

**CO-TREATMENT OF DOMESTIC AND OIL & GAS WASTEWATER WITH A
HYBRID SEQUENCING BATCH REACTOR-MEMBRANE BIOREACTOR**

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ABSTRACT

Oil and gas production has generated substantial volumes of wastewater over the past decade. Due to high salinity, which can exceed 100,000 mg/L, and the presence of organic and inorganic constituents, considerable challenges must be overcome to effectively treat O&G wastewaters for beneficial reuse (e.g., irrigation, livestock watering, industrial water, surface water recharge). Currently nearly 90% of wastewater produced during the life of an oil well is disposed of through deep-well injection. Produced water brought to the surface during the production process contains formation water of highly variable composition that was previously trapped in the rock. This wastewater contains high dissolved organic matter and salt concentrations, as well as various inorganic compounds. Advanced treatment technologies must be developed to remove this broad range of contaminants from O&G waste streams to maximize options for water reuse.

This study investigates the potential for publically owned treatment works using biological treatment processes to adequately co-treat produced water and municipal wastewater. This study utilized a pilot-scale sequencing batch reactor-membrane bioreactor (SBR-MBR) hybrid treatment system to remove organic compounds, primary nutrients, and suspended solids from a mixture of municipal and O&G wastewaters for beneficial reuse. The fate of dissolved organic compounds and metals of concern throughout the treatment train, how to optimize sodium chloride loading rates to achieve effluent goals, and the change in characteristics of the adapting biological community are addressed.

Produced water was initially dosed at 6% by volume, and the SBR-MBR system achieved comparable removal of primary (i.e., chemical oxygen demand, ammonia) and secondary constituents (i.e., trace organic compounds, inorganic contaminants) to control conditions. When produced water was increased to 20% of the influent by volume, nitrification was lost, indicating the threshold at which removal is effected by produced water dose lies between 6% and 20% by volume. Over this time, the biological community in the bioreactors remained stable providing evidence of a robust system.

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CHAPTER 1

INTRODUCTION

Water reuse has become a focal point of innovation due to drivers such as climate change, fresh water scarcity, ground water depletion, and population growth [1-4]. Competition for water resources is driven by increased industrial activities such as agriculture, energy production, and resource extraction [5]. For example, water for mining operations, including coal and petroleum, constitutes one percent, or two billion gallons annually, of the total water demand in the United States [3, 6, 7]. However, unlike other industrial applications, oil and gas (O&G) extraction operations generates waste streams that are primarily disposed of through deep well injection, rather than treated and released back into the environment for reuse downstream [8-10]. The loss of this stream to the subsurface, where it can no longer be utilized, is counterproductive to water reuse initiatives being implemented by other industries and municipal consumers [5]. The implications of injecting wastewaters into disposal wells are not well understood and therefore heavily debated [3, 11]. Technologies to treat O&G wastewater are available, but cannot currently compete economically with disposal in most regions [12]. A possible solution to this economic imbalance is to utilize existing treatment facilities at publically owned treatment works (POTWs) as a pretreatment option to membrane desalination technologies.

1.1 Oil and gas production in the United States

Total petroleum production in the United States increased from eight million barrels per day in 2006 to over 14 million barrels per day in 2014 [13]. This increase in production was made possible through technology advancements (i.e., hydraulic fracturing and horizontal drilling), but has in turn led to increased demand for fresh water resources. Hydraulic fracturing and horizontal drilling serve as an additional step (commonly referred to as completion) to conventional drilling to achieve higher recovery of hydrocarbons from the formation [14]. The amount of water used for a single well drilling and completion operation widely varies and reportedly ranges from 50,000 to 13 million gallons per well [7, 15, 16]. The volume of water used per well is dependent on the characteristics of the drilling operation, completion operations, and O&G formation [9]. Water for well development and operation is acquired primarily from fresh water sources such as groundwater, lakes, and rivers [16-21]. Water mixed with chemicals is necessary for drilling and

completion; it carries out soil and rock cuttings to the surface, it is used as a coolant and a lubrication medium, it is used for pressurizing the formation, and it is used as a medium to inject additives such as drilling mud and other chemicals during the drilling process [22]. Chemicals used for drilling and completion operations can vary in composition and are often proprietary.

After drilling and completion of a well, the water that flows first to the surface is defined as fracturing flowback (flowback). It is a waste stream comprised of water and chemicals that were initially injected into the well for completion purposes. After a short period of time (a few days to a couple weeks), the water flowing to the surface decreases and transitions from flowback to produced water. The amount of water recovered as flowback or produced water varies based on the resource being extracted (oil or gas), the characteristics of the formation, and how much water was injected into the formation [9]. Produced water is the largest (by volume) waste stream generated by O&G operations, and therefore, it was the waste stream of interest in this study [23].

Given its extended contact with the formation, produced water contains a broad range of organic and inorganic constituents. Organic constituents include volatile organic compounds (VOC), free oil and grease (FOG), and total petroleum hydrocarbons (TPH) [17]. Soluble chemical oxygen demand (sCOD) and chemical oxygen demand (COD) are important bulk measurements used in wastewater treatment as an indication of the dissolved and total organic contaminants present in the water. Produced water COD concentration ranges from 150 to 9,300 mg/L [17]. Produced water contains high concentration of total dissolved solids (TDS), the sum of charged ions and compounds dissolved in a solution that pass through a filter with a nominal pore size of 0.45 μm or less. TDS concentration in produced water has been reported as high as 285,000 mg/L, which is equivalent to 28.5% salinity [24], and includes constituents such as barium, boron, bromide, chloride, iron, magnesium, manganese, nitrogen, potassium, sodium, sulfate, and zinc [1, 9, 22, 25]. Other contaminants include microorganisms and total suspended solids (TSS). Thus, it is clear that produced water is highly contaminated and requires complex treatment.

Produced water generated in the Denver-Julesburg (D-J) basin (Colorado, US) is of particular interest in this study due its location in a water stressed region and the prevalence of deep well disposal facilities in the area [16]. The D-J basin is located in northeastern Colorado and contains oil and gas from tight oil and shale gas reserves in the Niobrara formation. In the D-J basin an average of 2.8 million gallons are used for a single drilling and completion operation, and of the total volume injected, only approximately 50% is returned to the surface [26].

1.2 Produced water treatment and disposal

Treating produced water has been proven a technically-viable wastewater management option; however, it can be difficult to compete economically with disposal methods such as deep well injection [27]. The economics of managing O&G waste streams, treatment or disposal, varies substantially with geographic location. In the D-J basin, deep well injection is inexpensive and in close proximity to drilling operations, which is why deep well injection is so abundantly exploited.

Due to highly variable organic and inorganic matter concentrations, produced water treatment requires robust, durable, versatile, redundant, and economical systems that can tolerate variation in influent quality and quantity. Pretreatment of produced water is often employed to reduce suspended solids and the concentration of primary constituents. Biological pretreatment of produced water is of particular interest as a pretreatment method due to the high organic content in produced water available for biodegradation. Biological pretreatment options, as well as a summary of other pretreatment alternatives are summarized in Figure 1.1. Pretreatment is a necessary step for implementing secondary treatment to minimize fouling and increase efficiency for desalination technologies such as nanofiltration (NF), reverse osmosis (RO), and membrane distillation (MD) [12]. Secondary treatment is not mandatory following pretreatment, but is necessary if the desired water reuse application requires desalination. While biological processes can efficiently be used for removal of organic constituents in waste streams, high salt concentration, as expected in produced water and co-treated produced water with domestic wastewater, may negatively impact the performance of the microorganisms in the treatment system. This study evaluated the salinity threshold at which microorganisms in an SBR-MBR system achieve optimal organic matter and nutrient removal.

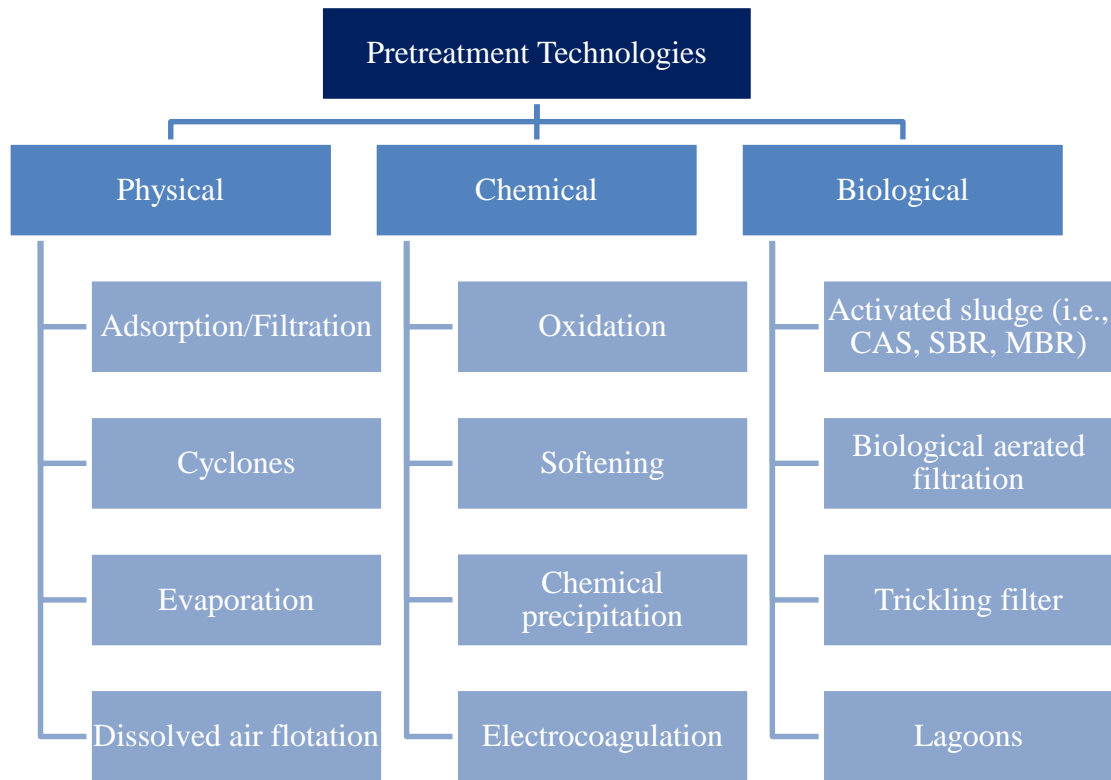


Figure 1.1. A summary of potential pretreatment technologies for O&G produced water that remove or reduce suspended solids and primary contaminants [12, 28].

1.3 Residential wastewater treatment

Throughout the United States, POTWs collect and treat wastewaters produced by both domestic and industrial sources; therefore, concentrations of contaminants in residential wastewater are dependent on source(s), time of day, flow, and season [29]. Composition of residential wastewater varies depending on the source of the wastewater, but generally contains organic carbon (fats, oils, etc.), nitrogen (human protein metabolism, fertilizers, etc.), phosphorus (soaps, detergents, cleaning products, etc.), inorganic compounds (salts, minerals, etc.), suspended solids, and microorganisms [30]. Processes in residential wastewater treatment have been developed specifically to remove these contaminants in a multi barrier approach.

An emerging group of contaminants found in residential wastewater are known as trace organic compounds (TOrcs). TOrcs include personal care and consumer products such as pharmaceuticals, insect repellants, antibiotics, artificial sweeteners, and flame-retardants. Depending on their chemical structure, some TOrcs are easily biodegraded while others are more persistent. Due to their potential risk to human health and the environment, it is important that

wastewater treatment processes are optimized to achieve high removal of TOxCs. When considering co-treatment of produced water with residential wastewater, it is necessary to ensure that salinity and other constituents present in produced water do not negatively impact TOxC removal that was previously achieved in the treatment process.

Various biological treatment processes dominate the residential wastewater treatment industry. Biological processes are designed to accomplish a similar goal—to remove organic matter, nutrients, and suspended solids in the waste stream – to allow for discharge back to the environment [31]. Common biological treatment trains include conventional activated sludge (CAS), sequencing batch reactor (SBR), and membrane bioreactor (MBR) systems.

An SBR operates under batch cycles using precise timing of dosing, aeration, settling, and decanting to achieve nitrification, denitrification, COD removal, biological phosphorus uptake, and clarification. As untreated influent flows into the reactor under anaerobic conditions, a mixer distributes the incoming nutrients to support denitrification. Phosphorus release also occurs during this time. Aeration then initiates ammonia conversion to nitrite and nitrate, the oxidation of organic matter, and biological uptake of phosphorus. Adequate floc formation allows for gravity settling, clarification, and decanting to take place before the next batch is dosed into the reactor. The concept behind an SBR is that equalization, biological treatment, and clarification take place in one basin, thus reducing the land-use footprint of the treatment facility. Due to the flexibility in timing, SBRs are capable of handling variable organic and nutrient loading rates present in both municipal and produced wastewater [4].

In an MBR, high mixed liquor suspended solids (MLSS) is used to achieve high COD removal, nitrification, and denitrification. Rather than settling the MLSS by gravity to decant the clarified water, a UF or an MF membrane is used to physically separate the suspended solids from the treated stream. Using an MBR reduces the need for floc formation and clarification. The biological treatment configuration used in this study is a hybrid sequencing batch reactor-membrane bioreactor (SBR-MBR) and will be further described in Chapter 2.

1.4 Co-treatment of produced water with residential wastewater

Increased awareness of water use in the O&G industry has led to new initiatives to effectively and economically treat produced water for water reuse purposes [3]. One option could involve transporting produced waters to nearby POTWs employing biological treatment processes.

There are numerous advantages for this option. First, biological treatment processes contain microorganisms capable of reducing the high concentrations of organic carbon present in produced water [32-34]. Also, the costs of transportation would most likely be low due to the abundance of POTWs throughout the country, and thus short hauling distances. Utilizing existing facilities would minimize capital costs, making it an economically competitive treatment alternative. Above all, treating O&G wastewater, rather than sequestering it in the subsurface, would mean availability to use the water for future applications. While studies have been conducted to address the feasibility of treating produced water with activated sludge, data pertaining to the impacts on nitrogen and phosphorus removal is insufficient [32-35].

In order for an industrial wastewater to be considered for treatment at a POTW, it must pass several criteria based on federal, state, and local regulations. The Clean Water Act (CWA) 40 CFR Part 403, commonly referred to as the National Pretreatment Program, establishes requirements for accepting industrial wastewaters at POTWs based on the quality of the industrial wastewater submitted for treatment [22]. In order to comply, industrial wastewaters cannot interfere with the overall operation of the POTW, cause a hazardous work environment for employees (i.e., explosives/fire hazard, radiation, toxic gases, etc.), or introduce pollutants that will pass through the process without treatment. Additionally, industrial wastewaters may not contain constituents (i.e., heavy metals) that have been demonstrated to negatively influence sludge reuse applications (i.e., land application) [22]. At the state and local levels, states and individual POTWs have the ability to ban produced water from entering headworks or to develop their own standards for acceptable industrial wastewater quality based on treatment concerns of individual facilities [15]. Regulations pertaining to other methods of treatment and disposal can be found in regulations such as the U.S. EPA Clean Water Act (40 CFR 435,144-148) and the Safe Drinking Water Act (Section 1421).

Sludge used for land application, also referred to as biosolids, are regulated under CWA 40 CFR Part 503 [36]. This regulation establishes maximum allowable pollutant limits in order to use biosolids for land application. Passed in 2010, this regulation aims to minimize leaching of toxic substances to the environment. Pollutants regulated under this code and their respective limits are summarized in Table 1.1.

Table 1.1. A summary of pollutants regulated in 40 CFR Part 503 for land application of biosolids.

Contaminant	Ceiling Concentration mg/kg
Arsenic	75
Cadmium	85
Copper	4,300
Lead	840
Mercury	57
Molybdenum	75
Nickel	420
Selenium	100
Zinc	7,500

Limited number of studies have evaluated whether or not accepting produced water at POTWs will influence the ability of the treatment process to adhere to the expectations outlined by the National Pretreatment Program [22]. These studies—primarily based on reports from POTWs in Pennsylvania that accepted produced water in the past—have been included in a March 2015 EPA rule proposal to ban POTWs from accepting produced water. The volume fraction of produced water mixed with the residential wastewater stream in these POTWs ranged from 0.04% to 21%.

A literature review was performed to identify possible concerns related to the co-treatment of produced water with residential wastewater using biological treatment processes. Salinity in produced water and other waste streams has been reported to increase effluent turbidity, reduce organic carbon removal efficiency, and inhibit nitrification in activated sludge operations [32-34, 37-41]. However, of the studies reviewed, synthetic influent was often used [33, 38, 39, 42]. The use of synthetic influents eliminates the introduction of native microorganisms and unidentified constituents from these wastewaters, which may bias the results. A summary of the findings of the literature review involving salt effects on nitrification and COD removal is provided in Table 1.2. Metals present in produced water such as copper and zinc have also shown to have an adverse effect on nitrification at concentrations of 0.6 mg/L and higher [43, 44].

Table 1.2. A summary of the literature review performed to investigate possible concerns related to salt concentration and the co-treatment of produced water with residential wastewater under biological treatment operations.

