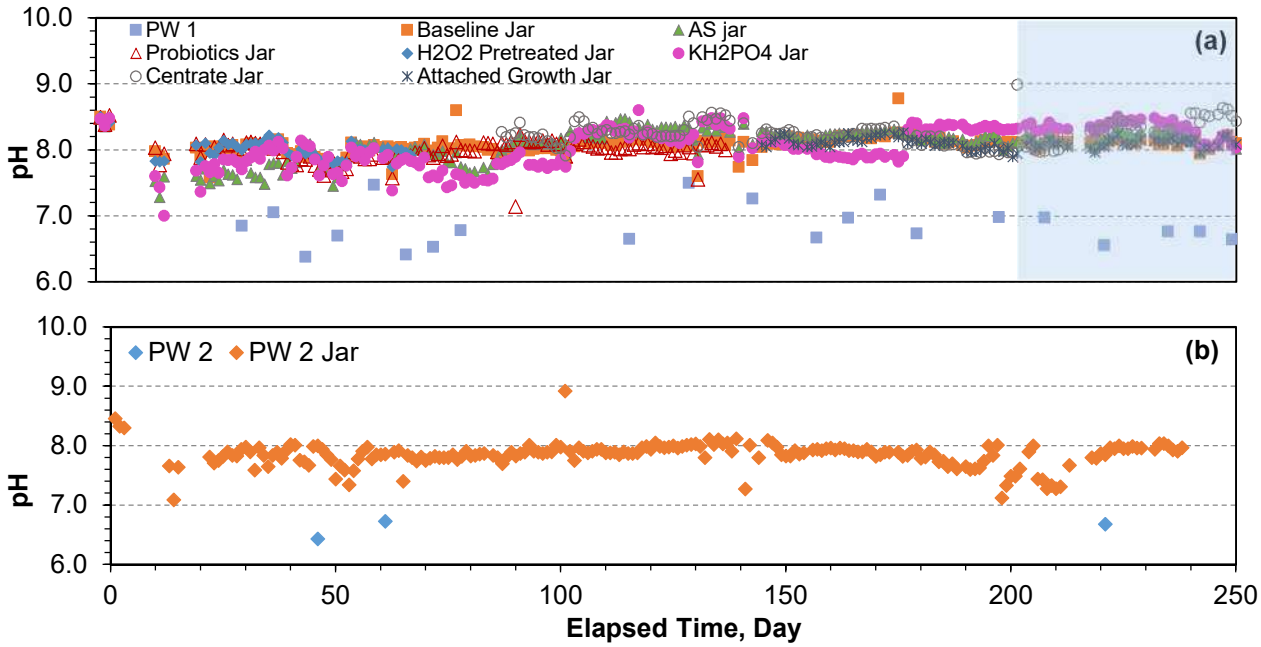

Figure 3.1. pH as a function of time for feed water and mixed liquor in the (a) baseline jar, AS addition jar, probiotic addition jar, KH_2PO_4 addition jar, centrate addition jar, attached growth jar, and H_2O_2 pretreated feed jar, and (b) PW2 feed water jar. Results show that all treatment conditions in the experimental bioreactors increased pH of the water during treatment. The blue shaded area marks the increase in phosphorus addition in the KH_2PO_4 jar from 7.5 to 15 mg-P/L.

Conductivity as a function of time for all bioreactor jars is shown in Figure 3.2. In all jars the conductivity slowly increased over time, and suddenly decreased. Each slow rise in conductivity was a result of

evaporation and each sudden decrease in conductivity was the result of the manual addition of deionized water to replace the evaporated water. PW2 jar had a higher conductivity than all other jars because it was fed with PW2, which has a higher average conductivity than PW1. PW2 conductivity varied from batch to batch because the batches of water were from a deep-well disposal site. Injection wells for disposal accept produced water from an entire region, which results in varying water quality over time, including salinity.

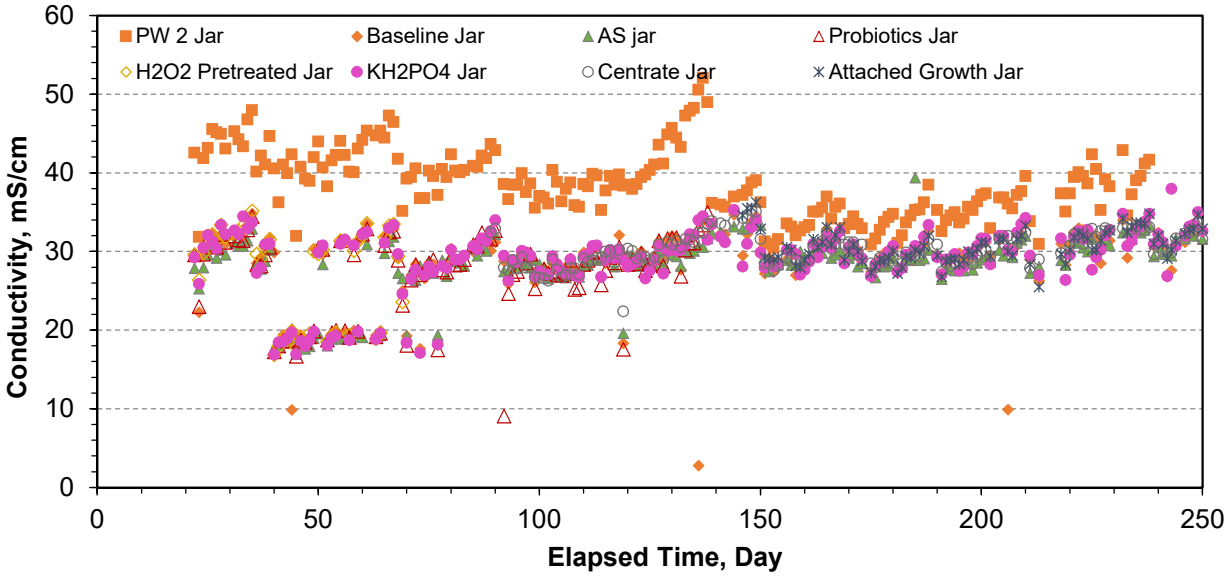

Figure 3.2. Conductivity in each jar over time, showing that the PW2 jar has higher conductivity than the other jars due the difference in feed water. All gradual increases in conductivity are due to evaporation and sharp decreases in conductivity are due to the manual addition of deionized water.

3.1.2 COD and sCOD removal

Total and soluble COD were used as a proxy to evaluate removal of organic matter in the bioreactor jars. The average concentrations and percent removal of total and sCOD are summarized in Table 3.1. The highest removal of sCOD was in the AS, the KH_2PO_4, and the centrate jars. Although the centrate jar had slightly lower sCOD removal than the AS jar, it had higher removal of COD. The H_2O_2 jar had almost no removal of sCOD and the lowest removal of COD compared to the other bioreactor jars. This may be due to the H_2O_2 not fully reacting and decomposing before the H_2O_2-pretreated feed was introduced into the bioreactor jar in the fill stage. If H_2O_2 was present in the feedwater, microorganisms in the bioreactor jar may have been oxidized and killed. The baseline and probiotic jars had comparable removal of both soluble and total COD, which may suggest that either the dosing may have needed to be increased, or the microorganisms in the probiotic jar are not able to treat the produced water. The probiotic and H_2O_2 jars were replaced with the attached growth and centrate jars on days 144 and 74, respectively.

Table 3.1. Average percent removal and concentration of COD and sCOD in the feed and bioreactor jars. The highest percent removal was observed in the AS jar, the KH_2PO_4 jar, and the centrate jar (bold). The jar with the lowest removal of COD was the H_2O_2-pretreated jar.

		PW1	Baseline	**AS**	Probiotic	**KH_2PO_4**	**Centrate**	Attached Growth	H_2O_2
		Feed	*Decant*	***Decant***	*Decant*	***Decant***	***Decant***	*Decant*	*Decant*
sCOD Removal	*%*	-	20.4	**48.1**	22.3	**45.9**	**43.1**	35.6	2.7
sCOD Conc.	*mg/L*	1509	1092	**717**	1005	**753**	**807**	1000	1509
COD Removal	*%*	-	21.5	**24.6**	20.2	**40.4**	**36.2**	43.2	21.9
COD Conc.	*mg/L*	1562	1139	**1067**	1117	**961**	**930**	978	1562

sCOD concentrations and percent removal for the top performing jars are shown in Figure 3.3. The COD and sCOD concentrations and percent removal for the remaining jars are provided in Appendix A (Figures A.1, A.2, and A.3).

The AS and centrate jars had more consistent percent removal than the KH_2PO_4 jar; however, the average decant concentrations were similar. The KH_2PO_4 jar had the same removal of sCOD with the addition of 7.5 mg-P/L or 15 mg-P/L. The AS jar had an estimated phosphorus addition of 1.25 mg-P/L using a municipal activated sludge cell formula of $C_{60}H_{87}O_{23}N_{12}P$.[13] The percent sCOD removal was similar in jars with a phosphorus supplement ranging from 1.25 mg-P/L to 15 mg-P/L, indicating that at a point less than or equal to 1.25 mg-P/L a different factor may have limited suspended biological growth or that all the bioavailable COD had been consumed.

The TOC:COD ratio was compared for the baseline and top three performing jars as summarized in 2.6. TOC measurements capture the total organic matter in a sample and COD measurements capture all the materials that can be oxidized (organic and inorganic). As expected, the DOC:sCOD ratios are very similar to the TOC:COD ratios of the corresponding samples. The jars with higher sCOD and COD removals (AS, centrate, and KH_2PO_4 jars) had lower ratios compared to the baseline. In municipal wastewater, the ratio of TOC:COD (or DOC:sCOD) also decreased with increased removal of organic matter, indicating that the AS, centrate, and KH_2PO_4 bioreactor jars removed organic matter better than the baseline or attached growth jars. A typical TOC:COD ratio for conventional municipal systems is 0.5 for raw wastewater and 0.1 for well-stabilized effluent.[34] The lower ratio of TOC:COD (and DOC:sCOD) in produced water compared to municipal water suggests that produced water has more oxidizable inorganic material (e.g., iron, sulfur) relative to municipal wastewater. Based on the TOC concentrations, the majority of the biodegradable portion of organic matter in produced water may have been consumed in the bioreactor with addition of a phosphorus supplement, with the remaining portion of organic matter too complex for microorganisms to easily break down. Inorganic constituents that are most likely the remaining COD can cause fouling of membranes during desalination and may need to be removed via chemical or physical treatment methods.

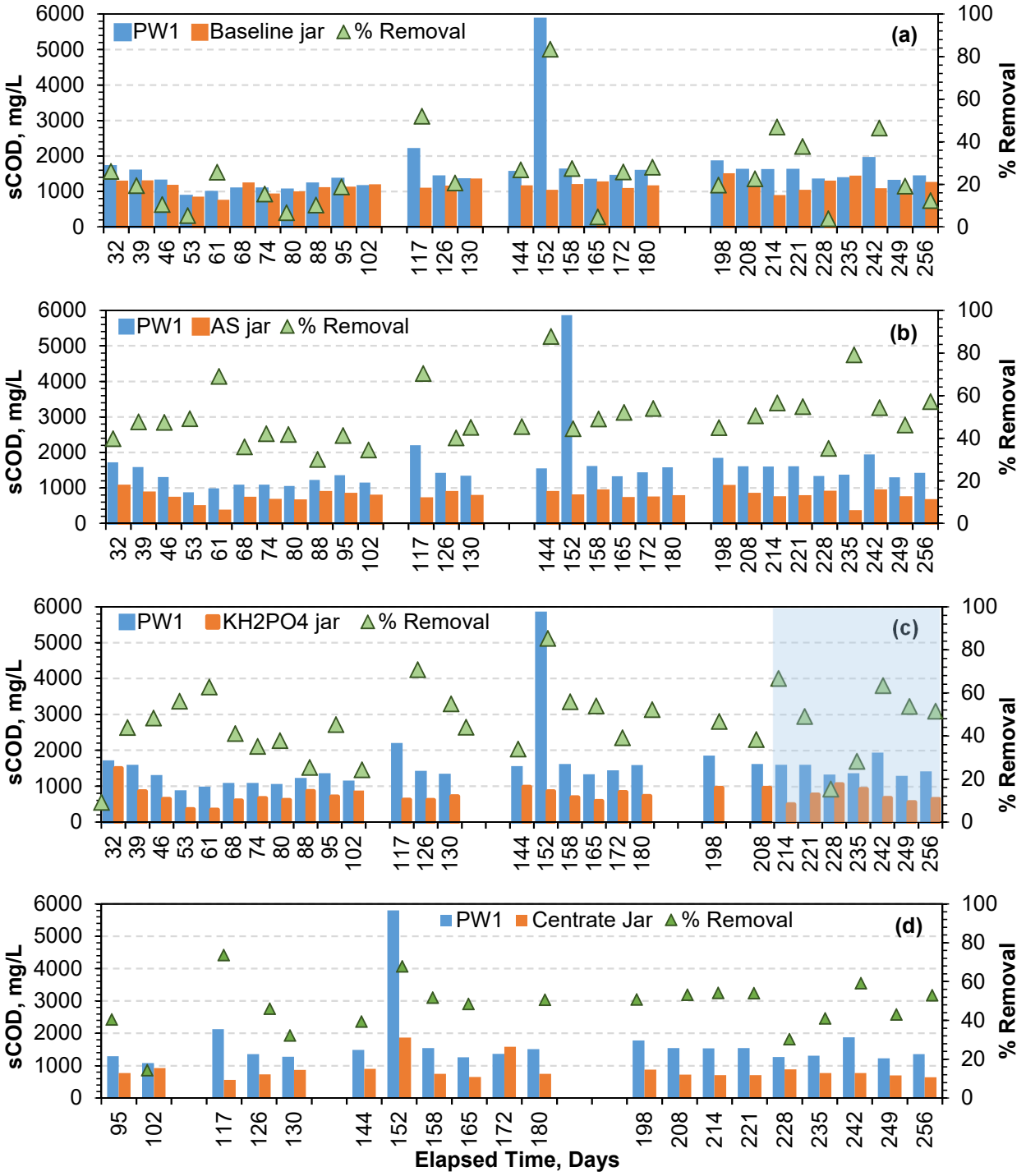

Figure 3.3. sCOD concentration and percent removal as a function of time in the (a) baseline jar, (b) AS jar, and (c) KH_2PO_4 jar. When the addition of KH_2PO_4 increased from 7.5 mg-P/L to 15 mg-P/L (blue-shaded area), the percent removal of sCOD did not change; and (d) the centrate jar had slightly lower sCOD percent removal than the AS and the KH_2PO_4 jars.

Table 3.2. Comparison of total and dissolved organic carbon with total and dissolved COD. The ratio of organic carbon to COD decreases with increased treatment (AS, Centrate, and KH_2PO_4 jars).

		Baseline	**AS**	**Centrate**	**KH_2PO_4**
TOC	*mg/L*	192	81.9	68.3	71.6
COD	*mg/L*	1024	1133	803	846
TOC:COD	-	0.19	0.07	0.09	0.08
DOC	*mg/L*	181	60.4	52	62.1
sCOD	*mg/L*	1186	580	638	655
DOC:sCOD	-	0.15	0.1	0.08	0.09

3.1.3 Nitrogen removal

Ammonia is the dominant form of nitrogen in both the feed water and the supernatant of each bioreactor jar. The average ammonia concentration and percent removal over time for all bioreactor jars is summarized in Table 3.3. The AS and the KH_2PO_4 jars had the highest ammonia removal of all jars. The centrate jar had a negative removal rate of ammonia because the daily centrate addition contained ammonia (57 mg-N) as well as phosphorus (15 mg-P). In all jars the nitrate concentration did not increase while the ammonia concentration decreased during treatment, which indicates that both nitrification and denitrification may be occurring in the bioreactors.

Table 3.3. Average concentration and percent removal of nitrogen species in feed and bioreactor jars. The jars with the highest percent removal were the AS and KH_2PO_4 jars (bold). The centrate jar had an increase in ammonia concentration due to the daily addition of centrate, which contained approximately 94 mg-N/L of ammonia. Less than 1.0 mg/L of nitrate was in the decant of each bioreactor jar throughout the experiment.

		PW1	Baseline	**AS**	Probiotic	**KH_2PO_4**	Centrate	Attached Growth	H_2O_2
		Feed	*Decant*	***Decant***	*Decant*	***Decant***	*Decant*	*Decant*	*Decant*
Removal	*%*	-	18.9	**58.8**	9.5	**58.6**	-238	26.2	9.4
Ammonia	*mg-N/L*	25.2	20.7	**10.4**	21.7	**10.1**	89.3	19.5	23.1
Nitrate	*mg-N/L*	1.03	0.57	**0.85**	0.62	**0.61**	0.70	0.52	0.89

Ammonia concentrations and percent removal as a function of time for the best performing bioreactor jars (AS and KH_2PO_4) compared to the baseline are shown in Figure 3.4. Both the AS and KH_2PO_4 jars had phosphorus addition and similar ammonia removal. The phosphorus addition via the 200 mg solids in the AS jar was estimated to be 1.25 mg-P/L using an average municipal activated sludge cell composition of $C_{60}H_{87}O_{23}N_{12}P$.[13] The probiotic solution that was used in the probiotic jar included nutrients to support biological growth; however, the dose only supplied a concentration of approximately 0.01mg-P/L to the bioreactor jar. The better ammonia removal in both the AS and KH_2PO_4 jars compared to the other jars suggests that PW1 is nutrient limited with respect to phosphorus for suspended microbial growth. The increase in phosphorus addition from 7.5 mg-P/L to 15 mg-P/L in the KH_2PO_4 jar did not change the level of ammonia removal. Additionally, the estimated 1.25 mg-P/L addition (AS jar) achieved similar removal to the KH_2PO_4 jar, suggesting that ≤1.25 mg-P/L needs to be added to improve treatment in the bioreactor.

