ABSTRACT

Title of Thesis:	INVESTIGATING THE DYNAMICS OF VOLATILE SULFUR COMPOUNDS FROM PRIMARY AND SECONDARY SYSTEMS IN WASTEWATER RESOURCE RECOVERY FACILITIES
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This study quantifies volatile sulfur compounds (VSCs) emissions from Wastewater Resource Recovery Facilities (WRRFs) and investigate their mechanisms of generation. In primary treatment, of the VSCs analyzed, hydrogen sulfide (H_2S) and methyl mercaptan (MM) concentrations in the off gas were dominant, while dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) were under their odor threshold for most sampling dates. H_2S emission in primary settling tanks was mainly the result of the stripping of dissolved sulfide (64%) generated in the sewers. MM emission was more dependent on the conditions in the primary clarifiers (only 16% stripping). Most significant prevention of odor emission in primary settling tanks can be achieved by managing biofilms and microbial reactions in the sewer network. This would control the biomass seeding and fermentation product availability in the primary settling tanks directly and will decrease the observed kinetics of H_2S and MM production.

Overall, management of sludge blanket heights and thus avoiding time at low oxidation reduction potential (ORP) minimized odor emission independent of sewer conditions. Our investigations in secondary reactors have shown that MM was 2 to 3 order of magnitude higher than dissolved MM in primary effluent, revealing that the production of MM took place in the activated sludge process itself, and the stripping of MM from the feed was very minimal. Furthermore, data showed that the depth of secondary sludge blanket plays an important role on the extent of MM emission. At high sludge blanket height, high MM emission was observed. It was concluded that low ORP conditions in sludge blanket, selector zones and RAS was the major source of VSCs. Increasing ORP could decrease odor emissions by targeting the zones where MM is emitted. This could be achieved by addition of nitrate in secondary settling tanks.

Key words: Methyl Mercaptan, hydrogen sulfide, sulfate reducing bacteria, active biomass, primary sludge blanket

INVESTIGATING THE DYNAMICS OF VOLATILE SULFUR COMPOUNDS
FROM PRIMARY AND SECONDARY SYSTEMS IN WASTEWATER
RESOURCE RECOVERY FACILITIES

by

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Table of Contents

List of Tables

List of Figures

List of Abbreviations

WRRFs – Wastewater Resources Recovery Facilities
WWTPs – Wastewater Treatment Plants
COD – Chemical oxygen demand
DO – Dissolved oxygen
DMDS – Dimethyl Disulfide
DMS – Dimethyl Sulfide
HRT – Hydraulic retention time
H_2S – Hydrogen Sulfide
MLSS – Mixed liquor suspended solids
MM – Methyl Mercaptan
OHOs – Ordinary Heterotrophic Organisms
SOR –Solids Overflow Rate
SRT – Sludge retention time
SLR – Solids Loading Rate
SRBs – Sulfate reduction bacteria
TIN – Total inorganic nitrogen
TSS – Total suspended solid
VSS – Volatile suspended solid

Chapter 1   Introduction

1.1   Problem Statement

Urban spread continues to encircle once-remote wastewater treatment plants (WWTPs), resulting in increasing complaints from neighbors due to nuisance odors emissions (Lebrero et al., 2011). Although odorous compounds are formed and emitted from each step of the treatment process, passive and active liquid surfaces exposed to the atmosphere are one of the major sources of odorous compounds related to WWTPs (Prata et al., 2018). Primary settling tanks (PSTs) and activated sludge reactors are important source of malodorous volatile sulfur compounds (VSCs) emissions due to their exposed large surface area (Catalan et al., 2009, Devai and DeLaune, 1999). In primary and secondary treatment, odorous compounds are largely composed of organic and inorganic sulfur compounds (Sekyiamah et al., 2008). Among them, hydrogen sulfide (H_2S), methyl mercaptan (MM), dimethyl sulfide (DMS) and Dimethyl Disulfide (DMDS) are the main odorous compounds. VSCs are characterized by their extremely low odor threshold (MM: 0.07 ppbv; DMS: 3 ppbv, DMDS: 2.2 ppbv; H_2S: 10 ppbv) (Catalan et al., 2009). Moreover, it is important to notice that organic VSCs have much lower odor threshold than H_2S, thus even small concentrations would have higher odor impact than H_2S.

Very few studies have reported the impact of collection systems and wastewater treatment process on VSCs emission from wastewater primary and secondary treatment. For this reason, this study investigated VSC emissions from both sources, with a focus on the potential impact of sewers odors downstream at the

plant. Additionally, other factors which could impact VSCs formation were assessed, resulting in a matrix correlating the impact of operational conditions and influent characteristics on VSCs emission.

1.2   Objectives

For decades, research and technologies have been focused on the treatment of foul air from treatment processes providing end-of-pipe solutions for VSCs removal, which incorporate capital and operational cost to utilities (Estrada et al., 2010). Technologies developed include physical-chemical approaches with the focus to remove mainly H_2S as well as biological approaches (i.e. biofilters and trickling filters) being able to also treat VOSCs (Giri et al., 2014). Treatment and cost effectiveness of these end-of-pipe approaches is mainly dependent on the ease to capture the foul air and therefore mostly applied for sewer networks, screening and grit chamber buildings, waste activated sludge treatment and biosolids storage facilities. However, one of the significant sources of nuisance odor emission within WWTP is the primary and secondary treatment system, which is mainly caused by VSCs (C. C. Koe & C. Tan, 1990).

Therefore, this research aimed to propose that through a better understanding of the microbiome involved in the in-situ production of VSC and especially VOSC, a significant part of the odor emission from the biological wastewater treatment systems can be minimized through operational control rather than odor treatment, thus minimizing capital investments. Specific objectives are:

1) To develop fundamental understanding of the mechanisms and conditions leading to production, consumption and emission of VSC in WRRFs

2) To measure key kinetic parameters in primary and secondary needed to predict odor emission potential within WWTP.

3) To determine effects of collection systems on odorous compounds production in primary systems

4) To investigate impact of wastewater treatment process of VSCs emissions

Chapter 2   Manuscript: Investigating the dynamics of Volatile Sulfur Compounds emission from primary systems at a Water Resource Recovery Facility

This paper was submitted to *Water Environment Research Journal.*

Abstract

This study quantifies volatile sulfur compounds (VSCs) emissions from primary settling tanks and investigate their mechanisms of formation. Of the VSCs analyzed, hydrogen sulfide (H_2S) and methyl mercaptan (MM) concentrations in the off gas were dominant, while dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) were under their odor threshold for most sampling dates. Due to the large variability in emission rates in summer 2018, the proposed Arrhenius model could not significantly explain the data and was not valid. H_2S emission in primaries was mainly the result of the stripping of dissolved sulfide generated in the sewers. MM emission was more dependent on the conditions in the primary clarifiers. The seeding of active biomass was found to be a critical factor impacting emissions due to short sludge retention time in primary systems. Low oxidation reduction potential conditions in the sludge blanket were shown to promote both H_2S and MM formation.

Practitioner points

- H_2S emission from primary clarifiers mainly originated from the stripping of the dissolved sulfide formed in the sewers

- MM emission contributed up to 89 % of total VSCs emitted from primary clarifiers

- Seeding of active biomass in the wastewater was be the main driver for both MM and H$_2$S formation

- Free nitrous acid (FNA) treatments to remove biofilm in sewers would control both stripping and production in primary settling tanks

Key words

Methyl Mercaptan, hydrogen sulfide, sulfate reducing bacteria, active biomass, primary sludge blanket

3.1 Introduction

Nuisance odors originating from Water Resource Recovery Facility (WRRF) has become a rising concern in the resource recovery sector. The increase of constraining regulations has created an urge to change the public perception of municipalities. In the past 50 years , the urban spread has encircled WRRFs, resulting in an increasing amount of neighboring residents complaints due to odors emissions (Lebrero et al., 2011). Although odorous compounds are formed and emitted from each step of the treatment process, passive liquid surfaces exposed to the atmosphere are one of the major sources of odorous compounds related to WRRFs (Prata et al., 2018). These passive surfaces are mainly encountered in primary, secondary and tertiary settlement tanks. Primary settling tanks are important source of malodorous volatile sulfur compounds (VSCs) emissions due to their exposed large surface area (Catalan et al., 2009, Devai and DeLaune, 1999). Although no active gas flow is applied to primary systems, the wind velocity promotes shear at the water surface and contribute significantly to odors dispersion. Odors emitted in primaries are potentially impacted by odors produced in the sewers and characterizing the emission rates of

specific odorous compounds from these surfaces is important to evaluate their impact on the environment. Additionally, understanding their mechanisms of formation and subsequent emissions is critical for developing better odor control initiatives.

In primary treatment, odorous compounds are largely composed of organic and inorganic sulfur compounds (Sekyiamah et al., 2008). Among them, hydrogen sulfide (H_2S), methyl mercaptan (MM), dimethyl sulfide (DMS) and Dimethyl Disulfide (DMDS) are the main odorous compounds. These compounds are known to have the potential to pose human health hazards and significant nuisances with odor phenomena (Giri et al., 2014, Lebrero et al., 2011). VSCs are characterized by their extremely low odor threshold (MM: 0.07 ppbv; DMS: 3 ppbv, DMDS: 2.2 ppbv; H_2S: 10 ppbv) (Catalan et al., 2009). Moreover, it is important to notice that organic VSCs have much lower odor threshold than H_2S, thus even small amounts would have higher odor impact.

Only few studies have investigated VSCs emission from primary clarifiers (Catalan et al., 2009, Jeon et al., 2009, Paing et al., 2003, Prata et al., 2018, Stuetz and Frechen, 2015). For example, H_2S, MM, DMS and DMDS emissions from Kraft Mill primary clarifiers of 0.39, 0.19, 0.17, 0.83 (ug S/m^2/s), respectively were found to be responsible of odor nuisance (Catalan et al., 2009). Total reduced sulfur emission from primary settling tanks of 0.3 (ug S/m^2/s) have caused odor issues at the Sun-Cheon WRRF in South Korea (Jeon et al., 2009). A similar study from an anaerobic pond in the South of France have shown H_2S emission rates ranging from 0.23 to 6.66 (ug S/m^2/s) generating nuisance for nearby inhabitants (Paing et al., 2003). There is a lack of sulfur studies in primary systems and, to our knowledge, none of the studies

6

have reported the impact of collection systems on VSCs emission from wastewater primary treatment. For this reason, this study focused on quantifying VSCs emission from primary clarifiers and investigated the potential impact of sewers odors downstream at the facility.

In the collection systems, high amount of VSCs are formed in the process of wastewater transportation (Hvitved-Jacobsen et al., 1998), and among them H_2S has been identified to be the main VSCs generated (Sun et al., 2015, Zhang et al., 2008). Sulfur cycle and microbiology involved has been well studied in the sewers and the reduction of the sulfate ion has been the most significant mechanism for the production of H_2S (Design, 1985, Du and Parker, 2012, Hvitved-Jacobsen et al., 1998, Park et al., 2014, Zhang et al., 2008). Other studies have shown that organic VSCs were also formed in the sewers through degradation of sulfur containing amino acids under anaerobic conditions (Hvitved-Jacobsen et al., 1998, Sun et al., 2015). In a suggested pathway, this degradation involved the sequential break down of proteins to form free amino acids of which cysteine and methionine were then broken down to form H_2S, MM, and NH_3 (Higgins et al., 2006). Before organic VSCs were released into the atmosphere, considerable quantities have undergone degradation by microbial populations. For instance, the degradation of DMS and MM was mainly attributed to methanogens, sulfate reducing bacteria (SRB) and denitrifying bacteria in systems where anaerobic or anoxic sludge retention time (SRT) were long enough to maintain these microbial communities (Chen et al., 2005).

As shown above, odorous compounds formed in the sewers could contribute to VSCs emission in the primary settling tanks. Furthermore, several factors could impact

VSCs formation, therefore investigating their mechanism of generation is of high interest and will contribute to developing better odor control initiatives. To our knowledge, continuous monitoring of VSCs from primaries has not yet been performed under different seasonal changes and operational conditions. Consequently, this study quantified VSCs emission from primary settling tanks and investigated the impact of sewers, seasonality and wastewater characteristics.

