

## AN ABSTRACT OF THE THESIS OF

Gavin A. Bushee for the degree of Master of Science in Environmental Engineering presented on September 16, 2016.

Title: Co-treatment of Municipal Wastewater and Landfill Leachate in an Activated Sludge Sequencing Batch Reactor.

Abstract approved: \_\_\_\_\_

Tyler S. Radniecki

A year-long bench-scale treatability study was performed to assess the feasibility of using an activated sludge sequencing batch reactor (SBR) to treat a mixture of domestic wastewater and landfill leachate. A 50/50 (v/v) of domestic wastewater and landfill leachate was treated in a 1 L SBR operated on a 12 hour cycle with a hydraulic retention time (HRT) of 4 days, mean solids retention time (SRT) no less than 25 days, and an average mixed liquor volatile suspended solids (MLVSS) of  $2500 \pm 500$  mg/L. The combined influent had high chemical oxygen demand (COD) and total ammonia nitrogen (TAN), with average concentrations exceeding 1500 mg/L and 450 mg N/L respectively. The combined influent had a carbonaceous biochemical oxygen demand (CBOD<sub>5</sub>) to COD ratio of  $40 \pm 10\%$ , a TAN to COD ratio of  $26 \pm 7\%$ , and also showed seasonal variability in pollutant loadings due to changes in rainfall. The SBR was capable of meeting effluent targets for 5-day carbonaceous biochemical oxygen demand (CBOD<sub>5</sub>) and TAN, which were 10 mg/L and 5 mg N/L respectively, at loadings of up to 100 mg CBOD<sub>5</sub>/L-d and 140 mg N/L-d. However, during the first 8 months, CBOD<sub>5</sub> removal was less consistent, with effluent values often above 20 mg/L, after which time effluent CBOD<sub>5</sub> was consistently below 20 mg/L. Filtration reduced effluent CBOD<sub>5</sub> by 50%, suggesting that a significant

fraction was association with particulate matter. Nitrification performance was inconsistent during the first 7 months of operation, with accumulation of both TAN and  $\text{NO}_2\text{-N}$ , although good nitrification performance was eventually attained with complete nitrification of TAN to  $\text{NO}_3\text{-N}$  and almost 100% TAN removal. The decreased nitrification performance was most likely related to factors such as excess ammonia loading, aeration intensity, and free ammonia, rather than other inhibitory substances in the landfill leachate such as metals or organics.

Aeration adjustments under different loading scenarios showed that the extent of nitrification was highly affected by aeration intensity, with improved nitrification observed with increased aeration. Increased aeration resulted in the complete nitrification of TAN to  $\text{NO}_3\text{-N}$  with effluent TAN and CBOD below target values for a combined influent of 67% landfill leachate and 33% wastewater. Denitrification was achieved only with the addition of methanol, which could provide another option for nitrogen removal in the SBR if reduction of  $\text{NO}_2\text{-N}$  or  $\text{NO}_3\text{-N}$  is needed. Average phosphorus removal in the SBR was approximately 10%. Based on mass wasting of reactor sludge, the reduction in phosphorus corresponded to normal microbial uptake and not to the presence of phosphorus accumulating organisms (PAOs). Metals analysis showed effluent manganese to be consistently below the preliminary target value of 5 mg/L and that reactor solids contained regulated heavy metals at concentrations well below the EPA ceiling limits for land application. Volatile organics and pesticides selected as additional preliminary target pollutants were either well below target limits or were not detected at all in the SBR effluent, although additional data may be needed to further verify whether these contaminants would be an issue in terms of effluent requirements.

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Co-treatment of Municipal Wastewater and Landfill Leachate in an Activated Sludge  
Sequencing Batch Reactor

by  
Gavin A. Bushee

A THESIS

submitted to

Oregon State University

in partial fulfillment of  
the requirements for the  
degree of

Master of Science

Presented September 16, 2016  
Commencement June 2017

Master of Science thesis of Gavin A. Bushee presented on September 16, 2016

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Gavin A. Bushee, Author

## ACKNOWLEDGEMENTS

I would like to give my sincere appreciation to my advisor Dr. Tyler Radniecki for his support and for giving me the opportunity to work on this excellent project for my Master's thesis. I would also like to thank Dr. Lewis Sempini for his involvement as Co-PI on the project, for serving on my committee, and for giving me the opportunity to be involved with the undergraduate seniors' capstone design class. It was a great experience and helped me to build confidence in my work by letting me share what I've learned to others. My appreciation also goes to Dr. Mark Dolan who served as a committee member and offered his support and feedback on my work. His experience and knowledge were a great resource. I would also like to express my gratitude to Amber Berger for serving as my Graduate Council Representative.

I would like to extend my thanks and appreciation to undergraduate students Catherine Mays and Matthew Palmer for their help in the lab and for being dependable and enjoyable to work with. I would also like to thank everyone in the Radniecki lab for being helpful, supportive, and great to work with as well. My most sincere gratitude goes to the CBEE graduate students who gave me their support and for helping to create a fun and friendly work environment. They were always willing to listen and were a great help, especially when I was having problems or questioning myself. It was great getting to know many of them, and I wish them the best in their lives and careers. I would also like to thank Elisha Brackett, Anita Hughes and all the rest of the graduate school staff for helping me with administrative things and for being very nice!

Finally, I would like to thank my wife Layla for her unending love and support. Her kind words of encouragement and willingness to listen were the most valuable resource for me.

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## NOMENCLATURE

AOB.....Ammonia oxidizing bacteria

CBOD.....Carbonaceous biochemical oxygen demand

CBOD<sub>5</sub>..... Five day carbonaceous biochemical oxygen demand

COD.....Chemical oxygen demand

DEQ.....Department of Environmental Quality

DO.....Dissolved oxygen

FA.....Free ammonia

FNA.....Free nitrous acid

HRT.....Hydraulic retention time

$K_N$ .....Ammonium half-saturation constant

$K_O$ .....Oxygen half-saturation constant

$K_s$ .....Soluble organic half-saturation constant

MLSS.....Mixed liquor suspended solids

MLVSS.....Mixed liquor volatile suspended solids

NOB.....Nitrite oxidizing bacteria

## NOMENCLATURE (Continued)

$\text{NO}_x\text{-N}$ .....Nitrite + nitrate nitrogen

PAC.....Powdered activated carbon

$q_{M,N}$  .....Maximum ammonium utilization rate

SBR.....Sequencing batch reactor

SRT.....Solids retention time

SVI.....Sludge volume index

TAN.....Total ammonia nitrogen

TDS.....Total dissolved solids

TN.....Total nitrogen

TSS.....Total suspended solids

VSS.....Volatile suspended solids

v/v.....Volume to volume ratio

## CHAPTER 1

### INTRODUCTION

Landfill leachate is a high strength liquid waste generated by the percolation of rainwater through landfills (Christensen *et al.*, 2001). It is usually collected and either discharged into the sewage system or stored prior to being sent for treatment (Henze & Comeau, 2008; Lema *et al.*, 1988). Landfill leachate poses a threat to the quality of both groundwater and surface waters as it often contains high concentrations of organics, ammonia, and heavy metals (Kurniawan *et al.*, 2006; Xu *et al.*, 2009). Biological treatment of combined landfill leachate and domestic wastewater has gained attention due to its relatively low cost and ease of operation (Renou *et al.*, 2006; Kelly, 1987). However, landfill leachate treatment can often cause difficulties in conventional treatment systems due to high pollutant loadings and the presence of inhibitory substances like heavy metals and chlorinated organics (Renou *et al.*, 2007; Kulikowska & Klimiuk 2008).

The activated sludge sequencing batch reactor (SBR), a type of fill-and-draw reactor, has gained popularity as a robust and cost effective biological treatment system capable of treating strong wastewaters, including landfill leachates (Dockhorn *et al.*, 1997; Artan & Orthon, 2005, Morling, 2009). Many studies have reported high removal efficiencies and low effluent concentrations for key pollutants such as ammonia nitrogen (Yalman & Ortiz, 2001; Li *et al.*, 2009; Doyle *et al.*, 2001). Since landfill leachates can vary widely in their constituents depending on the landfill type, age, and location, it is usually necessary to perform bench or pilot studies to determine the extent to which biological reactors are capable of effective treatment (Kelly, 1987; Lema *et al.*, 1988).

The Coffin Butte landfill in Benton County, OR, which began as a municipal solid waste landfill in 1973, is currently owned and operated by Republic Services. The landfill leachate is collected and sent via tanker trucks to the Corvallis wastewater treatment plant, where it is fed to the system at no higher than a 1% leachate to wastewater ratio. This process is very inefficient and costs Republic Services over two million dollars per year, mostly due to shipping of the leachate. Recently, the nearby City of Adair Village has been seeking to upgrade its wastewater treatment plant, which is past its design life. Adair Village and Republic Services have consulted with Civil West Engineering, Hemphill Water Engineering, and the Oregon Department of Environmental Quality (DEQ) in order to assess the possibility of implementing a system capable of treating the leachate in combination with the city's wastewater. The activated sludge SBR was chosen as the most suitable for the combined treatment, and a year-long bench-scale treatability study was proposed to assess its effectiveness and feasibility.

This thesis presents the results from the treatment study, which included the setup and operation of bench-scale SBRs and the monitoring of the SBRs' treatment performance, based on effluent water quality parameters. The main objectives for the study were as follows:

- Set up and operate SBRs with a 50/50 (v/v) wastewater and landfill leachate feed
- Quantify specified water quality parameters for the combined wastewater and leachate influent
- Monitor system performance based on SBR effluent quality and sludge characteristics
- Verify that the SBR can meet effluent requirements for target pollutants
- Determine if the sludge from the SBR is suitable for land application

Secondary goals of the study were to optimize operational parameters of the SBR, including aeration and cycle times, determine the need for chemical additions, *e.g.* alkalinity, and test the effectiveness of pre- and post-treatments, including filtration and powdered activated carbon (PAC) addition to improve system performance and effluent quality.

The feasibility of implementing the SBR system was to be determined by its ability to achieve effluent targets for pollutants regulated by the Oregon DEQ. Table 1.1 gives the target pollutants and effluent goals for discharge from the combined treatment system. Thus, these were used as the target effluent values for the bench-scale SBR. In terms of discharge regulations and permitting, other pollutants could be added to this list if detected at unacceptable levels in any of the samples.

**Table 1.1** Target effluent goals for the combined treatment system.

Parameter	Target Effluent	Units
Manganese, total	5	mg/L
Benzene	20	ppb
Vinyl chloride	1	ppb
Pentachlorophenol	7	ppb
Bis (2-ethylhexyl) phthalate	10	ppb
Lindane	0.07	ppb
CBOD <sub>5</sub>	10	mg/L
TAN	5	mg/L
TSS	30	mg/L

For the domestic wastewater, the regulated pollutants are the 5-day carbonaceous biochemical oxygen demand (CBOD<sub>5</sub>), total ammonia nitrogen (TAN), and total suspended solids (TSS), with the first two being based on a total monthly average oxygen demand allowance. Permits for discharge from a combined wastewater and landfill leachate treatment system required targets for additional pollutants that were expected to be present in the leachate based on previous data.

In addition to the pollutants given in Table 1.1, the following water quality parameters were monitored during the study:

- Chemical oxygen demand (COD)
- Total nitrogen (TN), nitrite (NO<sub>2</sub>-N), and nitrate (NO<sub>3</sub>-N)
- Alkalinity
- pH
- Conductivity
- Total dissolved (TDS) and volatile suspended solids (VSS)
- Phosphorus
- Color
- Heavy metals

Reactor performance was also evaluated based on sludge characteristics; in particular the biomass concentration, measured as mixed liquor volatile suspended solids (MLVSS), and settling properties, quantified using the sludge volume index (SVI). Sludge samples were also tested for regulated heavy metals in order to determine suitability for land application. Due to the high levels of ammonia nitrogen in the landfill leachate, nitrification was an important biological process in the SBR. Thus, the work presented in this thesis includes a more in depth

look at nitrification, including the effects of aeration and other process conditions on nitrification performance. Phosphorus removal, another important process in biological treatment, was also monitored. Results for all water quality and sludge parameters quantified during the study are presented with discussions.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Landfill leachate

##### 2.1.1 Introduction

Landfill leachate is a complex and high strength liquid waste generated by the flow of rainwater through solid waste landfills (Foo & Hameed, 2009, Christensen *et al.*, 2001). Landfill leachates are often characterized by high concentrations of organic matter, both refractory and readily biodegradable, TAN and organic nitrogen, and inorganic salts. They can also contain toxic substances such as halogenated organics, phenols, heavy metals, sulfides, phthalates, and pesticides (Christensen *et al.*, 2001; Kurniawan *et al.*, 2006; Kulikowska & Klimiuk 2008; Martins *et al.*, 2014; Oman & Junestedt, 2007; Xialoi, *et al.*,2010). Organic and TAN concentrations can often be in the thousands of mg/L, with CBOD as high as tens of thousands of mg/L (Christensen *et al.*, 2001; Henze & Comeau., 2008; Kurniawan *et al.*, 2006, Foo & Hameed, 2009). Due to the large amount of pollutants present, landfill leachate has the potential to contaminate both surface and groundwater if not collected and treated (Tatsi *et al.*, 2003; Lema *et al.*, 1988).

Landfill leachate treatment has gained growing attention due to increasingly stringent requirements for discharge to natural waters (Li *et al.*, 2009). There are many physico-chemical processes that can be effective in treating landfill leachate, including air stripping, adsorption, coagulation & flocculation, and membrane filtration (Ganigue *et al.*, 2007; Ozturk, *et al.*, 2003; Uyger & Kargi, 2004; Yuan *et al.*, 2015). However, these are expensive due to chemical costs and additional sludge production. Conventional biological treatment, *e.g.* activated sludge

systems, has become more popular due to its reliability, lower cost, and relative ease of operation (Renou *et al.*, 2007; Uygur & Kargi, 2004).

Due to the considerable variability between landfill leachates and the high concentrations of pollutants, many difficulties are encountered in biological treatment (Lema *et al.*, 1988). Also, the data for any particular landfill can be scarce, and since leachate quality between landfill sites can be very different, characterization of a particular leachate is essential in determining the appropriate treatment (Chu *et al.*, 1994; Kelly, 1987; Knox; 1984; Kurniawan *et al.*, 2006; Lema *et al.*, 1988). Characterization is also important in determining whether toxic substances, *e.g.* heavy metals or organics, may inhibit biological treatment processes (Chu *et al.*, 1994; Renou *et al.*, 2007).

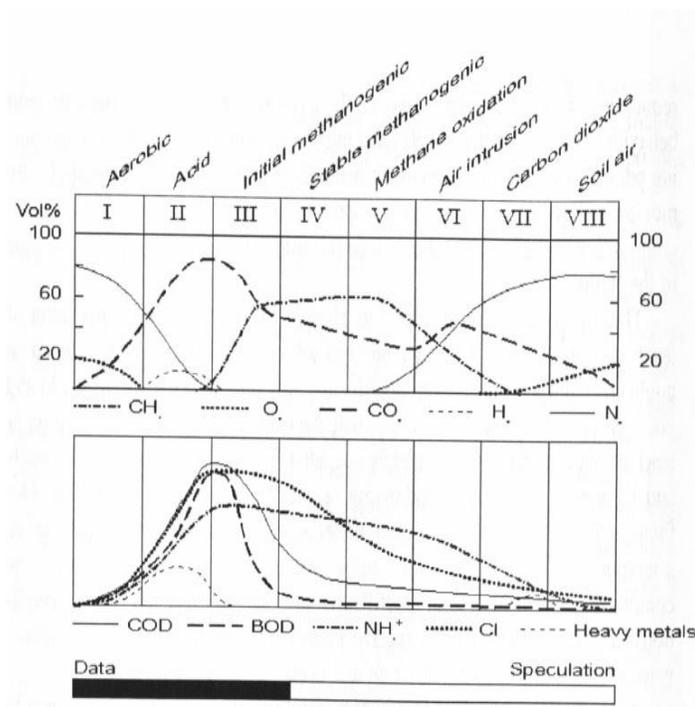
The following review begins with a discussion of landfill pollutants and conditions which lead to the variability in landfill leachate characteristics. Key biological processes in wastewater treatment relevant to landfill leachate treatment are also covered. The discussion ends with a brief overview of the history, uses, and operational principles of activated sludge SBRs, as well as a review of landfill leachate treatment studies using SBRs.

### *2.1.2 Landfill Stages & Landfill leachate Characteristics*

Landfills are known to go through various stages of maturation, which lead to production and degradation of certain compounds, leaching of pollutants, changes in pH, and production of methane (SWANA, 2004). The relative amounts of many pollutants in landfill leachates depend on a variety of factors including precipitation, landfill type, level of compaction, and age, which all have an effect on decomposition. Examples of pollutants that can vary in quantity over the life of a landfill are organics, ammonia, alkalinity, and heavy metals (Renou *et al.*, 2007;

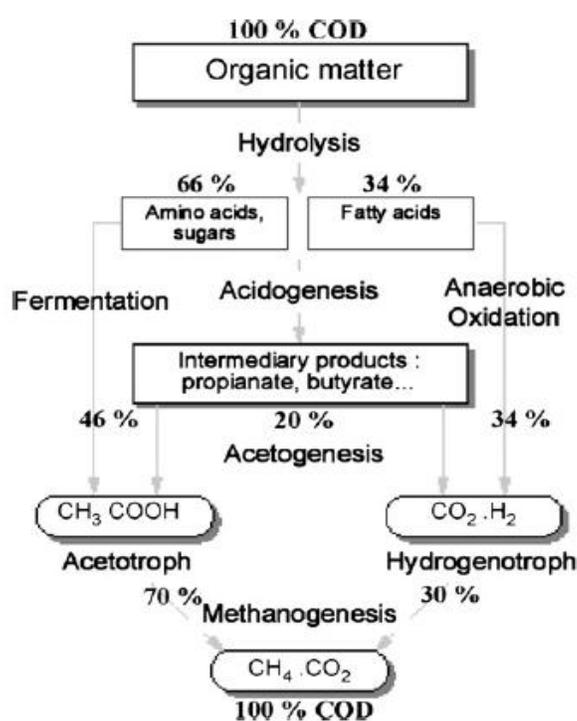
Kulikowska and Klimiuk 2008, Chen 1996). Figure 2.1 gives a diagram showing the various landfill stages and the relative abundance of pollutants at each stage taken from Kjeldsen *et al.* (2002).

After a relatively short initial aerobic phase, the landfill becomes anaerobic. This anaerobic phase is much longer and has two sub-phases associated with it: an early acidic phase, and a later methanogenic phase. As can be seen in Figure 2.1, the initial amount of ammonia is lower and increases more rapidly by the start of the anaerobic phase, as do the COD and CBOD. Metals concentrations are at their highest during the initial acidic stage and begin to decline. The initial methanogenic stage sees a rapid decrease in CBOD and increased methane production, analogous to an anaerobic digester. There is also an increase in sulfide production from sulfates during this stage due to the reducing environment (Aucott, 2006).



**Figure 2.1** Municipal landfill stages with relative pollutant abundance (adopted from Kjeldsen *et al.*, 2002).

The changes during the various decomposition stages lead to some important characteristics pertaining to treatment of landfill leachate. One important factor is the relative amount of COD and CBOD, or the CBOD/COD ratio, which changes significantly over the life of a landfill (Christensen *et al.*, 2001). This process is shown in detail by the diagram in Figure 2.2, which was taken from a comprehensive review of landfill leachate treatment by Renou *et al.* (2007).



**Figure 2.2** Balance of COD and organic fractions in landfill leachate (adopted from Renou *et al.*, 2007).

Landfills in an early acidic stage typically have a higher CBOD/COD ratio, with a large portion of the CBOD consisting of short chain organic acids and alcohols (Kjeldsen *et al.*, 2002; Chen, 1996). The CBOD to COD ratio then decreases over time due to the breakdown of these easily biodegradable organics, also resulting in a rise in pH, and production of carbon dioxide

and methane. The recalcitrant COD fraction becomes larger as does the amount of TAN, which is produced via release of nitrogen during anaerobic breakdown of the organics. This TAN has no pathway for removal in the anaerobic environment, and so it remains for many years (Kurniawan *et al.*, 2006; Kjeldsen *et al.*, 2002). Thus, older landfills in a methanogenic stage will have higher levels of both TAN, recalcitrant COD, and higher pH, whereas very young landfills in an acidic stage will have higher CBOD, and lower pH.

Figures 2.3 - 2.5 give pollutant concentrations, including CBOD to COD ratios, taken from Kjeldsen *et al.* (2002) Christensen *et al.*, (2001), and Chu *et al.* (1994), who presented compiled data from a variety of landfill leachate studies. The figures include comparisons between acidic and methanogenic landfills, CBOD to COD ratios for methanogenic landfills, and pollutant ranges for landfills of various ages, respectively. The ranges of values in these figures show the widely varying nature of landfill constituents, both between landfills and over the life of the landfills.

Parameter	Acid phase		Methanogenic phase		Average
	Average	Range	Average	Range	
pH	6.1	4.5–7.5	8	7.5–9	
Biological oxygen demand (BOD <sub>5</sub> )	13 000	4000–40 000	180	20–550	
Chemical oxygen demand (COD)	22 000	6000–60 000	3000	500–4500	
BOD <sub>5</sub> /COD (ratio)	0.58		0.06		
Sulfate	500	70–1750	80	10–420	
Calcium	1200	10–2500	60	20–600	
Magnesium	470	50–1150	180	40–350	
Iron	780	20–2100	15	3–280	
Manganese	25	0.3–65	0.7	0.03–45	
Ammonia-N					741

**Figure 2.3** Pollutant concentration ranges for leachates from a wide variety of landfills in acidic and methanogenic stages of decomposition (adopted from Christensen *et al.*, 2001).

Parameter	Landfill						
	JB, HK	GDB, HK	Keele Valley, Canada	Brock North, Canada	Beare Road, Canada	Bryn Posteg, UK	Pitsea, UK
Age	3.5	11	1.5	8	18	<4	>60
pH	7.2–8.0 <sup>b</sup>	7.2–8.4	5.8	6.35	6.58	5.8	8.0–8.5
Conductivity	8.5–12.0	2.5–11.8	—	—	—	—	13.7
Salinity	7.2–15.1	4.0–9.5	—	—	—	—	—
COD	489–1670	147–1590	13780	3750	1870	5518	850–1350
BOD <sub>5</sub>	—	—	9660	1100	930	3670	80–250
Total solids	2680–5580	920–4500	12730	5280	3070	—	—
Volatile solids	685–1580	498–1580	6300	1350	1300	—	—
Fixed solids	1770–4010	398–2923	6430	3930	1770	—	—
Kjeldahl N	675–1840	137–1060	212	42	75	157	—
Ammoniacal N	594–1610	65–883	42	36	10	130	200–600
Nitrate/nitrite N	0.06–0.31	21.6–179	—	—	—	—	0.1–10
Total P	2.72–14.1	0.36–3./78	0.77	0.11	0.15	—	0.2
Ortho P	1.17–12.8	0.35–2.78	—	—	—	—	—

**Figure 2.4** Pollutant concentration ranges for leachates from a wide variety of landfills of various ages (adopted from Chu *et al.*, 1994).

### Observed Values of BOD, COD and BOD/COD-Ratio for Landfill Leachates Samples from Landfills in the Methanogenic Phase

BOD (mg/l)	COD (mg/l)	BOD/COD	Reference
5.7–1100	76–6997	---	Concentration ranges from 21-30 year old German landfills (Krumpelbeck and Ehrig, 1999)
290	1225	0.24	Average concentrations from 21-30 year old German landfills (Krumpelbeck and Ehrig, 1999)
44	320	0.11	Average concentrations from old, Danish landfills (Kjeldsen and Christophersen, 2001)
39	398	0.10	Composite results at Sandsfarm Landfill, (Robinson, 1995)
11	190	0.06	Composite results at Bishop Middleham Landfill, (Robinson, 1995)
38	517	0.07	Composite results at Odsal Wood Landfill, (Robinson, 1995)
1.0	53	0.02	Composite results at East Park Drive Landfill, (Robinson, 1995)
2.5	64	0.04	Composite results at Marton Mere Landfill, (Robinson, 1995)
180	3000	0.06	Average concentrations in methanogenic leachate (Ehrig, 1988)

**Figure 2.5** CBOD to COD ratios for leachates from a wide variety of landfills in methanogenic stages of decomposition (adopted from Kjeldsen *et al.*, 2002).

A major organic constituent ubiquitous in nature and common to landfill leachates are humic substances, which are due to the large quantity of decaying organic matter (Gupta *et al.*, 2014) and have been shown to consist mainly of humic and fulvic acids (Park *et al.*, 2000). Analysis of many different landfill leachates has shown that humic substances, which have a high molecular weight, make up a large portion of the recalcitrant organics in leachate (Gupta *et al.*, 2014; Kulikowska & Klimiuk, 2008; Park *et al.*, 2000). They can be formed from almost any type of organic material (Kang *et al.*, 2002), and tend to give landfill leachate a characteristic deep brown 'peaty' color (Knox, 1986). Humic substances have been shown to interact with a wide variety of pollutants in both aqueous and soil systems, affecting speciation of metals and their toxicity, adsorbing hydrophobic compounds, and serving as electron acceptors for degradation of organic pollutants in anaerobic environments (Kang *et al.*, 2002; Lovely *et al.*, 1996; Plaza, 2006). Thus, humic substances can play an important role in the fate and transport of many pollutants in landfill leachates.

Although humics are not toxic or particularly harmful by themselves, they may have adsorbed pollutants including aromatics, phthalates, and heavy metals (Plaza *et al.*, 2006; Xiaoli, 2010), and are a significant contributor to COD and color (Knox, 1986; Aziz *et al.*, 2007). They are also known to react with chlorine to form toxic disinfection byproducts in the form of halogenated organic compounds, *e.g.* trihalomethanes (THMs) and haloacetic acids (HAAs) (Reckhow *et al.*, 1990; Yang and Shang, 2004). The degree of humification has been shown to increase with landfill age, affecting both the size of the organic molecules and the amount of adsorbed pollutants (Kang *et al.*, 2002; Park *et al.*, 2000). Due to their refractory nature, these organic compounds are typically not removed by biological processes and often pass through treatment systems (Henze *et al.*, 2008; Gupta *et al.*, 2014). Studies have reported successful

removal of both color and recalcitrant COD using physico-chemical treatment such as activated carbon, membrane filtration, and coagulation and flocculation (Aziz *et al.*, 2007; Cecen *et al.*, 2001; Kurniawan *et al.*, 2006; Tatsi *et al.*, 2003).

Heavy metals concentrations will be much lower in older landfill leachates due to leaching in the acidic stage, and precipitation during the later stages (Aucott, 2006; Morling, 2009; Kjeldsen *et al.*, 2002). Precipitation is a result of the increasing hydroxide and sulfide content in the leachate, leading to the formation of metal hydroxides and sulfides, respectively (Aucott, 2006; Morling, 2009). These metals remain in the landfill until a much later aerobic phase, where they may be subsequently released (Morling, 2009; Kjeldsen *et al.*, 2002). The LEACH 2000 database provides data from a large number of municipal solid waste landfills for heavy metals that are of concern in natural waters based on environmental standards. Table 2.1 gives values for selected metals from over 200 landfills, taken from Aucott (2006).

**Table 2.1** Selected metals from over 200 landfills given by the USEPA LEACH 2000 database (adopted from Aucott, 2006).

Heavy metals in landfill leachate, from LEACH 2000 database						
Metal	No. samples	Mean (mg/l)	90 <sup>th</sup> percentile (mg/l)	TCLP level (mg/l)	EPA Primary drinking water MCL (mg/l)	RCRA groundwater MCL (mg/l)
Arsenic	2,444	0.441	0.100	5	0.01	0.05
Barium	1,779	0.866	1.700	100	2	1
Cadmium	2,351	0.283	0.079	1	0.005	0.01
Chromium	2,776	0.235	0.341	5	0.1	0.05
Lead	2,539	0.133	0.250	5	0.015	0.05
Mercury	2,078	0.00715	0.0046	0.2	0.002	0.002
Selenium	1,754	0.585	0.180	1	0.05	0.01
Silver	1,830	0.0537	0.056	5	NA	0.05

The eight heavy metals shown in Table 2.1 are the metals for which groundwater limits were set by the Resource Conservation and Recovery Act (RCRA) (SWANA, 2004). The Toxic

Characteristic Leaching Procedure (TCLP) levels are a federal classification of whether or not the landfill leachate can be considered hazardous (SWANA, 2004). The mean values indicate that heavy metals for these landfill leachates were not at levels to be considered hazardous based on the TCLP.

The quality of landfill leachates is also significantly influenced by rainfall, thus, the relative concentrations of many pollutants can show seasonal variation (Lema *et al.*, 1988; Vadillo *et al.*, 1999). Concentrations of pollutants such as COD, TAN, and heavy metals have been shown to increase drastically with decreased rainfall (Chen, 1996; Salleh & Hamid, 2013). Rapid dilution has been seen during rainfall events after long dry periods (Vadillo *et al.*, 1999). It has also been reported that during an initial rainfall after a dry period, concentrations of certain pollutants can be temporarily elevated due to a wash out effect (Chen, 1996). The amount of precipitation a landfill receives is also directly related to both how quickly it matures, and to the amount of leachate produced (Lema *et al.*, 1988).

Though it is common practice to cover the top of a landfill to reduce leachate generation, it can directly affect not only the strength of the leachate by allowing less dilution, but it can slow decomposition (Lema, 1988; SWANA, 2004). Water that flows through a landfill not only picks up the pollutants, but provides an environment where pollutants can be degraded both abiotically and biologically (SWANA, 2004). The presence of water thus allows for faster decomposition and transport, so in dryer climates or well sealed landfills, degradation of leaching pollutants may be much slower, whereas in wetter climates or open top landfills, degradation and leaching will be more rapid (Kjeldsen *et al.*, 2002).

The variations in landfill leachate characteristics presented thus far are important, not only to understand better the complicated dynamics of leachates, but also because they can indicate how effectively the landfill leachate can be treated by physio-chemical or biological means. The lower proportion of BOD to COD in leachates from older landfill means that there will be less effective biological removal of organics (Alvarez-Vasquez *et al.*, 2004), and that removal of oxidized nitrogen forms by denitrification may require an external carbon source such as methanol, making treatment more costly (Ganigue *et al.*, 2007).

Additionally, the high ammonia concentrations may inhibit biological processes such as nitrification if not diluted (Li *et al.*, 1999). However, the low metals concentrations of older landfill leachates indicate less of a problem both in terms of effluent quality and inhibition of biological processes, since, in many cases, heavy metals can be at levels much lower than discharge requirements, and at low concentrations in the solids of biological treatment systems (Morling, 2009). Characterization of a landfill leachate can provide insight into the present decompositional stage of a particular landfill, offering not only necessary information pertinent to treatment, but also some predictive value as to the changes that may be expected in the leachate quality over the life of a landfill.

## 2.2 Biological Processes in Activated Sludge

### 2.2.1 Introduction

Landfill leachate contains many of the same contaminants seen in municipal wastewaters, although some, *e.g.* nitrogen, can be at very high concentrations. It is therefore necessary to review the important biological processes involved in activated sludge sewage treatment, since they will be the main processes involved in treating the leachate in the SBR. The following subsections present the key biological processes for removal of biodegradable organic matter, nitrogen, and phosphorus. The discussion of nitrification will include a review of inhibition and partial nitrification, which are often observed in treatment of high ammonia wastes such as landfill leachate. The effects of process conditions on nitrification are also discussed.

### 2.2.2 Biological Degradation of Organic Matter

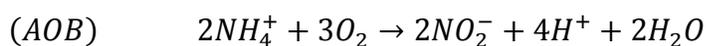
Biodegradable organic matter, also referred as carbonaceous biochemical oxygen demand (CBOD), is problematic in natural waters as it exerts oxygen demand and causes other water quality problems including color, taste, and odor, and has the potential to form halogenated compounds during disinfection processes in both wastewater and drinking water treatment systems (Tchobanoglous & Schroeder, 1987). The CBOD can be soluble, or it can be associated with particulate matter (Metcalf & Eddy, 2003). Organic substrates are degraded in sewage treatment systems by a wide variety of heterotrophic organisms, both aerobically and anaerobically.

The main removal process for biodegradable organics in wastewater is typically aerobic, and often takes place in aeration basin. The microbes break down the various organics, both as



require oxygen as a terminal electron acceptor, obtain energy in the form of electrons from their respective inorganic substrates, and use inorganic carbon as their only source for cell growth.

The overall nitrification process is given by the equations in Figure 2.7:



**Figure 2.7** Biological nitrification of ammonia to NO<sub>3</sub>-N by (1) AOB and (2) NOB

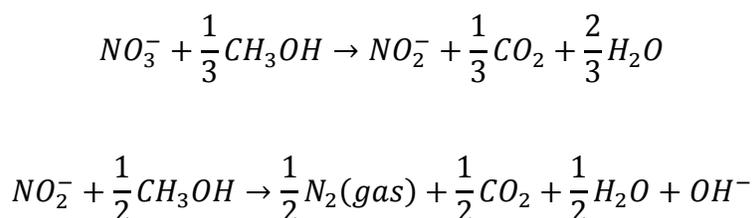
The rate limiting step during nitrification is generally considered to be ammonia oxidation (Davis, 2010; Antiniou *et al.*, 1989). As can be seen in Figure 2.7, the oxygen requirements for AOB are greater than for NOB, where the amount of oxygen necessary for conversion of TAN and NO<sub>2</sub>-N each step are 3.2 mg O<sub>2</sub>/mg NH<sub>4</sub>-N and 1.1 mg O<sub>2</sub>/mg NO<sub>2</sub>-N, respectively. Due to the low cell yields compared to heterotrophs, nitrifiers are usually a very low fraction of the total reactor biomass (Metcalf and Eddy, 2003; Davis, 2010; Barnes and Bliss, 1983), thus, oxygen demand due to endogenous decay should be comparatively small.

Nitrification requires alkalinity for pH buffering since protons are generated during ammonia oxidation, causing a drop in the pH (Gerardi, 2002). Carbonate alkalinity is usually a good choice for alkalinity addition, since it provides inorganic carbon for cell growth and has a lower pH than other sources, such as hydroxide salts (NEIWPCC, 2005).

#### 2.2.4 Denitrification

Denitrification is a process by which the oxidized forms of nitrogen (NO<sub>x</sub>-N) are ultimately converted into N<sub>2</sub> gas via nitrogen oxide intermediates by facultative anaerobic

heterotrophs (Bashkin & Howarth, 2002). Facultative anaerobes capable of denitrification often make up a significant fraction of the total heterotrophic population in activated sludge (Metcalf & Eddy, 2003). In the absence of oxygen,  $\text{NO}_x\text{-N}$  are used as alternate electron acceptors for oxidation of biodegradable organics, thus, this process requires an easily biodegradable organic carbon source under anoxic conditions. The overall process is shown in Figure 2.8, with methanol as the carbon source and omission of the intermediate steps. Denitrification results in the production of hydroxide ions which restores about half of the alkalinity destroyed during nitrification.