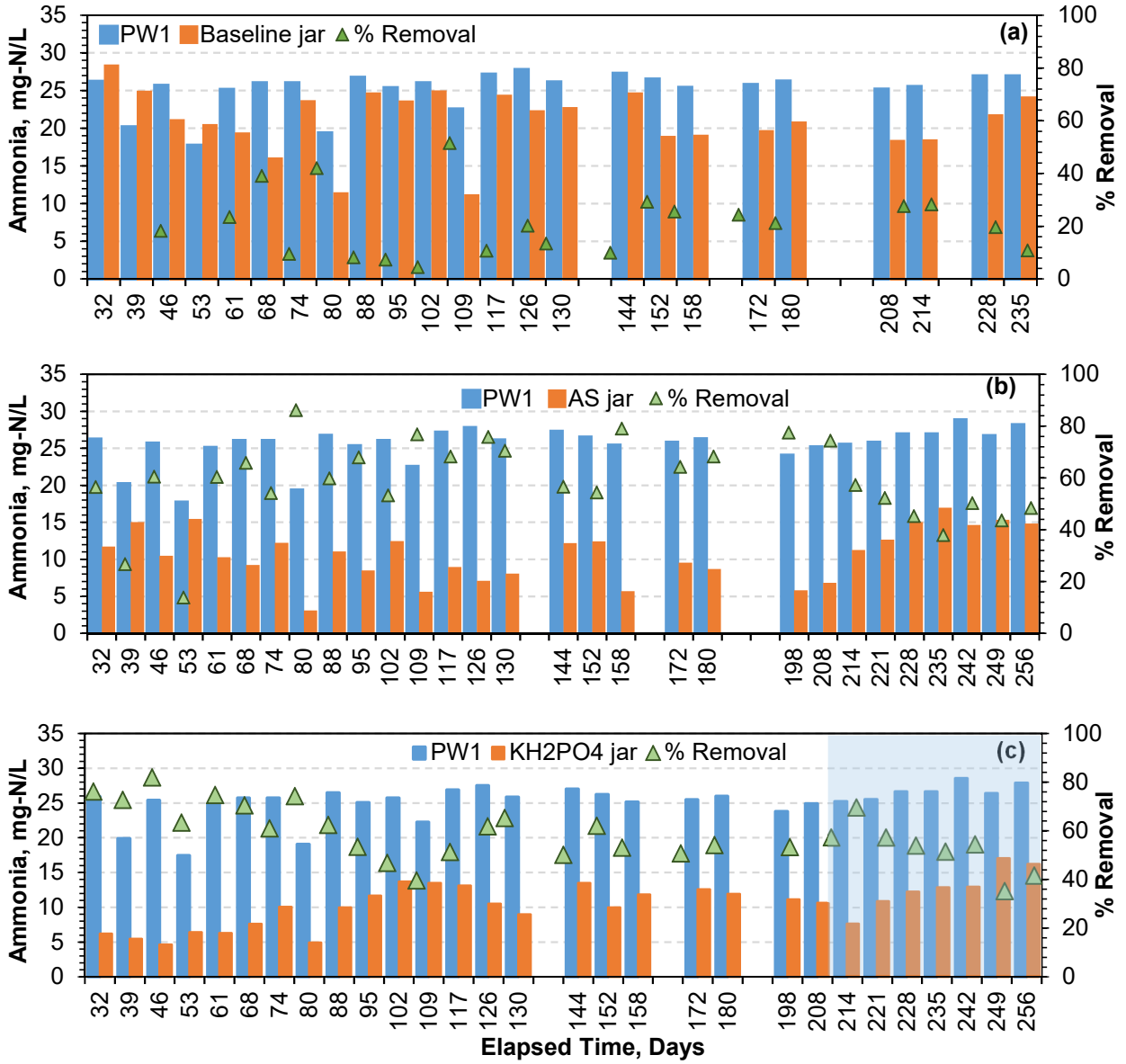

Figure 3.4. Ammonia concentrations and percent removal as a function of time in the (a) baseline jar, (b) AS jar, and (c) KH_2PO_4 jar. The AS jar and KH_2PO_4 jar had similar percent removal even when the addition of KH_2PO_4 increased from 7.5 mg-P/L to 15 mg-P/L (blue area).

3.1.4 Phosphorus effects

Phosphorus is an essential component of DNA, which is needed for cell growth. PW1 has little to no phosphorus; thus, soluble phosphorus concentration over time was monitored in the jars that had a phosphorus supplement, as shown in Figure 3.5. Only the KH_2PO_4 and centrate jars had a measurable amount of soluble phosphorus concentration in the decant. The 7.5 mg-P/L supplement to these jars may not be entirely utilized by the microbial communities. An average decant concentration of 3.3 mg-P/L and 3.8 mg-P/L in the KH_2PO_4 and centrate jars, respectively, may indicate that a supplemental dose of approximately 4 mg-P/L may be adequate to increase the performance in the bioreactors. Additionally, the

AS jar (1.25 mg-P/L dose) had an average residual concentration of 0.8 mg-P/L, indicating that not all the phosphorus was consumed. This supports the above results that the optimal phosphorus dosing concentration is less than or equal to 1.25 mg-P/L (section 3.1.2).

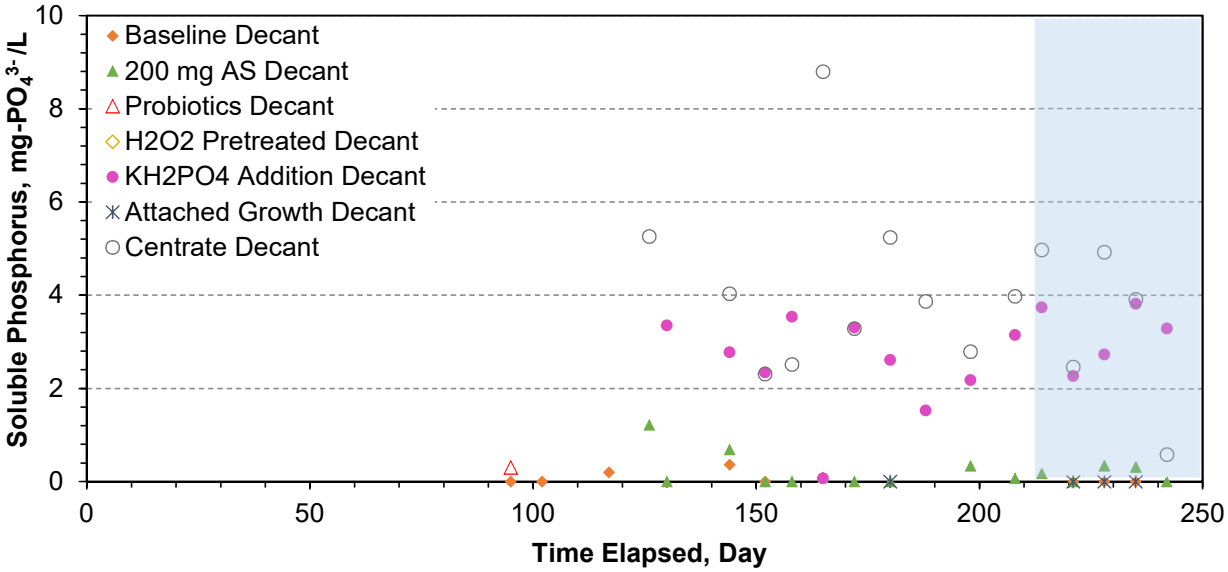

Figure 3.5. Soluble phosphorus over time in the bioreactor jars. The blue-shaded area is the period when phosphorus addition to the KH_2PO_4 jar was increased from 7.5 to 15 mg-P/L.

3.1.5 Suspended solids and turbidity

The TSS, and particularly the VSS, concentration of mixed liquor is used as an indicator of microbial growth in conventional wastewater treatment, with the higher concentration of suspended solids, the higher concentration of microorganisms. Turbidity is another way to gauge the relative amounts of suspended material in the liquids. The average turbidity, TSS concentration, and VSS concentration for the final 100 days of operation of the jars is summarized in Table 3.44. The AS jar had the highest solids concentration of all the bioreactor jars, which is due to the manual addition of 200 mg solids daily. The turbidity measurement does not test for activity of microorganisms, and it is unknown how many survive the transition from a municipal system (low salinity) to the AS jar treating produced water (high salinity).

Table 3.4. The average turbidity, TSS concentration, and VSS concentration of the feedwater and mixed liquor (ML) during the last 100 days of operation.

		PW1	Baseline	AS	Probiotic	KH_2PO_4	Centrate	Attached Growth	H_2O_2
		Feed	*ML*	*ML*	*ML*	*ML*	*ML*	*ML*	*ML*
Turbidity	*NTU*	93	81	858	186	339	178	33	73
TSS	*mg/L*	29	132	1741	173	50	124	44	112
VSS	*mg/L*	14	102	1409	72	42	59	25	39

TSS and VSS concentrations as a function of time in all jars are shown in Figure 3.6. In all the jars, except the AS jar, which has solids added from a municipal system, the TSS was consistently less than

300 mg/L. Typical municipal activated sludge systems have TSS concentrations an order of magnitude higher than the 300 mg/L maximum TSS concentration observed in the jars,[13] which indicates a low density of microbial communities in the bench-scale jars. The solids concentration in the AS jar increased over time due to the 200 mg solids added daily. However, this test does not designate how many of those municipal wastewater microorganisms were alive and breaking down contaminants in the produced water.

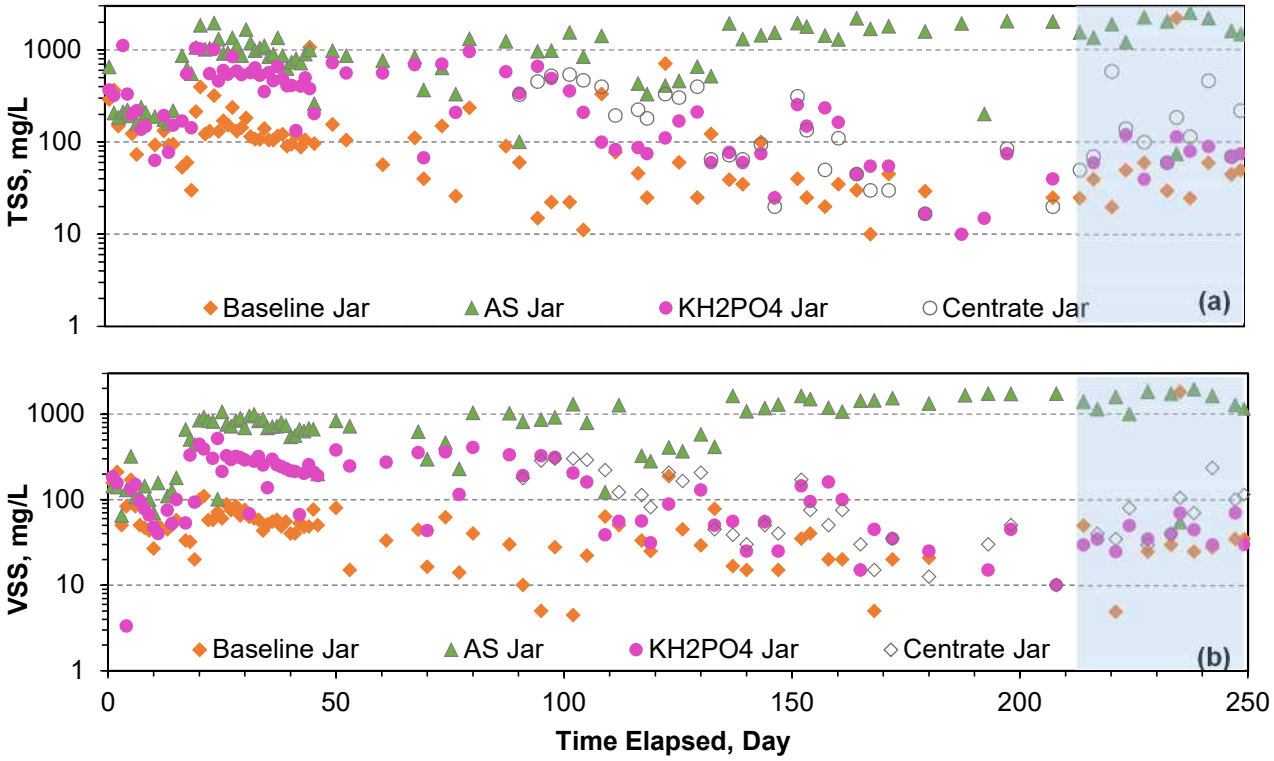

Figure 3.6. (a) TSS and (b) VSS concentration as a function of time for bioreactor jars with the highest percent removal of ammonia and COD. The blue-shaded area is the period when phosphorus addition to the KH_2PO_4 jar was increased from 7.5 to 15 mg-P/L.

Turbidity measurements support the TSS and VSS analysis described above, indicating a low concentration of suspended solids compared to municipal activated sludge. The turbidity of the AS jar increased due to the daily addition of solids; however, all other jars had turbidity values less than 500 NTU as shown in Figure 3.7.

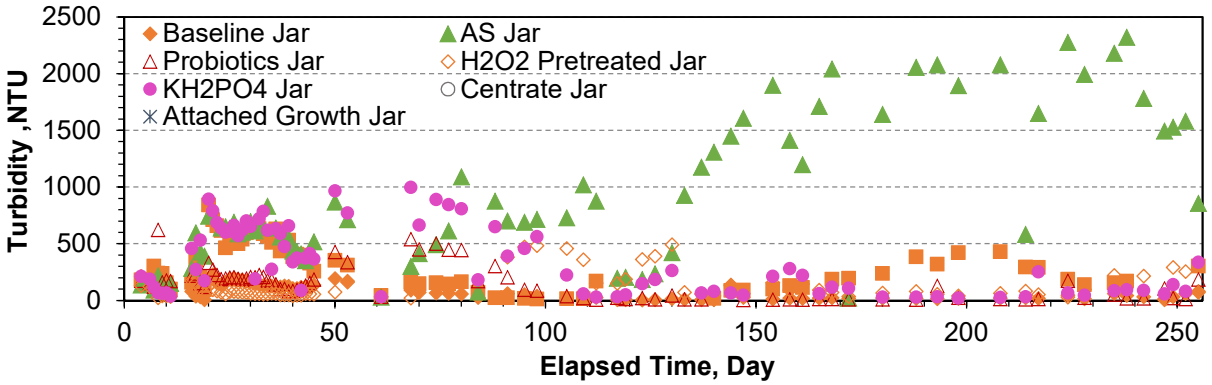

Figure 3.7. Turbidity of the mixed liquor in the bench bioreactor jars fed with PW1 as a function of time. The AS jar had increasing turbidity due to the 200 mg solids added daily. The other jars had consistently low turbidity, indicating a low concentration of solids in the mixed liquor.

3.1.6 PW2 bioreactor jar

The performance of the PW2 jar changed with each batch of PW2. The average performance of the PW2 jar is summarized in Table 3.5. Each batch of PW2 had varying feedwater characteristics such as salinity or phosphorous concentration. Differences in composition may also influence the type of active microorganisms present in the feedwater and limit growth of microorganisms introduced from past PW2 feedwater batches.

Table 3.5. The average performance of the PW2 jar throughout the 250-day test period.

		PW2 ***Feed***	**PW2 Jar** ***Decant***
Ammonia Removal	*%*	-	13.1
Ammonia Conc.	*mg-N/L*	33.3	27.2
Nitrate Conc.	*mg-N/L*	<1.0	.80
sCOD Removal	*%*	-	14.1
sCOD Conc.	*mg/L*	2887	1950
COD Removal	*%*	-	16.7
COD Conc.	*mg/L*	3338	2221
Turbidity	*NTU*	56	304
TSS	*mg/L*	59	203
VSS	*mg/L*	40	164

The concentration and percent removal as a function of time of sCOD for the PW2 jar is shown in Figure 3.8 and correlates to the COD concentration. The white and green shaded areas refer to various batches (1-5 from left to right) of PW2 and the grey shaded area refers to a single 20-day cycle. The sCOD concentration was highest in batch 4; however, when the jar was fed with batch 4 produced water it had the highest percent removal compared to all other PW2 batches. This supports the previously discussed results that there is not enough phosphorus in the produced water influent and a phosphorus supplement may be needed to support suspended biological growth for produced water treatment because batch 4 had a phosphorus concentration higher than the other PW2 batches.

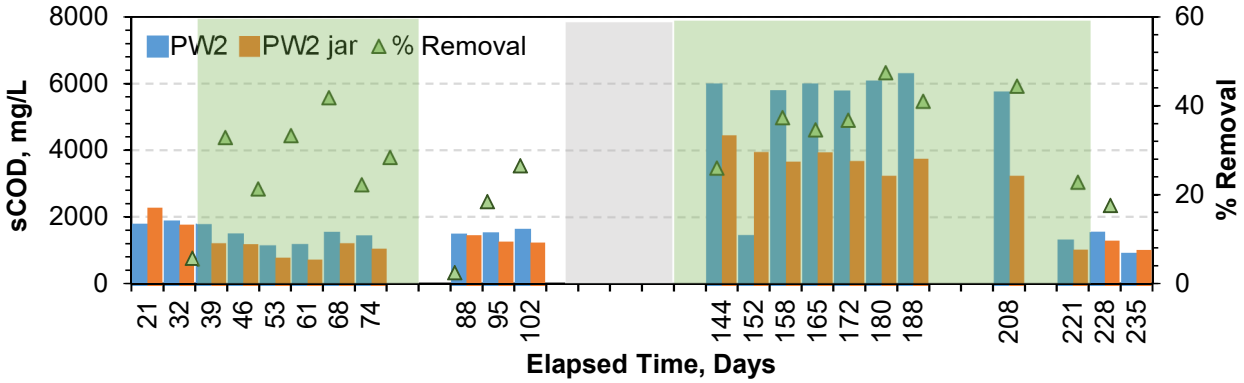

Figure 3.8. sCOD concentration and percent removal as a function of time in PW2 Jar influent and decant showing inconsistent removal rates. Changes in color-shaded (green and white) areas represent different batches of PW2 (from left to right batches 1 through 5). The greyed area designates a single 20-day cycle for PW2 jar.