3.2   Material and Methods

3.2.1   Site Description

A schematic diagram of the primary treatment at the Blue Plains Advanced Wastewater Treatment Plant (AWWTP) is shown in Figure 1. Blue Plains AWWTP is one of the largest advanced wastewater treatment facility in the world, treating over 1.1 million cubic meters of sewage per day and serving the District of Columbia and parts of Maryland and Virginia in the USA. Raw influent wastewater was split in two treatment streams named East and West receiving 60% and 40% of the flow respectively. Gravity thickening overflow was redirected to west influent. East and west were composed of twenty and sixteen primary clarifiers, respectively. A chemically enhanced primary treatment (CEPT) process was applied using ferric chloride and anionic polymer to enhance coagulation and flocculation for more effective organics and phosphorous removal. Clarifiers surface area were 192 m^2 for west and 172 m^2 for east. For consistency, sampling campaigns for odor monitoring were conducted on the third and twentieth primary settling tank on West and East side respectively.
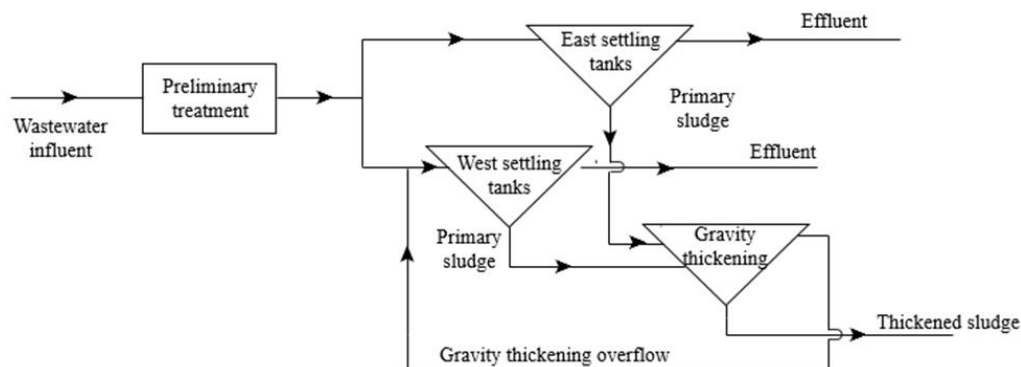
Figure 1. Schematic representation of wastewater process at the beginning of the plant at Blue Plains AWWTP.

3.2.2 Sampling campaigns

Sampling campaigns were performed once a month from May 2017 to August 2018 except in November 2017 and December 2017. An AC'SCENT surface emission isolation flux chamber (St. Croix Sensory, Inc., St. Croix River Valley, MN, USA) was used for gas phase sampling at the surface of clarifiers. A universal 44XR air sampling pump (SKC Inc., Eighty Four PA, USA) was used to pump the air out of the hood at a constant flow of 1.5 L/min. Air samples were collected into 1.4 L canisters coated with fused silica (Entech Instruments Inc., Simi Valley, CA, USA) for analysis of organic VSCs. Canisters were thoroughly cleaned prior to sampling. This ensured that the canisters were free from any volatile and semi-volatile compound. H2S measurements were carried out using an electrochemical sensor (Odalog, Detection Instruments Co. Phoenix, Az., USA) with a range of 0.1 ppm to 20 ppm and an accuracy of 0.1 ppm. The sensor included a sampling pump with a flow rate controlled at 1.5 L/min. Calibration of the sensor was performed using an H2S standard gas (Restek Corporation, Bellefonte, Pa., USA). The obtained

9

concentrations were used to calculate emission rates based on method described in Catalan et al., (2009).

Additionally, wastewater influent, effluent and primary sludge were sampled and analyzed for total suspended solids (TSS) and volatile suspended solids (VSS) according to standard methods. Nitrogen species (NH_4^+-N, NO_3^--N), phosphorus (PO_4^{3-}-P) and chemical oxygen demand (COD) were measured using HACH vials [HACH GmbH] and analyzed according to standard methods (American Public Health Association, 1999). Total Sulfur and total soluble sulfur in wastewater samples were analyzed using an inductively coupled plasma—atomic emission spectrometry (ICP-AES) following method described in Dewil et al., (2006). Soluble organic sulfur was determined as the difference between total soluble sulfur and sulfate. Total Kjeldahl Nitrogen (TKN) and soluble Kjeldahl nitrogen (sTKN) was analyzed using EPA standard method. Furthermore, starting October 2017, the sludge blanket height in the primary clarifiers was recorded simultaneously to VSCs monitoring using a 15 ft sludge judge (Sludge Judge® - 15 Ft, Nasco).

3.2.3 Headspace-Gas Chromatography-Mass Spectrometry

Analysis of canisters was performed within 24 hours of sampling using an Entech Model 7500 Autosampler followed by a Model 7200 Pre-concentrator coupled to an Agilent 5790N Gas Chromatographer-Mass Spectrometer (Agilent Technologies Inc., Wilmington, DE., USA) (Romero et al., 2017). Sample canisters were placed in the autosampler and air samples of 10 to 500 mL were withdrawn for pre-concentration using the following method: empty trap at -40 °C to remove most water vapor; VOCs captured on Tenax trap at -40 °C and flushed with helium to

remove remaining water; Tenax trap heated to 10 °C; VOCs trapped on fused silica

tube at -150°C; tube heated at to 50 °C onto the GC-MS column. All gas transfer lines

were coated with fused silica and heated to 100 °C. Gas chromatography conditions

were: Rtx1-MS Column (60 m x 0.32 mm x 1.0 μm) (Restek Corporation, Bellefonte,

Pa.); ultra high purity He carrier gas at a constant flow 172 of 1.5 mL min-1;

temperature program: 35 °C hold 5 min; 10 °C min^{-1} to 130 °C; 20 °C min-1 to 220°C

hold 5 min. Mass spectrometer source was operated in electron impact mode with

simultaneous total ion chromatography and selected-ion monitoring. Temperature

conditions were: transfer line 240 °C and source at 230 °C. Target ions for selected-

ion monitoring were: carbonyl sulfide (60 m/z); methanethiol (48 m/z); ethanethiol

(62 m/z); dimethyl sulfide (62 m/z); carbon disulfide (76 m/z); propanethiol 178 (76

m/z); butanethiol (90 m/z); dimethyl disulfide (94 m/z); and trimethylamine (59

m/z). 1,4 dichlorobenzene (63 m/z) was used as an internal standard. Calibration of

the GC-MS was carried out using certified gas standards from Restek Corporation

and Tech Air Companies (While Plains, NY, USA): 5 ppm (± 5%) mixture of

carbonyl sulfide, methanethiol, ethanethiol, dimethyl sulfide, carbon disulfide,

propanethiol and butanethiol; 5 ppm (± 2%) standard of dimethyl disulfide; 184

trimethylamine 5 ppm (± 5%); and 1ppm (± 5%) of TO-14 internal standard mixture

including bromochloromethane, 1,4 difluorobenzene, chorobenzene-d5 and 1,4

bromochlorobenzene. Standard gases were diluted into canisters to 250 ppbv and 25

ppbv as working standards using a 4600 dynamic dilutor (Entech Instruments Inc.,

Simi Valley, Ca) and ultra-high purity nitrogen as balance gas. Diluted standards

were prepared every 6 weeks for calibration curves and were used for calibration
check in every set of samples.

3.2.4   Batch experiments

To gain understanding of VSCs formation and impact of substrate availability,
batch studies were conducted with different wastewater streams including primary
sludge plus final effluent (S +FE), primary sludge plus influent (S + I) and primary
sludge plus influent plus GTO (S + I +GTO). These tests were carried out in 2 L
plexiglas jars, in which 1.6 L of sample (sludge + wastewater) was added, leaving 0.4
L headspace. Tests were performed at constant stripping rate of 1.5 L/min of nitrogen
gas and gas samples were collected at regular intervals (every 10 minutes) over a
period of 30 minutes. This method allowed for MM and H_2S production rate
calculation based on gas phase measurements for the given conditions and
sludge/food mixture (Romero-Flores et al., 2016).

Additionally, soluble MM and H_2S were estimated using a method described in
Romero-Flores et al., (2017). Batch testing were undertaken using samples from
primary influent, primary effluent and primary sludge. These samples were added to
20 L buckets at midpoint and the headspace gas samples were collected in evacuated
canisters at equilibrium. Dissolved concentrations were calculated based on the
headspace concentrations and their Henry constants (K_{H2S}: 0.087 M/atm at 25 °C;
K_{MM}: 0.2 M/atm at 25 °C).

3.2.5 VSCs emission rates calculation

VSCs emission rates were calculated based on the following equation (Catalan et al., 2009):

$$ER(i) = \frac{C(i) \; X \; Q \; X \; Ac}{Afc} \tag{1}$$

Where:

ER(i) = Emission rate of the target compound (g S/d)

C(i) = Concentration of the target compound (g S/m^3)

Q = Sweep gas flow rate (m^3/d)

A$_c$ = Exposed water surface area to the flux chamber (m^2)

A$_{fc}$ = Surface area of the clarifier (m^2)

No significant difference was found when measurements were undertaken at different location of the clarifier, therefore the samples were taken from the middle of the clarifier and the resulting flux was multiplied to the total surface area of the clarifier to determine the total mass emission of each compound.

3.2.6 Active biomass determination in influent wastewater

An aerated and mixed batch method was used to estimate the content of active heterotrophic organisms in influent wastewater (Wentzel et al., 1995). In this test, two liters of primary influent sample were added to a batch reactor and aerated with air. Dissolved oxygen level was maintained between 4 and 5 mgO2/L and the resulting oxygen uptake rate (OUR) was measured semi – continuously for approximately 5 to

10 hours. The test required an availability of readily biodegradable COD (rbCOD) at the start of the test which will translate in a logarithmic growth phase. Typically, OUR increased exponentially from its initial low value within the first 6 hours until rbCOD was depleted accompanied by a drop in OUR. Using OUR response and default Monod kinetics (4 d-1 growth rate, yield of 0.666 mg COD/mg COD, decay of 0.62 d-1) the biomass concentration was estimated.

3.3 Results

3.3.1 Sulfur mass balances

The overall CEPT performance in terms of TSS, total COD, total P and TKN removal efficiencies for both East and West systems is presented in Table 1. The highest variability in performance was related to the fluctuations in organic nitrogen content of the wastewater and thus the TKN removal efficiency fluctuated with 40% (Table 1). Additionally, a full overview of influent characteristics is also shown in Table 2. The sulfur balance was performed over both primary systems and showed an average removal of total sulfur of $30 \pm 7\%$ and $20 \pm 11\%$ for East and West systems respectively (Table 1). This included a $37 \pm 7\%$ and $32 \pm 4\%$ of SO_4^{2-}-S removal efficiency or $5 \pm 3\%$ mg SO_4^{2-}-S/L and $4 \pm 4\%$ mg SO_4^{2-}-S/L removal over the East and West primary system, respectively. The sulfur influent characterization was similar for both systems: 0.05 ± 0.01 g total S/g total COD and 0.47 ± 0.13 g SO_4-S/g Total Sulfur for the East system and 0.04 ± 0.01 g total S/g total COD and 0.33 ± 0.06 g SO_4-S/g Total Sulfur for the West system.

Table 1. Operational conditions and Removal efficiencies for total suspended solids (TSS), total COD, total Kjeldahl nitrogen (TKN), ammonium (NH4+), total phosphorous (Total P), total sulfur (Total S) and Sulfate (SO42-) over the EAST and WEST CEPT system at Blue Plains AWWTP over a period from 05/31/2017 to 08/20/2018.

		EAST	WEST
Clarifier rates			
Surface Overflow Rate	*m/d*	8.4 ± 0.6	9.2 ± 0.9
Surface Loading Rate	*Kg/m²/d*	2.4 ± 0.4	5.9 ± 2.1
pH		7.2 ± 0.4	7.3 ± 0.5
Clarifier performance			
HRT	*h*	3.8 ± 0.3	3.1 ± 0.2
TSS	*%*	70 ± 6	63 ± 8
Total COD	*%*	75 ± 8	72 ± 9
TKN	*%*	46 ± 11	37 ± 9
NH_4^+-N	*%*	23 ± 6	21 ± 11
Total P	*%*	59 ± 7	48 ± 5
Total Sulfur	*%*	30 ± 7	20 ± 11
SO_4^{2-}	*%*	37 ± 7	32 ± 4
Primary effluent			
TSS	*mgTSS/L*	64 ± 23	96 ± 37
Total COD	*mgCOD/L*	211 ± 56	207 ± 55
TKN	*mgN/L*	28 ± 5	35 ± 10
Total P	*mgP/L*	2.2 ± 1.9	2.6 ± 0.9
Total Sulfur	*mgS/L*	16 ± 8	23 ± 4
SO_4^{2-}-S	*mgS/L*	6.3 ± 1.3	7.9 ± 2.7

Table 2. Primary influent and gravity thickening overflow (GTO) concentration for COD, Suspended solids (SS), Nitrogen (N), Phosphorus (P) and Sulfur including total, particulate, and soluble fractions over east and west CEPT over a period from 05/31/2017 to 08/20/2018.