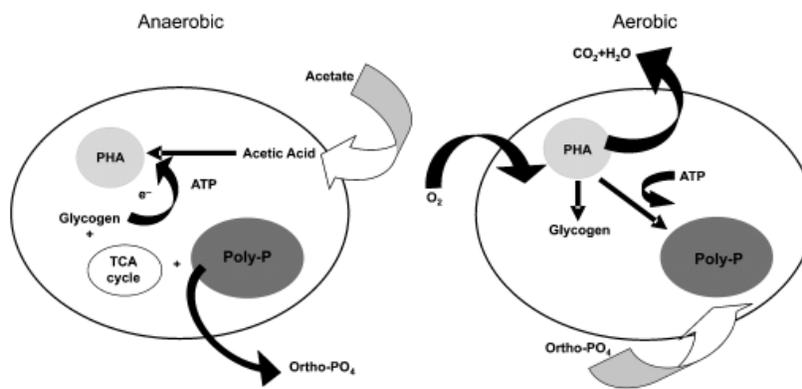
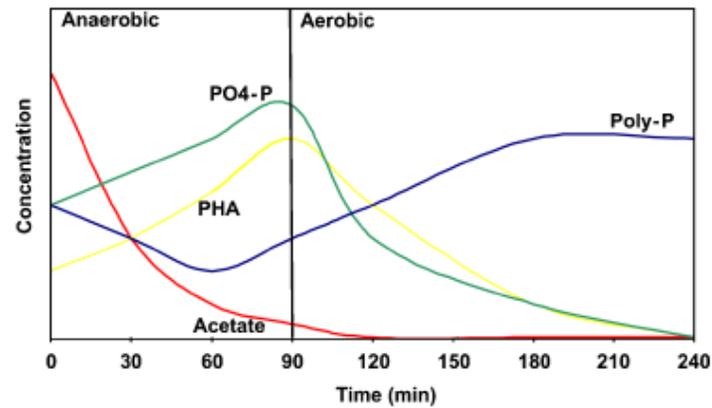
**Figure 2.8** Biological denitrification using methanol as carbon source.

The necessary ratio for biodegradable carbon to nitrogen in denitrification has been shown to be 2.86:1 (EPA, 1993), therefore it may be often necessary to add an external carbon source, *e.g.* methanol, if the C:N ratio is less than this value. External carbon addition is common in systems where an anoxic phase is preceded by an aerobic phase. Since biodegradable organics are oxidized in the preceding aerobic stage, there is insufficient residual carbon to convert all of the  $\text{NO}_x\text{-N}$  produced during nitrification (Davis, 2010). The need for an external carbon source is also widely reported in studies that attempt to use influent organics of older landfill leachates for denitrification, where the C:N ratio is low (Diamadopoulos *et al.*, 1997; Spagni & Marsili-Libelli, 2008).

### 2.2.5 Phosphorus Removal

Phosphorus is another nutrient found in wastewater that can be problematic if not removed before discharge, because like nitrogen, it can cause eutrophication (EPA, 2007). Some landfill leachates can contain a considerable amount of phosphorus (Miera de Oliveira *et al.*, 2015), although it is not typical as landfill leachates are often low in phosphorus (Amokrane *et al.*, 1997; Lema *et al.*, 1988). Phosphorus typically has a more stringent effluent requirement than nitrogen, due to the fact that it is more limiting in freshwater systems, and so algae growth can be better controlled by reducing discharged phosphorus (EPA, 2007). In wastewater, reactive phosphorus also provides the necessary phosphorus for microbial growth. However, phosphorus only constitutes roughly 2-3% of a cell's dry weight (Shuler & Kargi, 2002), thus, normal phosphorus uptake by activated sludge is minimal. Since sludge wasting is how phosphorus is ultimately removed in wastewater treatment systems (Artan & Orhon, 2005), normal microbial uptake and wasting may be insufficient to meet effluent requirements, which are often less than 1 mg/L depending on the region (EPA, 2007).

To achieve better phosphorus removal, special microbes termed phosphate accumulating organisms (PAOs) are enriched through a process known as enhanced biological phosphorus removal (EBPR) (Davis, 2010). EBPR requires an anaerobic zone preceded by an anoxic zone, as well as volatile fatty acids (VFAs) as substrate. The process of phosphate accumulation by PAOs is depicted in Figure 2.9 (Forbes *et al.*, 2009). The graph shows conversion of substrates during both the anoxic and aerobic phases and the diagram depicts the biological mechanisms for release and subsequent uptake of reactive phosphate.



**Figure 2.9** Enhanced biological phosphorus removal by PAOs (adopted from Forbes *et al.*, 2009).

In the anaerobic zone, PAOs store VFAs which can be fermentation products of organic substrates such as acetate (Davis, 2010). These VFAs are converted to polyhydroxoalkanoates (PHAs) using internally stored polyphosphate and glycogen, resulting in release of orthophosphate. In the subsequent aerobic phase, the PAOs use the stored PHAs as their energy source and use O<sub>2</sub>, or in some cases NO<sub>3</sub>-N as an electron acceptor, accumulating as much as 15% of their dry weight as phosphorus (Forbes *et al.*, 2009). However, if biodegradable carbon and nitrates are present during the anoxic cycle, problems can arise due to competition for

substrate with denitrifying bacteria (Ng *et al.*, 2001). The EBPR process is often implemented using SBRs (Artan & Orhon, 2005; Forbes *et al.*, 2009).

### 2.2.6 Biological Process Kinetics

Biological processes for the removal of organics and nitrogen are typically modeled based on Monod kinetics. The basic process rate equations for cell growth and substrate utilization, respectively, are given by the following equations, which are fundamental in wastewater treatment:

$$\frac{dX}{dt} = \frac{\mu_M SX}{K_S + S} - k_d X \quad [2.1]$$

$$\frac{dS}{dt} = -\frac{1}{Y} \frac{\mu_M SX}{K_S + S} \quad [2.2]$$

In Equations 2.1 and 2.2,  $X$  and  $S$  are cell and substrate concentrations, respectively, and  $\mu_m$ ,  $Y$ ,  $k_d$ , and  $K_s$  are the maximum specific growth rate (1/d), cell yield (g VSS/g S), decay coefficient (1/d), and substrate half-saturation constant (mg/L), respectively. The ratio  $\mu_m/Y$  is the maximum specific substrate utilization rate in mg substrate/mg VSS-time, and is often referred to as the variable  $\hat{q}_M$ . Thorough treatments of the kinetics of biological organic and nitrogen removal processes, along with typical parameter values used in design can be found in a vast amount of literature, including books on the design and operation of wastewater treatment systems (Metcalf & Eddy, 2003; Davis 2004; EPA, 1993; Kaelin *et al.*, 2009).

The basic forms of the process rates given by Equation 2.1 and 2.2 are the same for removal of organics and nitrification, except that the substrates and the values of the kinetic constants are different for each biological process. The kinetic constants often vary significantly

between systems and are affected by conditions such as temperature and pH (Antiniou *et al.*, 1989; Metcalf & Eddy, 2003; Wang *et al.*, 2009, Park *et al.*, 2007; Blackburne *et al.*, 2007).

Equations 2.1 and 2.2 typically include additional Monod terms for other important substrates such as oxygen and alkalinity (Kaelin *et al.*, 2009). The Monod terms are multiplicative, and act like ‘switches’ that have a significant effect on the rates based on both the substrate concentrations and the  $K_S$  values (Mulas, 2006). For example, oxygen is an important substrate for aerobic processes, thus the rates include a Monod oxygen term, which is shown in Figure 2.10.

$$\frac{S_O}{K_O + S_O}$$

**Figure 2.10** Monod oxygen term used in activated sludge modeling.

In Figure 2.10,  $S_O$  is dissolved oxygen concentration (mg/L) and  $K_{OH}$  is the oxygen half-saturation constant (mg/L). Heterotrophic organisms are generally considered to have a much greater oxygen affinity than nitrifying bacteria, and thus have a lower  $K_O$  value (. Typical  $K_O$  values used for plant design and activated sludge models are available in a wide variety of sources (Metcalf & Eddy, 2003; Kaelin *et al.*, 2008), and some are given in Table A.7 of the Appendix. Nitrification rates also include a term for alkalinity, which is identical to that shown in Figure 2.10, since it is a substrate that also affects growth.

For denitrification,  $S_O$  and  $K_O$  are swapped in the Monod oxygen term to provide an ‘off’ switch for when oxygen concentrations are significant and anoxic conditions no longer prevail (Mulas, 2006; EPA, 1993). The portion of heterotrophic biomass that are facultative anaerobic, which carry out denitrification, are accounted for by multiplying the process rates by their

fraction of the biomass (EPA, 1993). This fraction is typically 0.8 or higher for single-stage, post-anoxic processes (Davis, 2010).

### *2.2.7 Inhibition & Effects of Process Conditions on Nitrification*

#### 2.2.7.1 Introduction

Nitrification is widely considered to be the most sensitive of the major biological processes in activated sludge (EPA, 1993; Juliastuti *et al.*, 2003; Katipoglu-Yazan *et al.*, 2015; Morling, 2009; Pagga *et al.*, 2006; Sujarittanonta & Sherrard, 1981; Ward, 2011), which is also related to the low growth rates of nitrifiers (Sandborgh, 2011). Inhibition can affect both the growth and substrate utilization of nitrifying bacteria (Kim & Kim, 2003). Nitrification inhibition is widely reported in literature and can be caused by extreme environmental conditions such as temperature and pH (Gerardi, 2002), the presence of toxic compounds and heavy metals (You *et al.*, 2009; Kim & Kim, 2003; Sandborgh, 2011; Katipoglu-Yazan *et al.*, 2014), or their own substrates and products, in the form of free ammonia (FA) or free nitrous acid (FNA) (Anthonisen *et al.*, 1976). Some inhibition can also be reversible upon improved conditions, for example, as in some substrate inhibition (Shuler & Kargi, 2002; Suthersan & Ganczarczyk., 1986), or can be irreversible due to enzyme toxicity or chronic exposure to adverse conditions causing cell death (Hyman & Wood, 1985; Shuler & Kargi, 2002; Suthersan & Ganczarczyk., 1986).

Due to the presence of toxic pollutants found in many landfill leachates, conditions causing nitrification inhibition may be expected during treatment, therefore it is important to be familiar with some of the different types of inhibitions should they occur. The following

sections give a review of nitrification inhibition and the effects of various conditions on nitrification performance.

#### 2.2.7.2 Temperature

As with most microbial processes, growth and substrate utilization rates of nitrifiers have been shown to be significantly affected by temperature. Changes in temperature have been shown to significantly affect nitrification rates outside an optimal value (Gerardi, 2002). Nitrification has been shown to cease at extreme temperatures  $< 5\text{ }^{\circ}\text{C}$  and  $> 45\text{ }^{\circ}\text{C}$  (Metcalf & Eddy, 2003; Gerardi, 2002). Below  $30\text{ }^{\circ}\text{C}$ , a temperature change of  $1\text{ }^{\circ}\text{C}$  has been shown to result in a 10 % change in the ammonia oxidation rate (EPA, 1993; Gerardi, 2002). Kinetic parameters, including maximum substrate utilization rate and half-saturation constants, vary with temperature and thus optimal temperatures for nitrification vary somewhat in literature (Wang *et al.*, 2009; EPA, 1993).

Effects of temperature on AOB and NOB activity have been shown to differ, with AOB growth rates being higher than NOB at warmer temperatures (Kim *et al.*, 2007; Li *et al.*, 2008). Van Dongen *et al.* (2001) reported that the growth rate of AOB exceeds that of NOB at temperatures greater than  $25\text{ }^{\circ}\text{C}$ , a phenomenon that is utilized in the SHARON-ANAMMOX process. Wastewater temperatures can be fairly cool, although this depends on geographic location. Average annual wastewater temperatures in the U.S. vary between  $3 - 27\text{ }^{\circ}\text{C}$ , with a typical value of  $15.6\text{ }^{\circ}\text{C}$  (Metcalf & Eddy, 2003).

### 2.2.7.3 Alkalinity and pH

The pH range most effective for nitrification in activated sludge has been shown to be in the range of 7 - 8.2 (Gerardi, 2002; EPA, 1993; Tarre & Green, 2004). Ammonia oxidation is low to non-existent in wastewater below a pH of 6.5 (Tarre & Green, 2004), which is likely due to substrate limitations since the actual substrate is generally considered to be unionized ammonia (Suzuki, 1974). The  $pK_a$  of ammonia is 9.3, and at a  $pH < pK_a$ , most of the total ammonia is in the form of ammonium ions ( $NH_4^+$ ). Substrate inhibition of both AOB and NOB due to FA and FNA is also strongly dependent on pH (Anthonisen *et al.*, 1976).

The pH in wastewater treatment systems is controlled mainly by carbonate alkalinity, which, as previously mentioned acts as a buffer and also provides nitrifiers with a carbon source for growth. Thus, in order to keep the pH in an adequate range for nitrification, sufficient alkalinity must be provided. It is recommended to have a minimum of 50 mg/L as  $CaCO_3$  to keep the pH from dropping too low (Gerardi, 2002).

### 2.2.7.5 Dissolved Oxygen

As the Monod term shown in Figure 2.10 indicates, dissolved oxygen greatly affects nitrification rates. The  $K_O$  values for nitrifiers, which are generally higher than for heterotrophs (Kaelin *et al.*, 2009), have been shown to range from 0.2 - 0.5 mg/L for AOB and 0.35 - 2.5 for NOB (Van Hulle *et al.*, 2010), thus, AOB have a higher affinity for oxygen than NOB. The  $K_O$  values depend not only on temperature, but also on sludge characteristics such as floc size and density, and mixing and aeration intensity, all of which relate to mass transfer of DO from the bulk phase (Manser *et al.*, 2005; Van Hulle *et al.*, 2010), with decreasing mass transfer rates resulting in higher  $K_O$  values.

Low DO has been shown to negatively affect sludge characteristics, causing dispersed growth and formation of pin flocs (Richard, 2003). Low dissolved oxygen has also been shown to result in incomplete nitrification to nitrite due to the lower oxygen affinity of NOB (Ciudad *et al.*, 2004; Ruiz *et al.*, 2003, Van Hulle *et al.*, 2010; Sanchez *et al.*, 2007; Blackburne *et al.*, 2008; Ma *et al.*, 2015). Thus, in most wastewater treatment systems, a target concentration of at least 2 mg O<sub>2</sub>/L is used to ensure sufficient DO for nitrification (EPA, 1993).

#### 2.2.7.6 Toxic Substances and Heavy Metals

Many toxic substances such as xenobiotic compounds, sulfides, and heavy metals, which are often present in landfill leachates, have been found in many studies to inhibit nitrification (EPA, 1993; Bejerano-Ortiz *et al.*, 2015; Hu *et al.*, 2004; Kim & Kim, 2003; Sujarittanonta and Sherrard, 1981; Sandborgh, 2011; You *et al.*, 2009). Some examples of aromatic compounds that inhibit nitrifiers are phenols, cresols, antibiotics, toluene, and phthalates (Juliastuti *et al.*, 2003; Kim and Kim, 2003; Katipoglu-Yazan *et al.*, 2015; Pagga *et al.*, 2006). Some inhibition can cause chronic toxicity and subsequent failure of nitrification, which has been shown with the antibiotic tetracycline (Katipoglu-Yazan *et al.*, 2015). Inhibition has been reported for a great many organic compounds, although the concentrations are often reported in the 1 - 100 mg/L range or higher (EPA, 1993; Katipoglu-Yazan *et al.*, 2015; Kim and Kim, 2003), with the exception of some compounds, *e.g.* dichlorophenol, which can inhibit nitrification at concentrations much lower than 1 mg/L (Pagga *et al.*, 2006).

Heavy metals such as As, Cd, Cr, Cu, Hg, Ni, Zn and organotin compounds have been shown to inhibit nitrification (Hu *et al.*, 2004; Juliastuti *et al.*, 2003; You *et al.*, 2008). Inhibitory effects are highly variable for many metals, since their bio-availability depends on speciation and

complexation, as well as extent of adsorption and uptake based on sludge characteristics and metals concentrations (Cecen *et al.*, 2010; Hu *et al.*, 2003; Stasinakas and Thomaidis, 2003; You *et al.*, 2009). Due to complexation with organics or other compounds, or chemical precipitation, heavy metals can be less bio-available, thus reducing inhibition (Cecen *et al.*, 2010; Semerci and Cecen, 2007). For example, Hg toxicity to nitrifiers was shown to be reduced by its complexation with ammonium (Cecen *et al.*, 2010). It has also been shown that certain species of metals are more toxic than others, for example Cr (VI) has been shown to reduce nitrification rates significantly at much lower concentrations than Cr (III) (Novotnik *et al.*, 2014; Stasinakas and Thomaidis, 2003).

Low metals concentrations in landfill leachate have been associated with presence of sulfides (Morling, 2010; Aucott, 2006). An investigation of sulfide inhibition on enriched nitrifying cultures by Bejerano-Ortiz *et al.* (2015) showed that  $\hat{q}_M$  for AOB and NOB decreased significantly when exposed to sulfide concentrations of  $2.5 \pm 0.5$  mg HS<sup>-</sup>-S/L. They also observed that  $K_N$  values for NO<sub>2</sub>-N affinity of NOB increased dramatically. Thus, NOB was much more sensitive to inhibition than AOB, leading the authors to suggest the possibility of nitrite accumulation due to hydrogen sulfides.

Inhibition of nitrification by metals and other toxic substances can be complex and difficult to quantify in many cases, and can also affect growth and substrate utilization differently. Humic substances and other organics in landfill leachate can highly affect the bio-availability of metals and xenobiotic compounds by complexation and adsorption, as described previously. It has also been shown in many studies that inhibitory effects of toxic substances to nitrification can be much lower in treatment systems with longer sludge ages (Stasinakas *et al.*, 2002). Other factors affecting inhibition by toxic substances are acclimation time (Stasinakas *et*

al, 2002), exposure time, or in the case of organics, biodegradability of the compound of interest, e.g. dichlorophenol, which has a low biodegradability resulting in high toxicity (Pagga *et al.*, 2006).

#### 2.2.7.7 Free Ammonia & Free Nitrous Acid

Nitrifiers have been shown to be significantly inhibited by free ammonia (FA) and free nitrous acid (FNA). The inhibition of FA and FNA on AOB and NOB was studied in detail by Anthonisen *et al.* in 1976, a work that is widely cited in the literature. Based on their observations of a wide variety of treatment systems, the authors found that inhibition of AOB and NOB may likely occur in the threshold ranges shown in Table 2.2.

**Table 2.2** FA and FNA inhibition ranges for AOB and NOB as reported by Anthonisen *et al.*, 1976 that are often cited in literature.

	Reported range of AOB inhibition	Reported range of NOB inhibition
FA (mg/L)	10 - 150	0.1 - 1.0
FNA (mg/L)	0.22 - 2.8	0.22 - 2.8

It has been shown in many studies that NOB are generally much more sensitive to FA inhibition than AOB, which is also clear from Table 2.2. However, both organisms are much more sensitive to FNA than FA (Anthonisen, 1976; Vadivelu *et al.*, 2007; Fux *et al.*, 2003). The inhibition of FA and FNA greatly depend on pH, and to a somewhat lesser extent temperature, since the relative concentrations of each are dictated by these parameters based on equilibrium chemistry (Anthonisen, 1976). The  $pK_a$  for nitrous acid and ammonium are 3.3 and 9.3, respectively, and the relative abundance of FA and FNA will change drastically depending on how far the pH is from the  $pK_a$ . For example, at a higher pH, ammonium ions will dominate and

FNA will be very low, and at a lower pH, FA will be low and nitrous acid will be higher, provided that ammonia and nitrite are present at significant concentrations.

Inhibition of nitrification by FA and FNA has been investigated with enriched cultures and with activated sludge using synthetic wastewater, as well as in systems treating landfill leachate. Many studies report FA inhibition to be a major contributor to incomplete nitrification to nitrite (Bae *et al.*, 2002, Chung *et al.*, 2004), although some that reported FA inhibition operated experiments at low DO levels, which may also contribute to the incomplete nitrification to NO<sub>2</sub>-N (Zhang *et al.*, 2015; Kim *et al.*, 2003).

Inhibition ranges reported in the literature have been shown to vary somewhat from those given in Table 2.2. For example, a batch study on enriched nitrifying cultures found no inhibition of the catabolic processes of AOB up to 16 mg FA/L and below 0.40 of FNA (Vadivelu *et al.*, 2007). They also found no inhibition of NOB up to 0.024 mg/L FNA, and only 12% inhibition at 6 - 10 mg/L FA. However, in a separate publication, Vadivelu *et al.* (2007) found that FNA of 0.024 mg/L completely stopped growth of NOB. Fux *et al.* (2003) found that high FA in an SBR treating sludge dewatering liquor did not inhibit AOB, although 0.162 mg/L FNA resulted in 20-25% inhibition of AOB.

A study investigating the effects of temperature and pH on ammonia oxidation and nitrite accumulation found that FA on a range of 4.3 - 90 mg/L had no significant effect on TAN or NO<sub>2</sub>-N oxidation rates, although they cited the possible acclimation of the NO<sub>2</sub>-N oxidizers (Kim *et al.*, 2008). Another study investigating nitrification in cokes wastewater found inhibition of AOB starting at 9 mg/L of FA (Kim *et al.*, 2007). The negligible effect of FA inhibition on

ammonia oxidation was also reported by Kaczorek and Ledakowicz (2006), who modeled nitrogen removal in an SBR treating landfill leachate at high TAN loadings.

Thus, inhibitory concentrations can vary for both AOB and NOB depending on the system and the environmental conditions, and affect growth and catabolism differently. Extent of inhibition can also depend on factors such as acclimation time and MLVSS. For example, FA concentrations inhibiting NOB have been shown to increase with both increasing acclimation time and biomass concentration (Suthersan & Ganczarczyk., 1986).

#### 2.2.7.8 Partial Nitrification: Accumulation of Nitrite

Incomplete or partial nitrification is a widely occurring phenomenon in treatment of high ammonia waste streams and is the subject of a great many studies, including those involving treatment of landfill leachate (Ganigue *et al.*, 2012; Chung *et al.*, 2004; Spagni *et al.*, 2014). Partial nitrification occurs when TAN is oxidized to  $\text{NO}_2\text{-N}$ , but is incompletely converted to  $\text{NO}_3\text{-N}$ , which results in either  $\text{NO}_2\text{-N}$  bleed through in continuous flow systems or  $\text{NO}_2\text{-N}$  accumulation in batch systems. In general, partial nitrification is not desirable in sewage treatment, due to nitrogen limitations on effluent based on oxygen demand and toxicity, and the fact that  $\text{NO}_2\text{-N}$  carries significant chlorine demand which interferes with disinfection processes (Alleman, 1984; Gerardi, 2002).

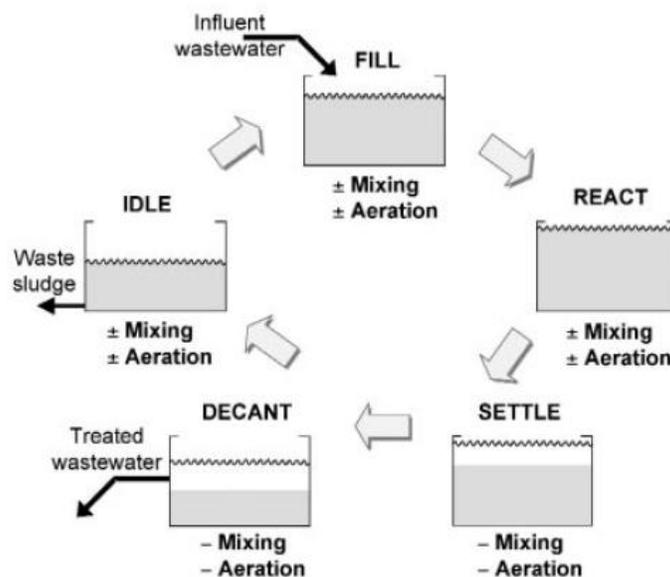
However, much work has been done to utilize partial nitrification as a means to cut down on operational costs through shortcut nitrification-denitrification by eliminating or suppressing the  $\text{NO}_2\text{-N}$  oxidation step and going directly from  $\text{NO}_2\text{-N}$  to  $\text{N}_2$  gas through anoxic processes (Zhang *et al.*, 2015; Ganigue, *et al.*, 2012). The common theme is the utilization of differences in AOB and NOB growth and metabolism under certain conditions, in order to operate so as to

aid in ammonia oxidation but suppress  $\text{NO}_2\text{-N}$  oxidation. Most studies rely on operating conditions including temperature, pH, dissolved oxygen, and sludge retention time, thus, they are all important contributors to incomplete nitrification (Chung *et al.*, 2004; Ciudad *et al.*, 2004; Zhang *et al.*, 2015; Bae *et al.*, 2001).

## 2.3 Activated Sludge SBRs

### 2.3.1 Uses and Operational Principles

The activated sludge SBR is often used as a robust system for the removal of organics and other nutrients from wastewater (Artan and Orhon, 2005; Kargi and Uygur, 2002). Due to their effectiveness at achieving low effluent pollutant concentrations, ability to resist shock pollutant loads, and operational flexibility, SBRs are being used more frequently for treating both sewage and industrial wastes (Dries, 2016; EPA, 1999; Irvine *et al.*, 1997). Sequencing batch reactors are fill-and-draw type reactors which run on cycles consisting of various stages. Common to most SBRs are a fill, react, settle, decant, and idle stage (Metcalf and Eddy, 2003). Figure 2.11 gives a schematic of a typical SBR operational scheme showing each stage of the operational cycle.



**Figure 2.11** Typical operational stages of SBRs (adopted from New England IWPC, 2005).

A typical cycle in an SBR begins with a fill phase where untreated waste is pumped into the vessel. This phase can either be mixed or aerated depending on the particular need. The fill volume and flow rate during the fill phase will be determined by the hydraulic retention time (HRT) chosen. The fill stage is followed by a reaction period, which can be aerobic, or anaerobic, or a sequence consisting of alternating aerobic and anoxic periods. SBRs designed for nutrient removal often require both an aerobic phase and an anoxic one, for example if phosphorus removal or denitrification is required (Davis, 2010; Kargi and Uygur, 2002). Organics, nitrogen reduction and cell growth during the reaction phases of an SBR follow the unsteady state process equations given by Equations 2.1 and 2.2. After the reaction phases, a settling phase allows for separation of solids from the mixed liquor, and is followed by a decant phase where treated waste in the supernatant above the settled sludge is pumped from the SBR. This is often followed by an idle phase, in which sludge can be wasted in order to maintain the operational SRT.

Cycles of an SBR can be tailored for the type of treatment necessary, which adds to their operational flexibility and control (Woodard and Curran, 2006). The SBR is also unique in that it can serve as a reaction vessel, either aerobic or anaerobic, a secondary clarifier to achieve solids settling, and an equalization basin (EPA, 1999). This allows treatment to be carried out with less unit operations, resulting in both a smaller footprint and lower operational costs (EPA, 1999).

### *2.3.2 Sludge Retention Time*

One of the most important parameters in both the design and operation of an SBR is the SRT, which is the average time that solids stay within the reactor. This parameter controls the growth of microorganisms and is based on maintaining a mixed liquor sludge concentration to

attain a desired treatment level (Davis, 2010). Control of SRT in SBRs is maintained by wasting sludge from the settled solids, although sometimes wasting can occur directly from the mixed liquor (Metcalf and Eddy, 2003; Davis, 2010). Due to the higher growth rates of heterotrophs compared with nitrifiers, the SRT needed for BOD removal is generally much less than for nitrification (Grady *et al.*, 2011).

Design SRTs of SBR systems for BOD and nitrogen removal are usually > 15 days, with a typical range of 20 - 40 days (Wang *et al.*, 2009; Metcalf and Eddy, 2003). There are advantages of maintaining longer SRTs, including higher MLVSS (Kargi and Uygur, 2002), improved nitrification rates (Klimiuk and Kulikowska, 2002), degradation of xenobiotic compounds, and biomass stabilization (Grady *et al.*, 2011). Longer SRTs also foster lower microbial growth rates, which can lessen the effects of inhibition by toxic substances (Stasinakas *et al.*, 2002; Stasinakas *et al.*, 2001; Sujarittanonta and Sherrard, 1981), although it also results in increased endogenous decay (Wang *et al.*, 2009).

### 2.3.3 Landfill Leachate Treatment in SBRs

In addition to applications in conventional wastewater treatment, the SBR has also been used for treating stronger wastes such as industrial effluents (Irvine *et al.*, 1997), anaerobic digester effluents (Graja and Wilderer, 2001), dairy wastes (Neczaj *et al.*, 2008), and landfill leachates (Artan and Orhon, 2005). Most studies of SBR treatment of landfill leachate focus on organics and nitrogen removal (Uyger and Kargi, 2004; Yalmaz and Oztur, 2001; Yabroudi *et al.*, 2013; Wei *et al.*, 2011), although some include phosphorus as well (Li *et al.*, 2009). High removal efficiencies of 95 - 98% for both CBOD and ammonia nitrogen have been reported (Li *et al.*, 2009; Laitenen *et al.*, 2009; Morling, 2009; Yalmaz and Ozturk, 2001).

One study of SBR treatment of leachate from 4 different landfills in Australia reported extremely high nitrification rates (Doyle *et al.*, 2001), which were much higher than rates reported in previous SBR studies (Karlberg *et al.*, 1993; Mena *et al.*, 1992). The authors reported that no inhibition was observed and that the high rates were likely due to long-term cultivation of a high concentration of nitrifiers due to a low C:N ratio. Nitrification rates reported in many SBR landfill leachate treatment studies are often comparable to, if not higher than typical ranges for nitrification in activated sludge treating municipal sewage (Barnes and Bliss, 1983; Dockhorn *et al.*, 1997; Kaczorek and Ledakowicz, 2006; Klimiuk and Kulikowska, 2006; Knox; 1984; Morling, 2010). Combined treatment with domestic wastewater has also been shown to be successful by lessening the effects of the leachate by dilution and mixing to control pollutant loads (Diamadopoulos *et al.*, 1997; Uygur and Kargi, 2004).

Many studies have tested the use of PAC in SBRs to improve both settling and removal of harmful organics. It has been found that nitrification of ammonia in landfill leachate can be improved by addition of PAC (Atkas and Cecen, 2001; Aziz *et al.*, 2011). Batch experiments by Atkas and Cecen (2001) observed higher nitrification rates for PAC treated samples compared with samples without PAC, suggesting the removal of inhibitory substances. This has been confirmed by other studies, including those done with landfill leachate treatment in SBRs, in which PAC addition improved performance (Aziz *et al.*, 2011; Uygur and Kargi, 2004). Pretreatments such as sonication, air-stripping, and coagulation-flocculation have also been shown in landfill leachate studies to improve the biological treatment process (Amokrane *et al.*, 1997; Neczaj *et al.*, 2006; Tatsi *et al.*, 2003; Uygur and Kargi, 2004).

Due to the high ammonia concentrations, there is also considerable focus on shortcut nitrification-denitrification via nitrite in SBR landfill leachate studies, which use methods as

previously described to achieve partial nitrification (Zhang *et al.*, 2015; Zhou *et al.*, 2012; Ganigue *et al.*, 2007; Gabarro *et al.*, 2012). However, denitrification of leachates from older landfill often requires the need for an external carbon source, due a low C:N ratio (Yalmaz and Ozturk, 2001; Diamadopoulos *et al.*, 1997; Hartmann and Hoffman, 1990).

In general, biological landfill leachate treatment via SBR technology has been proven successful for removal of organics and nitrogen, with and without chemical additions or pretreatment. The treatability study by Doyle *et al.* resulted in a full-scale treatment system being implemented, and currently there are numerous full-scale facilities designed for biological treatment of landfill leachate, although many also incorporate physico-chemical processes (Li *et al.*, 2009; Morling, 2009; Renou *et al.*, 2006; Doyle *et al.*, 2001). Due to the variable nature of landfill leachates presented thus far, treatability studies are likely to be a necessary pre-requisite for treatment of leachate at the full scale.

## CHAPTER 3

### MATERIALS AND METHODS

#### 3.1 Sample Collection and Storage

Raw landfill leachate and wastewater samples were collected on site from the Coffin Butte Landfill (29175 Coffin Butte Rd. Corvallis, OR) and Adair Village Wastewater Treatment plant (6030 NE William R Carr Ave, Adair Village, OR), respectively. New samples were obtained approximately once per month, or when needed. Samples were collected in 10 liter Nalgene bottles and stored at 4 °C.

#### 3.2 Laboratory Analysis of Water Quality and Reactor Solids

Section 3.2 describes the methods used for measuring all water quality parameters for SBR influent and effluent as well as metals analysis of reactor solids. Where test kits were used, such as for TAN, total nitrogen (TN), NO<sub>2</sub>-N, NO<sub>3</sub>-N, phosphorus, and COD, samples and reagent blanks were prepared as per manufacturer's specifications. Samples analyzed with Thermo-Scientific test kits or other colorimetric methods were read using a Thermo-Scientific Aquafast Orion spectrophotometer. Samples analyzed with Hach TNT test kits were read using a Hach DR 2000 UV-Vis Spectrophotometer. Any interference observed or modifications to methods are covered in the relevant sub-sections.

##### 3.2.1 Five-day carbonaceous biochemical oxygen demand (CBOD<sub>5</sub>)

Five-day CBOD (CBOD<sub>5</sub>) was measured according to *Standard Method 5210B* (APHA, 2005). All tests were done using 300 mL BOD bottles. Dilution water was prepared using Hach BOD buffer pillows and seed suspensions were prepared using Interlab *POLYSeedNX*, which

contained a nitrification inhibitor. Dissolved oxygen was determined using a Hach LBOD101 luminescent probe with a Hach HQ440d probe interface. Glucose-glutamic acid standards were prepared using 6 mL per BOD bottle of Hach 300 mg/L GGA ampules.

Average GGA standards were 250-300 mg/L, which was above the maximum acceptable range of  $198 \pm 30$  mg/L, as reported in the *Standard Methods*. Seed adjustments and preparation of dilution water from reagents did not remedy the problem, thus, the BOD test results should be used with caution. All seeded and unseeded dilution water blanks met the requirements for DO depletion of no greater than 0.2 mg/L, and all seed controls were within the acceptable range of 0.6 - 1 mg/L. Samples were immediately frozen after collection to prevent deterioration of CBOD during storage.

### 3.2.2 Chemical oxygen demand (COD)

Chemical oxygen demand (COD) was determined using Thermo-Scientific CODH00 dichromate reactor digestion method with a range of 0 - 1500 mg/L. Samples with  $\text{NO}_2\text{-N}$  present were corrected for interference. A standard curve of  $\text{NO}_2\text{-N}$  vs. COD was developed to determine the amount of COD associated with a given concentration of  $\text{NO}_2\text{-N}$ . The standard curve is given in Figure A.6 of the Appendix. COD measurements for samples containing  $\text{NO}_2\text{-N}$  were corrected by subtracting the  $\text{NO}_2\text{-N}$  COD, determined from the standard curve, from the total sample COD. Interference by the sample matrix for both influent and effluent were tested using known spikes of Hach COD standard and showed recoveries of almost 100% for all checks.

### 3.2.3 Nitrogen

#### 3.2.3.1 Total Ammonia Nitrogen (TAN)

Total ammonia nitrogen (TAN) was measured using Hach 10205 HR TNT plus 832 and Thermo-Scientific HR ACR011 (Salicylate Method) test kits, per manufacturer's instructions.

#### 3.2.3.2 Total Nitrogen (TN)

Total nitrogen (TN) was measured using Thermo-Scientific ACD007 kits per manufacturer's instructions. Sample spikes of known TAN and  $\text{NO}_3\text{-N}$  concentrations showed relatively poor recovery in some cases (<75 %) indicating possible interference by the sample matrix. This problem was not investigated further, and it was assumed that organic-N  $\ll$  TAN, thus, TAN  $\sim$  total Kjeldahl nitrogen (TKN).