Contaminant	Source	Influent Type	Biological Treatment Application	Removal	Salinity (g/L NaCl)
Organic Carbon	[42]	Synthetic sewage with salt	SBR	86%	60
	[33]	Synthetic produced water	MBR	83%	50
	[32]	Produced water	MBR	85%	7.0
	[34]	Produced water with nutrients	CAS	92%	48
	[41]	Sewage with salt	CAS	19%	20
Ammonia	[38]	Synthetic sewage with salt	CAS	40%	40
	[40]	Sewage with salt	SBR	44%	42
	[39]	Synthetic sewage with added salt	BAF	72%	70

1.5 Research purpose and hypothesis

Until now, minimal research has been conducted to investigate the impact of accepting produced water at POTWs. The main objective of this study was to evaluate the ability of a pilot-scale SBR-MBR system to co-treat produced water from O&G operations and residential wastewater. Over the course of 317 days, produced water was gradually introduced into a traditional residential wastewater stream to be treated by an SBR-MBR system. During this time the impact of increased COD, salt, and inorganic matter from increased produced water loading on effluent quality was evaluated. The research quantifies the optimal produced water load to the system, evaluates the fate and transport of inorganic matter throughout the treatment process, and assesses the adaptation of the native biological community present in the bioreactor with each increase of produced water dose.

CHAPTER 2

MATERIALS AND METHODS

A pilot-scale SBR-MBR was constructed and operated at the Colorado School of Mines' Advanced Water Technology Center (AQWATEC) research laboratory in Golden, Colorado. Raw residential wastewater from the Mines Park Apartments (MPA) was treated to establish baseline treatment conditions during Phase I of this study, then transitioned to introduce 6% and 20% by volume produced water into the residential wastewater stream for Phase II and Phase III of the study, respectively.

2.1 Experimental pilot-scale SBR-MBR system

The experimental pilot-scale SBR-MBR system (Figure 2.1) design was based on a 8,000 gallons per day (30 m³/d) demonstration-scale SBR-MBR system [4]. The experimental pilot-scale system was equipped with two bioreactors (BR) constructed from 113 L (30 gal) conical bottom tanks (U.S. Plastic Corp., Lima, OH). A peristaltic pump equipped with two pump heads (Cole-Parmer, Court Vernon Hills, IL) was used to dose clarified residential wastewater and produced water into the bottom of each BR. Actuated ball valves (Ashai, Ryan Herco, Denver, CO) were installed on the influent port of each BR and on the effluent ports of each BR feeding the membrane tank (MT) to control the timing of streams entering and exiting the BR. The BRs were equipped with a linear air pump (Alita Industries, Arcadia, CA) and a 4" (10 cm) diameter air diffuser to supply air and induce mixing in each bioreactor during aeration. Rotameters were installed between the air pumps and the air diffusers to monitor the air flow into the BRs. Aquatic heating elements (Aqueon, Franklin, WI) and external fiberglass insulation were installed during the winter months of the study to maintain a temperature between 14 and 20 °C in the BRs.

Schedule 80 PVC pipe, 1" (2.5 cm) in diameter, was used to transport clarified effluent from the BRs into an 8" (20 cm) diameter clear PVC pipe which served as the MT. The MT contained one submerged PURON® ultrafiltration (UF) hollow-fiber membrane bundle (Koch Membrane Systems, Wilmington, MA) having a total membrane surface area of 0.44 m². The nominal size of the membrane pores is 0.03 µm [45]. A gear micropump was used to pull permeate by vacuum through the membrane and into a 5 L permeate tank. A rotameter (McMaster-Carr, Elmhurst, IL) and a MicroTOL series turbidimeter (HF Scientific, Ft. Myers, FL) were installed

between the micropump and the permeate tank to monitor the flow of permeate and to monitor permeate turbidity, respectively. To minimize fouling on the membrane surface and sustain operation, continual air scouring during permeation and automated backwashing of the membrane (every 3 min for 30 s using water from the permeate tank) were performed and controlled by the SCADA system. Optimization of membrane operating parameters was not investigated in this study and will be the focus of future research.

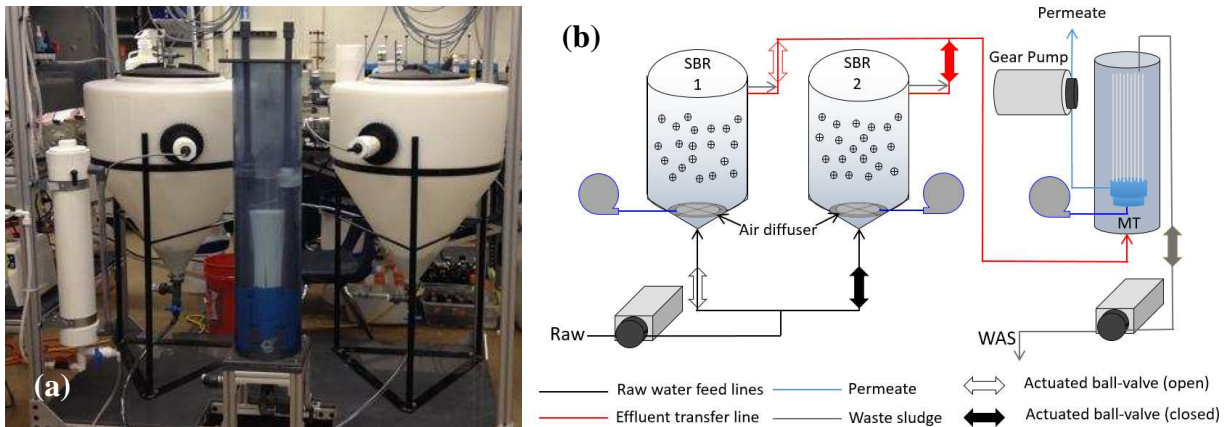


Figure 2.1. (a) Picture and (b) process flow diagram for the SBR-MBR system. Clarified residential wastewater and produced water enter through the bottom of the BRs while the treated effluent overflows into the MT. A gear micropump is used to withdraw water through the membrane while air scouring is applied within the membrane bundle to minimize membrane fouling. If the contents of the BR could not gravity drain to the MT (i.e., loss of power to micropump, reduced membrane efficiency), a wasting port located 1” above the port to the MT provided a redundant outlet to avoid sludge overflow from the top of the BR.

Oxidation-Reduction Potential (ORP; WALCHEM, Holliston, MA), pH (WALCHEM, Holliston, MA), conductivity (Hach, Loveland, CO), and dissolved oxygen (DO; Hach, Loveland, CO) probes were installed in each BR. Data from these probes were logged continuously by data acquisition software (LabVIEW, National Instruments Corp., Austin, TX), instrument control systems (LabJack, UE9-Pro, Lakewood, CO), and a WebMasterONE series controller (WALCHEM, Holliston, MA). The integration of this software and controls provided full automation of the pilot-scale SBR-MBR to maintain proper timing and execution of the operations described above.

2.2 Feed streams

In this study, screened, raw residential wastewater from the MPA and untreated produced water from the D-J basin were utilized for the mixed influent stream.

2.2.1 Residential wastewater

Raw residential wastewater from nearby student apartments was obtained continuously throughout the study using pre-existing infrastructure and was used to dose the SBR-MBR system intermittently over the course of the study. Prior to entering the BRs, the raw residential wastewater was clarified using a primary clarifier operated at a hydraulic retention time (HRT) of 75 min. The effluent from the primary clarifier was sieved through a 2 mm fine screen before being transferred into the BRs. The treatment train of the raw residential wastewater prior to entering the pilot-scale SBR-MBR is illustrated Figure 2.2.

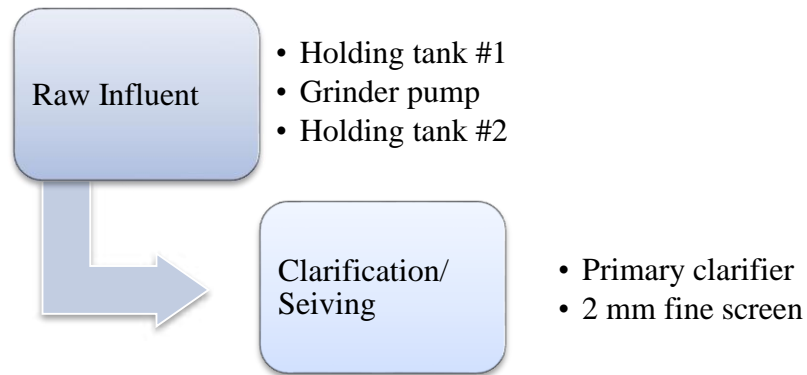


Figure 2.2. Raw residential wastewater pretreatment operations prior to entering the SBR-MBR system.

The occupancy of the MPA decreases during the summer months, and thus changes the raw municipal wastewater composition and flow. The months of June through August are considered summer months while September through May are school months. Seasonal averages of influent composition and characteristics are summarized in Table 2.1.

Table 2.1. Water quality parameters of clarified municipal wastewater. The number of tenants contributing to the wastewater treatment facility varies on a seasonal basis. The population is high from September to May, and low between June and August when school is not in session.

Parameter	Units	June-August	September-May
pH	-	7.17 ± 0.34	7.35 ± 0.29
Conductivity	µS/cm	430 ± 154	1177 ± 128
Temperature	°C	18.9 ± 2.4	14.1 ± 5.8
sCOD	mg/L	162 ± 63.7	185 ± 44.9
NH ₄ ⁺ - N	mg/L	29.6 ± 7.2	45.1 ± 5.8
Total PO ₄ ²⁻ - P	mg/L	10.5 ± 3.5	17.7 ± 5.6
NO ₃ ⁻ - N	mg/L	0.8 ± 1.7	0.6 ± 1.9
Sodium (Na ⁺)	mg/L	60.1 ± 2.0	58.2 ± 6.5
Iron (Fe ²⁺)	mg/L	0.1 ± 0.06	0.25 ± 0.90
Calcium (Ca ²⁺)	mg/L	46.8 ± 1.4	49.7 ± 8.1
Total suspended solids (TSS)	mg/L	234.4 ± 127.1	200.0 ± 114.5
Volatile suspended solids (VSS)	mg/L	223.4 ± 113.4	114.2 ± 16.9

2.2.2 Produced water

Saline produced water from the D-J basin was co-treated in the SBR-MBR system with clarified residential wastewater. Due to the nature of how produced water is acquired, it can be highly variable in composition. In order to minimize variability of produced water quality, a single batch was delivered to the lab from the well at the start of the study and was replenished using produced water from the same well. The well is located in Weld County, Colorado, and operated by Bayswater Exploration & Production. Over the course of the study, produced water was stored at ambient temperature in 275 gal sealed totes. Produced water was mixed and transferred from totes to 20 L containers as needed for the experiment. Characteristics of the produced water used in this study are summarized in Table 2.2.

Table 2.2. Average produced water quality parameters.

Parameter	Unit	Produced Water
pH	-	6.89±0.48
Conductivity	mS/cm	29.9±5.2
sCOD	mg/L	1521±398
NH ₄ ⁺ - N	mg/L	23.2±3.8
Total PO ₄ ²⁻ - P	mg/L	0.3±1.2
Iron (Fe ²⁺)	mg/L	15.9±28.6
Barium (Ba ²⁺)	mg/L	10.6±5.2
Bromide (Br ⁻)	mg/L	122.7±20.2
Boron (B)	mg/L	23.2±5.9
Copper (Cu ²⁺)	mg/L	0.07±0.04
Potassium (K ⁺)	mg/L	36.5±12.3

Parameter	Unit	Produced Water
Strontium (Sr^{2+})	mg/L	35.8±2.6
Lithium (Li^+)	mg/L	5.9±1.1
Zinc (Zn^{2+})	mg/L	0.31±0.24

2.3 Operating conditions

Each bioreactor operated independently of the other under the same timing and operating conditions. Two bioreactors were used in this study as a backup for possible inconsistencies in the biological activity. Unlike a common SBR, the pilot-scale SBR-MBR implements a fill/decant cycle in place of a mix/fill cycle and does not include mixers in the BRs. Each bioreactor was seeded with 50 L of activated sludge from the demonstration-scale SBR-MBR system, which is operated continuously with residential wastewater only. Cycle timing of the pilot-scale SBR-MBR system mimicked the cycle timing of the demonstration-scale SBR-MBR system, and was tested and adjusted during Phase I of the study to allow for adequate settling, nitrification, and denitrification. The time sequence (Figure 2.3) consisted of 20 min of influent flow into a BR, 6 min settling, 34 min aeration, 11 min anoxic phase, 19 min aeration, and 30 min settling for a total of 2 hr. Each BR maintained an HRT of 12 hours. The solids retention time (SRT) was not used as operating criteria due to the nature of solids lost to overflow. Solids accumulated in the MT were not recycled due to the poor settling characteristics of the MT solids.

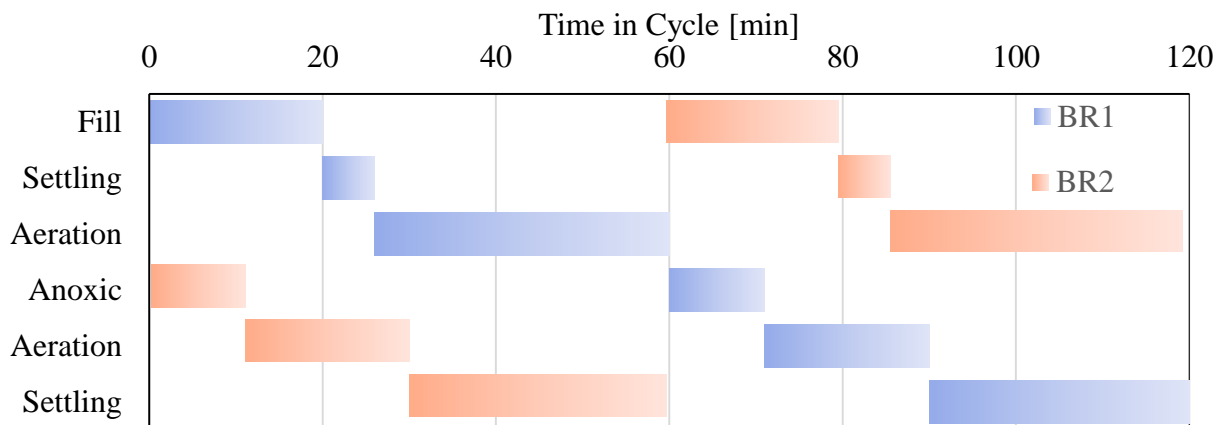


Figure 2.3. The time sequence in each BR during operation of the pilot-scale SBR-MBR system. Each BR operated under the same sequence with an hour offset to ensure continuous operation.

The study consisted of three phases, each based on the ratio between produced water and clarified residential wastewater as the influent to the BRs. Produced water dosing was adjusted according to the schedule shown in Table 2.3. Each phase of the study was conducted until the conductivity and nitrogen removal in the BRs reached steady state. Phase III was broken into three parts.

Table 2.3. Phases of operation of the pilot-scale SBR-MBR system and the volume ratio of produced water co-treated with the residential wastewater.

Date	Phase	Volume Ratio Produced Water to Residential Wastewater
May 2015 - August 2015	Phase I	0%
August 2015 - January 2016	Phase II	6%
January 2016 – February 2016		20%
February 2016 – March 2016	Phase III	6%
March 2016 – April 2016		20%

2.4 Samples collection and analysis

Residential wastewater, untreated produced water, BR effluents, and UF permeate were sampled regularly throughout the study and analyzed for target constituents. Activated sludge was sampled throughout the study to monitor sludge composition over time. Settled sludge from each BR was collected periodically for DNA extraction and metals composition.

2.4.1 Collection and analysis of liquid samples

Samples of clarified residential wastewater, produced water, BR effluents, and UF permeate were collected on a weekly basis throughout the study. At the end of each phase, when the ratio of produced water to clarified residential wastewater in the influent was changed, sampling was increased to three times a day for five continuous days to more closely monitor water quality fluctuations occurring in the BR effluents and membrane permeate. Clarified municipal wastewater samples were collected from the effluent of the 2 mm screen. Produced water samples were collected from a completely mixed, 20 L container. BR effluent samples were collected from just under the water surface of each BR during the final minute of the settling period, prior to overflowing into the MT. UF permeate was collected from a small port at the bottom of the permeate tank. A total of 150 mL of each sample was collected.

Conductivity, pH, and temperature were measured using handheld probes (Thermo Fisher

Scientific Inc., Waltham, MA) immediately after each sample was collected. Approximately 20 mL of each sample was filtered through a 0.45 μm polyethersulfone membrane filter (VWR International, Radnor, PA) and used for chemical analyses. Due to the high chloride concentration in the streams, samples were diluted with deionized water as necessary. Approximately 100 mL of remaining, unfiltered sample was used to measure alkalinity by digitally titrating sulfuric acid down to a pH of 4.68 following the standard method. Filtered samples were analyzed for chemical oxygen demand (COD), ammonia ($\text{NH}_3\text{-N}$), nitrate ($\text{NO}_3^-\text{-N}$), nitrite ($\text{NO}_2^-\text{-N}$), and total phosphate ($\text{PO}_4\text{-P}$) using Hach TNTplus kits (see summary in Table 2.4) and a Hach DR 6000 spectrophotometer.

