

## ABSTRACT

Title of Document:

UTILIZING ELECTRONIC NOSE  
AND GC-MS TO EXAMINE  
CRITICAL FACTORS  
INFLUENCING THE FORMATION  
OF ODOROUS VOC'S IN  
BIOSOLIDS.

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Despite the efforts to better manage biosolids field application programs, biosolids managers still lack of efficient and reliable tools to apply large quantities of material while avoiding odor complaints. Objectives of this research were to determine the capabilities of an electronic nose in supporting process monitoring of biosolids production and, to compare odor characteristics of biosolids produced through thermal-hydrolysis anaerobic digestion (TH-AD) to those of alkaline stabilization in the plant, under storage and in the field. A method to quantify key odorants was developed and full scale sampling and laboratory simulations were performed. The portable electronic nose (PEN3) was tested for its capabilities of

distinguishing alkali dosages in the biosolids production process. Frequency of recognition of unknown samples was tested achieving highest accuracy of 81.1%. This work exposed the need for a different and more sensitive electronic nose to assure its applicability at full scale for this process. GC-MS results were consistent with those reported in literature and helped to elucidate the behavior of the pattern recognition of the PEN3. Odor characterization of TH-AD and alkaline stabilized biosolids was achieved using olfactometry measurements and GC-MS. Dilution-to-threshold of TH-AD biosolids increased under storage conditions but no correlation was found with the target compounds. The presence of furan and three methylated homologues in TH-AD biosolids was reported for the first time proposing that these compounds are produced during thermal hydrolysis process however, additional research is needed to fully describe the formation of these compounds and the increase in odors. Alkaline stabilized biosolids reported similar odor concentration but did not increase and the 'fishy' odor from trimethylamine emissions resulted in more offensive and unpleasant odors when compared to TH-AD. Alkaline stabilized biosolids showed a spike in sulfur and trimethylamine after 3 days of field application when the alkali addition was not sufficient to meet regulatory standards. Concentrations of target compounds from field application of TH-AD biosolids gradually decreased to below the odor threshold after 3 days. This work increased the scientific understanding on odor characteristics and behavior of two types of biosolids and on the application of electronic noses to the environmental engineering field.

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FACTORS INFLUENCING THE FORMATION OF ODOROUS VOC'S IN  
BIOSOLIDS.

By

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Dissertation submitted to the Faculty of the Graduate School of the  
University of Maryland, College Park, in partial fulfillment  
of the requirements for the degree of  
Doctor of Philosophy  
2016

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## **Dedication**

*To my family*

## **Acknowledgements**

I want to thank the committee members for their willingness to participate in this process. Thank you for sharing your experience, for your commitment to my work and for enhancing the overall output of this effort. I would also like to thank my academic advisors, Alba Torrents and Laura McConnell for giving me the opportunity and providing me with the framework to become an independent researcher. I would like to thank Cathleen Hapeman and Mark Ramirez for always making sure that this project had what it needed to continue. I would like to thank to all of those that support and motivate the work of graduate students in many ways: Anh Nguyen and Peter Downey in USDA; Marya Orf in UMD and; Haydee De Clippeleir and Norman Docket in DC Water. And to the graduate students from these institutions that I enjoyed working with and that increased the level of motivation. I also want to thank Dan, Jaime and José for feeding the critical thinking of my surroundings, to remember its value and to celebrate it. Lastly, I would like to thank Sarah for showing me how to make of love a key driver to excel in our day-to-day work. That, without a doubt, helped to make of this work a better one.

## Table of contents

Dedication .....	ii
Acknowledgements.....	iii
List of Tables.....	vi
List of Figures .....	vii
Chapter 1. Introduction and Objectives .....	1
1.1 Introduction.....	1
1.2 Background .....	3
1.2.1. Odor formation and release .....	3
1.2.3. Odor monitoring for decision making .....	11
1.3 Objectives .....	15
1.3.1 Objective 2 .....	17
1.3.2 Objective 3.....	18
1.3.3 Objective 4 .....	19
1.3.4 Objective 5 .....	20
Chapter 2. Sampling and Analytical Methods .....	22
2.1 Biosolids Sample Collection .....	22
2.1.1 Description of the facility and biosolids production .....	22
2.2 Chemical Analysis by Gas Chromatography-Mass Spectrometry .....	24
2.2.1 Sampling .....	24
2.2.2 Sample analysis .....	24
2.2.3 Calibration curve .....	25
2.3 Electronic Nose .....	26
2.3.1 Introduction .....	26
2.3.2. Portable Electronic Nose (PEN3) .....	27
2.3.3 Pattern creation and sample recognition .....	29
Chapter 3. Evaluation of an Electronic Nose for Improved Biosolids Alkaline- Stabilization Treatment and Odor Management .....	33
3.1 Abstract .....	33
3.2 Introduction .....	34
3.3 Experimental Methods .....	36
3.3.1 Biosolids Sample Collection .....	36
3.3.2 Alkaline Stabilization .....	36
3.3.3 Analytical Methods .....	37
3.3.4 Statistical analysis .....	38
3.4 Results and Discussion .....	38
3.4.1 Trends in pH, Temperature and Hydrogen Sulfide .....	38
3.4.2 Electronic Nose Pattern Recognition .....	39
3.4.3 Recognition Frequency of Unknown Samples .....	42

3.4.4 Odorant profiles of alkaline-stabilized biosolids .....	42
3.4.5 Comparing electronic nose and GC-MS .....	44
3.5 Conclusions .....	48
3.6 Acknowledgements .....	48
Chapter 4. Odor characterization of TH-AD and alkaline stabilized biosolids under storage conditions .....	49
4.1 Abstract .....	49
4.2 Introduction .....	50
4.3 Experimental methods .....	53
4.3.1 Biosolids sampling collection .....	53
4.3.2 Alkaline stabilization .....	54
4.3.3 Storage Simulation .....	54
4.3.4 Olfactometry sampling and analysis .....	56
4.3.5 Headspace sampling for GCMS analysis. GCMS analysis .....	56
4.3.6 H <sub>2</sub> S analysis with Teledyne .....	56
4.4 Results and discussion .....	57
4.4.1 Chemical analysis .....	57
4.4.2 Olfactometry .....	63
4.4.3 Odor index .....	67
4.5 Conclusions .....	69
4.6 Acknowledgements .....	69
Chapter 5. Utilizing GC-MS and an electronic nose for the characterization of key odorants from TH-AD and alkaline stabilized biosolids after simulated field application .....	70
5.1 Abstract .....	70
5.2 Introduction .....	71
5.3 Materials and Methods .....	74
5.3.1 Biosolids Sample Collection .....	74
5.3.2 Alkaline Stabilization .....	75
5.3.2 Simulation of field application .....	75
5.3.3 Analytical Methods .....	76
5.3.4 Statistical analysis .....	76
5.4 Results and Discussion .....	76
5.4.1 Odorant profile for field application of alkaline stabilized biosolids .....	76
5.4.2 Odorant profile for field application of THAD biosolids .....	79
5.4.3 Electronic Nose Pattern Recognition .....	80
5.5 Conclusions .....	82
5.6 Acknowledgements .....	82
Chapter 6. Conclusions and future work .....	84
6.1 Conclusions .....	84



6.2 Future work on odor characterization from biosolids .....	87
6.3 Future work on odors in activated sludge .....	88
Appendices .....	90
Bibliography.....	94

## List of Tables

Table 1.1 .....	3
Table 2.1.....	26
Table 2.2.....	28
Table 3.1.....	47
Table 4.1.....	63
Table 4.2.....	66
Table 5.1.....	79

## List of Figures

Figure 1.1.....	300
Figure 1.1.....	7
Figure 2.1.....	23
Figure 2.2.....	29
Figure 2.3.....	29
Figure 2.4.....	30
Figure 3.1.....	39
Figure 3.2.....	41
Figure 3.3.....	41
Figure 3.4.....	43
Figure 3.5.....	44
Figure 3.6.....	46
Figure 4.1.....	55
Figure 4.2 .....	58
Figure 4.3.....	59
Figure 4.4.....	61
Figure 4.5.....	62
Figure 4.6 .....	64
Figure 4.7.....	65
Figure 4.8.....	68
Figure 4.9.....	68
Figure 5.1.....	77
Figure 5.2.....	78
Figure 5.3.....	80
Figure 5.4.....	83

# **Chapter 1. Introduction and Objectives**

## **1.1 Introduction**

Domestic wastewater treatment plants play an important environmental roll as nutrient recovering facilities while enhancing water quality before water is returned to the natural environment or for beneficial reuse. Physical, chemical and biological processes are used in a standard wastewater treatment plant (WWTP) to separate the solids from the liquid phase and to degrade, to some extent, pollutants that have been added to the water during its domestic and, sometimes, industrial use. During the treatment process, a high solids content mixture is generated as a by-product which has the potential to be converted to energy and to be reused for agricultural purposes due to its nutrient rich composition. In the United States, in order to do so, these solids have to be conditioned in accordance to the Federal rule 40 CFR Part 503 (EPA, 1995) regulation such that they do not pose a threat to human health or to the environment and can then be beneficially used as “biosolids”. Approximately 7,180,000 dry tons of solid residuals are generated each year from the treatment process at the more than 16,000 municipal wastewater treatment facilities in the U.S., from which about 55% are beneficial used as biosolids and 45% are disposed (landfilled or incinerated) (Beecher *et.al.*, 2007).

Biosolids application to agricultural fields represents a source of organic matter and plant nutrients instead of using fertilizers (Obreza and O’Connor, 2003; Laor *et.al.*, 2011). In the same way, for municipalities it is an end-of-pipe waste

disposal solution as well as a sustainable practice when compared to other alternatives such as incineration or landfilling (Singh and Agrawal, 2008; Lu *et.al.* 2012). Some of the concerns related to the agricultural use of biosolids are potential contamination by heavy metals and organic pollutants, malodors, and vectors attraction (EPA, 2000). In this sense, sanitary concern about biosolids field application due to nuisance odors can lead to public opposition and possible failure of a sustainable biosolids management program.

Public complaints due to biosolids field applications are a result of odor causing compounds being released from biosolids followed by transport to sensitive populations. Currently, application programs of biosolids to agricultural fields are regulated by state rules on nutrient management in order to control nutrients loadings, pursue a high crop yield and protect soils and waterways from contamination (EPA, 2000). However, ignoring the odor characteristics of the biosolids and of the location of application sites can result in public opposition (Iranpour *et.al.* 2004).

The aim of this project was to address odor-related challenges in a specific biosolids field application program, by means of **1)** increasing the understanding on the production and release of odor causing compounds in the treatment plant and in the field, as well as **2)** evaluating new technology for odor monitoring that would allow for a better decision making on the biosolids final destination.

## 1.2 Background

### 1.2.1. Odor formation and release

The main groups of odor-causing compounds released from the WWTP and biosolids application described in the literature are organic sulfur compounds, volatile fatty acids, and nitrogen based compounds. These compounds are presented in Table 1 with their human detection limits.

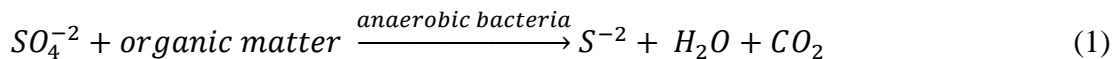
**Table 1.1** Odor thresholds for human detection limit of main odor-causing compounds from biosolids.

Compound	Odor	Odor threshold		
		ppbv	Source	ug/m <sup>3a</sup>
Hydrogen Sulfide	Rotten egg	10	OSHA	24.9
Dimethyl Sulfide	Decayed vegetables	2.2	Amoore and Hautala, 1983	5.6
Dimethyl Disulfide	Decayed vegetables	6.4	Fords, 1988	47.5
Carbon Disulfide	Rotten pumpkin	16	Verschueren, 1983	296
Methyl mercaptan	Rotten cabbage	1.1	Devos, 1990	2.2
Ammonia	Sharp, pungent	5754	Devos, 1990	
Trimethylamine	Fishy odor	5.49	Devos, 1990	0.11
Acetic	Vinegar	144-6.0	Devos, 1990-Nagata, 2003	356
Propanoic	Rancid	35-5.7	Devos, 1990-Nagata, 2003	108.3
Butyric	Rancid	3.8-19	Devos, 1990-Nagata, 2003	14.1

<sup>a</sup> Devos *et.al.* 1990.

### Wastewater treatment plant

Sulfur compounds form the majority of odorants associated with sewage treatment works. Domestic sewage typically contains 3-6 mg/L organic sulfur, derived mainly from proteinaceous material and, it can contain further organic sulfur resulting from sulfonates in household detergents (about 4 mg/L) (Boon, 1995). Inorganic sulfur, in the form of sulfate, is present in quantities depending on the hardness of the water, typically in concentrations of 30-60 mg/L (Boon, 1995). Hydrogen sulfide (H<sub>2</sub>S) is the predominant odorant associated with sewage (Bonnin et al., 1990; Vincent and Hobson, 1998). The formation of H<sub>2</sub>S arises from two sources: the reduction of sulfate and the desulfurisation of organic compounds containing sulfur in a reduced state (Harkness, 1980). The formation of H<sub>2</sub>S from sulfate is shown in the following equations:



The optimum redox potential (Eh) for this reaction is -200 to -300mV (Boon, 1995). H<sub>2</sub>S is a weak acid and dissociates according to pka<sub>1</sub> = 7.04 and pka<sub>2</sub> = 12.89. It is only molecular H<sub>2</sub>S that will lead to odor problems. At pH 7, approximately 50% of the sulfide is in this form. Thus, acidic conditions will enhance H<sub>2</sub>S odour problems and basic conditions will suppress them. On the other hand, sulfur occurs in a reduced

form in some amino acids (i.e. cysteine, cystine, methionine, taurine) where it provides a structural link within protein molecules (Harkness, 1980). Other sulfur-containing odorants can similarly be derived from sulfur-containing amino acids, and can also be formed from reactions between  $\text{H}_2\text{S}$  and unsaturated ketones (Harkness, 1980) as it is discussed in the following section (solids treatment).

Nitrogen-containing odorants can also be significant sources of odor. They are mainly ammonia, amines, indole and skatole. It has been reported that indole and derivatives (such as skatole) have a character similar to the general sewage treatment works odor when considered in isolation (Young, 1984). Nitrogen sources in sewage are urine, proteins and amino acids. Amines in particular are produced from amino acids by the removal of the carboxyl ( $\text{COOH}$ ) group (Harkness, 1980).

Volatile fatty acids, aldehydes, alcohols and ketones are the by-products of carbohydrate fermentation and are generally associated with anaerobic treatment and in particular with the treatment of sewage sludge (Bonnin et al., 1990).

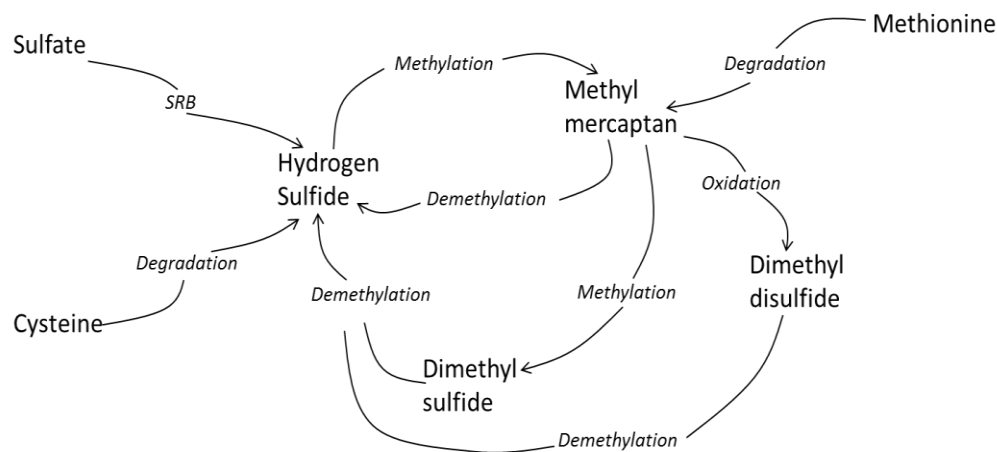
### Solids treatment

In a survey for the patterns of odorous chemicals within a WWTP, Kim et al (2002) found that carbon disulfide ( $\text{CS}_2$ ), dimethyl sulfide (DMS), dimethyl disulfide (DMDS) were more prevalent in samples collected from downstream processes and corresponded with decreased oxidation-reduction potential (ORP) conditions. Propionic acid (PA), and butyric acid (BA) were consistently identified in the primary gravity thickeners, while trimethylamine could only be detected from biosolids after alkaline stabilization.



Also in 2002, Novak *et al.* described the mechanisms for DMDS and trimethylamine (TMA) formation in limed biosolids. They showed that methyl mercaptan (MM) is sorbed by an acid-base reaction with lime and subsequently converted into DMDS. They also found that TMA is not produced by the liming treatment of biosolids but this process does convert TMA from the ionic form to the molecular form due to an increase in the pH that lead to TMA volatilization causing the “fishy” odor. Enzymatically degradation of acrylamide-based polymer (Kim *et al.*, 2003; Chang *et al.*, 2005) and protein (Kim *et al.*, 2003) in the wastewater and sludge has been found to be the overriding factor in TMA production.

Further research on the formation of VOSC in biosolids has shown that the production of MM that leads to the formation of DMDS, mainly occurs from biological degradation of the amino acid methionine and the methylation of hydrogen sulfide, the latter being formed from the degradation of cysteine and sulfate reduction; DMS is formed through the methylation of MM and; DMDS by MM oxidation (Higgins *et. al.*, 2003; Novak *et.al.*, 2006; Higgins *et. al.*, 2006). This VOSC cycling is shown in Figure 1. The demethylation of DMS, DMSD and MM is done by methanogens communities in the biosolids to produce H<sub>2</sub>S (Chen *et al.*, 2005).



**Figure 1.1** Cycling Pathway of Volatile Organic Sulfur Compounds

production and transformation in anaerobic digested biosolids.

Source: Higgings *et. al.*, 2006

### Field

Dimethyl disulfide, DMS, CS<sub>2</sub>, NH<sub>3</sub>, TMA, methyl ethyl ketone, and acetone have been identified as odorant emissions from biosolids application to forest soil, where sorbent tubes followed by thermal desorption into a gas chromatography-mass spectrometry (GC-MS) system was used as the analytical technique (Rosenfeld, 1999). Reduced sulfur compounds like hydrogen sulfide and methyl mercaptan are unstable in oxidized environments and oxidize to form DMDS in land-applied biosolids (Rosenfeld *et al.*, 2000; Higgins *et al.*, 2006). Banwart and Bremmer (1975) found that DMDS accounted for 55 to 98% of total S evolved from biosolids application to soil in aerobic conditions. Ammonia and TMA comprise most of the nitrogen emissions from land-applied biosolids (Rosenfeld *et al.*, 2000).

In a more recent project, Laor *et al.* (2011) identified VOC emissions from two types of biosolids during their production and over time after land application. They

detected high ammonia and amines concentrations in digested sludge followed by alkaline stabilization (higher biosolids quality) and these concentrations were below the detection threshold after soil incorporation. Nitrogen containing compounds were not detected in digested biosolids without alkaline stabilization (lower quality). The VOC's profiles for both biosolids behaved similarly after land application and differed from those chemical patterns at the treatment plant showing that handling operations, weather conditions and soil characteristics may influence the chemistry of the odor causing compounds. Other VOC's such as short chain alkanes, BTEX and terpenes were also identified in this study.

#### 1.2.2. Processes affecting the presence of odors.

In addition to the description of the odor causing compounds in the literature, there is evidence that these compounds are present depending on the biosolids treatment process and, sometimes, these processes are affected by the upstream waste water treatment operations. This evidence is described in this section.