The concentration and percent removal of ammonia as a function of time for the PW2 jar is shown in Figure 3.9. The white and green colored areas refer to various PW2 batches (1-5 from left to right) and the grey area refers to a single 20-day cycle. The ammonia concentration is highest in batch 4, which also has phosphorus concentration of 3.6 mg-P/L; however, the time PW2 jar was fed with batch 4 also corresponded to the time it had the highest percent removal of ammonia. This supports the results previously discussed that the produced water collected is nutrient limited with respect to phosphorus.

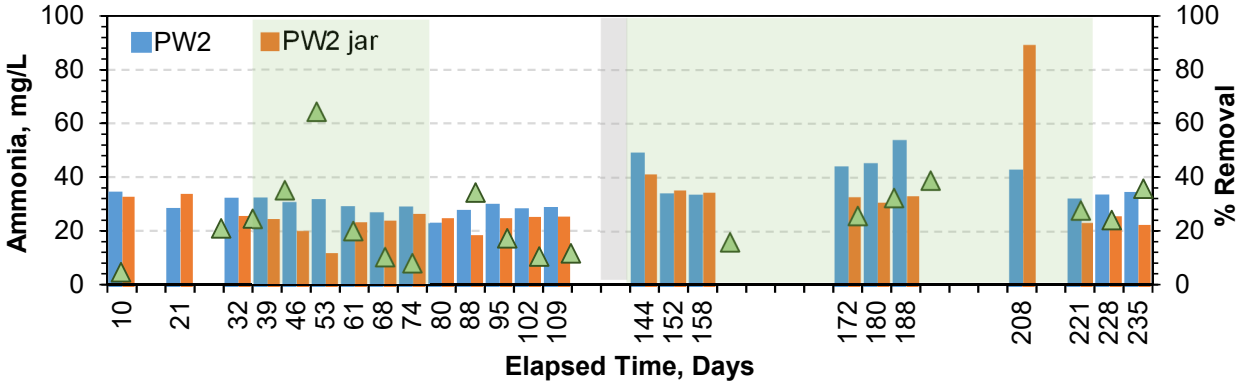

Figure 3.9. Ammonia concentration and removal in PW2 jar as a function of time showing inconstant removal with different feedwater composition. Each change in colored area (green and white) represents a different batch of PW 2 (batch 1-5 from left to right). The grey colored area designates a single 20-day cycle for PW2 jar. The highest removal rate of ammonia occurs during batch 4, which also had higher concentration of ammonia.

The concentration of soluble phosphorus as a function of time in the decant of the PW2 jar is shown in Figure 3.10. The green area corresponds to batch 4 feedwater, which had the higher phosphorus concentration and correlates to the times of higher sCOD, COD, and ammonia removal presented above. Again, this supports the concept that PW1 is nutrient limited, and phosphorus is needed to support suspended biological growth in the bioreactors.

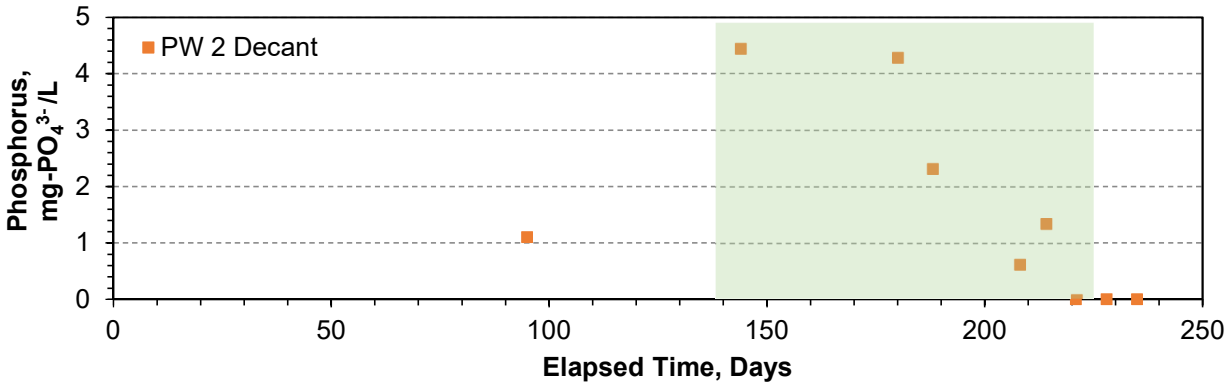

Figure 3.10. Concentration of phosphorus as a function of time in the decant of PW2 jar. The green area represents the time the jar was fed with PW2 batch 4, which had the higher phosphorus concentration.

The TSS, VSS, and turbidity of the mixed liquor of PW2 jar as a function of time are shown in Figure 3.11. During two periods of testing the PW2 jar had an increase in solids concentration. The first was during the first 36 days, when the jar was fed with batch 1, which had a phosphorus concentration of 1.06 mg-P/L. The second gradual increase in solids concentration started around day 144, which correlates with the change from batch 3 to batch 4 PW2. Around day 214, which correlates to the switch from batch 4 to batch 5 PW2, the solids concentration in the PW2 jar began to decline. The main difference that distinguishes batch 4 from all the other PW2 batches is the higher phosphorus concentration in batch 4. This also supports the previous bench scale results that suspended biological growth needs phosphorus to treat produced water.

3.2 Pilot system

PW1 was used as the feedwater for the pilot system. Initially, baseline performance was established before exploring the effect of hydraulic residence time (HRT) and phosphorus supplement (7.5 mg-P/L) on system performance. During bench-scale testing, the KH_2PO_4 jar was the best performing jar with respect to ammonia, COD, and sCOD removal. Therefore, KH_2PO_4 was chosen as the phosphorus supplement in the pilot system bioreactors. Results for ammonia, COD, and sCOD removal were used to evaluate treatment performance. Analysis of TSS, VSS, and turbidity was used to evaluate microbial growth in the mixed liquor and solids removal in the media filters.

3.2.1 pH and conductivity

The pH of PW1 was close to neutral throughout the study. Manual pH measurements as a function of time at each point in the treatment process is shown in Figure 3.12. The pH increased to 7.5-8.0 in the two bioreactors before decreasing slightly in the media filters; however, it remained higher than the influent. The pH range in the treatment train is within normal operating conditions of SBRs treating municipal wastewater.[34]

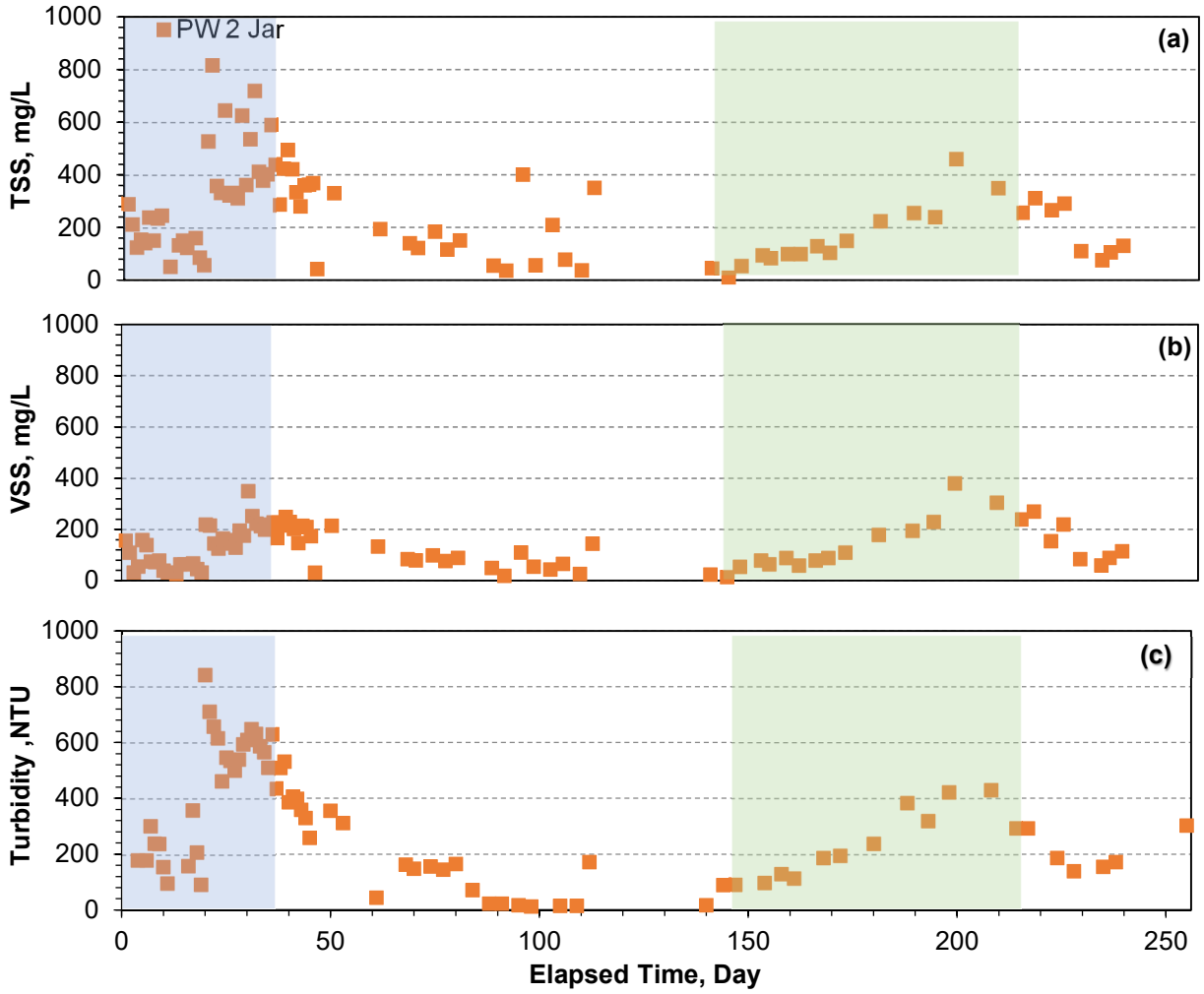

Figure 3.11. (a) TSS, (b) VSS, and (c) turbidity as a function of time in the PW2 jar. The phosphorus addition increased when fed with batches 1 and 4, which contained higher concentrations of phosphorus (blue and green time intervals respectively).

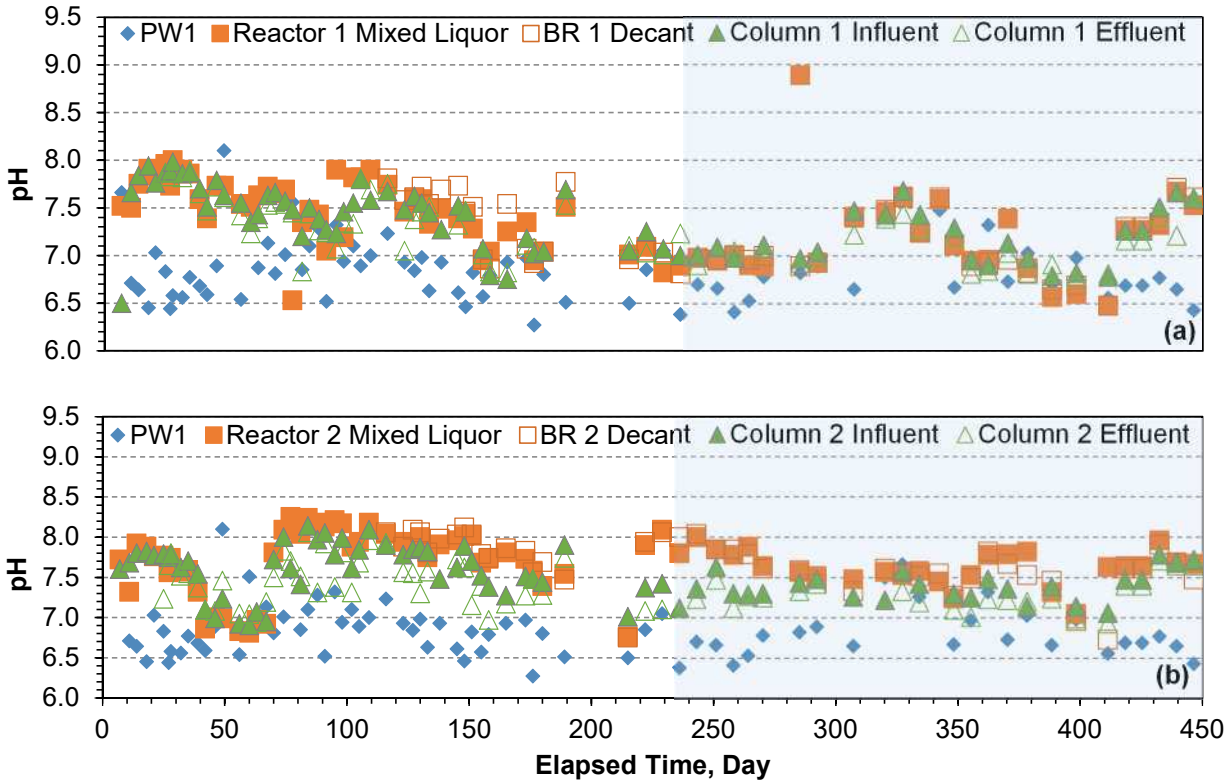

Figure 3.12. pH of (a) treatment train 1 and (b) treatment train 2 as a function of time. The average PW1 pH was 6.9 and increased through the treatment process to 7.2 in the effluent of train 1 and 7.7 in the effluent of train 2. The blue-shaded area designates time that 7.5 mg-P/L was added daily to the two bioreactors.

Conductivity in BR1 was stable throughout treatment. The biological treatment system was not designed to treat TDS and the influent TDS was relatively constant; therefore, conductivity was not expected to change. Additionally, the covers of the bioreactor tanks were closed during operation, reducing evaporation and preventing concentration of the TDS and increased conductivity in the bioreactors.

3.2.2 Organic removal

The concentrations of organic matter in the treatment trains in the pilot system and the average ratios of TOC:COD and DOC:sCOD concentrations for the first phase of the pilot system (days 1-93) are summarized in Table 3.6. In general, the concentrations of organic matter decrease along the treatment train (raw PW, BR, column influent, column effluent). The average TOC and DOC concentration across filter column 1 increased, which could be a result of breakthrough, sloughing of microorganisms, or material becoming biologically available. The COD and sCOD concentrations increased in the holding reservoir, which is the difference between the decant and the filter column influent. This is most likely due to lack of oxygen in the holding reservoirs for a range of 2-5 hours. Lack of oxygen can promote anaerobic bacterial growth, which may have different biochemical processes that solubilize oxidizable matter. The HRT in the holding reservoirs was dependent on the cycle time to match overall flow rates.

The two concentration ratios decrease in the bioreactors, and increase above the ratios of the influent after the filter columns. A decrease in the ratios observed in the bioreactors may indicate that the organic matter is being removed and the remaining inorganic portion of COD cannot be treated biologically. An increase in the two ratios, as seen in the columns, may suggest that inorganic matter that can be oxidized (e.g., iron or sulfur) is removed. After the first phase of the pilot testing, COD and sCOD was used as a proxy to evaluate organic removal in the two treatment trains.

Table 3.6. Comparison of the average total and dissolved organic carbon with average total and dissolved BOD, and average total and dissolved COD for the first phase (days 1-93) of the pilot system. The TOC:COD ratio (and DOC:sCOD ratio) increases with increased treatment.

	TOC *mg/L*	**COD** *mg/L*	**TOC:COD** *Ratio*	**DOC** *mg/L*	**sCOD** *mg/L*	**DOC:sCOD** *ratio*	**sCOD:COD** *%*
PW1	263	1611	0.16	254	1180	0.22	73
BR1 Decant	157	1409	0.11	149	1063	0.14	75
BR2 Decant	124	1255	0.10	115	713	0.16	57
Column 1 Influent	155	1461	0.11	146	1220	0.12	84
Column 1 Effluent	165	583	0.28	165	498	0.33	85
Column 2 Influent	117	982	0.12	115	766	0.15	78
Column 2 Effluent	113	408	0.28	117	284	0.41	70

sCOD concentration as a function of time in the bioreactors and media filters during the first 4 phases (Table 2.3) is shown in Figure 3.13. The sCOD was primarily removed in the media filters, which suggests that attached growth biological treatment is happening in the filters. Each change in shaded area represents a different phase. Most of the fluctuations of effluent sCOD concentrations appear to be directly related to a fluctuation in feedwater sCOD concentration. The first 4 phases vary in HRT, which does not appear to affect the treatment of sCOD. Trends in COD concentration are similar to those of sCOD and data can be found in Appendix A (Figure A.5). This suggests that either the treatment trains removed all the bioavailable organic matter with an HRT of less than 1.67 days or a stronger influential factor such as lack of micronutrients or inhibiting chemicals limited removal of organic matter.

sCOD concentration as a function of time in the bioreactors and media filters during the last 3 phases (Table 2.3) is shown in Figure 3.14. During the last three phases 7.5 mg-P/L was dosed into the two bioreactors. During the last three phases the bioreactors were removing most of the sCOD, with little to no removal in the filter columns. Additionally, the increase in aeration time (phase 6/blue shaded), and the increase in HRT (phase 7) did not affect the treatment of sCOD. This indicates that with phosphorus addition, the media columns have little to no biological treatment during the last three phases. COD concentration as a function of time during the last three phases is shown in Appendix A (Figure A.6).