Table 2.4. Analytes measured with their respective quantification ranges and chloride (Cl^-) interference limits.

Analyte	Hach TNT Number	Quantification Range mg/L	Cl^- Interference Limit mg/L
COD, Low Range	821	3-150	2,000
COD, High Range	822	20-1,500	2,000
$\text{NH}_3\text{-N}$, Ultra Low Range	830	0.015-2.0	1,000
$\text{NH}_3\text{-N}$, Low Range	831	1.0-12.0	1,000
$\text{NH}_3\text{-N}$, High Range	832	2.0-47.0	1,000
$\text{NO}_3\text{-N}$, Low Range	835	0.23-13.5	500
$\text{NO}_3\text{-N}$, High Range	836	22.0-155	500
$\text{NO}_2\text{-N}$, Low Range	839	0.001-0.60	2,000
$\text{PO}_4\text{-P}$, Low Range	843	0.05-1.50	2,000

Filtered samples were also analyzed for concentration of anions using ion chromatography (IC; ICS-900, Dionex, Sunnyvale, CA) and cations/metals using inductively coupled plasma optical emission spectroscopy (ICP-OES; Optima 5300 DV, PerkinElmer, Fremont, CA). Dissolved organic carbon (DOC) concentration was measured using a carbon analyzer (Shimadzu TOC-L, Columbia, MD). Samples that exceeded the chloride or sodium interference concentration, as denoted by the machine specifications, were diluted with deionized water as necessary.

At the end of Phases II and III, 50 mL samples of clarified residential wastewater, BR effluents, and UF permeate were collected at the same time in the morning for three consecutive days to analyze for a suite of 29 wastewater-derived TORCs such as pharmaceuticals, personal care products, artificial sweeteners, and flame retardants present in the different streams. In addition, a few samples from the produced water stream were analyzed as a control, although occurrence of pharmaceuticals and personal care products was not expected in produced water. Samples were

filtered through 0.45 μm filters at the time of collection and stored at 5 $^{\circ}\text{C}$ pending further analysis (<72 hours). TOrC analysis by liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) in positive and negative electrospray ionization mode was performed using isotope dilution method developed by Teerlink et al. and as described in Holloway et al. [31, 46]. Water samples (50 mL) were extracted by Waters Oasis HLB cartridges (500 mg adsorbate, Milford, MA) using an automated solid phase extraction unit (AutoTrace 280, Thermo Scientific, Waltham, MA). LC-MS/MS analysis was performed using an Agilent 1200 HPLC (Santa Clara, CA) and a CTC Analytics HTS PAL autosampler (Lake Elmo, MN) equipped with a 1 mL sample loop for chromatography, coupled with a Sciex 3200 QTRAP MS/MS (Framingham, MA) system. Compounds were separated using a 150 mm \times 4.6 mm Luna C₁₈ column (Phenomenex, Torrance, CA) with 5 μm particle size. Table 2.5 summarizes the detected 22 TOrCs in this study as well as their compound-specific limits of quantification.

Table 2.5. Average concentration and physicochemical properties of TOrCs detected in the clarified, residential wastewater adapted from Holloway et al [31].

TOrC	LOQ ng/L	Residential Conc. in WW, ng/L	MW g/mol	Log K _{ow}	pKa	Charge	LogD*
Acesulfame	100	47,919 \pm 7,839	163.2	-1.33 ^a	2.00 ^a	Neutral	-4.00
Acetaminophen	10	67,308 \pm 29,141	151.2	0.46 ^b	9.46 ^b	Neutral	0.40
Atenolol	10	0.0 \pm 0.0	266.3	0.56 ^b	9.87 ^b	Positive	-1.85
Benzophenone	250	694 \pm 385	182.2	3.79 ^c	11.3 ^d	Neutral	2.96
Bisphenol A	50	26 \pm 41	228.3	3.32 ^e	10.1 ^e	Neutral	3.63
Caffeine	10	31,392 \pm 8,368	194.2	0.79 ^b	1.50 ^b	Neutral	0.28
DEET	25	334 \pm 156	191.3	2.18 ^d	2.00 ^d	Neutral	2.24
Diclofenac	10	61 \pm 143	296.2	3.28 ^b	4.15 ^e	Negative	1.37
Diphenhydramine	25	678 \pm 322	255.4	3.27 ^f	8.98 ^f	Positive	2.34
Fluoxetine	5	0.0 \pm 0.0	309.3	4.05 ^b	10.5 ^b	Positive	1.75
Gemfibrozil	10	5.8 \pm 9.2	250.3	4.77 ^b	4.75 ^b	Negative	1.58
Ibuprofen	100	20,830 \pm 4,226	206.3	3.97 ^b	4.91 ^b	Negative	0.45
Naproxen	10	1,901 \pm 788	230.3	3.18 ^b	4.15 ^b	Negative	0.45
Oxybenzone	100	911 \pm 492	228.2	3.79 ^g	8.39 ^h	Neutral	3.65
Propylparaben	5	767 \pm 276	180.2	3.04 ^b	8.23 ^b	Neutral	2.81
Sucralose	500	41,257 \pm 18,097	397.6	-1.00 ^a	11.80 ^a	Neutral	-0.17
Sulfamethoxazole	5	8,442 \pm 4,344	253.4	0.89 ^b	6.16 ^b	Negative	-0.56
Triclocarban	10	47 \pm 31	315.6	10.6 ^b	5.74 ^b	Neutral	2.41
Trimethoprim	10	3,946 \pm 1,450	290.3	0.91 ^b	7.12	Positive	-1.15
TCEP	10	83 \pm 25	285.5	1.44 ^b	-	Neutral	1.42
TCPP	25	1,842 \pm 977	327.6	2.59 ^b	-	Neutral	2.14
TDCP	50	113 \pm 71	430.9	3.65 ^b	-	Neutral	3.26

*Values were calculated at a pH of 7.4 using ACD/Labs Percepta Platform (PhysChem Module). Average pH in the bioreactors was 7.2 during the study. ^aLange et al. [47], ^bDrewes et al. [48], ^cGago-Ferrero et al. [49], ^dJencks et al. [50], ^eHyland et al. [51], ^fTeerlink et al. [46], ^gWert et al. [52], ^hHolloway et al. [31]

A probability analysis, known as BIOWIN (v4.10, EPI Suite™, U.S. EPA), predicts the biodegradability of compounds based on a variety of models (i.e., linear, non-linear, etc.). A BIOWIN probability score greater than 0.5 indicates fast biodegradation. Linear model BIOWIN scores will be used in addition to the information provided in Table 2.5 to predict the fate and transport of TOxCs in the SBR-MBR system.

2.4.2 Collection and analysis of activated sludge

Activated sludge samples from both BRs were collected periodically throughout the study for metals composition and biological analysis. Activated sludge samples for biological analysis were collected in 14 mL falcon tubes during the 30-minute settling cycle from a port at the bottom of each reactor. 50 mL samples of unfiltered clarified residential wastewater and UF permeate, and 14 mL of produced water were also collected for biological analysis. All samples were immediately stored in a freezer at -20 °C. 50 mL activated sludge samples used for MLSS and metals extraction were collected during the last minute of the first aeration period to achieve a fully mixed sample.

Samples used for DNA analysis were thawed at room temperature for approximately one hour. Under sterile conditions, a fully mixed sample was filtered through 0.22 µm filters (Durapore®, Darmstadt, Germany) until clogging occurred. The rejected contents retained on the filter were transferred into a 2 mL microcentrifuge tube. Samples were then processed for DNA extraction using the PowerSoil® DNA Isolation Kit (MOBIO Laboratories, Carlsbad, CA) following the manufacturer's protocol. DNA was eluted into 100 µL of nuclease-free water (HyClone, Logan, UT). Extracted DNA was quantified using a Qubit® 2.0 Fluorometer Broad Range Assay Kit (Thermo Fisher Scientific Inc., Waltham, MA). Amplification, purification, and normalization of samples for 16S rRNA gene sequencing was performed in accordance with Kozich et al. [53] using V4 region primers (515F and 806R). Samples were sent to the Biofrontiers Laboratory in Boulder, Colorado for sequencing via the MiSeq platform (Illumina, Inc., San Diego, CA). Sequences provided by Biofrontiers were analyzed using bioinformatics software, Quantitative Insights into Microbial Ecology (Qiime).

Activated sludge samples collected for metals extraction were processed following EPA Method 3051. Method 3051 is a proven method to detect which metals are likely to leach from

solids (i.e., soils and sludge) in environmental applications such as land application. Samples were frozen immediately to $-20\text{ }^{\circ}\text{C}$ at the time of collection. The preparation for analysis involved thawing the samples at room temperature for approximately six hours, and gravity settled for an additional 30 minutes. To minimize the liquid in the sample, the supernatant was decanted. The remaining solids samples were thoroughly mixed and then divided into three weighing trays. The volume and wet weight of each sample was recorded prior to drying at $40\text{ }^{\circ}\text{C}$. After 24 hours, samples were cooled at room temperature for 20 minutes and measured to the nearest 0.001 g to obtain the dry weight of the solids. Samples were transferred from the weighing trays to fluorocarbon digestion vessels where 10 mL of concentrated nitric acid and 3 mL of hydrochloric acid were added.

The digestion vessels were properly sealed and placed in the microwave accelerated reaction system (CEM analytical, Matthews, NC). Digestion occurred at $175\text{ }^{\circ}\text{C}$ with a ramp time of 5 minutes and hold time of 5 minutes. The pressure during this time did not exceed 350 psi. The digestion vessels were removed from the digestion microwave and cooled at room temperature for 20 minutes. Each sample was transferred to a 50 mL falcon tube and digestion vessels were triple rinsed into the falcon tubes. Falcon tubes were then filled with deionized water to a total of 50 mL. Samples were centrifuged at 2700 rcf for 10 minutes before 1 mL of the supernatant was transferred to a 14 mL falcon tube. To dilute the concentration of acid in the sample, 10 mL of deionized water was added. Liquid samples were analyzed for metals using ICP-OES.

2.5 Statistical analysis

A student's t-test was used to compare the mean removal of the primary constituents during the three phases of the study. For each response variable (i.e., COD, NH_4^+) we conducted a t-test to determine whether average removal rate was significantly different across different levels of produced water dose (i.e., control, 6%, 20%). To use this test, we assume that the removal rates of each response under each treatment are normally distributed. For each response variable, removal rates were measured an equal amount of times for each treatment, thus resulting in a balanced design. The null hypothesis of the study assumes that the mean removal rates under each treatment are all equal for the given response variable. Treatments were compared at the 95% significance level, thus tests resulting in a p-value less than 0.05 are taken as evidence in favor of the alternative hypothesis.

CHAPTER 3

RESULTS AND DISCUSSION

Treatment performance of a pilot-scale SBR-MBR system was evaluated based on its ability to degrade organic carbon, ammonia, and phosphorus from a combined wastewater streams. The solids in the system were evaluated based on acclimatization adaptation of the activated sludge in terms of quantity, inorganic constituent composition, and microbial community over time. Data were collected and analyzed during each phase of the study; therefore, results of the SBR-MBR treatment performance are presented by constituent, beginning with removal of primary constituents, and then transitioning to fate and transport of metals and adaptation of the microbial community over the course of the study. Each section is further broken down by results from each phase—control conditions in Phase I, 6% produced water by volume in Phase II, and 20% produced water by volume in Phase III.

3.1 System startup

During system startup, at the beginning of Phase I, the SBR-MBR system was operated using only residential wastewater as the influent. The system was seeded by dosing 50 L of activated sludge from the demonstration-scale SBR-MBR system into each BR. The initial timing of the SBR-MBR cycle mimicked that of the demonstration-scale system. Due to differences in the design of the two systems, timing was adjusted to allow for adequate settling of the activated sludge prior to the fill/decant period (Figure 2.3). At the time of system startup, influent doses were approximately 18% of the total BR volume transferred at a flowrate of 20 L/hr. The doses were slowly reduced to 8% of the total BR volume at a transfer flowrate of 9 L/hr to decrease the up-flow velocity in the BRs and minimize mixing during the fill/decant period. Aeration was set at 9 L/min into each BR to ensure adequate dissolved oxygen concentrations during aeration periods.

Phase II began on day 153 by dosing 6% produced water by volume. All conditions remained constant for 80 consecutive days. Phase III began on day 235 by increasing produced water dose to 20% by volume. Nine days into Phase III, NH_4 concentration in the effluent started to increase, indicating loss of nitrification. To avoid complete loss of nitrification, produced water

dose was reduced back to 6% by volume on day 247 of the study. The recovery of nitrification at 6% produced water took place between days 247 and 299, reaching less than 5 mg/L NH_4^+ in the effluent. On the 300th day of the study, produced water dose resumed to 20% by volume until the end of the study on day 317. Results from phases I, II, and III are explained chronologically in each of the following subsections.

3.2 Effluent quality and characteristics

The ability of the SBR-MBR system to remove primary constituents from the combined waste stream served as the main focus of this study. The following subsections compare baseline removal efficiencies for each constituent from Phase I to removal at increased produced water dosing during Phase II and III. In order to adhere to the National Pretreatment Program, introducing produced water into the residential wastewater stream must not interfere with the removal of these constituents.

3.2.1 pH, conductivity, and temperature

Basic measurements such as pH, conductivity, and temperature were taken for each sample collected during the study. Average influent and UF permeate (effluent) composition during each phase of the study are summarized in Table 3.1. Phase II and III influents are denoted as “mix influent” to indicate that produced water and municipal wastewater are present in the sample. Phase III includes samples from both 20% produced water dosing periods, and does not include the period of time when produced water dose was reduced to 6% by volume.

Over time, conductivity in the influent and effluent increased due to the influence of high TDS concentration in the produced water. Conductivity in the effluent increased from approximately 1,000 $\mu\text{S}/\text{cm}$ in Phase I to 3,200 $\mu\text{S}/\text{cm}$ (approximately 1.6 g/L NaCl) in Phase II and eventually reached 6,400 $\mu\text{S}/\text{cm}$ (3.2 g/L NaCl) in Phase III. Temperature of the samples varied by season. Phase I took place during the summer while Phases II and III occurred in the fall and winter months. Submersible heaters and external thermal insulation were installed on the BRs toward the end of Phase II to mitigate the effect of cooler ambient temperatures. pH remained stable during the course of the study.

Table 3.1. Average influent and effluent pH, conductivity, and temperature over the three phases of the study.

	Phase I		Phase II		Phase III	
	Influent	Effluent	Mix Infl.	Effluent	Mix Infl.	Effluent
pH	7.17±0.3	7.11±0.4	7.37±0.4	7.26±0.4	7.37±0.3	7.46±0.2
Conductivity (µS/cm)	563±7.1	502±92	2,850±489	3,200±303	5,980±161	6,453±637
Temperature (°C)	18.9±2.4	19.5±1.5	15.1±2.8	13.1±3.2	13.4±1.2	14.1±1.2

3.1.1 Ammonia (NH₄⁺)

Ammonia (NH₄⁺), the primary form of nitrogen in raw residential wastewater, was closely monitored throughout the study. NH₄⁺ concentration in the system influent and effluent during Phases I, II, and III are shown in Figure 3.1 (a), (b), and (c), respectively. Due to the reduced conditions, by-products of nitrification, nitrite (NO₂⁻) and nitrate (NO₃⁻), were below 1.0 mg/L in the clarified residential wastewater.

During Phase I, the average effluent concentrations of NO₂⁻ and NO₃⁻ were 1.4 and 2.3 mg/L, respectively. Low concentrations of these three nitrogen species indicate adequate aeration and anoxic periods in the cycle, which support nitrification and denitrification. The concentration of NH₄⁺ in the effluent increased between days 26 and 33, but quickly regained adequate nitrification until day 80 when occupancy of the housing complex increased considerably, resulting in elevated nutrient loading. Average steady state NH₄⁺ removal during Phase I was 91%.

The system achieved consistent removal of NH₄⁺ during Phase II. Elevated NH₄⁺ concentration in the influent was not a result of adding produced water, but rather higher nutrient loading in the residential waste stream. Average steady state NO₃⁻ and NO₂⁻ concentrations in the effluent were 2.6 and 0.2 mg/L, respectively. Dissolved oxygen concentrations during aeration between days 219 and 226 were lower due to clogging of the air stone in BR1 due to biofilm growth in the diffuser pores. The air stone was replaced, and nitrification was restored by day 228. Elevated effluent concentrations triggered by this incident are marked as empty symbols in Figure 3.1(b). The average steady state removal of NH₄⁺ during Phase II was 88%.

On day 235, produced water dosing increased to 20% by volume. Over the first nine days NH₄⁺ concentration slowly increased, showing signs of nitrification loss. As a precautionary measure to avoid complete loss of nitrification, produced water dose was reduced to 6% by volume on day 247.