Raw Influent characterization				
		East	West	GTO
Solids				
TSS	mgTSS/L	230 ± 44	233 ± 72	2990 ± 843
VSS	mgVSS/L	168 ± 21	193 ± 43	2467 ± 956
Sulfur				
Total Sulfur	mgS/L	21 ± 6	29 ± 3	33 ± 11
Soluble Sulfur	mgS/L	15 ± 5	17 ± 5	27 ± 9
Sulfate	mgS/L	9 ± 3	10 ± 43	11 ± 7
COD				
Total COD	mgCOD/L	440 ± 102	475 ± 142	4726 ± 1300
Particulate COD	mgCOD/L	300 ± 176	359 ± 124	2110 ± 652
Soluble COD	mgCOD/L	74 ± 30	83 ± 35	553 ± 321
Nitrogen				
TKN	mgN/L	52 ± 33	52 ± 17	108 ± 51
Soluble TKN	mgN/L	33 ± 8	28 ± 9	39 ± 21
Ammonia	mgN/L	24 ± 6	23 ± 10	22 ± 13
Phosphorus				
Total P	mgP/L	4 ± 1	4 ± 1	7 ± 3
Particulate P	mgP/L	3 ± 3	2 ± 1	5 ± 3
Soluble P	mgP/L	2 ± 1	2 ± 2	4 ± 2

3.3.2   VSCs emission rates and odor impact

Off-gas testing was performed from May 2017 to August 2018 except in November 2017 and December 2017, and thus covered the different seasonal changes in temperature and wastewater characteristics. DMS and DMDS concentrations in the off gas were under the detection limit (< 0.5 ppbv) most of the time and under the odor threshold (MM< 3 ppbv, DMDS< 2.2 ppbv). Therefore, the study focused on the degree of H_2S and MM emissions (Figure 2). During the summer months, H_2S and MM emission rate were higher than in winter months. H2S emission rates were higher than MM emission rates. Only during the summer of 2018, MM emissions were in a similar range than H_2S emission rates (Figure 2 A&B). No clear difference

in emission rates was observed between East and West systems. The increased H2S peak during January 2018 on the West side was most probably attributed to the increase of blanket height (see Figure 3) or the result of a delivery of septic wastewater. At normal operational conditions, sludge blanket height was fluctuating between 0.1 and 0.3 meters (see Figure 3). Under normal conditions, only West H2S emission was well correlated with the sludge blanket height (correlation factor = 0.8).
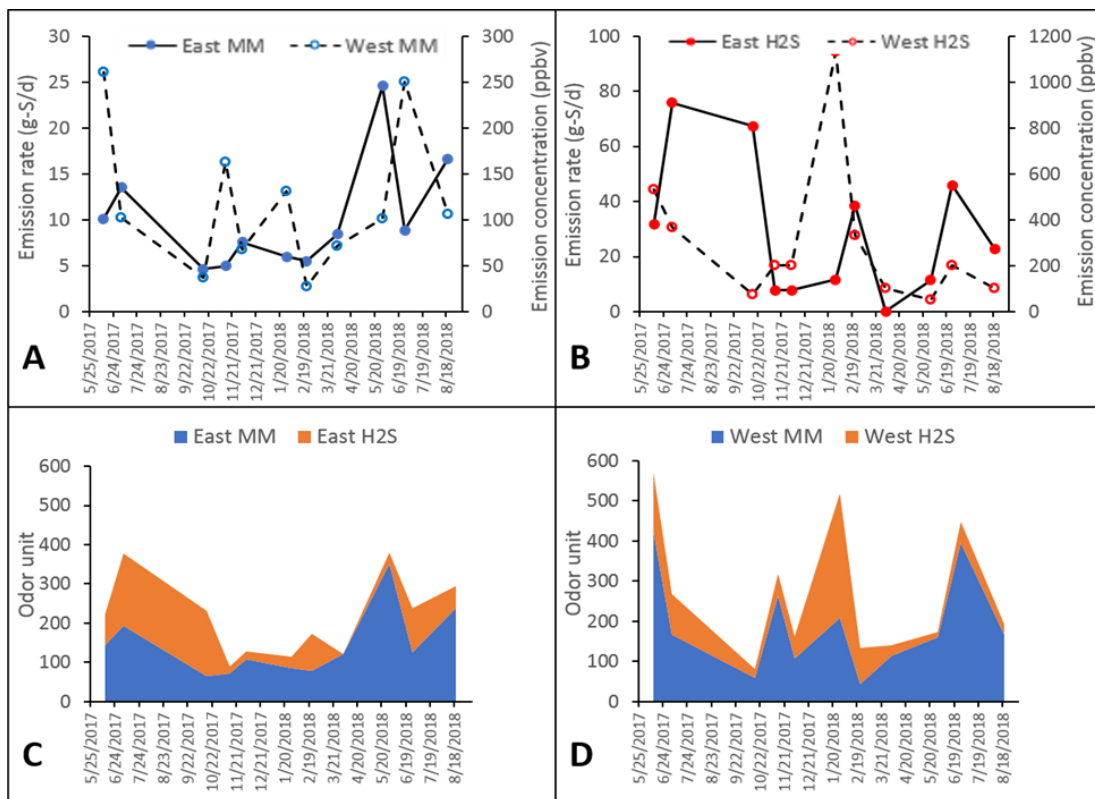
Figure 2. MM (A) and H2S (B) emissions as measured by the applied flux chamber on the EAST and WEST CEPT systems at Blue Plains AWWTP, and their contribution to the odor impact based on the ratio of emission concentration with their odor threshold (C: EAST; D: WEST).
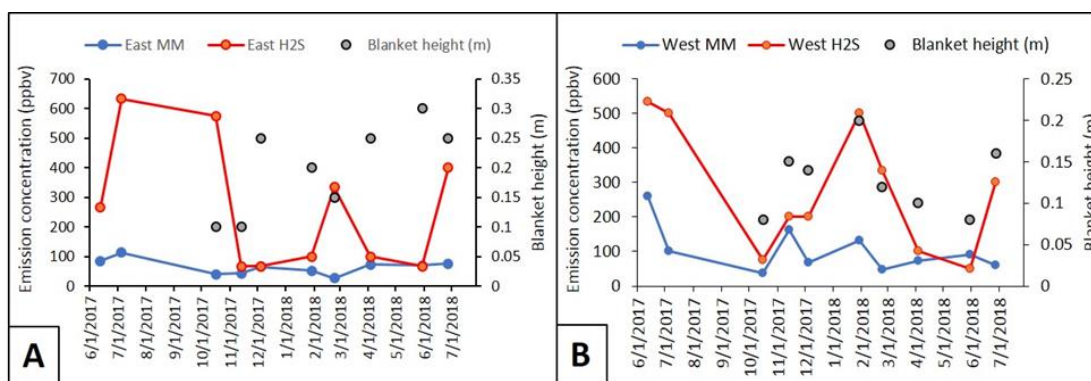
Figure 3. East (A) and west (B) emissions as measured by the applied flux chamber in relation to primary sludge blanket height. Primary sludge data were collected from October 2017 to August 2018 when VSCs emission were measured.

To elucidate the impact and importance of MM emissions over primary clarifiers, an odor unit defined as the ratio of odor concentration by the odor threshold was calculated for MM and H_2S for each sampling date. Fig. 2 C&D show that MM emission contributed $85 \pm 20\%$ and $89 \pm 24\%$ in VSCs for the East and West system respectively. In contrast, the MM emission only contributed $28 \pm 19\%$ and $30 \pm 21\%$ in mass basis for the East and West system, respectively.

3.3.3 Stripping versus production in primary systems

To separate the impact of the sewer system versus the primary system as a source for the observed MM and H_2S emission, soluble H_2S and MM concentration were measured in July 2017 in the primary influent, primary effluent and the primary sludge (see Table 3). When assuming that all soluble H_2S and MM in the primary influent was emitted to the atmosphere and thus captured within the off-gas measurements, the maximum stripping of VCSs was 64 % of the total observed emission for H_2S and 16% of the total MM emission (Figure 4). Thus, while the H_2S emission was more dependent on the levels produced in the sewer system, a

18

significant production of both H₂S and MM took place in the primary systems itself. This observation was correlated well with the high soluble H₂S and MM levels in the primary sludge samples (Table 3).

Table 3. Dissolved concentration for H2S and MM in West primary influent, effluent and sludge (PS) for 07/05/2017.

		Primary influent	Primary effluent	Primary sludge
H_2S	µg S/L	0.043	0.021	0.129
MM	µg S/L	0.085	0.071	0.601
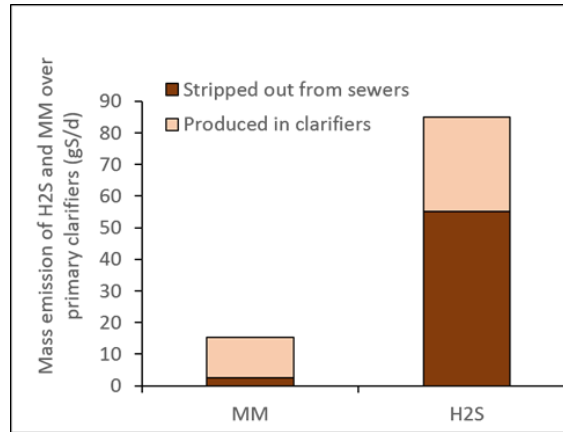
Figure 4. Mass emission of MM and H2S over primary clarifier showing impact of sewers and production within the clarifier on 07/05/2017

3.3.4 Temperature impacts on odor production

Microbial processes are impacted significantly by temperature changes and follow an Arrhenius model type of temperature dependency. To assess how MM and H₂S emission rates were correlated with temperature, an Arrhenius model was fitted using full-scale data in relation to influent wastewater temperature (Figure 5). Due to the large variability in emission rates, especially during the summer period (22-25 °C), the proposed Arrhenius model could not significantly explain the data (p values >

0.01; Figure 3) and was not valid. Looking into the summer data for 2017 and water temperature between 22-25 °C, there was a 75% probability to get a H_2S emission higher than 45 g S/d (or 383 ppbv) and 66% probability to get a MM emission lower than 25 g S/d (or 212 ppbv) (Figure 5). The exact opposite was true for the summer of 2018. This indicated that temperature was not the only determining factor and thus wastewater composition and operational conditions in the primary treatment systems played an important role in the observed odor emission rates.
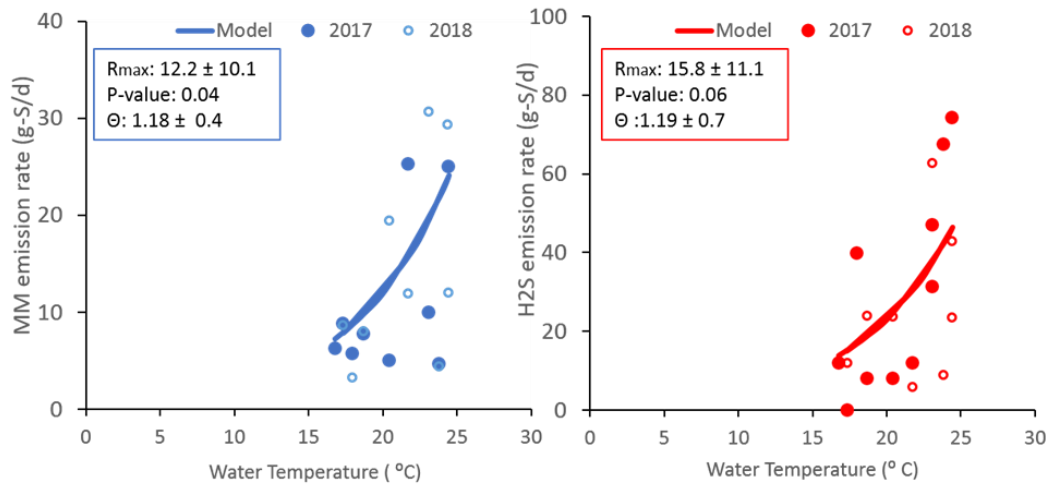
Figure 5. Impact of temperature on the formation and emission of MM and H2S in primary system at Blue Plains, including Arrhenius model fit

3.3.5   Active biomass seeding impact on odor production

As the retention time was only a few hours, microbial production of H_2S and MM was dependent on the amount of active biomass available in the primary influent. The quantification of active biomass concentration was based on the conventional method for ordinary heterotrophic organisms (OHOs) and showed a

linear correlation with the observed emission rates for both MM and H$_2$S (Figure 6A).

The correlation was stronger for MM (R^2 of 0.86) as MM emission was mostly the

result of microbial production in the primary systems, while H$_2$S depended partly on

H$_2$S stripping originating from the sewer system (Figure 6A). Moreover, OHOs

concentration showed a linear correlation with water temperature (R^2 of 0.84) (Figure

6C).