Several treatments can be used to produce biosolids. Aerobic digestion, anaerobic digestion (AD), alkaline stabilization, composting and, lagoons are among the main technologies used in the United States (EPA, 1995). Each technology produces biosolids with different odor characteristics and quality. According to an estimate made by Beecher *et.al.* (2007) approximately 66% of the biosolids produced in the US is by using anaerobic digestion or alkaline stabilization. Dewatering strategies are commonly used to reduce the amount of material and the cost of hauling. Belt-filters, drying beds and centrifuges are the main ones described in literature

(EPA, 1995). These dewatering technologies can lead to odor problems due to shear and re-activation of microorganisms that produce odors.

Higgins *et al.* (2008) published an evaluation of in-plant parameters on biosolids odors from eleven facilities that use anaerobic digestion and dewatering in their biosolids production. The highest concentrations of sulfur compounds found after dewatering were in facilities using high speed centrifuges. The same effect had been observed by Muller *et al.* (2007). Higgins *et al.* (2008) also found that longer solids retention times and higher ratio of secondary solids (waste activated sludge) to primary solids reduced the odors from the final material. There was an observed reduction in biosolids odor with the addition of ferric salts but variability in the effect among the eleven plants did not allow for strong conclusions. However, Zeynep *et al.*, (2008) further described the effect of iron on sulfur compounds where the presence of iron reduces the odor characteristic of biosolids by precipitation as ferrous sulfide. Novak *et al.* (2002) found sulfur compounds as the main chemicals associated with the odor properties from anaerobic digested biosolids and described the concentrations profiles to be specific to each facility and sampling event (within the same facility).

Both, Novak *et al.* (2002) and Kim *et al.* (2003) examined the mechanism of odor generation in limed biosolids. The main difference between anaerobic digested biosolids and limed biosolids is the presence of TMA due to an increase in the pH that will lead to TMA emission. The sulfur compounds profile changed from AD process with a reduction of H<sub>2</sub>S and an increase in organic reduced sulfur compounds. Kim (2003) described the effect of upstream processes on the odor profile of the final material where untreated biosolids storage increased odor problems, and the addition

of cationic polymer was the main source of amine compounds. The breakdown of cationic polymer to produce amines was further described by Chang *et al.* (2005).

Other research has focused on the use of statistical models to describe the odors or odor compounds as a dependent variable on the upstream processes. Gabriel *et al.* (2005) found strong correlations between DMDS emissions measured by SPME-GC-MS from limed biosolids and the ratio of primary solids to secondary solids, oxidation-reduction potential (ORP) in the gravity thickening process and the amount of material dewatered by the centrifuges. In the same way, Janpengpen *et al.* (2007) found that the secondary sedimentation basins blanket depth and the polymer addition were the variables that better described the emissions of H<sub>2</sub>S and ammonia (NH<sub>3</sub>) from the biosolids production process (limed).

Emphasis has been put in recent years on pre-treatments enhancing AD to increase loading rates and biogas yields (Carlsson *et.al.* 2012). Several methods have been studied with some of them already operating at full scale. This pretreatment methods can be classified in mechanical, thermal, chemical and biological (Ariunbaatar *et.al.* 2014). Thermal hydrolysis (TH) prior anaerobic digestion to produce high quality biosolids is a promising technology that has recently been introduced in the United States. In Europe, more than 30 facilities already use this technology and the impact on the odor reduction seems to be clear. However, few scientific studies have addressed this topic to make any conclusions related to odor characterization and control. In an evaluation of enhance digestion processes for biosolids treatment, Murthy *et al.* (2009) showed that the advantage of the thermal hydrolysis pretreatment is that high solids can be achieved with belt filter press

dewatering that are equivalent to centrifuge dewatering. Belt filter press cakes have generally been shown to have lower odors and less likelihood of indicator bacteria regrowth in the cake (Higgins *et.al.* 2007), which further helps the thermal hydrolysis process minimize risks related to odors and indicators. Electro-Dewatering of anaerobically digested biosolids showed better odor characteristics under storage conditions when compare with heat drying (Navab-Daneshmand *et.al.* 2014). However, literature on the impact of these enhanced treatments on the quality of biosolids from an odor perspective is still limited.

#### 1.2.3. Odor monitoring for decision making

An odor is a mixture of volatile molecules present at very low concentrations in the inhaled air that, upon coming in contact with the human sensory system, is able to stimulate an anatomical response. Odors are recognized *via* the memory effect of previous experienced smells, thus accounting for the high subjectivity of the odor perception (Freeman, 1991). Therefore, measuring odors in any form represents a challenge due to the low concentrations of compounds at which an odor can be perceived. Often times, analytical techniques are not designed to detect nor quantify concentrations at the detection threshold. In addition, odor detection is subjective and highly variable from person to person. In wastewater and biosolids studies, odors have been monitored using several approaches. Some of these utilize human sensory panels; others seek to simulate the human olfactory system; while still others are based on concentration measurements in comparison to measured detection thresholds.

## Olfactometry

Odor characterization become of particular importance when designing processes and management strategies for biosolids production and reuse. Sensory measurements employ the human nose as the odor detector, relating directly to the properties of odors as experienced by humans. Dynamic olfactometry is the sensory measurement of choice for odor assessments in wastewater facilities (Lebrero, 2011). Odor concentrations (dilution to threshold –DT–) are quantified by determining the amount of dilution needed to bring the odorous air sample to its threshold. The higher the threshold value, the more dilution is needed to bring the odor to threshold, thus the stronger the odor. In addition, hedonic tone may be reported as a mean to measure how pleasant or unpleasant an odor is as well as the level of dilution required to characterize the type of smell. Olfactometry measurements are performed by sensory panel members selected according to EN-13725.

Sampling techniques and sampling containers for olfactometry analysis may affect the results reported, especially when odor compounds are unstable and reactive, which is the case of sulfur compounds. Trabue *et al.* (2007) found background contamination that can lead to bias on the final result when using Tedlar bags, a container commonly used to sample air for olfactometry determinations as well as for the determination of specific compounds using analytical techniques. Laor *et al.* (2011) concluded the similarly when testing and comparing different materials of sampling bags (Tedlar vs. Nalophan). Nevertheless, due to the use of the human nose as a detector, olfactometry is still a preferred approach for reporting odors (Boeker, 2014).

### Chemical analysis

In contrast with more general olfactometric measurements, information on specific compound concentrations provide valuable insight when evaluating process and mechanisms of odor generation and emissions as well as to monitor strategies for odor reduction. In order to obtain this information, analytical techniques are used.

Odorous emissions are composed of a complex mixture of hundreds of chemical compounds at ppb and ppt concentrations, which presents a challenge to the sensitivity and separation capacity of gas chromatography (GC). These low concentrations present in odors are very often below the detection limits of most common GC detectors (mass spectrometry and flame ionization), commonly in the parts per billion range. Studying odor compounds in environmental applications (agricultural or wastewater/biosolids), this low concentrations have forced the use of pre-concentration of the odorants either via cryogenic trapping (Trabue, *et.al.*, 2008a) or via adsorption into porous polymers or carbon-based adsorbents (Trabue, *et.al.* 2008b; Kim, *et.al.* 2002). One of the main limitations of using gas chromatography when monitoring odor compounds is a major capital investment and a significant technological challenge with high trained personnel to operate it.

In the same way that for olfactometric measurements, sampling techniques and containers play an important role in chemical analysis of air samples. For the majority of air toxic compounds, canisters present a fair option for sampling; however, when sulfur compounds are to be measured, reactivity represents an issue. In this sense, fused-silica lined canisters have shown to be the preferred option (Trabue, *et. al.* 2008a).



### Online sensors

Online odor monitoring presents a number of challenges in odor management. Traditionally, single odorants such as H<sub>2</sub>S and NH<sub>3</sub> have commonly been used for online monitoring as surrogate compounds. Specific gas sensors for these surrogates are based on chemical, electrochemical, catalytic, and optical detectors with a high sensitivity and selectivity for some target odorants (Lebrero, 2011). They present low response times, low detection limits (ppb levels in some cases), low cost and provide a direct reading of the concentration of the target odorants. However, specific sensors only provide a partial characterization of odorous emissions because H<sub>2</sub>S and NH<sub>3</sub> are not always responsible for the entire odor profile. In addition, because most specific sensors are based on odorant adsorption, they are susceptible to interferences from reduced sulfur compounds and humidity (Lebrero, 2011).

### Electronic nose

Electronic noses are arrays of electronic sensors capable of detecting and differentiating complex mixtures of volatile compounds. The instruments contain an array of one to 32 sensors, using a variety of different sensor technologies from organic polymers to metal oxides to micro-balances (Lebrero, 2011). According to Harper (2001), advantages of electronic noses include high sensitivity and correlation to human sensory panels for many applications.

Electronic nose sensors have been used in the food industry to monitor quality of decaying fruits (Brezmes *et.al.*, 2000) and meats (Ghasemi-Varnamkhasti *et al.*, 2009) as well as processed food such as rice extrudes (Feng *et.al.*, 2011). Application

of electronic nose technologies in the environmental engineering field has been reported for the quantification of odors from composting facilities (Sironi *et.al.*, 2007a; Sironi *et.al.*, 2007b and; Delgado-Rodriguez *et.al.*; 2012), within wastewater treatment plants (Stuetz *et.al.*, 1999; Bourgeois and Stuetz, 2002 and; Sohn *et.al.*, 2009) and at receptor locations downwind from treatment facilities (Sironi *et.al.*, 2008).

Challenges still exist as electronic nose sensors can exhibit drift in response due to changing environmental conditions and over time (Harper, 2001; Romain and Nicolas, 2009). Sampling techniques (*i.e.* static and dynamic) and sample characteristics (*i.e.* temperature and humidity) have shown to limit their performance in full scale applications (Knobloch *et.al.*, 2009). Moreover, the concept of using sensor arrays for odor measurements has recently been evaluated by Boeker (2014) concluding in part that the response of an electronic nose should not be correlated to that of human perception of smell.

### **1.3 Objectives**

Despite the efforts to better manage biosolids field application programs and to reduce the likelihood of complaints related to odor emitted from biosolids, managers still lack efficient and reliable tools to successfully apply large quantities of material while avoiding odor complaints from communities and cities.

The main limitations in achieving improvements are the lack of deep understanding on the interaction between the upstream variables affecting the odors in the final material and at the application sites. On the other hand, technologies for odor

monitoring that would support a decision making process as to the biosolids allocation have not proven to be reliable. Furthermore, the use of technologies to provide real time feedback to the facility operation have not been yet explored with the complementary scientific tools and framework needed to support the output of such strategy.

Therefore, this research aimed to develop a methodology whose output will help fulfilling the gap between the scientific understanding and the process engineering on the production and field application of biosolids with the goal of exploring tools for decision making that would lead to a successful biosolids management program.

Specific objective were:

1. To develop a methodology to quantify key odorant compounds commonly found in biosolids to support the evaluation of new monitoring technologies.
2. To determine the capabilities of an electronic nose in supporting an on-line process monitoring scheme in a biosolids management program.
3. To compare odor characteristics of biosolids produced through thermal hydrolysis anaerobic digestion to those of alkaline stabilization from the same initial sludge.
4. Conduct biosolids storage simulation to assess biosolids stability from an odor perspective.
5. Conduct biosolids field application under controlled conditions to study key odorant compounds behavior over time depending on the biosolids treatment process.

Objective 1 is non-hypothesis driven and the importance of meeting this objective relies on that it becomes a key tool to achieve objective 2-5, for which a series of questions have been stated to support reaching the goals of this study.

#### 1.3.1 Objective 2. Evaluating an electronic nose for process monitoring of biosolids.

##### *Questions:*

- a) Is an electronic nose capable of providing reliable feedback to the biosolids production system?
- b) Is it capable of distinguishing between different process conditions that affect odors from biosolids?

##### *Hypotheses*

- a) With the information provided by the electronic nose, it will be possible to recognize and classify 90% of the treatment process operational conditions.

##### *Experimental approach*

Electronic nose sensors are designed to detect differences in complex air sample matrices. For example, they have been used in the food industry to monitor process performance and quality control. However, no information is available on the application of sensor arrays to monitor process performance of biosolids treatment processes.

Selection of a commercial electronic nose that has been studied for environmental applications and that allows for conducting research was an import step to achieve this goal. Two instruments were evaluated based on technology (number

and type of sensors), publications, cost and communication with manufacturers. The Portable Electronic Nose -PEN3- (Airsense Analytics, Schwerin, Germany) showed the best balance with the main advantage that it allowed for deeper and more versatile data analysis for pattern creation and sample recognition.

This work examined the feasibility of the PEN3 to discriminate between treatment conditions of alkaline stabilized biosolids and to explore its performance by comparison with quantitative analysis of key odorants. Untreated sludge samples were collected from Blue Plains Advanced Waste Water Treatment Plant in Washington, D.C. Seven quick lime treatment rates from 0 to 30% (w/w) were prepared and the off gas was monitored by GC-MS and with an electronic nose with ten metal oxide sensors. Pattern recognition models were created from the electronic nose data using Linear Discriminant Analysis and Principal Component Analysis. Details of the experimental design and results can be found in Chapter 3.

### 1.3.2 Objective 3. Odor characterization of biosolids.

#### *Questions:*

- a) What are the odor characteristics of biosolids produced by TH-AD process?
- b) Are these characteristics better than the ones from alkaline stabilized biosolids?

*Hypothesis:*

- a) The thermal hydrolysis-anaerobic digestion process will reduce odors in biosolids by 50%, measured as dilution to threshold, compared to alkaline stabilization.

*Experimental approach*

There are clear advantages of incorporating novel pretreatment process to enhanced anaerobic digestions, such as thermal hydrolysis, as well as new technologies for dewatering of biosolids based on these novel pretreatment. The reported advantages have focused on the intensification of resource recovery and less and safer material to be disposed. However, literature on the impact of these enhanced treatments on the quality of biosolids from an odor perspective is still limited. This work established the odor characteristics of THAD biosolids and compared them with three levels of alkaline stabilized biosolids. Odor characterization was achieved by using olfactometry measurements and chemical analysis by GCMS. Details on methodology used and results can be found in Chapter 2 and Chapter 4.

1.3.3 Objective 4. Stability of odors from biosolids under storage conditions.

*Questions:*

- a) Do odor concentration from TH-AD biosolids increase over time when stored in anaerobic conditions?
- b) How does this changes, if any, compare to the stability of alkaline stabilized biosolids?

*Hypothesis:*

- a) Odors from TH-AD biosolids will increase 20% over a 28 day storage period due to a further destruction of volatile solids. However, its characteristics will be less offensive compared to that of alkaline stabilized biosolids.

*Experimental approach*

Odor characterization from the treatments used in objective 3 were used as starting point for the simulation of storage under anaerobic conditions for 28 days. Target compounds included carbonyl sulfide, methyl mercaptan, ethanethiol, dimethyl sulfide, carbon disulfide, propanethiol, butanethiol, dimethyl disulfide and trimethylamine. Dilution to threshold, recognition threshold, hedonic tone and odor descriptors were reported as well. Details on the methodology and results can be found in Chapter 2 and Chapter 4.

1.3.4 Objective 5. Key odorants emission from field applied biosolids.

*Questions:*

- a) Does the chemical composition of key odorants emitted from TH-AD biosolids change over time under controlled field application conditions?

*Hypothesis:*

- a) Concentration of target compounds measured from TH-AD biosolids in field application will decrease below detection limits in a period of 5 days after being applied.

### *Experimental approach*

Target compounds described in Chapter 2 were used to monitor the behavior of key odorants emission from biosolids when they are subject to field application.

Laboratory tests under controlled temperature and wind speed were performed in order to isolate independent variables. The tested variables were then the treatment processes and the soil application techniques. Surface application and soil incorporation were studied. TH-AD biosolids as well as three levels of alkaline stabilized biosolids (under-dosed, properly dosed, and over-dosed) and an untreated control were tested. Details on the experimental design and the results can be found in Chapter 5.



## **Chapter 2. Sampling and Analytical Methods**

This chapter covers in detail the main analytical methods used in achieving the objectives of this study as well as the description of the facility where untreated sludge and biosolids samples were collected. In chapters 3 to 5 specific materials and methods are described as needed and the ones presented in this chapter have been omitted to avoid duplication.

### **2.1 Biosolids Sample Collection**

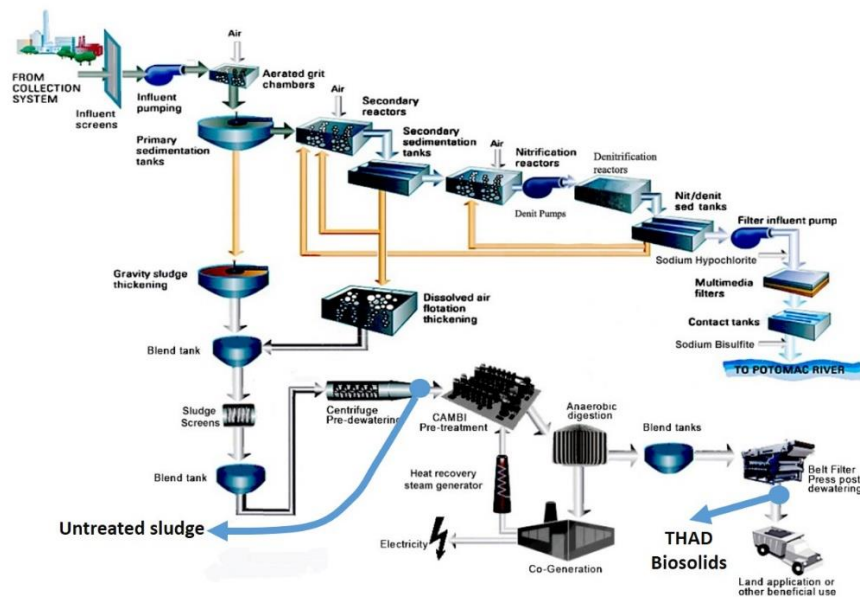
Untreated sludge and biosolids were collected from DC Water Blue Plains Advanced Waste Water Treatment Plant (AWWTP) located in Washington, D.C., USA. Over the duration of this study, Blue Plains underwent major changes in the biosolids treatment system from alkaline stabilization to anaerobic digestion enhanced by thermal hydrolysis pre-treatment.

#### **2.1.1 Description of the facility and biosolids production**

Blue Plains AWWTP has a capacity of treating 370 MGD ( $970 \text{ L min}^{-1}$ ) of domestic wastewater using a treatment train consisting on preliminary treatment (screening and grit removal), chemical enhanced primary treatment, conventional activated sludge, secondary clarification, nitrification-denitrification, tertiary sedimentation, filtration, chlorination and dechlorination to finally discharge on the Potomac River under strict regulations. Solids from tertiary sedimentation are fully recycle. Primary solids undergo gravity thickening and secondary solids thicken by dissolved air flotation. Currently, solids blend and go further screening, followed by dewatering by high speed centrifuges before entering thermal hydrolysis process. After hydrolysis, solids cool down by heat exchangers and enter anaerobic digestion for 15 days (solids retention time). Final dewatering is achieved by belt filter press

before hauling for beneficial reuse. A schematic of the treatment processes is shown in Figure 2.1. Class A biosolids production to March 2016 is approximately 400 wet metric tons per day. Additional high speed centrifuges are still in place for alkaline stabilization for flow peaks. If needed, primary and secondary solids would blend and undergo dewatering, by high speed centrifugation, and alkaline stabilization with quick lime (CaO) to produce class B biosolids and beneficially reused.

The untreated sludge samples used in this study before the plant upgrade (before December 2014) were collected using a metal shovel from a sampling port in the screw conveyor system after centrifugation, before alkaline stabilization, and were stored in 22-L plastic buckets. Average total solids of the samples collected in this period was 26.2% ( $\pm 4.1$ ). In 2015 and after, samples were collected from a mechanical sampling port after preliminary dewatering (before THP) for untreated samples (Appendix A) and manually from the conveyor system after the belt filter press for stabilized biosolids (TH-AD biosolids). Average total solids of the samples collected in this period was 16.5% ( $\pm 2.1$ ). Sampling points are marked in Figure 2.1.