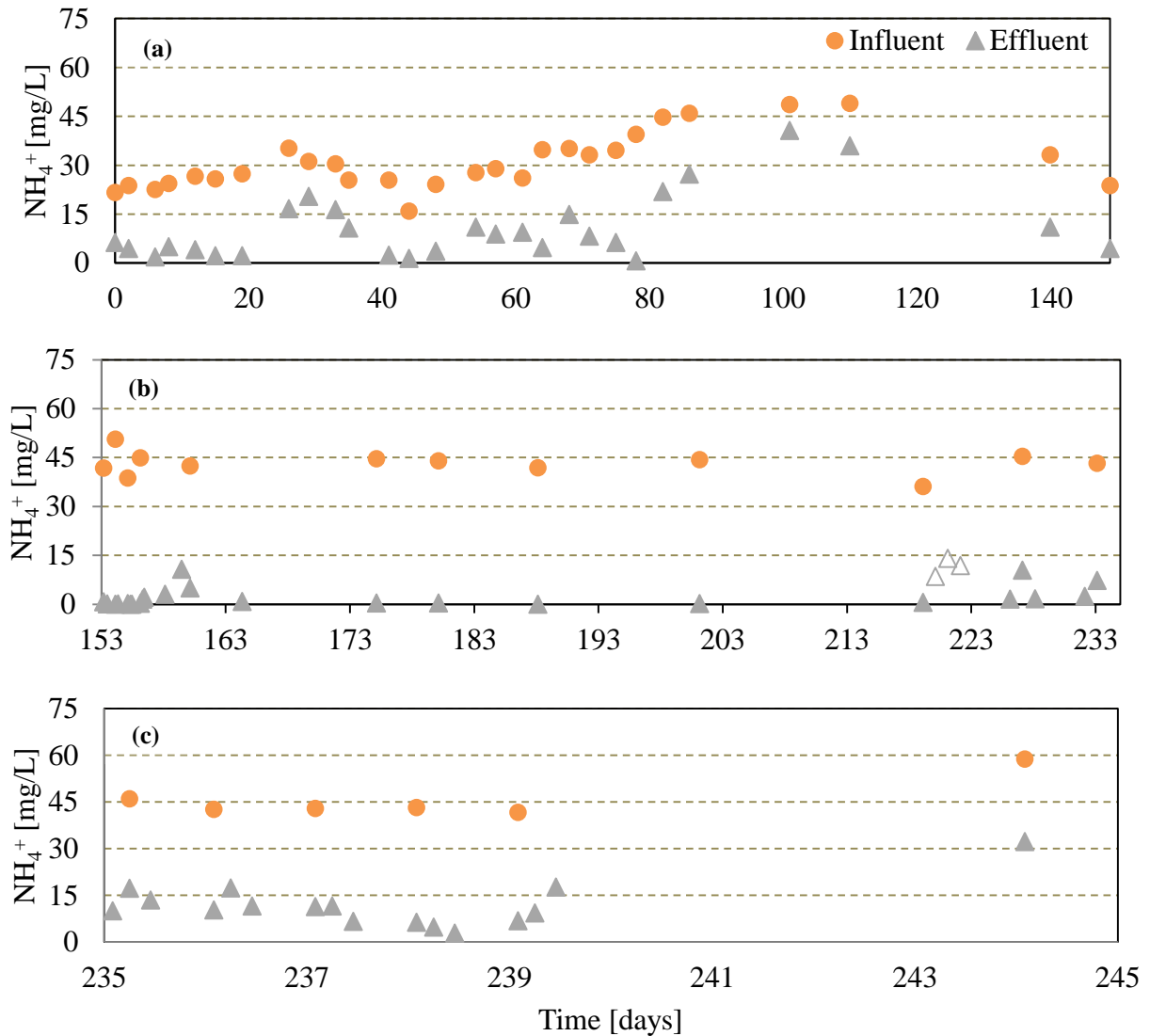


Figure 3.1. Ammonia concentration in the influent (orange) and effluent (grey) during (a) Phase I, (b) Phase II, and (c) Phase III. An influx of MPA residents occurred at approximately day 80, which caused an increase in influent concentrations. Empty symbols indicate that the air stone at the bottom of BR1 was clogged due to biofouling and was replaced on day 222.

A profile of NH_4^+ concentrations from the beginning of Phase II through the end of Phase III is shown in Figure 3.2. The percent of produced water dosed at each point in time is denoted in the shaded areas on the graph. After produced water was decreased back to 6% on day 247, nitrification removal improved over the following 38 days. On the 299th day of the experiment, produced water was increased to 20% once again. A sharp increase in effluent NH_4^+ was observed between days 300 and 302 from insufficient DO concentrations due to clogging of the air stone in BR2. Despite the installation of the new air stone, which led to adequate DO concentrations in the

BR, NH_4^+ in the effluent continued to increase until NH_4^+ removal reached only 19% on the final day of the study. When 6% and 20% conditions were repeated, similar results were reproduced. A combined steady state NH_4^+ removal of 24% was achieved during 20% by volume produced water dosing.

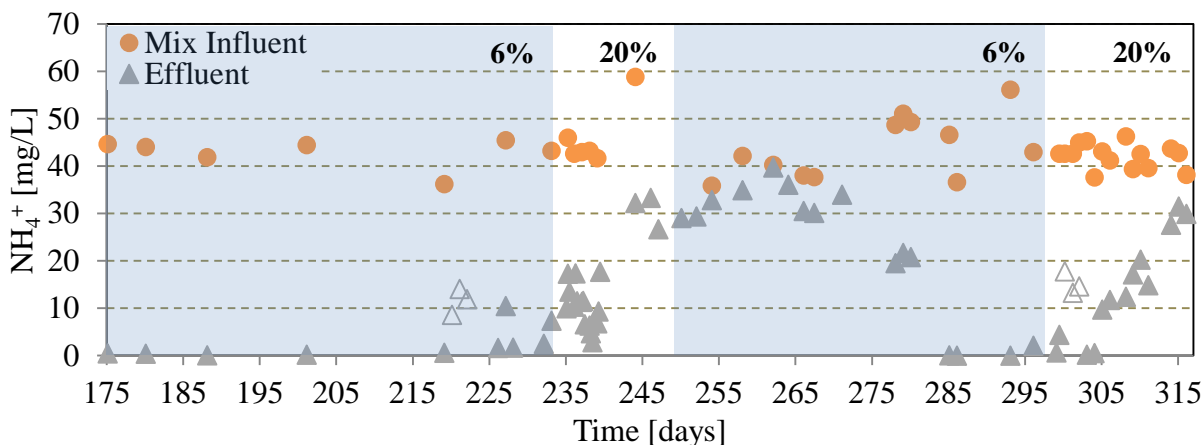


Figure 3.2. Ammonia concentration in the influent (orange) and BR effluent (grey) over the course of 142 days. Produced water was dosed at 6% by volume on days 175 through 234 and 247 through 299. Dosing changed to 20% by volume on days 235 through 246 and 300 through 317. Empty symbols indicate times of insufficient aeration.

Nitrification loss was not anticipated at 20% produced water dose. Dosing 20% produced water led to salinity concentrations in the BRs reaching approximately 3.2 g/L NaCl. This salinity is much lower than values reported in the literature to inhibit nitrification [37-40]. Additionally, metals were not present in the BRs at concentrations as high as those reported to cause loss of nitrification [44, 54]. These unexpected findings could be the result of other constituents in the produced water that inhibit nitrification. For example, there could have been traces of biocides from fracturing fluids in the produced water that negatively impacted the sensitive nitrifying bacteria, but did not impact the more robust heterotrophic bacteria responsible for oxidation of organic matter.

A t-test was performed to compare the mean NH_4^+ removal during Phases II and III with the mean NH_4^+ removal during Phase I. When comparing the control (Phase I) results with 6% (Phase II) results, there was not evidence that the means were significantly different (t-test, $P=0.34$). However, there was evidence that the means were significantly different (t-test, $P=4.48 \times 10^{-13}$) when comparing the results of Phases I and III.

Loss of nitrification at 20% produced water dose indicates that the threshold at which the SBR-MBR system can adequately remove NH_4^+ lies between 6 and 20% produced water influent by volume. Accepting produced water at volumes of more than 6% by volume may influence a POTW's ability to achieve NH_4^+ discharge standards. Our results do not indicate that NaCl concentration was the cause of nitrification loss. Further tests need to be performed to better understand the composition of produced water to determine if other known nitrification inhibitors are present.

3.1.2 Soluble COD (sCOD)

sCOD removal is another important feature of the SBR-MBR treatment process due to the high influent concentrations introduced into the system. Removals of sCOD over time during Phase I, II, and III are shown in Figure 3.5 (a), (b), and (c), respectively. sCOD concentration in the effluent remained relatively stable and low throughout Phase I. Reduction in effluent sCOD concentration can be accredited to the presence of well-developed microorganism community utilizing oxygen to reduce, and thus stabilize, the organic materials in the influent stream. An upset in sCOD removal took place between day 26 and 33 of the study for unknown reasons. However, following this upset, sCOD removal recovered and was stable for the remainder of Phase I. Average steady state sCOD removal of the pilot-scale SBR-MBR system during Phase I was 83%.

sCOD in the influent increased by approximately 80 mg/L from Phase I to Phase II, as shown in Figure 3.5 (b). Despite the higher sCOD concentration in the mixed influent caused by produced water dosing, sCOD concentration in the effluent was consistently low over the 80 days of Phase II, indicating that a large portion of the sCOD present is biodegradable. The average steady state removal of sCOD during Phase II was 89%.

For the first nine days of Phase III (20% produced water in the influent), effluent sCOD concentration increased from 40 mg/L to 85 mg/L while influent sCOD concentrations increased from approximately 300 mg/L in Phase II to 500 mg/L in Phase III. The average steady state removal of sCOD during 20% produced water dosing was 78%.

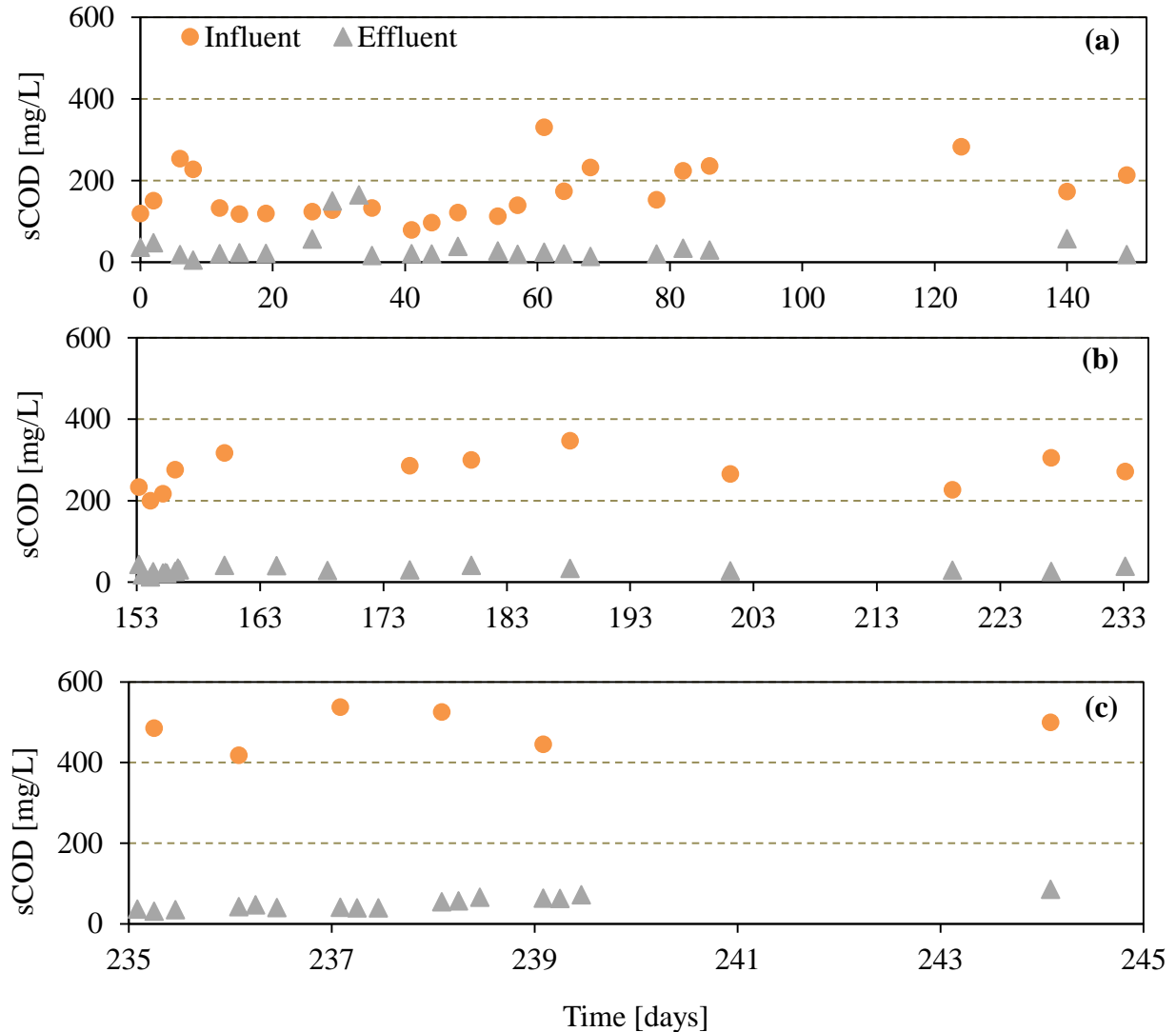


Figure 3.3. sCOD concentration in the influent (orange) and effluent (grey) over the course of the three phases. (a) Phase I sCOD concentrations over the first 152 days of the study to establish baseline conditions (produced water not added to the influent). A decline in sCOD removal was observed between days 26 and 33, but nitrification was restored on day 40 for the remainder of the study. An influx of MPA residents occurred around day 80 of the experiment, yielding higher loading rates; (b) sCOD concentration during Phase II over the course of 80 days. Produced water was dosed at 6% by volume during this period of time; and (c) Phase III sCOD concentrations over the first nine days at 20% produced water influent by volume.

sCOD concentrations in the mixed influent and in the effluent from the beginning of Phase II to the end of Phase III are shown in Figure 3.4. Effluent sCOD increased during times of 20% produced water dose. The influent sCOD concentration during the first period of 20% produced water increased to approximately 500 mg/L. The second period of 20% produced water contained lower mixed influent sCOD concentrations due to lower sCOD concentrations of the municipal

wastewater. Average steady state removal during 20% produced water dosing was reduced to 78% from the 89% removal achieved at 6% produced water and 84% removal achieved during Phase I.

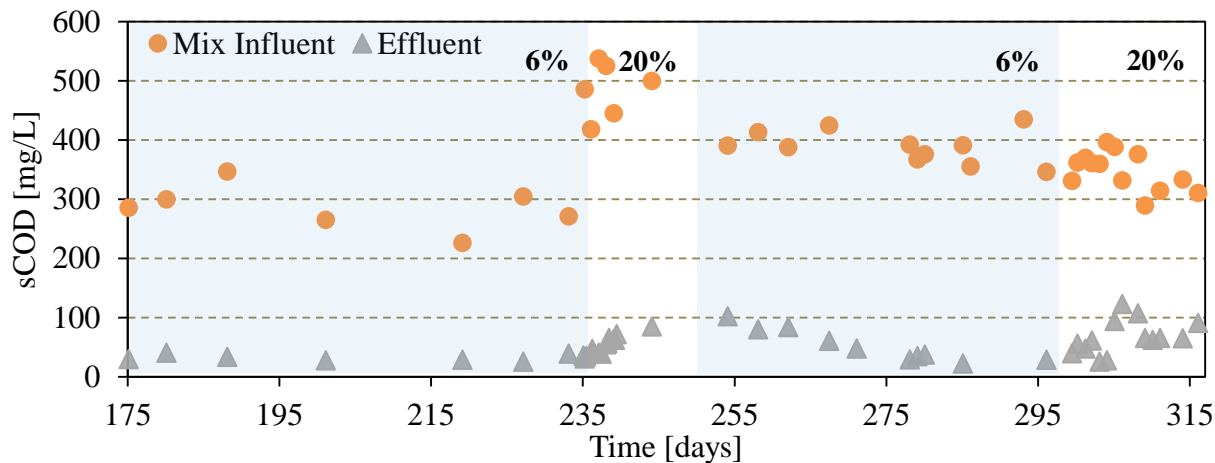


Figure 3.4. sCOD concentration in the influent (orange) and BR effluent (grey) during the course of 142 days in Phases II and III. Produced water was dosed at 6% days 175 through 234 and 247 through 299. Dosing changed to 20% for days 235 through 246 and 300 through 317.

Despite the fluctuation in sCOD concentration in the mixed influents, acceptable sCOD removal took place throughout the study. A t-test was performed to compare the mean sCOD removal during each phase to determine if the means were statistically different. When comparing the results from the control phase (Phase I) with the results from Phase II (6% produced water in the influent) there was evidence that the means were significantly different (t-test, $P=0.005$). However, average sCOD removal improved from Phase I (average removal 84.6 ± 6.4) to Phase II (average removal 90.4 ± 2.8), indicating that better treatment occurred during Phase II. When results from Phase I were compared to results from Phase III, no statistical difference was determined (t-test, $P=0.015$). These results provide evidence that in order to abide by the regulations set by the National Pretreatment Program, introducing produced water at 6% or 20% of the total volume should not significantly impact sCOD removal at POTWs.