During the summer of 2018, despite similar temperatures than 2017,

decreased H$_2$S emission rates took place which indicated decreased formation of H$_2$S

in the sewer (decreasing stripping of H$_2$S) and decreased production in the primary

systems indicating decreased seeding of SRBs. This might have been caused by

heavy rain storm during summer of 2018 (8 events with rain > 50 mm, during May to

August). This was combined with an overall wet summer period (18 mm overall rain

fall in summer 2018 versus 11 mm in summer 2017) which might have slowed down

the formation of biofilms in the sewer system (Figure 6B). The impact on MM

emission was not as severe as H$_2$S emission rates.
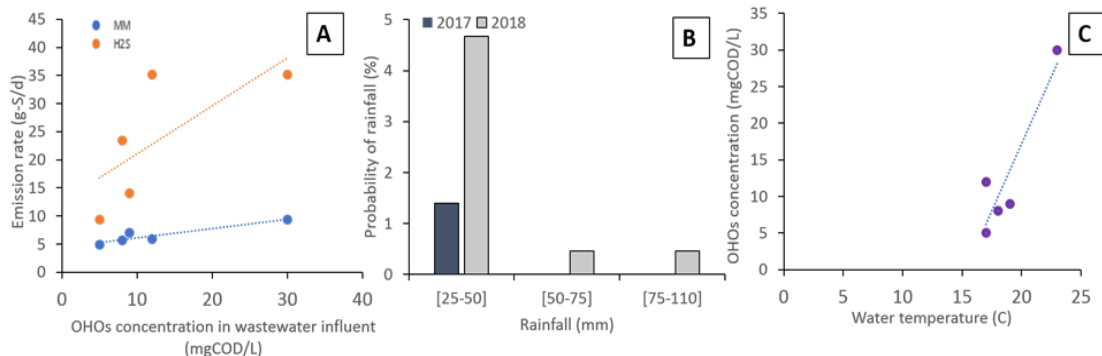
Figure 6. A: Relation between influent OHOs concentration and odor emissions presented as concentration in the flux chamber; B: Probability of rainfall > 25 mm in the Washington D.C area for 2017 and 2018; C: Relation between influent OHOs concentration and wastewater temperature

3.3.6 Substrate availability for odor production

Substrate levels are another important factor determining the odor production. Sulfate and sCOD levels were varied during batch experiments by the use of different wastewater streams (Table 4). Only when SO_4^{2-}-S levels were below 10 mg SO_4^{2-}-S /L, a clear relationship between H_2S and SO_4^{2-}-S concentration was observed (see test 3, Table 4, Fig 7A). In most other tests, the degree of H_2S emission was driven by sCOD concentrations when lower than 124 mg sCOD/L (test 2, test 4, Table 4, Fig 7A). The largest difference in emission rate was observed between tests, despite similar substrate levels indicating that the amount of active SRBs in the wastewater might be the main driver for H_2S emission. This was also observed in full scale sampling, where the correlation matrix shown in Figure 9 indicated low correlation coefficients between H_2S and influent sulfate (correlation factor: 0.3). Despite similar sulfate concentration in the primary effluent, large differences in H_2S emission was recorded. This could be explained by the impact of the fluctuating active SRBs seeding and the change in primary sludge blanket height between each sampling date.

Table 4. Mix liquor chemical measurements from of batch testing including primary sludge mixed with final effluent (S+FE), sludge mixed with influent (S+I), and sludge mixed with Influent and GTO (S+I+GTO).

		Test 1		Test 2		Test 3			Test 4		
	Unit	S + I	S + I+ GTO	S + FE	S + I	S + FE	S + I	S + I+ GTO	S + FE	S + I	S + I+ GTO
Date		06/07/18		06/12/18		06/19/18			06/26/18		
tCOD	mgCOD/L	3297	4075	4665	4160	6490	7092	8037	5020	3377	4125
pCOD	mgCOD/L	2902	3572	4502.5	3954.5	3651.5	6821	7736.5	4910	3217	3958
sCOD	mgCOD/L	149	146	102.6	149.5	178	211	231	115	124	153
VSS	mgVSS/L	1832	1862	2185	2135	4490	3910	5340	3485	2090	2530
NH3	mgN/L	16.95	16.85	11.2	23.7	14.8	24.8	25.6	13	23	22.8
OP	mgP/L	1.8	1.2	0.9	1.3	1.4	0.8	1.2	12	1.2	1.3
sTKN	mgN/L	32.2	32.7	25	29.5	20.2	27.1	19.4	1.2	33	40.8
sOrgS	Mg-S/L	11.4	11.5	9.8	12.5	13.2	12.2	8.9	10.5	11.4	16.4.9
SO_4^{2-}	mg-S/L	14	13.7	10.5	10	7.7	3.6	11	8.5	9.5	.1
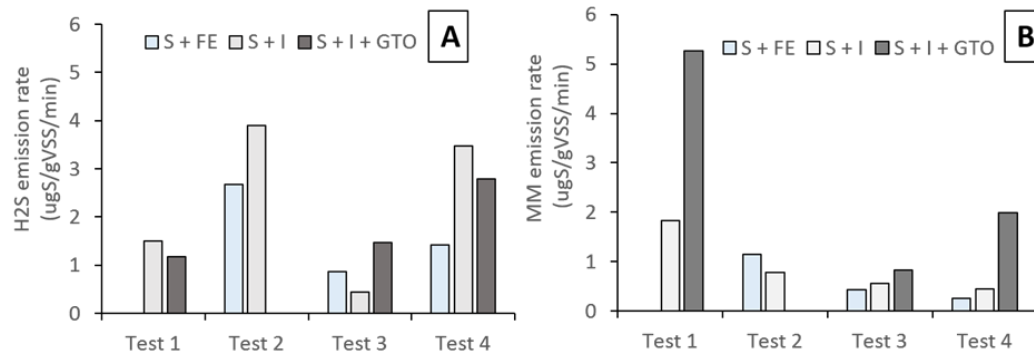
Figure 7. (A) H2S and (B) MM emission rate for Sludge mixed with final effluent (S+FE), sludge mixed with influent (S+I), and sludge mixed with Influent and GTO (S+I+GTO)Due to lack of easy methionine measurements, soluble TKN

(sTKN) and soluble organic sulfur (sOrgS) were used as indicators for substrate availability for MM production. A slight trend was observed between sTKN levels and MM production (Table 4, Figure 7B). However, the tests with gravity thickener overflow (GTO) addition showed sharp increases in MM production despite the minor changes in sTKN and sOrgS concentrations (Test 1,3,4, Table 4, Figure 7B). Fermentation products present in the gravity thickener might have resulted in a better substrate source for MM production. Low concentration of sOrgS (< 9 mg S/L) seemed too low to allow for increased MM production when GTO was added in test 3 in comparison to test 1 and 4 (Table 4). Overall trends between tests did show increased MM production when sTKN levels were above 30 mg N/L (test 1 versus test 2 and3, Table 4, Figure 7B). This might indicate, unlike H_2S production, a more determined impact of substrate limitation on MM production rather than biomass seeding limitation. Furthermore, at full scale, MM emission seemed to be more driven by influent substrate content for most sampling dates. A correlation was found between MM emission with influent sTKN and sOrgS content (Correlation factor: 0.6). Additionally, for most sampling dates, MM emission seemed to follow s.Org.S and sTKN patterns.

3.3.7   Impact of sludge blanket height on odor production

The impact of sludge blanket height on MM and H_2S emission rates was investigated on July 1st, 2017, June 27th, 2018 and July 5th, 2018 (Figure 8). Results have shown a strong linear correlation between sludge blanket height and emission. Correlations were stronger for 2017 (R^2: 0.8 for H_2S; R^2: 0.9 for MM)) which correlated with increased emission rates (Figure 1) and potentially increased active biomass seeding

24

(Figure 8A). For 2018 data points, decreased levels of emission were observed, with a

weaker linear correlation (R^2: 0.3 for H_2S).
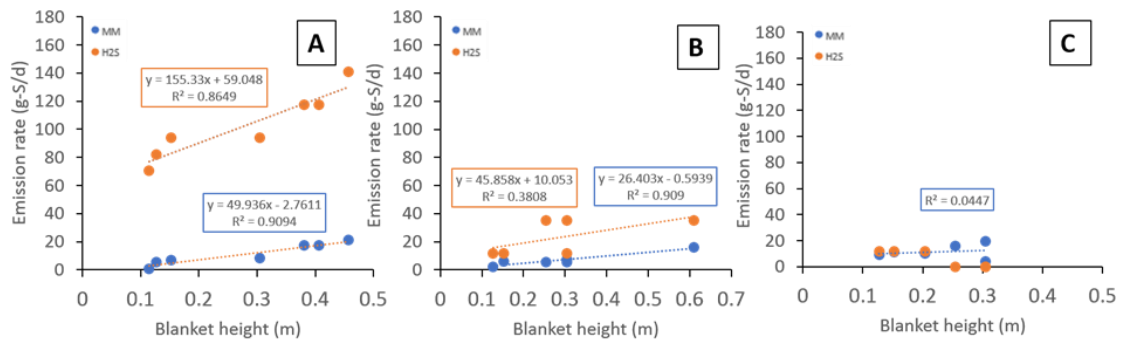
Figure 8. MM and H₂S gas phase concentration in primary settling tank in relation to sludge blanket height for 07/01/2017 (A), 06/27/2018 (B), 07/05/2018 (C).
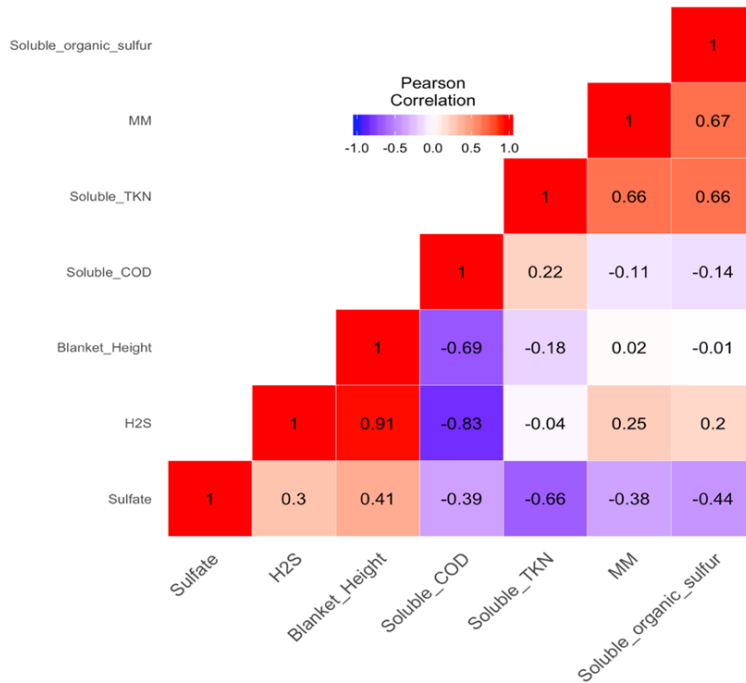
Figure 9. Correlation matrix between H₂S and MM emission in relation to influent characteristics and sludge blanket height

3.4   Discussion

A large variety of studies have quantified VSCs emission in sewers, while only few have investigated VSCs emission from primary treatment (Calvo et al., 2018, Easter et al., 2005, Hvitved-Jacobsen et al., 1998, Jeon et al., 2009, Paing et al., 2003, Sekyiamah et al., 2008). While in sewers, H_2S was the dominant VSC generated and MM levels were low (Hvitved-Jacobsen et al., 1998, Sun et al., 2015) , this study showed the importance of MM emission in primary systems. The observed impact of sewer conditions, and mechanisms for MM and H_2S production within primary settling tanks are discussed in the subsequent sections.

3.4.1   Mechanism of H2S emission in primaries

To develop better odor control initiatives, it is essential to understand the mechanism of H_2S emission. Our data showed that H_2S emission from primary clarifiers mainly originated from the stripping of the dissolved sulfide formed in the sewers. The second source of H_2S emission was through sulfate reduction within the clarifier which was principally favorized by the seeding of active SRBs over substrate availability.

In the sewers, the sulfur cycle has been well studied (Park et al., 2014, Sharma et al., 2008, Sun et al., 2015, Zhang et al., 2008). These studies have reported that the sulfide formed in the sewers would either be oxidized under aerobic conditions, react with metals to form insoluble complexes, or released to the sewer atmosphere while a significant fraction would diffuse towards water phase. The dissolved sulfide formed in sewer would then be stripped out downstream confirming the impact of sewers on the H_2S emitted in the primaries. Given the measured 64% contribution of sewer H_2S

stripping compared to measured H_2S emission in the primary system, this would imply that lowering sulfide formation in the sewers could reduce H_2S stripping in the primaries. In addition to stripping of formed H_2S from the sewer system, formation of H2S was mainly driven by active biomass seeding (Figure 6A) rather than sulfate levels. Our data showed the relation between H_2S and SO_4^{2-} was more pronounced when SO_4^{2-}-S /L levels were below 10 mg SO_4^{2-}-S /L (Figure 7A or Table 4). This could be explained by the fact that SO_4^{2-}-S affinity constant was higher than the actual SO_4^{2-}-S concentration in these cases, thus the growth rate of SRBs would depend on the SO_4^{2-}-S concentration (Barker and Dold, 1997). Several studies have reported sulfate affinity constant ranging from 1.15 SO_4^{2-}-S /L to 64 SO_4^{2-}-S /L (Ingvorsen, 1984, Roychoudhury and McCormick, 2006), with 10 mg SO_4^{2-}-S /L being in this reported range.