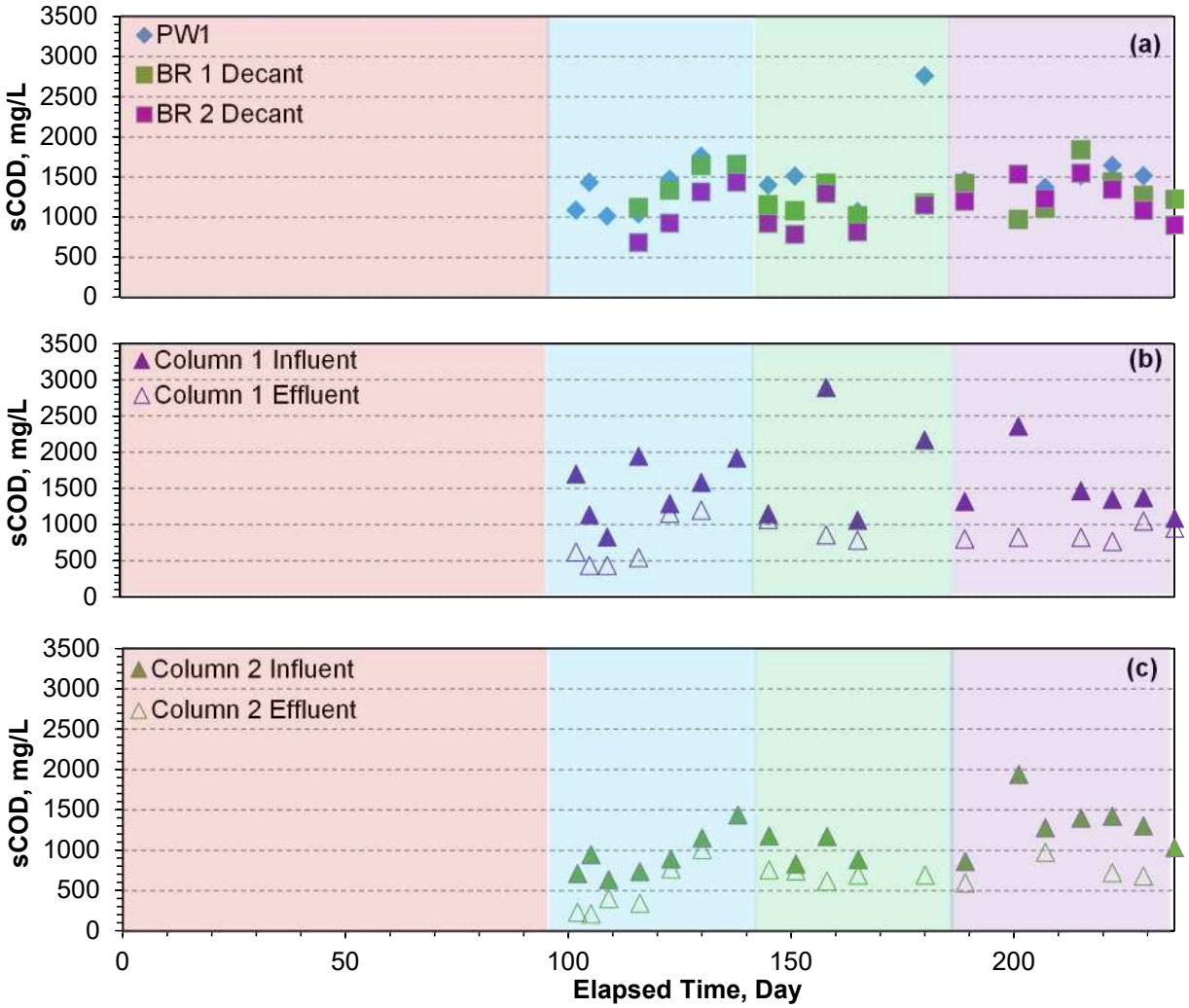

Figure 3.13. Concentration of sCOD as a function of time in the first 4 phases in (a) the bioreactors, (b) column 1, and (c) column 2. Colors from left to right represent the different phases (Table 2.3) during pilot operation (pink = phase 1, blue = phase 2, green = phase 3, purple = phase 4). The amount of sCOD removed did not vary with respect to HRT during the first 4 phases. The majority of the sCOD removal occurred in the filter columns.

The average concentration and percent removal of total and soluble COD in the pilot system before and after phosphorus addition is summarized in Table 3.7. During phases 1-4, the majority of the organic removal occurred in the filter columns. Both the glass and the sand media had an average sCOD removal of 41%, and the glass media (column 1) had slightly higher COD removal. During phases 5-7, 7.5 mg-P/L was added to the bioreactors and resulted in increase in soluble and total COD removal in the bioreactors and a decreased removal in the filter columns. The shift in location where COD was primarily removed indicates that the location of treatment of organic matter can be determined by the addition of phosphorus. The filters removed organic material without a phosphorus supplement, suggesting that they may be a more efficient treatment method than suspended growth. Additionally, the overall sCOD removal did not change

significantly, indicating a recalcitrant or biologically unavailable portion of sCOD that will need to be removed by means of physical or chemical treatment.

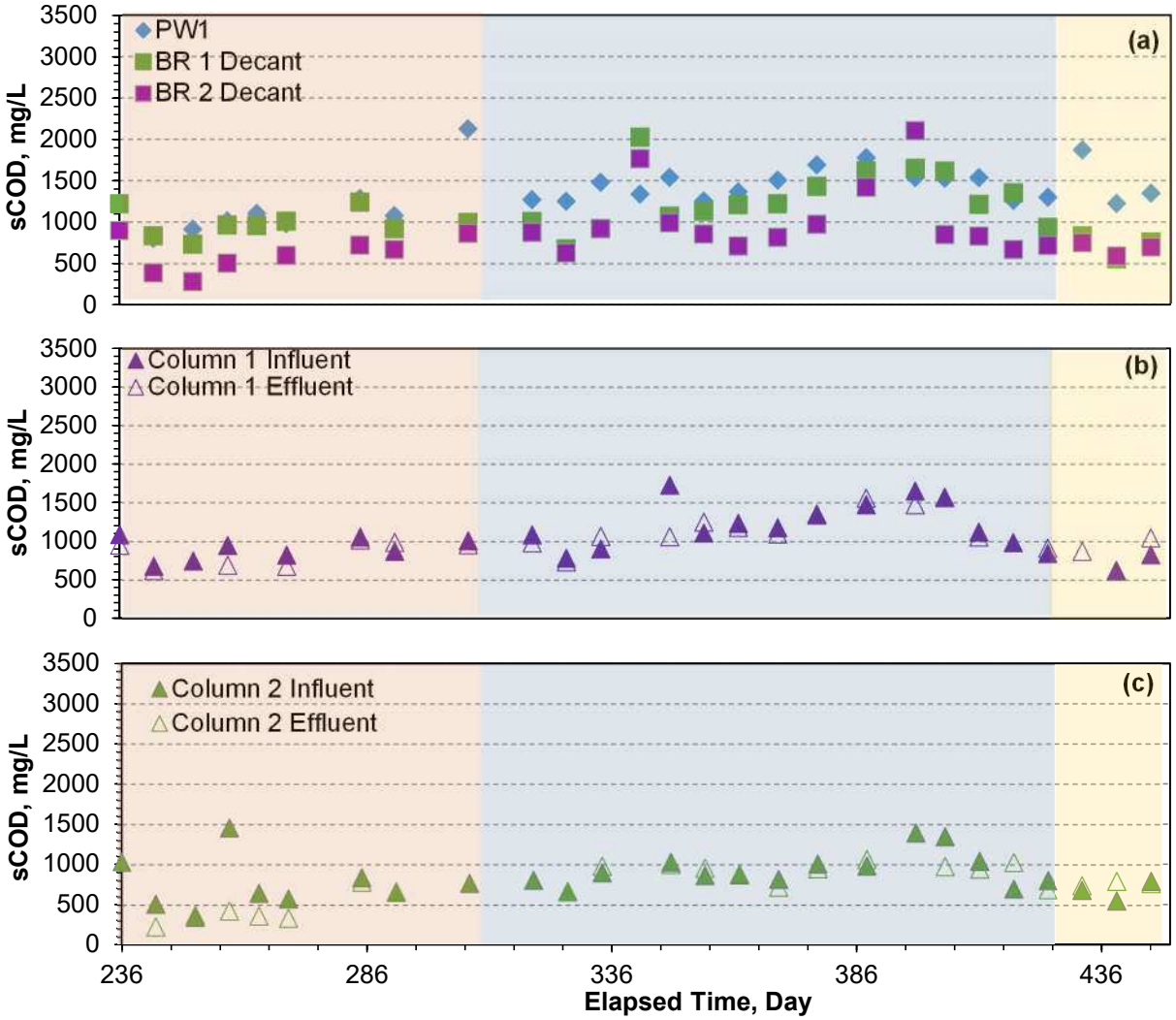

Figure 3.14. Concentration of sCOD as a function of time in the (a) bioreactors, (b) column 1, and (c) column 2 during the last 3 phases of testing (Table 2.3). During the three phases 7.5 mg-P/L was added to each bioreactor. The colors from left to right represent a different phase during pilot testing (orange = phase 5, blue = phase 6, yellow = phase 7). The majority of sCOD removal took place in the bioreactors, with little to no removal occurring in the filter columns. The increase in aeration (phase 6) and the increase in HRT (phase 7) did not affect the performance of the system.

3.2.3 Nitrogen removal

During the first 110 days of testing, ammonia accounted for over 88% of the total nitrogen, the average nitrate concentrations was below 1.3 mg-N/L, and the average nitrite concentrations were lower than 0.1 mg-N/L at all sampling points in both treatment trains. The average total nitrogen and average ammonia concentration through the first 110 days of treatment are summarized in Table 3.8. Due to the strong

correlation between ammonia and total nitrogen, ammonia and nitrate were used to evaluate nitrogen removal after the first 110 days.

Table 3.7. Concentration and percent removal of COD and sCOD in the pilot system before and after phosphorus addition. Before phosphorus was added to the system, the soluble and total COD was primarily removed in the filter columns, and after phosphorus was added to the system, the location of soluble and total COD removal changed to the bioreactors.

		PW1 Feed	BR1 Decant	BR2 Decant	Column 1 Influent	Column 2 Influent	Column 1 Effluent*	Column 2 Effluent*
Before Phosphorus Addition (Phases 1-4)								
sCOD Removal	*%*	-	14	28	-	-	41	41
sCOD Conc.	*mg/L*	1676	1306	1136	1566	1368	822	632
COD Removal	*%*	-	9.6	7.5	-	-	21	57
COD Conc.	*mg/L*	1587	1450	1127	1496	1224	693	497
After Phosphorus Addition (Phases 5-7)								
sCOD Removal	*%*	-	17	39	-	-	2.7	7.2
sCOD Conc.	*mg/L*	1363	1113	850	1071	844	1038	743
COD Removal	*%*	-	14	26	-	-	15	36
COD Conc.	*mg/L*	1384	1193	1034	1389	1504	1126	968

*percent removal relative to column influent

Table 3.8. Average total nitrogen (TN) and ammonia concentrations in the pilot system during the first 110 days. The first 93 days occurred in phase 1 and the remaining days were during phase 2. Both total nitrogen and ammonia concentrations decrease in the treatment trains, indicating that both nitrification and denitrification may be occurring during the first 110 days.

	Days 1-93 (Phase 1)			Days 93-110 (Phase 2)		
	TN mg-N/L	Ammonia mg-N/L	Ammonia:TN ratio	TN mg-N/L	Ammonia mg-N/L	Ammonia:TN ratio
PW1	28.1	28.4	~1*	29.9	27.4	0.92
BR1 Decant	23.2	23.6	~1*	27.9	26.3	0.94
BR2 Decant	23.1	22.1	0.96	20.8	20.4	0.98
Column 1 Influent	23.8	23.8	~1	27.6	25.8	0.93
Column 2 Influent	22.9	22.6	0.99	24.1	21.1	0.88
Column 1 Effluent	23.9	23.8	~1	28.5	25.5	0.89
Column2 Effluent	20.7	22.9	~1*	20.9	21.1	~1*

* Actual ammonia concentration is not greater than TN. Salinity interference with the ammonia test method may account for an ammonia measurement higher than the TN measurement.

Ammonia concentration as a function of time for the first four phases (Table 2.3) is shown in Figure 3.15. In all samples nitrite concentration was consistently less than 0.5 mg-N/L and nitrate concentration was consistently below 1 mg-N/L. Almost all ammonia removal occurred in the bioreactors, with little to no change in the filter columns. There is no aeration in the filter columns; therefore, ammonia removal is not expected in the columns. Throughout the first four phases of the pilot study the ammonia removal was

independent of HRT (Table 2.3), suggesting either a lack of nitrifying microbial communities in the bioreactors or that growth is inhibited because of lack of nutrients or presence of toxic chemicals.

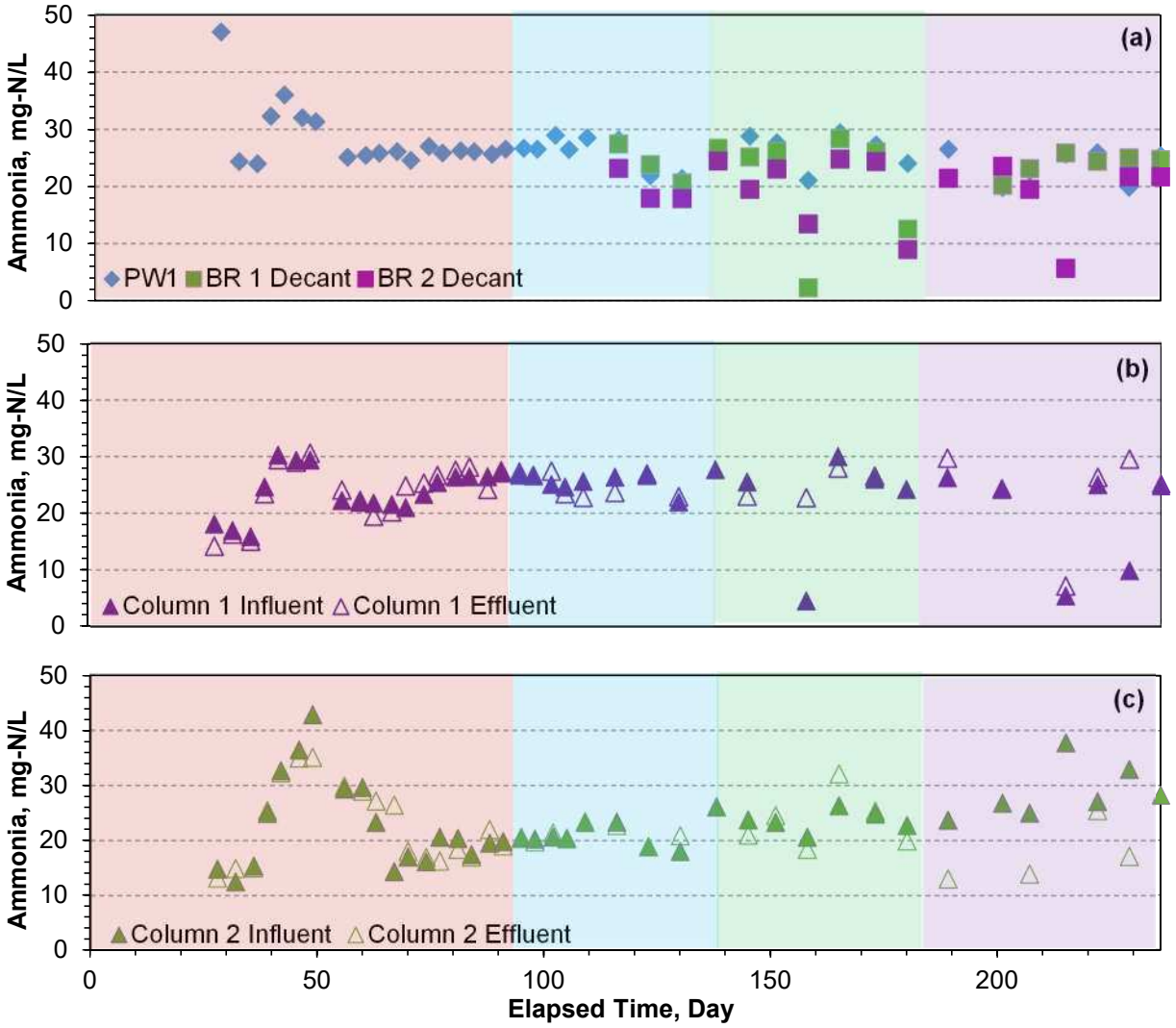

Figure 3.15. Ammonia concentration as a function of time in (a) the bioreactors, (b) column 1, and (c) column 2 during the first four phases of the pilot-scale testing. Color-shaded areas from left to right represent different phases (Table 2.3) during pilot operation (pink = phase 1, blue = phase 2, green = phase 3, purple = phase 4). Ammonia removal did not vary with changing phases. There was little to no change in ammonia concentration in the filter columns.