3.1.3 Phosphorus

Phosphate (PO_4^{3-}) concentrations were measured as phosphorus ($\text{PO}_4^{3-}\text{-P}$) periodically during the study to analyze biological phosphorus removal. PO_4^{3-} in the influent and effluent over time is shown in Figure 3.5. The demonstration-scale SBR-MBR, from which the activated sludge

for this study was obtained, achieved very low PO_4^{3-} removal (9.7%) prior to seeding the pilot-scale system; therefore, it was not anticipated that the pilot-scale system would achieve high PO_4^{3-} removal. Over the course of Phase I, the pilot-scale SBR-MBR achieved an average of 56% PO_4^{3-} removal, but did not remain stable during the duration of the phase. This increase in PO_4^{3-} removal, when compared to the demonstration-scale system, can most likely be attributed to selection of polyphosphate accumulating organisms (PAOs) in the pilot-scale system due to dissimilarities in cycle timing and system configuration when compared to the demonstration-scale system.

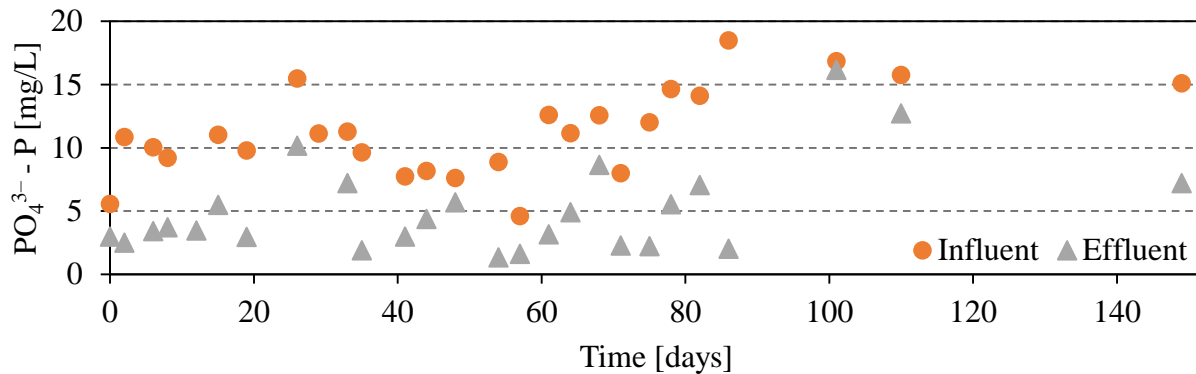


Figure 3.5. PO_4^{3-} concentrations in the influent (orange) and effluent (grey) over the course of 152 days of Phase I. Phosphate removal was not anticipated during this study due to lack of PAOs in the seeding sludge. Produced water was not dosed during this phase.

PO_4^{3-} removal over the course of Phase I was higher than expected, based on the low removal of PO_4^{3-} in the demonstration-scale sludge used for seeding the BRs. Despite higher average PO_4^{3-} removal, the results were highly variable ($55.5\% \pm 22.2$) and never reached a steady state. PO_4^{3-} was measured intermittently throughout Phase II and Phase III. PO_4^{3-} concentrations in the mixed influent and in the effluent as a function of time are shown in Figure 3.6.

PO_4^{3-} was not detected at very low concentrations (0.3 ± 1.2 mg/L) in the produced water, which indicates that the fluctuation of PO_4^{3-} concentration in the mixed influent was primarily due to changes in the residential wastewater. When PO_4^{3-} concentrations measured by Hach kits were compared to PO_4^{3-} concentrations measured by IC (not shown), the results did not correlate to one another for results during Phase II and III, indicating a source of interference in the samples. Due to the inconsistency of this data, results are inconclusive and need to be further investigated.

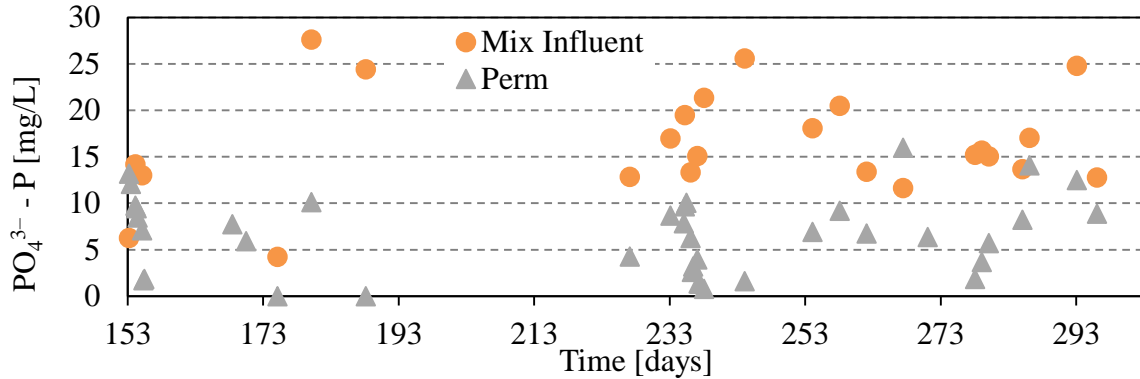


Figure 3.6. $\text{PO}_4^{3-}\text{-P}$ concentration in the influent (orange) and effluent (grey) over the course of Phase II and Phase III. Produced water was dosed at 6% days 175 through 234 and 247 through 299. Dosing changed to 20% for days 235 through 246 and 300 through 317.

3.1.4 Cycle profile sampling

Due to the unique nature of each period in the cycle, a series of grab samples from BR1 were taken every five minutes over the course of a single two-hour cycle. This series of grab samples, referred to as “profile sampling,” took place on the last day of each phase. Samples were analyzed for COD, NH_4^+ , NO_3^- , NO_2^- , and PO_4^{3-} concentrations. DO concentration was recorded continuously throughout the cycle. Each profile sampling event took place at the same time of day to minimize variation in residential influent composition.

Each constituent concentration in BR1 with respect to time in the cycle during Phases I, II, and III are shown in Figure 3.7. Samples during the fill/decant period (0-20 min) were taken from the clarified effluent prior to overflow into the MT. Samples during aeration and settling were taken from the center of the BR contents to ensure a fully mixed sample. The spike in organic matter and nutrient concentrations during the beginning of the cycle (fill/decant period) of Phase I and Phase III profiles (Figure 3.7 (a), (b), and (g)) indicates that more mixing took place than during the fill/decant period of Phase II (Figure 3.7 (d) and (e)). The influent pump was calibrated prior to each sampling; therefore, mixing could likely be a result of constrictions in the influent tubing and fittings, resulting in higher velocity of the influent into the BR. During Phase I, organic carbon was consumed while ammonia was converted to NO_2^- and NO_3^- between the 25th and 30th minutes of the cycle. sCOD and NH_4^+ concentrations quickly dropped during the first aeration period.

Profile sampling was conducted for Phase II at the end of the phase (day 234). Similar to the Phase I sampling, when aeration began at 26 minutes, organic carbon was consumed while

ammonia was converted to NO_3^- . We would expect NO_3^- concentrations to decrease over the anoxic period (59-70 minutes); however, there was no mixing in the BR during the anoxic phases; therefore, grab samples do not represent a homogenous sample during times without aeration.

The final profile sampling took place on day 317 for Phase III. Similar to previous profile sample events, sCOD concentration decreased at the start of the first aeration period. NH_4^+ concentration over the entire cycle remained constant, indicating no conversion took place. To further support this, NO_2^- and NO_3^- concentrations were below zero during the entire cycle.

Major differences in profile sample events can be broken down by constituent. For sCOD, mix influent sCOD concentrations increased at each phase of the experiment; yet, decline in sCOD concentration during each phase occurred over the first 15 minutes of the first aeration cycle. The NH_4^+ , NO_2^- , and NO_3^- profile sampling results were consistent for Phases I and II. No noticeable degradation of NH_4^+ occurred during the profile sampling taken during Phase III; indicating that there was little to no nitrification taking place. PO_4^{3-} concentrations throughout the cycle in Phases I and III were stable, demonstrating that little to no biological phosphorus removal occurred. For Phase II, peaks and valleys of PO_4^{3-} concentration indicate inconsistent release and uptake of phosphorous by PAOs.

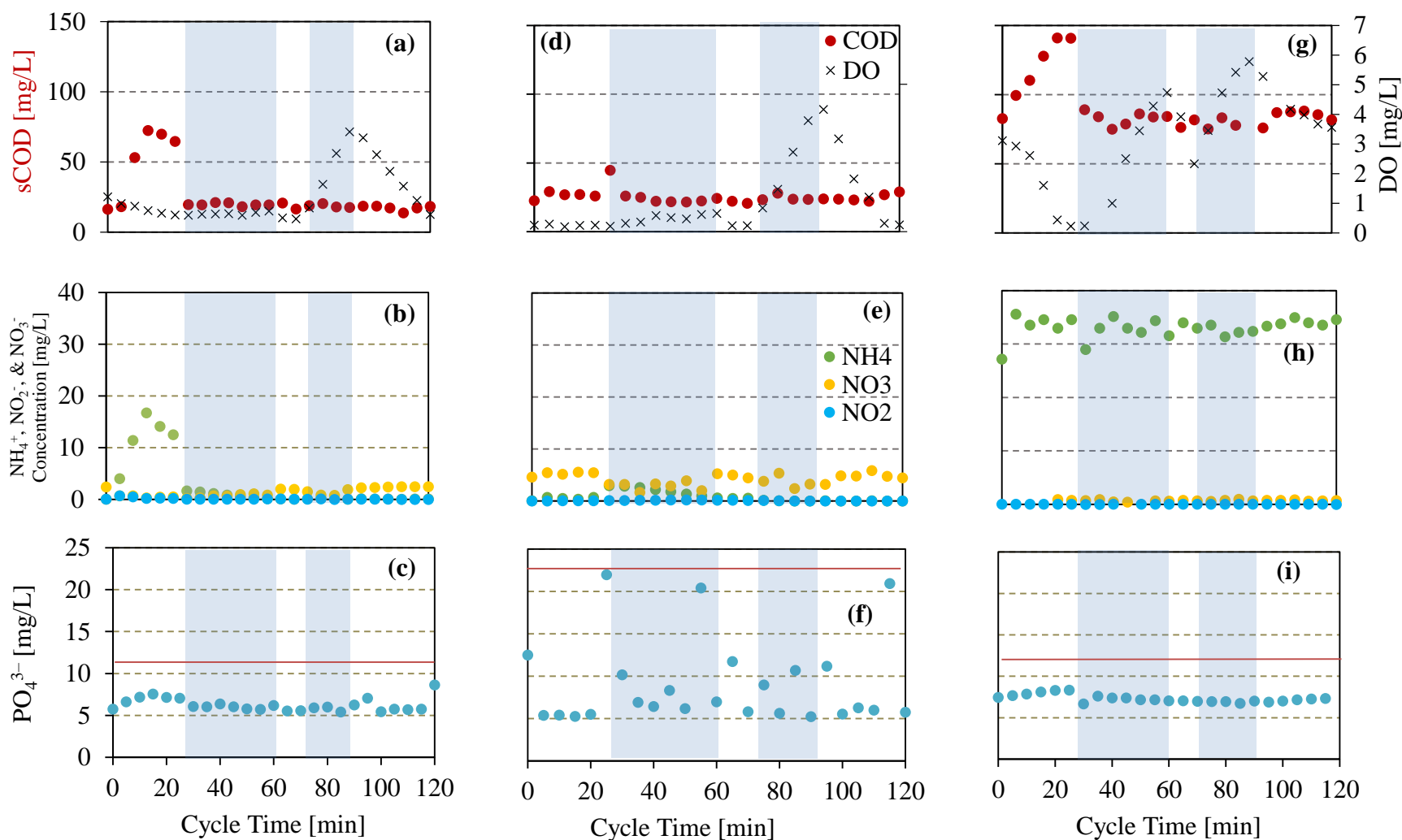


Figure 3.7. sCOD, ammonia, nitrate (NO₃⁻), nitrite (NO₂⁻), and phosphate (PO₄³⁻) concentrations in the BR over the course of one cycle during (a-c) Phase I, (d-f) Phase II, and (g-i) Phase III. Areas highlighted in blue indicate aeration times. During Phase I, influent concentrations of sCOD and NH₄⁺ were 273 mg/L and 40 mg/L, respectively. During Phase II influent sCOD concentration increased to 311 mg/L and NH₄⁺ concentration increased to 56 mg/L. During Phase III, influent sCOD increased further to 407 mg/L and concentration of NH₄⁺ was 31 mg/L. Influent concentrations of PO₄³⁻ are provided by the orange lines in graphs (c), (f), and (i).

3.1.5 Trace organic compounds (TOrcs)

Aqueous samples were collected from the clarified residential wastewater, produced water, BR effluents, and UF permeate during Phases II and III to measure TOrc concentrations in each stream. Of the TOrc that were investigated (i.e., pharmaceuticals, personal care products, artificial sweeteners, flame retardants), most contribution of TOrc in the BR effluents and UF permeate originated from the residential wastewater. High concentrations in the residential wastewater were observed for sulfamethoxazole ($8,442 \pm 4,344$ ng/L), acetaminophen ($67,308 \pm 29,141$ ng/L), caffeine ($31,392 \pm 8,368$ ng/L), and acesulfame ($47,919 \pm 7,839$ ng/L). A complete list of the TOrc influent concentrations is shown in Table 2.5. Except TCP and bisphenol A, none of the analyzed TOrc were detected in produced water samples. Produced water contained low concentrations of the flame retardant TCP and the plasticizer bisphenol A that likely leached from the high-density polyethylene storage tanks. Removal was normalized using mass balance calculations to incorporate dilution effects from absent/lower TOrc concentrations in produced water. Samples were not analyzed for TOrc concentrations during Phase I; therefore, this section only compares results from Phases II and III. A summary of the overall removal for select TOrc during both phases is shown in Figure 3.8.

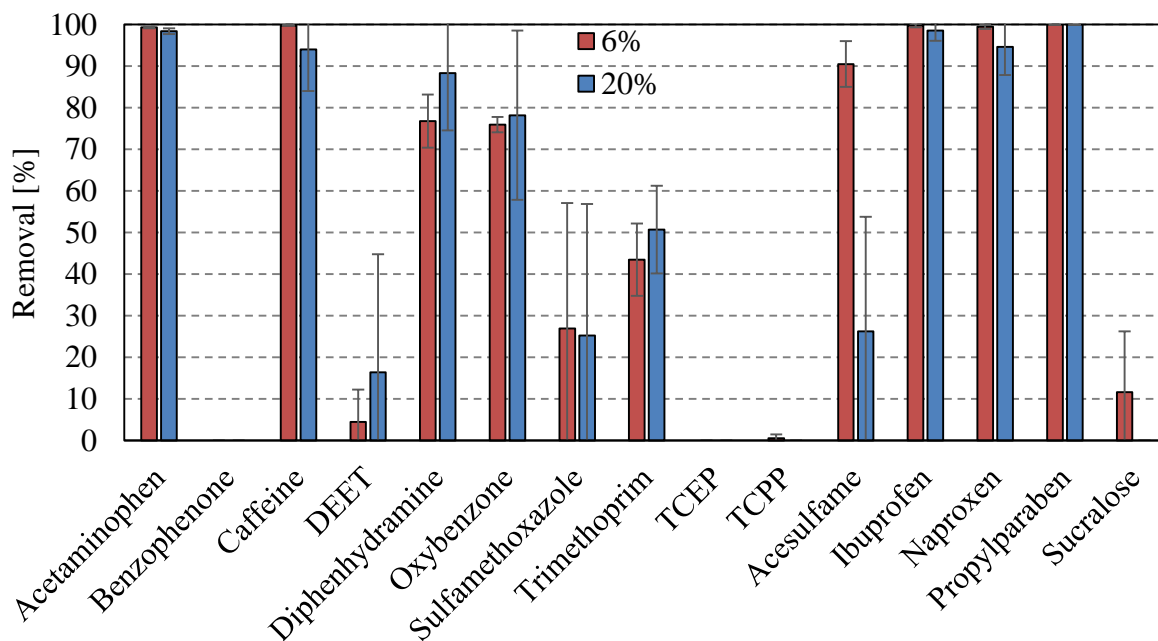


Figure 3.8. Average removal of select TOrc during Phase II and II of the study.

Removal by volatilization or photodegradation was considered to be negligible within the bioreactors; biotransformation and adsorption were assumed to be the main removal pathways for the selected TOxC. Physiochemical properties (i.e., charges, log K_{ow} , pKa, and logD values) for individual TOxC are summarized in Table 2.5. Furthermore, linear model BIOWIN (v4.10, United States Environmental Protection Agency) probability scores were used to predict the biodegradability of analyzed TOxC. Removal during Phase II ranged from 0% for triclocarban, TCEP, TCPP, and benzophenone to 99.7% for ibuprofen. During Phase III removal ranged from 0% for TCEP, TCPP, sucralose, and benzophenone to 99.4% for propylparaben.

Concentrations of the pharmaceuticals acetaminophen, ibuprofen, and naproxen in the mixed influent, BRs, and effluent over the course of a three consecutive day sampling period as well as corresponding sCOD concentrations are illustrated in Figure 3.9.