During intense and continuous raining events, the rapid flushing of active biomass, sediment and biofilm in the sewer system decreased the production of H_2S in the sewer and primaries over the whole summer season. The heavy rain potentially removed biofilm and sediment from the sewer creating a lag in H_2S production despite the higher temperatures. Management of biofilms in the sewer, and thus controlling both production of H_2S (stripping source) and seeding of SRB (production source) could therefore allow for minimization of H_2S emission in primary settling tanks.

Several studies have successfully minimized H_2S emission in the sewers (Camarillo et al., 2013). Chemical options include nitrates, chlorine, metal salts, hydrogen peroxide, and potassium permanganate (Zhang et al., 2008). Additionally, other

biological treatment could be used for H_2S removal (Easter et al., 2005). To control both stripping and production of H_2S in primary settling tanks, methods such as free nitrous acid (FNA) treatments to remove biofilm in sewers has shown to be successful in creating extensive lags in H_2S production (Jiang et al., 2013). This type of approach would control both stripping and production in both sewers and primary settling tanks.

Production of H_2S in primary clarifiers was managed by sludge blanket heights, controlling anaerobic conditions present in the system needed to drive sulfate reduction. The high H_2S emission observed in sludge sample confirmed the generation of H_2S in the sludge blanket. Low oxidation reduction potential conditions in sludge blanket favorized the activity of SRBs. Our data has shown about 40% of total H_2S emission originating from the primary sludge. Previous studies have shown that H_2S was produced in wastewater sludge (Devai and DeLaune, 1999, Rosenfeld and Suffet, 2004). Sekyiamah et al., (2008) have reported the difference of dissolved sulfide concentration between the top and bottom of the secondary sedimentation basin (98 ppb versus 0.73 ppb), indicating the activity of SRBs in the activated sludge blankets at the bottom of the sedimentation basin. Similarly, dissolved H_2S levels were higher in the primary sludge sample compared to influent or effluent samples (Table 3). Similar results were observed in our primary full-scale data where a positive linear correlation was observed between sludge blanket height and H_2S emission. Thus, operating at minimal sludge blanket could lower H_2S emission from the clarifiers independent of SRB seeding from the sewer system.

3.4.2 Mechanism of MM emission in primaries

In contrast to H_2S, MM emission in primaries was driven by the conditions in primary clarifier (84% of emission attributed to production) rather than the stripping of MM formed in the sewers. Furthermore, substrate content in primary influent seemed to impact MM emission more than in the case of H_2S potentially due to the fact that a more diverse group of microorganisms are capable of MM generation (Kadota and Ishida, 1972, KIENEt and Visscher, 1987, Segal and Starkey, 1969). One of the major issues in assessing the mechanisms of MM formation is the difficulty to directly measure methionine and cysteine in wastewater. The degradation of methionine and the cysteine have been identified to be the main pathways for MM formation in anaerobic digestion (Chen et al., 2005, Du and Parker, 2012, Higgins et al., 2006). Romero-Flores et al.,(2016) have confirmed the same for activated sludge process and showed that no methylation or oxidation to DMS and DMDS occurred. Methanogens and SRBs were found to be responsible for MM degradation (Sun et al., 2015) and this might explain the low MM emission in sewer system. Methane emissions in sewer systems have been quantified to range from 19 Kg CH4/d to 25 Kg CH4/d) ((Liu et al., 2015). Short SRT (in matter of hours) in the primary systems would not allow methanogens growth on MM which would explain higher release of MM in primaries.

Additionally, MM emission was significantly higher when the GTO was added to the sludge samples. This indicated that the partial breakdown of organic matter by fermentation in gravity thickeners would result in the formation of volatile fatty acids which could be predominant carbon source for MM producers

(Glindemann et al., 2006, KIENEt and Visscher, 1987). It was reported that methionine degraders were anaerobic fermentative organisms (KIENEt and Visscher, 1987), so the other explanation of GTO impact could be related to biomass seeding. In reviewing the literature, we have found a variety of anaerobic bacteria including Pseudomonas, Achromobacter, or Flavobacterium capable of sulfur containing amino acids degradation resulting in organic sulfur formation (Kadota and Ishida, 1972, Lomans et al., 2002, Segal and Starkey, 1969). No clear distinction was found between MM producers and SRBs. Our data have shown a strong linear relationship OHOs and MM emission (R^2: 0.9). Thus, for facility operations, OHOs estimation through the conventional OUR based method could be good indication of MM producers content in influent wastewater.

Although MM emission in the sewer system was minimal (Sun et al., 2015), MM producing organisms seeded from the sewer as well as protein degradation products originating from hydrolysis and fermentation reactions in the sewer will drive MM production in primary systems based on the results of this system. So, to prevent MM emission in primary system, odor control mechanisms that decrease biofilm growth and overall microbial reactions in the sewer, and thus apply toxicity-based mechanisms will result in lower MM emissions. To minimize MM emission in primary systems, increased frequency of free nitrous acids treatments (Jiang et al., 2013) in sewer systems might be needed to manage faster fermentation reactions rather than just sulfate reduction. To minimize MM production in primary systems, management of sludge blankets will be essential, similar to H_2S production. This study suggested a need for close collaboration between sewer odor management and

facility odor management as even when production is separated the interaction between sewer and facility can not be ignored.

3.4 Conclusion

In conclusion, this study reveals the mechanisms of H_2S and MM emissions in wastewater primary systems. While H_2S and MM were the dominant VSCs measured, their mechanisms of formation were quite different. H2S emission in primaries was mainly the results of the stripping of dissolved sulfur generated in the sewers. MM emission was more dependent on the conditions in the primary clarifiers driving the production of MM. The reduction of H_2S levels in the sewers would decrease emission in the primaries. However, for both H_2S and MM most prevention of odor emission in primary systems can be achieved to managing biofilms and microbial reactions in the sewer system. The latter would directly control biomass seeding to the primary systems and decrease production rates substantially. As MM production can be done by a more diverse group and potentially faster growing organism, management of primary sludge blanket will remain essential for minimization of both H_2S and MM emission.

3.5 Acknowledgement

Chapter 3   Characterization and mitigation initiatives of odors emission from secondary activated sludge systems

Abstract

The purpose of this study was to quantify and investigate on the source of volatile sulfur compounds (VSCs) associated with secondary activated sludge systems. Floating flux chamber was used to capture and monitor VSCs emission in secondary bioreactor on top of mix liquor at the Blue Plains Advanced Wastewater Treatment Plant. The main VSCs identified in activated sludge were MM, DMS, DMDS and H_2S. MM emission was consistently dominant ranging from 5 to 175 kg S/d and from 2 to 27 kg S/d for west and east reactors respectively.MM emission accounted to 90 % of total VSCs emission. Most emission occurred in the first and second pass.

Our study has shown that MM emitted in secondary reactors was 2 to 3 order of magnitude higher than dissolved MM in primary effluent, revealing that the production of both MM took place in the activated sludge process itself, and the stripping of MM from the feed was very minimal. A similar observation was found for H_2S. Furthermore, data showed that the depth of secondary sludge blanket plays an important role on the extent of MM emission. At high sludge blanket height, high MM emission was observed. It was concluded that low ORP conditions in sludge blanket, selector zones and RAS was the major source of VSCs. The latter explained the spike of VSCs emission when aeration was initiated. kinetics tests were performed to elucidate the kinetic parameters of methionine degradation to MM

through methionine spikes in batch experiments under fully anaerobic conditions. Results show a maximum MM production of 50 ug S/g VSS/d and half saturation coefficient of 0.5 mg methionine/L. Further tests are needed to confirm these results and to understand the kinetics of this mechanism more into detail in relation to microbial composition of sludge samples. Increasing ORP could decrease odor emissions by targeting the zones where MM is emitted. This could be achieved by addition of nitrate in secondary settling tanks.

Keywords: Methyl Mercaptan, hydrogen sulfide, activated sludge

3.1   Introduction

Odors from wastewater treatment plants (WWTPs) have become a significant source of environmental annoyance. Public complaints from communities surrounding WWTPs have increased in the past years (Choi et al., 2012, Kim et al., 2014). In the wastewater treatment process, each unit can be a potential source of volatile sulfur compounds (VSCs) formation (Lebrero et al., 2011, Sekyiamah et al., 2008).

VSCs were found to be the main odorous compounds formed in sewers and sludge processing units. Among VSCs, hydrogen sulfide (H_2S), methyl mercaptan (MM), dimethyl sulfide (DMS) and Dimethyl Disulfide (DMDS) were the main odorous compounds identified in these systems. These compounds are known to have the potential to pose human health hazards and significant nuisances with odor phenomena (Giri et al., 2014, Lebrero et al., 2011). VSCs are characterized by their extremely low odor threshold (MM: 0.07 ppbv; DMS: 3 ppbv, DMDS: 2.2 ppbv; H2S: 10 ppbv) (Catalan et al., 2009). VSCs interactions and pathways of formation

have been well studied in anaerobic digestion. These studies have shown that the production of MM mainly occurs via two pathways, a) biological degradation of the amino acid methionine and, b) the methylation of hydrogen sulfide (H_2S), the latter being formed from the degradation of cysteine and sulfate reduction. Additionally, DMS was formed through the methylation of MM and DMDS by MM oxidation (Chen et al., 2005, Higgins et al., 2006, Novak et al., 2002). Lastly, it has been found that the demethylation of DMS, DMDS and MM is done by methanogens communities in AD to produce H_2S (Chen et al., 2005, Higgins et al., 2006).

VSCs emission and control have been well investigated in sludge processing streams and sewers, however more studies are needed for activated sludge process. Due to its large surface area, secondary aeration basins are one of the main source of VSCs emission from WWTPs (Koe, 1985, Sekyiamah et al., 2008). Odor emission from activated sludge has become an important challenge for resource recovery facilities due to its high cost and off-gas treatment. For instance, Philadelphia's Northeast Water Pollution Control Plant had spent USD 2.5 million a year to abate odor emission on neighboring community (Cheng et al., 2005). Kim et al., (2014) has shown that VSCs were the main group of chemicals emitted from activated sludge process that relate to odor problems. In a survey for the patterns of odorous chemicals within a WWTP, Kim et al., (2002) found that carbon disulfide (CS_2), DMS, DMDS were more prevalent in samples collected from downstream processes, correlating with decreased oxidation-reduction potential (ORP) conditions. Later, Sekyiamah et.al. (2008) found that DMDS and DMS were the main compounds being emitted from activated sludge reactors. The study concluded that returned activated sludge

(RAS) was potentially the main source of these compounds, which were produced in the clarifiers where the sludge bed lead to anaerobic conditions. During an odor control master plan for Blue Plains Advanced Wastewater Treatment Plant (AWTP) (data not published, 2012), it was found that MM accounted for up to 96% of total reduced sulfur compounds. Furthermore, MM showed a strong correlation with olfactometry measurements. With the intensification of resource recovery in WWTPs, new technologies and processes are being developed and implemented to redirect carbon from secondary treatment to the solids stream to increase energy production potential. For instance, decreasing sludge retention time (SRT) in activated sludge, aims for carbon sorption in the aerobic tanks rather than oxidizing it. This system allows high loading rates and energy recovery is often maximized by capturing organics for anaerobic digestion and biogas production. This approach, however, challenges proper bio-flocculation, often requiring longer retention times in clarifiers (Van Winckel et al., 2019). Therefore, the potential for higher VSCs production in RAS increases due to longer periods under anaerobic conditions. On the other hand, in addition to being implemented as a carbon capture strategy, bio-augmentation of activated sludge is an already established cost-effective method for better flocculation, enhanced microbial community (Estrada et al., 2015, Limbergen et al., 1998), degradation of recalcitrant compounds and improved removal of suspended solids (Stephenson and Stephenson, 1992). Moreover, it has been implemented in full-scale operations with carbon removal processes to enhance nitrification of special interest (Leu and Stenstrom, 2010).