#### 3.2.3.3 Nitrite Nitrogen ( $\text{NO}_2\text{-N}$ )

Nitrite nitrogen ( $\text{NO}_2\text{-N}$ ) was measured using a colorimetric assay adapted from EPA method 354.1(EPA, 1983). Sample absorbance was determined using a spectrophotometer at 540 nm and concentrations were calculated based on a standard curve. To check for possible sample interference, a standard curve was developed using known  $\text{NO}_2\text{-N}$  concentrations in landfill leachate diluted by a factor of 6 (17% leachate). The curve was identical to curves developed using DI water which indicated that no interference was to be expected when using the assay for combined influent samples. Standard curves are given in Figure A.5 (a) and (b).

#### 3.2.3.4 Nitrate Nitrogen

Nitrate nitrogen was determined initially determined using Hach TNT 832 and Thermo-Scientific ACR007 test kits per manufacturer's instructions. However, false positive  $\text{NO}_3\text{-N}$  readings were observed in effluent samples for both kits. This was suspected to be due to the high  $\text{NO}_2\text{-N}$  concentrations in the samples even when diluted. No information about this interference was provided in the either Hach or Thermo-Scientific documentation. As of November 19th, the test method was changed to Merck Spectroquant 1.09713.0001 (Aquamate method 09713H10), which report interferences for  $\text{NO}_2\text{-N}$  concentrations above 5 mg N/L. All effluent samples using this method were diluted to achieve  $\text{NO}_2\text{-N}$  concentrations below this value.

#### *3.2.4 Phosphorus*

Total and reactive phosphorus was determined using Hach TNT 843 and 844, and Thermo-Scientific ACD095 ascorbic acid method test kits per manufacturer's instructions.

#### *3.2.5 Total suspended, volatile suspended, and total dissolved solids*

Sample volumes of typically 20 - 30 mL were filtered through Whatman 934AH fiberglass filters. Total and volatile suspended solids and total dissolved solids were determined following the *Standard Methods* 2540d, 2540c, and 2540e, respectively (APHA, 2005).

#### *3.2.6 Conductivity and pH*

Conductivity and pH were measured using VWR Symphony 89231-618 and 89231-578 probes respectively connected to a VWR Symphony B40PCID interface. The conductivity probe

was calibrated weekly using a Hach 1000  $\mu\text{S}/\text{cm}$  NaCl standard and the pH probes were calibrated daily using pH buffers of 4 and 7.

### 3.2.7 Alkalinity

#### 3.2.7.1 Alkalinity Titrations

Alkalinity was quantified by titration of the samples with 0.02 N sulfuric acid using either a Pyrex burette, or a Brinkmann 665 Dosimet digital titrator when available. Samples were brought to a pH of approximately 4.3 and alkalinity was calculated using Equation [3.1]

$$\text{Alkalinity} \left( \frac{\text{mg}}{\text{L}} \text{ as CaCO}_3 \right) = \frac{50000 * (0.02 \text{ N}) * V_{\text{acid}}}{V_{\text{sample}}} \quad [3.1]$$

In Equation [3.1],  $V_{\text{acid}}$  and  $V_{\text{sample}}$  are the acid and sample volumes in mL, and 50000 is a conversion factor with units of mg  $\text{CaCO}_3/\text{eq}$ .

#### 3.2.7.2 Alkalinity Additions

Due to high ammonia concentrations, the influent mixture required the addition of alkalinity, which was supplied in the form of a saturated (0.8 M)  $\text{NaHCO}_3$  solution. First, the TAN concentration and initial alkalinity of the influent was quantified. Next, the amount of alkalinity necessary for complete nitrification, which is approximately 7.1 mg as  $\text{CaCO}_3$  per mg TAN, was calculated. Then, the amount of alkalinity that needed to be added was calculated by subtracting the amount already present in the mixture from the amount required for full nitrification. An additional amount, which varied based on influent volume, was added to ensure remaining alkalinity in the effluent of at least 100 mg/L in order to maintain a final pH of 7-8.

### *3.2.8 Metals*

Arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), selenium (Se), and zinc (Zn) were quantified for the influent mixture, the reactor effluent, and the reactor solids. Due to the complex analytical methods necessary for determination of As and Hg, samples were collected and sent to CH2MHill Analytical Laboratory (Corvallis, OR) for their analysis. All other metals were determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) analysis in the Keck Laboratory at Oregon State University using a Prodigy ICP-OES (Leeman Labs, Hudson, NH) in axial view.

The following two sub-sections describe preparation methods used for all liquid and solid samples respectively. VWR Aristar Plus ppb grade nitric acid and 18 M $\Omega$  reverse osmosis (RO) water were used for preparation of all samples and equipment. Initially, no digestion method was used in the preparation step, although later samples digested at 80 °C for 1 hour showed no difference in concentrations compared with undigested samples.

#### *3.2.8.1 Liquid Samples*

All glassware and tubes to contain prepared samples or standards were pre-soaked overnight with ppb grade 5% HNO<sub>3</sub>. Glassware was also rinsed with the samples to be contained. Polypropylene 15 mL culture tubes were used to contain liquid samples for analysis. Influent samples were pumped directly from the influent bottle and effluent samples were taken from the SBR supernatant during the idle phase via serological pipette. Samples were diluted by a factor of no more than 2.5 and were not filtered since the mass of solids present was negligible

compared to liquid sample mass. Diluted samples were acidified with ppb grade HNO<sub>3</sub> to achieve a final acid concentration of 1-2% (v/v) and pH of 1.

Due to the wide range of concentrations expected, standards were prepared with a range of 5 ppb to 5 ppm. A custom metals standard purchased from CPI International containing 10 ppm Cd, Cr, Mo, Ni, and Se, and 1000 ppm Zn, Cu, Mn, and Ba was used for standard dilutions. Standards were prepared in Class A volumetric flasks then transferred to 50 mL Nalgene centrifuge tubes for analysis.

#### 3.2.8.2 Solid Samples

Reactor solids samples were obtained from settled sludge using a serological pipette. Samples of approximately 5 mL were transferred to a culture tube and allowed to settle for 20 - 30 minutes. After decanting the supernatant, the settled solids were poured into pre-weighed 10 mL VWR United quartz crucibles and dried for 6 hours on a hot plate at 100 °C. The dried samples and crucibles were weighed before being heated for 3 hours at 550 °C to ash the solids. Ashen samples were dissolved in 3 mL of 2 N HNO<sub>3</sub>. The 2N HNO<sub>3</sub> was then dripped slowly down the sides of the crucible while being warmed at about 50 °C on a hot plate. Aliquots of 1 mL were immediately transferred from each crucible into clean culture tubes and diluted by a factor of 10 using 18 mΩ water resulting in a final acid concentration of ~7%, which was acceptable for the ICP analysis.

#### *3.2.9 Color*

Color was determined for influent and effluent using a Hach CO-1 color kit. Samples were diluted per manufacturer's instructions and color was reported in Pt-Co units.

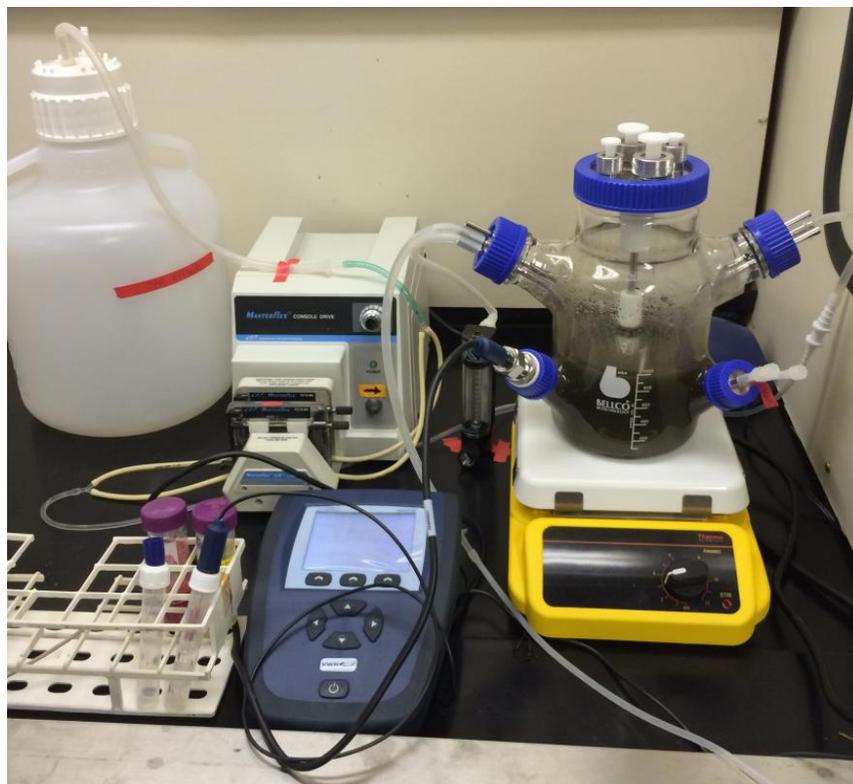
### 3.2.10 Pesticides, Volatile Organic Compounds (VOCs), & Semi-VOCs

Influent and effluent samples were collected and sent to CH2MHill analytical laboratory in Corvallis, OR for determination of pesticides (method(s) described by Millar *et al.*, 1984), VOCs (method(s) E624: SW5030), and semi-VOCs (method(s) E625: SW3510) via gas chromatography-mass spectroscopy (GC-MS).

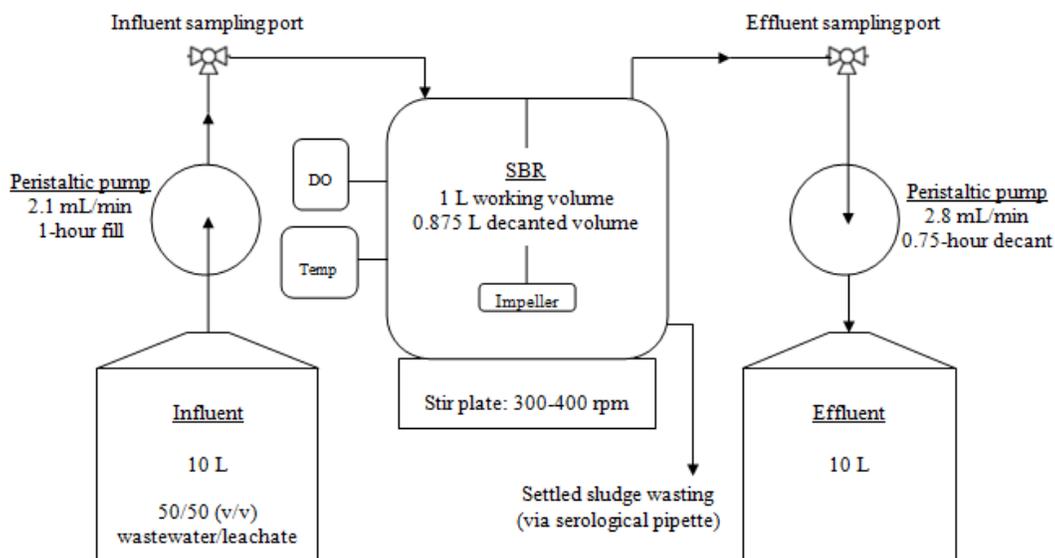
## 3.3 Sequencing Batch Reactor Setup and Operation

### 3.3.1 Reactor Setup and Components

Sequencing batch reactors were constructed with Belco USA Bioprobe 1000 mL glass vessels equipped with magnetic stir paddles. The reactor vessels contained ports for influent and effluent liquid flows, air supply, mixed liquor sampling, sludge wasting, and temperature and dissolved oxygen measurements. Mechanical mixing of SBRs during the reaction phases was done using Thermo-Scientific Ciramec stirrers set to 350 rpm. Air was supplied via Tetra ‘Whisper’ aquarium pumps with air flow controlled using VWR 0.1 - 2 L/min gas flow meters. Influent and effluent flows were controlled by Masterflex L/S peristaltic pumps with digital display from Cole Parmer. The SBRs were fed by pumping directly from a 10 L Nalgene bottle containing the landfill leachate and wastewater mixture. A paint strainer bag was folded and wrapped around the influent tube to reduce clogging. Reactor temperature was controlled as of December 12th, using a Thermo-Scientific Neslab Merlin M33 chiller connected to silicon tubing wrapped around the base of the SBRs. Dissolved oxygen was measured using a Hach LDO101 luminescent probe with a Hach HQ440d probe interface following manufacturer’s instructions. Figures 3.1.1 and 3.1.2 show an image of the initial SBR setup and process flow diagram respectively.



**Figure 3.1** Initial SBR setup for the landfill leachate treatability study.



**Figure 3.2** Simple process flow diagram of SBR setup for the landfill leachate treatability study.

### 3.3.2 *Sludge Inoculum*

The SBRs were seeded with activated sludge from the Corvallis wastewater treatment plant aeration basin effluent, which contained a mixture of heterotrophic and autotrophic microorganisms. The SBRs were inoculated to achieve an initial MLSS of 3000 mg/L. There were no further seed additions in either SBR after initial start-up.

### 3.3.3 Operational Parameters

Table 3.1 gives the initial operating conditions for the SBRs. Two SBRs were used in the study with each SBR being initially fed with only wastewater from Adair Village.

**Table 3.1** Operational parameters for SBRs during the treatment study.

Parameter	Value	Units
Working volume	1	L
Hydraulic retention time ( <i>HRT</i> )	4	d
Total solids retention time ( <i>SRT</i> )	25 <sup>a</sup>	d
Fill time	1	h
Aerated react time	7	h
Air Flow Rate	9	L/h
Anoxic react time	2	h
Settle time	1	h
Decant time	0.75	h
Idle time	0.25	h
Total cycle time	12	h
Cycles per day	2	(-)

<sup>a</sup>*SRT* was above 100 d for the first 6 mo. of the study then reduced to 25 d through wasting of settled sludge. Sludge wasting as calculated by Equation 3.3 was based on this total *SRT*.

After 1 week of operation, one of the SBRs (SBR 1) was fed of a 50/50 landfill leachate wastewater mixture and became the primary SBR, referred to as SBR 1 for the duration of the

study. The second SBR, (SBR 2), was fed only wastewater for the first 8 months, after which it was fed a combined leachate:wastewater mixture. All reported results are for SBR 1 unless explicitly indicated.

### 3.3.4 Estimated Pollutant Loadings and Oxygen Demand

Daily SBR pollutant loadings were based on a 4 day HRT and concentrations for the 50/50 (v/v) landfill leachate:wastewater influent. CBOD<sub>5</sub> and TAN concentrations were assumed from historical data available for the Adair Village WWTP and Coffin Butte leachate (Figures A.3 and A.4 of the Appendix) in order to estimate the daily oxygen demand. Maximum concentrations were used for determining an initial air flow rate, and are shown in Table 3.2.

**Table 3.2** Estimated maximum TAN and BOD influent concentrations based on historical data for the Adair WWTP influent and the Coffin Butte landfill leachate.

	<i>CBOD<sub>5</sub></i> (mg/L)	<i>TAN</i> (mg N/L)
Landfill leachate	1750	1000
Wastewater	300	50
50/50 (v/v) mixture	1025	525

Table 3.3 shows estimated maximum BOD and TAN loadings and oxygen demand for the SBRs treating a 50/50 (v/v) landfill leachate:wastewater mixture using the values from Table 3.2. Daily pollutant loadings in mg/L-d were based on a 4-day HRT, and thus, was the estimated influent concentrations divided by four. Oxygen demand was assumed to be 1 mg O<sub>2</sub>/mg CBOD and 4.6 mg O<sub>2</sub>/mg TAN based on stoichiometric requirements for the associated catabolic reactions. Estimated oxygen demand in mg/L-h was determined as the daily oxygen demand divided by 14 hours per day of aerated react time as follows:

$$\text{Hourly oxygen demand } \left( \frac{\text{mg O}_2}{\text{L-h}} \right) = \left( \frac{1 \text{ d}}{14 \text{ h}} \right) \left[ \text{CBOD} \left( \frac{\text{mg}}{\text{L-d}} \right) + 4.6 * \text{TAN} \left( \frac{\text{mg}}{\text{L-d}} \right) \right] \quad [3.2]$$

**Table 3.3** Estimated maximum daily TAN and BOD loadings and corresponding hourly oxygen demand using Equation [3.2].

	<i>BOD</i> <sub>5</sub> (mg/L-d)	TAN (mg N/L-d)	O <sub>2</sub> demand (mg/L-h)
50/50 (v/v) mixture	256	130	61

An initial air flow rate was calculated using the oxygen demand from Table 3.3 assuming 20°C and using the ideal gas law divided by a factor 0.21, since air contains 21% oxygen. A value of 9 l/h was chosen as a starting air flow rate, which was higher than the calculated value by a factor of 40, in anticipation of low oxygen transfer efficiency, fluctuating room temperatures, and residual oxygen demand due to endogenous decay of microorganisms.

### 3.3.5 Temperature

The SBRs were operated at room temperature for the first 8 months of the study which varied on a range of 22 - 26 °C, with maximum temperatures reaching 28 - 30 °C in July. Fall temperatures in the SBR fell in a range of 18 - 25 °C with an average of 22 °C. Temperature of SBR 1 was controlled at 17 ± 2 °C as of December in order to simulate more realistic temperature conditions.

### 3.4 Influent and Effluent Sampling

Influent samples were collected by pumping directly from the feed into a storage container, typically a 150 mL Wheaton bottle or 50 mL centrifuge tube, depending on the volume needed for analysis. Effluent samples were collected by bypassing the effluent feed into a 1 L flask before being transferred to 150 mL Wheaton bottles, although later in the study some

effluent samples were retrieved via serological pipette during the idle phase. All collected samples were immediately stored at 4 °C until used for analysis.

### 3.5 Reactor Solids Analysis and Sludge Wasting

#### 3.5.1 Mixed liquor total suspended (MLSS) and volatile suspended solids (MLVSS)

Mixed liquor suspended and volatile solids were determined by sampling directly from the SBR during the mixing phase using a serological pipette. Sample volumes were 5 mL initially, and were collected almost daily. After wasting from the settled sludge began, the volume was reduced to 2 - 3 mL to reduce the volume extracted from the SBR. Solids analyses were carried out using the methods described in section 3.2.5 for TSS and VSS.

#### 3.5.2 Sludge volume index

Sludge volume index (SVI) was measured by placing a 50 mL reactor sample in a graduated VWR centrifuge tube and allowed to settle for 30 minutes. Final settled volume was recorded and SVI was calculated using Equation [3.3]:

$$SVI \left( \frac{mL}{g} \right) = \left( \frac{\text{Settled Volume mL}}{\text{Sample Volume L}} \right) \left( \frac{1}{MLSS \frac{mg}{L}} \right) \left( \frac{1000mg}{g} \right) \quad [3.3]$$

#### 3.5.3 Sludge wasting

Sludge was wasted directly from the settled volume during the idle phase using a serological pipette. Sludge wasting rate was based on achieving a  $SRT_{TOT}$  of 25 d. The required volumetric wasting rate  $Q_w$  of settled sludge in mL/d was calculated using Equation [3.4], which assumes complete settling and no influent or effluent sludge:

$$Q_W = (V_R * MLSS)/(SRT * X_W) \quad [3.4]$$

In Equation [3.4],  $V_R$  is the SBR working volume in liters and  $X_W$  is the sludge concentration in mg TSS/L in the settled volume. Prior to July, 5 mL of mixed liquor was wasted for daily MLSS measurements resulting in an average SRT > 100 d. After July 1, settled sludge volumes typically ranging from 4 - 6 mL were collected and discarded to maintain an SRT of ~25 d.

### **3.5 Effluent Filtration**

It was desired to determine the extent to which COD, BOD, and phosphorus would be reduced through removal of suspended solids via filtration. This was done by filtering samples through Whatman 934AH fiberglass filters then comparing results with those of unfiltered samples.

### **3.5 Nitrification Profiles**

Concentration profiles for TAN,  $\text{NO}_2\text{-N}$ , and  $\text{NO}_3\text{-N}$  during the aeration phase were determined by taking mixed liquor samples at 0.5 to 1 hour time intervals. Sample volumes of 1.5 mL were collected using a Thermo-Scientific micropipettor and placed into 1.5 mL VWR centrifuge tubes. Samples were immediately centrifuged at 9000 rpm for 4-5 minutes. One mL of supernatant was transferred to a separate 1.5 mL centrifuge tube and frozen at  $-80\text{ }^\circ\text{C}$ . Samples were later thawed and then analyzed for TAN and  $\text{NO}_x\text{-N}$  using methods described in Sections 3.2.3.1, and 3.2.3.3 - 3.2.3.4. The remaining solids were re-suspended in 1 mL of BOD dilution water and returned to the reactor. Temperature and pH measurements in the mixed liquor were recorded for each sample point.

### **3.6 Aeration Effects on Nitrification**

To study the effects of aeration intensity on nitrification, a 50/50 landfill leachate and wastewater mixture with a TAN concentration of approximately 430 mg N/L was fed to SBR 2 with the same operational parameters as given in Table 3.1. The SBR was operated at 17-19 °C and the air flow rate was adjusted between 9 L/h to 60 L/h every 4 to 5 days. Influent and effluent nitrogen species and pH were measured on consecutive days at each flow rate.

To determine aeration effects at a higher loading, a mixture of 67% landfill leachate and 33% wastewater with a combined TAN concentration of 570 mg N/L was fed to SBR 2. Airflow rates tested were 60 L/h, 30 L/h, then 9 L/h with DO monitored continuously. As before, influent and effluent nitrogen species and pH were measured on consecutive days at each air flow rate.

### **3.7 Denitrification**

#### **3.7.1 Methanol Addition**

To test the possibility of denitrification, methanol was added to SBR 1 over a 3 day period. One mL of methanol was added directly to the mixed liquor at the beginning of the anoxic cycle on 3 consecutive days and effluent  $\text{NO}_x\text{-N}$  was monitored. This was done only once during the study.

## CHAPTER 4

### RESULTS AND DISCUSSION

#### **4.1 Wastewater and Landfill leachate Characteristics**

The combined influent to be treated in SBR 1 was a 50/50 (v/v) mixture of Adair Village wastewater and Coffin Butte landfill leachate. The following sub-sections focus on characterization of the combined influent, including a comparison of the wastewater and leachate portions, as well as a look at some of the seasonal variability seen in the combined influent during the study.

##### *4.1.1 Comparison of Wastewater and Combined Influent*

Table 4.1 gives water quality parameters for both the combined influent and the wastewater only during the first 3 months of the study. The landfill leachate portion was not measured directly, but was estimated by accounting for the wastewater contribution in the 50/50 (v/v) mixture. Initially, the wastewater was analyzed for the same parameters as for the combined influent in order to determine the relative contributions of the wastewater and landfill leachate, although due to the time constraints, analysis of wastewater only was not continued through the entire study, with the exception of a few CBOD<sub>5</sub> and COD measurements.

**Table 4.1** Comparison of 50/50 (v/v) combined influent and wastewater only for selected water quality parameters during the first 3 months of the study.

Parameter	Combined Influent	Adair Wastewater	Estimated Landfill leachate Portion	Units
COD	1350 ± 140 <sup>a</sup>	316 ± 41	2380	mg/L
CBOD <sub>5</sub>	240 ± 57 <sup>a</sup>	117 ± 5	360	mg/L
TAN	354 ± 14	42 ± 5	670	mg N/L
PO <sub>4</sub> <sup>3</sup> -P	6 ± 1	4 ± 1	8	mg P/L
TSS	71 ± 28 <sup>b</sup>	21 ± 16 <sup>b</sup>	120	mg/L
TDS	2040 ± 100	294 ± 55	3800	mg/L
Alkalinity	2040 ± 100	220 ± 15	3860	mg/L as CaCO <sub>3</sub>
pH	7.6 ± 0.2	7.2 ± 0.3	7.5 - 8	(-)
Color	1390 ± 250	210 ± 70	NA	Pt-Co

<sup>a</sup>Values should be taken with caution and were likely higher due to breakdown in unfrozen samples before analysis.

<sup>b</sup>Influent was pre-filtered using a fine mesh screen.

The values in Table 4.1 show clearly that the leachate contributed the majority of pollutants to the combined influent with high concentrations of COD, TAN, alkalinity, and TDS, very typical of landfill leachates (Aucott, 2006; Christensen *et al.*, 2001; Chu *et al.*, 1994; Renou *et al.*, 2008). The wastewater was shown to be low to medium strength for all water quality parameters compared to typical values of pollutants for municipal wastewaters (Henze and Comeau, 2008; Metcalf and Eddy, 2003). The wastewater CBOD to COD ratio was about 30-40%, which is on the low end of typical ranges reported for wastewater (Metcalf and Eddy, 2003). The CBOD to COD ratio for the leachate portion was < 20%, indicating a higher

percentage of refractory organics, *e.g.* humic substances, which is common in landfill leachates (Kjeldsen *et al.*, 2002). The combined influent also had much more color, which was peaty brown due to the leachate (Chu *et al.*, 1994; Knox, 1984).

Table 4.2 shows a comparison of CBOD<sub>5</sub> data collected during the fall and winter months for both combined influent and wastewater only. There was a significant decrease in wastewater CBOD<sub>5</sub> during winter months, likely due to infiltration of stormwater into the piping system. Combined influent samples collected after November 19<sup>th</sup> were immediately frozen to avoid degradation of organics, and after doing so, larger CBOD<sub>5</sub> values were observed for each new batch, which is clear by comparing the values in Tables 4.1 and 4.2. The lower values for the combined influent measured during summer and early fall were most likely due to degradation of CBOD<sub>5</sub> in the influent bottle. The later measurements show the CBOD<sub>5</sub> of the raw landfill leachate to be ~1000 mg/L or greater (Table 4.2), which is high for a methanogenic landfill (Figure 2.3), suggesting an earlier methanogenic stage of decomposition (Christensen *et al.*, 2001).

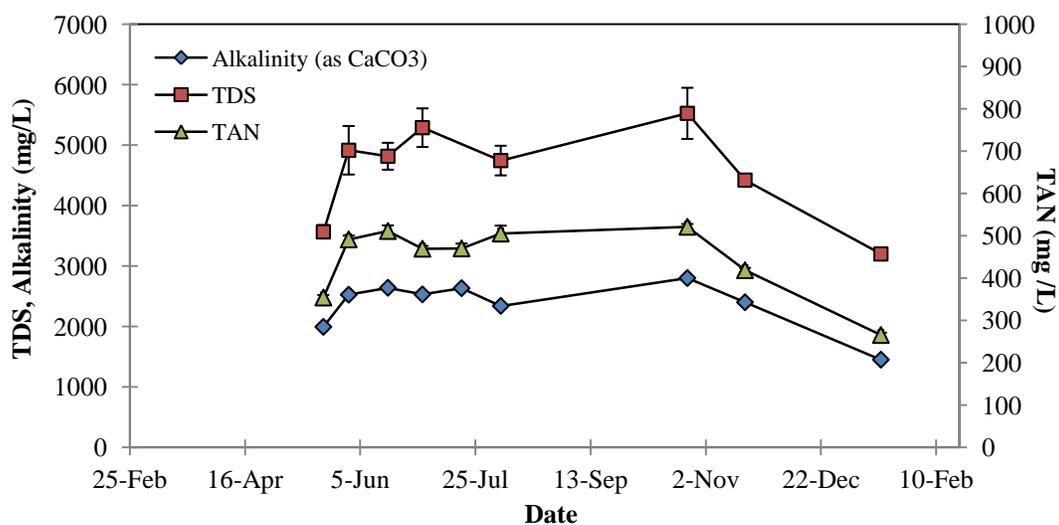
**Table 4.2** Comparison of 50/50 (v/v) combined influent and wastewater only CBOD<sub>5</sub>. Data is shown with a 95% confidence interval for sample triplicates.

Date	(CBOD <sub>5</sub> ) Combined Influent	(CBOD <sub>5</sub> ) Adair Wastewater	Estimated Landfill leachate Portion	Units
19-Nov	594 ± 66 <sup>a</sup>	223 ± 7	965	mg/L
17-Jan	893 ± 184	86 ± 4	1700	mg/L
9-Feb	649 ± 62	39 ± 3	1300	mg/L

<sup>a</sup>The sample was also run by a professional water quality analyst at the Corvallis WWTP for comparison, who measured a CBOD of 650 mg/L.

#### 4.1.2 Combined Influent Characterization and Seasonal Variability

The strength of the combined influent varied over the study, with lower concentrations for some pollutants seen during wetter months, which is a commonly reported phenomenon in landfill leachate studies (Chu *et al.*, 1994). Figure 4.1 gives average concentrations of TAN, TDS, and alkalinity for different batches of combined influent. Total dissolved solids were corrected to account for alkalinity additions where necessary. The parameters shown in Figure 4.1 were chosen because they showed a clear pattern of seasonal change. The COD and CBOD<sub>5</sub> were expected to vary in much the same way based on historical data (Figure A.4), although no clear pattern of seasonal variability was observed.



**Figure 4.1** Combined influent TAN, alkalinity, and TDS for SBR 1. Bars represent 95% confidence intervals for measurement averages over each new influent batch. Alkalinity measurements are initial values for each batch before NaHCO<sub>3</sub> additions.

An interesting trend of note, based on the data in Figure 4.1 is the relatively constant ratio between all of these parameters throughout the year, since the ratio of TAN to alkalinity was  $20 \pm 1\%$  and the ratio of TAN to TDS was  $10 \pm 1\%$ . The data shows that the concentrations of

these contaminants relative to one another are roughly constant, and that landfill leachate strength in terms of ‘macro’ constituents throughout the year depends on rainfall. These trends may indicate some predictability in pollutant loadings due to the leachate, and could be useful in determining how much additional alkalinity would be required based on TAN concentration alone.

Ranges for all parameters observed during the study are given in Table 4.3. Assuming only a small contribution by the wastewater (~ 10% or less), the estimated average TAN and COD of the leachate portion were 800 mg N/L and 3500 mg/L (~ double the middle range values from Table 4.3), respectively, which compare well with mean values reported by Chu *et al.*, (1994) for old landfill, methanogenic stage landfill leachate.

**Table 4.3** Combined influent parameters over the range of the treatment study.

Parameter	Concentration range in combined influent	Units
COD	1218 - 2212	mg/L
CBOD <sub>5</sub>	400 <sup>a</sup> - 890	mg/L
TAN	243 - 575	mg N/L
PO <sub>4</sub> <sup>3</sup> -P	6 ± 1	mg P/L
TSS	24 - 160 <sup>b</sup>	mg/L
NO <sub>3</sub> -N	3 - 6	mg/L
TDS	3198 - 5525	mg/L
Alkalinity	1450 - 2800	mg/L as CaCO <sub>3</sub>
pH	7.6 ± 0.2	(-)
Color	1390 ± 250	Pt-Co

<sup>a</sup>Minimum estimated value based on average rate of initial degradation in the influent.

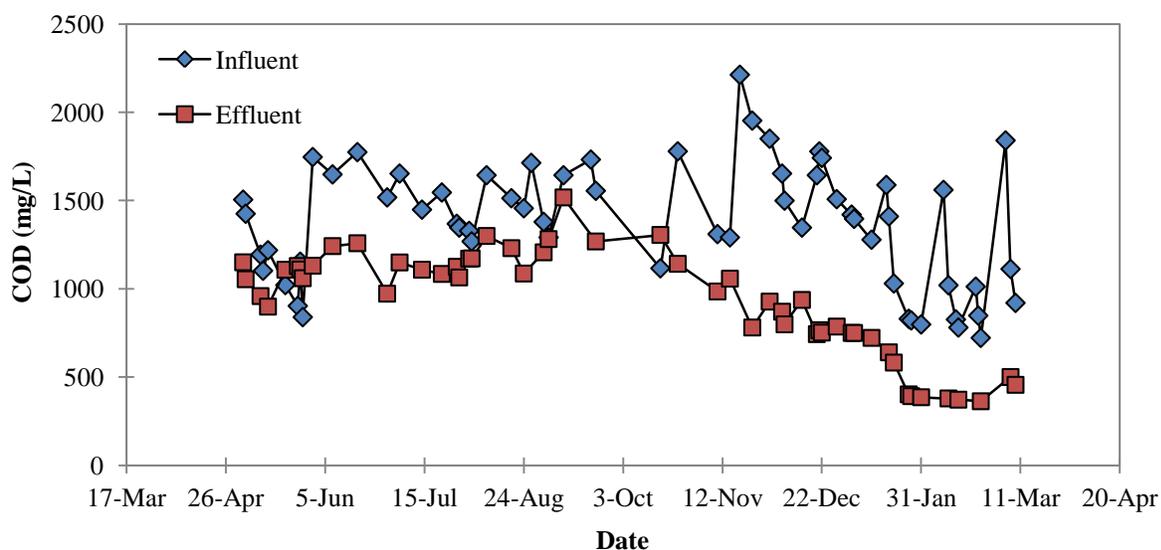
The landfill leachate concentrations for all parameters also compared well with values reported by Kulikowska and Klimiuk (2008), who studied the effects of landfill age on leachate quality. The high TAN ( $>500$  mg/L), low COD ( $< 4000$  mg/L), low CBOD/COD ratio ( $< 40\%$ ), and higher pH ( $> 7.5$ ) indicate that the Coffin Butte landfill is in a methanogenic (if early methanogenic) phase of decomposition (Kjeldsen *et al.*, 2002; Kulikowska & Klimiuk, 2008; Tatsi *et al.*, 2003; Aucott, 2006). Although older landfills like Coffin Butte are generally methanogenic, it should be noted that the term ‘young’ landfill may not necessarily indicate an acidic stage, as it has been shown that the methanogenic stage can be reached quickly, even less than 1 year (Lo, 1996). A similar phenomenon was reported by Kulikowska and Klimiuk (2008), who observed a methanogenic phase within 2 years for a polish landfill.

Values of pollutant concentrations comparing ‘high’ and ‘low’ strength landfill leachates are presented by Henze and Comeau (2008), and by comparison, the Coffin Butte leachate would be considered low strength for COD, but high strength for TAN and phosphorus. Despite the higher CBOD<sub>5</sub> after November, the CBOD to COD ratio was still relatively low (40% or less), albeit on the high end of reported values for methanogenic landfills (Figure 2.3 and 2.5). However, as previously stated, the high TAN and alkalinity, and pH  $> 7.5$  still suggest a methanogenic stage of maturation. In fact, the landfill owner Republic Services captures a significant amount of methane to power electrical generators on site (Tedder, 2012). The higher CBOD to COD may be due to the fact that although the landfill is relatively old ( $> 40$  years) and receives a large amount of yearly rainfall, it is still active, with some parts of the landfill being newer than others, and so it continues to be a significant source of BOD.