Ammonia concentration as a function of time in the bioreactors, column 1, and column 2 during the last three phases is shown in Figure 3.16. During these three phases, a daily dose of 7.5 mg-P/L KH_2PO_4 was added to the bioreactors. Following phosphorus addition, ammonia concentration in the decant of BR2 decreased to approximately 12.5 mg-N/L; however, ammonia concentration in BR1 did not significantly change after phosphorus addition, which was most likely due to lack of adequate aeration and mixing. During operation we discovered that the fluctuations in ammonia concentration in the decant of BR1 are a result of loss of aeration—every increase in ammonia concentration corresponded to times when aeration

was lost and every decrease corresponded to recovering aeration in the bioreactor. BR2 had consistent aeration and steady ammonia removal, and was not affected by the increase in aeration time (phase 6) or increase in HRT (phase 7). This indicates that nitrifying microorganisms are in the produced water; however, other factors may have limited nitrification and thus nitrogen removal. Limiting conditions may include lack of micronutrients or growth-limiting chemicals found in the produced water. The bioreactors were not inoculated and the microorganisms present are native to the produced water environment; therefore, it is more likely that the produced water is nutrient limited.

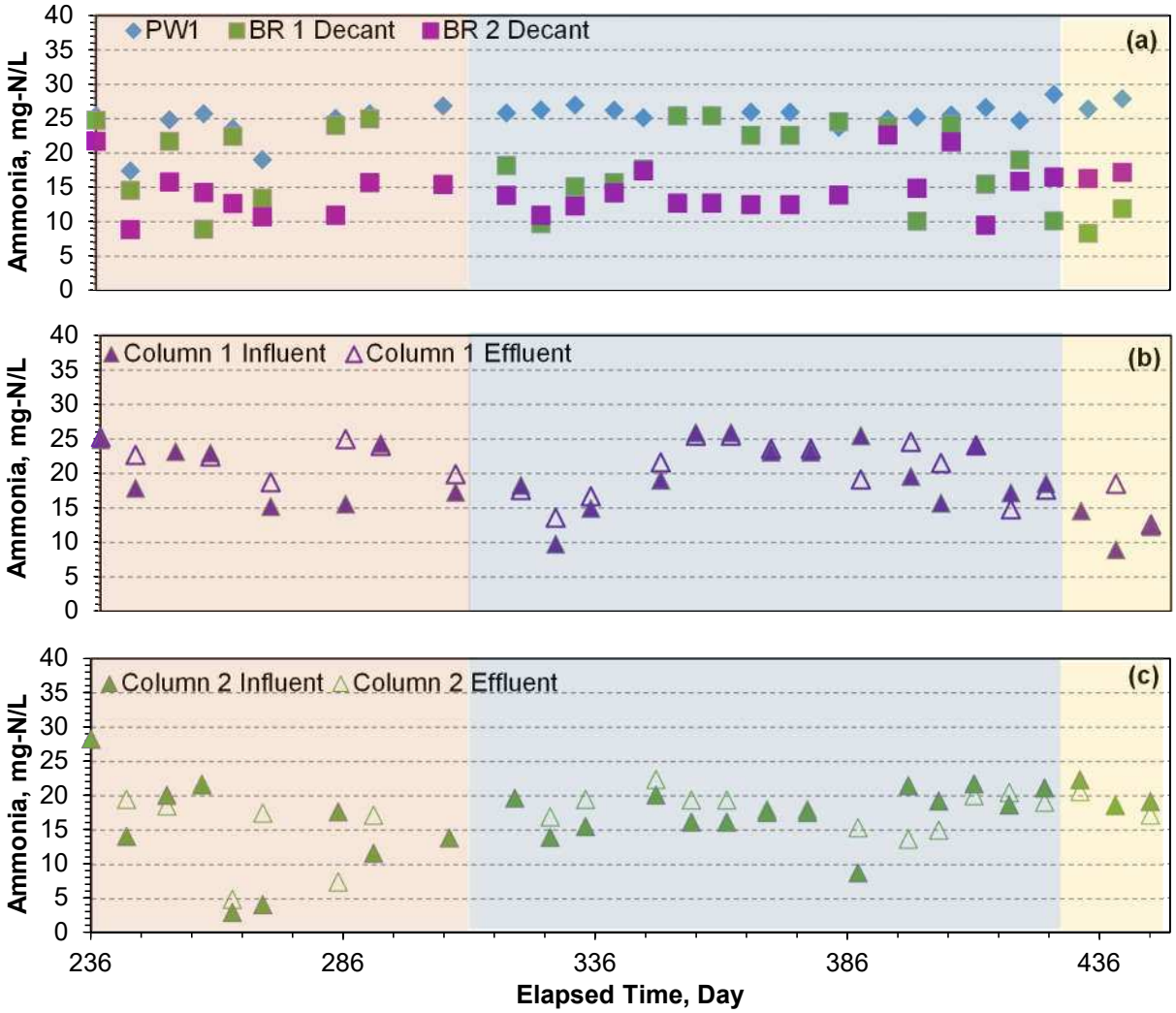

Figure 3.16. Ammonia concentration as a function of time in (a) the bioreactors, (b) column 1, and (c) column 2 during the last three phases of the pilot study. During all three phases 7.5 mg-P/L was added to the two bioreactors. The color-shaded areas from left to right represent different phases (Table 2.3) during the pilot test (orange = phase 5, green = phase 6, yellow = phase 7). Ammonia removal was consistent in BR2, and corresponded to changes in aeration in BR1.

The average concentration and percent removal of ammonia and nitrate at each sampling point is summarized in Table 3.99. The ammonia removal significantly increased in the bioreactors after the addition

of phosphorus, indicating that PW1 is nutrient limited with respect to phosphorus to sustain suspended biological growth and treatment. The nitrate concentration did not increase when the ammonia concentration decreased, indicating that both nitrification and denitrification may have occurred in the bioreactors. The negative removal rate in the columns indicates that nitrogen species (e.g., organic nitrogen) in the filter columns are most likely being converted to ammonia and complete denitrification did not occur.

Table 3.9. Average concentration and percent removal of ammonia and nitrate before and after phosphorus addition in the pilot system. The removal of ammonia in the bioreactors significantly increases with the addition of phosphorus.

		PW1 Feed	**BR1** Decant	**BR2** Decant	**Column 1** Influent	**Column 2** Influent	**Column 1** Effluent*	**Column 2** Effluent*
Before Phosphorus Addition (Phases 1-4)								
Ammonia Removal	%	-	8.5	21	-	-	-17	-2.7
Ammonia Conc.	mg-N/L	26.8	21.3	19.5	23.3	23.6	24.2	22.0
Nitrate Conc.	mg-N/L	1.02	1.08	1.20	1.06	1.04	0.66	0.60
After Phosphorus Addition (Phases 5-7)								
Ammonia Removal	%	-	27.6	43.2	-	-	-14.1	-2.98
Ammonia Conc.	mg-N/L	25.2	18.0	14.3	18.9	16.6	20.6	17.4
Nitrate Conc.	mg-N/L	0.55	0.68	0.73	1.09	1.68	0.58	0.56

*% removal relative to column influent

3.2.4 Iron removal

Iron concentration as a function of time for the first four phases (Table 2.3) in the bioreactors, column 1, and column 2 is shown in Figure 3.17. Iron concentration slightly increased in BR1 and slightly decreased in BR2, most likely due to differences in aeration. BR1 lost aeration intermittently, which corresponded to black liquor in the bioreactor and may indicate that iron in its reduced form was present in the water. The mixed liquor in BR2 had a rusty tan color throughout operation, which is most likely an indicator of oxidized iron due to the consistent aeration. The iron removal did not change with HRT, and most of the removal takes place in the media columns. This may be one of the reasons for the increase in TOC:COD ratio through the filter columns (see section 3.2.2 for TOC:COD ratio discussion).

Iron concentration as a function of time in the bioreactors, column 1, and column 2 during the last three phases (Table 2.3) is shown in Figure ***3***3.18. During the phosphorus addition phases (phases 5-7), iron was primarily removed in the filter columns, which may be the cause of the TOC:COD ratio increase through the filter columns (see section 3.2.2 for ratio discussion). Yet, the iron concentration was not affected by the increase in aeration time (phase 6) or the increase in HRT (phase 7).

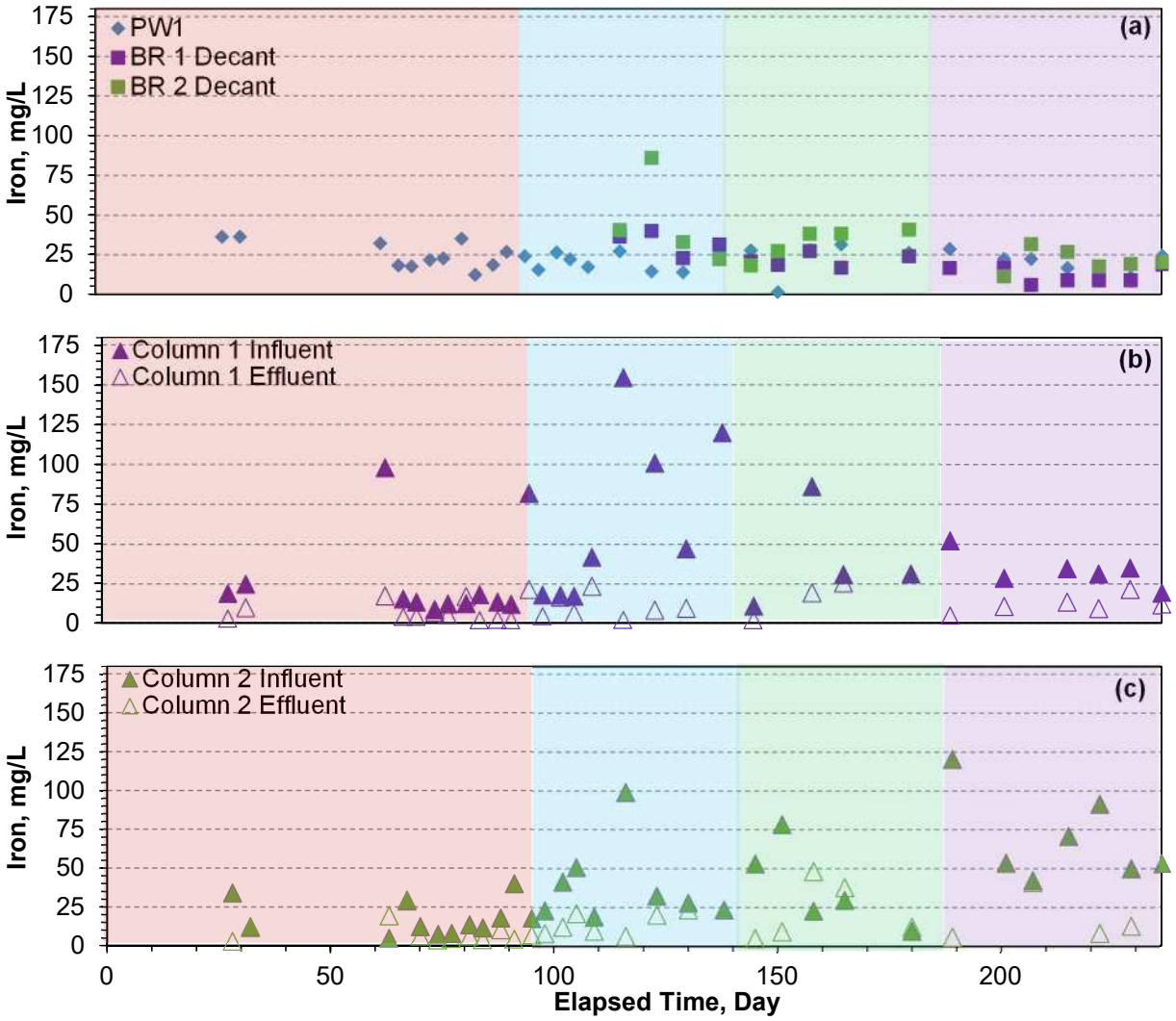

Figure 3.17. Iron concentration as a function of time for the first four phases in (a) the bioreactors, (b) column 1, and (c) column 2. The color-shaded areas from left to right represent different phases (Table 2.3) during pilot operation (pink = phase 1, blue = phase 2, green = phase 3, purple = phase 4).

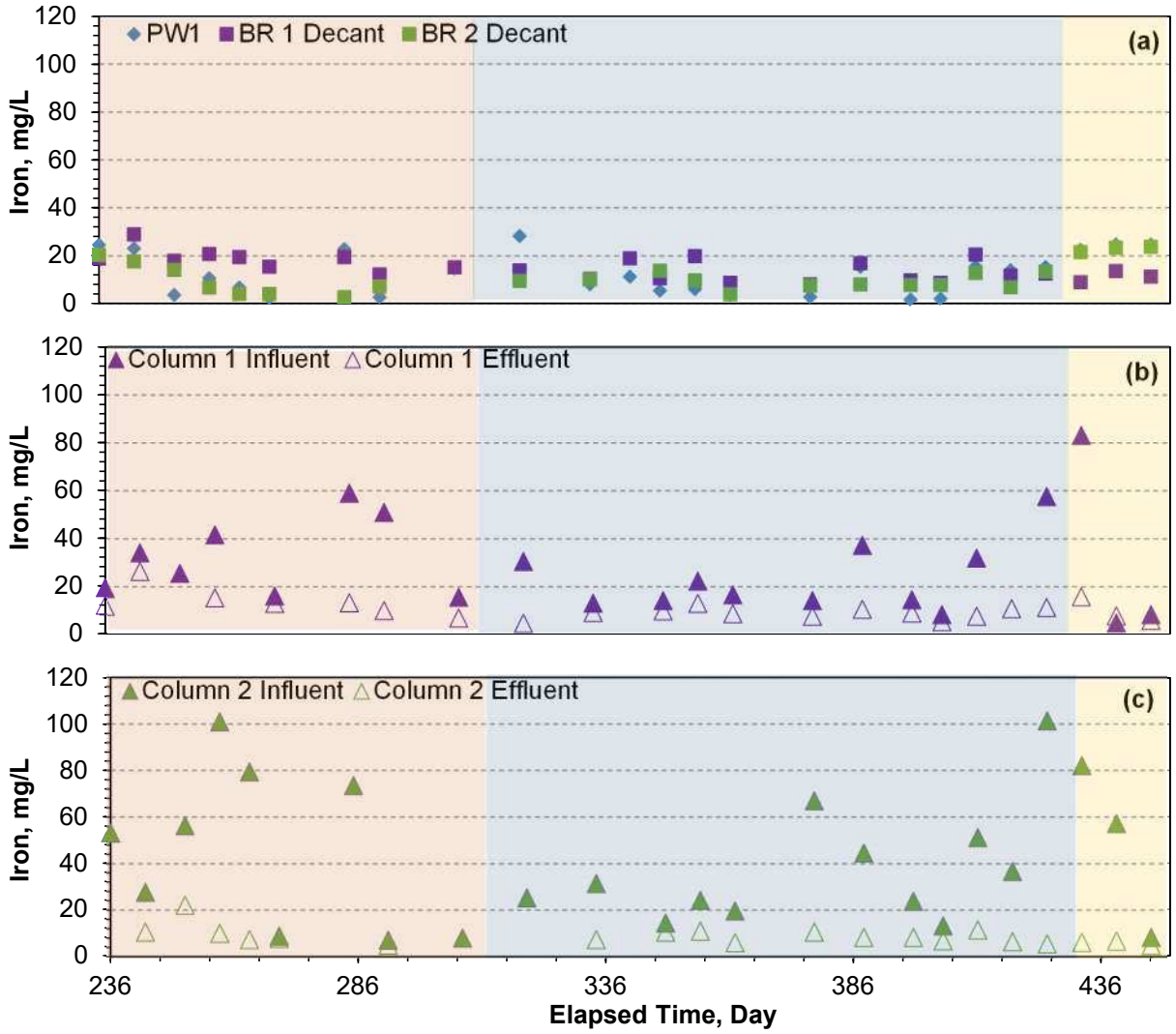

Figure 3.18. Ammonia concentration as a function of time in (a) the bioreactors, (b) column 1, and (c) column 2 during the last three phases of the pilot study. During the three phases, 7.5 mg-P/L was added to the two bioreactors. The color-shaded areas from left to right represent different phases (Table 2.3) during the pilot test (orange = phase 5, green = phase 6, yellow = phase 7). Most of the iron removal occurred in the filter columns and did not change with increased aeration (phase 6) or increased HRT (phase 7).

3.2.5 Phosphorus supplement

Phosphorus concentration over time for treatment trains 1 and 2 is shown in Figure 3.19. The phosphorus concentration during the baseline period (days 0-20) was consistently less than 0.5 mg-PO_4^{3-}/L in the column bioreactors, and was not measured again until a phosphorus supplement was added to the system. During the phosphorus addition phases (days 378 – 456), the phosphorus concentration in the system slightly increased initially, but remained insignificant. This suggests that the full daily dose of 7.5 mg-P/L was consumed in the bioreactors. The bioreactors may achieve better performance if the phosphorus dose increased. Additionally, no phosphorus remained after the bioreactor treatment step and the effect of supplemental phosphorus on the filter columns is unknown.