Although some studies have investigated VSCs emissions in secondary systems, only little is known on their kinetics of formation and inhibition. Additionally, most studies found in the literature were focused on odor analysis to quantify odorants concentrations in headspace of in the mixed liquor of bioreactors, while less consideration was given the source and pathways of VSCs formation in activated sludge process. Consequently, in this study, odor emission characteristics from full-scale secondary activated sludge after chemically enhanced primary treatment (CEPT) were studied under different operational conditions and VSCs kinetics were investigated using batch experiments. Furthermore, potential mitigation strategy through ORP control due to the presence of NOx obtained by nitrification in bio-augmented secondary activated sludge was studied.

3.2   Materials and Methods

3.2.1   Activated sludge reactors

Blue Plains AWWTP is one of the largest advanced sewage treatment plants in the world, treating over 1.1 million cubic meters of sewage per day and serving the District of Columbia and parts of Maryland and Virginia in the USA. Secondary treatment was composed of two different systems.

- The West system: a high-rate secondary treatment process for the removal of organic carbon and phosphorous. The system consists of two step feed reactors of similar size/dimensions. The West system was operated at a SRT between 1 and 2 days.

- The East system: a high-rate secondary treatment process for the removal of organic carbon and phosphorous. The system consists of a total of four reactors; two step feed of similar size/dimensions and two smaller reactors of similar size/dimensions. The East system is operated at a SRT between 1 and 2 days.

Air flows and operational data was collected from the process control system at Blue Plains. Most important operational conditions and influent characterizations are summarized in Table 5 for east and west systems. Sampling was conducted across west secondary reactor 1 and east secondary reactor 4. Sampling locations for both east and west systems in are shown in figure 10 in summer 2017. After gaining better understanding of the activated sludge process and VSCs emissions, the number of sampling points was reduced to key locations.

Table 5 Overview of the operational conditions and wastewater characterizations for primary effluent (PE), secondary effluent (SE) and waste activated sludge (WAS) at Blue Plains AWWTP over a period from 06/19/2017 to 08/20/2018.

|		East			West		
		PE	SE	Sludge	PE	SE	Sludge
Wastewater characterization							
Total S	mg S/L	15.9 ± 3.5	11.4 ± 2.1	49 ± 18	19.9 ± 2.8	10.8± 2.9	54 ± 21
SO$_4^{2-}$-S	mg S/L	9.5 ± 3.5	13.3 ± 5.5	9 ± 3	8.1 ± 3.5	12.2 ± 6.1	11 ± 5
Soluble S	mg S/L	10 ± 2	8 ± 4	14 ± 6	12 ± 3	9 ± 1	16 ± 7
Total COD	mg COD/L	200 ± 67	49 ± 13	6583 ± 2388	205 ± 41	57 ± 14	7146 ± 2467
Soluble COD	mg COD/L	59 ± 17	28 ± 9	106 ± 30	60 ± 17	34 ± 10	128 ± 68
Total P	mg P/L	2.1 ± 0.6	0.9 ± 0.8	57 ± 27	2.8 ± 1.3	0.5 ± 1.3	67 ± 31
TKN	mg N/L	38 ± 14	35 ± 4	204 ± 84	37 ± 6	34 ± 4	211 ± 91
TSS	mg TSS/L	83 ± 20	33 ± 5	5869 ± 1773	102 ± 26	27 ± 8	6189 ± 1083
Reactors conditions		West Reactor			East reactor		
SRT	day	1.5 ± 0.5			1.5 ± 0.5		
pH		7.2 ± 0.4			7.3 ± 0.5		
MLSS	mg TSS/L	2627 ± 632			2873 ± 801		
Inflow (*Qin*)	MGD	175 ± 46			117 ± 20		
RAS recycle	% Qin	30 % ± 5%			35 % ± 7%		
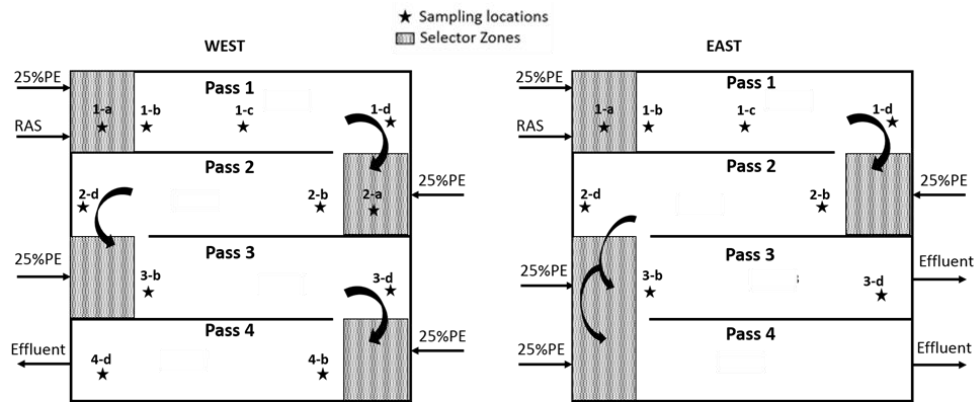
Figure 10 Schematic representation of full-scale reactor at Blue Plains AWTP characterized for VSCs emission

3.2.2 Sampling campaigns

Sampling campaigns were performed once a month from June 2017 to July 2018 except in August and September 2017. An AC'SCENT surface Emission Isolation Flux Chamber was used for gas phase sampling at the surface of reactors. A universal 44XR air sampling pump was used to pump the air out of the hood at a constant flow of 1.5 L/min. Air samples were collected into 1.4 L canisters coated with fused silica (Entech Instruments Inc., Simi Valley, CA, USA) for analysis of organic VSCs. Canisters were thoroughly cleaned prior to sampling. This ensured that the canisters were free from any volatile and semi-volatile compound. H_2S measurements were carried out using an electrochemical sensor (Odalog, Detection Instruments Co. Phoenix, Az., USA) with a range of 0.1 ppm to 20 ppm and an accuracy of 0.1 ppm. The sensor included a sampling pump with a flow rate controlled at 1.5 L/min. Calibration of the sensor was performed using an H_2S standard gas (Restek Corporation, Bellefonte, Pa., USA). The obtained concentrations were used to calculate emission rates based on method described in Catalan et al., (2009).

Additionally, wastewater influent, effluent and sludge were sampled to analyzed for total suspended solids (TSS) and volatile suspended solids (VSS) according to standard methods. Nitrogen species (NH_4^+-N, NO_3^--N), phosphorus (PO_4^--P) and chemical oxygen demand (COD) were measured using HACH vials [HACH GmbH] and analyzed according to standard methods (American Public Health Association, 1999). Sulfur in wastewater samples were analyzed using an inductively coupled plasma-atomic emission spectrometry (ICP-AES) following

method described in Dewil et al., (2006). Total Kjeldahl Nitrogen (TKN) were analyzed using EPA standard method.

3.2.3 Batch experiments

Batch testing were undertaken to investigate the effect of aeration and nitrate addition on the production of VSCs. Activated sludge samples were collected from the full-scale reactors of Blue Plains AWTP to measure the production potential of sulfur compounds in batch tests under different oxygen levels ranging from 0.5 to 1.5 L/min.

A 2 L Plexiglass jar was filled with 1.4 L of mixed liquor suspended solids (MLSS) and kept the remaining volume (0.6 L) as headspace. MLSS concentration was about 2700 mgTSS/L in all batch tests. To evaluate the effect of aeration, blend of pure nitrogen and air at different ratios was introduced into the reactor at a total flow of 1.5 L/min using a diffuser stone. Headspace samples were taken at regular intervals for 60 minutes with an evacuated 1.4 L canisters at an average flow rate of 1.5 L/min and analyzed by GC-MS as previously described. The same setup was used to study the effect of nitrate addition on VSCs emissions.

3.2.4 Headspace-Gas Chromatography-Mass Spectrometry

Analysis of canisters was performed within 24 hours of sampling using an Entech Model 7500 Autosampler followed by a Model 7200 Pre-concentrator coupled to an Agilent 5790N Gas Chromatographer-Mass Spectrometer (Agilent Technologies Inc., Wilmington, DE., USA). Sample canisters were placed in the autosampler and air samples of 10 to 500 mL were withdrawn for pre-concentration

using the following method: empty trap at -40 °C to remove most water vapor; VOCs

captured on Tenax trap at -40 °C and flushed with helium to remove remaining water;

Tenax trap heated to 10 °C; VOCs trapped on fused silica tube at -150°C; tube heated

at to 50 °C onto the GC-MS column. All gas transfer lines were coated with fused

silica and heated to 100 °C. Gas chromatography conditions were: Rtx1-MS Column

(60 m x 0.32 mm x 1.0 μm) (Restek Corporation, Bellefonte, Pa.); ultra high purity

He carrier gas at a constant flow 172 of 1.5 mL min-1; temperature program: 35 °C

hold 5 min; 10 °C min^{-1} to 130 °C; 20 °C min^{-1} to 220°C hold 5 min. Mass

spectrometer source was operated in electron impact mode with simultaneous total

ion chromatography and selected-ion monitoring. Temperature conditions were:

transfer line 240 °C and source at 230 °C. Target ions for selected-ion monitoring

were: carbonyl sulfide (60 m/z); methanethiol (48 m/z); ethanethiol (62 m/z);

dimethyl sulfide (62 m/z); carbon disulfide (76 m/z); propanethiol 178 (76 m/z);

buthanethiol (90 m/z); dimethyl disulfide (94 m/z); and trimethylamine (59 m/z). 1,4

dichlorobenzene (63 m/z) was used as an internal standard. Calibration of the GC-MS

was carried out using certified gas standards from Restek Corporation and Tech Air

Companies (While Plains, NY, USA): 5 ppm (± 5%) mixture of carbonyl sulfide,

methanethiol, ethanethiol, dimethyl sulfide, carbon disulfide, propanethiol and

buthanethiol; 5 ppm (± 2%) standard of dimethyl disulfide; 184 trimethylamine 5

ppm (± 5%); and 1ppm (± 5%) of TO-14 internal standard mixture including

bromochloromethane, 1,4 difluorobenzene, chorobenzene-d5 and 1,4

bromochlorobenzene. Standard gases were diluted into canisters to 250 ppbv and 25

ppbv as working standards using a 4600 dynamic dilutor (Entech Instruments Inc.,

Simi Valley, Ca) and ultra-high purity nitrogen as balance gas. Diluted standards were prepared every 6 weeks for calibration curves and were used for calibration check in every set of samples.

3.3   Results and discussion

3.3.1   Characterization of odors in secondary HRAS

3.3.1   Wastewater characterization

Wastewater characteristics for both east and west systems is presented in table 5. The total COD removal efficiency was about 71% ± 8% for both east and west systems. The average mix liquor concentration was 2627 ± 632 mg TSS/L and 2873 ± 801 mg TSS/L for west and east reactor respectively. The influent sulfate-S concentration was about 9.5 ± 3.5 mg SO_4^{2-}-S/L for east and 8.1 ± 3.5 mg SO_4^{2-}-S/L for west and increased to 13.3 ± 5.5 mg SO_4^{2-}-S/L and 12.2 ± 6.1 mg SO_4^{2-}-S/L respectively due to oxidation of dissolved sulfide concentration present in the influent and RAS.

The highest difference in performance between east and west was observed in sulfur balances. Total sulfur balance performed over both secondary systems has shown an average removal of total sulfur of 25% ± 8% and 44% ± 9% for East and West systems respectively (Table 5). The sulfur influent characterization slightly differed for both systems: 0.08 ± 0.03 g total S/g total COD and 0.6 ± 0.3 g SO4-S/g Total Sulfur for the East system and 0.09 ± 0.03 g total S/g total COD and 0.4 ± 0.2 g SO4-S/g Total Sulfur for the West system.

3.3.2 Source of VSCs in secondary activated sludge

Off-gas testing was performed from June 2017 to July 2018 except in August and September 2017.VSCs emission rates and concentrations from west reactor and east reactor are presented in Figure 11. Although high DMS concentrations ranging from 5 to 150 ppb were measured in summer 2017, for most sampling date both DMS and DMDS concentrations in the off gas were quite low and sometimes under the odor threshold (DMS< 3 ppbv, DMDS< 2.2 ppbv). It is important to note that prior studies have reported high DMDS emission in secondary treatment while MM was considerably low and sometimes below the detection limit. For instance, Sekyiamah et.al. (2008) studied VSCs emission profile in AS showing that DMDS and DMS were the main compounds being emitted and suggested the blanket depths in secondary clarifier as the main parameter causing these emissions. However, they employed an analytical method based on Solid Phase Micro Extraction (SPME) and GC-MS which converts MM, a key odorant, to DMDS and thus lacking the accuracy in VSCs measurements.