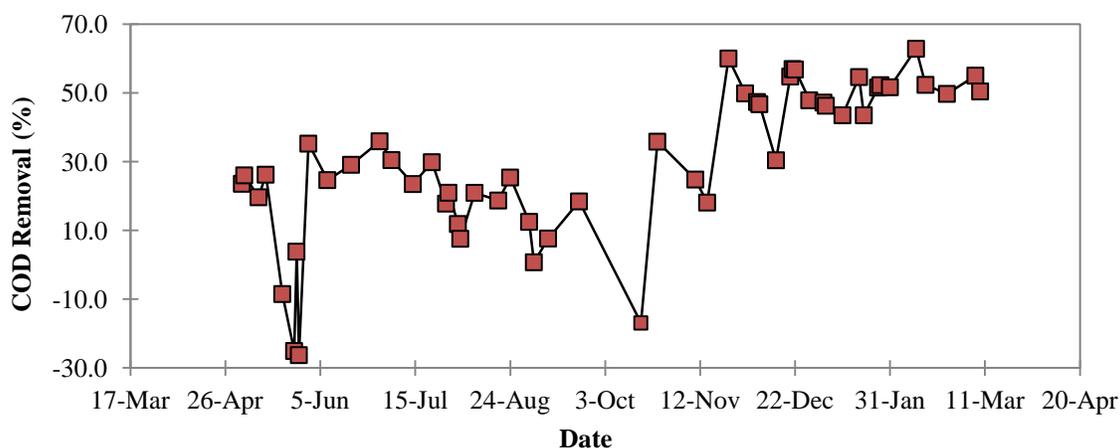
## 4.2 SBR Performance - Pollutant Removal and Sludge Characteristics

### 4.2.1 COD and CBOD

The influent mixture contained large amounts of both COD and CBOD. Figure 4.2 and 4.3 show influent and effluent COD and estimated removal percentage respectively for SBR 1. Removal of COD was inconsistent throughout the first half of the study. During the first 7 months, the removal ranged from -26% to 36% with a standard deviation of 16% which was the same as the average. As of late November, COD removal improved significantly with an average removal percentage of 50% and a standard deviation of 6%, indicating more stable operation. Removal efficiency remained above 40% even after reactor temperature was lowered to 17-19 °C in late December, indicating little temperature effect on COD removal.



**Figure 4.2** Influent and effluent COD for SBR 1 treating 50/50 (v/v) wastewater and landfill leachate.

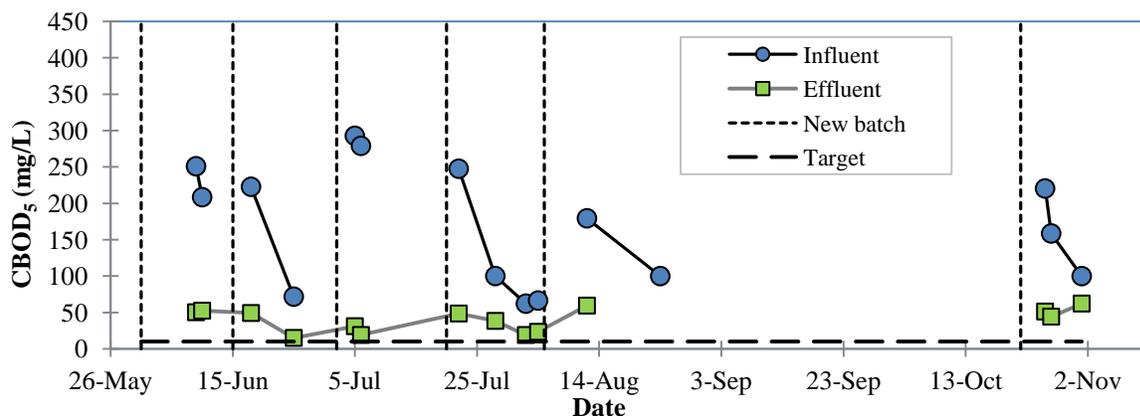


**Figure 4.3** COD removal percentage for SBR 1 treating 50/50 (v/v) wastewater and landfill leachate.

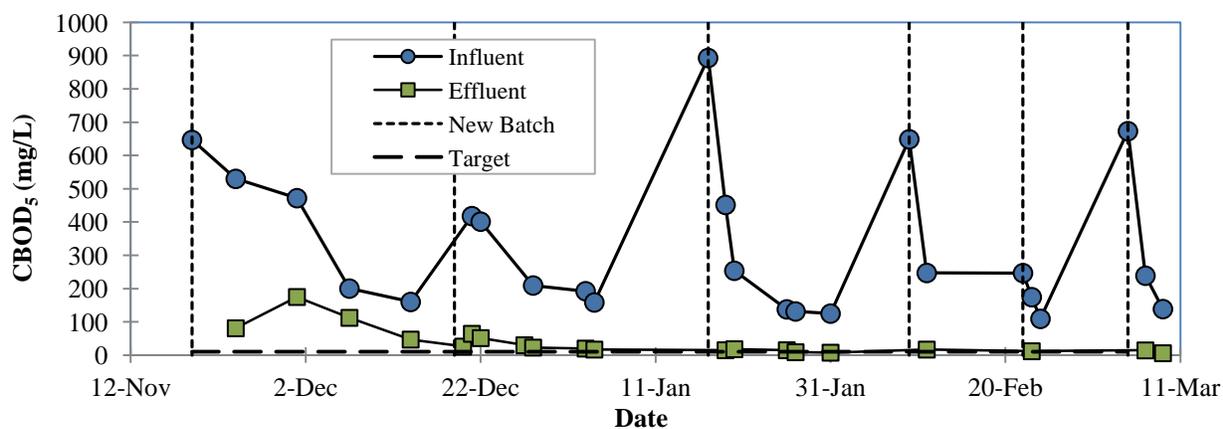
COD removal is generally attributed to the heterotrophic oxidation of readily biodegradable organics, and was therefore limited in this system, due to the relatively low average CBOD<sub>5</sub> to COD ratio (< 40%). The limited removal of refractory COD is commonly reported in landfill leachate treatment studies (Cecen and Aktas, 2004; Cecen and Cakiroglu, 2001; Kulikowska and Klimiuk (2004); Morling, 2006). The recalcitrant nature of the remaining organics, as indicated by the low CBOD<sub>5</sub> to COD of the effluent (< 5 ± 1 %) suggests that a physico-chemical process would likely be required for further reduction of COD, which has been shown effective by other authors of landfill leachate SBR studies (Cecen and Cakiroglu, 2001; Li *et al.*, 2009; Neczaj *et al.*, 2008; Uygur and Kargi, 2004). Removal of remaining COD may be necessary if chlorine disinfection is to be implemented, in order to avoid the formation of disinfection byproducts upon reaction with humic substances (Reckhow *et al.*, 1990; Yang and Shang, 2004).

Influent and effluent CBOD<sub>5</sub> is shown in Figures 4.4 and 4.5, with the vertical dashed lines indicating when a fresh batch was mixed for the feed, and horizontal dashed line for the target effluent value of 10 mg/L. As is clear in both figures, influent CBOD<sub>5</sub> fluctuated greatly

due to breakdown in the influent bottle. The wastewater and leachate were stored in separate bottles and refrigerated at 4 °C prior to mixing in order to reduce biodegradation, as was done in other combined wastewater and landfill leachate SBR treatment studies (Diamadopoulos *et al.*, 1997; Kulikowska and Klimiuk (2004)). However, after mixing of wastewater and leachate, the feed bottle was at room temperature (> 20 °C) for many days and exposed to air through a ventilation tube, thus, breakdown occurred. One batch was premixed and refrigerated at 4 °C (Figure 4.5, February 9th), and when that same batch was used for the feed on February 22nd, analysis showed that 400 mg/L of CBOD<sub>5</sub> breakdown occurred during refrigeration.



**Figure 4.4** Influent and effluent CBOD<sub>5</sub> for SBR 1 treating 50/50 (v/v) wastewater and landfill leachate. The effluent target was 10 mg/L (horizontal dashed line).



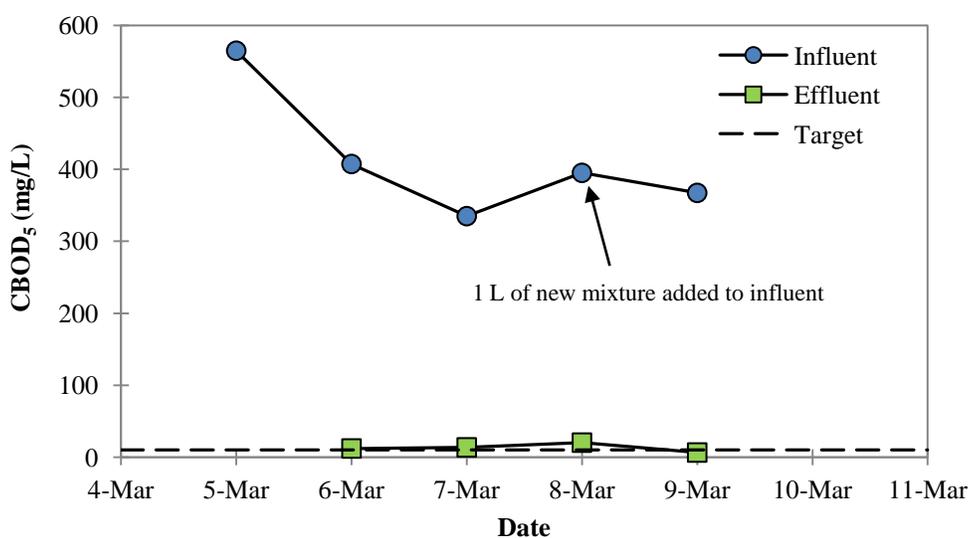
**Figure 4.5** Influent and effluent CBOD<sub>5</sub> for SBR 1 treating 50/50 (v/v) wastewater and landfill leachate. The effluent target was 10 mg/L (horizontal dashed line).

Measurements of CBOD<sub>5</sub> taken before November were not always performed for a fresh batch and so initial influent CBOD<sub>5</sub> to the SBR would have been higher in those cases. By examining the rapid decrease of CBOD<sub>5</sub> for each new batch, it is clear that the initial values (corresponding to the vertical dashed lines in Figure 4.4) would have been considerably higher than the first measurements taken. The estimated range of initial CBOD<sub>5</sub> values were 400 - 900 mg/L, based on the average initial rates of degradation seen in Figure 4.5. This estimated range is very similar to the initial values seen in Figure 4.5, suggesting that CBOD<sub>5</sub> during summer and fall (Figure 4.4) were high as in winter and spring (Figure 4.5).

Before January, effluent CBOD<sub>5</sub> never reached a target value of 10 mg/L, and was only measured below 20 mg/L on three occasions (Figures 4.4 and 4.5). Beginning in late December and early January, when winter leachate was fed to the reactor, CBOD<sub>5</sub> removal was excellent regardless of the high influent values for each new batch. It was unclear as to why there was sudden improvement in COD and CBOD<sub>5</sub> removal as of winter, or why there was limited removal during summer and fall (Figures 4.4 and 4.5). It was possible that a longer aeration time may have been necessary to reduce CBOD<sub>5</sub> to achieve the effluent target.

Another possibility for reduced CBOD removal performance was dissolved oxygen in the SBR, which was unknown until late December. However, it was necessary to maintain sufficient DO levels for biological processes (Metcalf and Eddy, 2003). To test the effects of increased aeration on reactor performance, an aeration study was performed in which the air flow rate was increased from 9 L/h to 60 L/h. The aeration study was performed using SBR 2 at 17 °C, with all operating parameters being the same as for SBR 1 (Table 3.1), except with a combined influent of 33% wastewater and 67% November landfill leachate. The landfill leachate during November was more dilute than in summer, so this mixture was chosen to simulate the higher

summer leachate loadings. Influent and effluent CBOD<sub>5</sub> measurements during the period of increased aeration are given in Figure 4.6. An air flow rate of 60 L/h resulted in low effluent CBOD<sub>5</sub>, with effluent values less than 15 mg/L and one as low as 6 mg/L being achieved. Thus, with increased aeration, the SBR was capable of producing low effluent CBOD<sub>5</sub> for a combined influent with a higher leachate concentration, suggesting that low DO could have been a factor when treating the more concentrated leachate during summer and fall.



**Figure 4.6** Influent and effluent CBOD<sub>5</sub> during an aeration study for SBR 2 treating 33/67 (% v/v) wastewater to landfill leachate. Operating parameters from SBR 2 were the same as for SBR 1.

Effluent was measured for CBOD remaining after more than 20 days in order to estimate the ultimate CBOD leaving the SBR. Table 4.4 shows the long-term CBOD values compared with corresponding CBOD<sub>5</sub> for effluent samples from SBR 1. The CBOD<sub>5</sub> was approximately  $40 \pm 7\%$  of the long-term CBOD indicating slow biodegradability of effluent organics.

**Table 4.4** Long-term CBOD and CBOD<sub>5</sub> for effluent from SBR 1 treating 50/50 (v/v) wastewater and landfill leachate. Data is given with 95% confidence intervals for sample replicates.

Date	Effluent CBOD <sub>5</sub> (mg/L)	Effluent CBOD <sub>20</sub> (mg/L)
Dec 1, 2015	175 ± 64	446
Dec 27, 2015	23 ± 14	78 ± 24
Jan 3, 2016	12 ± 2	39 ± 7
Mar 9, 2016	6 <sup>a</sup>	50 ± 13 <sup>b</sup>

<sup>a</sup>Insufficient sample volume to provide replicates.

<sup>b</sup>37-day CBOD value

Effluent BOD was able to be reduced by filtration, suggesting association with particulate matter (Section 4.2.5). The data is shown in Table 4.4. Although it is a very limited data set, and the effluent values are already quite low, it shows a possibility for reducing effluent CBOD<sub>5</sub> via filtration.

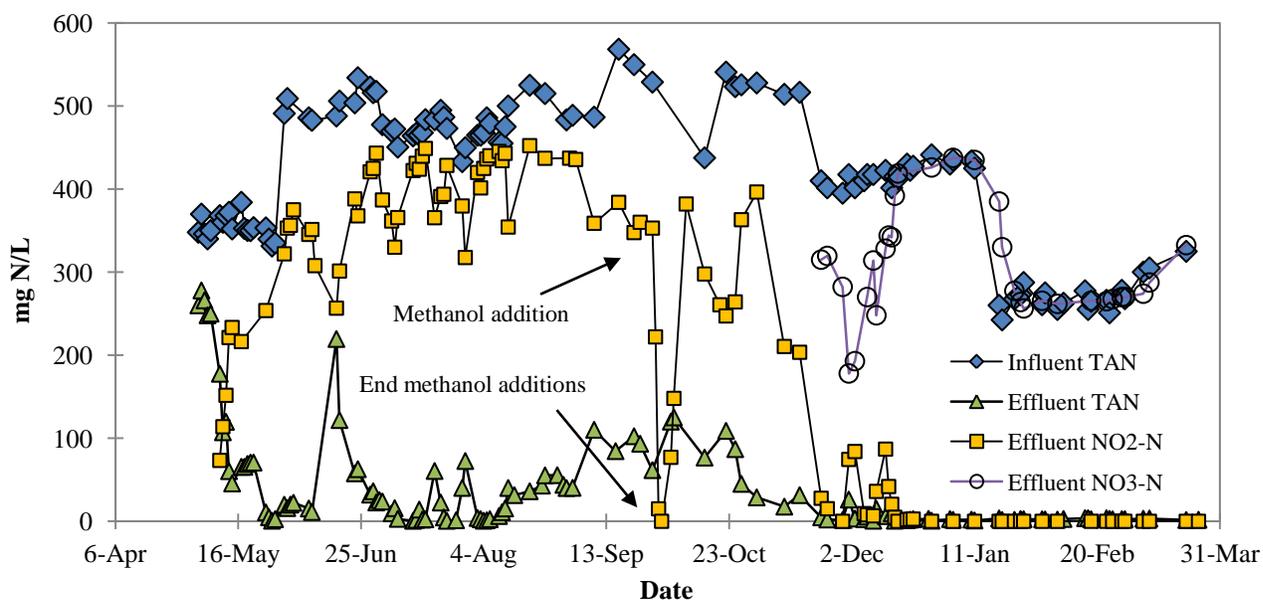
**Table 4.5** Filtered and unfiltered effluent CBOD<sub>5</sub> for SBR 1 treating 50/50 (v/v) wastewater and landfill leachate.

Sample date	Effluent CBOD <sub>5</sub> , dil 1 (mg/L)	Effluent CBOD <sub>5</sub> , dil 2 (mg/L)	Effluent CBOD <sub>5</sub> , avg (mg/L)	
20-Jan	10	18	14	<i>unfiltered</i>
	8	6	7	<i>filtered</i>

## 4.2.2 Nitrogen

### 4.2.2.1 Nitrogen Removal

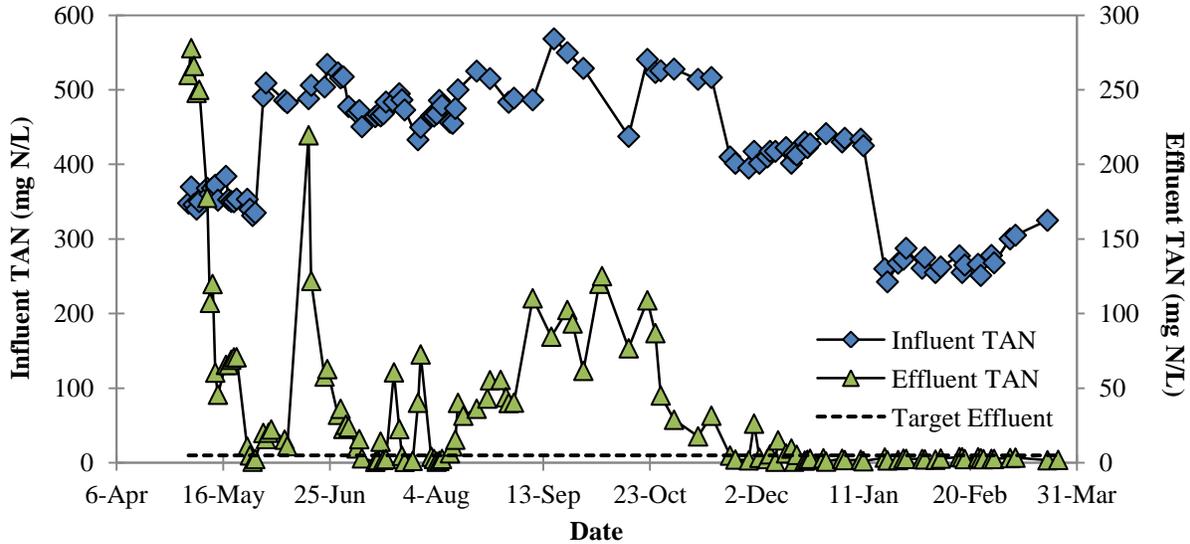
Figure 4.7 shows nitrification performance for SBR 1 during the entire study. After the first few days of initial start up, the HRT was increased from 1 day to 4 days. The 1 day HRT caused excessive TAN loading to the reactor and therefore removal was poor during this time. Once the HRT was increased, ammonia oxidation improved with effluents of less than 5 mg N/L being achieved, although there was incomplete nitrification to nitrite (Figure 4.7). There were a few spikes in effluent TAN due to reactor perturbations, although in each case the SBR recovered. The spikes that occurred on June 17<sup>th</sup> and October 19<sup>th</sup> were due to extra fill causing an increased loading. Similar occurrences caused brief spikes in both effluent TAN and NO<sub>2</sub>-N on December 1<sup>st</sup> and 10<sup>th</sup>. The spike in effluent TAN observed July 28<sup>th</sup> - 29<sup>th</sup> was due to the air being accidentally shut off for 4 cycles.



**Figure 4.7** Influent and effluent nitrogen species for SBR 1 treating 50/50 (v/v) wastewater and landfill leachate.

Nitrite accumulation continued throughout the first 7 months of operation, followed by complete nitrification to nitrate for the remainder of the study (Figure 4.7). Due to test interferences,  $\text{NO}_3\text{-N}$  was only given under conditions of low  $\text{NO}_2\text{-N}$  concentrations beginning in November. However, an effluent sample from September 14th sent for testing by EMD Millipore contained 67 mg/L of  $\text{NO}_3\text{-N}$ , indicating NOB activity at some point, although it was still a relatively small portion of the  $\text{NO}_x\text{-N}$ . The sharp drop in  $\text{NO}_2\text{-N}$  that occurred between Sept 28<sup>th</sup> and Oct. 5<sup>th</sup> was due to denitrification, by spiking the SBR with methanol. Complete nitrification to  $\text{NO}_3\text{-N}$  was consistently observed after a drop in the TAN loadings in November.

Although the SBR was able to achieve effluent TAN < 5 mg/L at higher loadings, it was not consistent during the first 6 ½ months (Figure 4.7). There were some periods of time in which TAN accumulated in the SBR as indicated by high effluent values, especially during September and October, which can be seen more clearly in Figure 4.8. The data suggests that under higher TAN loadings, the SBR was prone to TAN accumulation (Figure 4.8). This was a cause for concern as one of the main goals of the treatment study was the reduction of TAN to effluent quality standards. However, when TAN loadings decreased in November and complete nitrification to  $\text{NO}_3\text{-N}$  was observed, effluent TAN consistently met the effluent target.



**Figure 4.8** Influent and effluent TAN concentrations for SBR 1 treating 50/50 (v/v) wastewater and landfill leachate.

Reactor performance in terms of TAN removal can also be visualized by plotting average TAN oxidation rates, which were based on estimated loading and effluent values by Equation 4.1:

$$\Delta TAN/\Delta t = (TAN_i - TAN_f)/t_{aer} \quad [4.1]$$

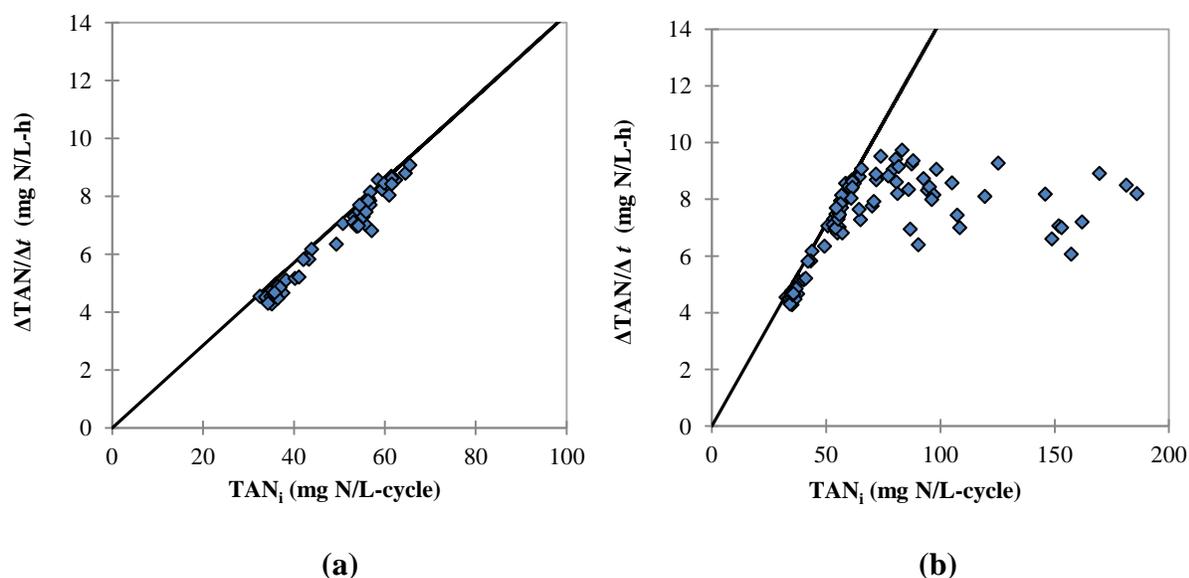
In Equation 4.1,  $TAN_f$  and  $TAN_i$  are the final and initial TAN concentrations in mg/L respectively and  $t_{aer}$  is the aerobic react time in hours. The assumption in using Equation 4.1 is that the majority of TAN oxidation occurs during the 7-hour aerobic phase. To estimate the loading,  $TAN_i$ , the following mixing Equation was used:

$$TAN_i = [V_{fill}TAN_{inf} + (V_R - V_{Fill})TAN_{eff}]/V_R \quad [4.2]$$

In Equation 4.2,  $V_R$  and  $V_{fill}$  are the reactor working volume and fill volume respectively in L, and  $TAN_{eff}$  is the effluent TAN after decant during the previous cycle. Interpolation and averaging was used for estimating effluent TAN from previous cycles, since there was at least 1 cycle in between measured effluent values.

Figure 4.9 (a) and (b) display the rates estimated by Equation 4.2 plotted versus total  $TAN_i$  using (a) only the data in which most TAN was oxidized (effluent TAN < 10 mg/L) and (b) all of the data including rates that could be reasonably estimated. The straight line represents 100% removal. As shown in Figure 4.9 (a), for TAN loads less than 70 mg/L-cycle the plot is linear and near the 100% removal line as would be expected since  $\Delta TAN \sim TAN_i$  and the estimated rate is almost proportional to  $TAN_i$  by a factor of  $1/t_{aer}$ . Under increased loading,  $\Delta TAN$  should continue to increase. However, as shown in Figure 4.9 (b), the estimated rate curve flattens out, and TAN removal was limited to ~ 6 - 9 mg N/L-h (Figure 4.9 (b)) above a loading of 60 - 70 mg/cycle. This resulted in residual TAN after the 7 h aeration period. Thus, a longer aeration period was required for complete TAN removal.

Based on the average MLVSS of 2500 mg/L, the corresponding range of average specific rates were 2.4 - 3.6 mg N/g VSS-h. Typical rates reported in activated sludge have been reported on a range of 1 - 7 mg N/g VSS-h (Barnes and Bliss, 1983; Choubert *et al.*, 2005; Wang *et al.*, 2009). Due to high concentrations of residual TAN, these rates at loadings above 60 mg/cycle (Figure 4.9 (b)) were likely to be very near the actual kinetic rates in the SBR, as opposed to rates shown at lower loadings, which could have been higher since near complete removal was achieved during the cycles.



**Figure 4.9** Estimated average TAN oxidation rates using (a) data where effluent TAN < 10 mg/L and (b) all data where rates could be estimated through interpolation. The straight line represents 100% removal.

As discussions in Section 2.27 of the literature review, some possible reasons for decreased TAN removal and excess  $\text{NO}_2\text{-N}$  accumulation under higher loadings were suspected to be due to inhibitory concentrations of FA or FNA, low dissolved oxygen levels, or other inhibitory substances present in the leachate like metals or organics (Anthonisen et al., 1976; Ciudad *et al.*, 2004; Kaczorek and Ledakowicz, 2006; Kim and Kim, 2003; Ruiz *et al.*, 2003; Sandborgh, 2011; You *et al.*, 2009).

#### 4.2.2.2 Free Ammonia and Free Nitrous Acid

It was suspected that FA or FNA could have been a source of nitrification inhibition, thus it was necessary to estimate their concentrations in the reactor. FA and FNA concentrations were calculated by converting the TAN and  $\text{NO}_2\text{-N}$  data using the following relationships taken from Anthonisen *et al.* (1976):

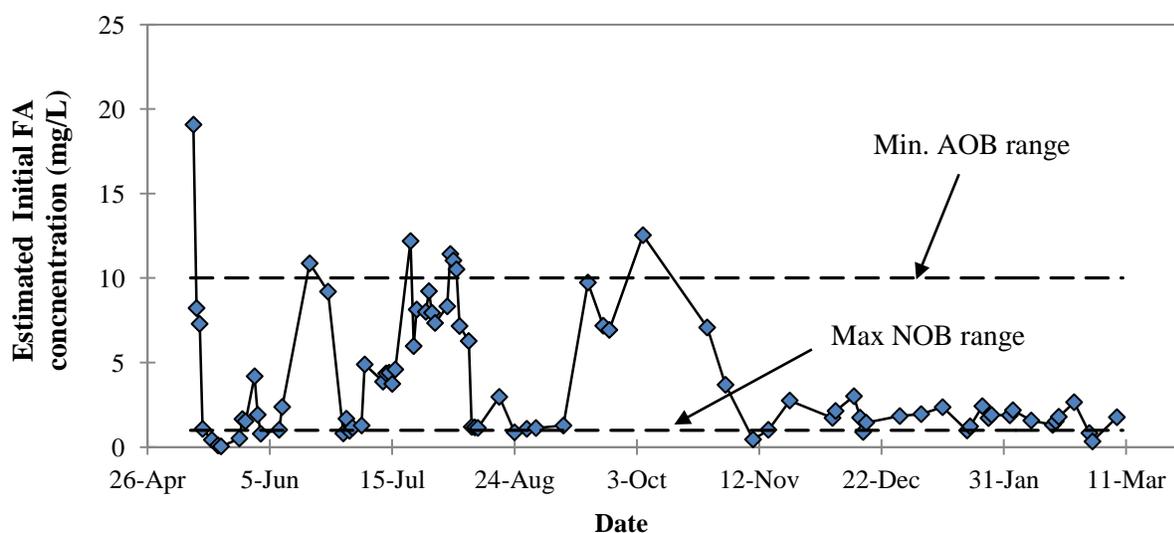
$$FA \left( \frac{mg}{L} \right) = \left( \frac{17}{14} \right) \frac{TAN * 10^{pH}}{\left( \frac{K_b}{K_w} \right) + 10^{pH}} \quad [4.3]$$

$$FNA \left( \frac{mg}{L} \right) = \left( \frac{46}{14} \right) \left( \frac{NO_2-N}{K_a * 10^{pH}} \right) \quad [4.4]$$

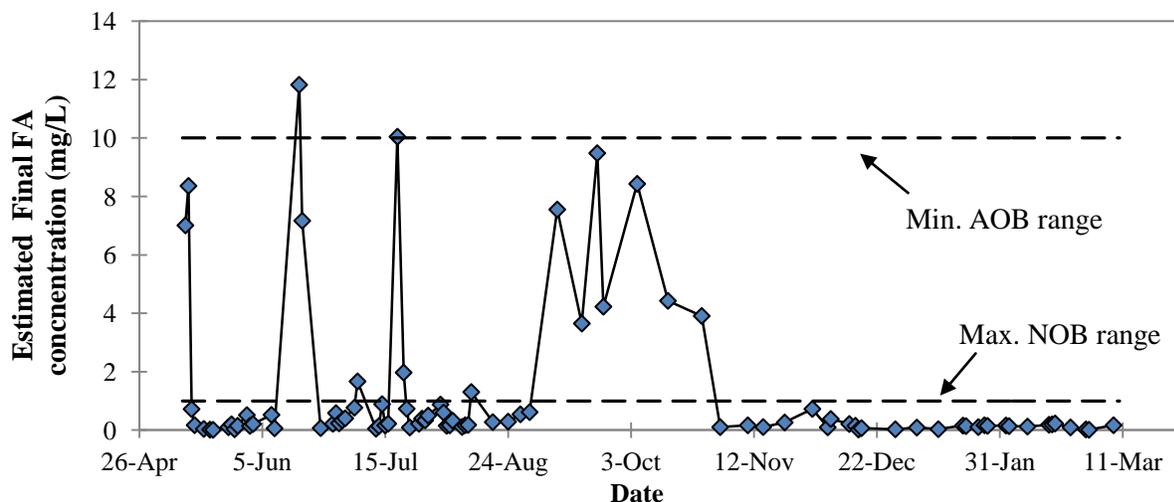
In Equation 4.3,  $K_b$  and  $K_w$  are the temperature dependent ionization equilibrium constants for ammonia and water respectively where  $K_b/K_w = \exp(6344/(273+^{\circ}C))$ . In Equation 4.4,  $K_a$  is the temperature dependent ionization constant of nitrous acid equilibrium where  $K_a = \exp(-23300/(273+^{\circ}C))$ . Initial FA and FNA in the SBR were estimated using TAN and  $NO_2-N$  influent values with Equation 4.3 and 4.4 respectively, and final concentrations were estimated using effluent values.

Estimated FA concentrations in the SBR are shown in Figure 4.10 and Figure 4.11 respectively and maximum FNA is shown in Figure 4.12. The higher sensitivity of NOB to FA than AOB may help explain the accumulation of  $NO_2-N$ , since FA concentrations were often above reported inhibitory levels for NOB (Figures 4.10 and 4.11). Incomplete TAN removal due to high FA was not likely, since estimated concentrations were rarely, if ever, at inhibitory concentrations for AOB (Figure 4.10 and 4.11). Furthermore, these concentrations were only observed after significant TAN accumulation occurred in the reactor. It should be noted that concentrations above 10 mg/L of FA does not necessarily result in a significant decrease in AOB rates. For example, a landfill leachate treatment study by Chung *et al.* (2004) found only a 10 % decrease in the maximum specific substrate utilization rate from 10 - 50 mg FA/L, and no effects below 10 mg/L. Negligible effects of high FA on TAN oxidation have also been reported in other landfill leachate studies (Kaczorek and Ledkowicz, 2006).

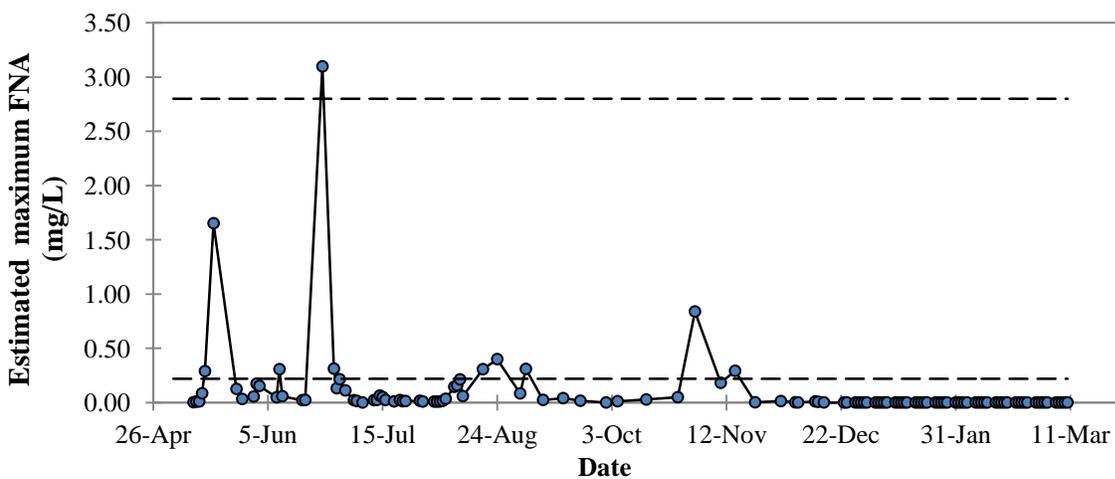
The sharp spike in FNA on June 24<sup>th</sup> shown in Figure 4.12 was due to a drop in pH by ammonia oxidation before starting alkalinity additions. This seemed to have no lasting effect on AOB since TAN concentrations steadily dropped over subsequent cycles. The most likely cause for the decreases in AOB activity at pH < 7 was lack of sufficient substrate, which has been shown to be FA (Suzuki *et al.*, 1974). Due to dilution at the start of each cycle and pH buffering by alkalinity, initial and average FNA concentrations would have been considerably lower than those shown in Figure 4.12, thus, FNA was most likely at low enough levels as to not significantly inhibit nitrification, although it could not be completely ruled out at times since inhibitory FNA concentrations can be quite low for both AOB and NOB (Figure 4.12).



**Figure 4.10** Estimated initial FA concentrations in SBR 1 based on total TAN loading and estimated initial pH values. Dashed lines indicate concentration range where AOB/NOB inhibition may occur as reported in literature (Anthonisen *et al.*, 1976).



**Figure 4.11** Estimated final FA concentrations in SBR 1 based on effluent TAN and pH values. Dashed lines indicate concentration range where AOB/NOB inhibition may occur as reported in literature (Anthonisen *et al.*, 1976).