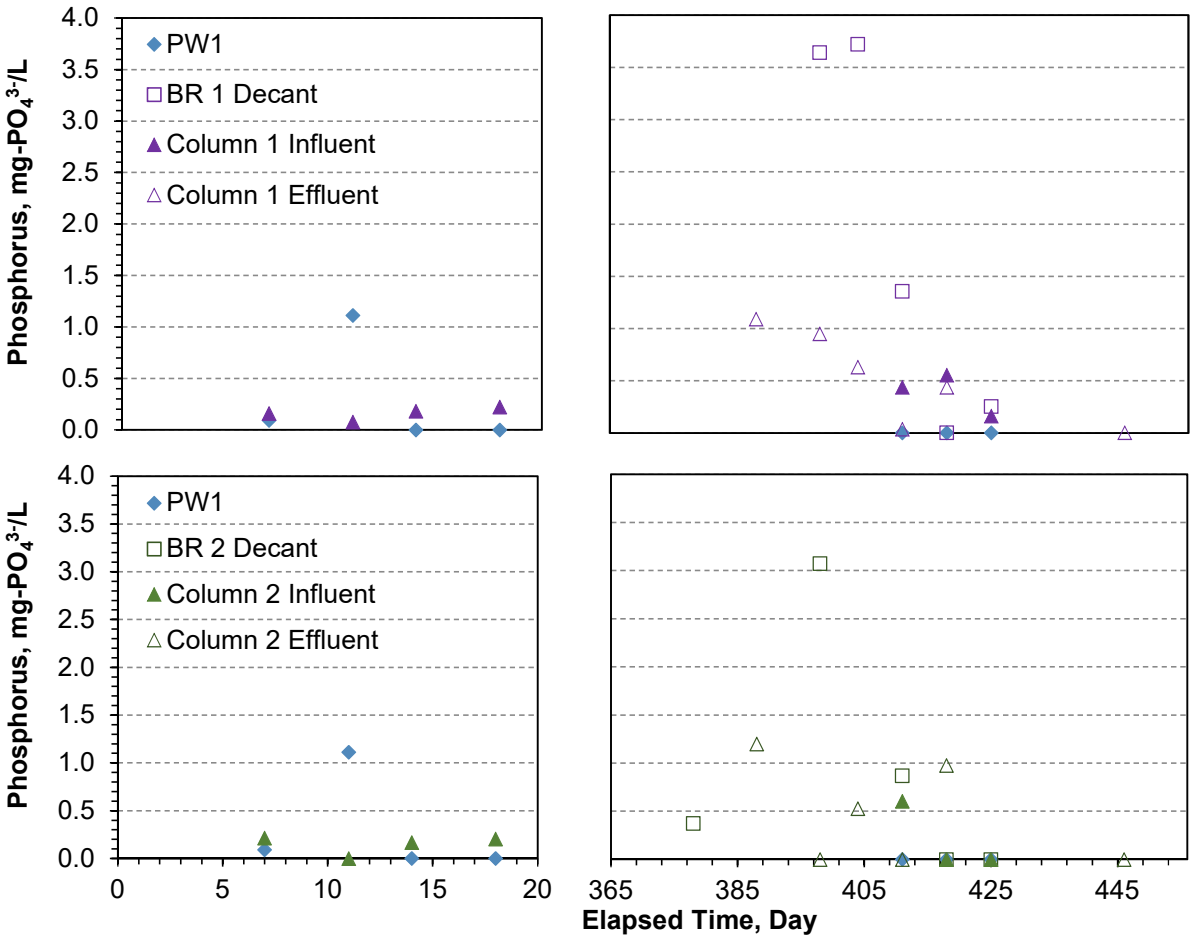

Figure 3.19. Phosphorus concentration as a function of time in the two treatment trains. Days 0 to 20 were during phase 1 (baseline testing) and days 365 to 456 were during phases 6 and 7 (supplemental phosphorus addition). The concentrations did not change significantly in the decant or column influent, indicating that all the phosphorus dose was consumed in the bioreactors.

3.2.6 Suspended solids and turbidity

The suspended solid concentration and turbidity of the mixed liquor in the bioreactors are shown in Figure 3.20. The TSS concentration in BR1 was highly variable, while the TSS concentration in BR2 was mostly consistent. The TSS fluctuations in BR1 are most likely due to changes in aeration in the bioreactor. Because aeration in the reactors also induces mixing, any loss of aeration, equates to no mixing. Corrosion and fouling on the air stone in BR1 were the primary factors resulting in frequent loss of aeration. BR2 had relatively consistent aeration, and thus relatively consistent mixing. In both bioreactors, the mixed liquor TSS concentration is significantly lower than the TSS concentration of municipal mixed liquor, indicating that a low density of microbial communities is in the bioreactors. Furthermore, despite returning solids from the decant and filter backwash into the bioreactors, the low TSS concentration indicates that the bioreactors are populated with slow-growing bacteria.

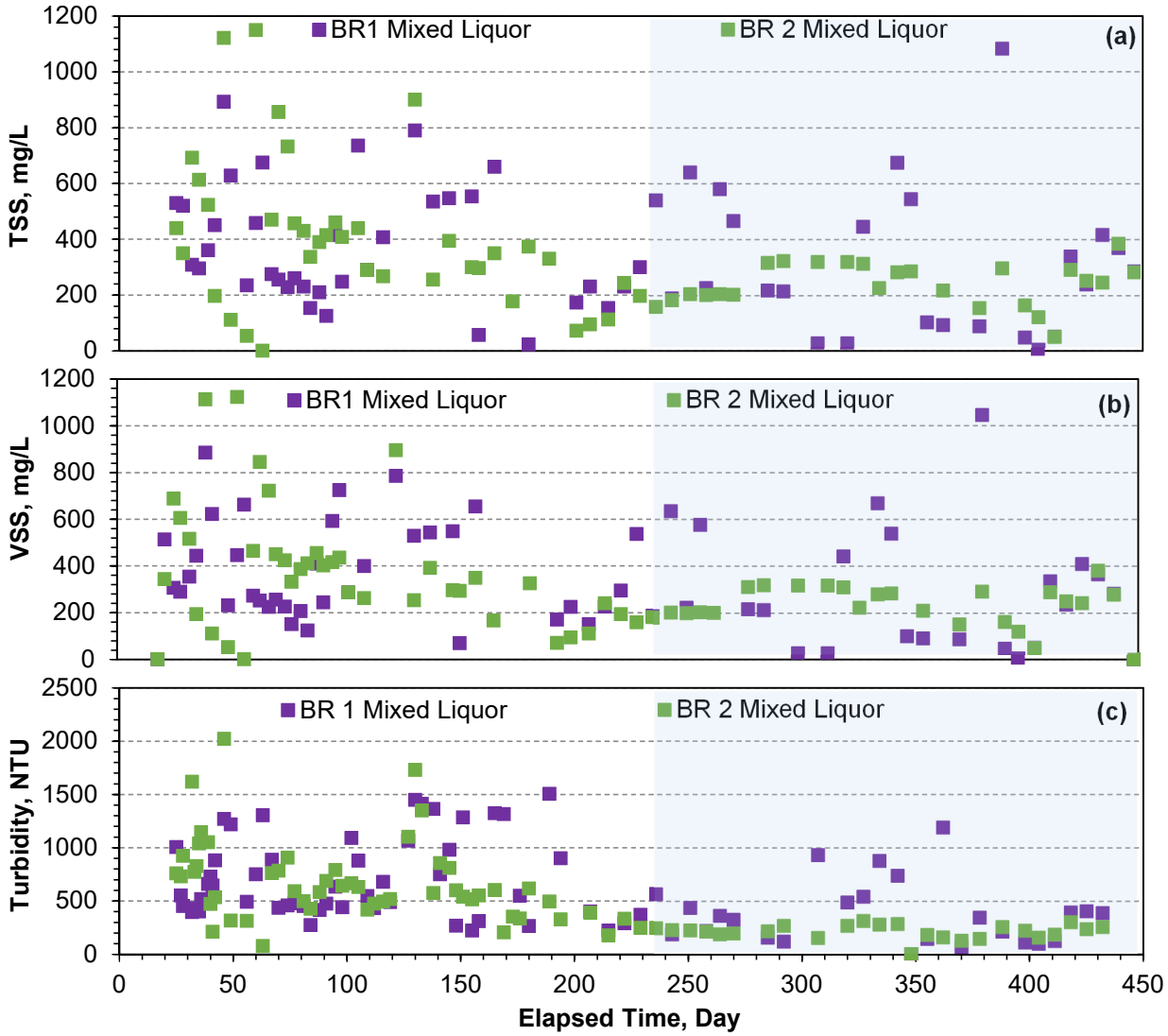

Figure 3.20. (a) TSS, concentration (b) VSS concentration, and (c) turbidity of the mixed liquor in the two bioreactors as a function of time during the pilot study. The TSS concentration in BR1 was more variable over a short time; however, averages to approximately the same as BR2. Throughout all phases of the study, the concentration of TSS and VSS did not change, indicating that more limiting factors besides phosphorus concentration may have prevented increased suspended biological growth.

3.4 Microbial analysis

Microbial samples throughout the operation of the bench and pilot systems system were sequenced and preliminary analysis was conducted. A heat map of the microbial class abundance in the baseline jar, AS jar, centrate jar, and KH_2PO_4 jar is shown in Figure . All jars were dominated by the Proteobacteria phylum. In the Proteobacteria phylum, Gammaproteobacteria and Alphaproteobacteria are the dominant classes. The AS jar had much more diversity compared to the other jars. This is most likely because microorganisms from a municipal SBR were introduced daily to the bioreactor jar. The narrow range of class types, especially in the top performing bioreactor jars (AS, centrate, and KH_2PO_4 jars) indicate that the microorganisms that remove organic matter and ammonia are most likely Gammaproteobacteria or

Alphaproteobacteria. Proteobacteria are often chemoautotrophs, and the gammaproteobacteria and epsilonproteobacteria classes are often found around deep hydrothermal heat vents.[35] The Alphaproteobacteria bacteria class is very diverse; however, they are often associated with marine environments and can have nitrogen fixation or ammonia oxidation metabolisms.[36] Microbial classes are a very broad and diverse classification system. Moving forward, it would be useful to look at the order or family of the DNA sequences processed to narrow in on metabolic pathways in the bacteria present in the bioreactors.

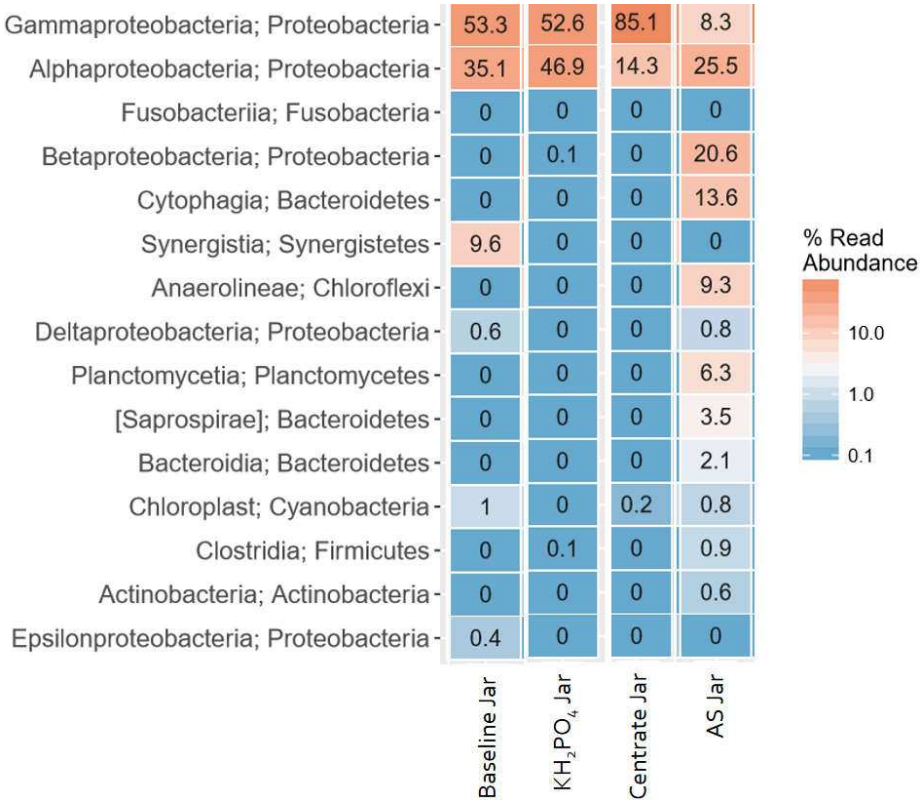

Figure 3.21. Heat map of the microbial class abundance in the (A) PW2 jar, (B) baseline jar, (C) AS jar, (D) H_2O_2 jar, (E) centrate jar, and (F) KH_2PO_4 jar. The numbers on the x-axis refer to sample date (MMDDYY). The (C) AS jar had the most diversity with respect to both phylum and class. The baseline jar had class Synergistia from the Synergistetes phylum, unlike any other jar during sampling events. The lack of diversity with respect to phylum and class in the top performing jars (AS, centrate, and KH_2PO_4 jars) indicates that the bacteria that remove sCOD, COD, and ammonia are in the Proteobacteria phylum.

The heat map of microbial classes in the mixed liquor of BR1 and BR2 in the pilot system is show in Figure 3.22. In the pilot system bioreactors, Alphaproteobacteria appears to have been the dominant class of bacteria; however, there was more diversity and less Gammaproteobacteria compared to the jar bioreactors. Comparing same samples across various sample dates, it appears as though the microbial communities changed with time. BR1 became more diverse and BR2 became less diverse by selecting for Alphaproteobacteria. This may have resulted from more malfunctions in the BR1 aeration system relative

to the BR2 system. Lack of aeration creates a different treatment environment and results in a different evolution of microorganisms. Bacteroidia appeared in both BR1 and BR2; however, BR1 had a higher abundance of Clostridia and Epsilonproteobacteria. Clostridia are commonly anaerobic or aerotolerant, which is another indication that BR1 received less aeration over time than BR2.

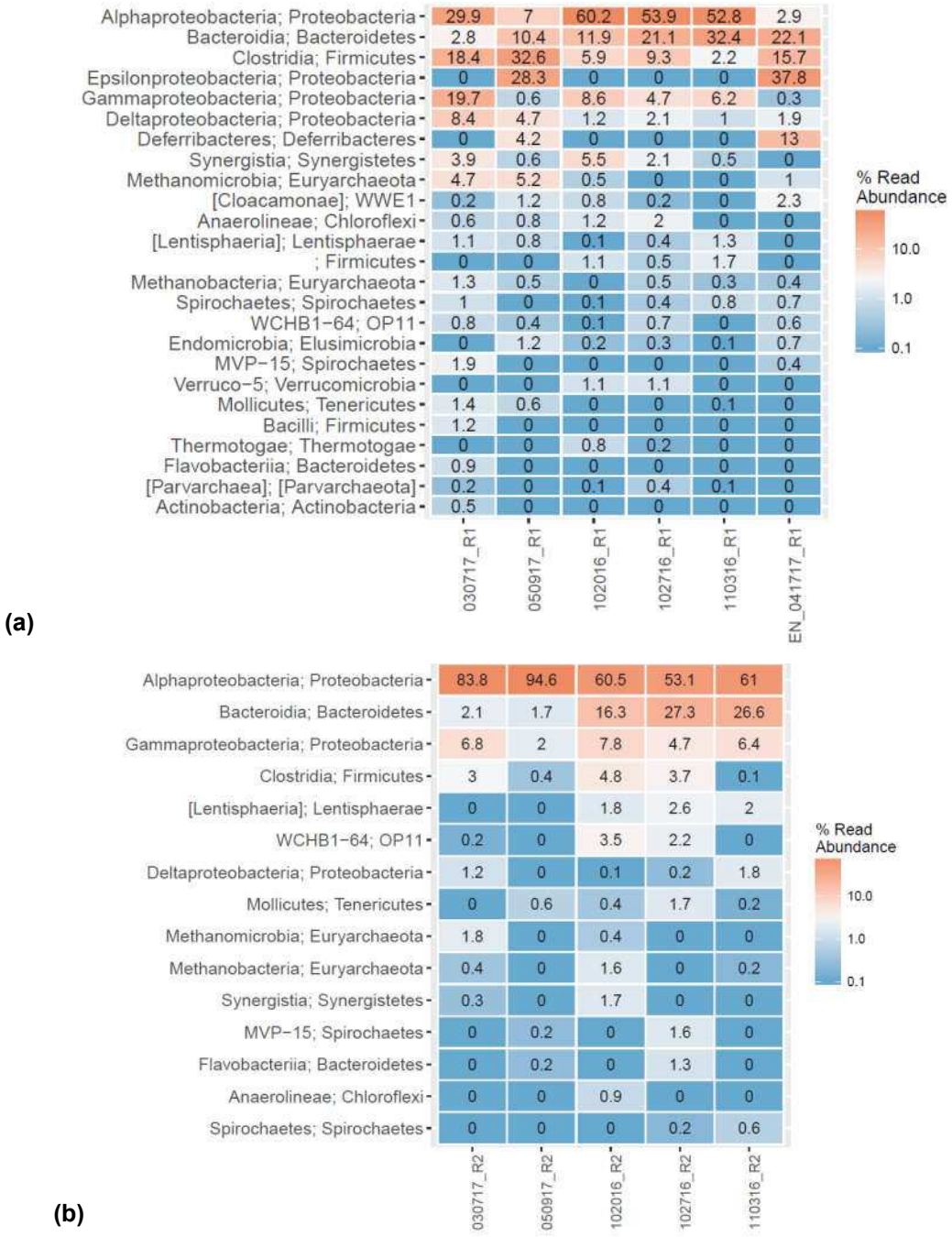

Figure 3.22. Heat map of microbial classes in the (a) BR1 (R1) and (b) BR2 (R2) at various sample days.

Nonmetric multidimensional scaling (NMDS) of pilot system samples is shown in Figure 3.23. Each shaded area represents one of three categories (grey area contains all the PW1 influent samples, the purple area contains all treatment train 1 samples, and green area contains all of treatment train 2 samples). This plot suggests that the microbial communities in each treatment train varies from the influent water quality, and that each treatment train may have unique communities.