**Figure 2.1** General layout of Blue Plains AWWTP. Source: (DCWater, 2015)

## 2.2 Chemical Analysis by Gas Chromatography-Mass Spectrometry

### 2.2.1 Sampling

Headspace samples were collected into evacuated 1.4 L canisters coated with fused silica (Entech Instruments Inc., Simi Valley, Ca., USA) and were analyzed within 24 hours.

Canisters were prepared prior sampling using an Entech 3100A automated cleaning system (Entech Instruments Inc., Simi Valley, Ca.) using the following program: canisters heated to 70 °C; filled to  $2.0 \times 10^5$  Pa with zero air; evacuated to 130 Pa; repeated for 10 cycles; final evacuation to 1.3 Pa for 12 h before being used for sampling. This ensured that the canisters were free from any volatile and semi-volatile compound. Clean tests were performed as part of quality assurance by randomly selecting one canister per batch of 10 to be filled with ultra-high purity nitrogen and analyzed by GC-MS using the same method as that for samples.

### 2.2.2 Sample analysis

Analysis of canisters was performed within 24 hr of sampling using an Entech Instruments Inc. (Simi Valley, Ca., USA) system consisting of a Model 7500 Autosampler followed by a Model 7200 Preconcentrator 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. Components of the analytical system including details of the Preconcentrator are shown in Appendix B.

Gas chromatography conditions were: Rtx1-MS Column (60 m x 0.32 mm x 1.0  $\mu$ m) (Restek Corporation, Bellefonte, Pa.); Helium carrier gas at a constant flow of 1.5 mL min<sup>-1</sup>;

temperature program: 35 °C hold 5 min; 10 °C min<sup>-1</sup> to 130 °C; 20 °C min<sup>-1</sup> 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*); methyl mercaptan (48 *m/z*); ethanethiol (62 *m/z*); dimethyl sulfide (62 *m/z*); carbon disulfide (76 *m/z*); propanethiol (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.

### 2.2.3 Calibration curve

Calibration of the GC-MS was carried out using certified gas standards from Restek Corporation and Tech Air Companies (White Plains, NY, USA): 5 ppm (± 5%) mixture of carbonyl sulfide, methyl mercaptan, ethanethiol, dimethyl sulfide, carbon disulfide, propanethiol and buthanethiol; 5 ppm (± 2%) standard of dimethyl disulfide; trimethylamine 5 ppm (± 5%); and 1ppm (± 5%) of TO-14 internal standard mixture including bromochloromethane, 1,4 difluorobenzene, chlorobenzene-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.

Calibration curves were created by withdrawing different volumes of gas mixtures from the working standard canisters and a set volume of internal standard gas. The calibration range for VOSCs was 0.4 ppb (v/v) to 17.5 ppm (v/v) using injection volumes of 500 mL and 10 mL respectively (Appendix C). The method detection limit (MDL) for VOSCs was calculated as the standard deviation of eight replicate injections of a 0.25 ppb standard, multiplied by the *t*-student value at seven degrees of freedom. This resulted in MDL values of 0.04 ppb for VOSC except for buthanethiol at 0.02 ppb and DMDS at 0.09 ppb (Table 2.1).

The chromatographic peak shape for trimethylamine on the RTx1-MS column was wide and tailing due to its inherent polarity. However, as a separate chromatographic analysis method was not available, and TMA has been identified in previous research as an important odorant, the ratio of peak height to internal standard peak height was used for calibration. The linear range of TMA concentrations was 100 ppb (v/v) to  $1.0 \times 10^6$  ppb (v/v). The estimate method detection limit for TMA was 80 ppb (v/v).

**Table 2.1 Target analytes for GC-MS.**

Compound	MW (g/mol)	Odor threshold <sup>a</sup> (ppbv)	Target ion ( <i>m/z</i> )	MDL <sup>b</sup> (ppbv)	Vapor pressure (bar at 20°C)	Solubility in water (g/L at 20°C)	pKa 25°C
Carbonyl sulfide	60	55	60	0.05	10.1	1.22*	N/A
Methyl Mercaptan	48	1.1	48	0.06	2.05	23.3	10.33
Ethyl Mercaptan	62	0.1 to 1 <sup>b</sup>	62	0.04	0.58	6.8	10.61
Dimethyl sulfide	62	2.2	62	0.04	0.45	22*	N/A
Carbon disulfide	76	95.16	76	0.05	0.53	2	N/A
1-Propanethiol	76	0.1 to 1 <sup>b</sup>	76	0.03	0.2	1.9*	10.7
1-Buthanethiol	90	0.1 to 1 <sup>b</sup>	90	0.02	0.04	0.56*	10.78
Dimethyl disulfide	94	12.33	94	0.09	0.03	2.5	N/A
Trimethylamine	59	5.49	59	80 <sup>d</sup>	1.8	890**	9.8

MW Molecular Weight

<sup>a</sup> Devos *et.al.* 1990

<sup>b</sup> Bingham *et.al.* 2001

<sup>c</sup> Method Detection Limit

<sup>d</sup> Estimated Method Detection Limit

N/A Not Applicable

\* At 25°C

\*\* At 30°C

## 2.3 Electronic Nose

### 2.3.1 Introduction

The basic principle of operation of an electronic nose has been introduced recently as a new technology for classification of chemical samples. A sensor array consists of a combination of chemical sensitive sensors, which change their resistance with the presence of gaseous

compounds. The signals obtained from these sensors are related to the gas composition being measured and can be compared with previously stored patterns through recognition algorithms. Due to the broad range sensitivity of the sensing principle used, an electronic nose is capable of detecting single compounds or whole gas mixtures and many different applications.

The subsequent analysis is always a comparison of pattern. Such an instrument does not provide any information about the chemical content (species, quantification) of a sample. With a training set (pattern) it is capable of distinguishing quality features for a given problem (discrimination). Or it may be easily used for discovering deviations between standards and differing samples. During the training phase, single points from a known sample set are “taught” into the device. Once trained, the electronic nose can be used for classification of unknown samples.

### 2.3.2. Portable Electronic Nose (PEN3)

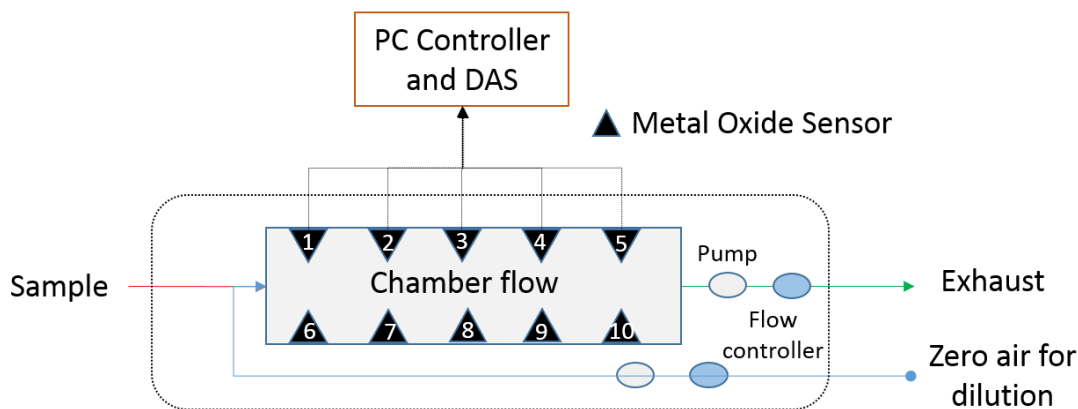
Selection of an electronic nose should be specific to the application since each instrument consists of an array of different sensors providing inherent specificity. Selection of a commercial electronic nose that has been studied for environmental applications and that allows for conducting research was an import step in this project.

The Portable Electronic Nose PEN3 (Airsense Analytics, Schwerin, Germany) was selected due to the number and type of sensors, literature, cost and communication with manufacturers. The PEN3 was equipped with ten different heated metal oxide sensors (150 – 500° C) that, although non-specific, they are slightly sensitive to different classes of compounds. Sensor affinity and sensitivity to particular test compounds are listed in Table 1.

**Table 2.2 Affinity and sensitivity of PEN3 electronic nose sensors.**

Key	Sensor	Affinity	Sensitivity (mg Kg <sup>-1</sup> )
A	W1C	Aromatic compounds	Toluene, 10
B	W5S	Broad range. Nitrogen oxides.	NO <sub>2</sub> , 1
C	W3C	Aromatic compounds	Benzene, 10
D	W6S	Hydrogen	H <sub>2</sub> , 0.1
E	W5C	Aromatic compounds. Alkanes	Propane, 1
F	W1S	Broad range. Methane.	CH <sub>4</sub> , 100
G	W1W	Sulfur compounds, H <sub>2</sub> S. Many terpenes and sulfur organic compounds.	H <sub>2</sub> S, 1
H	W2S	Broad range. Alcohols.	CO, 100
I	W1W	Aromatic. Sulfur organic compounds.	H <sub>2</sub> S, 1
J	W3S	Methane and aliphatic compounds.	Not determined

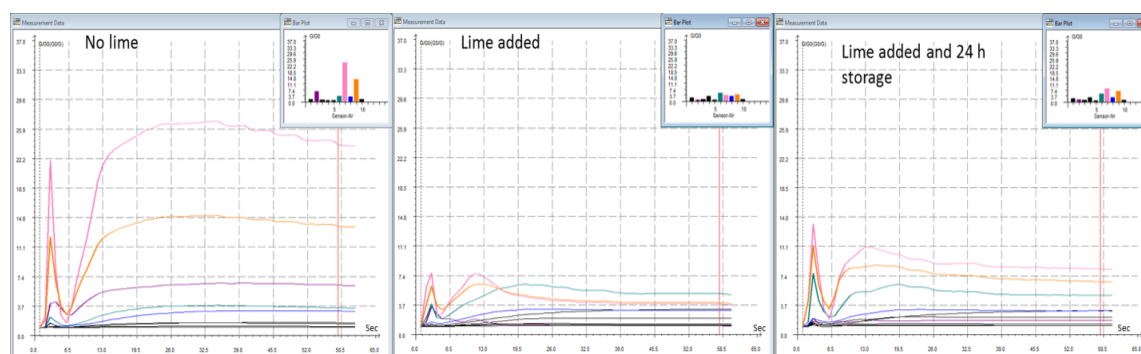
The PEN3 utilized an internal sampling pump at a flow rate of 400 mL min<sup>-1</sup> and an activated charcoal filter to produce clean air as reference gas to flush and zero the sensors. The method used for all headspace samples was: 60 seconds of flushing the sensor surfaces to a base line; 10 seconds of zeroing; and 60 seconds of sampling. Sensor response data was recorded every second and only the final 1-second reading, once the signal prove to be stabilized, was used for statistical analysis and pattern creation. The PEN3 was controlled and sensor data was processed using WinMuster software (Version 1.6.2.15, Airsense Analytics, Schwerin, Germany). A schematic of the PEN3 is shown in Figure 2.2



**Figure 2.2** Elements and flow path in the Portable Electronic Nose (PEN3)

### 2.3.3 Pattern creation and sample recognition

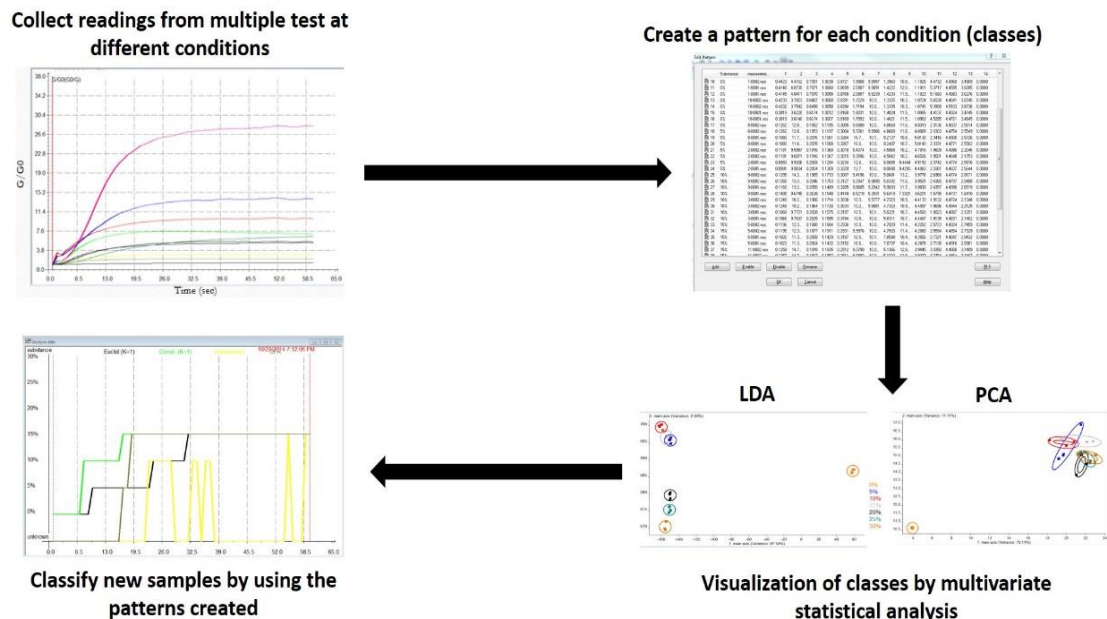
Based on the monitoring time set for the PEN3 method (60 seconds) and the 10 sensors in it, a total of 600 data points are collected per reading (Figure 2.3). As described in Chapter 3 and Chapter 4, each sample was recorded in triplicate and several samples were tested in each test. To reduce the amount of data and to eliminate inconsistency in the data due to instability of the sensors response at the beginning of each reading, only the response of individual sensors in the last second of the measuring time, once the response was consistent, was used for analysis. Examples of measurements with the PEN3 are shown in Figure 2.3. Even with this data reduction, handling large amount of data requires the application of powerful statistical tools.



**Figure 2.3.** Example of the response of the sensor array.



The main goal of applying multivariate statistical analysis is to create a model with patterns that display classes based on a well-known data set. These groups are then correlated with the characteristics of unknown samples measured with the PEN3 under the same conditions for classification. Two tools were evaluated for pattern creation: Principal Component Analysis and Linear Discriminant Analysis and; three algorithms were applied for identification of unknown samples based on the distance between the data collected from the sample and the classes in the pattern created: Mahalanobis, Euclidean and Discriminant Function Analysis (DFA). Figure 2.4 shows the flow diagram for the classification of unknown samples. WinMuster software was used for this purpose.



**Figure 2.4** Flow diagram for sample classification with the PEN3.

### Principal Component Analysis

Principal component analysis (PCA) is recommended to perform on a set of data in preparation for subsequent statistical analyses (Johnson, 1998). For a set of data that are n-dimensional, PCA creates a new n-dimensional space that each dimension, or axis, is orthogonal to the others (Huang, 2011). These new axes are called principal component axes and they are uncorrelated. The principal components (PCs) are in a decreasing order of importance in the sense that the first PC accounts for the maximal variance in the data set, and each succeeding PC accounts for as much of the remaining variance as is possible (Johnson, 1998). Therefore, the first few PCs might have captured most of the variance over the data and can be selected as new variables. The values in PCA space for the variables are called PC scores and can be plotted in 2D or 3D to create patterns. Training patterns from measurements with the PEN3 of similar samples are located close to each other after transformation. Hence, the graphical output is used for determining the difference between groups and comparing this difference to the distribution of pattern within one group. Additional tools can then be used for classification of unknown samples.

### Linear discriminant analysis

Linear discriminant analysis (LDA) is a supervised classification method (Huang, 2011). Data from known classes need to be available before the analysis. Similar to PCA, this data is called training group and it can be used for classification of unknown observations. LDA is designed to create linear functions, which can best separate the

classes in the training group. The linear functions are found by maximizing the ratio of the between-group variance to the within-group variance (Otto, 1999) being this the main difference with PCA. The criterion of observations being one of the classes is made and compared to when an unknown observation is projected to that function and determined which class it belongs to.

#### Identification of unknown samples

Mahalanobis distance is calculated based on how many standard deviations away A is from the mean of B. This distance is zero if A is at the mean of B, and grows as A moves away from the mean (De Maesschalck *et.al.*, 2000). Considering A mean value of an unknown sample and B the mean value for a known class given by PCA or LDA, the identification of the sample can be made by correlating the distance to any class set in the training phase. Similarly, Euclidean distance is used with the difference that instead of using the mean values, it handles all data points from the unknown sample and calculate the distance to the pattern points. Lastly, DFA applies only when LDA is used for pattern creation. LDA is applied to the unknown sample and correlating it to the classes for classification based on  $p$ -values using F-function.

## **Chapter 3. Evaluation of an Electronic Nose for Improved Biosolids Alkaline-Stabilization Treatment and Odor Management**

This chapter has been submitted to Sensors and Actuators B: Chemical.

Adrian Romero-Flores, Laura L. McConnell, Cathleen Hapeman, Mark Ramirez, Alba Torrents.

### **3.1 Abstract**

Electronic nose sensors are designed to detect differences in complex air sample matrices. They are used in the food industry to monitor process performance and quality control. However, no information is available on the application of sensor arrays to monitor process performance of biosolids treatment. The objective of this work was to examine the feasibility of an electronic nose to discriminate between treatment conditions of alkaline stabilized biosolids and to explore its performance by comparison with quantitative analysis of key odorants. Seven quick lime treatment rates from 0 to 30% (w/w) were prepared and the off gas was monitored by GC-MS and with an electronic nose with ten metal oxide sensors. Pattern recognition models were created from the electronic nose data using LDA and PCA. LDA performed better than PCA and showed clear discrimination when single tests were evaluated. However, when the full data set was included in the pattern creation, the discrimination of classes (lime dosages) was not as clear as with single test data. Frequency of recognition was tested by three algorithms with Euclidan and Mahalonbi performing at 81.1% accuracy while DFA at 69.8%. These limitations are shown to be due to the intrinsic variability of the wastewater treatment process and the low specificity of the sensor evaluated in this study. It appears that the electronic nose can discriminate from 0%, 15% and 30% lime

providing the opportunity to create classes of under-dosed and over-dosed, assuming that 15% lime is the dosage needed to safely achieve a pH of 12 required for 99% pathogen reduction for alkaline stabilized biosolids. Full scale application needs to be evaluated considering that the loss in accuracy is expected to increase with the addition of external variables and environmental conditions.

### **3.2 Introduction**

Improved gas monitoring tools are needed in a wide range of fields from the food industry, to disease detection, as well as in many agricultural and environmental engineering applications (Lebrero *et.al.*, 2011; Liu *et.al.*, 2012; Ram *et.al.*, 2015; Loutfi *et.al.*, 2015). Electronic nose technology has evolved over the last decade as a promising approach for applications which require continuous monitoring of specific volatile organic compounds (VOC's) or patterns of odorants. Electronic nose sensors provide several desirable characteristics for the continuous monitoring of complex gas mixtures. These sensors can provide rapid and automated detection of volatile compounds with low operational costs. Sensor data can be processed and used to discriminate between air samples containing complex mixtures of compounds (Feng *et.al.*, 2011).

Electronic nose sensors have successfully been used in the food industry to monitor quality of decaying fruits (Brezmes *et.al.*, 2000) and meats (Ghasemi-Varnamkhasti et al., 2009) as well as processed food such as rice extrudes (Feng *et.al.*, 2011). Application of electronic nose technologies in the environmental engineering field has been reported for the quantification of odors from composting facilities (Sironi *et.al.*, 2007a; Sironi *et.al.*, 2007b and; Delgado-Rodriguez *et.al.*; 2012), within wastewater treatment plants (Stuetz *et.al.*, 1999; Bourgeois and Stuetz, 2002 and; Sohn *et.al.*, 2009) and at receptor locations downwind from treatment facilities (Sironi *et.al.*, 2008). Challenges still exist and are often overseen in research projects as electronic nose sensors can exhibit drift in response due to changing

environmental conditions and over time (Romain and Nicolas, 2009). Sampling techniques (*i.e.* static versus dynamic) and sample characteristics (*i.e.* temperature and humidity) have shown to limit their performance in full scale applications (Knobloch *et.al.*, 2009). Moreover, the concept of using sensor arrays for odor measurements has recently been evaluated by Boeker (2014) concluding in part that the response of an electronic nose should not be correlated to that of human perception of smell and thus the focus of process monitoring rather than odors measurements results in a better goal.