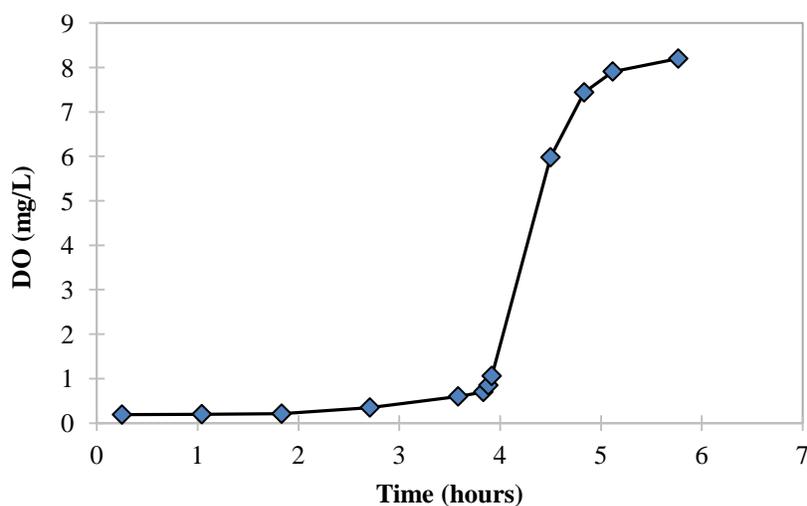
**Figure 4.12** Estimated maximum FNA concentrations in SBR 1 based on effluent  $\text{NO}_2\text{-N}$  and pH values. Dashed lines indicate concentration range where both AOB/NOB inhibition may occur as reported in literature (Anthonisen *et al.*, 1976).

As previously discussed, reported inhibitory FA and FNA concentrations for both AOB and NOB have been shown to vary between studies, and depend on a variety of factors including acclimation time, temperature and pH, and biomass concentration (Anthonisen *et al.*, 1976; Bae

*et al.*, 2002; Suthersan & Ganczarczyk., 1986). Actual inhibitory conditions will depend on the system, and can only be determined through controlled experiments in which other substrates such as DO are not significant rate limiting factors. It is nonetheless important to take measures to avoid extremely high TAN and NO<sub>2</sub>-N concentrations in the SBR to avoid inhibitions, which could be done through adjustments in loading (or HRT), pH, or aeration.

#### 4.2.2.3 Dissolved Oxygen

Elevated effluent TAN during summer and early fall (Figure 4.8) may have been due to a reduction in ammonia oxidation rates by DO limitations, although no DO data was available during the period of high observed TAN concentrations. However, the DO profile shown in Figure 4.13, measured during February under a TAN loading of approximately 30-35 mg N/L-cycle, shows that the bulk DO concentration was below 0.5 mg/L during the first half of the cycle and around 0.2 mg/L (anoxic) during the first 2 hours.



**Figure 4.13** Dissolved oxygen profile for SBR 1 treating 50/50 (v/v) landfill leachate and wastewater during low winter loadings of 35 mg TAN/L-cycle and <15 mg BOD/L-cycle. The air flow rate was 9 L/h.

Nitrification rates have been shown to be significantly reduced by  $DO < 0.5$  mg/L, also resulting in transient  $NO_2-N$  (Metcalf and Eddy, 2003). Typical  $K_O$  values for nitrifiers have been reported on a range of 0.4 - 2.0 mg/L (Kaelin *et al.*, 2009; Metcalf and Eddy, 2003). Furthermore, incomplete nitrification has been shown in many studies as a result of low DO (Ciudad *et al.*, 2004; Ruiz *et al.*, 2003, Van Hulle *et al.*, 2010; Sanchez *et al.*, 2007; Blackburne *et al.*, 2008; Ma *et al.*, 2015).

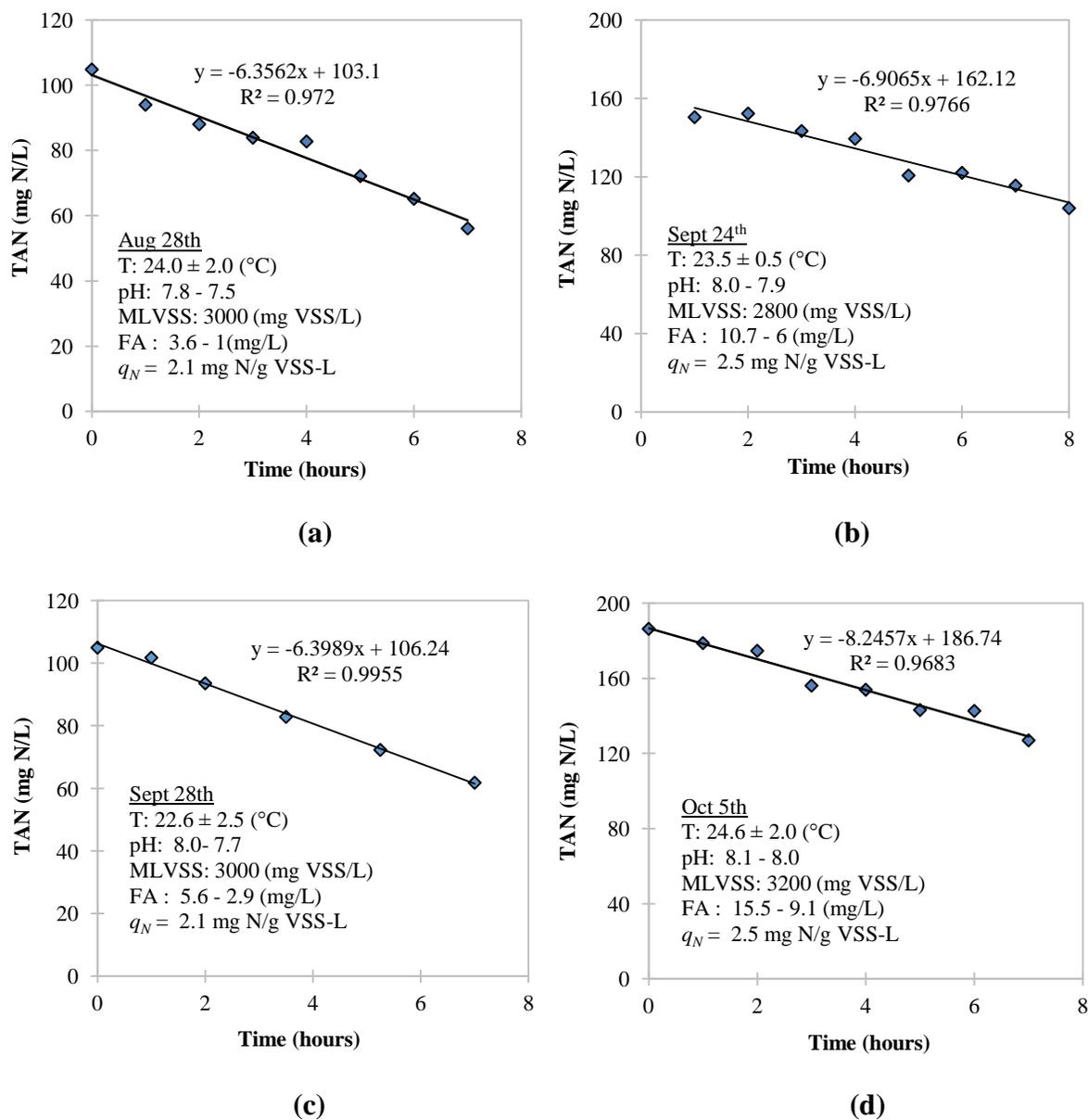
It therefore possible that the DO concentration was below levels for sufficient nitrification during the first half of the aeration cycle, even during a period of relatively low oxygen demand loadings. The TAN loading corresponding to the DO profile shown in Figure 4.19 was only about 50-60 % of previous feed loadings to the SBR, and an much smaller fraction of the total TAN loadings seen during summer and fall (Figures 4.13 (a) - (b)). In addition, there were also periods of high  $CBOD_5$  loading, thus, oxygen demand would have been at least double what is represented by the DO profile in Figure 4.13. Thus, low DO may have had a detrimental effect on nitrification activity, and could have contributed to both the TAN and  $NO_2-N$  accumulation seen previously in the SBR.

Complete nitrification at low DO levels ( $< 0.5$  mg/L) after long-term operation at high SRTs (10 - 40 days) have been previously reported in literature (Liu and Wang, 2013). This was shown to be due to a shift in the NOB culture in the reactor from *Nitrobacter* to *Nitrospira*, leading to less sensitivity of NOB to low DO, although the authors did report short term (weeks long) accumulation of both TAN and  $NO_2-N$  after lowering DO concentrations. This could be one possible explanation for the complete conversion of  $NO_2-N$  after the long period of  $NO_2-N$  accumulation (Figure 4.7). It has been shown that *Nitrobacter*, which is often assumed to be the representative NOB in activated sludge, have a lower oxygen affinity than *Nitrospira* (Manser *et*

*al.*, 2005). Thus, a shift to, or enrichment of *Nitrospira* could be a plausible explanation for the increased NOB activity. However, a molecular analysis of the nitrifying culture, as well as further testing under various DO concentrations would be needed to verify this hypothesis.

#### 4.2.2.4 Ammonia Oxidation Kinetics and Nitrification Profiles

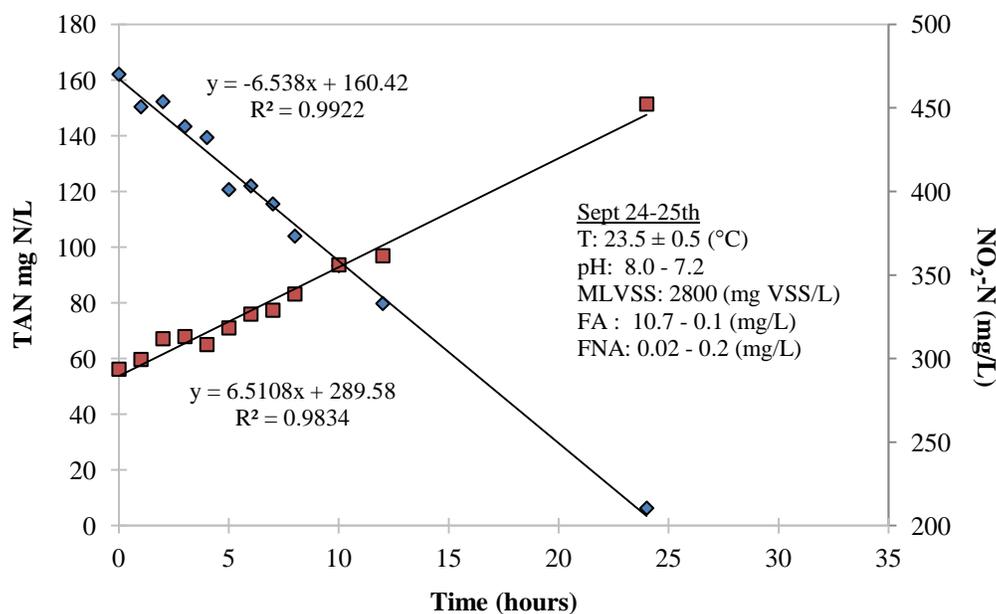
Kinetic profiles for ammonia oxidation under high oxygen demand loading conditions observed in late summer and early fall are given in Figure 4.14 (a) - (d). Profiles which include  $\text{NO}_2\text{-N}$  production can be found in the Figures A.11 (a) - (c) of the Appendix.



**Figure 4.14** (a) - (d) TAN profiles for SBR 1 treating 50/50 (v/v) landfill leachate and wastewater during elevated TAN loadings in summer and early fall.

The rates determined by the slope of the TAN curves in Figure 4.14 were similar to the estimated rates at higher loadings shown in Figure 4.9 (b), and were also included in that figure. The average specific rate ( $q_N$ ) using the MLVSS was  $2.4 \pm 0.2$  mg N/g VSS-h, which as stated previously, fall in a typical range for activated sludge (1-7 mg/g VSS-h). However, they were insufficient to oxidize all the TAN in the SBR during the aeration cycle. The rates were similar to those reported by Gorfelt (2008), who achieved minimum rates of 7.6 mg N/L-h (2.9 mg N/g VSS-h) in landfill leachate treating SBRs containing 2700 mg VSS/L mixed liquor solids. However, the author cited low oxygen levels as a possible rate limiting factor, and found that specific nitrification rates improved by over 50% with increased DO from 0.5 mg/L to 6.0 mg/L.

To lower the TAN in the reactor and decrease the FA concentration, the aeration cycle represented by the TAN curve in Figure 4.14 (b) was allowed to continue for 27 hours. TAN was reduced to 6 mg/L after 24 hours with a final TAN < 3 mg/L (data point not shown). The complete TAN curve is given in Figure 4.15 with NO<sub>2</sub>-N. The data suggests that the ammonia oxidation rate did not significantly increase during the cycle, even with FA concentrations well below 10 mg/L. Inhibition by FNA was unlikely since after 12 hours FNA was only 0.04 mg/L, well below the inhibitory range for AOB (Figure 4.12). Although no NO<sub>3</sub>-N data was obtained, the slopes of the TAN and NO<sub>2</sub>-N curves were the same, indicating no NOB activity (*i.e.* no NO<sub>3</sub>-N production) during the cycle.

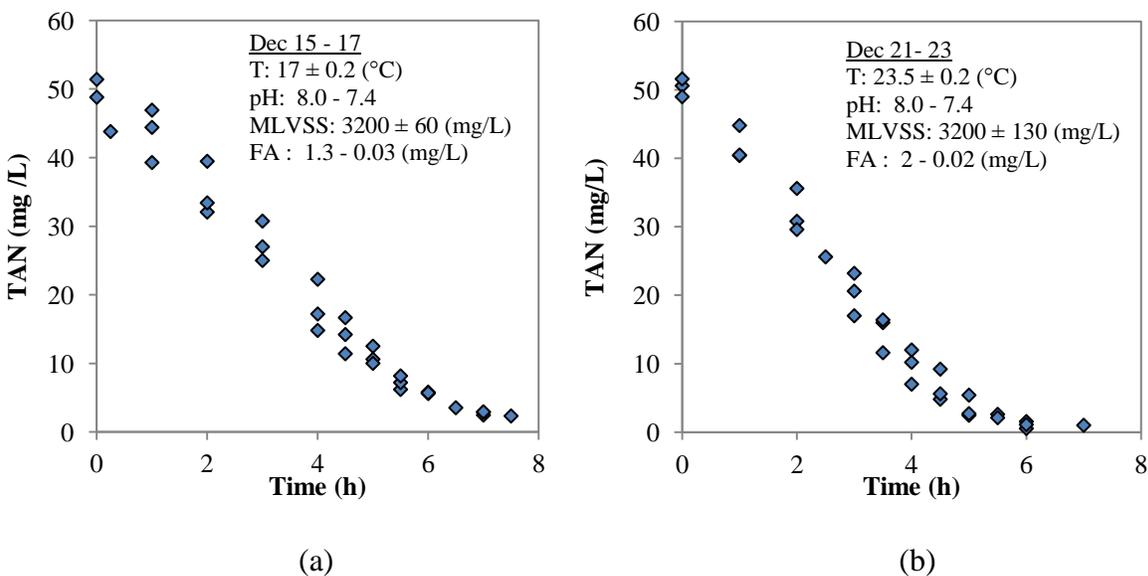


**Figure 4.15** Nitrification profile for SBR 1 treating 50/50 (v/v) landfill leachate and wastewater during September.

After TAN was allowed to decrease to almost zero, the next effluent value recorded on Sept. 28<sup>th</sup> was about 62 mg/L (Figure 4.7). This indicated that TAN had subsequently accumulated in the SBR by about 15 mg/L-cycle. The ammonia oxidation rate of 6.5 mg N/L-h (or ~50 mg TAN/cycle) observed during this time was insufficient to convert all of the TAN in the feed, which at this time was roughly 65 - 70 mg/L-cycle. Therefore, once normal operation was resumed, TAN accumulation was observed. This could not be explained by high FA concentrations since the initial FA during the subsequent aeration cycle could not have been higher than 4 mg/L, based on the initial TAN concentration (70 mg/L) pH (7.8 - 8), and temperature (24 °C) during this time.

Replicate TAN profiles measured during December, under an average loading of 50 mg N/L-cycle are given in Figure 4.16 (a) and (b) along with pH, MLVSS, average FA range, and temperature conditions. The temperatures 23.5 °C and 17 °C were chosen to represent the

temperature of previous kinetic profiles and cooler wastewater temperatures, respectively, as well as to quantify the temperature effects on nitrification rates.

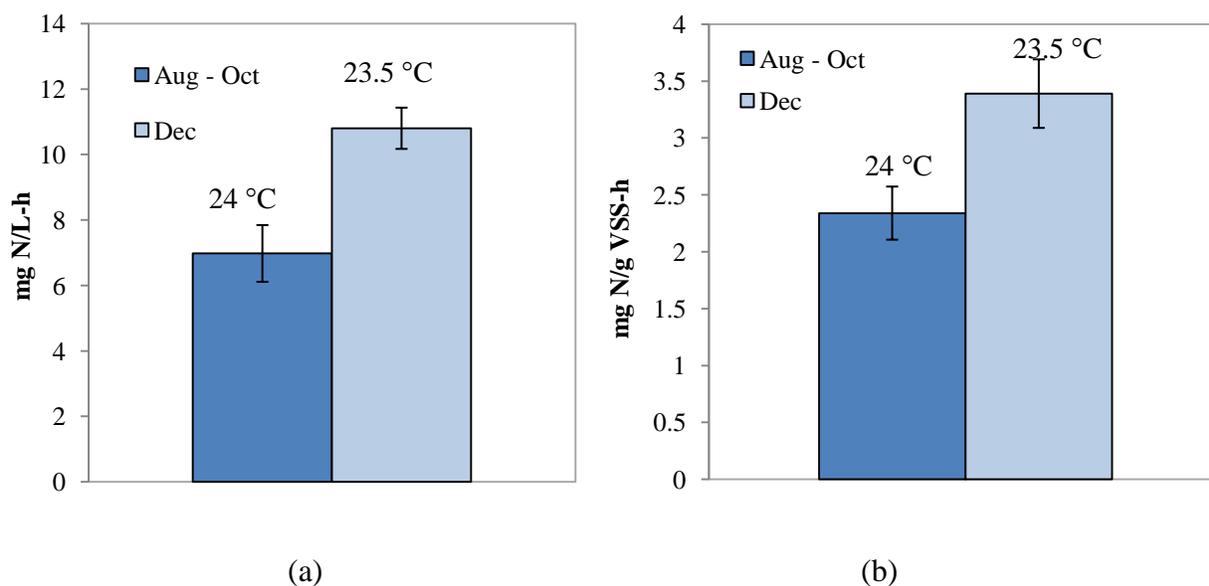


**Figure 4.16** Combined TAN profiles at (a) 17 °C and (b) 23 °C in SBR 1 treating 50/50 (v/v) wastewater and landfill leachate.

The target effluent TAN concentration of 5 mg/L was achieved after 6 hours at 17 °C and 5 hours at 23.5 °C, therefore at cooler wastewater temperatures under the given conditions, the 8 h length of the aerobic phase was adequate to achieve sufficient TAN conversion. The TAN profiles also show a significant decrease in the rate (~ 50 %) after 10 mg/L, indicating a relatively high ammonium half-saturation constant as compared with reported values, which range from 0.2 - 1.0 mg/L (Manser *et al.*, 2005; Metcalf and Eddy, 2003). From the curves in Figure 4.16, the ammonia oxidation rates observed at 17 °C and 23.5 °C were 7.9 mg/L-h and 10.4 mg N/L-h, respectively, with specific rates of 2.5 mg N/g VSS-h and 3.4 mg N/g VSS-h, respectively. The rates at 23.5 °C were about 30% higher than those compared to summer and

fall at the same temperature, and were sufficient for complete conversion of TAN, thus, no accumulation was observed during December (Figure 4.7).

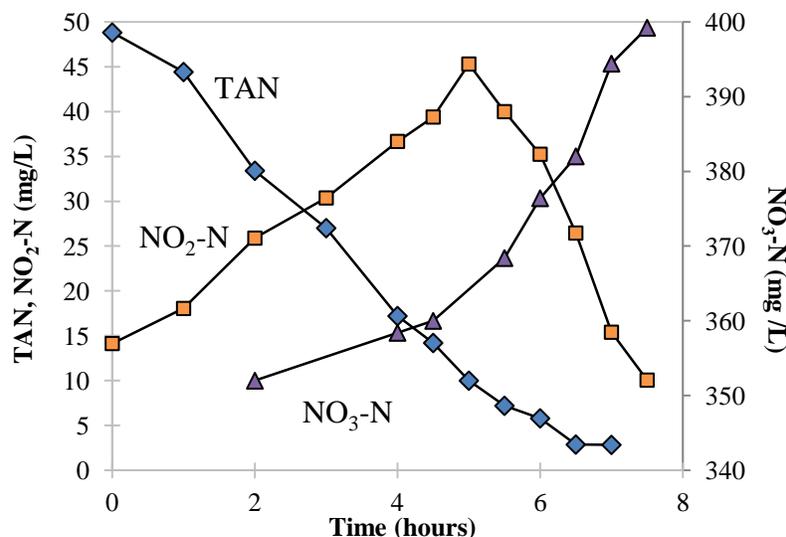
Rates compiled from all kinetic profiles during the study are shown in Figure 4.17 (a) and (b). An increase in ammonia oxidation was observed with increasing temperature from 17 °C to 23.5 °C. The rates at 17 °C during December are also slightly greater than those during summer and fall at 23 - 24 °C. This suggests that the higher TAN oxidation rates seen in December at lower TAN loadings were not due to a temperature increase, but rather some other conditions favoring higher rates. As previously discussed, this is likely to have been a higher bulk DO leading to increased TAN oxidation rates, rather than a reduction in FA concentrations in the SBR, although no DO data was available.



**Figure 4.17** (a) Volumetric ammonia oxidation and (b) specific ammonia oxidation rates in SBR 1 treating 50/50 (v/v) wastewater and landfill leachate. Error bars represent 95% confidence intervals.

The specific ammonia oxidation rates given in Figure 4.17 (b) are lower than those reported for many landfill leachate treatment studies. In separate studies using continuous flow activated sludge systems treating landfill leachate, Knox (1986) reported rates of 5 mg/g VSS-h and Chung reported rates of up to 30 mg N/g VSS-h. Rates on a range of 5.0 - 7.0 mg N/g VSS-h were reported for SBRs treating landfill leachate in separate studies by Kulikowska and Klimiuk, (2006) and Kaczorek and Ledakowicz (2006). Doyle *et al.* observed even higher specific rates of 37 mg N/g VSS-h in leachate treating SBRs with initial TAN concentrations up to 300 mg/L per cycle. However, the study by Dotle *et al.* was run for 2 years with mature landfill leachates containing very low amounts of COD, and therefore the extremely high rates could have been attributed to long-term acclimation and cultivation of a very high specific nitrifying biomass concentration (Doyle *et al.*, 2001). In fact, increasing TAN removal rates at lower N/COD ratios have also been reported in other landfill leachate studies (Kulikowska and Klimiuk, 2004). It is difficult to draw comparisons between specific TAN oxidation rates observed in this study (Figure 4.17) to reported specific rates in literature, since rates based on total VSS are highly dependent on the fraction of AOB in the total biomass (Barnes and Bliss, 1983; Wang *et al.*, 2009), which can vary greatly between studies depending on conditions and relative concentrations of COD and TAN in the feed.

A complete nitrification profile showing conversion of TAN to NO<sub>2</sub>-N then NO<sub>3</sub>-N is given in Figure 4.18, which was taken in December. Replicate profiles at 17 °C and 23.5 °C are given in Figures A.7 of the Appendix. Significant NO<sub>2</sub>-N build-up was observed during the cycle indicating low initial NOB activity, which was the same for all profiles measured during this time. Only about 10 mg of NO<sub>2</sub>-N was converted in the first 5 hours, thus the NO<sub>2</sub>-N oxidation rate was no greater than 2 mg N/L-h and there was a significant NO<sub>2</sub>-N lag.



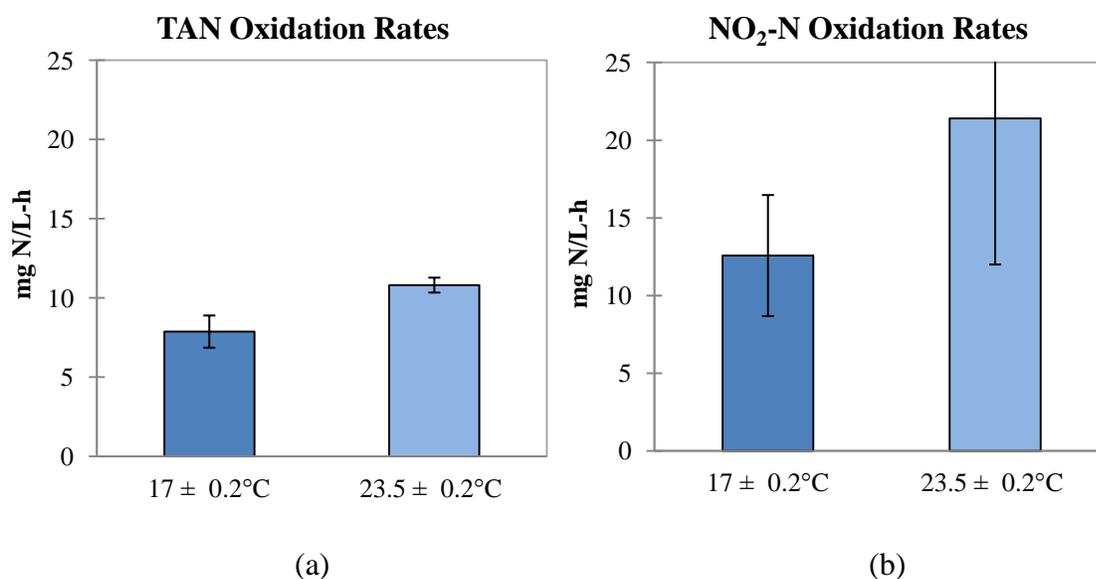
**Figure 4.18** Full nitrification profiles at 17 °C in SBR 1 treating 50/50 (v/v) wastewater and landfill leachate during December.

Once most of the TAN was oxidized, the rate of NO<sub>2</sub>-N oxidation increased significantly until complete conversion to NO<sub>3</sub>-N was achieved. This raised the question of which had a greater effect on NOB activity, low DO or FA. Due to the low NO<sub>2</sub>-N half-saturation constants (~ 0.3 mg/L) reported for NOB, substrate limitation was unlikely (Kaelin *et al.*, 2009). Based on the temporary accumulation of NO<sub>2</sub>-N seen in Figure 4.17, higher pollutant loadings could have led to even lower NOB rates due to effects of low DO, oxygen competition, or high FA. This could have led to incomplete conversion during the reaction cycle, resulting in NO<sub>2</sub>-N build-up over subsequent cycles.

When TAN loadings decreased in November, conditions favored complete nitrification to NO<sub>3</sub>-N as shown in Figure 4.18. Effects of loading, FA, and DO on partial nitrification will be discussed further in Section 4.2.2.6. As will be shown, increased aeration led to complete nitrification under TAN loading conditions significantly higher than those shown in Figure 4.18.

#### 4.2.2.5 Comparison of Ammonia and Nitrite Oxidation Rates

Nitrite curves were also used to estimate  $\text{NO}_2\text{-N}$  oxidation rates by measuring the slope during maximum  $\text{NO}_2\text{-N}$  utilization shown in Figure 4.18 and Figures A.7 (a) - (e), which occurred during the last 2 hours of the aeration cycle in each case. Limited data points were available for rate estimations for some profiles, however no less than 3 data points were able to be used to estimate the slopes. Compiled nitrification rates taken from December kinetic profiles are given in Figure 4.19 (a) and (b). The average rates of  $\text{NO}_2\text{-N}$  oxidation (b) were roughly 1.5 - 2 times higher than TAN oxidation rates (a), which makes sense given that ammonia oxidation is generally considered the rate limiting step in nitrification (Antiniou *et al.*, 1989; Davis, 2010), although under some conditions such as low DO, the opposite has been observed (Liu and Wang, 2013).



**Figure 4.19** (a) Ammonia oxidation and (b)  $\text{NO}_2\text{-N}$  oxidation rates in SBR 1 treating 50/50 (v/v) wastewater and landfill leachate. Error bars represent 95% confidence intervals.

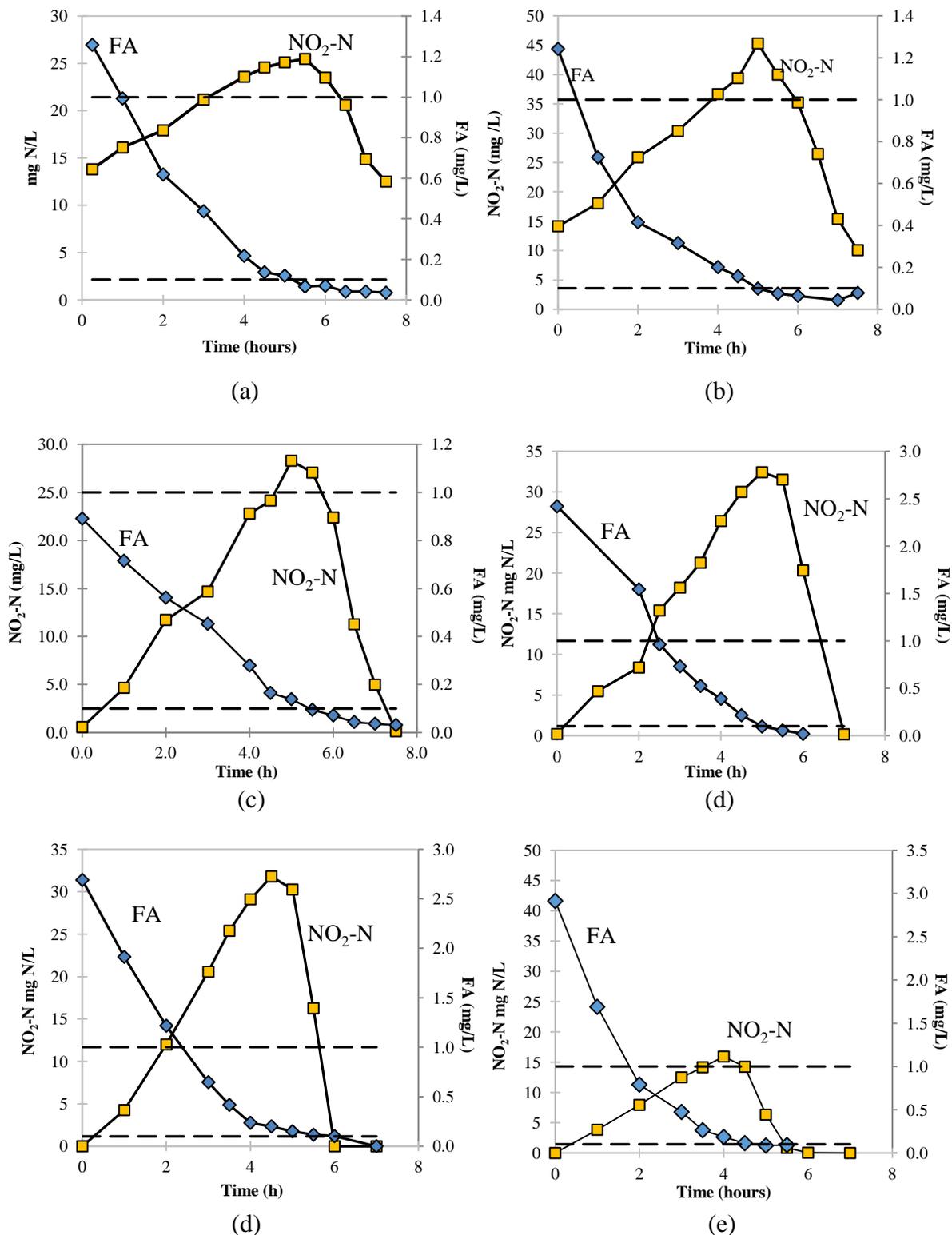
#### 4.2.2.6 Temperature Effects

The estimated rates given in Figure 4.17 and 4.19 also show the temperature effects on TAN and NO<sub>2</sub>-N oxidation. As expected, nitrification kinetics increased with increasing temperature. The TAN oxidation rate increased by approximately 26% for a 6.5 °C temperature increase, which corresponds very well with literature studies of temperature effects on AOB growth and substrate utilization rates (EPA, 1993). Temperature also seemed to have a much larger effect on NO<sub>2</sub>-N oxidation with a 70% increase in the average rate, although there was much more variation in this data as shown by the large error bars. The variation in estimated NOB rates could indicate other effects besides temperature. Nonetheless, increased temperature led to increases in both TAN and NO<sub>2</sub>-N oxidation.

#### 4.2.2.7 Effects of Aeration and Free Ammonia on Nitrification

As previously discussed, NO<sub>2</sub>-N accumulation was observed for several months after start up due to incomplete nitrification causing elevated levels in the SBR (Figure 4.7). The most likely factors responsible for NO<sub>2</sub>-N accumulation during the study were low DO and high FA concentrations. Although it was not a major concern based on the primary goals of the treatability study, it was an interesting problem that warranted further investigation. High effluent NO<sub>2</sub>-N could be problematic in a full-scale treatment system in that NO<sub>2</sub>-N constitutes about 1/3 of the oxygen demand associated with ammonia oxidation, it is toxic at high concentrations, and can significantly interfere with disinfection processes since it exerts chlorine demand (Gerardi, 2010; Richard, 2003). It could also inhibit biological treatment processes due to FNA at a high enough concentration and a low enough pH.

Using the nitrification profiles from December, TAN curves were converted to FA curves and plotted with NO<sub>2</sub>-N concentrations over time, which is shown in Figure 4.20 (a) - (e). What can be seen is that when FA concentrations drop below 0.1 mg/L, the minimum reported inhibition concentration for NOB (Anthonisen *et al.*, 1976), the NO<sub>2</sub>-N oxidation rate increases rapidly until either aeration ceases (at 7 hours) or no more NO<sub>2</sub>-N is present.



**Figure 4.20** Nitrite and FA profiles at (a) - (c) 17 °C and (d) - (e) 23.5 °C for SBR 1 treating 50/50 (v/v) wastewater and landfill leachate during December, 2015. Dashed lines represent reported inhibition threshold range of 0.1 - 1.0 mg/L for NOB (Anthonisen et al., 1976).