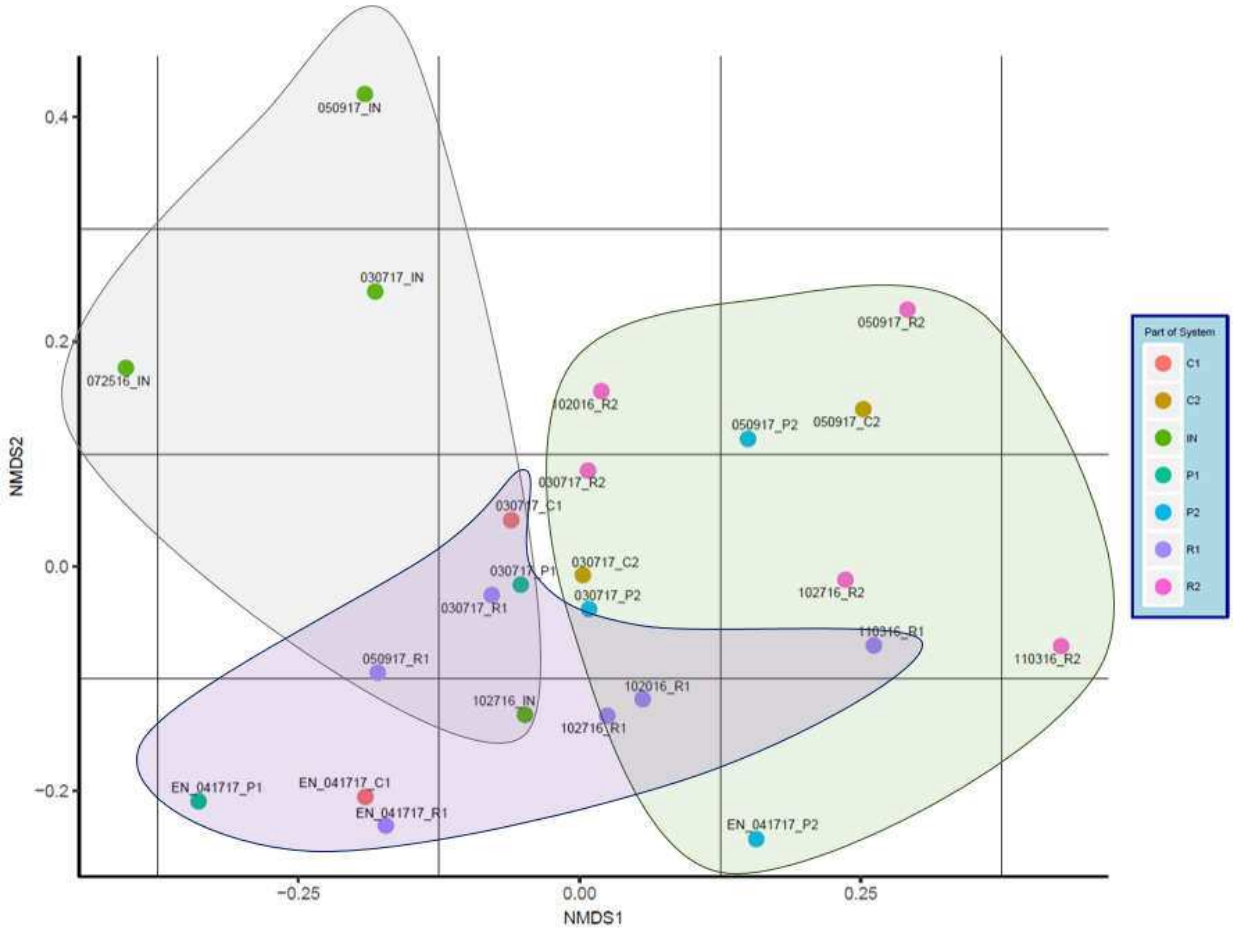

Figure 3.23. Nonmetric multidimensional scaling (NMDS) of pilot system samples showing three distinct groupings. The grey area contains all the PW1 influent samples, the purple area contains all treatment train 1 samples, and green area contains all of treatment train 2 samples. R1=BR1, R2=BR2, C1=Column 1 Influent, C2=Column 2 Influent, P1=Column 1 Effluent, and P2=Column 2 Effluent.

3.5 Bench and pilot system comparison

The baseline and KH_2PO_4 jars can be compared to the pilot system bioreactors before phosphorus addition (baseline jar) and after phosphorus addition (KH_2PO_4 jar). The KH_2PO_4 jar, and the pilot system bioreactors had the same feedwater (PW1); however, the pilot system was operated for a longer time period. The comparison of average concentrations and percent removal is summarized in Table 3.100. The baseline jar had better COD removal compared to the bioreactors, but was out-performed by BR2 with respect to sCOD and ammonia removal. BR1 did not have high removal rates of sCOD, COD or ammonia

most likely due inconsistent aeration. Once supplemental phosphorus was dosed into the bioreactors, the percent sCOD, COD, and ammonia removed increased in all three bioreactors. The KH_2PO_4 jar performed better than both pilot system bioreactors. The higher performance of the KH_2PO_4 jar may be due to a more controlled environment. For example, the pilot system was located in a building with little climate control. The bench scale system was inside a laboratory and consistently held at room temperature. Other differences include the HRT, which was variable (relative to the test phases) in the pilot system and held constant at 3.33 days in the bench system.

Table 3.10. Average concentration and percent removal of sCOD, COD, and ammonia in the baseline and KH_2PO_4 jars compared to the pilot system bioreactors. BR2 had better sCOD and ammonia removal than the baseline jar during the baseline; however, BR1 had the least removal of sCOD and ammonia most likely due to inconsistent aeration. During the time KH_2PO_4 was added, the KH_2PO_4 jar performed better than the pilot system with respect to all three constituents.

		Baseline			Phosphorus Addition		
		BR1	**BR2**	**Baseline Jar**	**BR1**	**BR2**	**KH2PO4 Jar**
sCOD Removal	%	14	28	20.4	17	39	45.9
sCOD	mg/L	1306	1136	1092	1113	850	753
COD Removal	%	9.6	7.5	21.5	14	26	40.4
COD	mg/L	1450	1127	1139	1193	1034	961
Ammonia Removal	%	8.5	21	18.9	27.6	43.2	58.6
Ammonia	mg/L	21.3	19.5	20.7	18.0	14.3	10.1

CHAPTER 4
CONCLUSION

Produced water from the D-J Basin can be treated with a conventional activated sludge system. The produced water used in this study was nutrient limited with respect to phosphorus and a supplemental dose was added to the bioreactors to increase removal of sCOD, COD, and ammonia in the bioreactors. When phosphorus was added to the pilot system, the overall COD removed was relatively constant; however, the location of treatment changed from the media filters to the bioreactors. The comparison of TOC to COD suggests that there is a recalcitrant portion of COD in produced water that is not biologically available. The remaining portion of COD is likely recalcitrant material that will need to be removed via physical or chemical treatment methods. Remaining COD most likely includes inorganic material such as iron and sulfur.

Further studies will need to be conducted to determine the effect of the remaining COD on nanofiltration or reverse osmosis membranes during desalination. Tests using effluent from the bioreactor system in a membrane desalination setup would provide valuable insight into what further pretreatment may be needed to make membrane desalination economically viable. Moving forward, other treatment methods for treatment of inorganic material will need to be tested as they are coupled with a sequencing batch bioreactor to achieve higher treatment of produced water.

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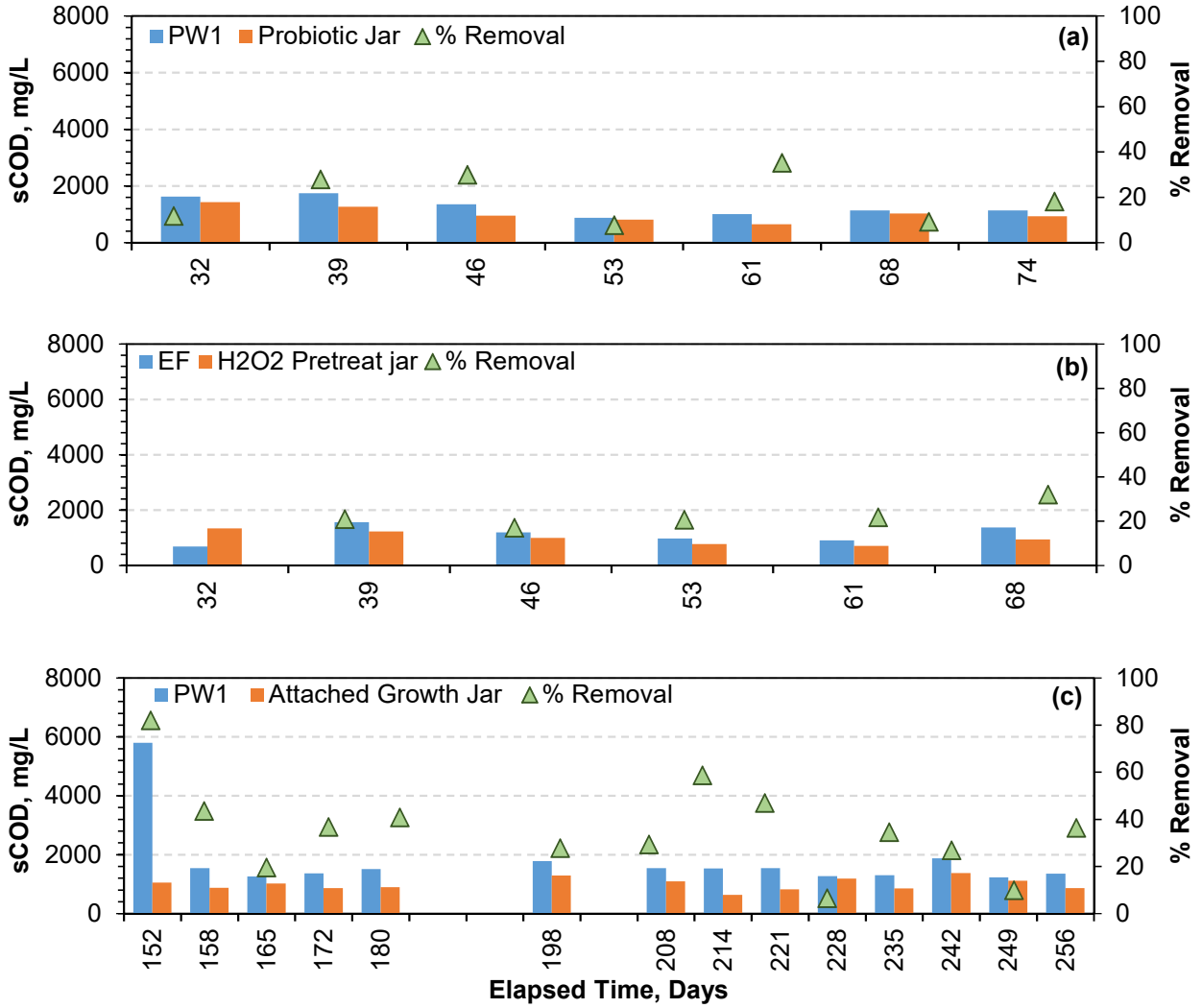

Figure A.1. sCOD concentration and percent removal over time in (a) probiotic jar, (b) H_2O_2 jar, (c) attached growth jar.

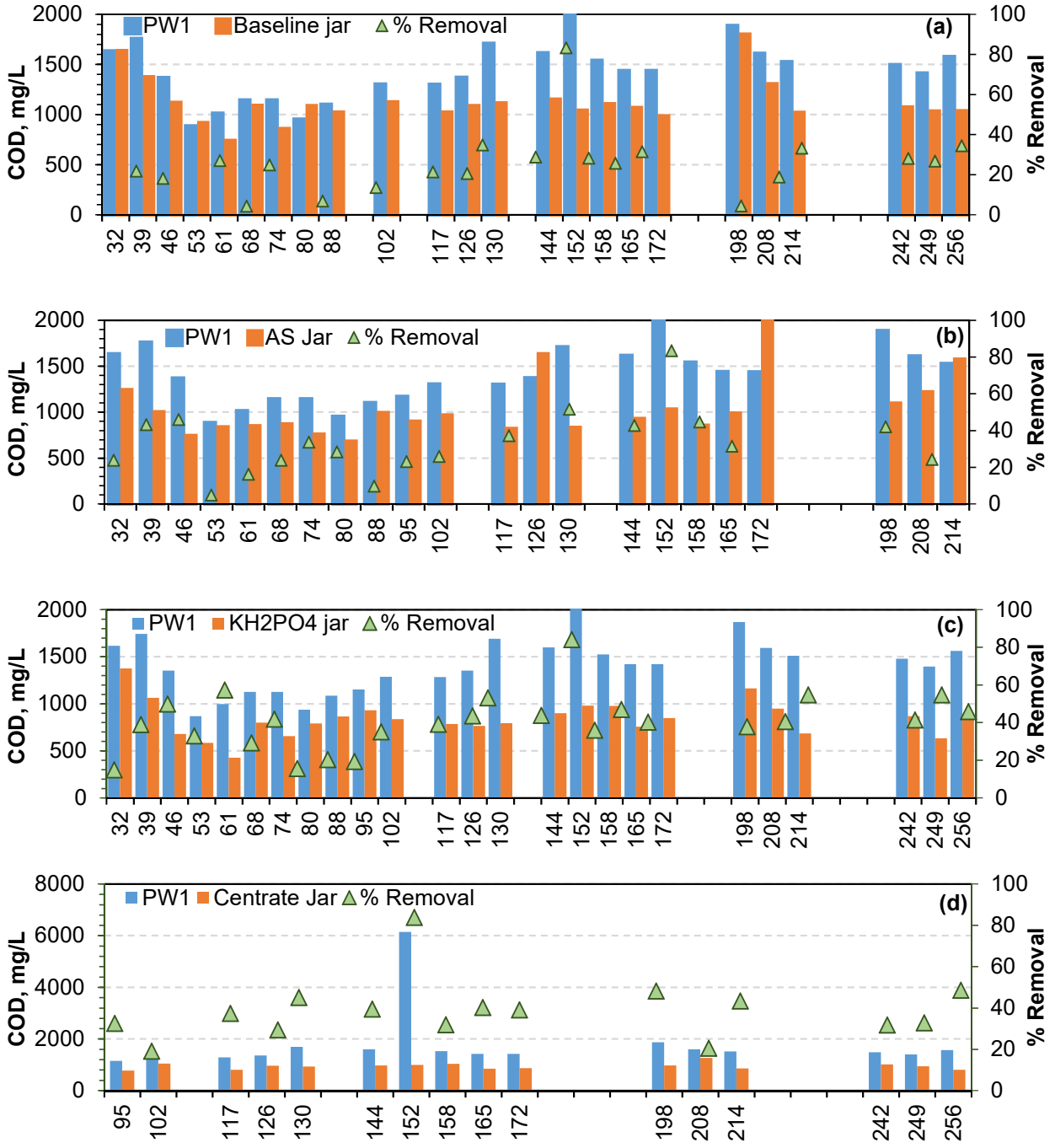

Figure A.2. COD concentration and percent removal over time in the top performing jars (a) baseline jar, (b) AS jar (c) KH_2PO_4 jar, and (d) centrate jar.

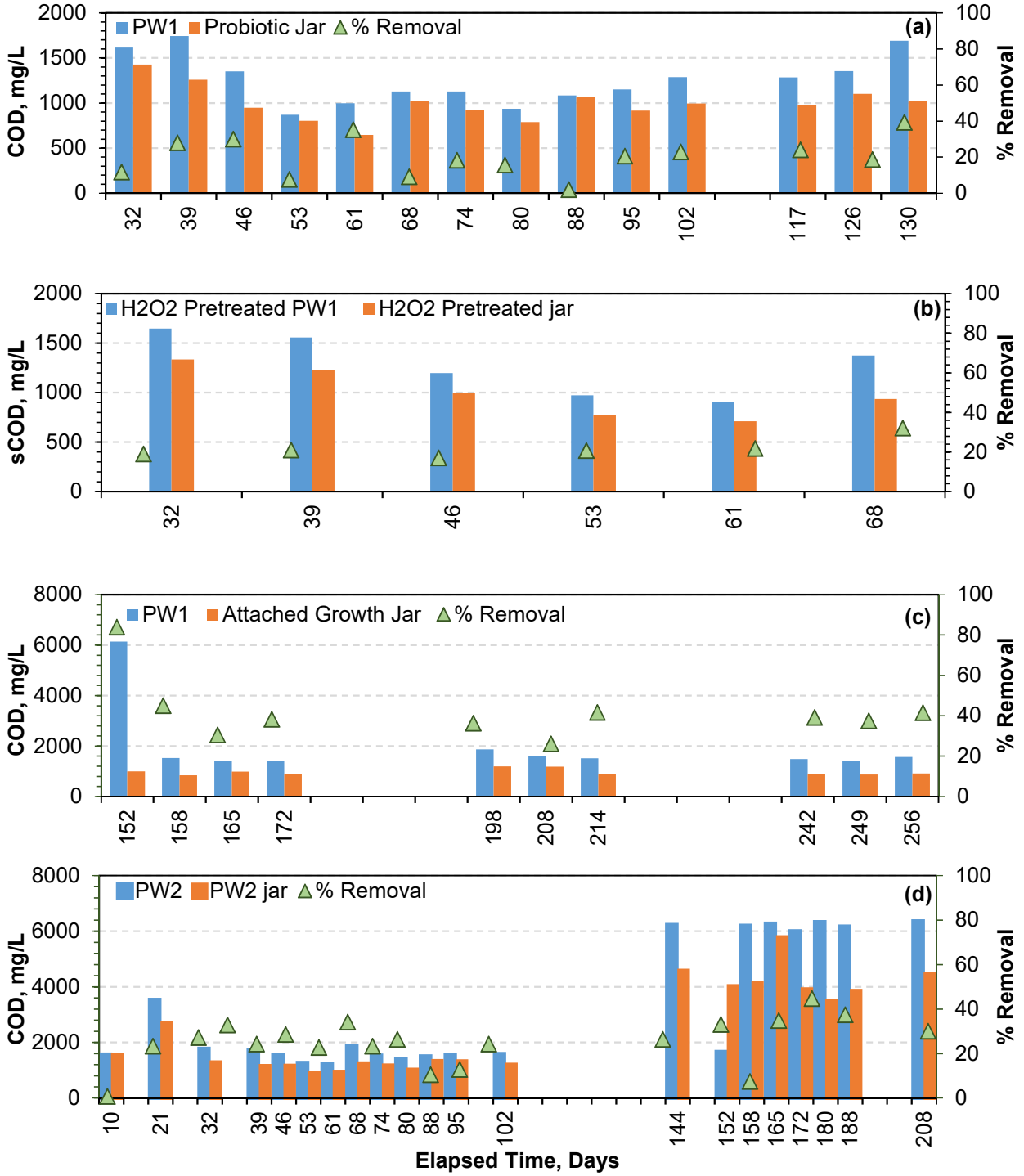

Figure A.3. COD concentration and percent removal over time in (a) probiotic jar, (b) H_2O_2 jar, (c) attached growth jar, and (d) PW2 jar.