An engineering application where electronic nose technology could be conceptually useful is in biosolids production for both, process monitoring and odor management to support field application programs. Reuse of biosolids has proven to be a sustainable practice where nutrients are safely recycled into the environment while providing utilities with an economical and socially responsible way to dispose a wastewater treatment byproduct (Obreza and O'Connor, 2003; Singh and Agrawal, 2008). However, biosolids material that has not been sufficiently stabilized prior to application in the field can create nuisance odors for nearby residents, leading to complaints and resistance to biosolids application programs.

US Environmental Protection Agency regulations require stabilization of biosolids prior to application for pathogen reduction and vector control (EPA 1993). Alkaline stabilization, which increases the pH of biosolids to 12, is utilized by approximately 20% of the biosolids operations in the United States (Beecher *et.al.* 2007) and has been shown to change the odorant profile of biosolids (EPA 1993). Volatile sulfur compounds and trimethylamine (TMA) were found to be among the main odorants emitted from alkaline stabilization (Rosenfeld *et al.* 1999 and 2000; Kim *et al.*, 2003; Higgins *et al.*, 2003; Chang *et al.*, 2005; Novak *et al.*, 2002; and Laor *et al.* 2011). However, limited information exists to correlate alkaline treatment with specific odorant reduction in biosolids. More precise control over alkali addition could be useful in reducing nuisance odors in the plant and in the field as well as reducing cost by avoiding over dosing.

Objectives of this work were 1) to determine the feasibility of utilizing an electronic nose to discriminate between alkaline-stabilized biosolids treated at different rates; 2) examine the odorant profiles of alkaline-stabilized biosolids treated at different rates in an effort to assess the minimum rates required to achieve key odorant reduction in the plant; and 3) compare the response of the electronic nose with measurements of odorants associated with biosolids to assess the predictive capability and limitations of this technology.

Results are expected to provide important information on the use of commercially-available electronic nose technology to increase the effectiveness of biosolids treatment programs and to reduce odor complaints in the field. This approach may also be useful in other industries such as composting operations to reduce nuisance odors.

### **3.3 Experimental Methods**

#### **3.3.1 Biosolids Sample Collection**

Untreated biosolids were collected from Blue Plains Advanced Waste Water Treatment Plant (Washington, DC, USA). This treatment plant has a capacity of treating 370 MGD (970 L min<sup>-1</sup>) of domestic wastewater and produces approximately 600 wet metric tons of alkaline-stabilized biosolids per day. The untreated biosolids utilized in the study consisted of a dewatered 1:1 blend of primary solids and secondary solids. Samples of approximately 10 Kg were collected using a metal shovel from a sampling port in the screw conveyor system and were stored in 22-L plastic buckets. Samples were immediately transported to the department of Civil and Environmental Engineering of the University of Maryland, College Park for alkaline stabilization.

#### **3.3.2 Alkaline Stabilization**

Aliquots (~500 g) of untreated biosolids were transferred to 4.7 L stainless steel bowls for mixing with calcium oxide (CaO, dry quick lime) and treated at 0 (untreated control), 5, 10,

15, 20, 25, and 30 % CaO by mass. The quick lime utilized in this study is the same industrial grade material utilized in the wastewater plant. Mixing was achieved using a stand mixer (model RKSM500wh, Kitchen Aid, Benton Harbor, MI, USA) at low speed for 3 min with an aluminum flat beater. After mixing, a stainless steel dome was placed over the mixing bowl for headspace analysis with the electronic nose (Section 2.3) and a H<sub>2</sub>S sensor (Section 3.3.3). Head space samples were also collected simultaneously in the last six tests for GC/MS analysis as described in Section 2.2. Temperature and pH (Hach sensION156) were measured in duplicate as minimum using standard methods after head space sampling was completed. A total of 10 alkaline stabilization tests were performed over 18 months between October 2013 and April 2015.

### 3.3.3 Analytical Methods

#### Electronic nose

Refer to section 2.3 for a detailed description of the instrument and methodology used.

#### Hydrogen Sulfide

H<sub>2</sub>S 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 0.5 L min<sup>-1</sup>. Calibration of the sensor was performed annually by the manufacturer using an H<sub>2</sub>S standard gas (Restek Corporation, Bellefonte, Pa., USA) and calibration checks were performed before each test using the same standard gas.

#### Headspace-Gas Chromatography-Mass Spectrometry

Refer to section 2.2 for detailed explanation of the analytical method.



### 3.3.4 Statistical analysis

For electronic nose results, the WinMuster software was used to conduct linear discriminant analysis (LDA) and principal component analysis (PCA) for comparison of alkaline stabilization results. Euclidean distance, Mahalanobi, discriminant function analysis (DFA) algorithms were used to determine the recognition frequency of unknown samples. For this purpose, a sample of 53 readings were taken out from the training data set one by one and tested as unknown for classification by the patterns created. A percentage of positive recognition was calculated for each algorithm. A Student's *t*-test at  $p = 0.05$  was used to compare lime treatments with odorant concentration data collected by GC-MS analysis.

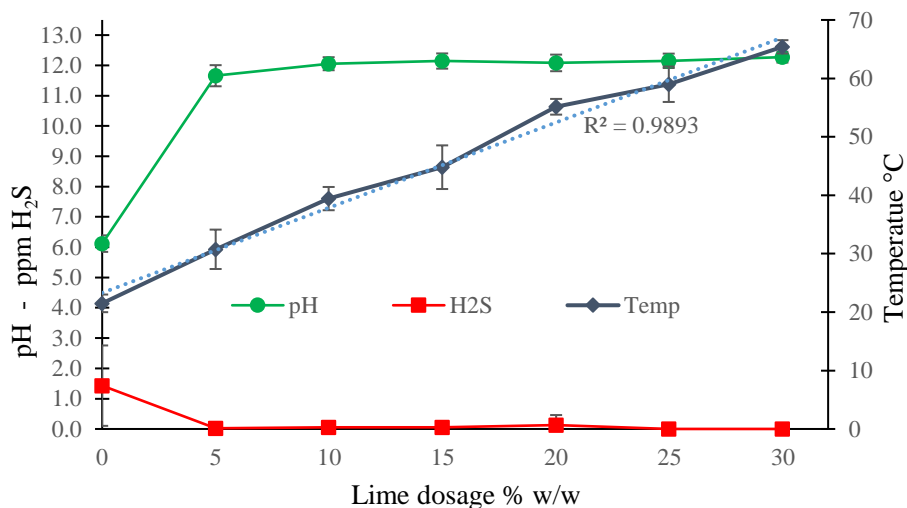
## 3.4 Results and Discussion

### 3.4.1 Trends in pH, Temperature and Hydrogen Sulfide

Comparison of pH results among treatments indicate that addition of only 5% lime increased the pH to 11.66 (SD = 0.35) (Figure 3.1) which is just under the recommended pH 12 established by the U.S.EPA for alkaline stabilized biosolids (1993). At 10% lime and above, pH remained in average between 12.1 and 12.3, clearly illustrating the limitation of pH measurement alone for process control of lime addition. This effect is due to the solubility of CaO which precipitates at pH of 12.44 at 25°C and to a potential alkaline error of pH measurements when working in this range (Cheng 2005). Temperature increased linearly ( $R^2 = 0.989$ ) with the increase in lime dosage (Figure 3.1) due to the exothermic reaction of quick lime. Results of these experiments indicate that for process monitoring, temperature could be used as a more effective indicator of lime addition than pH in plants where alkaline stabilization is utilized.

H<sub>2</sub>S sensors have been used for monitoring both hazardous conditions and process performance (Janpengpen 2007). However, in the case of alkaline stabilization, measurement of H<sub>2</sub>S is of limited value as its pK<sub>a</sub> is 7.05 (Boon 1995). Therefore at even low treatment

levels,  $\text{H}_2\text{S}$  will only be present in the non-volatile ionic form ( $\text{HS}^-$ ). This effect was observed in the current study where  $\text{H}_2\text{S}$  concentrations dropped from 1.4 ppm (SD = 1.3 ppm) in the untreated control to below detection limit in all treatments (Figure 3.1).

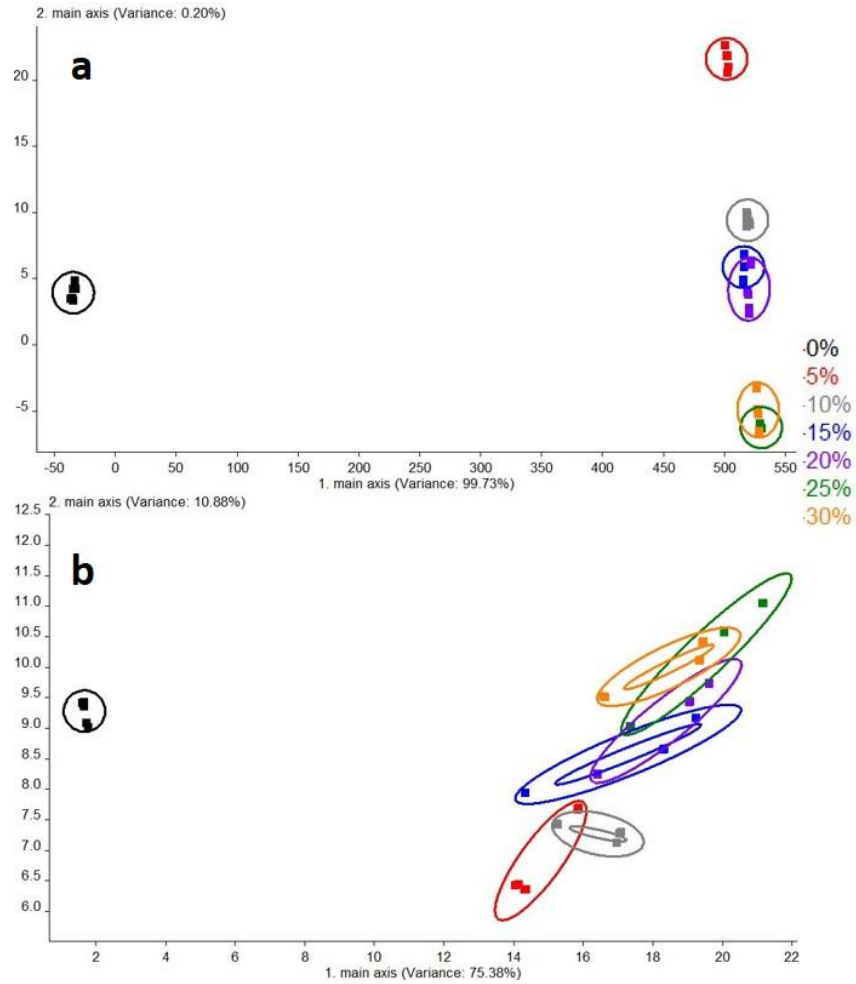


**Figure 3.1** Results of pH, Temperature and  $\text{H}_2\text{S}$  in alkaline stabilized biosolids (average;  $n = 10$ , error bars correspond to the standard deviation). Discrete data. Continuous line for graphic's communication purposes only.

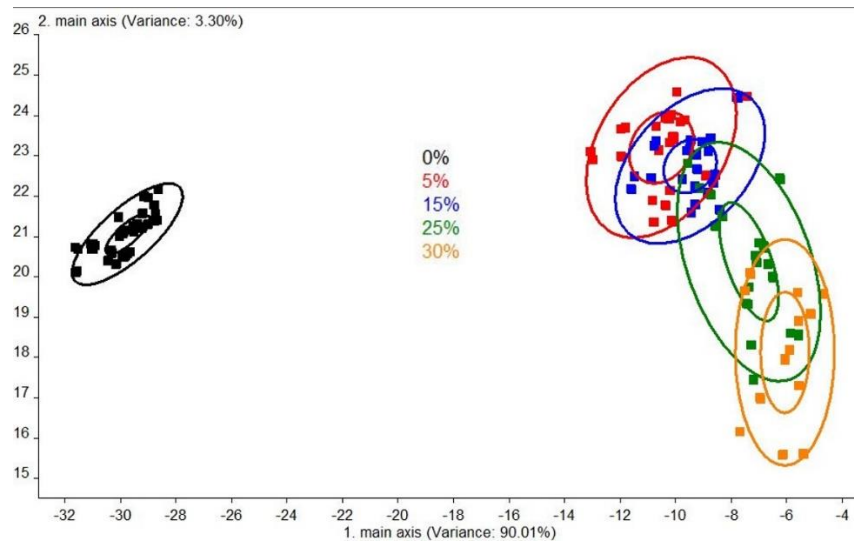
### 3.4.2 Electronic Nose Pattern Recognition

Performance of the PEN3 electronic nose to distinguish between alkaline treatments was evaluated for samples collected on a single day and then across all 10 tests. For single a test data analysis, LDA showed higher discrimination performance (Figure 3.2a) when compared to PCA (Figure 3.2b), accounting for 99.52% of the total variance in a two dimensional plane and an increase in the y-axis value with the increase of lime dosage. A clear difference between untreated biosolids and alkaline stabilized material is seen in both analysis (LDA and PCA). These results were consistently seen for the ten individual tests performed over the duration of this study. Under these conditions, the use of the PEN3 with LDA pattern recognition appears to be a promising method to apply for the monitoring of alkaline stabilization process.

When the full data set was included in the pattern creation, the discrimination of classes (lime treatments) is not as clear as with data from only one test. Using LDA it was possible to create some discrimination showing a separation of classes. The difference between untreated and treated samples is clear, and the 30% lime treatment could be differentiated from 5% and 15% but not from the remaining treatments (Figure 3.6, 10 and 20% results not shown). While some precision in the model appears to be lost with the inclusion of all data, these initial results are encouraging and could be further developed into a process monitoring scheme. It appears that the electronic nose can discriminate from 0%, 15% and 30% lime (Figure 3.3) providing the opportunity to create classes of under-dosed and over-dosed, assuming that 15% lime is the dosage needed in this samples to safely achieve a pH of 12 (Figure 3.1) required for 99% pathogen reduction for alkaline stabilized biosolids (EPA, 1993).



**Figure 3.2** LDA (a) and PCA (b) applied to the same data from a single test



**Figure 3.3** LDA applied to the complete data set.

### 3.4.3 Recognition Frequency of Unknown Samples

The pattern recognition model for the PEN3 was further tested for accuracy by removing sample data from the dataset, recreating the model and then testing the sample removed as unknown. The new model was tested using the unknown reading for classification by three different algorithms available in the WinMuster software. A total of 53 tests were performed showing that the Euclidan and Mahalanobis performed best ones with 81.1% of accurate recognitions followed by DFA with 69.8%.

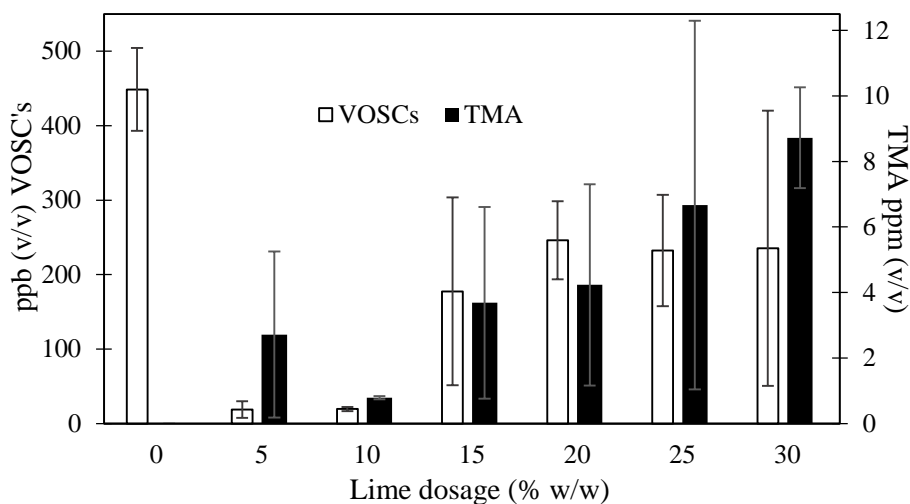
For the readings not accurately classified by Euclidan and Mahalanobis algorithms, the model classified them as a lower lime dosage. Therefore this approach is conservative and protective with respect to lime addition measurements for agricultural field application of biosolids. Results from the DFA algorithm indicate that 90% of the readings were improperly identified as a higher lime dosage, potentially leading to under-dosed biosolids applied in the field. Therefore use of Euclidan and Mahalanobis algorithms are recommended for unknown classification in this application.

### 3.4.4 Odorant profiles of alkaline-stabilized biosolids

Headspace samples from each of the 10 alkaline stabilization tests were analyzed for TMA and eight VOSCs: methyl mercaptan (MT), ethanethiol (ET), propanethiol (PT), buthanethiol (BT), carbonyl sulfide (COS), carbon disulfide (CDS), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) (Table 2.1). TMA concentrations in headspace were below the detection limit in the untreated biosolids and increased with lime dosage corresponding to higher pH values as would be predicted from its pKa of 9.81 (Perrin 1972) (Figure 3.4). Under high pH conditions, TMA is present in its molecular form leading to its volatilization (enhanced by increased temperatures) and a characteristic fishy odor (O'Neil 2006). Enzymatic degradation of acrylamide-based polymer and proteins in the wastewater and

sludge has been found to be a significant source of TMA in biosolids (Kim *et al.*, 2003; Chang *et al.*, 2005).

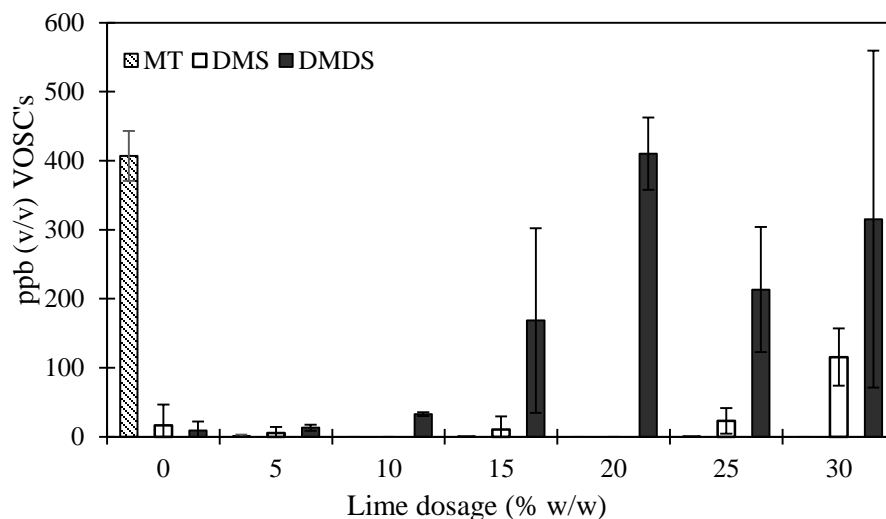
Total VOSCs in headspace were highest in untreated biosolids at >400 ppb. Lower total VOSC concentrations of approximately 20 ppb were observed in the 5 % and 10% lime treatments, suggesting that an increase in pH decreased VOSC levels in headspace. However, total VOSCs were greater in the 15 % lime treatment at 177 ppb and then remained between 235 and 246 ppb at the higher dose rates, in contrast to results observed for H<sub>2</sub>S (Figure 3.1).



**Figure 3.4** Total VOSC's and TMA emitted from alkaline stabilized biosolids treated at different dosages. Error bars represent the standard deviation.