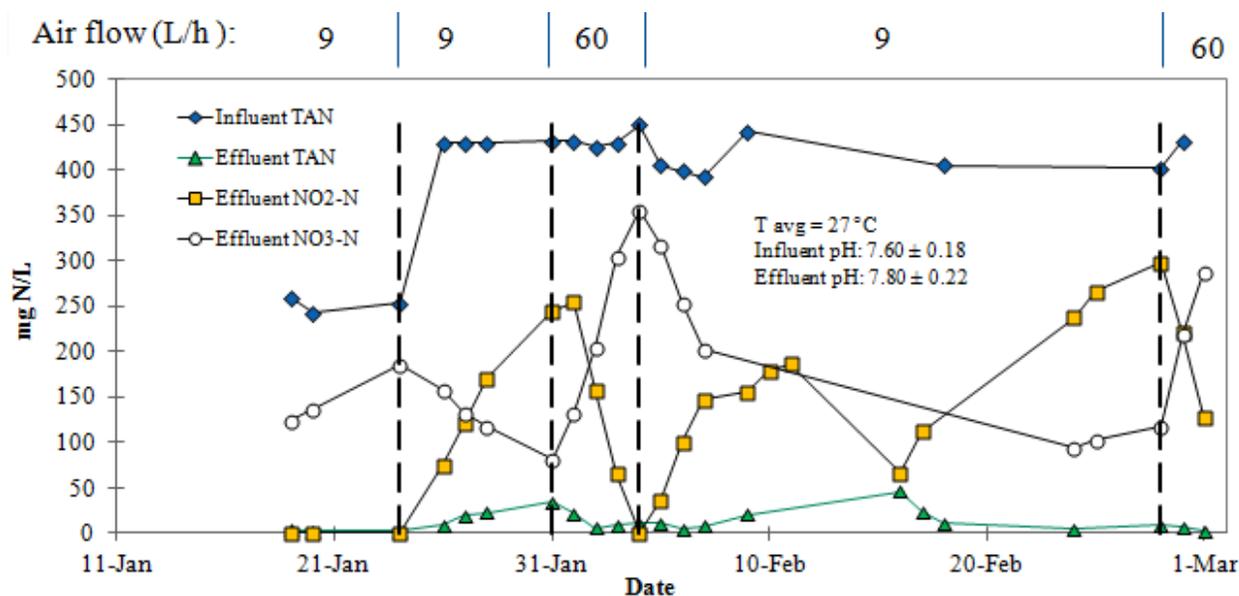
This may be an interesting find operationally, since it could show a connection between aeration, TAN oxidation rate and extent of  $\text{NO}_2\text{-N}$  oxidation. One hypothesis is that DO limitations cause a slowing of ammonia oxidation, which at high pH and TAN loadings could lead to FA concentrations remaining at inhibitory levels. The combination of low initial DO and high FA thus keeps NOB activity low, leading to incomplete conversion during the cycle and accumulation. This assumes that inhibition is completely reversible with limited recovery time needed, meaning that as soon as FA concentrations drop to non-inhibitory levels, activity resumes unimpeded. Based on nitrification profiles obtained for bench-scale SBRs, it was hypothesized by Alleman (1985) that a short aeration time (3 h) led to TAN oxidation through the entire reaction stage, resulting in FA stress on NOB, and subsequent  $\text{NO}_2\text{-N}$  accumulation. Although  $\text{NO}_2\text{-N}$  lags similar to those shown in Figures 4.18 and 4.20 were seen during the longer aeration phases (5 h and 9 h), lengthening of the aeration phase led to longer periods of low FA and thus  $\text{NO}_2\text{-N}$  was able to be completely oxidized to  $\text{NO}_3\text{-N}$  (Alleman, 1985).

Unfortunately, DO data was not available during collection of the profiles in Figure 4.20, and thus could not be ruled out as a major cause of the  $\text{NO}_2\text{-N}$  build-up, therefore a repeat of these tests under excess aeration while monitoring DO would be needed to validate this hypothesis. Some studies have reported increases in  $\text{NO}_2\text{-N}$  oxidation once TAN was depleted, which could be due to either DO limitations or FA, although it is not always the case as it has been shown that the rate can remain roughly constant even after TAN is completely consumed (Doyle *et al.*, 2001).

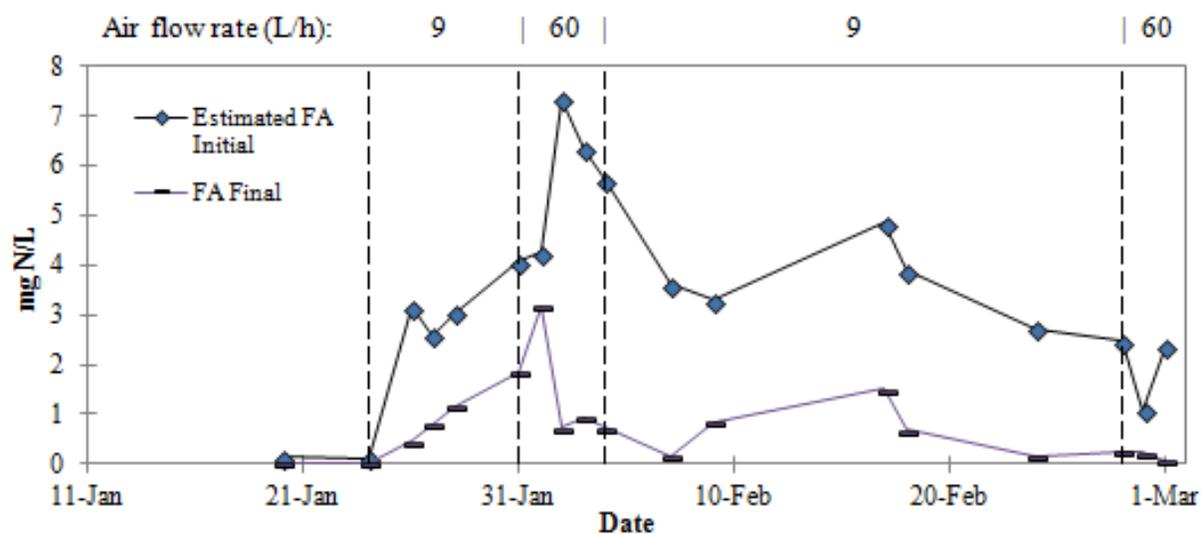
To investigate aeration effects on nitrification, the air flow rate was adjusted while operating under various landfill leachate loadings. Tests were done on SBR 2 which had been previously fed with higher ammonia concentrations by spiking the wastewater only influent with

$(\text{NH}_4)_2\text{SO}_4$ . At the start of the aeration study, the SBR was completely nitrifying the wastewater only influent with a TAN concentration and loading of approximately 125 mg/L and 16 mg N/cycle, respectively. The air flow rate was at 9 L/h, the same as for SBR 1.

Figure 4.21 shows nitrogen species under two different landfill leachate concentrations (blue diamonds) with aeration adjustments during the higher concentration. Temperature and pH measurements were recorded during the aeration study to allow for calculation of FA concentrations. Maximum and minimum FA concentrations, which were based on estimated initial pH and measured effluent pH respectively, are given in Figure 4.22.



**Figure 4.21** Influent and effluent nitrogen species for SBR 2 treating 50/50 (v/v) wastewater and landfill leachate during aeration study. The first vertical dashed line represents a change to November leachate, and the remaining dashed lines represent a change in the air flow rate.



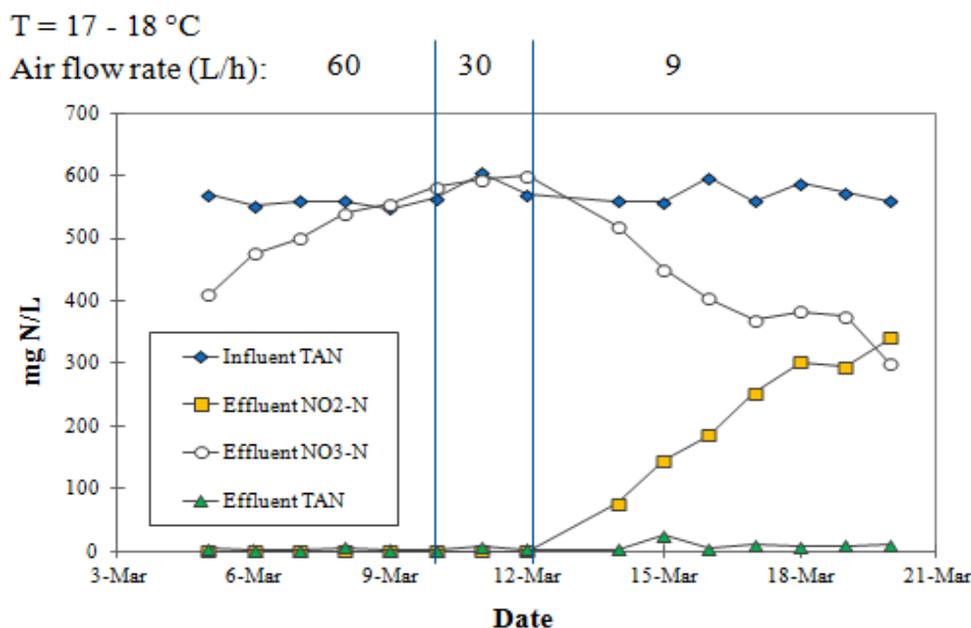
**Figure 4.22** Initial and effluent FA for SBR 2 treating 50/50 (v/v) wastewater and landfill leachate during aeration study. The first vertical dashed line represents a change to November leachate, and the remaining dashed lines represent a change in the air flow rate.

After adding a combined influent using winter landfill leachate, complete nitrification to ( $\text{NO}_3\text{-N}$ ) was observed with no  $\text{NO}_2\text{-N}$  in the effluent over a 3-day period. The influent bottle was then switched with a 50/50 (v/v) mixture using stronger landfill leachate from November with no aeration adjustment. Immediate  $\text{NO}_2\text{-N}$  accumulation was observed which lasted for several days as well as some TAN accumulation. A decrease in effluent  $\text{NO}_3\text{-N}$  was also observed further indicating a decrease in NOB activity. The air flow rate was then increased from 9 L/h to 60 L/h, and a decrease in  $\text{NO}_2\text{-N}$  with an increase in  $\text{NO}_3\text{-N}$  was observed. The process was repeated with the same pattern observed, with  $\text{NO}_2\text{-N}$  and TAN accumulation at the lower air flow rate, and decreasing effluent TAN and increasing  $\text{NO}_3\text{-N}$  at the higher air flow rate.

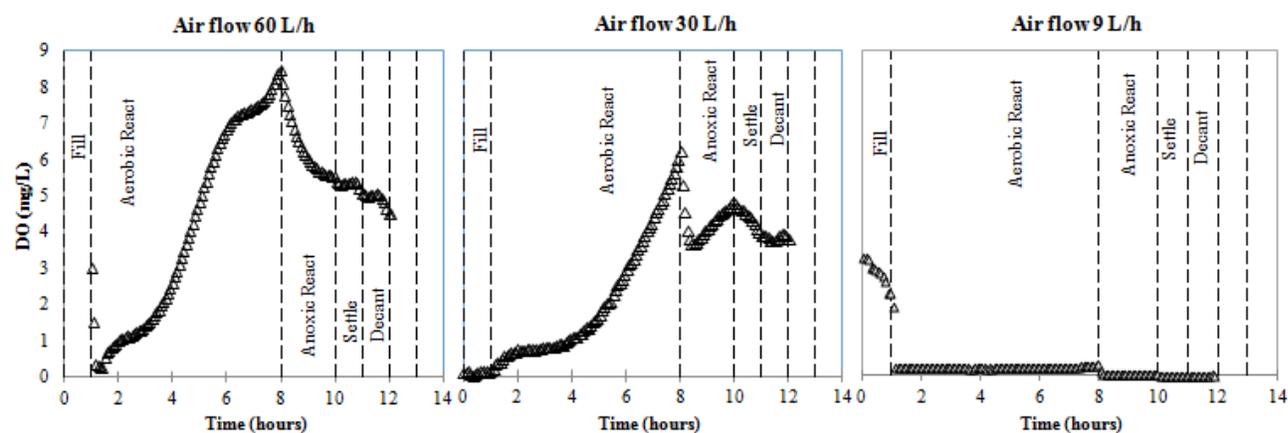
Based on the influent and effluent pH during the aeration adjustments, the estimated FA concentrations were above the minimum inhibitory range of 0.1 mg/L for NOB. During the first

aeration increase, FA concentrations were at the highest (Figure 4.22), yet the increase in  $\text{NO}_3\text{-N}$  was significant (Figure 4.21), thus indicating that NOB activity increased even though FA was above the typical range of inhibition. TAN oxidation also increased during this time which demonstrated that TAN oxidation improved with increased aeration, further suggesting that DO was limiting at the lower air flow rate of 9 L/h. These results indicated that AOB were sensitive to aeration adjustments, and that in addition to FA, aeration had a significant effect on NOB activity. In fact, aeration has been shown to be an effective process control for inducing partial nitrification to  $\text{NO}_2\text{-N}$ , due to the lesser affinity of NOB to oxygen than AOB (Blackburne *et al.*, 2007; Ma *et al.*, 2015; Ciudad *et al.*, 2005).

After observing the trends in Figure 4.21, SBR 2 was fed with a higher percentage of landfill leachate in order to simulate the high TAN loadings seen during summer and early fall. Temperature was controlled at 17-18 °C and DO was continuously monitored. Figures 4.23 and 4.24 show influent and effluent nitrogen species and representative DO profiles respectively for each air flow rate tested.



**Figure 4.23** Influent and effluent nitrogen species during the aeration study for SBR 2 treating 33/67 (v/v) wastewater to landfill leachate. Vertical lines represent a change in the air flow rate.

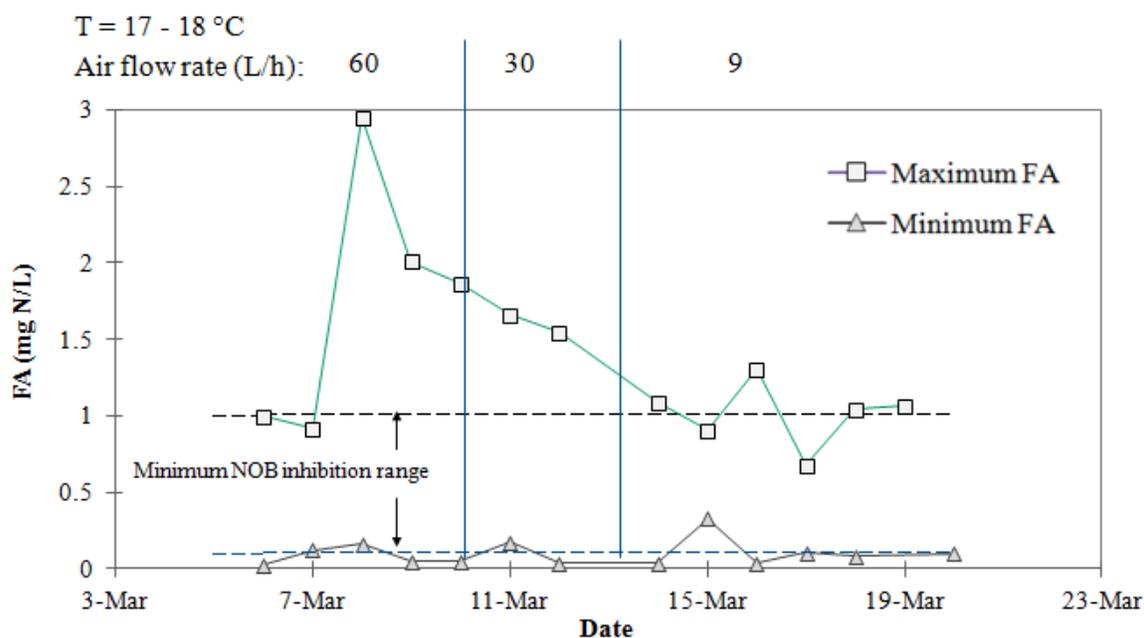


**Figure 4.24** Representative DO profiles for each air flow rate during aeration study for SBR 2 treating 33/67 (v/v) wastewater to landfill leachate.

For the higher air flow rates (30 and 60 L/h), DO was at a sufficient level for complete nitrification to NO<sub>3</sub>-N, with effluent TAN < 5 mg/L (Figure 4.23). When the air flow rate was reduced to 9 L/h, the SBR was anoxic and NO<sub>2</sub>-N build-up was immediately observed (Figure 4.23). Effluent TAN was not quite as low as for the higher airflow rates, but no significant accumulation was observed. This was interesting in that DO seemed to have a much greater

effect on NOB activity than AOB, which has been shown in some studies where decreases in DO have led to  $\text{NO}_2\text{-N}$  accumulation with little effect on ammonia oxidation (Ruiz *et al.*, 2002; Gao *et al.*, 2008). The low effluent TAN values even under anoxic conditions may also indicate that the AOB had a relatively low oxygen half-saturation constant under the given conditions. Another possibility is that the increased aeration broke apart the floc, thus improving substrate mass transfer (Manser *et al.*, 2005), since much higher TSS was observed in the SBR supernatant after settling.

Figure 4.25 shows corresponding FA concentrations for the results given in Figure 4.23. Average FA was higher during the period with the higher air flow rate however no accumulation of  $\text{NO}_2\text{-N}$  was observed. It is possible that the increased aeration may have helped counter the effects of FA on NOB by allowing DO to not be rate limiting.



**Figure 4.25** Estimated initial (squares) and final (triangles) free ammonia concentrations during aeration study for SBR 2 treating 33/67 (v/v) wastewater:landfill leachate. Dashed lines indicate minimum inhibition range for NOB (Anthonisen *et al.*, 1976). Vertical lines represent a change in the air flow rate.

The results from the aeration study showed that complete nitrification could be achieved for a combined influent with higher TAN loadings than were seen in summer and fall (>70 mg/cycle), even with a pH of 7.5 - 8.2, provided that aeration is sufficient to give an adequate bulk DO concentration that does not limit AOB and NOB activity. In general, adequate aeration is expected to keep ammonia oxidation rates high, thus avoiding accumulation of both TAN and NO<sub>2</sub>-N. This will also keep FA and FNA concentrations lower, thus reducing the possibility of nitrification inhibition.

#### 4.2.2.8 Parameter Estimation from Ammonia Oxidation Data

With the kinetic profiles from December given in Figures 4.15, the process rate for ammonia oxidation, given by Equation 4.5, was used to estimate the ammonia half-saturation constant  $K_N$  and maximum substrate utilization rate ( $q_{M,N}$ ):

$$\frac{d(TAN)}{dt} = \hat{q}_{M,N} X_N \left( \frac{TAN}{K_N + TAN} \right) \left( \frac{DO}{K_O + DO} \right) \quad [4.5]$$

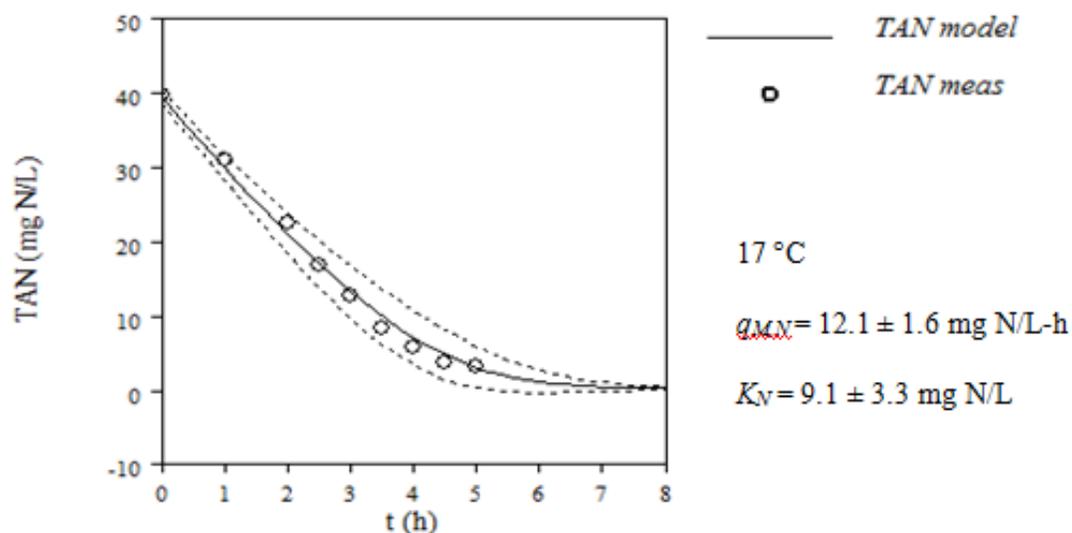
In Equation 4.5, ( $\hat{q}_{M,N}$ ) is the maximum specific substrate utilization rate in mg/L-h, DO is the dissolved oxygen concentration in mg/L,  $X_N$  is the cell concentration in mg/L, and  $K_N$  is the ammonium half saturation constant in mg N/L.

The experimental TAN data (Figure 4.16) was fitted using the model given by Equation 4.6. The somewhat curvilinear nature of some TAN profiles in Figure 4.16 during the first 1 -2 hours suggested rate limitations, and based on the DO profile in Figure 4.13, this was assumed to be due to low DO levels. Therefore, the parameter estimations and curve fitting were started at  $t = 2$  hours into the aeration cycle. No DO data was available, therefore modeling required omission of the Monod oxygen term. Neglecting the Monod oxygen term and substituting  $q_{M,N} = \hat{q}_{M,N} X_N$  where  $q_{M,N}$  is the maximum substrate utilization rate in mg/L-h:

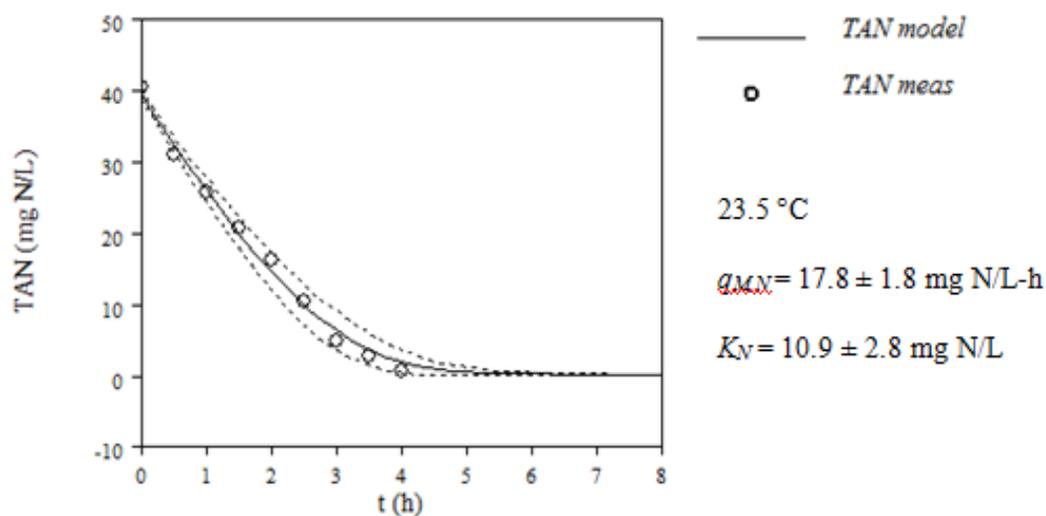
$$\frac{dTAN}{dt} = \frac{q_{M,N} TAN}{K_N + TAN} \quad [4.6]$$

Figures 4.26 and 4.27 show best fit curves for TAN profiles at 17 °C and 23.5 °C respectively, using the computer program Aquasim for simultaneous parameter estimation and non-linear least squares regression. Estimated parameters are shown with one standard deviation as computed by the program. Initial TAN concentration was also used as a parameter to be

estimated in order to improve the fit (Reichert *et al.*, 1994). The dotted lines represent a standard error of the model fit based on sensitivity analysis of the parameter estimations. Details on the methods and statistical analysis carried out by the program for regression and parameter estimates are given by Reichert *et al.* (1994).



**Figure 4.26** Best fit and parameter estimates for ammonia oxidation at 17 °C in SBR 1 during December.



**Figure 4.27** Best fit and parameter estimates for ammonia oxidation at 23.5 °C in SBR 1 during December.

The estimated maximum rates ( $q_M$ ) (Figures 4.26 and 4.27) are given as mg N/L-h which include the AOB concentration  $X_N$  which was unknown, and are assumed to be relevant for the given reactor conditions and loading since the SBR was being operated at constant SRT and TAN loading during this time. It was also assumed that  $\Delta X_N$  was very small compared with initial biomass. Any effect of FA on ammonia oxidation was assumed negligible due to the low concentrations. However, the estimated maximum rates may be underestimates due to the possible invalidity of the DO assumption in neglecting the Monod oxygen term. Without DO data, further tests would be needed to verify this. Normalizing by the MLVSS gives maximum specific rates of 3.8 mg N/g VSS-h and 5.6 mg N/g VSS-h at 17 °C and 23.5 °C, respectively. These rates were very similar to those reported by Kaczorek and Ledakowicz (2006), who operated under similar conditions, although the authors did not combine wastewater with the influent, and so TAN loadings were higher.

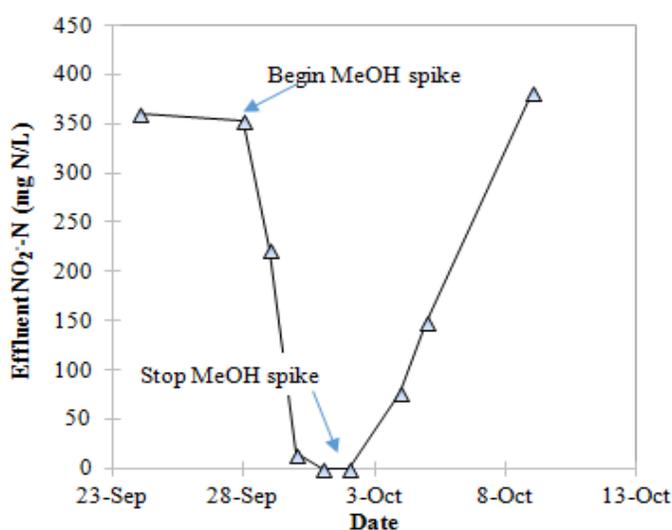
One interesting aspect of the results was the high  $K_N$  values. It was clear that the rates decreased significantly after 10 mg/L, with final TAN values of greater than 2 mg/L in most cases. The estimated  $K_N$  values were much higher than most reported  $K_N$  values for AOB, which are typically about 1-2 mg/L or less (Berge *et al.*, 2007; Kaelin *et al.*, 2007). This suggests significant substrate mass transfer limitations, with the measured  $K_N$  value actually being an effective  $K_N$ . The high  $K_N$  values were very comparable with those reported in other studies involving landfill leachate treatment by activated sludge, in which the effective  $K_N$  can be an order of magnitude higher than the 'true'  $K_N$  value (Doyle *et al.*, 2001; Kaczorek and Ledakowicz, 2006). Mass transfer limitations in activated sludge has also been shown for other substrates such as DO, which has been correlated to floc particle size, where better mass transfer was seen for smaller floc particles (Blackburne *et al.*, 2007; Manser *et al.*, 2005). Thus, mass

transfer limitations could have had a negative impact by reducing ammonia and nitrite oxidation rates.

Increased aeration may lead to different results for this analysis, not only by increasing the  $q_{M,N}$  estimates by making the Monod oxygen term sufficiently small to be neglected, but also by changing the half saturation constant if changes in floc characteristics are observed. For example, increased aeration intensity and mixing may lead to a less dense floc, thus reducing mass transfer limitations and lowering the effective  $K$  value. In any case, both treatment and the analysis of kinetic constants would likely be improved by ensuring adequate DO levels over the aeration cycle.

#### 4.2.2.9 Denitrification

Figure 4.28 shows the decrease in nitrite due to denitrification upon addition of 1 mL of methanol (MeOH) during the 2-hour anoxic phase in SBR 1. A rapid decrease in  $\text{NO}_2\text{-N}$  was observed indicating that with addition of a biodegradable carbon source, denitrification can be achieved when treating the landfill leachate. After MeOH additions were stopped, a build-up of  $\text{NO}_2\text{-N}$  was once again observed.



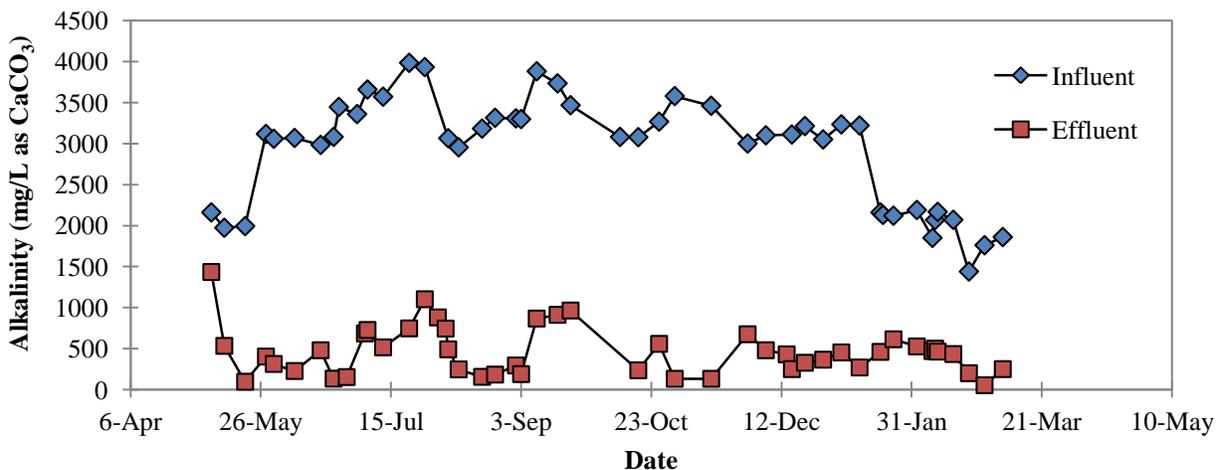
**Figure 4.28** Decrease in effluent  $\text{NO}_2\text{-N}$  by denitrification in SBR 1 treating 50/50 (v/v) wastewater and landfill leachate upon MeOH addition during the anoxic phase.

Without external carbon addition, minimal to no denitrification was observed (Figure 4.7), which has been seen in many landfill leachate treatment studies (Diamadopoulos *et al.*, 1997; Spagni and Marsili-Libelli, 2008) due to a low CBOD to N ratio. The fact that the aerated react phase preceded the anoxic phase meant that the more easily biodegradable organics would most likely be consumed, and would not be available for denitrification. To test denitrification in SBR 1 using influent organics, the anoxic phase was switched to precede the aeration phase

beginning on February 10, 2016 (Figure 4.7). Although DO profiles indicated adequate anoxic conditions during the cycles (Figure A.8), no noticeable denitrification occurred as can be seen in Figure 4.7, since effluent  $\text{NO}_3\text{-N}$  was roughly equal to influent TAN. The average  $\text{CBOD}_5\text{:N}$  ratio in the feed during this time was approximately  $< 1:1$ , which was lower than the required ratio which has been shown to be 2.86:1 (EPA, 1993). Also, the  $\text{NO}_3\text{-N}$  concentration in the SBR was 260 mg N/L; therefore a carbon addition would have also been required to reduce that amount. Denitrification was shown to be a viable option for reducing  $\text{NO}_x\text{-N}$ , but would almost certainly require an external source of carbon.

#### 4.2.3 Alkalinity and pH

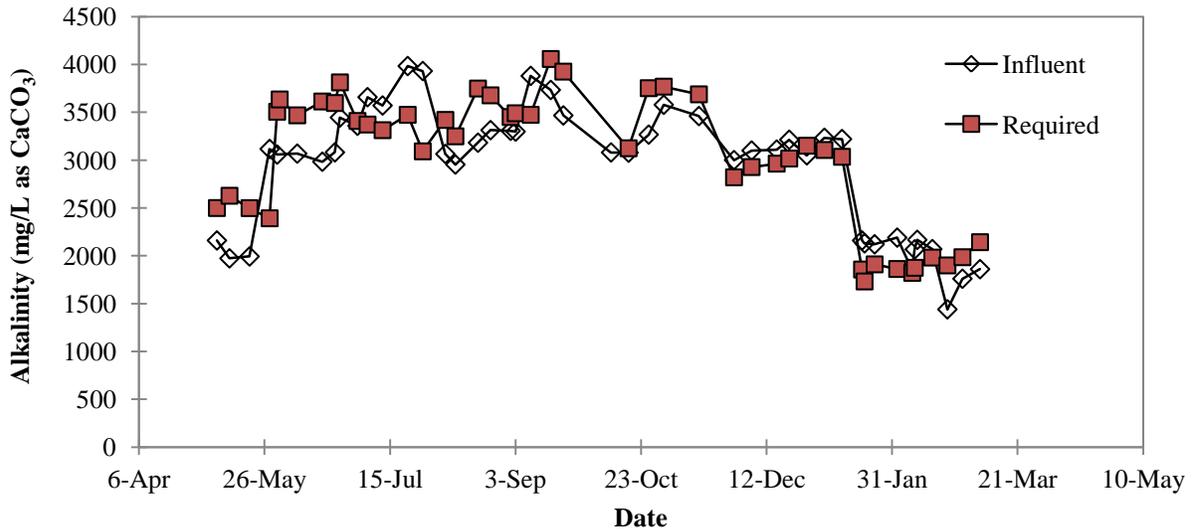
Figure 4.29 shows influent and effluent alkalinity for SBR 1 during the study. Alkalinity additions using  $\text{NaHCO}_3$  were required since the 50/50 (v/v) mixture had a constant alkalinity to TAN ratio of 5.3 mg/mg, which was less than the required 7.1:1 mg/mg ratio for complete nitrification and maintaining adequate effluent alkalinity. Sodium bicarbonate has a pH of 8.4, and was therefore a good choice for alkalinity additions to avoid extremely high pH in the SBR.



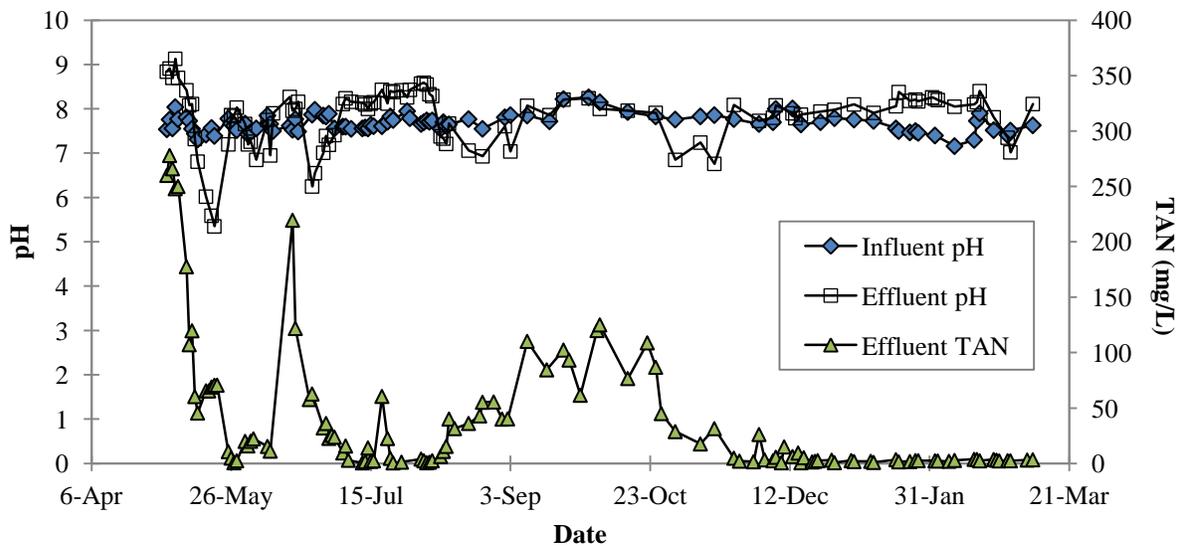
**Figure 4.29** Influent and effluent alkalinity for SBR 1 treating 50/50 (v/v) wastewater and landfill leachate.

Figure 4.30 shows the combined influent alkalinity plotted with the required stoichiometric amount for nitrification, which is approximately 7.14 mg as  $\text{CaCO}_3/\text{mg TAN}$ .

Figure 4.31 shows influent and effluent pH plotted with effluent TAN.