In our study, of the organic VSCs measured, MM emission was consistently 2 to 3 order of magnitude higher than DMS and DMDS, therefore the study was focused on the degree of MM emission. MM emission rates was ranging from 5 to 175 Kg S/d and from 2 to 27 Kg S/d for west reactor and east reactor respectively (Figure 11 A, B). H_2S emission concentrations were much lower than MM and sometimes below the detection limit. Kim et al., (2014) has shown that odors in secondary treatment system were mainly caused by organic sulfur compounds as MM rather than H_2S. Furthermore, organic sulfur compounds have been found to be the

main group of chemicals emitted from AS process that relate to odor problems rather

than H_2S (Kim et al., 2002).
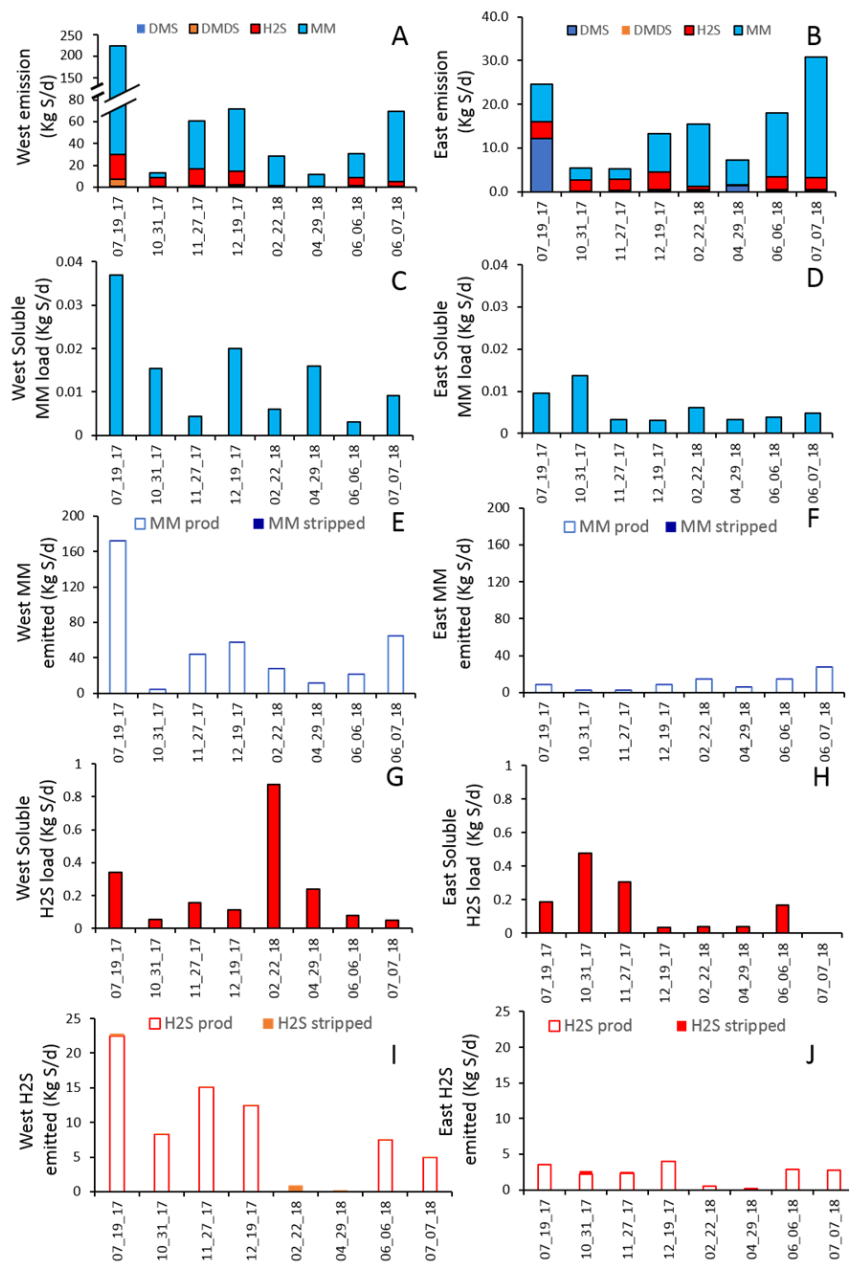

Figure 11 Mass emissions of VSCs from west and east reactors (A, B); Soluble MM loading into east and west secondary systems (C, D); MM mass emitted from east and west reactors (E, F). Soluble H2S loading into east and west secondary systems (E, F). Empty bars indicate most MM and H2S are formed with secondary system rather than being stripped out from Primary effluent (I, J).

The sulfur cycle has been well studied in sewers and anaerobic digestion revealing that H_2S was significantly generated in these systems rather organic sulfur (Chen et al., 2005, Park et al., 2014, Sharma et al., 2008). Later on , Sun et al., (2015) has shown that methanogens and SRBs were found to be responsible for MM degradation in anaerobic digestion. The formed MM was degraded by methanogens during digestion, with this degradation at higher rate (Higgins et al., 2006). MM would thus accumulate when methanogens are not fully functional. Shorter SRT in activated sludge systems would not allow methanogens growth on MM which would explain higher release of MM. The role of SRBs or methanogens in MM degradation is minimal in secondary treatment.

To separate the impact of the feed and activated sludge process itself and to elucidate if VSCs emission was originating from the stripping of dissolved sulfide in CEPT effluent, soluble VSCs loading into secondary systems was compared to the emitted VSCs to the atmosphere. Soluble MM and H_2S loading into west reactor and east reactor are presented in figure 12. Soluble MM loading was only ranging from 5 to 35 g S/d while MM emission rate was between 10 and 170 kg S/d for West secondary reactor (Figure 12 E & F). On the east side, soluble MM loading was ranging from 2 to 14 g S/d while MM emission rate was between 3 and 30 Kg S/d (Figure 12 C & D). A similar observation was found for H_2S where H_2S emission rates (Figure 12 I, J) was about 2 order of magnitude higher than soluble H_2S loading for both reactors (Figure 12 G &H). These results clearly explained that the production of both MM and H_2S took place in the AS process itself, and the stripping of MM and H_2S from the feed was very minimal.

Additional batch experiments were performed with sludge diluted either with final effluent (and thus minimal protein content) or primary effluent (proteins present) to elucidate if MM was formed from the sludge itself or from the wastewater matrix. Results have shown a high rate of MM production even in a matrix with minimal protein content (Figure 12). It was concluded that most MM production observed in the secondary sludge samples was originated from protein degradation from the microbial biomass in AS and not from influent protein.
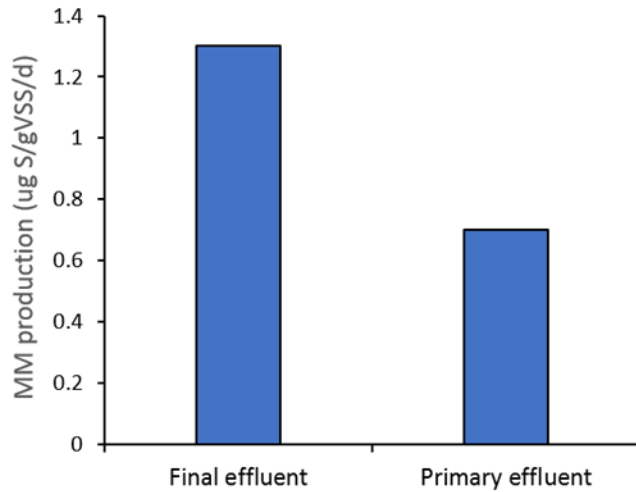
Figure 12 MM production under response of primary effluent and final effluent addition under anaerobic conditions

3.3.3 Impact of operational conditions VSCs emissions

MM emissions from all four passes of west and east reactor measured over sampling campaigns are shown in Figure 13. Our data showed that most emission was from pass 1 and 2, while emission from pass 3 and 4 was negligible (figure 13A, B). On average, pass 1 contributed to 80% of total MM emission from the reactors. Mean concentration in pass 1 was consistently the highest ranging from100 to 1700 ppb for west (figure 13C, D) and from 50 to 350 ppb for east (Figure 13E&F). For each

sampling campaign, there was a consistent trend of peak VSCs concentrations at the beginning of aeration after selector zones in pass 1 and 2. MM spike right after the selector zone was about three times higher for pass 1 than pass 2. The rise of MM emission was most likely caused by the fully anaerobic conditions developed in the selector zones. When the aeration is initiated, air bubbles from the diffusers provide sufficient interfacial surface between the liquid and the gas phases which resulted in significant stripping of VSCs from aeration basin. It was concluded that VSC emission were originated from accumulated VSCs in selector zone as well as from dissolved sulfide compounds present RAS.
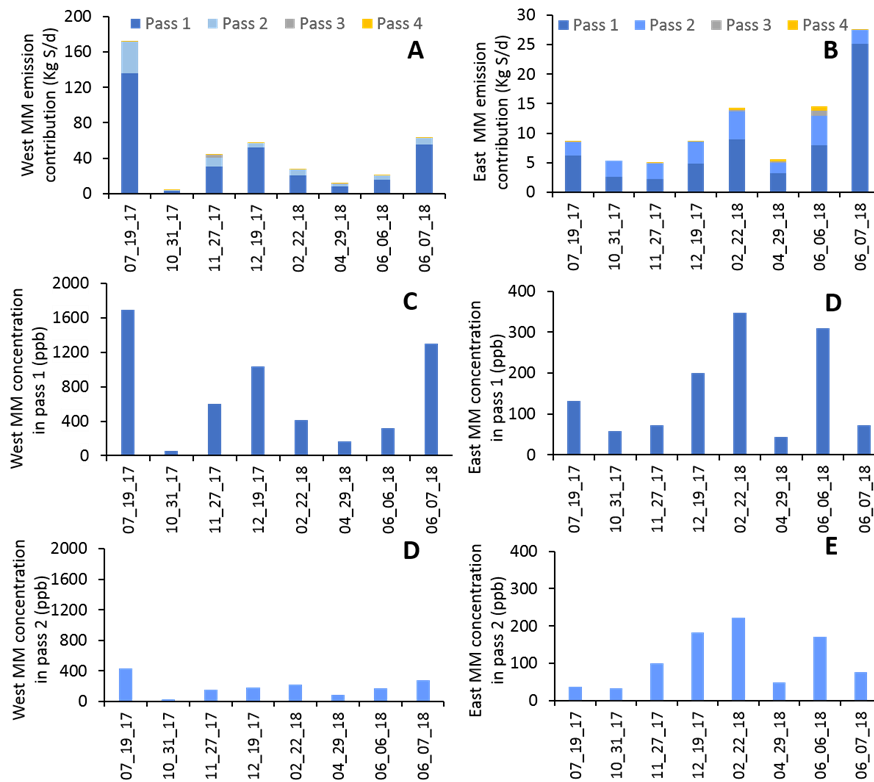

Figure 13 Mass emission of MM showing contribution from each pass for west and east (A, B); Mean emission concentration measured in floating flux chamber from pass 1 (C, D) and 2 (D, E)

Previous investigations have shown that the depth of sludge blanket in secondary settling basin have an impact on odor emission due to low ORP conditions. Sekyiamah et al., (2008) have reported the difference of dissolved sulfide concentration between the top and bottom of the secondary sedimentation basin (98 ppb versus 0.73 ppb), indicating the activity of SRBs in the activated sludge blankets at the bottom of the sedimentation basin. Kim et al., (2014) have shown that RAS recycle provides some reduced sulfur compounds to the aeration tank. In the same study, dissolved sulfide measured in RAS was three times higher than feed.

To elucidate the impact of sludge blanket height, the measured MM emission was compared to blanket height data obtained from PCS data. Results showed the extent of MM emission was influenced by secondary sludge blanket height. Figure 14 shows MM emission in pass 1 in relation to sludge blanket height. A linear correlation between sludge blanket height and MM emission (R^2: 0.65 for east; R^2: 0.5 for west) was determined. Additionally, a correlation matrix table was developed between MM emission and operation conditions. The highest correlation coefficient was found between MM emission in pass 1 and the blanket height depth (X: 0.81). No clear difference was observed between cold and hot weather, revealing that the impact of temperature was potentially disguised the change in sludge blanket height.