Examining the VOSC results as individual compounds clarified the observations. Only three compounds (MT, DMS, and DMDS) were observed above the limit of detection. The primary VOSC detected in headspace of untreated biosolids was MT (Figure 3.5) at an average of 406 ppb with small concentrations of DMS and DMDS averaging <20 ppb each. In the 5% and 10% treatments, MT is no longer detected in headspace since it has a pK<sub>a</sub> of 10.4 (Serjeant 1979) while DMS and DMDS concentrations remain approximately the same. With increasing lime treatment, the concentration of DMDS was highly variable but appeared to increase averaging between 168 and 406 ppb while concentrations of DMS remained low.

It is unclear if the increased concentrations of DMDS were due to formation from MT or were driven only by increasing temperatures. MT can undergo an acid-base reaction with lime to then form DMDS (Novak *et.al.* 2006). The production of MT that leads to the formation of DMDS primarily occurs from biological degradation of the amino acid methionine. DMS is formed through the methylation of MT and DMDS by MT oxidation (Higgins *et. al.*, 2006; Novak *et. al.*, 2006). Based on odorant profiles of the different lime treatment samples, there is a clear difference in constituents and magnitude between the untreated (primarily MT and H<sub>2</sub>S) and treated samples (primarily DMDS and TMA both increasing with dosage). However, the differences in odorant profile at the higher treatment levels were not dramatic. This supports results observed using the PEN3 sensor where it was more difficult to distinguish between samples at higher dose rates.



**Figure 3.5** Speciation of VOSC's emitted from alkaline stabilized biosolids treated a different dosages. Error bars represent the standard deviation.

### 3.4.5 Comparing electronic nose and GC-MS

The results for pattern recognition and identification of unknown samples suggest that the electronic nose could be successfully tested in a full scale scenario. However, results indicate

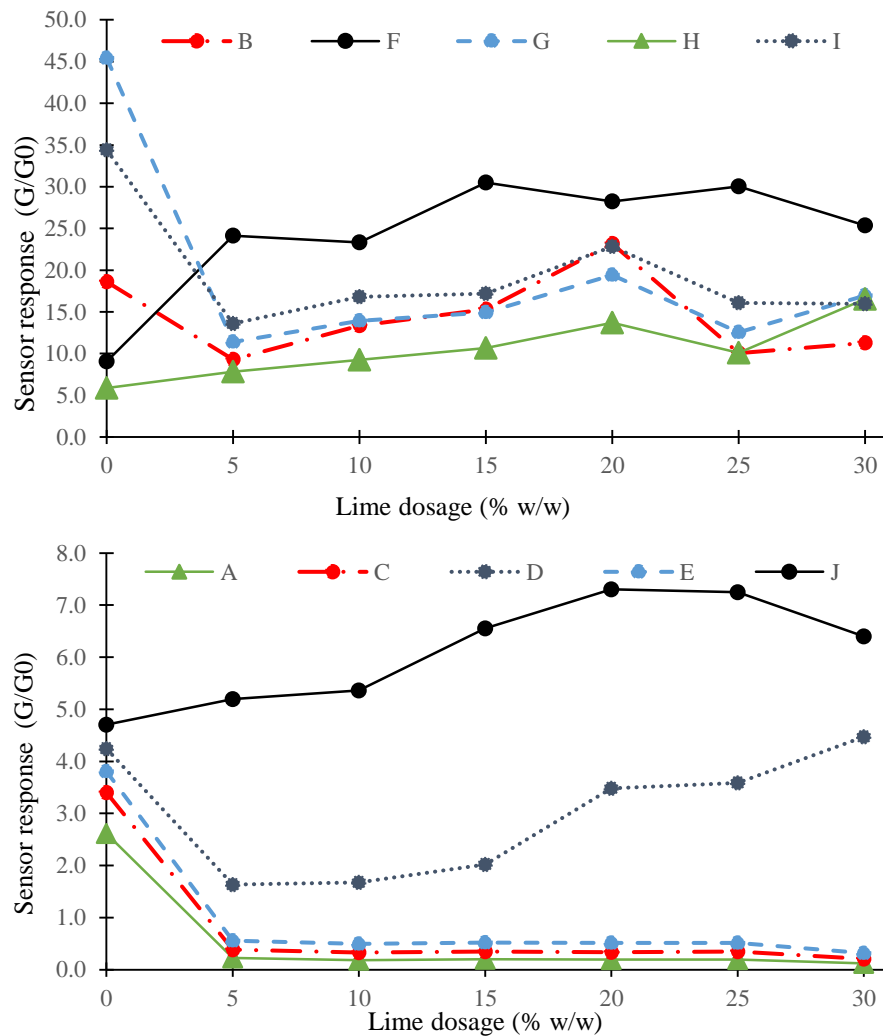
that the electronic nose may have a limited ability to distinguish between the higher lime dosages tested in this research. To further investigate the potential reasons behind this limitation, individual sensor responses examined. Sensors showing significant change over the lime dosages are the ones that respond to sulfur compounds (G and I) (Figure 3.7). These sensors followed similar trend observed for Total VOSC's (Figure 3.4). In addition, sensor F followed a similar trend to that observed for TMA even though its affinity is reported as a broad range and methane (Table 2.2). Methane has not been previously reported in literature as a constituent emitted from alkaline stabilized biosolids without previous anaerobic digestion.

While only three sensors in the electronic nose showed significant change with lime dosage, information from the ten sensors was required to build the best pattern recognition. LDA performs best when a larger data set is utilized optimizing for both the difference between groups and the similarities within each group (Otto, 1999). The high variability in composition of the emissions from alkaline stabilized biosolids does not allow for the creation of a cleaner pattern recognition and subsequent higher accuracy in the classification of unknown samples. The standard deviation of H<sub>2</sub>S concentrations (Figure 3.1), solids content of the untreated material (30.3% TS; SD 5.25% TS) and the TMA emissions, which responds not only to the lime dosage but to the amount and type of polymer commonly used to dewater biosolids and main source of TMA, explain in part the variability in the process. In other words, upstream operation of the biosolids treatment process highly affects the characteristics of the VOC's profile.

Results of the VOSC speciation (Figure 3.5) explained the differences in VOSC profile with treatment, demonstrating a large difference between untreated and treated material, but less difference between the different doses of treatment. A statistical analysis of GC-MS measurement results for DMS, DMDS, MT and TMA by treatment indicates that most of the treatments can be distinguished from each other with the exception of 30% from 25%, 30%



from 20% and 15% from 20% given the high variability of the process (Table 3.1). This indicates that with data from two groups of compounds (VOSC's and TMA), GC-MS was able to distinguish between most of the lime dosages unlike the PEN3 where at least 10 groups of compounds were accounted for. Moreover, including data from other VOC's emitted from biosolids, higher resolution may be achieved and multivariate statistical tools could be applied. However, continuous GC-MS measurements would be expensive and not feasible over the long term.



**Figure 3.6** PEN3 sensors response to different lime dosages in alkaline stabilized biosolids. Average values. Discrete data. Continuous line for graphic's communication purposes only.

**Table 3.1** Calculated  $p$  values for  $t$ -tests at 0.05 significance level comparing VOC's concentrations between lime treatments (as % w/w CaO).

	5%		10%		15%		20%		25%		30%	
0%	<b>0.0000</b>	0.4338	<b>0.0000</b>	0.2425	<b>0.0000</b>	0.7056	<b>0.0000</b>	0.2425	<b>0.0000</b>	0.6716	<b>0.0000</b>	0.1112
	0.4092	<b>0.0059</b>	<b>0.0103</b>	<b>0.0417</b>	<b>0.0255</b>	<b>0.0000</b>	<b>0.0154</b>	<b>0.0000</b>	<b>0.0038</b>	<b>0.0052</b>	0.0598	<b>0.0019</b>
5%	5%		0.2276	0.1849	<b>0.0255</b>	0.5698	0.2276	0.1849	0.2721	0.1089	0.2276	0.0937
			<b>0.0222</b>	0.0689	<b>0.0281</b>	0.5083	<b>0.0160</b>	0.4319	<b>0.0041</b>	0.0999	0.0623	<b>0.0007</b>
	10%				0.1133	0.2263	*	*	0.1021	<b>0.0470</b>	*	0.0813
					<b>0.0453</b>	<b>0.0397</b>	<b>0.0191</b>	0.1106	<b>0.0068</b>	<b>0.0212</b>	0.0750	<b>0.0020</b>
	15%				0.1133	0.2263	0.4149	0.3159	0.1133	0.1097		
					0.0845	0.7818	0.5242	0.2163	0.3357	<b>0.0046</b>		
	20%						0.1021	<b>0.0470</b>	*	0.0813		
							0.1512	0.3548	0.5696	0.0591		
	25%								0.1021	0.1512		
									0.5184	0.3603		
30%												

MT      DMS

DMDS    TMA

**Key**

**Bold** captions indicate  $p$ -values below the significance level of 0.05.

\*No calculation was possible since concentrations in treatments being compared was reported as zero in both cases.

### **3.5 Conclusions**

The portable electronic nose PEN3 was able to discriminate between lime dosages for alkaline stabilized biosolids using LDA when a single sample is tested. However limitations in the pattern recognition and unknown samples classification appeared when a larger data set was included due to the intrinsic variability of the biosolids treatment process and the low specificity of the sensor evaluated in this study.

The results obtained by GC-MS were in agreement with those reported in literature and helped to elucidate the behavior of the pattern recognition via comparison with individual sensor response to different biosolids treatment conditions. Despite the lower sensitivity and resolution of the PEN3 when compared to GC-MS analysis, the demonstrated capabilities for pattern recognition and on-line applicability could motivate full scale testing. However, transitioning from laboratory scale testing to full scale training and deployment of an electronic nose requires intensive investigation and further work is required to assure that sensor array technology is suitable for this type of application where environmental conditions and process variability are important parameters that may affect overall performance of an electronic nose. This work exposed the need for a different and more sensitive sensor array for the monitoring of alkaline stabilized biosolids production process.

### **3.6 Acknowledgements**

Funding support was received from DC Water and Sewer Authority. In addition, a scholarship from the National Council for Science and Technology (CONACyT, Mexico) was awarded to Mr. Romero-Flores for graduate studies. In kind support from ARS-USDA is also greatly appreciated.

## **Chapter 4. Odor characterization of TH-AD and alkaline stabilized biosolids under storage conditions.**

This Chapter is in preparation for submission to the International Journal of Integrated Waste Management, Science and Technology.

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### **4.1 Abstract**

Environmental conditions such as, snow, frozen ground, rain and spring thaw as well as agricultural practices typically make storage of biosolids needed for weeks or months before land application becomes possible. During this period of storage, biosolids may change some characteristics such as odors, which can lead to public opposition to land application. Emphasis has been put in recent years on pre-treatments enhancing anaerobic digestion to increase loading rates and biogas yields, but few scientific studies have addressed this topic to make any conclusions related to odor characterization and control strategies. This work aimed to establish the odor characteristics of THAD biosolids and their changes occurring during storage before final beneficial reuse, and to compare it with three levels of alkaline stabilized biosolids. Odor characterization was achieved by using olfactometry measurements and chemical analysis by GCMS. Target compounds included carbonyl sulfide, methyl mercaptan, ethanethiol, dimethyl sulfide, carbon disulfide, propanethiol, butanethiol, dimethyl disulfide and trimethylamine. Dilution to threshold, recognition threshold, hedonic tone and odor descriptors were reported as

well. Over 28 days period of storage in air tight containers, THAD biosolids showed an increase in dilution to threshold but no correlation was found with the target organic reduced sulfur compounds suggesting that other not-targeted chemicals are being produced while further stabilization is occurring during storage. Alkaline stabilized biosolids reported similar odor concentration but without increasing over time. The fishy odor given by TMA emissions resulted in more offensive and unpleasant odors when compared to THAD. Finally, the presence of furan and three methylated homologues in THAD biosolids is reported, proposing that these compounds are produced during thermal hydrolysis process.

## **4.2 Introduction**

Reuse of biosolids has proven to be a sustainable practice where nutrients are safely recycled into the environment while providing utilities with an economical and socially responsible way to dispose a wastewater treatment byproduct (Obreza and O'Connor, 2003; Singh and Agrawal, 2008).

Storage of biosolids in the field, tanks, basins, or lagoons is a common practice until the time is suitable for final land application (EPA, 2000). Environmental conditions such as, snow, frozen ground, rain and spring thaw as well as agricultural practices typically make storage of biosolids needed for weeks or months before land application becomes possible, particularly in colder climates (Miller *et.al.* 2014). During this period of storage, biosolids may change some characteristics such as odors, which can lead to public opposition to land application.

Odor characterization become of particular importance when designing processes and management strategies for biosolids production and reuse. Sensory measurements employ the human nose as the odor detector, relating directly to the properties of odors as experienced by

humans. Dynamic olfactometry is the sensory measurement of choice for odor assessments in wastewater facilities (Lebrero, 2011). Odor concentrations (dilution to threshold –DT–) are quantified by determining the amount of dilution needed to bring the odorous air sample to its threshold. The higher the threshold value, the more dilution is needed to bring the odor to threshold, thus the stronger the odor. In addition, hedonic tone may be reported as a mean to measure how pleasant or unpleasant an odor is as well as the level of dilution required to characterize the type of smell. Olfactometry measurements are performed by sensory panel members selected according to EN-13725.

Odorous emissions are composed of a complex mixture of hundreds of chemical compounds at ppb and ppt concentrations, which presents a challenge to the sensitivity and separation capacity of gas chromatography (GC). These low concentrations present in odors are very often below the detection limits of most common GC detectors (mass spectrometry and flame ionization), commonly in the parts per billion range. Studying odor compounds in environmental applications (agricultural or wastewater/biosolids), these low concentrations have forced the use of pre-concentration of the odorants either via cryogenic trapping (Trabue, 2008a) or via adsorption into porous polymers or carbon-based adsorbents (Trabue, *et.al.* 2008b; Kim, *et.al.* 2002).

The importance of chemical analysis of odorants resides in the support they provide when studying specific changes and their sources, and to design strategies to improve odor characteristics. Therefore, the need of using chemical analysis of odorants is complementary to olfactometry measurements in order to achieve a complete odor characterization.

Several treatments can be used to produce biosolids. Aerobic digestion, anaerobic digestion (AD), alkaline stabilization, composting and lagoons are among the main technologies used in the United States (EPA, 1995). Each technology produces biosolids with different odor characteristics

and quality. According to an estimate made by Beecher *et.al.* (2007) approximately 66% of the biosolids produced in the US is using anaerobic digestion or alkaline stabilization. Dewatering strategies are commonly used to reduce the amount of material and the cost of hauling. Belt-filters, drying beds and centrifuges are the main ones described in literature (EPA, 1995). These dewatering technologies can lead to odor problems due to shear and re-activation of microorganisms that produce odors.

Novak *et al.* (2002) and Kim *et al.* (2003) examined the mechanism of odor generation in limed biosolids. The main difference between anaerobic digested biosolids and limed biosolids is the presence of TMA due to an increase in the pH that will lead to TMA emission. Also, the sulfur compounds profile changed from AD process with a reduction of H<sub>2</sub>S and an increase in organic reduced sulfur compounds. Kim (2003) described the effect of upstream processes on the odor profile of the final material where untreated biosolids storage increased odor problems, and the addition of cationic polymer was the main source of amine compounds. The breakdown of cationic polymer to produce amines was further described by Chang *et al.* (2005).

Emphasis has been put in recent years on pre-treatments enhancing AD to increase loading rates and biogas yields (Carlsson *et.al.* 2012). Several methods have been studied with some of them already operating at full scale. This pretreatment methods can be classified in mechanical, thermal, chemical and biological (Ariunbaatar *et.al.* 2014). Thermal hydrolysis (TH) prior anaerobic digestion to produce high quality biosolids is a promising technology that has recently been introduced in the United States. In Europe, more than 30 facilities already use this technology and the impact on the odor reduction seems to be clear. However, few scientific studies have addressed this topic to make any conclusions related to odor control. In an evaluation of enhance digestion processes for biosolids treatment, Murthy *et al.* (2009) concluded that TH may have the

potential to produce odorous material in addition to the enhanced AD, higher solids loading and increase in biogas production. The advantage of the thermal hydrolysis pretreatment is that high solids can be achieved with belt filter press dewatering that are equivalent to centrifuge dewatering. Belt filter press cakes have generally been shown to have lower odors and less likelihood of indicator bacteria increases in the cake which further helps the thermal hydrolysis process minimize risks related to odors and indicators (Higgins *et.al.* 2007). Electro-Dewatering of anaerobically digested biosolids showed better odor characteristics under storage conditions when compare with heat drying (Navab-Daneshmand *et.al.* 2014). However, literature on the impact of these pre-treatments on the quality of biosolids from an odor perspective is still limited.

The specific objectives of this research were 1) to examine the behavior of target odorous compounds and other VOC's from THAD biosolids and compare it with alkaline stabilize biosolids, both under storage conditions; 2) to characterize THAD and alkaline stabilized biosolids by olfactometry measurements; and 3) to determine the feasibility of an odor index from the target compounds to correlate with olfactometry measurements. This work is expected to establish the odor characteristics of THAD biosolids and their changes occurring during storage before final beneficial reuse.

## **4.3 Experimental methods**

### **4.3.1 Biosolids sampling collection**

Sludge samples were collected from Blue Plains Advanced Waste Water Treatment Plant (Washington, DC, USA). This treatment plant has a capacity of handling 370 MGD (970 L min<sup>-1</sup>) of domestic wastewater and produces approximately 600 wet metric tons of alkaline-stabilized biosolids per day. TH-AD biosolids were collected after final dewatering by belt filter press at



full scale. For alkaline stabilization, pre-dewatered sludge was collected from full scale before going to thermal-hydrolysis and consisted of a 1:1 blend of primary solids and secondary solids. Samples of approximately 30 Kg were collected in 22-L plastic buckets for each treatment using a mechanical sampling port in the piping system. Untreated samples were immediately alkaline stabilized as described below.

#### 4.3.2 Alkaline stabilization

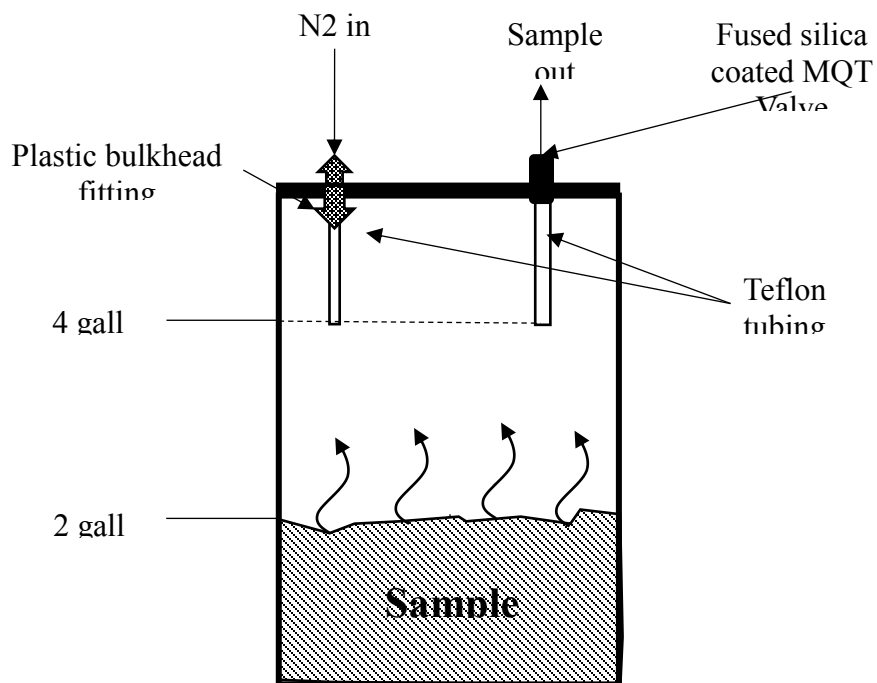
28 kg of untreated biosolids were transferred to a 38L stainless steel bowl for mixing with calcium oxide (dry quick lime) and treated at 5, 15, and 25 % CaO by mass. The quick lime utilized in this study is the same industrial grade material utilized in the wastewater plant. Mixing was achieved using an industrial mixer (model Globe SP40) at low speed for 5 min with an aluminum flat beater. Temperature and pH were measured in duplicate as minimum using standard methods after mixing was completed. Aliquots (7 kg) of lime stabilized biosolids were weighted and placed in containers fitted for storage simulation.