**Figure 4.30** Influent and required alkalinity for SBR 1 treating 50/50 (v/v) wastewater and landfill leachate.



**Figure 4.31** Influent and effluent pH plotted with effluent TAN for SBR 1 treating 50/50 (v/v) wastewater and landfill leachate.

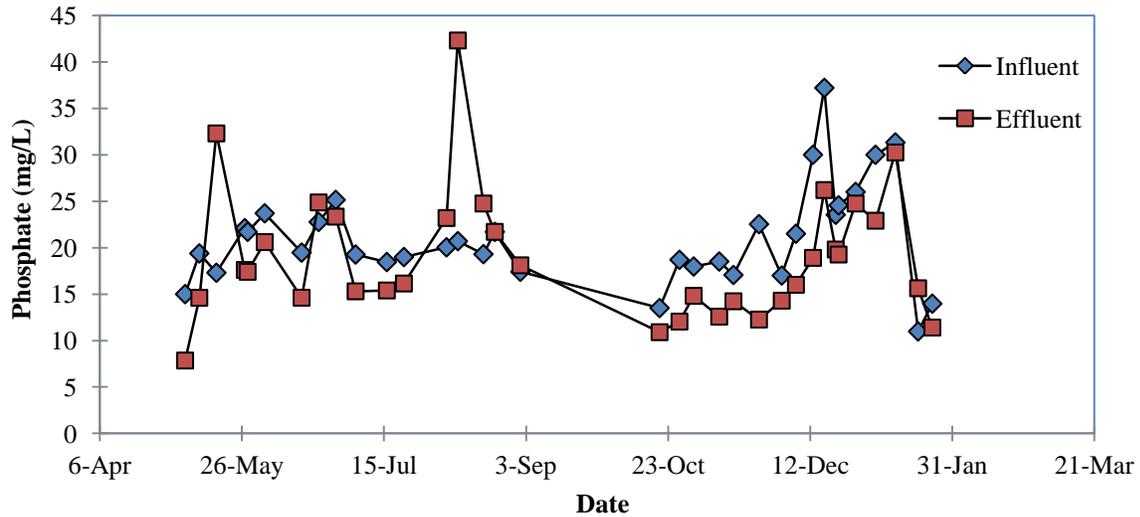
Figure 4.30 and 4.31 show that when the influent alkalinity was significantly lower than the stoichiometric amount, a drop in pH was observed due to ammonia oxidation. In fact when pH dropped close to 6.5, spikes in effluent TAN were observed due to substrate limitations. With the exception of the period of TAN accumulation during late summer and early fall, which was likely caused by rate limitations due to low DO, alkalinity in excess of the stoichiometric amounts resulting in average pH nearer to 8 corresponded to low effluent TAN. This indicates that a pH of 8 was better for ammonia oxidation, since more TAN is in the form of FA. However, at higher TAN loadings it likely had a negative effect on NOB activity due to high FA concentrations.

#### *4.2.4 Phosphorus*

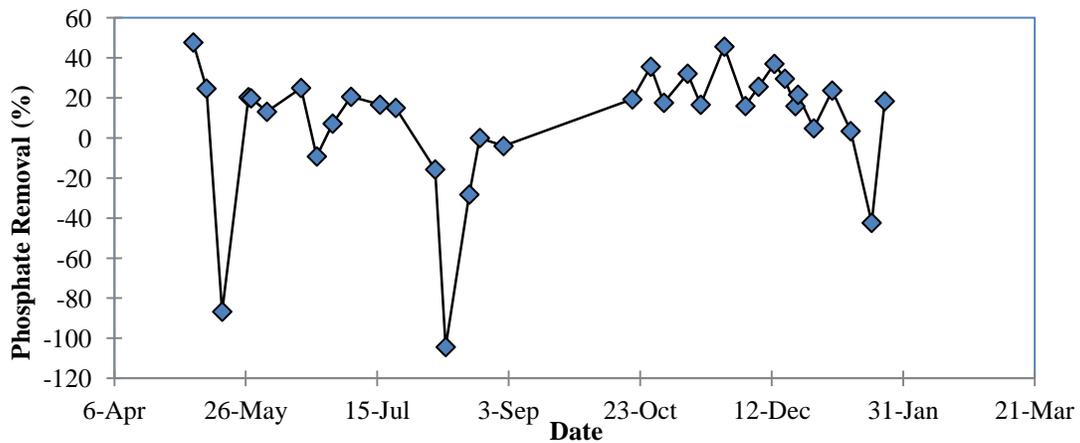
Figure 4.32 shows influent and effluent total reactive phosphorus concentrations for SBR 1 and Figure 4.33 shows percent removal. Phosphorus (P) removal was low during the study with an average removal percentage < 20 %, or ~2 mg/L. The average wasting rate was about 4 - 5 mL of settled sludge, corresponding to ~ 100 - 120 mg/d. This results in ~ 2 mg P/100 mg VSS, or 2%, which corresponds to normal P uptake for cell maintenance (Shuler and Kargi, 2002). This indicates that the sludge was not enriched for phosphorus accumulating organisms (PAOs).

Occasionally, the P detected in the effluent was greater than in the feed (Figure 4.32), suggesting release of P from the sludge. The anoxic and aerobic phases in SBR 1 were swapped in order to possibly improve P removal, although no data was able to be obtained. In general, the very high NO<sub>x</sub>-N concentrations were not conducive to enhanced P removal by PAOs, due to possible competition with denitrifiers for VFAs, which has been shown in SBR treatment studies

(Ng *et al.*, 2001). It could also be the case that organics in the form of fermentation products, which are necessary for PAO enrichment (Forbes *et al.*, 200, were at insufficient levels in the SBR.

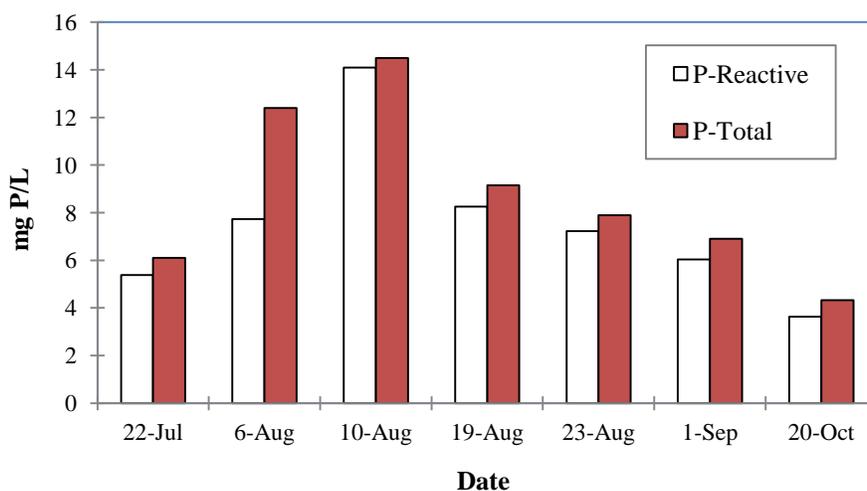


**Figure 4.32** Influent and effluent reactive phosphate for SBR 1 treating 50/50 (v/v) wastewater and landfill leachate.



**Figure 4.33** Reactive phosphate removal percentage for SBR 1 treating 50/50 (v/v) wastewater and landfill leachate.

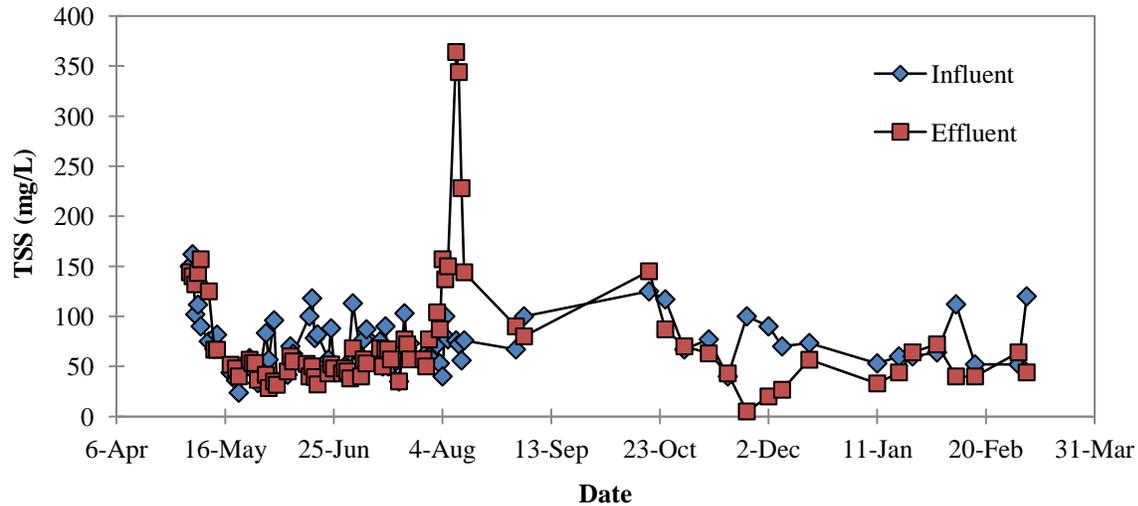
Total phosphorus was measured for a 4 month period during the study (July - October, 2015). Figure 4.34 shows a comparison of reactive P (orthophosphate) to total P in SBR 1 effluent. Only a small portion of the total P was in organic or condensed form, with the exception of one sample taken on August 6<sup>th</sup> during a period when PAC was still being added to the reactor. Effluent filtration showed only 6% P removal (data not shown). Thus, the high percentage of soluble P indicates that any significant removal would require a chemical process such as precipitation, or an additional reactor with operating conditions and necessary substrates favoring biological uptake by PAOs.



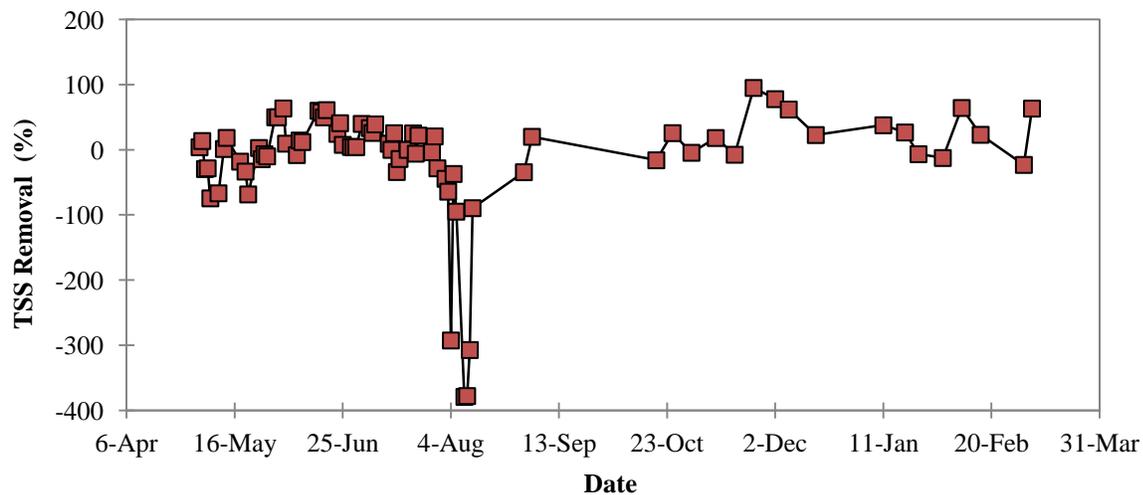
**Figure 4.34** Reactive and total phosphorus for SBR 1 treating 50/50 (v/v) wastewater and landfill leachate.

#### 4.2.5 Total Suspended Solids, Total Dissolved Solids, and Conductivity

Removal of TSS was mostly poor throughout the study. Figures 4.35 and Figure 4.36 show TSS for SBR 1 influent and effluent and TSS removal percentage respectively.



**Figure 4.35** Influent and effluent TSS for SBR 1 treating 50/50 (v/v) wastewater and landfill leachate.

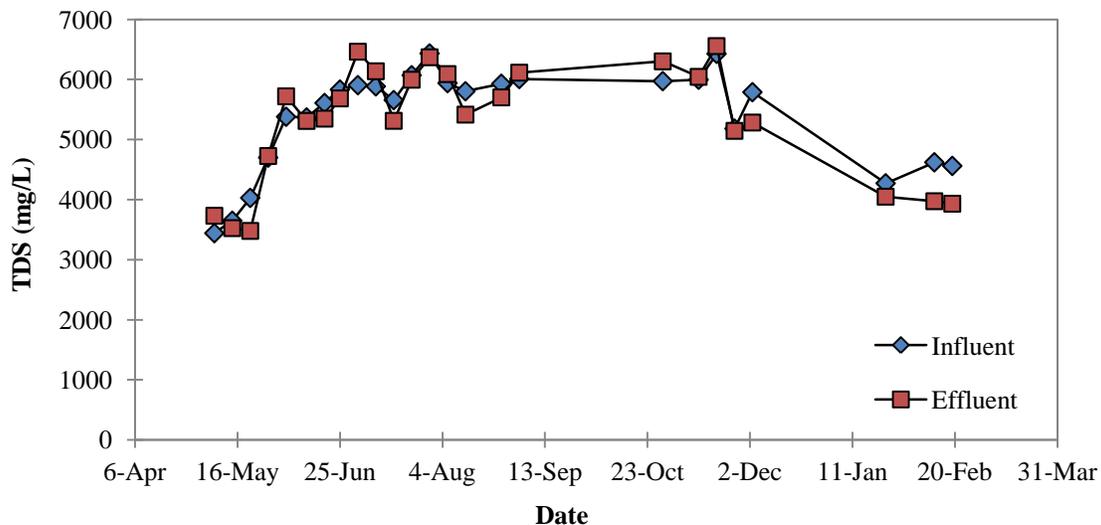


**Figure 4.36** TSS removal percentage for SBR 1 treating 50/50 (v/v) wastewater and landfill leachate.

Effluent TSS exceeded influent TSS on many occasions Figures (4.35 and 4.36), especially during PAC addition from July 14<sup>th</sup> to August 14<sup>th</sup> in which the effluent TSS reached more than triple the influent. PAC addition was subsequently stopped. Although the SBR was expected to act as a clarifier during the settling phase, the floc alone was unable to trap much of the fine suspended solids and sweep them from the mixed liquor during settling. As is discussed in the later sections, the floc characteristics could have played a role in poor TSS removal due to lack of a filamentous backbone and shearing of weak floc particles (Richard, 2003). Based on the data, filtration would be required as an effluent polishing step to bring the TSS below the target 30 mg/L, which was almost never met during the study with the exception of a few days.

A large portion of the suspended solids were volatile compounds. The ratio of VSS to TSS in the combined influent was 67% with a standard deviation of 17%, and in the effluent was 67% with a standard deviation of 12%, which are very typical values in wastewater treatment systems (Von Sperling, 2007). This indicates that a portion of the effluent organics was associated with particulate matter, which is often seen with wastewater treatment system effluents with high TSS (Von Sperling, 2007). It was therefore possible that a filtration step could remove some COD and BOD, and in fact that was the case as shown in Section 4.2.1.

Figure 4.37 shows influent and effluent TDS for SBR 1, which ranged from 3400 - 6400 mg/L, with much lower TDS during spring and winter. The TDS is a measure of all of the organic and inorganic dissolved substances present. The influent TDS includes the  $\text{NaHCO}_3$  which was added for alkalinity. The limited TDS removal reflects the fact that during the first 6 1/2 months, poor COD removal was observed with high  $\text{NO}_2\text{-N}$  concentrations and little to no denitrification. Even during times of improved COD removal during winter, TAN was being converted to  $\text{NO}_3\text{-N}$ , which added significantly to effluent TDS.



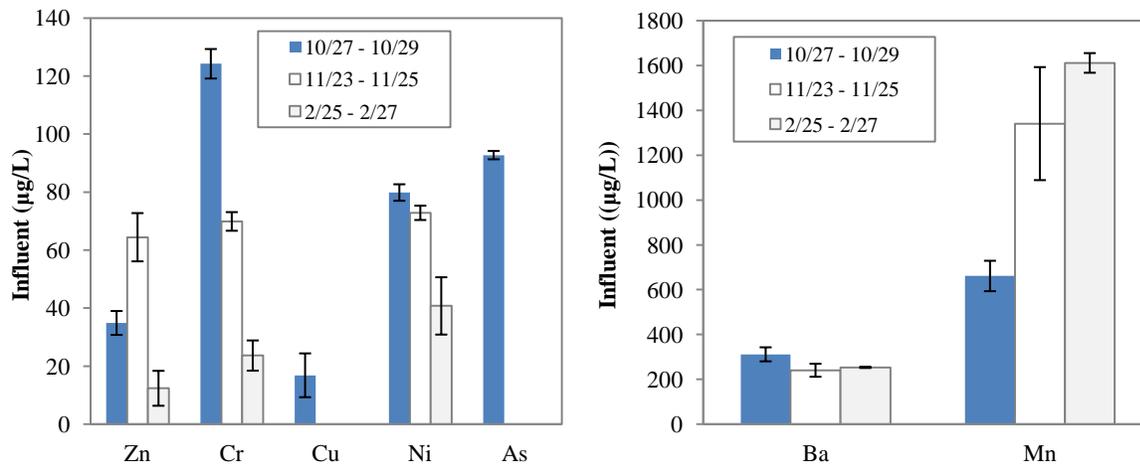
**Figure 4.37** Influent and effluent TDS for SBR 1 treating 50/50 (v/v) wastewater and landfill leachate.

Conductivity, a parameter directly related to TDS, was also measured during the study. The TDS was shown to be proportional to conductivity by a factor of 0.48 with a standard deviation of 0.02 and 95% confidence of 0.01. Although measurement of both TDS and conductivity is somewhat redundant, the high correlation between the two does provide more confidence in the data. The high TDS and conductivity are typical of landfill leachates and indicate a high salt content (Figure 2.4).

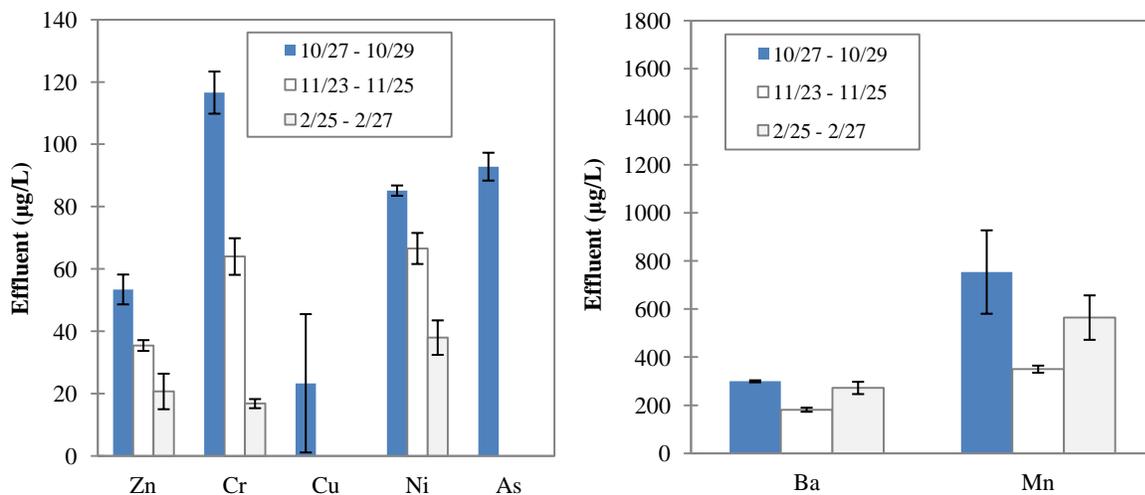
#### 4.2.6 Heavy Metals

Figures 4.38, 4.39, and 4.40 give concentrations of heavy metals in the influent, effluent, and reactor solids (WAS), respectively. Figure 4.41 gives estimated removal percentages. As can be seen in Figure 4.38, combined influent heavy metals concentrations were generally very low, except for Mn, which are very comparable to, or less than heavy metals concentrations

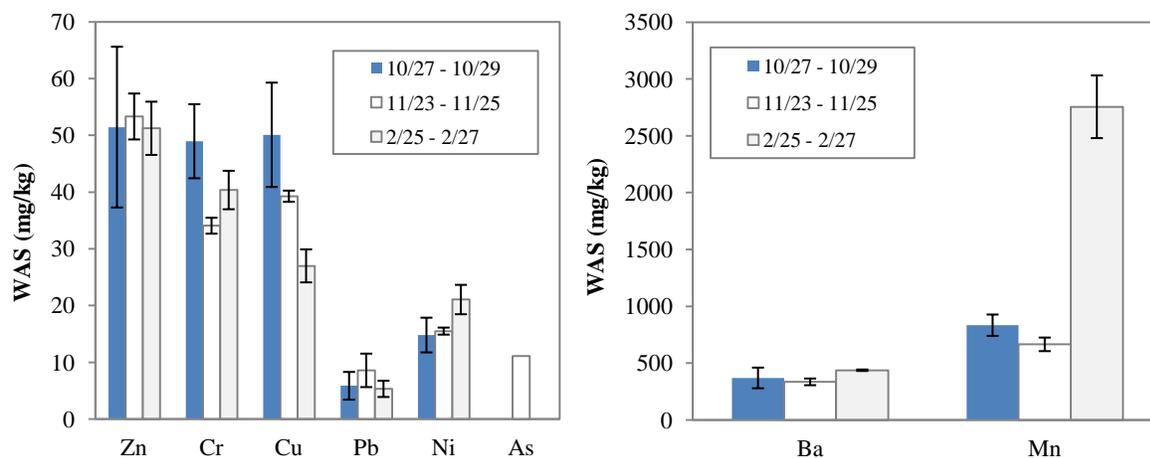
reported by Christensen *et al.* (2001) for a wide range of landfill leachates, as well as the values given in Table 2.1 from the LEACH2000 database.



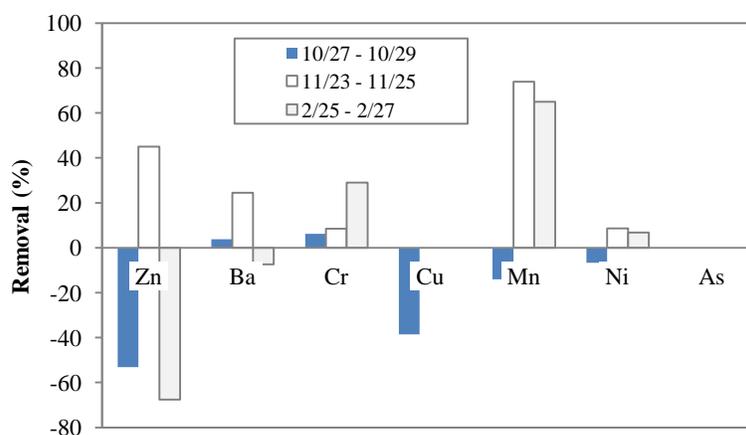
**Figure 4.38** Metals concentrations in the combined influent to SBR 1 treating 50/50 (v/v) wastewater and landfill leachate. Bars represent 95% confidence intervals.



**Figure 4.39** Effluent metals concentrations from SBR 1 treating 50/50 (v/v) wastewater and landfill leachate. Error bars represent 95% confidence intervals.



**Figure 4.40** Sludge (WAS) metals concentrations in SBR 1 treating 50/50 (v/v) wastewater and landfill leachate, given as mg per kg dry wt. solids. Error bars represent 95% confidence intervals.



**Figure 4.41** Metals removal percent in SBR 1. Error bars represent 95% confidence intervals

There was no Mo, Se, Pb, Cd, or Hg detected in any of the liquid samples and only the samples from October had Cu present. Manganese was < 1 mg/L in all influent and effluent samples, which met the target goal of < 5 mg/L. Only one data set was obtained for As and Hg, and for reactor solids, As and Hg levels are for a month-long conglomerate of sludge. The sludge contained only a trace amount of Hg at 0.17 mg/kg (not shown in Figure 4.40) and low levels of most metals, especially As, and Pb. The low concentrations of As and Hg in the WAS

are very similar to those reported for activated sludge systems (Stasinakis and Thomaidis, 2010). Low uptake of Hg and As has also been reported in landfill leachate treating SBRs (Morling, 2006). The highest concentrations in the WAS were Zn, Cr, and Cu, which were all ~ 50 mg/kg or less. Similar sludge uptake was reported in pilot SBR landfill leachate studies by Morling (2006), where Cu and Zn were at 100 mg/kg and 77 mg/kg, respectively, whereas lower levels of Pb (5 mg/kg), Cd (1 mg/kg), and Ni (8 mg/kg) were seen. Figure 4.40 shows much higher levels of Ba and Mn present in the WAS than any other metals, however these are not currently regulated for biosolids.

Overall, metals removal was low except for Mn, which suggests that sludge wasting from the SBR may not provide significant removal, especially with the long SRT. Limited metals removal has been found to be typical in activated sludge SBR systems (Morling, 2006). Zn and Cu were higher in the effluent in some cases which suggests some leaching from the sludge over time if the sludge becomes saturated.

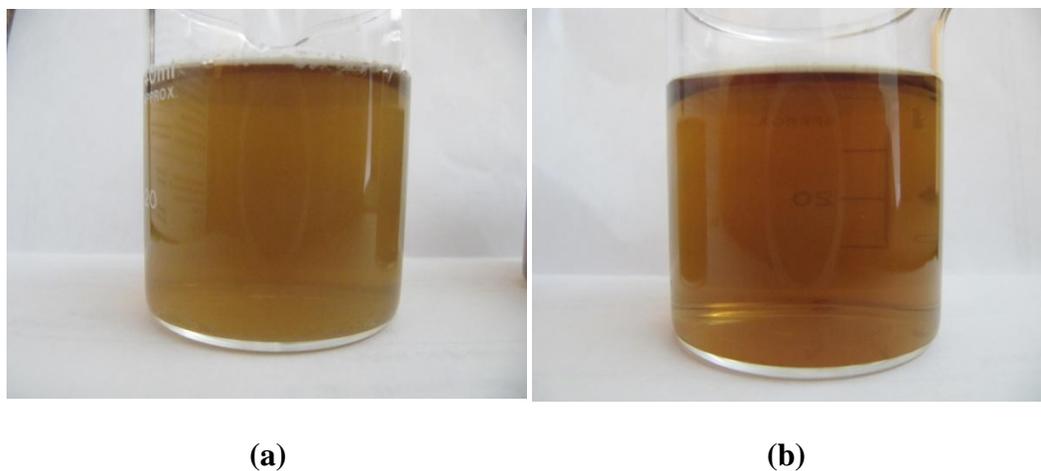
Based on the data for the WAS (Figure 4.40), metals concentrations in the sludge were well below EPA ceiling levels for land application, which are given in Figures A.9 and A.10 of the Appendix (EPA, 2014). However, further regulations for land applications also include limits on pathogens and viruses (EPA, 2014); therefore quantification of those pollutants may be necessary to fully determine whether the sludge meets those requirements. In terms of effluent criteria, the only metal specified as a target pollutant was Mn, however other metals such as Cr, Ni, and As were present in the effluent at concentrations that may be subject restrictions if not removed in the treatment system prior to discharge.

Metals concentrations in the influent were very comparable with typical values which have been compiled for many municipal landfills in the U.S. (Aucott, 2006), which are in the 1 - 1000  $\mu\text{g/L}$  range, and are characteristic of methanogenic landfills (Aucott, 2006; SWANA, 2004). The concentrations measured in this study also correspond well with data monitored by the Coffin Butte landfill with the exception of Se, which was not detected. Metals data for the raw landfill leachate measured by CH2MHill in August 2015 can be found in Figure A.2 in the Appendix for comparison.

It is difficult to determine whether some of these metals were at levels which might have inhibited biological processes. Many different metals have been shown to effect wastewater treatment processes as described in Chapter 2, which are highly dependent on metals speciation and adsorption under certain conditions. However, it appears that inhibition by the heavy metals analyzed in this study may not have been an issue, given the relatively low influent concentrations compared with reported inhibitory values in literature (Rios *et al.*, 2014; Novotnik *et al.*, 2014; Cecen *et al.*, 2010).

#### 4.2.7 Color

Color was measured for both the influent mixture and the reactor effluent. Figures 4.42 (a) and (b) show images of samples taken and placed in a beaker for comparison, where (a) is influent and (b) is effluent. The influent appeared slightly paler than the effluent for most samples, likely due to the turbidity of the influent in which the suspended material seemed to be colloidal in nature. The dark brown amber color was typical of solutions with high concentrations of humic substances (Knox, 1984).



**Figure 4.42** Images showing color of (a) combined influent and (b) effluent of SBR 1 treating 50/50 wastewater and landfill leachate in December 2015.

Table 4.6 shows influent and effluent color data which is given in Pt-Co units.

**Table 4.6** Influent and effluent color for SBR 1 treating 50/50 (v/v) wastewater:landfill leachate. Values are given with 95% confidence intervals.

	<b>Influent</b>	<b>Effluent</b>
<b>Color (Pt-Co)</b>	1340 ± 140	1770 ± 210

The lack of color removal correlates with the limited removal of recalcitrant COD, which has been reported in other SBR landfill leachate studies (Aziz *et al.*, 2011). Reduction of color will thus require an effective physico-chemical process such as PAC adsorption or coagulation-flocculation, which has been shown to be effective for landfill leachates (Aziz *et al.*, 2011; Aziz *et al.*, 2007; Renou *et al.*, 2007).

#### 4.2.8 Pesticides and Volatile Organic Compounds (VOCs)

Samples were collected and analyzed for a suite of semi-volatile organic compounds and pesticides. Table 4.7 shows analysis results for the major pollutants of concern in terms of the

project goals. Data for the entire suite of organic pesticides, VOCs, and semi-VOC analyzed can be found in Tables A.1 - A.6 of the Appendix.

**Table 4.7** Selected influent and effluent semi-VOC and pesticide concentrations for SBR 1 treating 50/50 (v/v) landfill leachate and wastewater. Values are shown with 95% confidence intervals for sample triplicates.

	Influent (ppb)	Effluent (ppb)
bis (2-Ethylhexyl) phthalate	8.5 ± 5.3	0.9
Lindane	0.0	0.00040

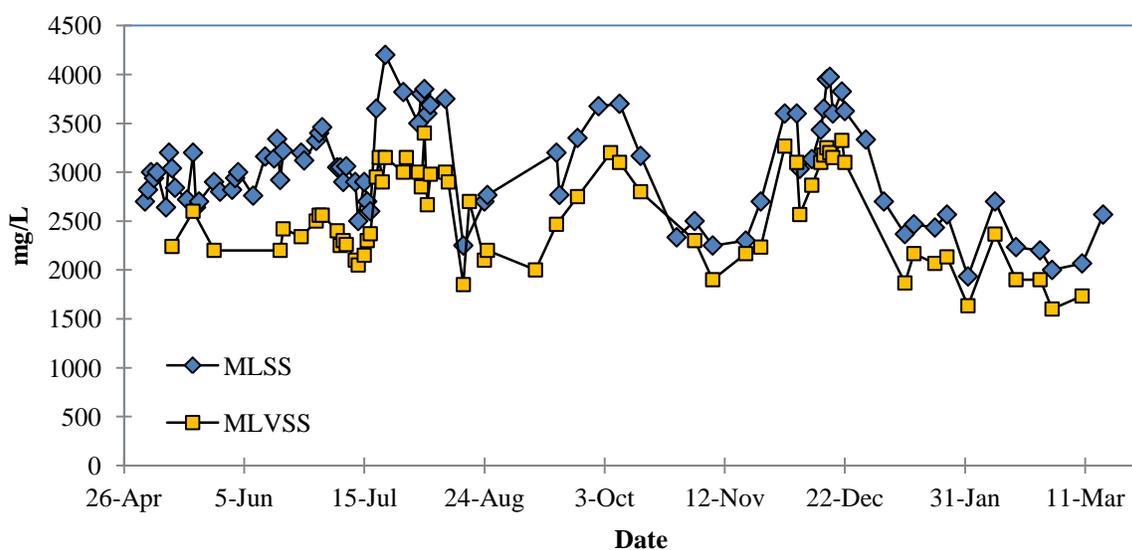
All VOCs, semi-VOCs, and pesticides were either well below requirements for discharge or were not detected at all in either the influent or effluent (Tables A.1 - A.6). Aromatic compounds such as benzene, xylene, and naphthalene were less than 1 µg/L in the combined influent, although none were detected in the effluent. The highest concentrations of any of the organic pollutants in the influent were 38 µg/L acetone, which was more than 3 orders of magnitude lower than that which has been shown to inhibit nitrifying activated sludge (EPA, 1993), and 30 µg/L phenol and 170 µg/L methylphenol (a cresol), both of which have been shown to inhibit nitrification in the hundreds of mg/L range (Kim, 2007). Acetone, at 63 µg/L, was the only significant VOC in the effluent, which is almost 5 orders of magnitude lower than reported inhibitory levels (EPA, 1993). Chloromethane and benzoic acid were both less than 5 µg/L in the effluent, but were not detected in the influent, and thus were likely produced through conversion of other organic compounds in the SBR.

Although the results are promising, there is a somewhat limited data set, thus it may be advisable to run more samples to ensure that toxic organics and pesticides will not pose a threat to the treatment system or to the environment via the discharged effluent. It is worth noting that

all of the contaminants that were monitored in this study for the combined influent are also periodically monitored by the landfill for the raw landfill leachate. As of August, 2015, all pesticides were shown as non-detectable in the landfill leachate as analyzed by CH2MHill.

#### 4.2.9 Mixed liquor total suspended (MLSS) and volatile suspended solids (MLVSS)

Daily to weekly measurements were made for MLSS and MLVSS which are both shown in Figure 4.43. The average MLVSS concentration during the study was 2500 mg/L with a 95% confidence of 130 mg/L, which was a good level for pollutant removal in an SBR system based on typical design criteria (Wang *et al.*, 2009). The MLVSS is a rough measure of the biological fraction of the total solids, which overall was 82% of the total MLSS with a 95% confidence interval of 2% using data for the entire study. This is a very typical value for the MLVSS to MLSS ratio in activated sludge systems (Metcalf and Eddy, 2003), and are similar to ratios reported in other landfill leachate SBR studies (Aziz *et al.*, 2011; Doyle *et al.*, 2001).



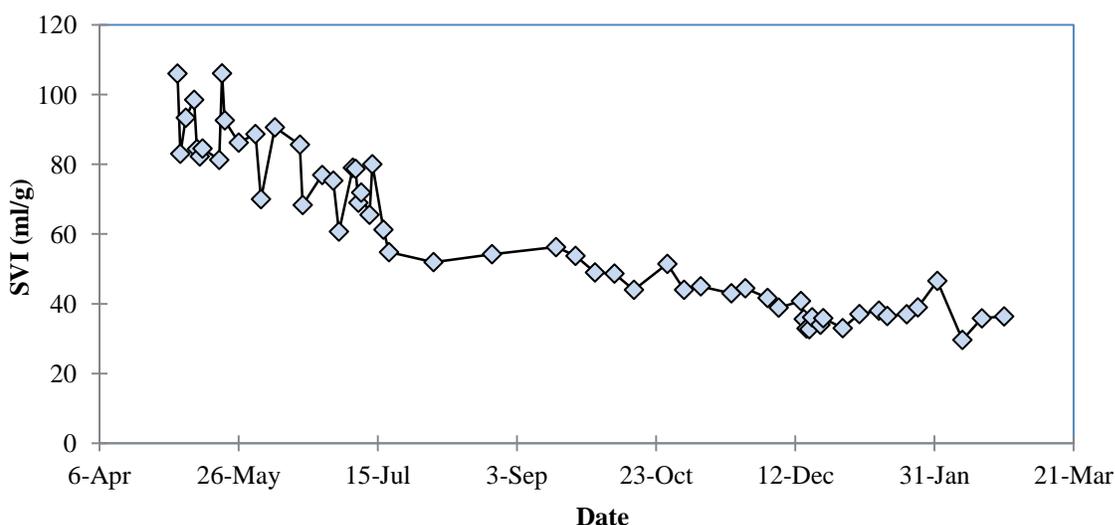
**Figure 4.43** MLSS and MLVSS for SBR 1 treating 50/50 wastewater and landfill leachate in December 2015 treating 50/50 (v/v) wastewater and landfill leachate.