Effective odor control initiative should address foul air treatment from pass 1 where aeration is initiated. Some studies have found that ORP control could be a good option in minimizing odors in secondary treatment. The latter is further discussed in our study.
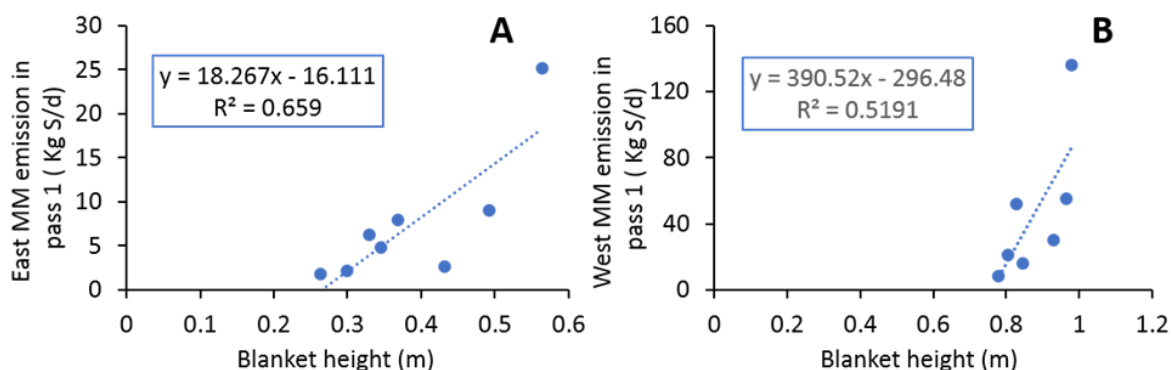
Figure 14 MM emission rate in east reactor (A), and west reactor (B) in relation to sludge blanket height at Blue Plains. Secondary sludge blanket data were collected from July 2017 to July 2018 when VSCs emission were measured

3.3.4   Kinetics of MM formation and inhibition

In accordance with the literature, the main organic sulfur compounds observed from activated sludge in batch testing were MM, DMS and DMDS. During batch testing, only MM was consistently produced at an average rate of 1.2 ± 0.3 ($\mu gS/(gVSS`\text{-}d)$) under anaerobic conditions. DMS was present in the initial sample and stripped out over the duration of the test. No DMS production was observed under the condition tested. This suggested that the mechanisms under which DMS is produced may require longer incubation times to convert MM to DMS (Du and Parker, 2012). Otherwise, low concentrations of DMSO may have been present in the plant influent and reduced to DMS (Glindemann et al., 2006, Kim et al., 2014).

To better examine the main mechanism of MM formation, H_2S and methionine was added to secondary mix liquor samples in the batch testing. Results on secondary sludge samples showed no increase in MM production when H_2S was added, indicating that the methylation of H_2S might not be significant in secondary systems (Figure 15A). Moreover, when methionine was spiked (1.5 mg/L) an increase

49

in MM was observed (Figure 15A). These results showed the potential importance of the `methionine degradation to MM` mechanism in secondary systems. In addition, kinetics tests were performed to elucidate the kinetic parameters of methionine degradation to MM through methionine spikes in batch experiments under fully anaerobic conditions. Results show a maximum MM production of 50 ug S/g VSS/d and half saturation coefficient of 0.5 mg methionine/L (Figure 15B). Further tests are needed to confirm these results and to understand the kinetics of this mechanism more into detail in relation to microbial composition of sludge samples.
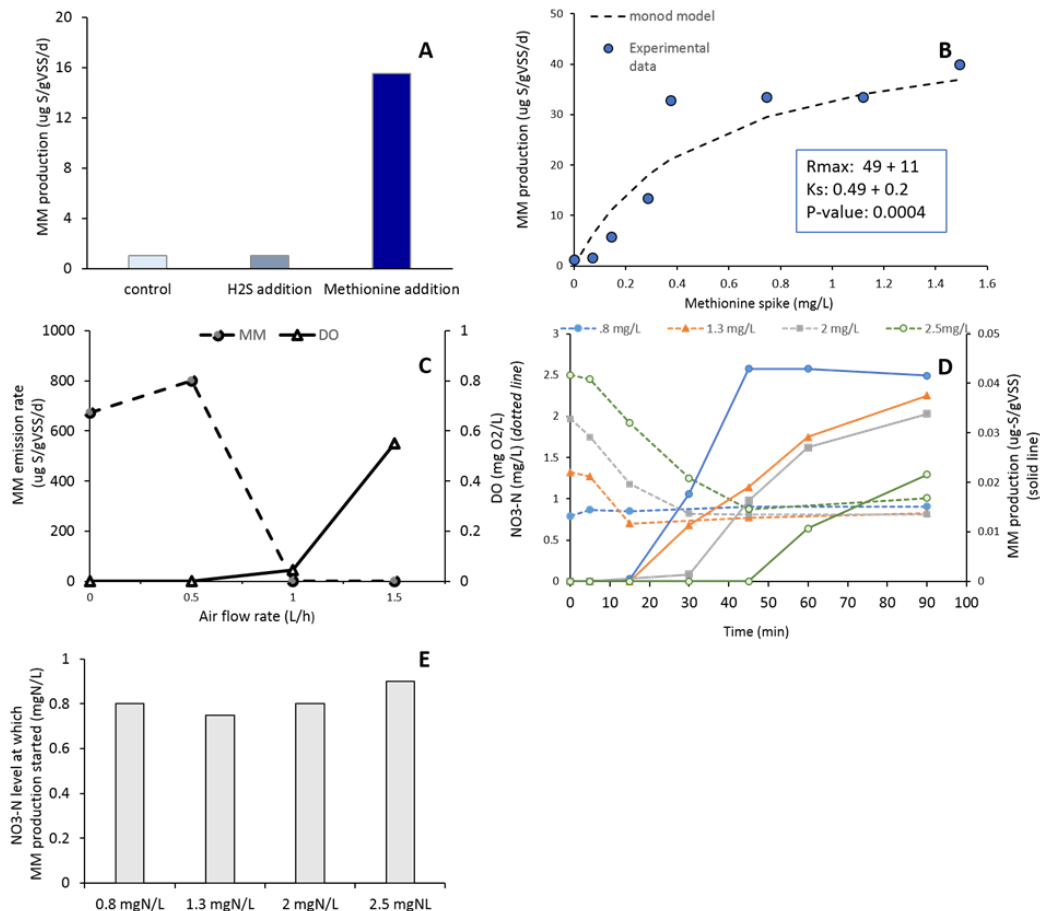

Figure 15 MM production under response of H2S and methionine addition at 1.5 mg/L under anaerobic conditions. No chemical was added in control sample (A), MM production kinetics in function of methionine concentration under anaerobic conditions (B);MM production response (round points, dotted line) to elevated DO levels (triangles) (C); MM production response (solid

lines) to nitrate levels (dotted line) (D); Minimum nitrate concentration at which MM was produced in batch testing (E).

Additionally, as suggested in previous studies (Kim et al., 2002, 2014), increased ORP decreases the potential of organic sulfur compounds production. In this respect, initial kinetic experiments were performed with secondary sludge to identify kinetic inhibition constants related to dissolved oxygen (DO) and nitrate (NO_3^-N) levels. MM production was inhibited at DO concentrations above 0 mg O_2/L (figure 15C). This suggested that increasing the oxygen reduction potential by increasing the DO concentration in the reactor resulted in the inhibition of MM formation. Furthermore, in order to assess if NOx may be responsible for decreasing the production of MM in sludge, a series of batch test were performed where nitrate was spiked at different concentrations ranging from 0.8 to 2.5 mgN/L and the concentrations of organic sulfur compounds were monitored (see figure 15D). It was found that increasing NO3-N concentrations increased the lag phase for MM detection when compared to the control and slightly decreased the rate of production. Additionally, our data have shown an apparent threshold of approximately 1 mg/L of NO3-N for MM inhibition in all batch tests. It appeared that maintaining a concentration above 1 mg/L of NO3-N in the secondary systems could potentially inhibit the production of MM.

In both cases MM production was minimized at measurable DO (Figure 15C) and when nitrate levels where above 1 mg N/L (Figure 15D). The mechanisms that relate the increase in ORP due to the presence of nitrate to MM inhibition are yet to be understood. It is hypothesized that the enzyme responsible for MM production,

methionine gamma lyase, is subject to negative feedback at higher ORP, allowing for an oxidative pathway for ATP production.

3.3.5   Bioaugmentation of nitrifiers as a practice of odor mitigation

Two approaches could be taken to elevate NOx-N levels within secondary systems to minimize odor emission: (i) optimization of bio-augmentation of waste sludge in secondary system through operation at increased SRT while enhancing bioaugmentation rates, (ii) addition of nitrate flow coming from sidestream deammonification to either the (a) head of plant, (b) beginning of secondary system or (c) just before secondary clarifiers. Estrada et al., (2015) has reviewed odor prevention techniques including Activated Sludge Recycling (ASR) and Oxidized Ammonium Recycling (OAR). These technologies have the potential to lower investment and operating costs regarding odor control decisions.

Our data has shown a clear relationship between MM emission and Nitrate concentration. Figure 16 shows MM emission in pass 1 in relation to NO3-N level in pass 1at three different ranges of sludge blanket height. The impact of NO3-N was better observed at lower blanket height. When the blanket height was ranging between 0.2 to 0.8 m, high NO3-N level would decrease MM emission. The impact of NO3-N was not observed at higher blanket (0.8 – 1m) (figure 16).

Previous investigations undertaken by our group has revealed that controlling ORP was potentially a key to reduce odors in AS process (Romero et al., 2016). Bio-augmentation of waste activated sludge from nitrification/denitrification process was being applied on one of the secondary systems allowing for side by side

determination of its impact independent of environmental changes. Full-scale

experiments were conducted across non bio-augmented and bio-augmented reactors

at the Blue Plains AWTP at SRT of 1.5 days. The effect of bio-augmentation on
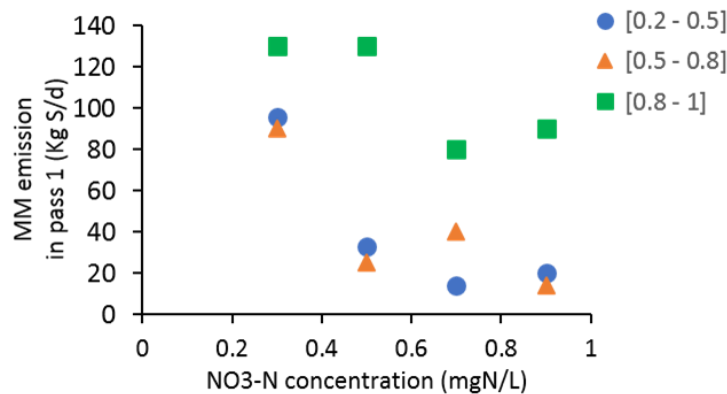
organic sulfur emission was clarified.

Figure 16 MM emission in pass 1 at three different sludge blanket height ranges in relation to nitrate concentration

Data showed the highest concentration of MM generated at the beginning of

the reactor in process B (bio-augmented), where RAS was fed into it. Similar to non

bio-augmented process, an increase of MM production after selector zones was

observed, again confirming that anaerobic conditions in RAS and selector zones

rapidly produced MM with subsequent stripping over the reactor (Romero et al.,

2016). Anaerobic selectors as well long retention times in clarifiers (anaerobic sludge

blankets) have shown to cause organic sulfur emission (Kim et al., 2002, Sekyiamah

et al., 2008). As anaerobic selectors are commonly used in secondary systems to

increase settleability, which is one of the major limitations within the treatment. The

emission of MM and its production in the selector zone was significantly lower in the

bio-augmented sludge compared to the non bio-augmented one (Romero at al.,

2016)). It was suggested that the nitrate and nitrite (NOx) found in bio-augmented sludge and not in non bio-augmented may be the factor contributing to the decrease in organic sulfur production and emission. NOx production through nitrification increase the ORP preventing the chemical reduction of sulfates to H_2S and a similar effect could be inhibiting the production of MM. It was found that bio-augmentation of waste sludge from the biological nutrient removal step into the secondary system, allowed nitrifying activity within secondary system despite the low SRT, thus increased nitrate concentration could be achieved within the secondary system minimizing MM production even further.

This study showed that increasing ORP could decrease odor emissions by targeting the zones where MM was emitted. This could either be achieved by addition of NOx or by increasing aeration. However, as the latter challenges application in clarifiers and selector zones, AS bio-augmentation with nitrifying sludge which allows for some NOx residual seemed a promising initiative.

3.4   Conclusion

Our study has shown the mechanism of VSCs emission in secondary activated sludge systems. Of the VSCs measured, MM was the dominant compounds accounted to 90 % of total emission. The stripped MM from both reactors was originating the AS itself rather than dissolved MM from the feed. Most MM was emitted in the first and second pass. Our study showed that the depth of secondary sludge blanket plays an important on the extent of MM emission. At high sludge blanket height, high MM

emission was observed. It was concluded that low ORP conditions in sludge blanket, selector zones and RAS was the major source of VSCs.

This study showed that increasing ORP could decrease odor emissions by targeting the zones where methyl mercaptan is emitted. This could either be achieved by addition of nitrate or by increasing aeration. However, as the latter challenges application in clarifiers and selector zones, AS bio-augmentation with nitrifying sludge which allows for some NOx residual seemed a promising alternative as long as the secondary clarifiers are well management. Addition of nitrate from an external source in clarifiers could support a strategy for overall reduction of MM.

Acknowledgement

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