#### 4.3.3 Storage Simulation

20 liters HDPE containers with air tight lids were used for storage of biosolids. Two ports, a Teflon bulkhead and a Silonite Micro-QT valve (Entech Instruments Inc., Simi Valley, Ca., USA), were adapted for headspace sampling. A schematic of these containers can be seen in Figure 4.1. Two storage simulation tests were performed. First, comparison between storage of alkaline stabilized and TH-AD biosolids was evaluated. 7 kg of three alkaline stabilized biosolids (5, 15 and 25% CaO by mass), a control (untreated material) and TH-AD biosolids were placed in the containers in four replicates and closed. For each treatment, two containers were used for

sampling for GC-MS analysis, one for Olfactometry and the fourth one for H<sub>2</sub>S analysis, randomly selected. In addition, two empty containers were used as blanks. Headspace sampling occurred in days 1 through 7, 14, 21 and 28. After the last sampling event (day 28), the containers were opened and pH, temperature and total and volatile solids were measured. Containers were stored undisturbed in a room with artificial light, no wind and an average temperature of 24.1°C ( $\pm 3.5$ ).

In a second experiment, 7 kg of TH-AD biosolids were placed in 28 storage containers and closed. After the first set of samples were taken (time = 0 days), 4 containers were left opened to simulate field storage of biosolids. The rest of containers (24) were kept closed and used in a semi-sacrifice test with sets of four replicates used for day 0 and 7, day 1 and 14, day 2 and 21, day 3, day 4 and 28, and for day 6. Total solids, volatile solids and pH were determined at days 0, 3, 7 and 28. Storage conditions were similar to those in the first experiment with average temperature of 22.1°C ( $\pm 4.1$ ).



**Figure 4.1.** Schematic of storage containers and sampling ports.

#### 4.3.4 Olfactometry sampling and analysis

Dynamic headspace method was used to sample from the storage containers for olfactometry analysis. Nitrogen gas was input through the Teflon port at a rate of 2 L/min for 1 minute while the sample was collected from the Micro-QT valve into a 10L Tedlar bag. The volume collected was used to pre-condition the sampling bag. Using a suction pump (224-PCXR4, SKC, Eighty Four, Pennsylvania), the bag was emptied and the sampling was resume for 4 more minutes for a total sample volume of 8 L. Samples in Tedlar bags were shipped overnight to St. Croix Sensory (Lake Elmo, Minnesota) for olfactometric analysis. The detection and recognition threshold concentrations of each sample were determined by an odor panel using a dynamic olfactometer (AC'SCENT). The procedures for sensory evaluation complied with industry standards (ASTM E679, 2004; EN13725, 2003). The odor panel presentation rate was 20 L/min to satisfy both ASTM E679 and the EN13725 standards. Odor descriptors and the hedonic tone of each sample were reported as well.

#### 4.3.5 Headspace sampling for GCMS analysis. GCMS analysis.

Refer to section 2.2 for detailed explanation of the analytical method.

#### 4.3.6 H<sub>2</sub>S analysis with Teledyne

Hydrogen sulfide emissions were monitored on-site with API-101E analyzer (Teledyne Instruments, San Diego, CA) equipped with an internal sampling pump a rate of 600 mL/min for 5 minutes. Dynamic headspace was used to monitor H<sub>2</sub>S using nitrogen as carrier gas. The API-101E determines the concentration of hydrogen sulfide in a sample gas drawn through the instrument. In the sample chamber the H<sub>2</sub>S in the sample gas is converted into SO<sub>2</sub> which is

then exposed to ultraviolet light causing the SO<sub>2</sub> molecules to change to an excited state (SO<sub>2</sub>\*). As these SO<sub>2</sub>\* molecules decay back into SO<sub>2</sub>, they fluoresce. The instrument measures the amount of fluorescence to determine the amount of SO<sub>2</sub> is present in the sample chamber and by inference therefore the amount of H<sub>2</sub>S present in the sample gas. The calibration range of the analyzer was set between 0.1 and 15 ppm.

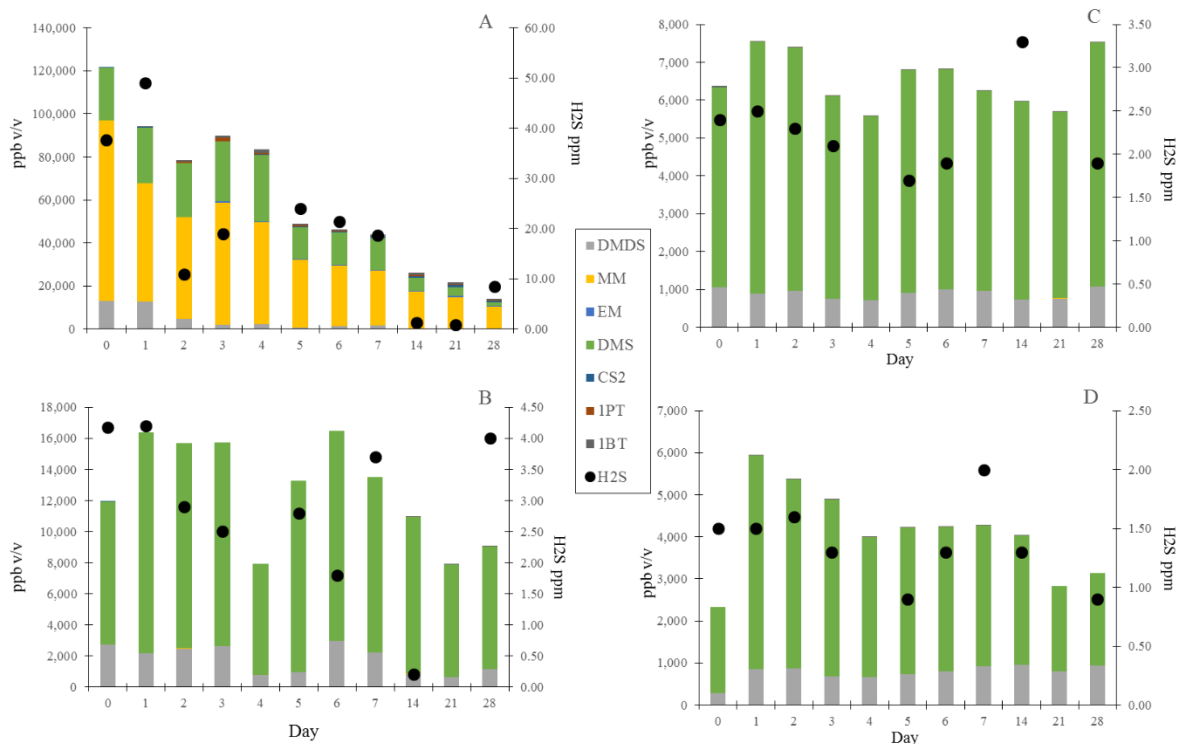
#### **4.4.Results and discussion**

##### **4.4.1 Chemical analysis**

###### *Alkaline stabilized biosolids.*

Analysis by GC-MS and using the API-101E analyzer provided with a profile of target compounds emitted from each treatment under storage conditions. Figure 4.2 shows the results obtained from the alkaline stabilized biosolids where MT and H<sub>2</sub>S were the main compounds in untreated material (Figure 4.2a) with very high concentrations in the order of 80 ppm and 40 ppm, respectively. Both concentrations are above the linear range reported for their calibration curves and the accuracy of these concentrations decreases. For untreated material, the concentration of MT, DMS and DMDS decreased over time presumably due to anaerobic conditions under storage with conversion to H<sub>2</sub>S (Du et. al. 2012, Higgins et.al. 2006). However, increase in H<sub>2</sub>S concentrations was not observed. Overall erratic concentration readings from the API-101E throughout the tests and across treatments bring the conclusion of not reliable H<sub>2</sub>S results. This lack of consistency and accuracy were believed to be due to the fact that the API-101E analyzer is designed for ambient air concentrations and the nature of the samples coming from the storage containers and sampling technique used in this study differ greatly from the recommended application of the analyzer.

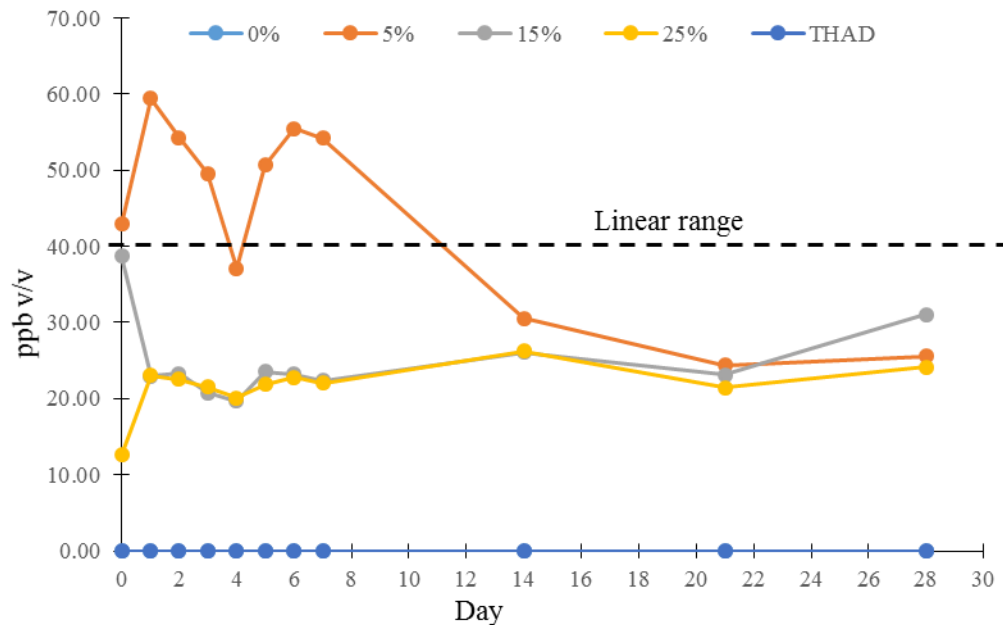
Methyl mercaptan has a pKa of 10.6 at 25°C (Tsonopolus et. al. 1976) and therefore is ionized when CaO is added increasing the pH to 12 and above with as much as 5% of CaO (Figure 4.2b), making MM unavailable to be emitted and was not observed in alkaline stabilized biosolids. No clear trend was observed in DMS and DMDS concentrations over time from the storage of alkaline stabilized material but concentrations of DMS decreased from a range of 7 ppm to 14 ppm in 5% CaO to a range of 2 ppm to 6.5 ppm in 15% and 25% CaO (Figures 4.2c and 2d).



**Figure 4.2.** VOC's and H<sub>2</sub>S from alkaline stabilized biosolids treated at different dosages and under storage conditions. a) Control (0%lime), b) 5% lime, c) 15% lime, and d) 25% lime.

As previously reported for alkaline stabilized biosolids (Kim *et al.*, 2003; Chang *et al.*, 2005, Laor et. al 2011) TMA becomes present in emissions when pH of the material is above

9.81. In this conditions, TMA is present in its molecular form leading to its volatilization (enhanced by increased temperatures) and a characteristic fishy odor (O'Neil, 2006). Enzymatic degradation of acrylamide-based polymer and proteins in the wastewater and sludge has been found to be a significant source of TMA in biosolids (Kim *et al.*, 2003; Chang *et al.*, 2005). Figure 4.3 confirms this was the case in this study where TMA was not observed in untreated material nor in TH-AD (pH of 6.55 and 8.6, respectively) but high concentrations were found in all three treatments with CaO at pH above 12.



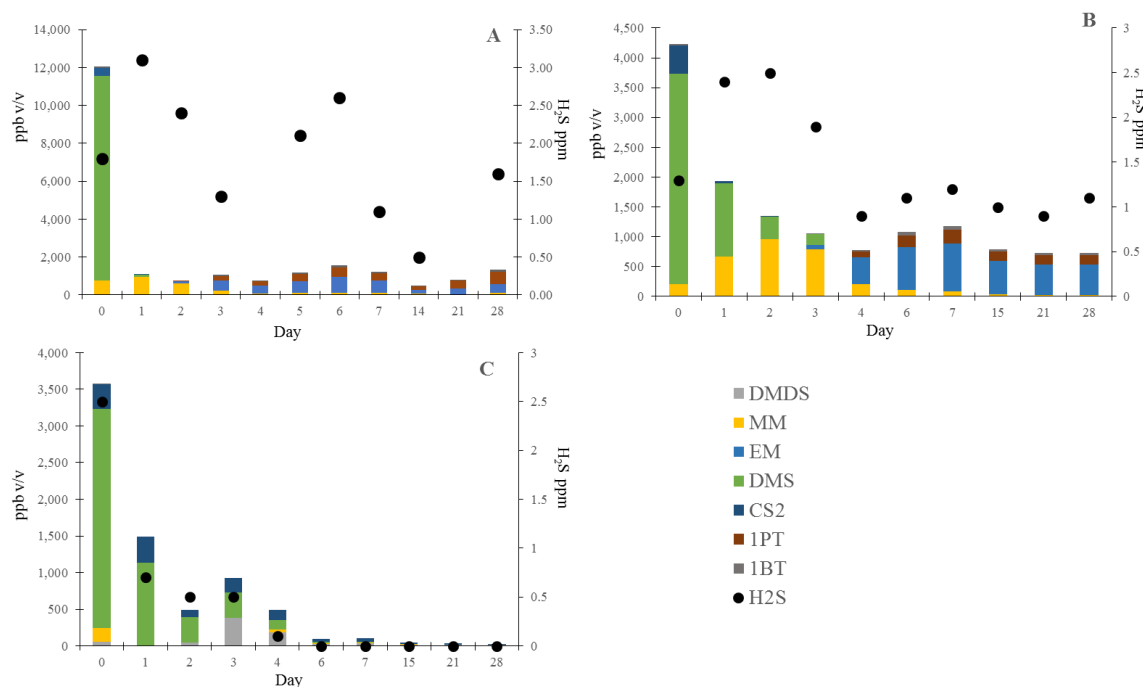
**Figure 4.3.** TMA concentrations emitted from biosolids under storage conditions. Percentage of grams of CaO/grams of wet sludge. THAD: Thermal Hydrolysis-Anaerobic Digestion.

#### Thermal hydrolyzed-anaerobic digested biosolids

Initial concentrations of total VOSC's from THAD biosolids differ between the two test performed, as shown in Figure 4.4, with 12,060.5 ppb in test one to 4,135.1 ppb in test two. VOSC's levels are consistent between the replicates of closed storage and open field storage in the second test (Figure 4.4b and 4.4c). Chemical profile and concentrations were similar over

time in both tests, making the results from of non-sacrificed samples comparable to those from the sacrificed samples test. DMS is the main compound emitted from THAD biosolids at initial time with presence of MM and CS<sub>2</sub>, the later likely formed from the interaction of H<sub>2</sub>S and CO<sub>2</sub> during anaerobic digestion (Heinen and Lawers, 1996). Increase in MM and a decrease in DMS over the first two days (Figure 4.4a and 4.4b) suggests microbial activity under anaerobic conditions, given that in such conditions DMS is de-methylated to MM (Kiene et. al. 1986). A decrease in MM after day 3 with an increase in EM and PM was also observed. The latter compounds have been included in some studies (WERF 2003) but their presence has not been reported, this may be to the fact that analytical techniques for mercaptans analysis are complex and highly specialized. It has been shown that the methylation of mercaptans produce sulfides (Kienes and Hines, 1995) and the presence of these two mercaptans are presumed to be from the methylation of hydrogen sulfide rather than methylation of MM and EM to produce EM and PM, respectively. However, although short chain alkanes were present in the samples which could have reacted with H<sub>2</sub>S, their rol as methyl donor group has not been reported. Finster et. al. (1990) suggested that methoxylated aromatic compounds such as syringic acid could be a source of methyl groups for the methylation of sulfides in marine and freshwater anoxic sediments. Further research on the methylation of H<sub>2</sub>S to produce EM and PM under storage of biosolids is needed.

DMS is the prevalent VOSC's from THAD in open field storage with declining concentrations over time due to volatilization, data shown in Figure 4.4c. No MM is produced in these samples due to the lack of anaerobic conditions. Moreover, an increase in DMDS in day 3 and 4 confirms that DMS undergoes oxidation unlike the observed de-methylation to MM in the stored samples.



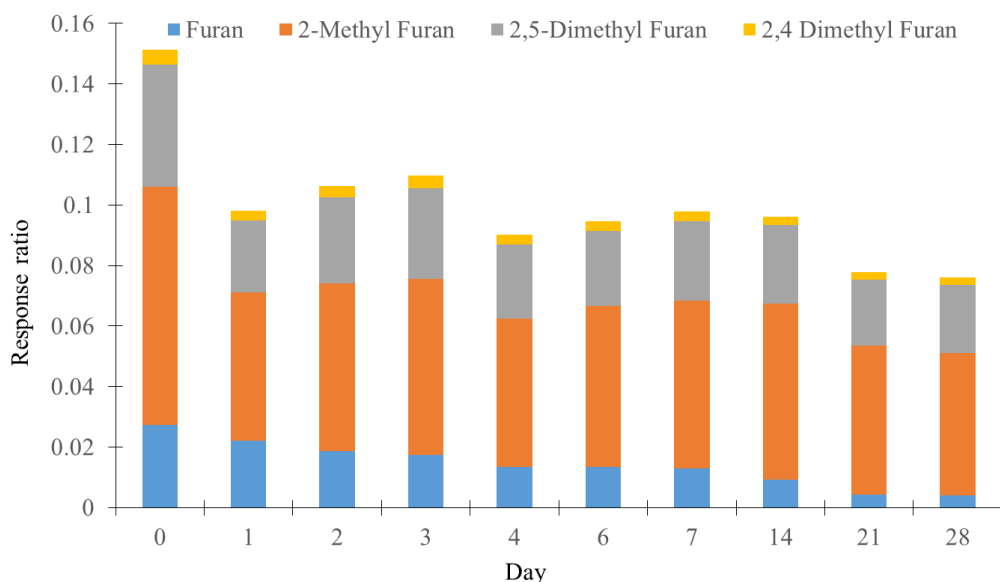
**Figure 4.4** VOSC's and  $H_2S$  from THAD biosolids under storage conditions. a) Replicate 1, b) Replicate 2, and c) Open field storage.

Other compounds were identified in the samples using National Institute of Standards and Technology MS library (NIST) and are listed in Table 4.1. One group of compounds of special interest and found in TH-AD biosolids in this study are furans and its methylated analogues. Furan is an aromatic hydrocarbon emitted mainly by biomass burning and the combustion of fossil fuel (Villanueva *et.al.* 2007; Stockwell *et.al.*, 2014) and as a byproduct of Maillard reaction, a chemical reaction between an amino acid and a reducing sugar such as glucose and fructose in the presence of heat, involved in the production of aromas and flavors (Hofmann, 1998; Mottram, 1998) and thus, potentially providing odors to the final biosolids. However, different pathways for production and degradation of furan and its methylated analogues have been reported (Kuhn *et.al.*, 1989; Villanueva *et.al.*, 2007; Vranova and Ciesarova, 2009).



Presence of chlorinated benzofurans and dioxins in biosolids has been described in literature (Lakhwinder *et.al.*, 2008; Bright and Healey 2003; O'Dette, 2002; Oberg *et.al.*, 1992) with *in-situ* formation from pentachlorophenols (Oberg *et.al.* 1992), incineration and from atmospheric deposition (Jones and Sewart, 1997) as potential sources.