All three compounds showed good removal (94.6-99.7%) during Phase II and III, which is consistent with previous studies that investigated activated sludge treatment [55-57]. Due to their negative charge (ibuprofen and naproxen) and low logD (acetaminophen), sorption of these pharmaceuticals to the activated sludge in the bioreactors is negligible. Their calculated BIOWIN indices indicate fast biotransformation.

Average removal of acetaminophen, ibuprofen, and naproxen in BR2 during Phase II was 99.3%, 99.7%, and 99.4%, respectively. During this series of testing, BR2 had consistently low concentrations of the three compounds, whereas the concentrations in BR1 were higher and much less consistent. Due to the biodegradability of these specific TOxCs, concentrations in the effluent may be linked to sCOD removal. Higher sCOD removal likely indicates the presence of more active microorganisms. sCOD concentrations in BR1 gradually increased over the three-day period, which may be the reason for inconsistent TOxC removal during this time. As mixed influent TOxC concentrations were extremely variable, sampling was performed for three consecutive days.

The TOxC sampling was repeated over a three-day period during the 20% produced water dosing period in Phase III of the study. Concentrations of the biodegradable pharmaceuticals acetaminophen, ibuprofen, and naproxen during Phase III are shown in Figure 3.10. Average removal of acetaminophen, ibuprofen, and naproxen in BR2 during Phase III were 98.3%, 98.5%, and 94.6%, respectively. Concentrations of biodegradable TOxCs in the BRs and effluent during Phase III (20% produced water by volume in the influent) are not as steady as the removal in BR2 during Phase II (6% produced water by volume in the influent). BR1 performed slightly better than

BR2 based on TOxC and sCOD removal.

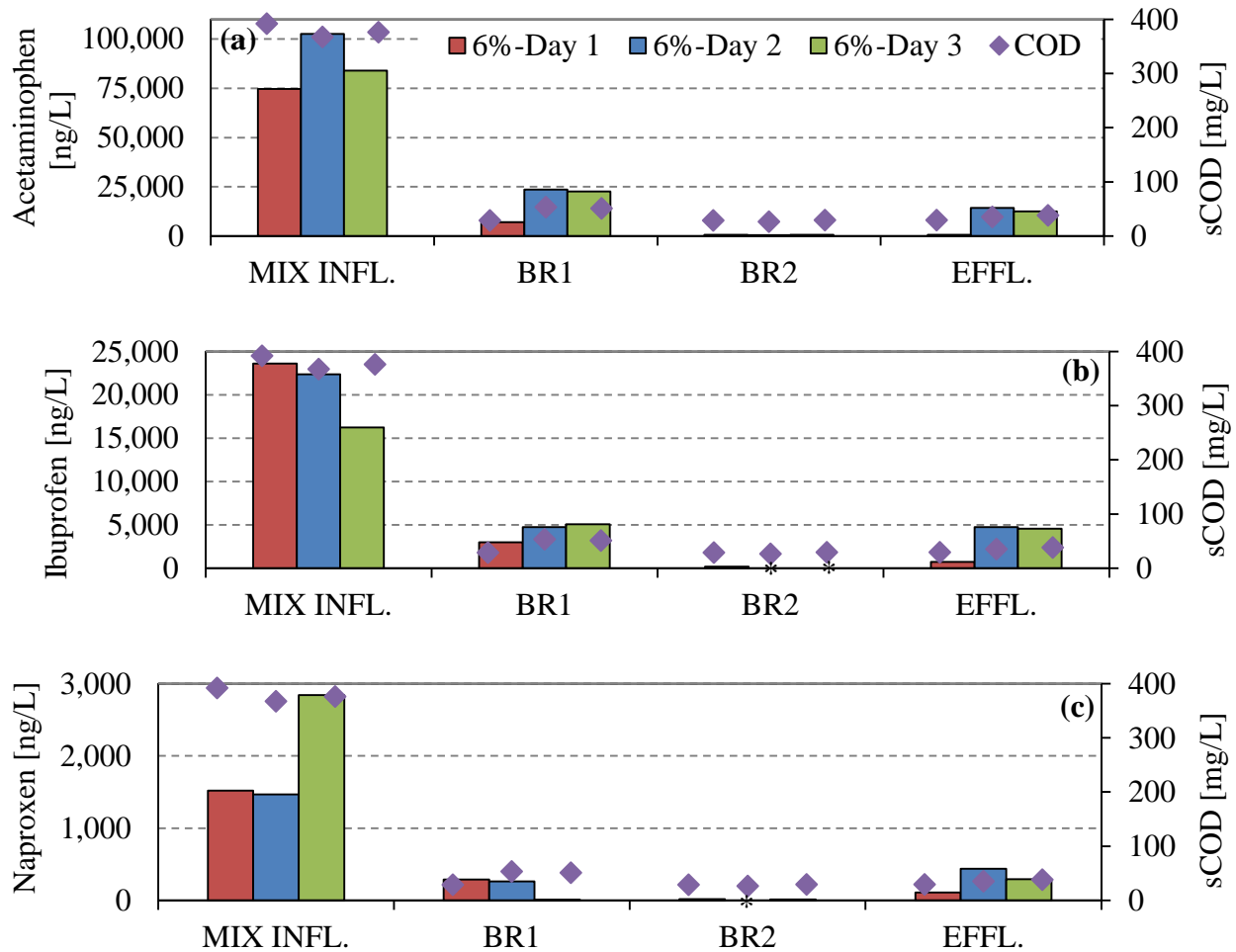


Figure 3.9. Concentrations (ng/L) of biodegradable compounds; (a) acetaminophen, (b) ibuprofen, (c) naproxen in the mixed influent, BRs, and effluent (UF permeate) during Phase II of the study (6% produced water by volume in the influent). Corresponding sCOD concentration (mg/L) is shown on the secondary axis. Concentrations below the limit of quantification are shown with asterisks.

A comparison by percent removal of selected biodegradable TOxCs during Phase II (in BR2) and Phase III (in BR1) is shown in Figure 3.11. Removal of select biodegradable TOxC during Phases II and III were generally high and consistent, indicated by the error bars in Figure 3.11. Results are consistent with removal of acetaminophen, caffeine, ibuprofen, naproxen, and propylparaben in other activated sludge systems [58-60].

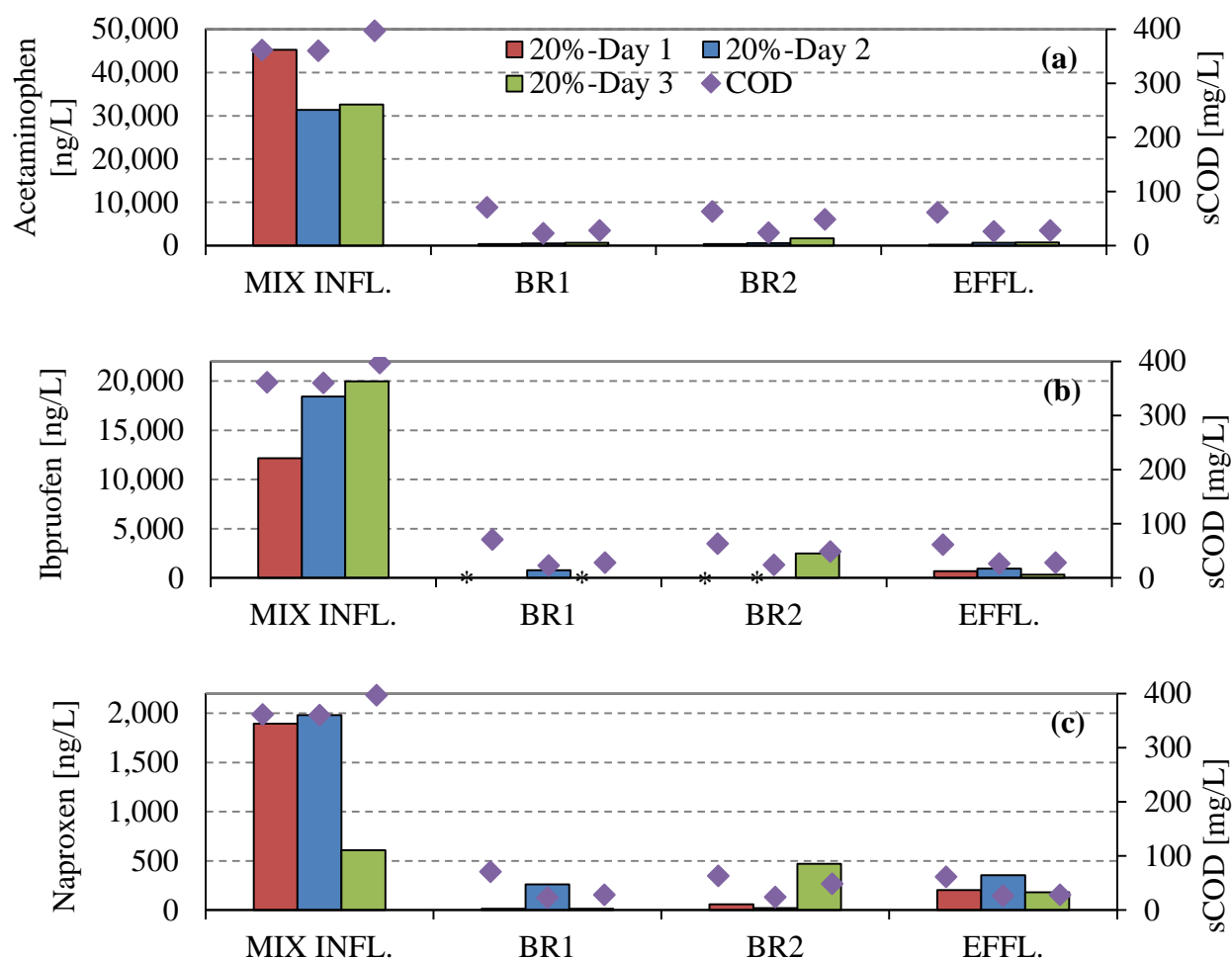


Figure 3.10. Concentrations of biodegradable compounds; (a) acetaminophen, (b) ibuprofen, (c) naproxen in the mixed influent, BRs, and effluent (UF permeate) during Phase III of the study (20% produced water by volume in the influent). sCOD concentration is shown on the secondary axis. Concentrations below the limit of quantification are shown with asterisks.

While biodegradable TO_{RC}s were consistently removed during both phases, the same cannot be said for TO_{RC}s that are more likely to sorb or persist in the waste stream. Acesulfame and sucralose are artificial sweeteners that have lower tendencies to biodegrade and are not likely to sorb to organic matter (i.e., neutral charge, and negative log K_{ow}). Phase II concentrations of these two compounds are shown with respect to sample source and time in Figure 3.12.

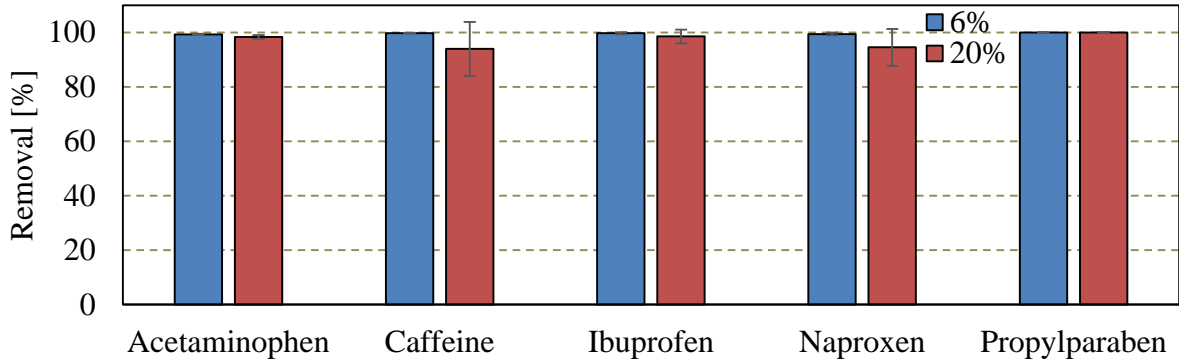


Figure 3.11. Removal of select biodegradable TOCs at 6% and 20% produced water dosing.

Due to the persistence of acesulfame and sucralose in the aqueous environment, they are often used as indicators of anthropogenic influence on groundwater and drinking water sources [61, 62]. Surprisingly, acesulfame was substantially removed during Phase II of the study ($90.5\% \pm 5.5$), but not during Phase III (26.2 ± 27.5). Similar to Phase II removal of acesulfame was reported by Holloway et al. [31] during activated sludge treatment in a hybrid ultrafiltration-osmotic membrane bioreactor. Concentrations of both artificial sweeteners during Phase III sampling are shown in Figure 3.13.

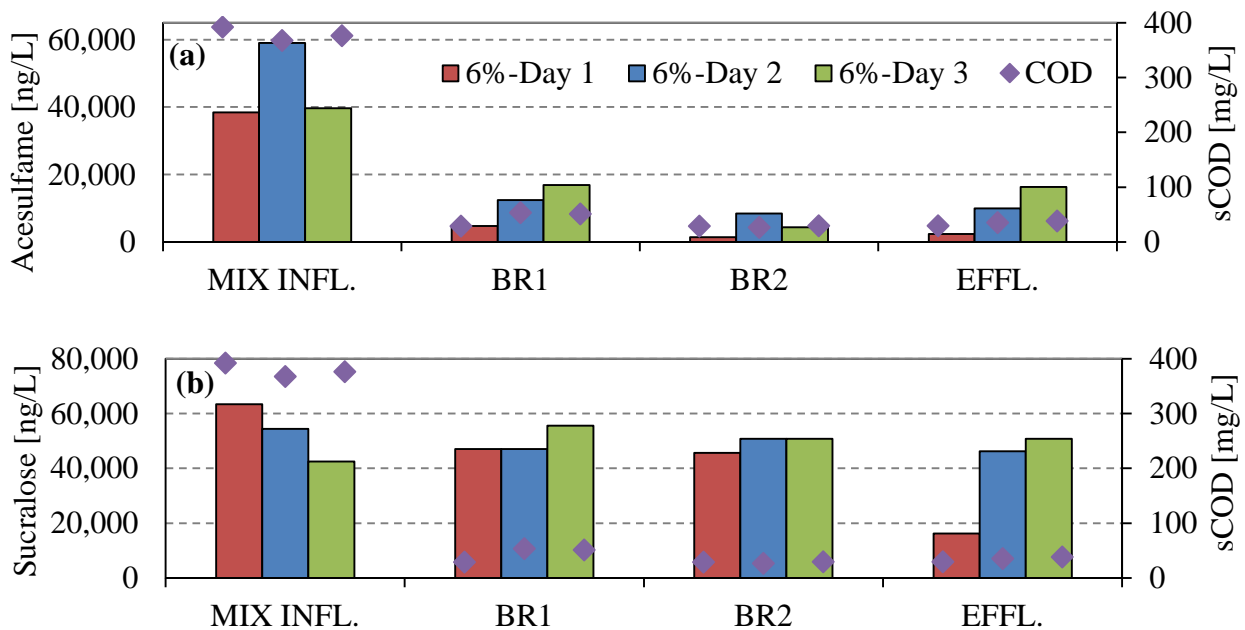


Figure 3.12. Concentrations (ng/L) of artificial sweeteners, (a) acesulfame and (b) sucralose, in the mixed influent, BRs, and permeate (effluent) at 6% produced water.

Sucralose removal during Phase III was negligible. Interestingly, acesulfame removal was much more inconsistent ($26.2\% \pm 27.5$) than in Phase II. Possible reasons for this change (e.g., loss of metabolic microbial function) need to be further explored. The removal of TOxC with higher partition coefficients is more dependent on sorption than biodegradation. Diphenhydramine and triclocarban possess high $\log D$ and $\log K_{ow}$ values, indicating high affinity to sorb to activated sludge. Both compounds are shown in Figure 3.14 during Phase II conditions.

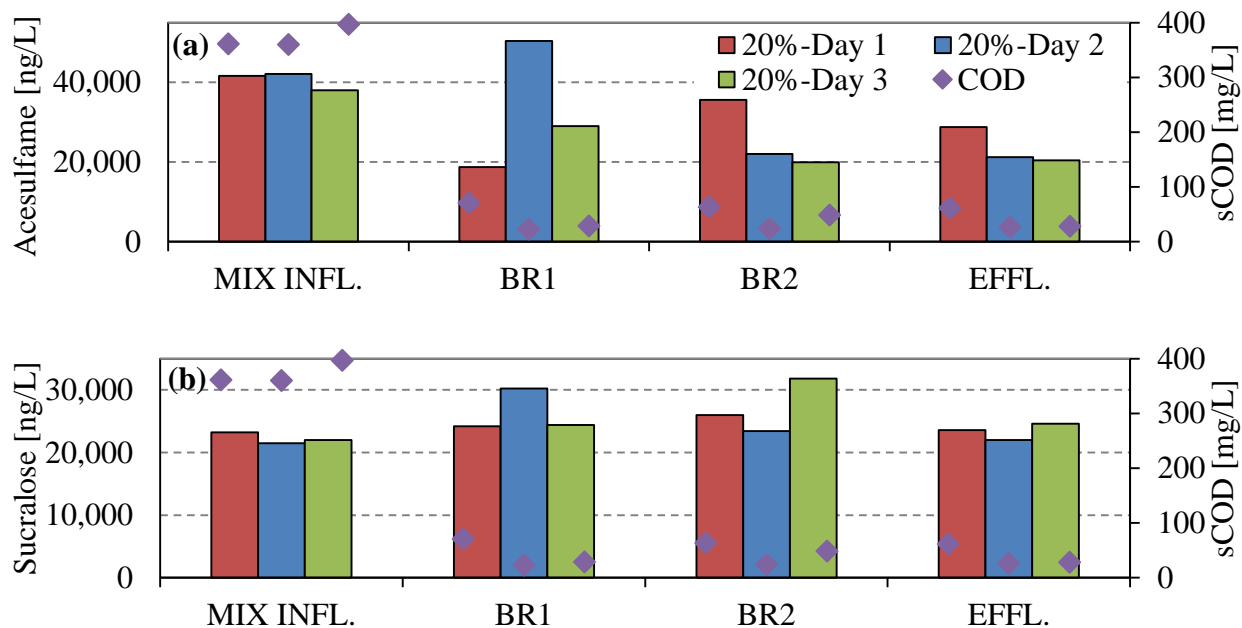


Figure 3.13. Concentrations (ng/L) of artificial sweeteners, (a) acesulfame and (b) sucralose, in the mixed influent, BRs, and permeate (effluent) at 20% produced water.