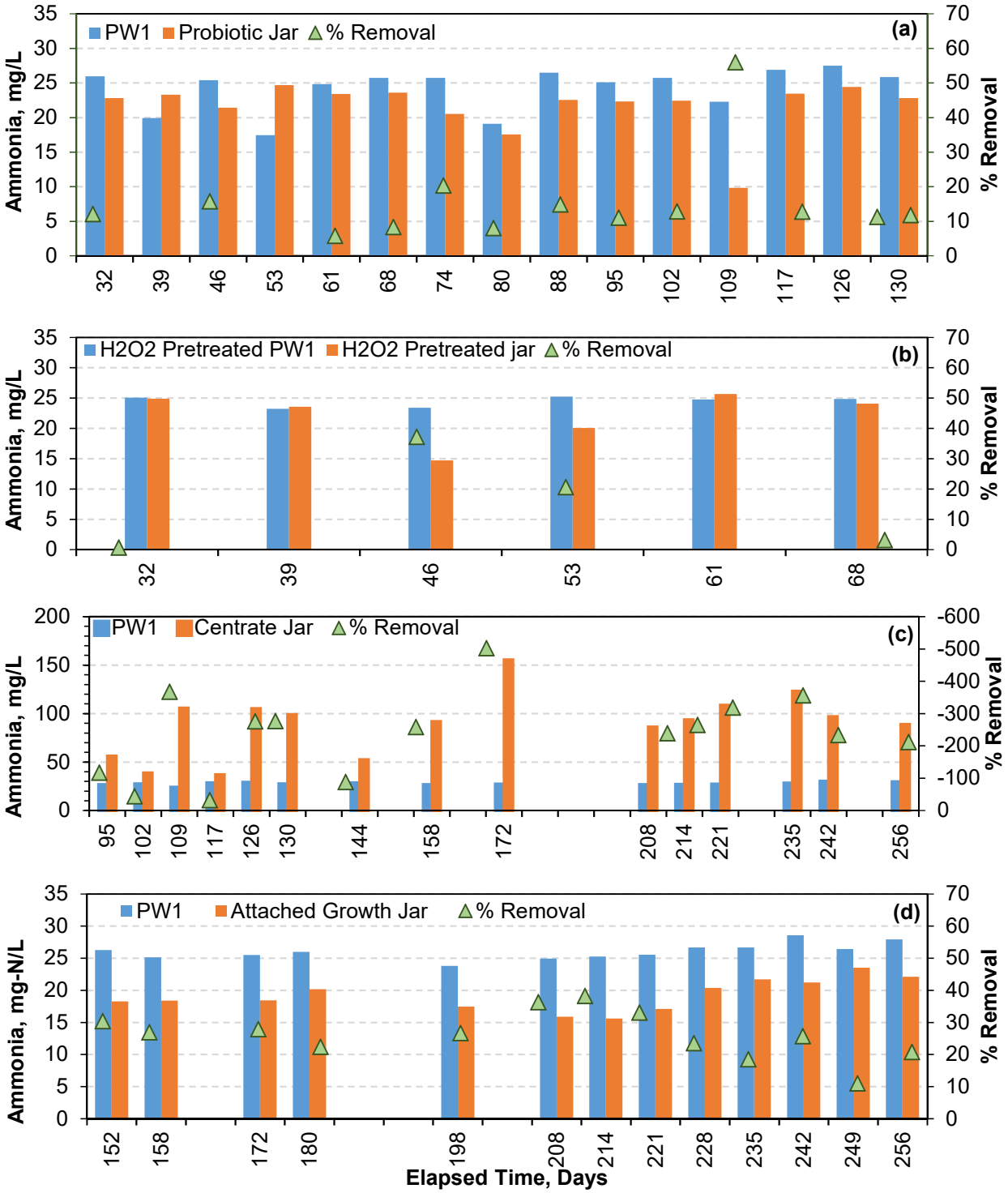

Figure A.4. Ammonia concentration and percent removal over time in (a) probiotics jar, (b) H_2O_2, (c) centrate jar, and (d) attached growth jar.

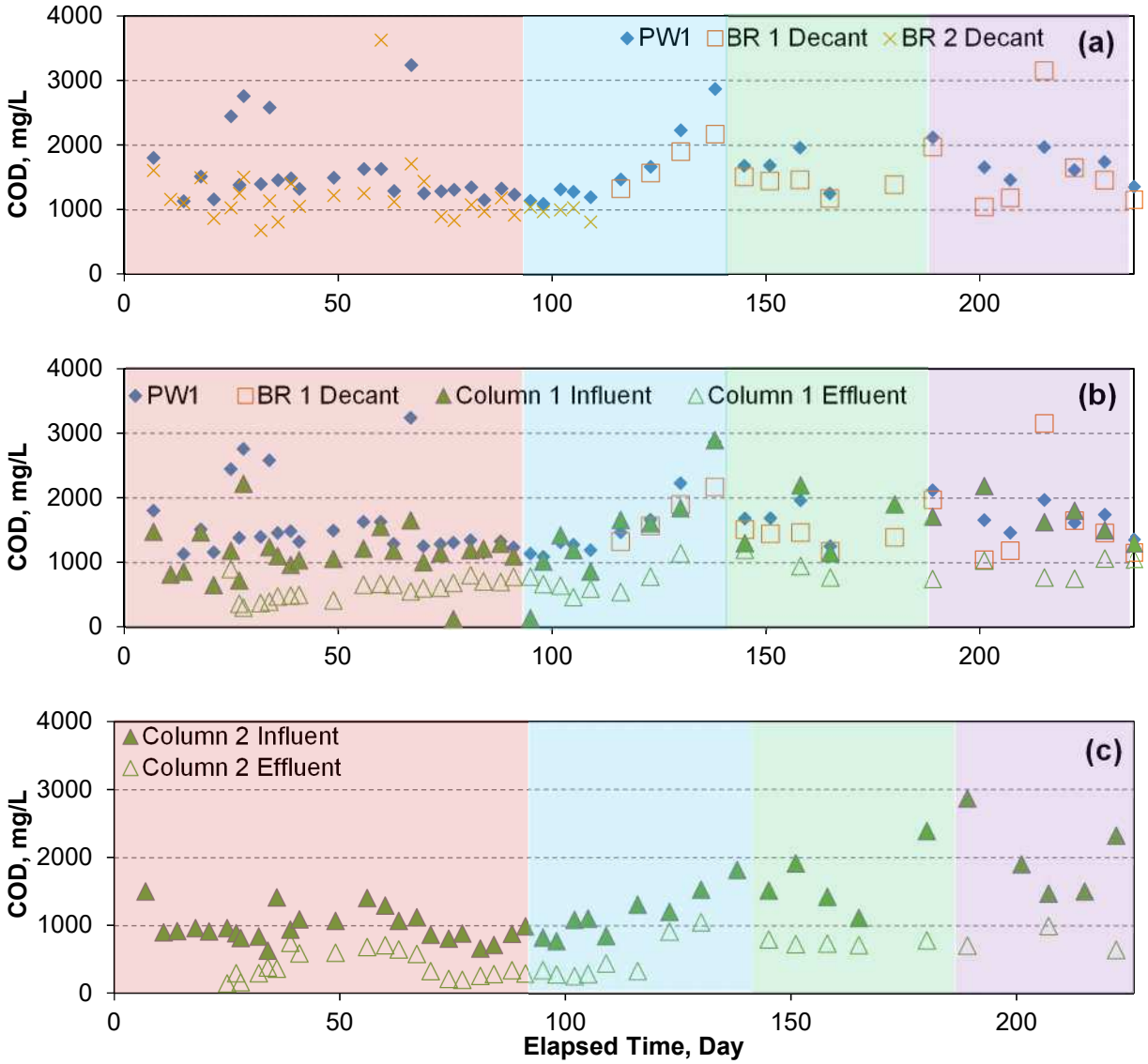

Figure A.5. Concentration of COD as a function of time in the first 4 phases in (a) the bioreactors, (b) column 1, and (c) column 2. Colors from left to right represent the different phases (Table 2.3) during pilot operation (pink = phase 1, blue = phase 2, green = phase 3, purple = phase 4). The amount of sCOD removed did not vary with respect to HRT during the first 4 phases. The majority of the COD removal was occurring in the filter columns.

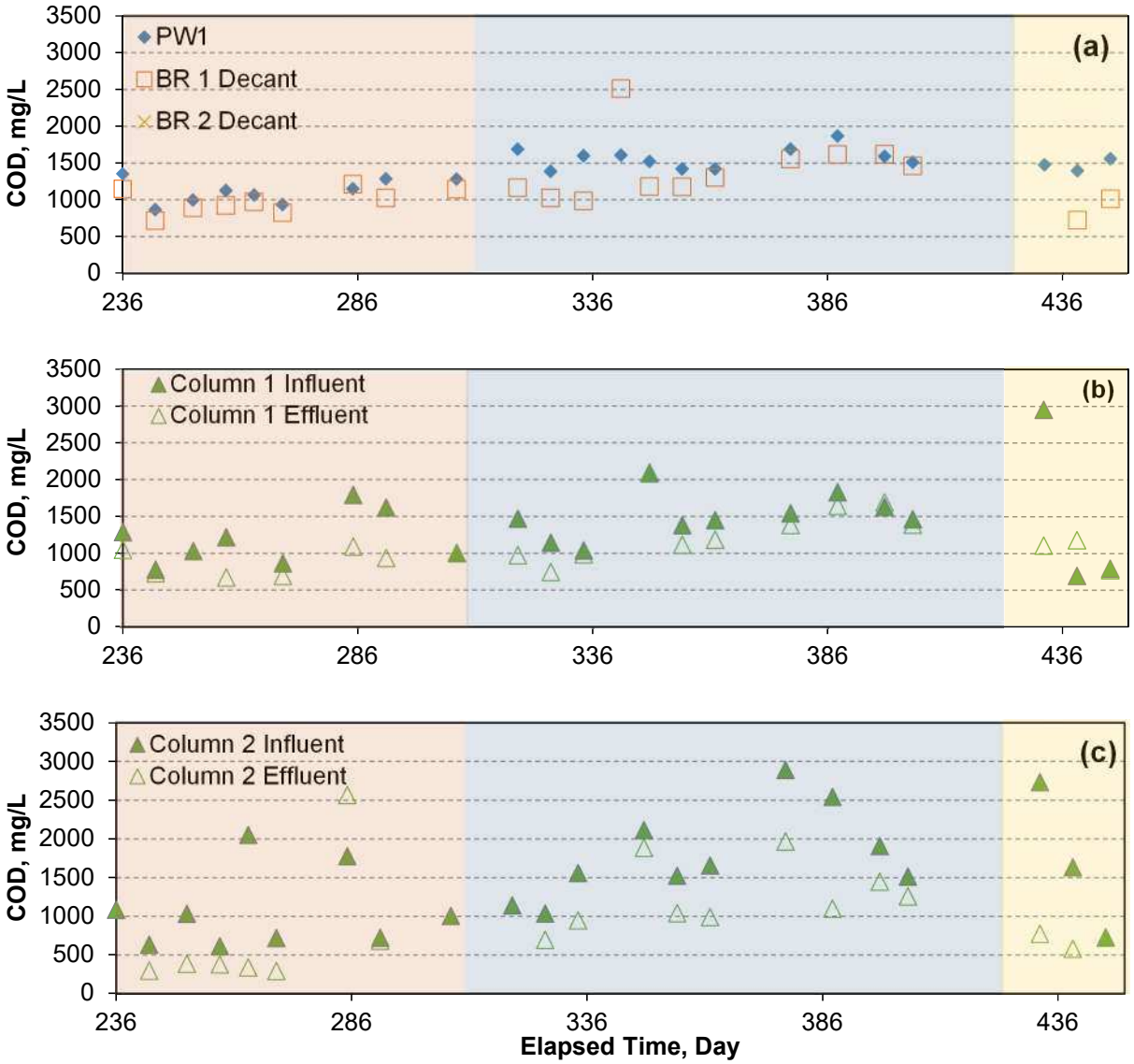

Figure A.6. Concentration of COD as a function of time in the (a) bioreactors, (b) column 1, and (c) column 2 during the last 3 phases of testing (Table 2.3). During the three phases 7.5 mg-P/L was added to each bioreactor. The colors from left to right represent a different phase during pilot testing (orange = phase 5, blue = phase 6, yellow = phase 7). The majority of COD removal took place in the bioreactors, with some removal occurring in the filter columns. The increase in aeration (phase 6) and the increase in HRT (phase 7) did not affect the performance of the system.

Table A.1. Statistical variation in PW1 feed.

	Average	Standard Deviation	Minimum Value	Maximum Value
pH	6.66	0.4	6.1	7.3
Conductivity (mS/cm)	28	5.3	24.8	36.0
COD (mg/L)	1562	769	1121	3320
sCOD (mg/L)	1509	571	1225	2590
NH_3 (mg-N/L)	25	2.4	25.0	31.3
TDS (g/L)	13.6	1.2	15.3	18.9
TSS (mg/L)	109	91.7	2.0	300.0
VSS (mg/L)	106	89.8	2.0	290.0
Chloride (mg/L)	10384	1001	8938	12077
Phosphorus (mg/L)	< 1	0.2	0.8	1.1
Sum Cations (mg/L)	5289	811	5590	8255
Sum Anions (mg/L)	8359	887	9736	12259

Table A.2. 95% confidence intervals of average percent removal in decant for COD, sCOD, and ammonia for each bench scale bioreactor jar.

		PW2	Baseline	AS	Probiotic	KH_2PO_4	Centrate	Attached Growth	H_2O_2
					sCOD				
Average Removal	%	14.1	20.4	48.1	22.3	45.9	43.1	35.6	2.7
Confidence Interval	+/-	20.4	7.2	4.8	6.3	4.1	8.4	10.1	38.9
					COD				
Average Removal	%	16.7	21.5	24.6	20.2	40.4	36.2	43.2	21.9
Confidence Interval	+/-	16.8	7.5	11.0	5.6	5.8	7.2	9.8	15.9
					Ammonia				
Average Removal	%	13.1	18.9	58.8	9.5	58.6	-238	26.2	9.4
Confidence Interval	+/-	13.1	6.8	5.8	10.2	6.0	64.8	4.0	12.9

Table A.3. 95% confidence intervals of average percent removal for COD, sCOD, and ammonia for each PW2 batch.

		PW2 Batch 1	PW2 Batch 2	PW2 Batch 3	PW2 Batch 4	PW2 Batch 5
			sCOD			
Average Removal	%	-12.2	30.0	15.6	36.3	2.61
Confidence Interval	+/-	35.0	6.15	13.8	5.88	29.3
			COD			
Average Removal	%	17.2	27.5	15.9	30.6	-
Confidence Interval	+/-	16.2	3.38	8.28	8.67	-
			Ammonia			
Average Removal	%	1.65	21.9	18.4	19.1	29.9
Confidence Interval	+/-	23.7	17.3	10.8	12.7	11.4

Table A.4. 95% confidence intervals of average percent removal for COD, sCOD, and ammonia for each sample point of the pilot system.

		BR1 Decant	BR2 Decant	Column 1 Effluent*	Column 2 Effluent*
Before Phosphorus Addition					
sCOD Removal	%	14	28	41	41
sCOD Confidence Int.	+/-	12.3	9.37	11.4	12.0
COD Removal	%	9.6	7.5	21	57
COD Confidence Int.	+/-	10.8	7.32	5.87	5.32
Ammonia Removal	%	8.5	21	-17	-2.7
Ammonia Confidence Int.	+/-	11.5	12.7	3.26	8.69
After Phosphorus Addition					
sCOD Removal	%	17	39	2.7	7.2
sCOD Confidence Int.	+/-	9.15	4.60	6.25	11.6
COD Removal	%	14	26	15	36
COD Confidence Int.	+/-	8.87	5.71	12.4	13.4
Ammonia Removal	%	27.6	43.6	-14.1	-2.98
Ammonia Confidence Int.	+/-	9.55	4.58	11.8	16.1

Table A.5. Total and dissolved BOD concentrations compared to total and dissolved organic carbon concentrations and total and dissolved COD concentrations on day 434 of pilot system.

	TOC ***mg/L***	**BOD_{20}** ***mg/L***	**COD** ***mg/L***	**DOC** ***mg/L***	**$sBOD_{20}$** ***mg/L***	**sCOD** ***mg/L***
PW1	267	508	1467	259	544	1527
Column 1 Effluent	300	572	1548	238	542	1272
Column 2 Effluent	73	103	807	54	56	623