No analytical method to quantify furans was available at the time of this study. However, Figure 4.5 shows the average of the response ratio for the peak area of four furans found over the peak area of the internal standard normalized by the sample volume injected into the GC-MS system. Both tests were considered. Furan decreased over the duration of the study unlike methylated furans, which remained stable due to its lower reactivity (relative to furan) under anaerobic conditions (Kuhn, 1989). No furans were found in the control nor in alkaline stabilized biosolids suggesting that these compounds were formed during THP from thermal degradation of organic matter. However, no correlation was found between these compounds and odor measurements from TH-AD biosolids, as shown in section 4.4.2.



**Figure 4.5** Furans speciation from THAD biosolids under storage conditions. Ratio of peak area: furans over internal standard.

Table 4.1 VOC's identified in THAD and alkaline stabilized biosolids under storage.

<b>Compound</b>	<b>Control</b>	<b>5%</b>	<b>15%</b>	<b>25%</b>	<b>THAD1</b>	<b>THAD2</b>	<b>THAD Open</b>
Acetone	P	P	P	P	P	P	P
2-Butanone	P	P	P	P	P	P	P
2-Pentanone	No ID	No ID	No ID	No ID	P	P	P
Isobutane	No ID	No ID	No ID	No ID	P	P	P
Propane	No ID	No ID	No ID	No ID	P	P	P
Butane	No ID	No ID	No ID	No ID	P	P	P
Pentane	No ID	No ID	No ID	No ID	P	P	P
Hexane	No ID	No ID	No ID	No ID	P	P	P
Octane	No ID	P	P	P	P	P	P
Decane	No ID	P	P	P	No ID	No ID	No ID
Isopropyl alcohol	P	P	P	P	No ID	No ID	No ID
2-Butanol	P	P	P	P	No ID	No ID	No ID
2-Pentanol	P	No ID	No ID	No ID	No ID	No ID	No ID
Benzene	P	P	P	P	P	P	P
Toluene	P	P	P	P	P	P	P
Ethyl Benzene	P	P	P	P	P	P	P
p-Xylene	P	P	P	P	P	P	P
Limonene	P	P	P	P	P	P	P

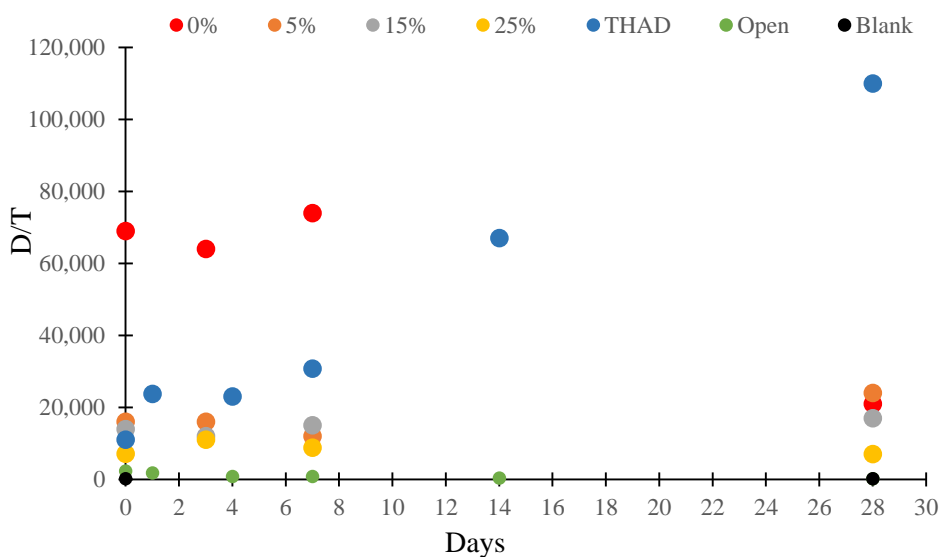
P Present

No ID No identified

#### 4.4.2 Olfactometry

Dilution to threshold for all treatment are reported in Figure 4.6. All three alkaline stabilized biosolids reported similar levels of odors measure by the panelist however, an increase is seen from 5% CaO treatment going from 16,000 D/T to 24,000 D/T over the 28 day storage period which indicates that full stabilization was not achieved. Volatile solids destruction for 5% CaO in the storage time was 22.5% and pH decreased from 12.4 (SD .16) to 11.9 (SD 0.035) consistent with the statement of stabilization. However, this dynamic is not seen in VOSC's from

Figure 4.2 nor in TMA emissions and therefore other compounds may have been produced and are responsible for the increase in odor concentration (Figure 4.3). The odor descriptors presented in Table 4.2 for 5% CaO suggests similarly, a fishy odor characteristic of the presence of TMA is consistent with the concentration measured and a medicinal descriptor at the end of the storage time (day 28) indicates that additional compounds not measured in this study may be increasing the Dilution to Threshold. This medicinal descriptor is seen at day 28 in all treatments, including THAD. The blank (empty container) did not presented these characteristics which eliminates the possibility of background odor from the containers. Some chemicals that commonly produce this character are phenols (Chen *et.al.*, 2009; Strube *et.al.*, 2009).

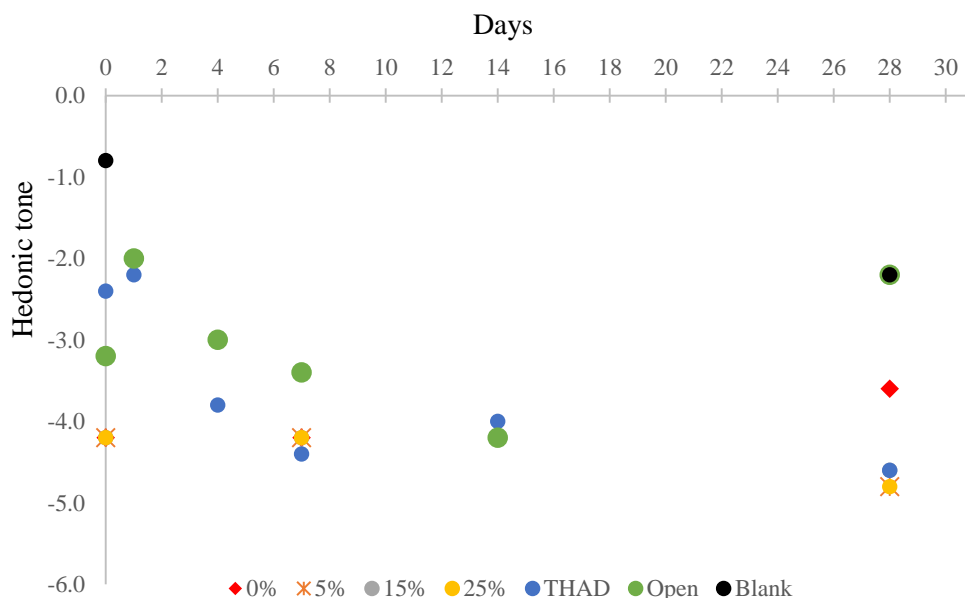


**Figure 4.6** Dilution to threshold of air samples from biosolids under storage conditions. Percentage of grams of CaO/grams of wet sludge. THAD: Thermal Hydrolysis-Anaerobic Digestion.

Concentrations of TMA for 15% and 25% CaO did not decrease over the storage period (Figure 4.3) whereas the fishy smell reported in the olfactometry results was not present for these treatments. A masking effect by the medicinal descriptor may be covering the fishy smell. The

main descriptor is still offensive and the hedonic tone shown in Figure 4.7 suggest that alkaline stabilization produces the most unpleasant odor from the treatments tested in this study.

A VSR of 21.8% was observed from THAD biosolids under storage conditions. This reduction even after an efficient anaerobic process is indicative of further stabilization under storage and was reflected in the increase in the dilution to threshold reported in Figure 4.6. VOSC's did not increase during the time of this study and an unpleasant (HT = -4.6) offensive and chemical descriptors only do not allow for correlation to specific group of compounds emitted causing this increase in odor. Field application of stored THAD biosolids could lead to public complaints due to the evident increase in D/T found in this study and further management of this stored material would be required. On the other hand, THAD stored in the open field showed low D/T values in the order of 1,400 to 110 over the 28 day period being earthy character the second most predominant one. At the end of the storage period, the THAD in the open field showed similar olfactometry characteristics to that of the blank.



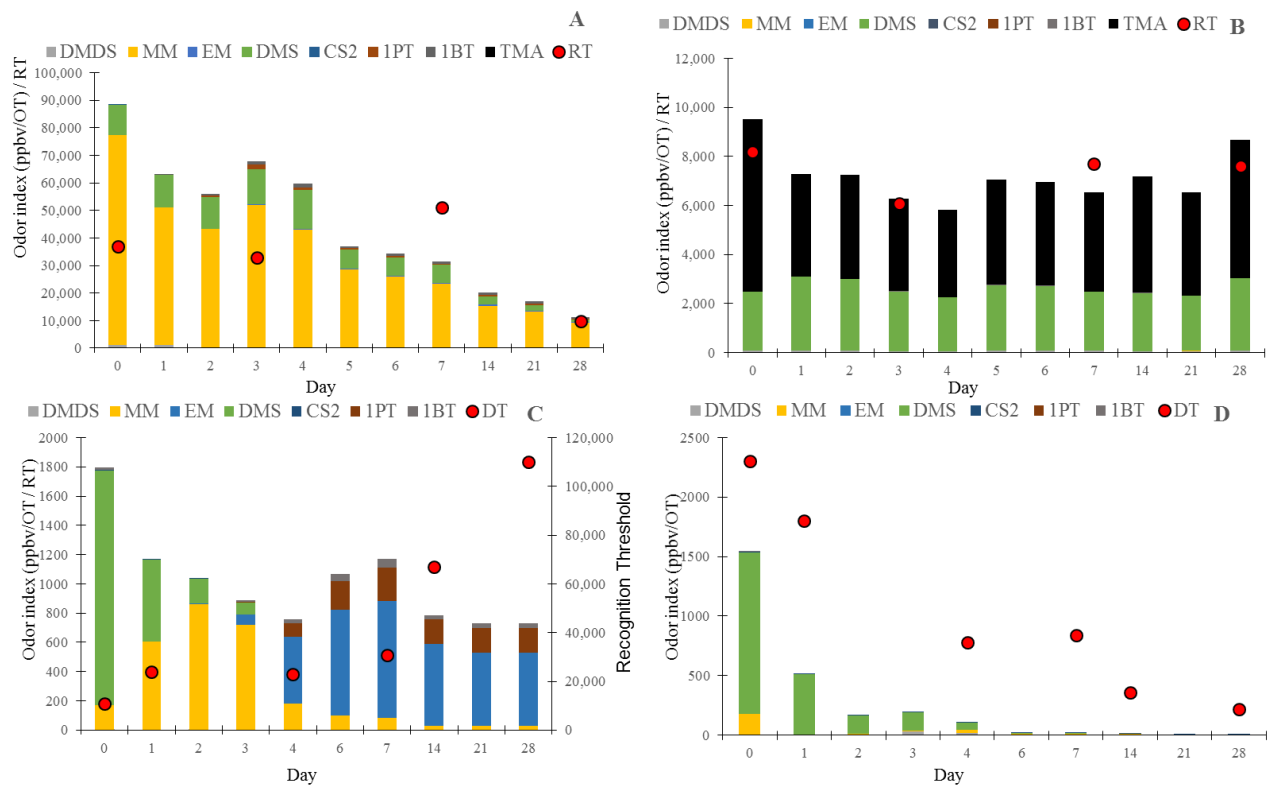
**Figure 4.7** Hedonic tone from biosolids under storage conditions. Percentage of grams of  $\text{CaO}_2$ /grams of wet sludge. THAD: Thermal Hydrolysis-Anaerobic Digestion.

**Table 4.2** Odor descriptors of biosolids at different treatment under storage conditions

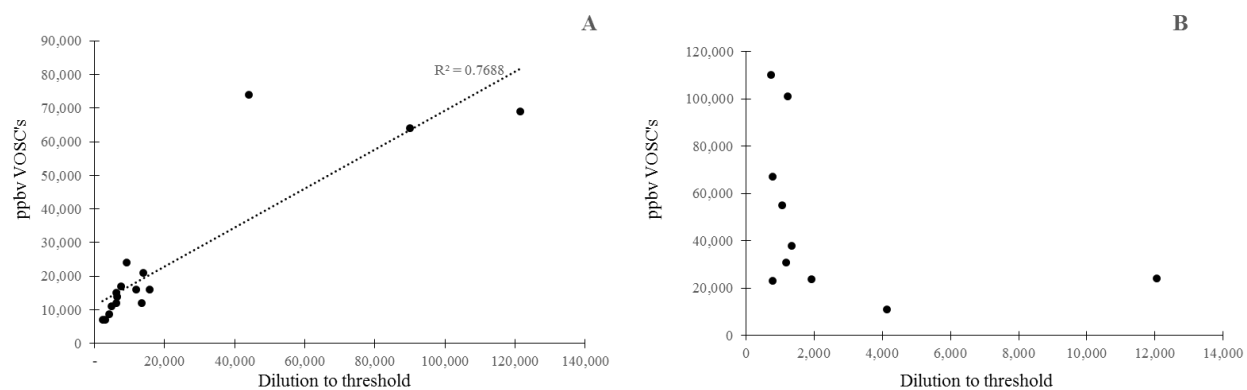
Day	0% CaO <sub>2</sub>	5% CaO <sub>2</sub>	15% CaO <sub>2</sub>	25% CaO <sub>2</sub>	THAD1	THAD2	Open	Blank
0	Offensive, Earthy	Offensive, Fishy, Earthy	Offensive, Fishy, Earthy	Offensive, Fishy, Earthy	Offensive, Chemical, Vegetable, Earthy	Offensive, Chemical, Vegetable, Earthy	Offensive, Chemical, Vegetable, Earthy	Chemical, Earthy, Floral, Offensive
1						Offensive, Chemical, Earthy	Offensive, Chemical, Earthy, Vegetable	
4						Offensive, Chemical, Fishy, Vegetable	Offensive, Vegetable, Chemical Earthy,	
7	Offensive, Earthy	Offensive, Fishy, Earthy	Offensive, Fishy, Earthy	Offensive, Fishy, Earthy	Offensive, Chemical, Earthy	Offensive, Chemical, Earthy	Offensive, Chemical, Medicinal, Vegetable Offensive, Earthy,	
14						Offensive, Chemical, Earthy	Vegetable, Chemical	
28	Offensive, Medicinal, Chemical	Offensive, Medicinal, Fishy, Earthy	Offensive, Medicinal, Chemical	Offensive, Medicinal, Earthy	Chemical, Offensive, Medicinal	Offensive, Chemical, Earthy, Medicinal	Offensive, Earthy, Chemical, Medicinal, Vegetable	Chemical, Offensive, Earthy, Vegetable

#### 4.4.3 Odor index

In order to better visualize the relationship between the concentration of the target compounds measured in this study with the Olfactometry characteristics reported for the same samples, an odor index was created by dividing the concentration of each compound by the odor threshold reported in Table 1.1. This ratio (odor index-OI-) was compared to the recognition to threshold. Figure 4.8a shows that the reported RT for the untreated control is below the calculated OI. The main compound increasing this index in the control is MM. Alkaline stabilized material at 15% CaO (Figure 4.8b) showed that the index calculated based mainly on DMS and TMA correlate well with the RT reported for this sample indicating that these two compounds are the responsible ones for the odor characteristics of alkaline stabilized biosolids. Odor index for THAD did not account for the levels of RT reported over the duration of the test (Figure 4.8c and 4.8d) confirming that the main odor causing compounds emitted from this treatment are not the ones in the target list presented here. This is further represented in Figure 4.9, where the correlation between VOSC's and DT was made for alkaline stabilized biosolids (Figure 4.9a) and THAD material (Figure 4.9b). Finally, a decrease in the RT along with the concentration of target compounds in THAD stored in the open field responds to a volatilization and further stabilization of this material under aerobic conditions.



**Figure 4.8** Odor index for biosolids under storage conditions. Based on VOSC's. a) Control, b) 15% lime, c) THAD, d) THAD open storage.



**Figure 4.9** Correlation of DT and VOSC's. a) Limed biosolids, b) THAD.

## **4.5 Conclusions**

Odor characterization of two types of biosolids was possible using olfactometry measurements and chemical analysis by GCMS. The changes in the characteristics of biosolids under storage conditions was also monitored.

THAD process produced biosolids with similar odor concentrations to alkaline stabilization when measured by DT but with different characteristics and less offensive measured by hedonic tone. The fishy odor from alkaline stabilized biosolids given by TMA drove the unpleasantness whereas MM was reported in high concentrations in THAD before storage. An increase in DT over the storage time was observed for THAD biosolids. No correlation with reduced sulfur compounds and the increase in DT was found and there's still a need to further examine the chemicals being produced from the degradation of organic matter (VSR), which are likely to be causing the increase in the odors from THAD biosolids. The use of an odor index based on VOSC's and TMA is not recommended for THAD but worked well for alkaline stabilized biosolids. Finally, the presence of furan and three methylated homologues in THAD due to the high temperature and high pressure nature of the process was reported.

## **4.6 Acknowledgements**

Funding support was received from DC Water and Sewer Authority. In addition, a scholarship from the National Council for Science and Technology (CONACyT, Mexico) was awarded to Mr. Romero-Flores for graduate studies. In kind support from ARS-USDA is also greatly appreciated.



## **Chapter 5. Utilizing GC-MS and an electronic nose for the characterization of key odorants from TH-AD and alkaline stabilized biosolids after simulated field application.**

This Chapter is in preparation for submission to Atmospheric Environment.

Adrian Romero-Flores<sup>a</sup>, Laura L. McConnell<sup>a</sup>, Cathleen Hapeman<sup>b</sup>, Mark Ramirez<sup>c</sup>, Alba Torrents<sup>a</sup>.

### **5.1 Abstract**

Public complaints due to biosolids field applications are a result of odor causing compounds being released from biosolids followed by transport to sensitive populations. Electronic noses are arrays of electronic sensors capable of detecting and differentiating complex mixtures of volatile compounds. However, no application of the electronic nose to monitor key odorants from the field application of biosolids has been reported. Objectives of this work were 1) to compare target odorants profiles from THAD and alkaline-stabilized biosolids after field application to assess the potential for public complaints; and 2) to determine the capabilities of an electronic at recognizing variations in the time after biosolids application. Results are expected to provide important information on the use of commercially-available electronic nose technology to support biosolids management programs. Surface field application was simulated under controlled conditions for three levels of alkaline stabilized biosolids and THAD biosolids. In addition, soil incorporation application techniques was tested for THAD biosolids. Under-dosed of alkaline stabilized biosolids showed a spike in VOSC's whereas properly dosed

biosolids did not, with low concentrations by day 1. Comparing THAD with alkaline stabilized biosolids, the former presented higher VOSC's at day 0 but the latter presented TMA which has been seen as a more unpleasant character for biosolids odors. No clear difference in the application technique of THAD on the behavior of the odorants was found. The electronic nose was able to distinguish the treatments by applying LDA at the beginning of the test with both THAD applications overlapping with the blank (soil) suggesting that there was no difference in odor characteristics. Taking into account the inherent limitation of the electronic nose, further testing would be needed at laboratory scale as well as under different environmental conditions in order recommend its use to support an odor monitoring program in the field where biosolids are land applied.

## **5.2 Introduction**

Biosolids application to agricultural fields represents a source of organic matter and plant nutrients instead of using fertilizers (Obreza and O'Connor, 2003; Laor *et.al.*, 2011). In the same way, for municipalities it is an end-of-pipe waste disposal solution as well as a sustainable practice when compared to other alternatives such as incineration or landfilling (Singh and Agrawal, 2008; Lu *et.al.* 2012). Some of the concerns related to the agricultural use of biosolids are potential contamination by heavy metals and organic pollutants, malodors, and vectors attraction (EPA, 2000). In this sense, sanitary concern about biosolids field application due to nuisance odors can lead to public opposition and possible failure of a sustainable biosolids management program.

Public complaints due to biosolids field applications are a result of odor causing compounds being released from biosolids followed by transport to sensitive populations.