The higher concentrations of triclocarban in BR2 and the UF permeate compared to mixed influent concentrations may be the result of desorption of previously sorbed triclocarban onto sludge.

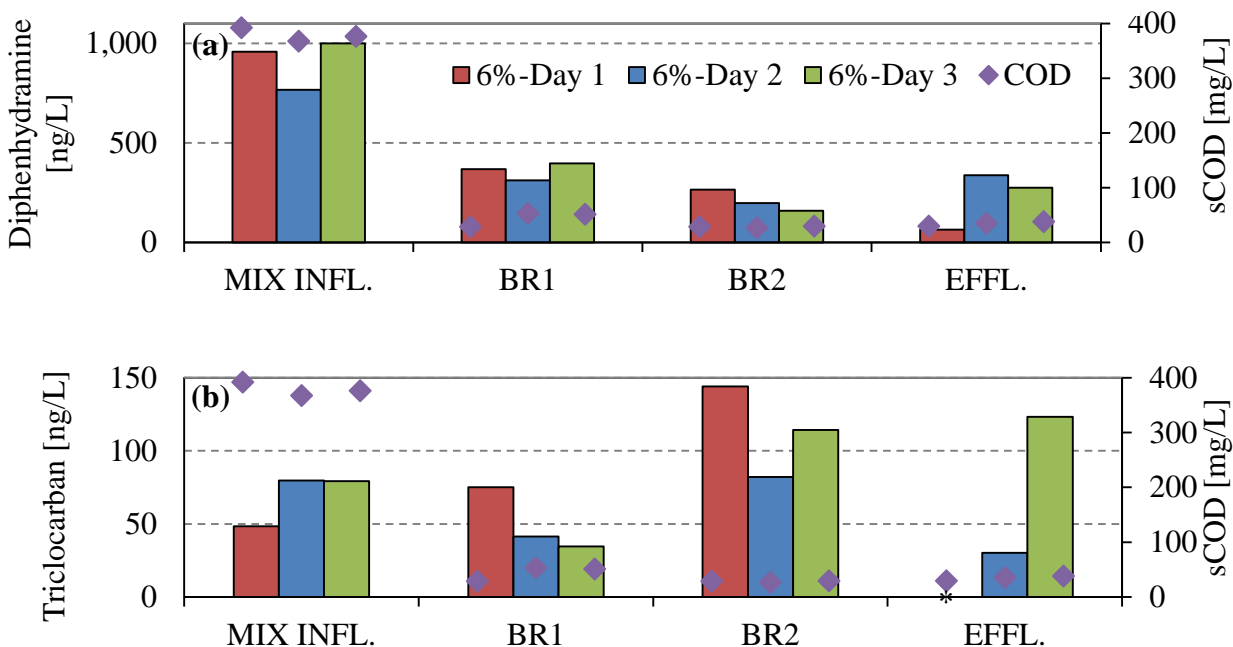


Figure 3.14. Concentrations (ng/L) of (a) diphenhydramine and (b) triclocarban in the mixed influent, BRs, and effluent (UF permeate) during Phase II dosing of produced water. sCOD concentration is shown on the secondary axis.

The antibiotics sulfamethoxazole and trimethoprim which are commonly ingested together, were present during both sampling events as shown in Figure 3.15. Sulfamethoxazole was found at particularly high concentrations in the mixed influent ($8,442 \pm 4,344$ ng/L). The original use of these compounds is to inhibit microorganism growth; therefore, high concentrations could influence the effectiveness of biological treatment. Effective concentrations (EC_{50}) of sulfamethoxazole on microorganisms common to biological wastewater treatment (i.e., *Bacteroides*, *Clostridium*, and *Fusobacterium*) have been reported at concentrations (e.g., 11,000,000-53,000,000 ng/L) much higher than what was present in the mixed influent—indicating concentrations are not high enough to produce an adverse effect on microorganisms during treatment [63].

BR1 effluent sulfamethoxazole concentrations remained consistent during Phase II testing while trimethoprim concentrations gradually increased over time. This resulted in an increase in trimethoprim concentration in UF permeate (effluent). During Phase III, trimethoprim concentrations in the BR effluent and UF permeate (effluent) fluctuated less over the three day period. Both compounds showed no significant differences in overall removal performance in

regard to produced water percentage (Figure 3.8).

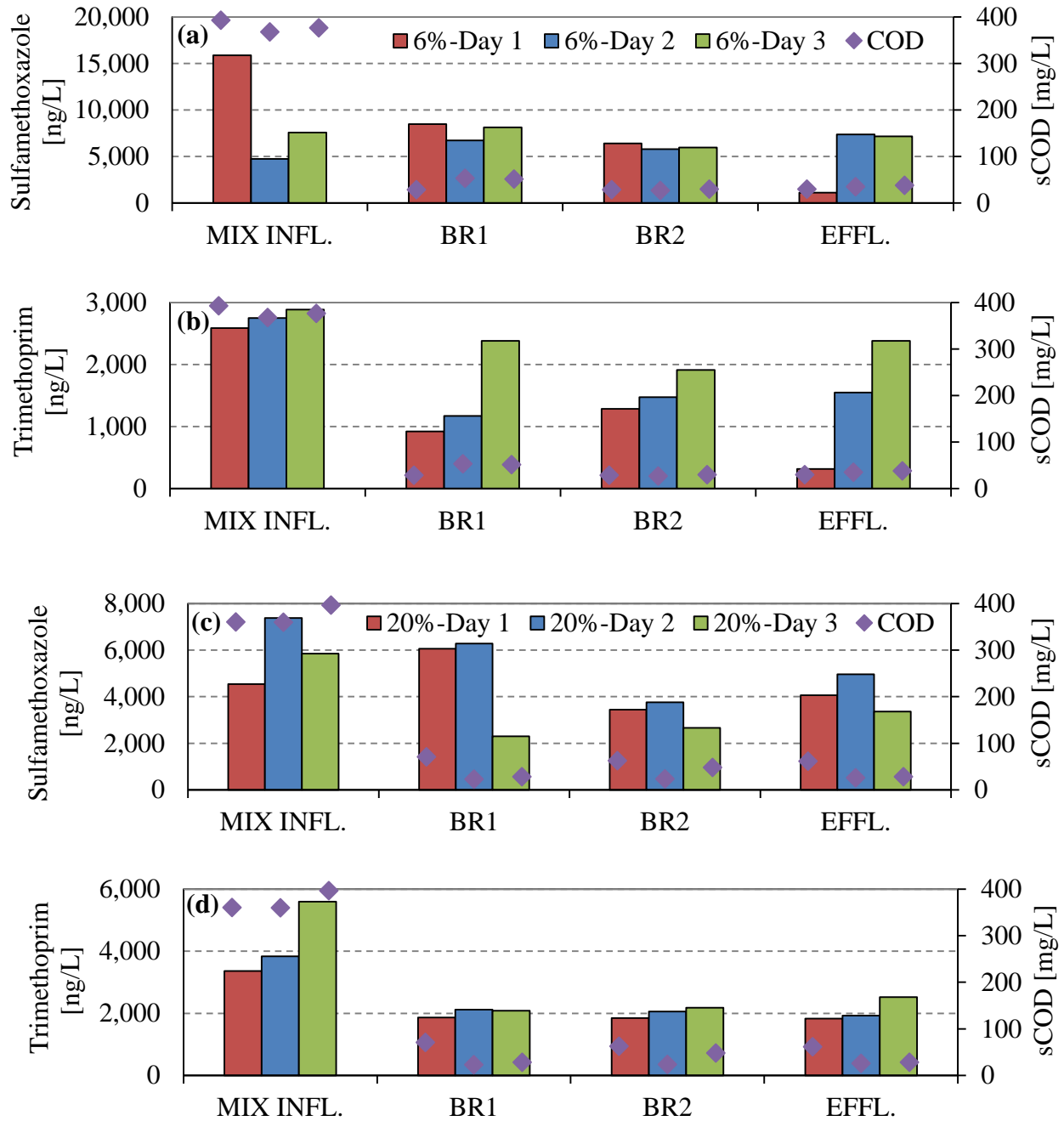


Figure 3.15. Concentrations (ng/L) of (a) sulfamethoxazole and (b) trimethoprim during Phase II dosing of produced water; (c) sulfamethoxazole and (d) trimethoprim during Phase III. Concentrations in the mixed influent, BRs, and effluent (UF permeate) are shown for each. sCOD concentration is shown on the secondary axis.

Overall, the SBR-MBR system achieved high removal of more readily biodegradable compounds during both phases, and achieved less removal of compounds unlikely to biodegrade. In order to evaluate TO₅C removal when compared to not dosing produced water, future research will gather TO₅C data during control conditions.

3.1.6 Inorganic constituents

According to the National Pretreatment Program, industrial wastewater must not introduce contaminants that will pass through the treatment process without treatment. Mixing produced water with a residential wastewater treatment stream presented an influx of inorganic constituents into the pilot-scale SBR-MBR system. In general, POTWs operating secondary treatment systems, such as SBR systems, typically exhibit low removal of inorganic contaminants while POTWs operating advanced treatment are able to achieve higher removal [22]. Low removals in typical POTWs emphasize the importance of evaluating the fate and transport of inorganic constituents during this study.

Average arsenic, selenium, barium, lithium, boron, zinc, copper, and strontium concentrations dissolved in the mixed influent and effluent during each phase are shown in Figure 3.16. A general increase in concentration of each constituent can be seen with increasing fraction of produced water in the influent.

Copper and zinc are of importance because they have been proven to inhibit nitrification; however, concentrations of both constituents were much lower in the mixed influent than what is reported in the literature to cause nitrification inhibition [43, 44]. Although POTWs are not required to meet discharge standards of the National Primary Drinking Water Regulations (NPDWR), this regulation serves as a legitimate basis to determine severity of effluent concentrations. Copper, barium, selenium, nitrate, and nitrite are regulated by the NPDWR [64].

Of these constituents, average concentrations in the effluent were below the maximum contaminant level (MCL) provided in the NPDWR. Arsenic was present in the effluent at concentrations above the MCL during each phase of the experiment, including Phase I; however, effluent concentrations remained below the maximum chronic concentration of 0.15 mg/L recommended for aquatic life by the EPA [65]. Due to the inconsistencies of the arsenic concentration measurements, more information is needed to determine if arsenic release would be a risk to the environment.

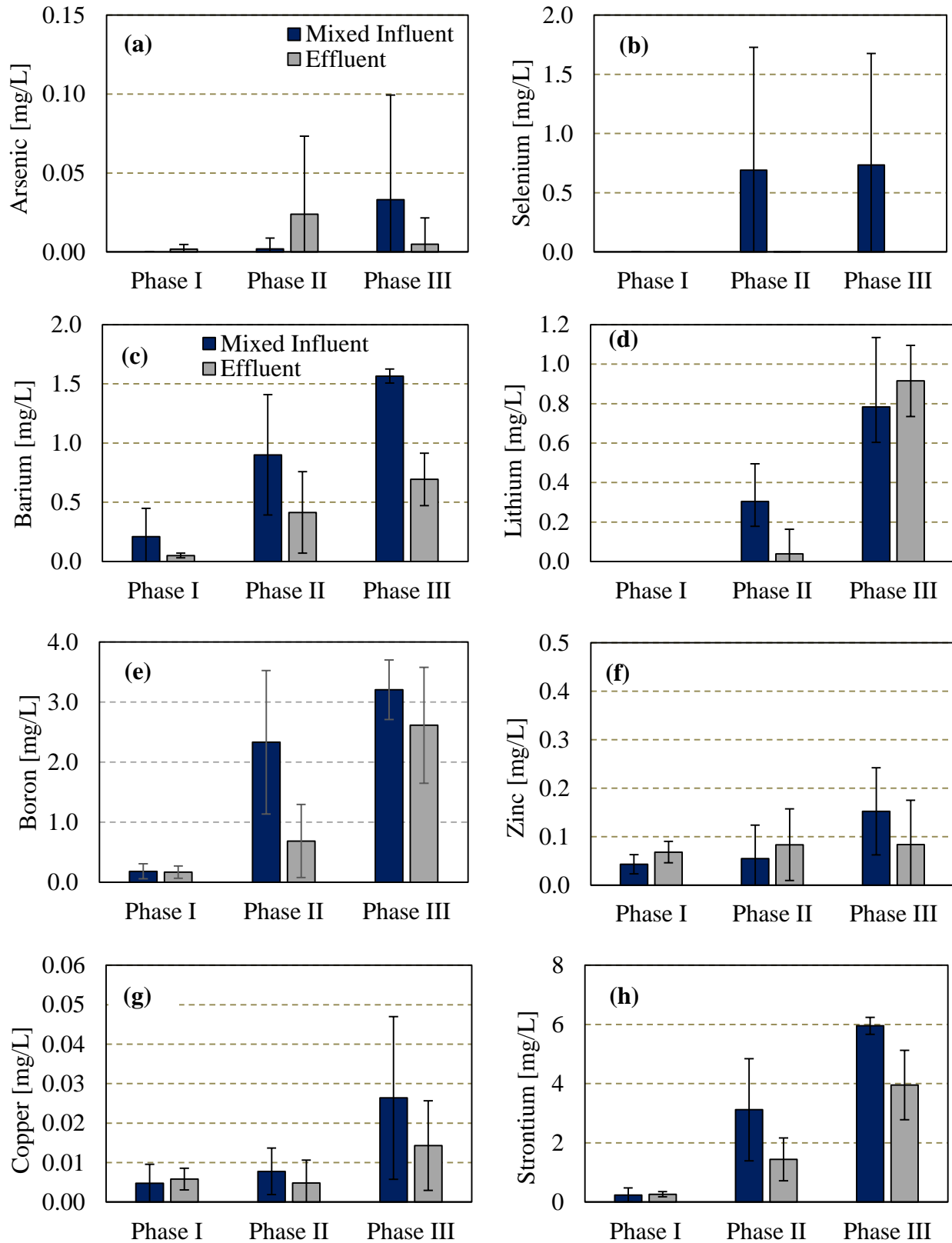


Figure 3.16. Influent and effluent concentrations of (a) arsenic (b) selenium, (c) barium, (d) lithium, (e) boron, (f) zinc, (g) copper, and (h) strontium during Phases I, II, and III.

Overall, if abnormally high concentrations of inorganic constituents are not removed during the treatment process, POTWs could be in violation of the National Pretreatment Program. Specific effluent guidelines need to be addressed on a case-by-case basis based on discharge permit limits.

3.2 Sludge characteristics and composition

The ability of the SBR-MBR system to remove primary constituents from the mixed waste stream was dependent on the sludge characteristics for the duration of the study. The following subsections compare activated sludge quality and quantity.

3.2.1 Sludge characteristics

Solids in the form of TSS (MLSS), VSS (MLVSS), and FSS are all important parameters to calculate sludge age, substrate growth rates, and SRT for traditional SBR systems. MLSS from BR1, BR2, and the MT during Phase I and after settling for 30 minutes are shown Figure 3.17.



Figure 3.17. Sludge settling characteristics of BR1, BR2, and the MT over a 30-minute period. The poor settling of the MT sludge is the reason for not recycling sludge back into the BRs.

This photo exemplifies the poor settling characteristics of the MT sludge compared to the BR sludge. Poor settling characteristics of the MT sludge didn't allow for recirculation into the BRs due to loss of this sludge once again during the fill/decant period. For this reason, the pilot-scale SBR-MBR system is unique in that no sludge was recirculated or intentionally wasted during operations, indicating an undefined SRT.

Average concentrations of TSS, VSS, and FSS in the BRs during the three phases of the study are summarized in Table 3.2. Concentrations of TSS, VSS, and FSS were consistent over time in both BRs; therefore, values from both BRs were combined to calculate the average.

Table 3.2. Average TSS, VSS, and FSS concentrations during the three phases of the study.