Interestingly, the average ratio of MLVSS to MLSS increased from an average 78 % for the first 6 months to 86 % for the remainder of the study, possibly indicating a slight increase in the active biomass in the reactor after September. However, this does not directly correspond with the improved COD and nitrification observed in Figures 4.2 and 4.7, respectively. Some relatively large fluctuations in MLVSS were observed during the study. During summer and fall, there were intermittent periods where MLVSS rose to > 3000 mg/L and dropped to < 2000 mg/L, which could be indicative of the drastic changes in organic loading due to breakdown of CBOD in the feed bottle. The large spike in MLSS during late July and early August was due to addition of PAC. A lower average MLVSS was observed in winter, possibly due to more dilute combined influent and thus, lower pollutant loadings.

Due to the very low reported yields (Table A.7), nitrifiers were assumed to represent a smaller fraction of the MLVSS than heterotrophs; therefore the periods of higher MLVSS suggest higher CBOD<sub>5</sub> loadings. Although CBOD data was insufficient to corroborate this, past data for CBOD<sub>5</sub> of the landfill leachate given in Figure A.6 of the Appendix follows a very similar pattern when compared with the MLSS/MLVSS data shown in Figure 4.43, in that it is higher on average in summer and fall and lower in winter. However, large periodic drops in MLSS and MLVSS were observed, likely due to breakdown of the feed organics, causing a low F/M ratio. Thus, the correlation between CBOD<sub>5</sub> and MLSS/MLVSS is less noticeable.

#### 4.2.11 Sludge volume index

Figure 4.44 shows the SVI of SBR 1 over the period of the entire study. After addition of landfill leachate to the feed, there is a gradual decrease in SVI which started above 100 ml/g and dropped to below 50 ml/g after 2 ½ months of operation, with a minimum near 30 mL/g after 7 months.



**Figure 4.44** SVI for SBR 1 treating 50/50 (v/v) wastewater and landfill leachate.

Low SVI values are often reported in landfill leachate SBR studies, with reported values being as low as 25 mL/g (Yalmaz and Ozturk, 2001; Doyle *et al.*, 2001). An SVI of 100 or less indicates good settling sludge whereas an SVI greater than 150 indicates sludge bulking and possible filamentous growth (Davis, 2004). A low SVI is good because it suggests compact settling which minimizes disturbance of the sludge blanket and loss of biomass during the decant phase.

Although it is desirable to have a low SVI in the SBR, this type of floc showed some characteristics of dispersed growth, and could have had issues with TSS removal and associated

CBOD. This is due to the lack of any filamentous backbone and formation of pin flocs associated with dispersed growth which, although may settle well and give a low SVI, are easily sheared, leaving particles in the supernatant (Jenkins *et al.*, 2004). A dense floc could have also caused some substrate mass transfer limitations in the sludge, reducing removal rates by increasing the effective half-saturation constants as discussed previously (Manser *et al.*, 2005). This type of dispersed floc has been related to starvation conditions (low F/M ratio), long SRTs, and toxicity due to organic acids, surfactants, or sulfides (Jenkins *et al.*, 2004).

It is unclear how the periodic changes in influent CBOD, and ultimately the F/M ratio, may have affected the sludge characteristics, since MLVSS fluctuated greatly at times, even though SVI seemed to steadily decrease. Increasing aeration would be expected to increase the SVI by increasing DO leading to more filamentous growth. However there are many conditions that effect floc characteristics which include SRT, waste type, pH, DO concentrations, F/M ratio, temperature, and toxicity (Richard, 2003). Thus, it is a very complicated topic which is beyond the scope of the work presented here. To attempt to quantify the effects of sludge characteristics on biological treatment in this system, analysis of floc characteristics, *e.g.* particle size, density, and size distribution would be needed in conjunction with treatment data.

### **4.3 PAC Addition**

Powdered activated carbon (PAC) was added to SBR 1 for about a month during summer between July 10<sup>th</sup> and August 14<sup>th</sup>. This was expected to improve biological treatment due to sorption of refractory organics as well as remove some toxic organics, which has been shown to be effective in other landfill leachate SBR studies (Uyger and Kargi, 2003; Cecen and Atkas, 2001). However, no noticeable effects in treatment were observed. Due to poor settling of the

PAC which caused spikes in effluent TSS (Figure 4.35) and caking in the SBR, PAC addition was discontinued. Further testing may be needed if toxic organics are detected, or if reduction of COD and color are required in the future.

## CHAPTER 5

### CONCLUSIONS

The combined influent was characterized as having high concentrations of COD, CBOD<sub>5</sub>, TDS, TAN, and alkalinity. It had a neutral pH (7.5 - 8), and showed seasonal variability in TDS, TAN, and alkalinity due to precipitation. The Coffin Butte leachate, although having a higher CBOD<sub>5</sub> typical of younger landfills, showed all of the characteristics of leachate from a landfill in a methanogenic phase of decomposition. The higher CBOD<sub>5</sub> may be related to the landfill still being actively used, and thus a full scale plant should be prepared for significant CBOD<sub>5</sub> in the combined influent. The SBR was shown to be an effective means for reducing TAN and CBOD<sub>5</sub> in the combined leachate and wastewater influent to achieve target treatment goals. Although treatment of TAN and CBOD<sub>5</sub> was inconsistent during the first part of the study, some likely causes for decreased performance (*e.g.* low DO, high FA, and excess loading) were identified. This provided a means to better understand how the treatment process was affected by these factors in order to avoid issues if implemented at the full-scale.

The NO<sub>2</sub>-N accumulation that was observed is a widely reported phenomenon in other studies involving treatment of landfill leachates and other high TAN waste streams. As data from this study suggests, this was most likely related to adjustable operating parameters such as aeration rate, pH, and HRT (as related to pollutant loadings). It was shown that with adequate aeration, substrate build-up leading to high TAN and NO<sub>2</sub>-N concentrations in the SBR and possible inhibition of the nitrification process can be avoided. Thus, this study demonstrated the SBR can perform well, even at higher concentrations of landfill leachate in the combined influent, as long as adequate aeration is provided. Denitrification was shown to be a viable

option in further reduction of nitrogen with addition of an external carbon source, such as methanol. Filtration was shown to eliminate TSS and thus further reduce effluent CBOD<sub>5</sub>. Removal of phosphorus was minimal, and was likely due to inadequate operating conditions (*e.g.* the aerobic phase preceding the anoxic phase), insufficient fermentation products, or high concentrations of NO<sub>x</sub>-N making PAO enrichment infeasible.

The 50/50 (v/v) mixture used in this study would be considered a 'worst case' scenario in terms of a combined influent and it is most likely that actual percentage of landfill leachate will be less, based on relative seasonal flows of the wastewater and leachate. The TAN and CBOD<sub>5</sub> removal performance under adequate aeration, the low heavy metals concentrations, and the low to non-existent levels of toxic organics and pesticides in the combined influent, indicate that the SBR, especially if coupled with physico-chemical processes, can provide adequate treatment to achieve an effluent quality acceptable for discharge and less hazardous to the environment.

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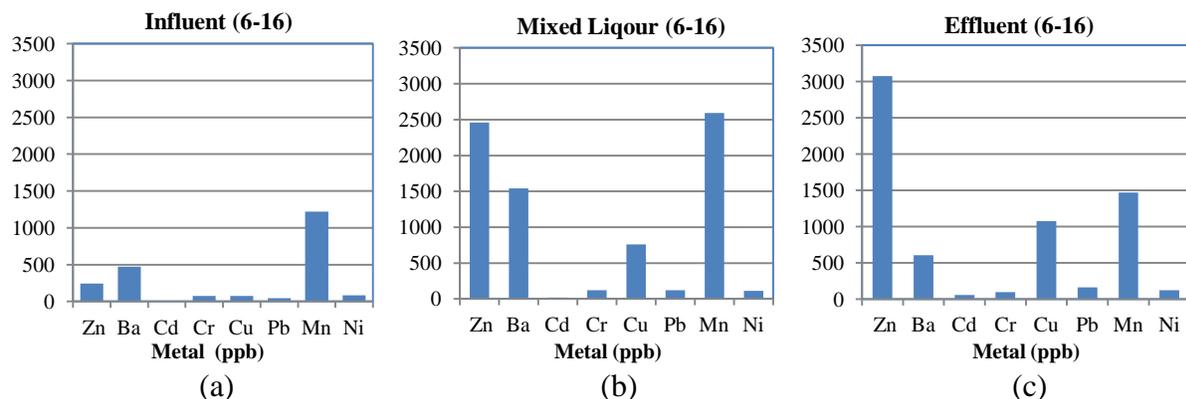
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APPENDIX

## APPENDIX



**Figure A.1** June (a) influent, (b) mixed liquor, and (c) effluent metals concentrations in SBR 1 treating 50/50 (v/v) wastewater and landfill leachate. No replicates were obtained.

**Table A.1** VOCs in the 50/50 (v/v) combined influent, as determined by CH2MHill. Values in red indicate false positives that were likely due to a contamination issue during analysis.

VOCs						
All Concentrations = ppb						
	10/9/2015	10/18/2015	10/21/2015	Average	Std Dev	95% CI
<b>Influent</b>						
Acetone	91.6	21.6	0	37.7	47.9	118.9
2-Butanone (MEK)	21.3	0	0	7.1	12.3	30.5
Benzene	0.84	0	0	0.3	0.5	1.2
4-Methyl-2-pentanone (MIBK)	26.8	0	0	8.9	15.5	38.4
Toluene	4.17	0	0	1.4	2.4	6.0
Ethylbenzene	0.96	0	0	0.3	0.6	1.4
m,p-Xylene	1.73	0	0	0.6	1.0	2.5
o-Xylene	1.25	0	0	0.4	0.7	1.8
Naphthalene	1.32	0	0	0.4	0.8	1.9
Methylene chloride	0	0	96900	32300.0	55945.2	138975.7
Chloromethane	0	0	0	0.0	0.0	NA

**Table A.2** Effluent VOCs for SBR 1, as determined by CH2MHill.

<b>VOCs</b>						
All Concentrations = ppb						
	10/14/2015	10/21/2015	10/26/2015	Average	Std Dev	95% CI
<b>Effluent</b>						
Acetone	66.1	55.5	68.7	63.4	7.0	17.4
2-Butanone (MEK)	0	0	0	0.0	0.0	NA
Benzene	0	0	0	0.0	0.0	NA
4-Methyl-2-pentanone (MIBK)	0	0	0	0.0	0.0	NA
Toluene	0	0	0	0.0	0.0	NA
Ethylbenzene	0	0	0	0.0	0.0	NA
m,p-Xylene	0	0	0	0.0	0.0	NA
o-Xylene	0	0	0	0.0	0.0	NA
Naphthalene	0	0	0	0.0	0.0	NA
Methylene chloride	0	0	0	0.0	0.0	NA
Chloromethane	3.65	4.36	3.73	3.9	0.4	1.0

**Table A.3** Semi-VOCs in the 50/50 (v/v) combined influent, as determined by CH2MHill.

<b>Semi-VOCs</b>						
All Concentrations = ppb						
	10/9/2015	10/30/2015	11/3/2015	Average	Std Dev	95% CI
<b>Influent</b>						
Pyridine	4.82	5.53	5.74	5.4	0.5	1.2
Aniline	6.57	9.92	4.95	7.1	2.5	6.3
Phenol	56.6	0	34.6	30.4	28.5	70.9
2-Methylphenol	5.84	3.77	5.9	5.2	1.2	3.0
3,4-Methylphenol	442	0	44.8	162.3	243.3	604.4
2,4-Dimethylphenol	5.1	0	0	1.7	2.9	7.3
bis(2-Ethylhexyl)phthalate	7.34	7.29	11	8.5	2.1	5.3
Benzyl alcohol	0	0	2.36	0.8	1.4	3.4
Benzoic acid	0	0	0	0.0	0.0	NA

**Table A.4** Effluent semi-VOCs for SBR 1, as determined by CH2MHill.

<b>Semi-VOCs</b>						
All Concentrations = ppb						
	11/2/2015	10/18/2015	11/17/2015	Average	Std Dev	95% CI
<b>Effluent</b>						
Pyridine	0	0	0	0.0	0.0	NA
Aniline	0	0	0	0.0	0.0	NA
Phenol	0	0	0	0.0	0.0	NA
2-Methylphenol	0	0	0	0.0	0.0	NA
3,4-Methylphenol	0	0	0	0.0	0.0	NA
2,4-Dimethylphenol	0	0	0	0.0	0.0	NA
bis(2-Ethylhexyl)phthalate	0	0	2.6	0.9	1.5	3.7
Benzyl alcohol	0	0	0	0.0	0.0	NA
Benzoic acid	0	7.22	6.94	4.7	4.1	10.2

**Table A.5** Pesticides in the 50/50 (v/v) combined influent, as determined by CH2MHill.

<b>Pesticides</b>						
All Concentrations = ppb						
	10/9/2015	11/6/2015	11/9/2015	<b>Average</b>	Std Dev	95% CI
<b>Influent</b>						
Heptachlor	0	0	0	0.0	0.0	NA
Endrin ketone	0	0	0	0.0	0.0	NA
4,4'-DDD	0	0	0	0.0	0.0	NA
Lindane	0	0	0	0.0	0.0	NA
4,4'-DDE	0	0	0	0.0	0.0	NA

**Table A.6** Effluent pesticides for SBR 1, as determined by CH2MHill.

<b>Pesticides</b>						
All Concentrations = ppb						
	10/25/2015	10/28/2015	11/9/2015	<b>Average</b>	Std Dev	95% CI
<b>Effluent</b>						
Heptachlor	0.0004	0	0	0.00013	0.00023	0.00057
Endrin ketone	0.0014	0	0	0.00047	0.00081	0.00201
4,4'-DDD	0	0.0007	0	0.00023	0.00040	0.00100
Lindane	0	0	0.0012	0.00040	0.00069	0.00172
4,4'-DDE	0	0	0.0012	0.00040	0.00069	0.00172

### CH2M HILL Applied Sciences Laboratory (ASL)

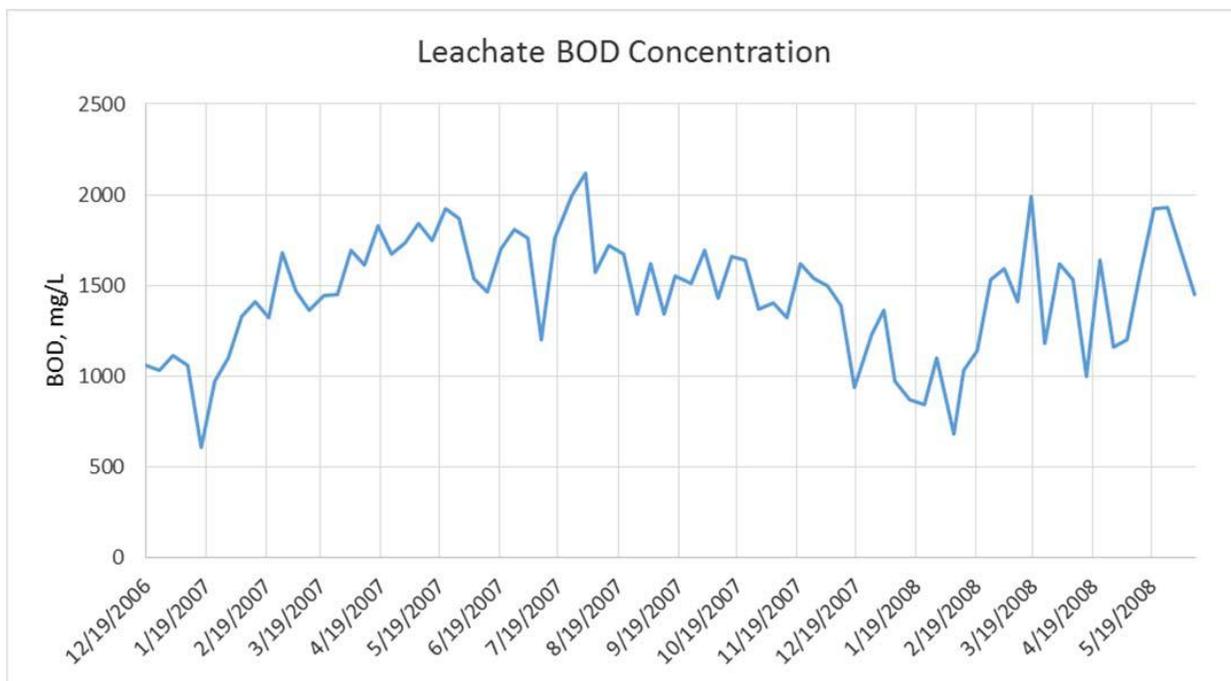
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Project Name: Valley Landfill, INC				Date Received: 08/04/15			
Sample Date: 08/04/15				Report Revision No: 0			
Sample Time: 09:00							
Type: Grab							
Matrix: Water							

Analyte	Dilution Factor	DL	RL	Result	Qual	Units	Analysis Method	Prep Method	Date Analyzed
<b>Metals</b>									
Antimony	20	0.62	10.0	33.7		ug/L	E200.8	E200.2	08/04/15
Arsenic	20	0.60	10.0	159		ug/L	E200.8	E200.2	08/04/15
Beryllium	20	0.50	10.0	0.50	U	ug/L	E200.8	E200.2	08/04/15
Cadmium	20	0.60	10.0	0.60	U	ug/L	E200.8	E200.2	08/04/15
Chromium	20	2.00	20.0	220		ug/L	E200.8	E200.2	08/04/15
Copper	20	10.0	40.0	58.2		ug/L	E200.8	E200.2	08/04/15
Lead	20	0.81	10.0	2.56	J	ug/L	E200.8	E200.2	08/04/15
Mercury	20	5.62	20.0	15.0	J	ng/L	E1631E	METHOD	08/06/15
Molybdenum	20	1.00	20.0	15.0	J	ug/L	E200.8	E200.2	08/04/15
Nickel	20	0.50	10.0	182		ug/L	E200.8	E200.2	08/04/15
Selenium	20	1.38	10.0	93.5		ug/L	E200.8	E200.2	08/04/15
Silver	20	0.50	10.0	0.50	U	ug/L	E200.8	E200.2	08/04/15
Thallium	20	0.50	4.00	0.50	U	ug/L	E200.8	E200.2	08/04/15
Zinc	20	50.0	200	150	J	ug/L	E200.8	E200.2	08/04/15

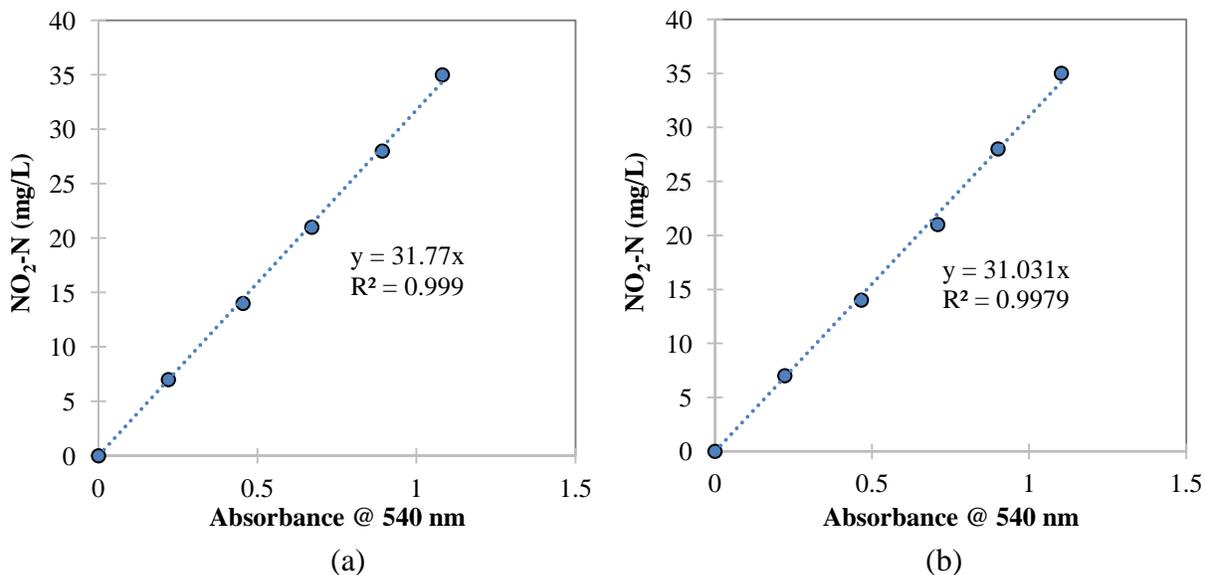
**Figure A.2** Metals data for Coffin Butte landfill leachate analyzed by CH2MHill on 8/15/2015 (provided as a supplementary reference).

Current Wastewater Composition Summary						
Flow Parameter	BOD		TSS		pH	
	Composition (mg/L)	Loading (lbs)	Composition (mg/L)	Loading (lbs)		
Annual Average	132	79	95	61	7.34	
	Average		Average		Minimum	Maximum
Winter (Nov-Apr)	94	78	78	69	5.51	8.41
Summer (May-Oct)	172	80	113	53	6.23	8.58
Maximum Month	318	210	302	178	8.12	
Maximum Day	450	300	492	286	8.58	
	Minimum Month				6.44	
	Minimum Day				5.51	

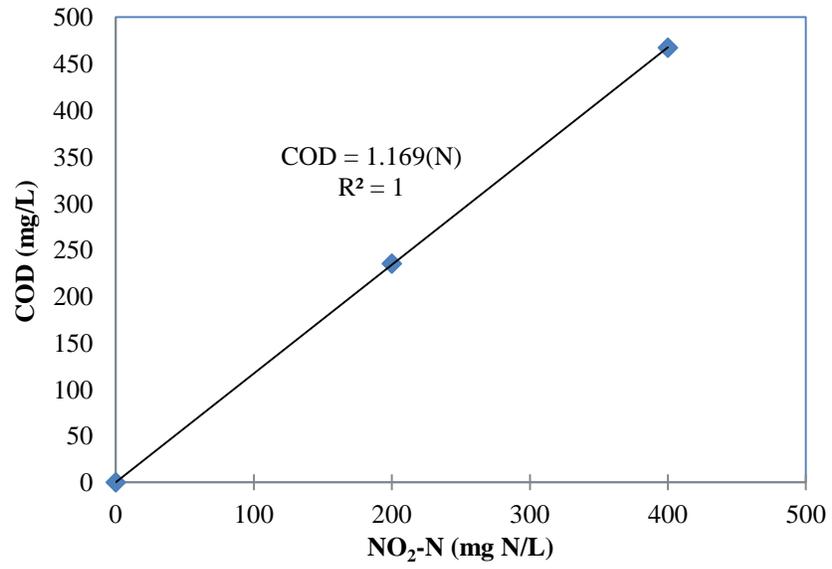
**Figure A.3** Influent BOD, TSS, and pH of Adair Village wastewater as monitored by the City of Adair (taken from Civil West Engineering design proposal, provided as a reference).



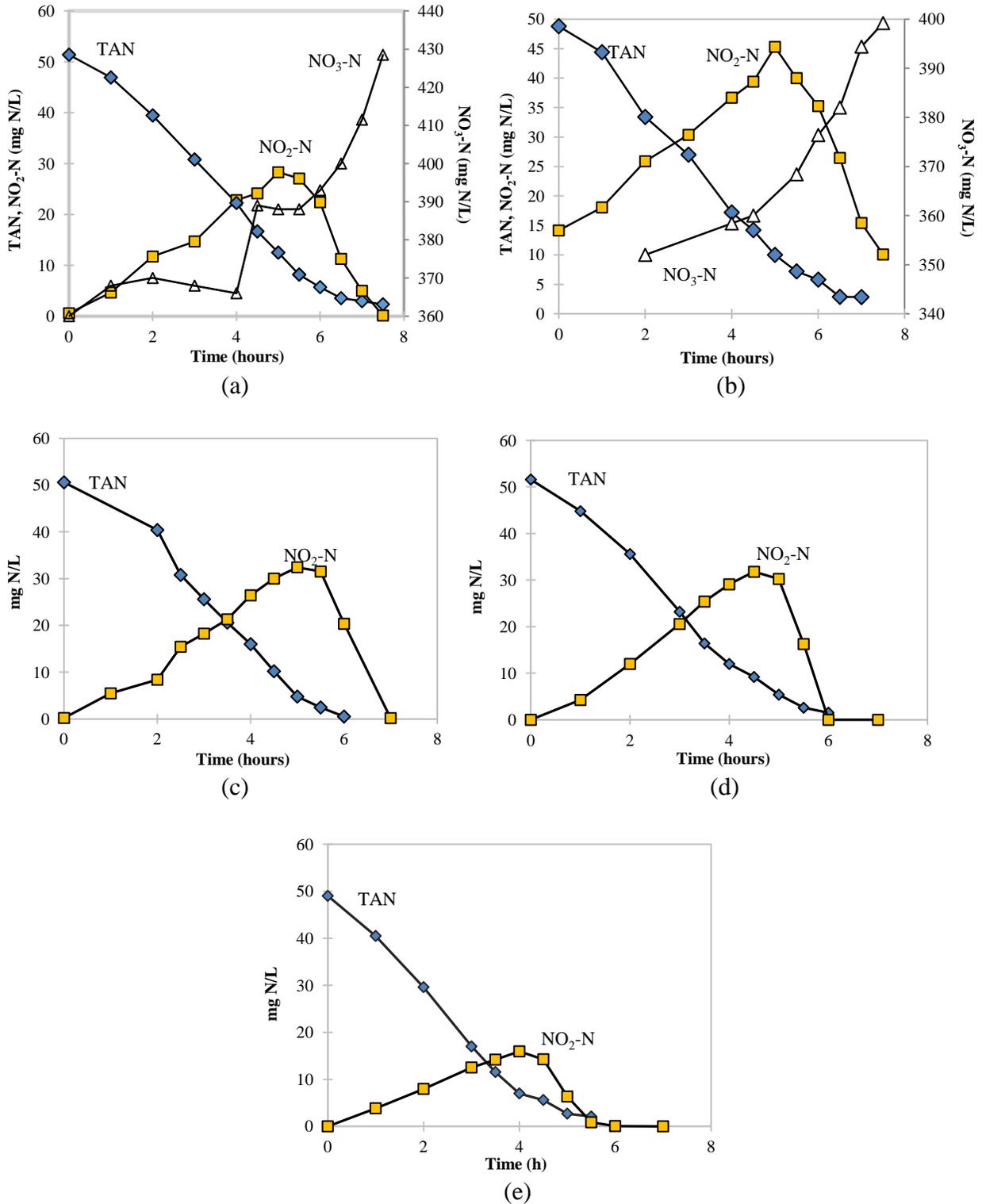
**Figure A.4** Historical BOD data for Coffin Butte Landfill leachate (taken from Civil West Engineering design proposal, provided as a reference).



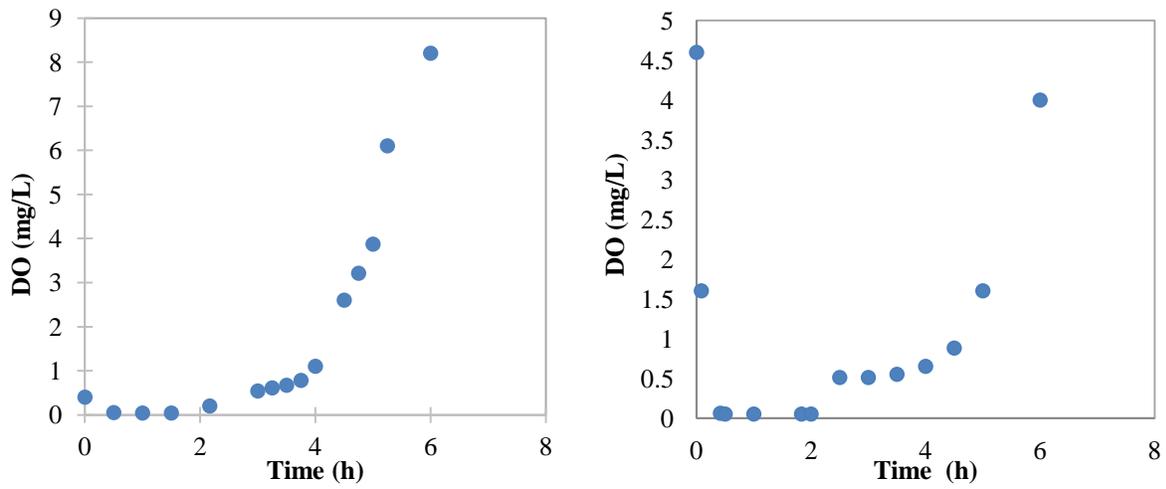
**Figure A.5** Nitrite assay standard curves using (a) only DI water and (b) 17% landfill leachate. The curves show only a 2% difference indicating very little if any interference by landfill leachate components.



**Figure A.6** Standard curve used to correct COD measurements for NO<sub>2</sub>-N interference.



**Figure A.7** Nitrification profiles at (a) - (b) 17 °C and (c) - (e) 23.5 °C for SBR 1 treating 50/50 (v/v) landfill leachate and wastewater (Dec 2015).



**Figure A.8** DO profiles for SBR 1 treating 50/50 (v/v) landfill leachate and wastewater, with the anoxic phase preceding the aerobic phase (Feb 2016).

**Table A.7** Constants and kinetic parameters for aerobic activated sludge processes taken from literature.

Parameter	Description	Range/Value (20 °C)	Units	Source
$\mu_{max,H}$	Max specific growth rate (heterotrophic)	0.125	(1/h)	<i>Henze et al. (2002)</i>
$k_{d,H}$	Decay constant (heterotrophic)	0.004	(1/h)	<i>Kaelin et al. (2009)</i>
$K_S$	Half saturation constant (heterotrophic)	20	(mg BOD/L)	
$K_{O,H}$	Half saturation constant oxygen (heterotrophic)	0.20	(mg DO/L)	
$Y_H$	Heterotrophic cell yield	0.67	(mg VSS/mg BOD)	
$\mu_{max,NH}$	Max specific growth rate (AOB)	0.033	(1/h)	
$k_{d,NH}$	Decay constant (AOB)	0.006	(1/h)	<i>Kaelin et al. (2009)</i>
$K_{O,NH}$	Half saturation constant oxygen (AOB)	0.5	(mg DO/L)	<i>Kaelin et al. (2009)</i>
$Y_{NH}$	AOB cell yield	0.18	(mg VSS/mg N)	<i>Ahn et al. (2008)</i>
$\mu_{NO}$	Max specific growth rate (NOB)	0.027	(1/h)	<i>Kaelin et al. (2009)</i>
$k_{d,NO}$	Decay constant (NOB)	0.009	(1/h)	<i>Ahn et al. (2008)</i>
$K_{NO}$	NO <sub>2</sub> -N half saturation constant	0.8	(mg N/L)	
$K_{O,NO}$	Half saturation constant oxygen (NOB)	1.8	(mg DO/L)	
$Y_{NO}$	NOB cell yield	0.06	(mg VSS/mg N)	

**Table A.8** EPA ceiling concentrations for heavy metals in land applied biosolids (adopted from <https://www.law.cornell.edu/cfr/text/40/503.13>; accessed 9/2/2016).

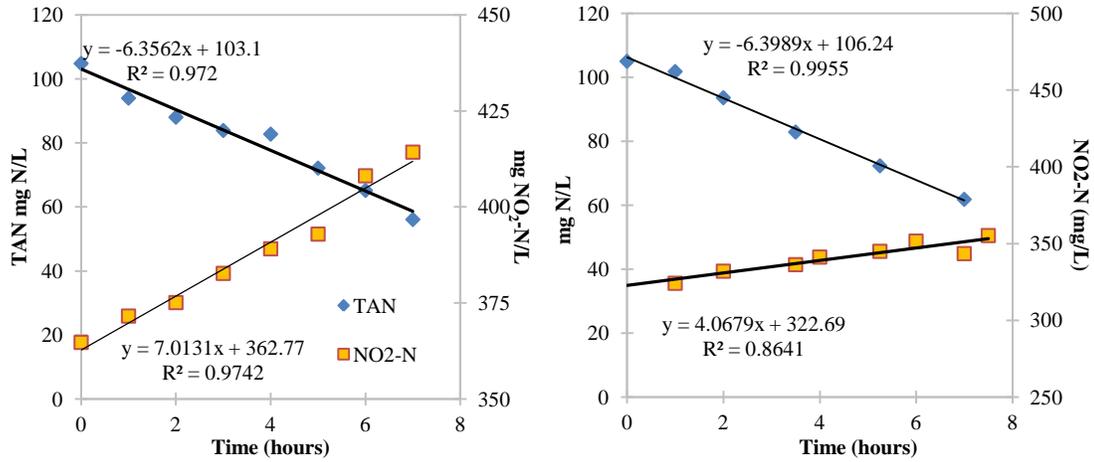
Pollutant	Ceiling concentration (milligrams per kilogram) <sup>1</sup>
Arsenic	75
Cadmium	85
Copper	4300
Lead	840
Mercury	57
Molybdenum	75
Nickel	420
Selenium	100
Zinc	7500

<sup>1</sup> Dry weight basis.

**Table A.9** EPA monthly average concentration limits for heavy metals in land applied biosolids (adopted from <https://www.law.cornell.edu/cfr/text/40/503.13>; accessed 9/2/2016).

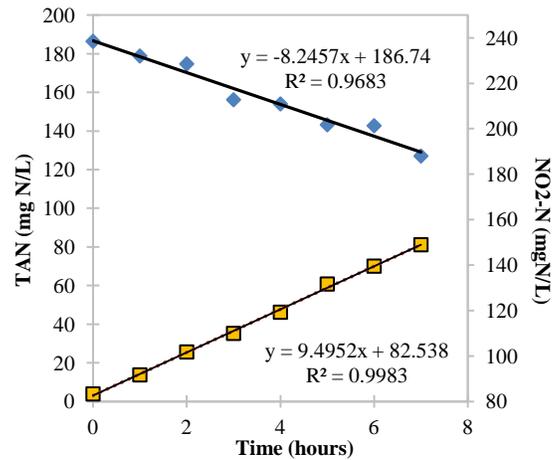
Pollutant	Monthly average concentration (milligrams per kilogram) <sup>1</sup>
Arsenic	41
Cadmium	39
Copper	1500
Lead	300
Mercury	17
Nickel	420
Selenium	100
Zinc	2800

<sup>1</sup> Dry weight basis.



(a)

(b)



(c)

**Figure A.9** Nitrification profiles for SBR 1 treating 50/50 (v/v) landfill leachate and wastewater on (a) Aug 28th, (b) Sept 28th, and (c) Oct 5 (2015).