	Phase I	Phase II	Phase III
TSS, mg/L	2,065±602	2,632±790	3,958±244
VSS, mg/L	1,878±464	2,328±548	3,274±225
FSS, mg/L	292±118	331±267	673±60

The sludge from the demonstration-scale system does not possess good settling characteristics and was easily wasted into the membrane tank during the early days of Phase I. MLSS concentrations (shown as TSS in Table 3.2) remained lower than desired until the sludge acquired better settling ability. Desired MLSS concentrations of approximately 4,000 mg/L were not met until Phase III; therefore, sludge was not wasted throughout the study. While each variable individually increased over time, the ratio of VSS to TSS (VSS:TSS) remained constant throughout the study with average values of 0.85 ± 0.16 and 0.83 ± 0.15 for BR1 and BR2, respectively. VSS:TSS indicates the impact of organic matter on sludge composition as well as the relative sensitivity to sludge age, and a steady VSS:TSS ratio indicates stable sludge production over the entire study. Because TSS is the sum of VSS and FSS, this ratio also indicates that the inorganic material (FSS) associated with the sludge remained stable over the entire study.

3.2.2 Sludge composition

Sludge samples were analyzed for inorganic constituents to determine if leaching would be a concern for POTWs interested in land application of biosolids. Concentrations of arsenic, cadmium, copper, lead, mercury, molybdenum, nickel, selenium, and zinc in biosolids are regulated under the Clean Water Act, 40 CFR 503. Concentrations of these inorganic constituents were measured using solids extraction methods followed by ICP analysis of the leached ions. Measurements were corrected to include only the metals present in the solids samples. This correction was made due to the high water content in the solids samples; however, to normalize the data to typical solids water content (80%) often used for regulatory compliance, a correction factor was implemented. The values of the solids concentration as well as the corrected solids concentration are summarized in Table 3.3.

Table 3.3. Concentration of regulated inorganic constituents found in sewage sludge during the study.

Constituent	Concentration based on dry solids only mg/kg			Corrected concentration using 80% water content mg/kg		
	Phase I	Phase II	Phase III	Phase I	Phase II	Phase III
Copper	158±31	208±105	106±30	158±31	167±105	107±30
Molybdenum	6.2±1.5	6.7±2.0	0.5±0.7	6.2±1.5	6.7±2.0	0.50±0.78
Zinc	734±135	735±209	441±100	734±135	736±209	442±100

All the regulated contaminants tested were found in concentrations lower than regulation requirements. It is important to note that arsenic, cadmium, lead, nickel, and selenium were not detected in any samples, and mercury was not tested for. Concentrations of copper and zinc increase between Phase I and Phase III; however, concentrations of all three ions are lower during Phase III. pH remained stable during all three phases, so complexation of metals in the sludge should be held constant. This anomaly of lower concentrations in Phase III is a finding that will require further research.

3.3 Microbial analysis

DNA extraction and Illumina sequencing were used to analyze the microbial community present with respect to time over the course of the study. Samples of residential wastewater and produced water were collected and analyzed to establish a baseline of the microbial community present in each of the influent streams. Activated sludge samples from both BRs were taken to compare the relative abundance of microorganisms in the mix influent and in the BRs over time. Sequence data was processed using QIIME to calculate the relative abundance of microorganisms in each sample.

While a single sample provides a snapshot of the relative abundance of microorganisms present at a single point in time, it does not distinguish between living or dead cells. However, taking multiple samples over time, allows us to distinguish live cells by comparing the relative abundance of microorganisms in each sample. If the relative abundance of any microorganism persists over time, it indicates that the species is alive. The relative abundance of the microbial community (by phylum) present in the residential wastewater is shown in Figure 3.18.

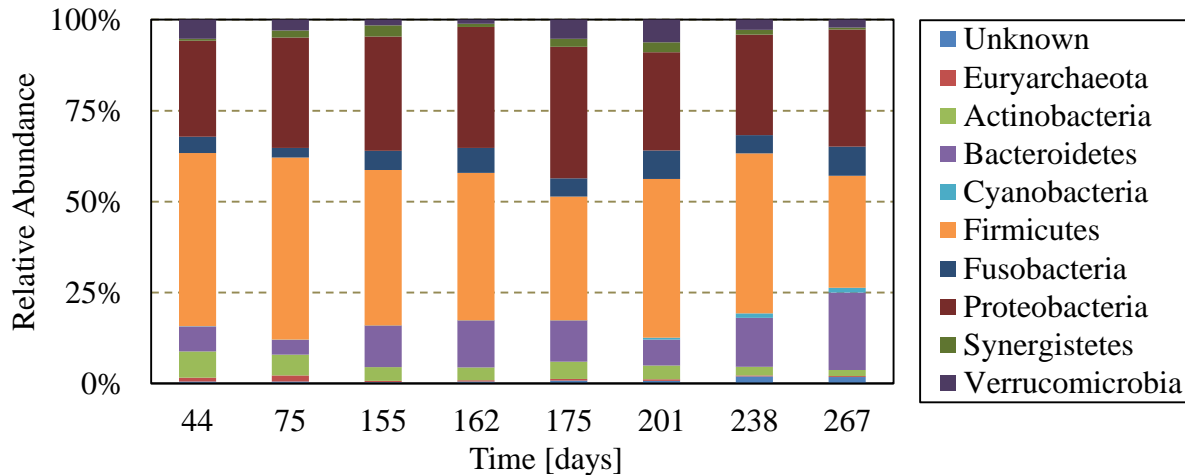


Figure 3.18. Relative abundance of microorganisms by phylum that were present in residential wastewater over the course of the study.

The consistency of the microbial community entering the BRs from the municipal wastewater is notable. Organisms belonging to the phyla Firmicutes (30-48%) and Proteobacteria (25-35%) dominated the influent community. The phylum Firmicutes contains organisms common to municipal wastewater streams such as Clostridiales and Lactobacillales. Both of these classes exhibit fermentative metabolic processes under anaerobic environments for the conversion of sugar to acids, gases, or alcohols [66]. Proteobacteria present in the residential wastewater include classes such as Alphaproteobacteria, Betaproteobacteria, and Gammaproteobacteria that specialize in metabolizing carbohydrates [66]. Microorganisms of the phylum Fusobacteria (4-7%) primarily ferment carbohydrates to produce organic acids. The relative abundance of the order Fusobacteriales increased in the residential wastewater samples over time. Known to have a fermentive metabolism, these organisms are essential for the breakdown of carbohydrates in wastewater to produce soluble sugars, proteins, and acids [66]. These by-products supplement other microbial processes, such as methanogenesis, to further digest contaminants. The presence of multiple anaerobic microorganisms that specialize in the degradation of carbohydrates provides the BRs with a diverse, healthy microbial community to allow for further removal of contaminants during the treatment process.

The relative abundance of microorganisms in produced water with respect to time is shown in Figure 3.19. Microorganisms present in produced water are from the phyla Proteobacteria (27-60%) and Bacteroidetes (13-35%). Notably, none of the Proteobacteria present in the produced water were similarly expressed in municipal wastewater, indicating significant differences

between each unique community. Flavobacteriales (p_Bacteroidetes) have been reported in produced water, saline waters, and freshwaters—indicating its ability to survive in a variety of environments [17]. They have also been associated with the degradation of hydrocarbons present in contaminated soils [67].

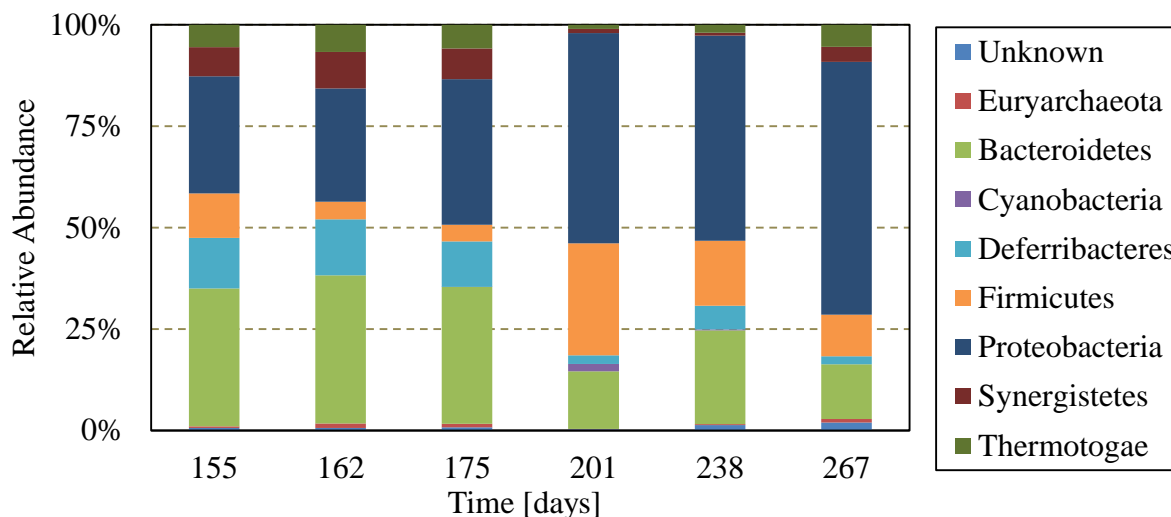


Figure 3.19. Relative abundance of microbial community in the produced water as a function of time.

Over the course of the study, the relative abundance of Bacteroidetes in the produced water gradually decreased. Bacteroidales, Flavobacteriales, and Saprospirales are three dominant orders present in the produced water samples at a relative abundance greater than 1%. Bacteroidales abundance decreased from 29% on day 155 to 8% on day 267 while Flavobacteriales and Saprospirales remained constant. Bacteroidales, often present in fecal matter, primarily ferment sugar under anaerobic environments but may also utilize proteins if needed [66]. A potential cause for the decrease in abundance of these microorganisms over time may involve a diminishing food source while stored in the produced water storage tank. During this same period of time, the presence of Proteobacteria, primarily Kiloniellales, increased. Kiloniellales are mesophilic organisms commonly found in marine environments [68]. The saline environment and ambient temperatures likely led to growth in relative abundance of this organism. Fluctuations determined in relative abundance may also be attributed to changes in how the produced water was stored during this time (i.e., fully mixed, aerated, sun exposure).

Relative abundance of microorganisms in the two BRs over the course of the study is

shown in Figure 3.20. Abundance during Phase I is indicated by red boxes while abundance during Phase III (20% produced water) is emphasized by blue boxes. Despite slight variations in constituent removal, both BRs demonstrated similar relative abundance trends over time. The stability in the relative abundance of the microbial community demonstrates that these microorganisms are robust under changing environments.

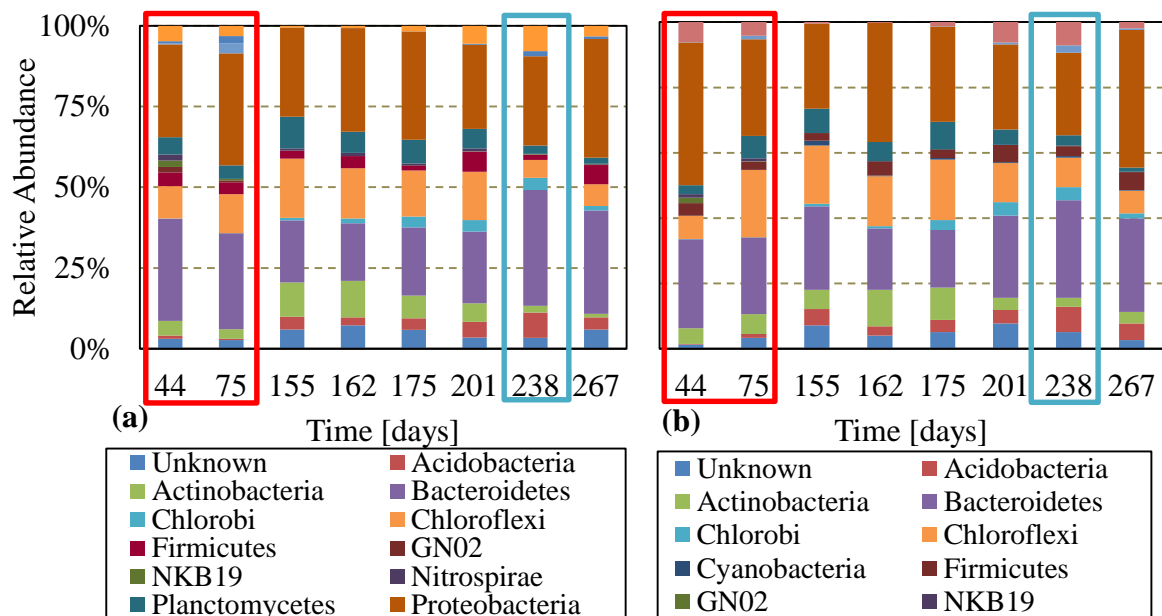


Figure 3.20. (a) BR1 and (b) BR2 trends of microbial community relative abundance over time. Days 44 and 75 (marked in red) represent control samples taken during Phase I. Phase II samples include days 155, 162, 175, 201, and 267. Day 238 was taken during 20% produced water, indicated by the blue box.

Trends of relative abundance in the BRs are similar at the phylum level. Bacteroidetes (17-35%) and Proteobacteria (24-34%) dominate the communities in the BRs over the entire course of the study. The Proteobacteria present represent microbial communities from the residential wastewater influent (Bacteroidales) as well as the produced water influent (Flavobacteriales). Relative abundance analysis provides evidence that a mixture of these microbial clades stems from the unique influent communities. Interestingly, the relative abundance of Firmicutes in the municipal wastewater drastically decreases when exposed to the BR communities. The aeration processes in each BR may contribute to this loss because Firmicutes thrive in anoxic conditions. Despite the greater portion of residential wastewater in the mixed influent, dominant microorganisms from the produced water were able to proliferate and impact overall community

function by contributing to organic matter degradation. Organisms of the phylum Bacteroidetes are common throughout the samples, most likely due to their affinity to warm, saline environments [69]. A possible reason for the slight decline in this community of microorganisms during Phase II may be the cooler ambient temperatures. Nitrospirales tend to be prevalent in biological wastewater treatment due to their ability to degrade ammonia; however, they were only found in small abundance (<1%) throughout the study.

The stability of relative abundance at the phylum level indicates robustness of the microbial community in the BRs over time. Fluctuations in produced water community did not have an adverse effect on BR community. No difference in community composition could be associated with the nitrogen and sCOD removal upsets that occurred during Phase I or at the end of Phase II. A more detailed analysis using specific species from the phylum outlined here would be helpful in making these correlations. Further sampling events are needed in order to evaluate if the microbial community present at 20% produced water remains consistent over time. Additional samples will provide evidence as to whether the microbial community present at 20% produced water is stable.

CHAPTER 4

CONCLUSIONS

Utilizing existing POWTs for produced water treatment has the potential to minimize capital costs to provide treatment as an economically competitive alternative to deep well injection for O&G operations. Treating O&G wastewater will result in availability of water for future applications instead of rendering it unavailable through subsurface injection.

The fraction of produced water mixed with municipal wastewater increased over the course of the study to allow time for the microorganisms to adapt to the varying influent conditions. The use of an SBR-MBR allowed the cultivation of specific microorganisms to degrade organic compounds, nutrients (e.g., phosphorus and nitrogen), and remove colloids.

sCOD removal remained stable during all three phases of the study. NH_4^+ removal remained steady at 6% produced water dose, but decreased substantially when produced water dose increased to 20% of the influent by volume. Accepting produced water at volumes of more than 6% may negatively influence POTWs' ability to achieve NH_4^+ discharge standards. Loss of nitrification is not likely due to the salinity or metal loading on the system. Further tests need to be performed to better understand the loss of nitrification at this fraction of produced water. The SBR-MBR system achieved high removal of more readily biodegradable TO_{RC} during both phases, and achieved lower removal of compounds unlikely to biodegrade. In order to evaluate TO_{RC} removal when compared to not dosing produced water, future research will gather TO_{RC} data during control conditions.

Salinity concentrations in the effluent reached 3.2 g/L NaCl which may violate NPDES permit limits which would require RO treatment prior to discharge. Other inorganic constituent concentrations in the effluent passed the strict NPDWR levels for all constituents throughout the study, except arsenic. Arsenic was present in the effluent during each phase of the experiment, including the control; however, effluent concentrations were below the maximum chronic concentration of 0.15 mg/L recommended for aquatic life by the EPA. Concentrations of inorganic constituents in the biosolids were analyzed at each phase. All regulated contaminants were found in concentrations lower than regulation requirements, with many constituents below detection limit. Relative abundance comparisons showed consistency and robustness of the BR sludge over

the course of the study. Both BRs showed evidence of similar microorganisms present, originating from both the municipal wastewater and the produced water. Further analysis at the order and species level may determine correlations between constituent removal and microbial community.

Ultimately, results from this study indicate that POTWs operating biological treatment processes may be capable of treating produced water up to 6% by volume without exceeding their current effluent permit requirements. Additionally, biosolids chosen for land application purposes should not be negatively affected at this fraction of produced water. In addition to further studies involving the characterization of produced water, it is recommended to investigate the ability of using an SBR-MBR system to pretreat mixed influent in order to implement more advanced processes such as NF and RO to reduce or remove salt concentrations when necessary.

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