Currently, application programs of biosolids to agricultural fields are regulated by state rules on nutrient management in order to control nutrients loadings, pursue a high crop yield and protect soils and waterways from contamination (EPA, 2000). However, ignoring the odor characteristics of the biosolids and of the location of application sites can result in public opposition (Iranpour *et.al.* 2004).

Dimethyl disulfide, DMS, CS<sub>2</sub>, NH<sub>3</sub>, TMA, methyl ethyl ketone, and acetone have been identified as odorant emissions from biosolids application to forest soil where sorbent tubes followed by thermal desorption into a gas chromatography-mass spectrometry (GC-MS) system was used as the analytical technique (Rosenfeld, 1999). Reduced sulfur compounds like hydrogen sulfide and methyl mercaptan are unstable in oxidized environments and oxidize to form DMDS in land-applied biosolids (Rosenfeld *et al.*, 2000; Higgins *et al.*, 2006). Banwart and Bremmer (1975) found that DMDS accounted for 55 to 98% of total S evolved from biosolids application to soil in aerobic conditions. Ammonia and TMA comprise most of the nitrogen emissions from land-applied biosolids (Rosenfeld *et al.*, 2000).

In a more recent project, Laor *et al.* (2011) identified VOC emissions from two types of biosolids during their production and over time after land application. They detected high ammonia and amines concentrations in digested sludge followed by alkaline stabilization (higher biosolids quality) and these concentrations were below the detection threshold after soil incorporation. Nitrogen containing compounds were not detected in digested biosolids without alkaline stabilization (lower quality). The VOSC's profiles for both biosolids behaved similarly after land application and differed from those chemical patterns at the treatment plant showing that handling operations, weather conditions and soil characteristics may influence the chemistry

of the odor causing compounds. Other VOC's such as short chain alkanes, BTEX and terpenes were also identified in this study.

According to an estimate made by Beecher *et.al.* (2007) approximately 66% of the biosolids produced in the US is using anaerobic digestion or alkaline stabilization. Emphasis has been put in recent years on pre-treatments enhancing AD to increase loading rates and biogas yields (Carlsson *et.al.* 2012). Thermal hydrolysis (TH) prior anaerobic digestion to produce high quality biosolids has recently been introduced in the United States and more than 30 facilities already use this technology. In an evaluation of enhance digestion processes for biosolids treatment, Murthy *et al.* (2009) showed that the advantage of the thermal hydrolysis pretreatment is that high solids can be achieved with belt filter press dewatering that are equivalent to centrifuge dewatering. Belt filter press cakes have generally been shown to have lower odors and less likelihood of indicator bacteria regrowth in the cake (Higgins *et.al.* 2007), which further helps the thermal hydrolysis process minimize risks related to odors and indicators. However, literature on the impact of these enhanced treatments on the emission of key odorants from field application of biosolids from these treatment has not been reported

Electronic noses are arrays of electronic sensors capable of detecting and differentiating complex mixtures of volatile compounds. Application of these arrays in the environmental engineering field has been reported for the quantification of odors from composting facilities (Sironi *et.al.*, 2007a; Sironi *et.al.*, 2007b and; Delgado-Rodriguez *et.al.*; 2012), within wastewater treatment plants (Stuetz *et.al.*, 1999; Bourgeois and Stuetz, 2002 and; Sohn *et.al.*, 2009) and at receptor locations downwind from treatment facilities (Sironi *et.al.*, 2008). To our knowledge, no application of the electronic nose to monitor key odorants from the field application of biosolids has been evaluated. The portability of such instruments position them as

a potential tool for monitoring key odorants where biosolids have been applied with the goal of supporting communication with nearby populations and evaluate the risk of public complaints.

Objectives of this work were 1) to compare target odorants profiles from THAD and alkaline-stabilized biosolids after field application to assess the potential for public complaints; and 2) to determine the capabilities of an electronic at recognizing variations in the time after biosolids application. Results are expected to provide important information on the use of commercially-available electronic nose technology to support biosolids management programs.

### **5.3 Materials and Methods**

#### **5.3.1 Biosolids Sample Collection**

Sludge samples were collected from Blue Plains Advanced Waste Water Treatment Plant (Washington, DC, USA). This treatment plant has a capacity of handling 370 MGD (970 L min<sup>-1</sup>) of domestic wastewater and produces approximately 600 wet metric tons of alkaline-stabilized biosolids per day. For alkaline stabilization, pre-dewatered sludge was collected from full scale before going to thermal-hydrolysis and consisted of a 1:1 blend of primary solids and secondary solids. Samples of approximately 10 Kg were collected using a metal shovel from a sampling port in the screw conveyor system and were stored in 22-L plastic buckets. Samples were immediately transported to the department of Civil and Environmental Engineering of the University of Maryland, College Park for alkaline stabilization. Approximately 3 Kg TH-AD biosolids were collected after final dewatering by belt filter press at full scale and stored in 4 1-L Teflon jars and transported with untreated sludge samples and use for field application simulation.

### 5.3.2 Alkaline Stabilization

Aliquots (~500 g) of untreated biosolids were transferred to 4.7 L stainless steel bowls for mixing with calcium oxide (CaO, dry quick lime) and treated at 0 (untreated control), 5, 15, and 25% CaO by mass. The quick lime utilized in this study is the same industrial grade material utilized in the wastewater plant. Mixing was achieved using a stand mixer (model RKSM500wh, Kitchen Aid, Benton Harbor, MI, USA) at low speed for 3 min with an aluminum flat beater. After mixing, temperature and pH (Hach sensION156) were measured in duplicate as minimum using standard methods after head space sampling was completed. Samples were then used for field application simulation.

### 5.3.2 Simulation of field application

Field application was simulated in 1-L glass jars (10 cm diameter) containing 100 grams of commercially-available garden top soil. A mass of 60 grams of biosolids was surface applied (SA) to the soil surface ( $n = 4$  per treatment), corresponding to an application rate of 67.2 metric tons hectare<sup>-1</sup>. A set of four jars containing untreated blank soil was also included as a control. In addition, a set of four jars was used to test a different type of biosolids application technique for THAD by manually mixing the biosolids with the soil at the same rate as the rest of the treatments.

Odorant measurements were carried out on two of the four replicates on day 0, 1, 2, 3, 4, 5, 6, 7, 15 and 22. The third jar of each treatment was used for electronic nose measurements and the fourth one for pH measurements. Jars were placed open in a fume hood (Appendix D) at a face velocity of 0.5 m s<sup>-1</sup>, corresponding to a wind speed of 1.8 km h<sup>-1</sup>. At each sampling point, sample jars were closed with air-tight lids 30 minutes before sampling. Stainless steel Jar lids were coated with fused silica and were equipped with a Micro-QT valve (Entech Instruments Inc., Simi Valley, CA, USA). Headspace samples were analyzed by GC-MS (Section 2.2).

### 5.3.3 Analytical Methods

#### Electronic nose

Refer to section 2.3 for a detailed description of the instrument and methodology used.

#### Headspace-Gas Chromatography-Mass Spectrometry

Refer to section 2.2 for detailed explanation of the analytical method.

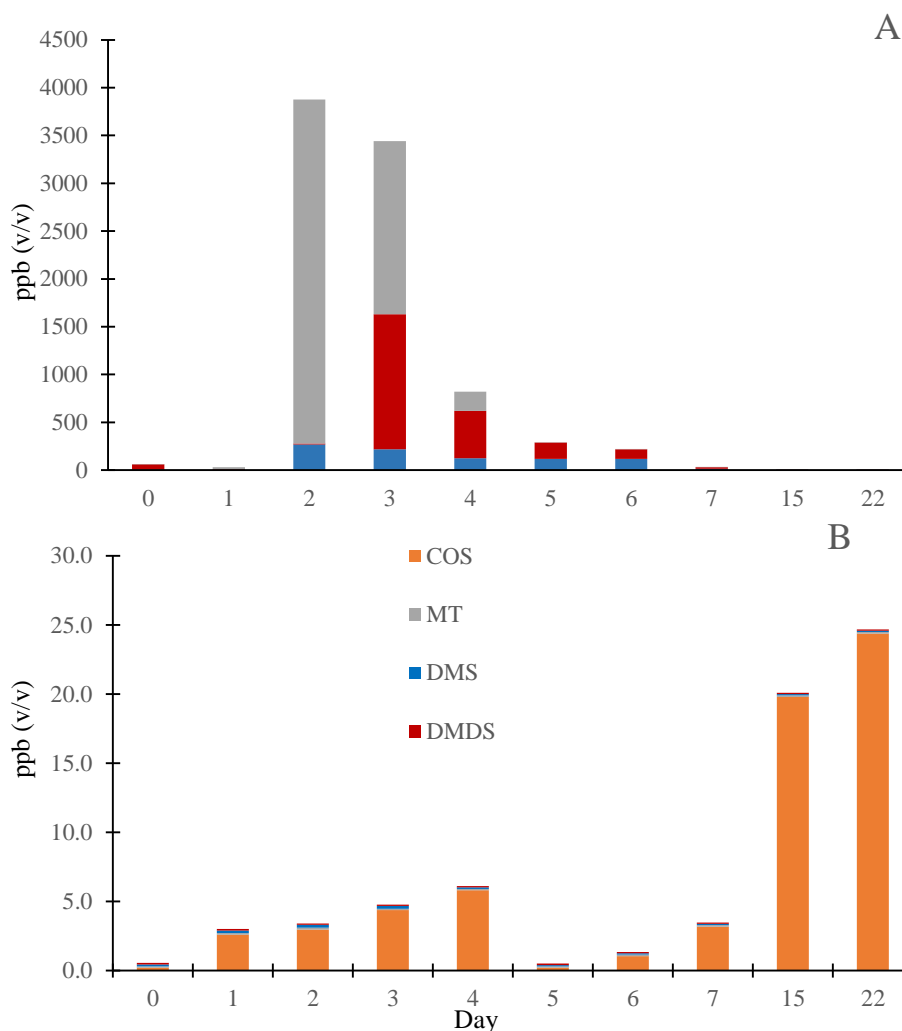
### 5.3.4 Statistical analysis

For electronic nose results, the WinMuster software was used to conduct linear discriminant analysis (LDA) and principal component analysis (PCA) for comparison of alkaline stabilization results and time after field application. Details of the methodology can be found in section 2.3.3.

## **5.4 Results and Discussion**

### 5.4.1 Odorant profile for field application of alkaline stabilized biosolids

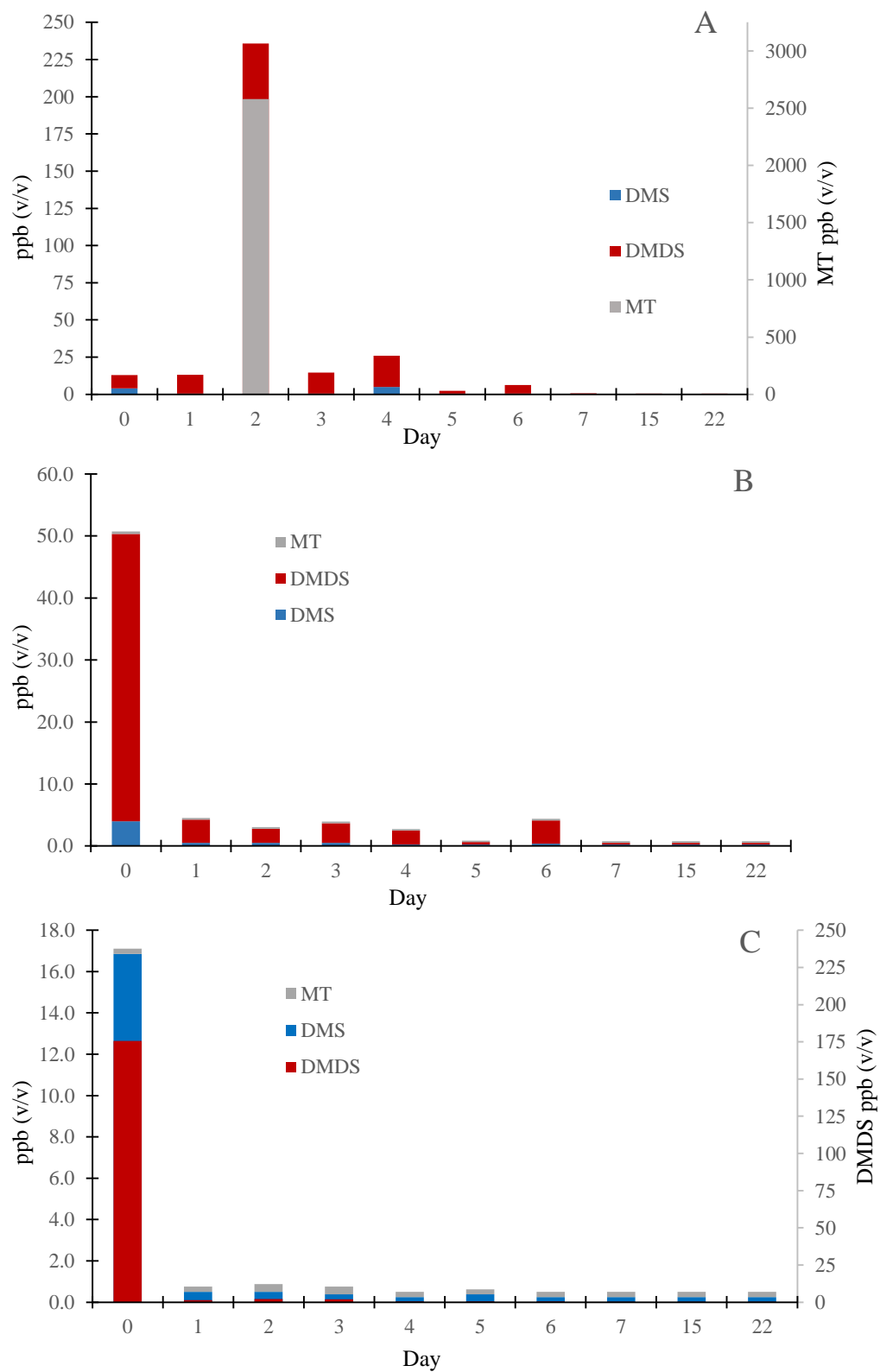
Overall, results support the use of lime stabilization to control odorant release in the field. Results indicated that 5% lime did not completely stabilize the biosolids producing sulfur compounds at day 2 with concentrations of total VOSCs increasing to 4000 ppb in untreated biosolids (Figure 5.1) and 2800 ppb in the 5% treatment (Figure 5.2). High concentrations of total VOSCs continued to day 8 days in untreated biosolids and to day 3 in the 5% treatment. In the remaining treatments all VOSC's and TMA were close or below odor threshold (Table 1.1) from day 1 indicating reduced odor associated with these samples. Values for TMA concentrations are shown in Table 5.1.



**Figure 5.1** VOSC's concentration from a) untreated control and; b) blank (soil)

In other research by Laor et al. (2011) an increase in odorants was observed in the field from alkaline-stabilized biosolids. However, the biosolids underwent anaerobic digestion prior to stabilization. Therefore a different microbial community was present due to the optimized anaerobic digestion process. Temperatures in the treated material did not increase during the treatment and microorganisms responsible for generating odorant compounds may not have been stabilized. Moreover, the rate and higher scale of the application may well have played a part when with the potential for anaerobic pockets within the samples, condition that could have led to odor production.





**Figure 5.2** VOSC's concentration from a) 5% CaO; b) 15% CaO and; 25% CaO.

**Table 5.1** TMA concentrations after field application of biosolids (day 0)

Treatment	TMA (ppm)
Untreated	BDL
5%	3.6
15%	5.09
25%	3.72
THAD	BDL
Soil	BDL

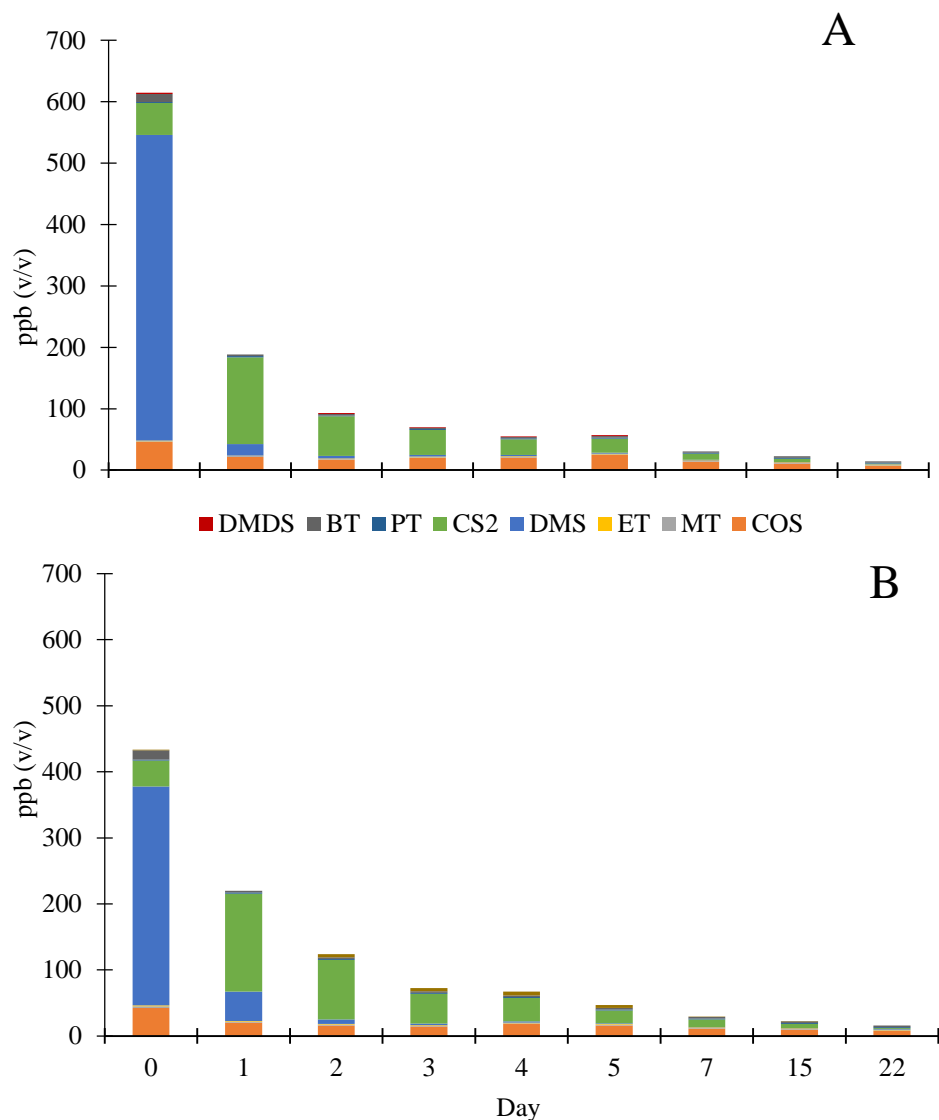
BDL Below detection limit

#### 5.4.2 Odorant profile for field application of THAD biosolids.

Results from the simulation of field application of THAD biosolids are in agreement with what it was observed in Chapter 4 for the open field storage of biosolids (Figure 4.4.c) with DMS being the main VOSC emitted and CS<sub>2</sub> found as well (Figure 5.3). A gradual decrease of sulfur compounds was observed with concentrations falling below odor threshold for individual compounds by day 5, again, similar to what it was found for the open field storage of biosolids. A difference of about 100 ppb in DMS between mixed biosolids and surface application was observed for day 0. This is likely to be due to an increase in the transfer of DMS by the mixing increasing the initial emission. Concentrations were similar from day 1 and for the rest of the duration of the test suggesting that soil incorporation of THAD biosolids could lead to slight higher odor concentrations when they are applied. However, the use of equipment for both types of application would impact these conditions. Similarly to the THAD biosolids tested in Chapter 4, Furan and the three methylated homologues were observed at day 0 and they were not identified by day 1.

The blank showed and increased in concentrations of carbon disulfide over time with concentrations above odor threshold at day 15. It is likely that constant temperature in the fume hood allow for the development of microbial community capable of degrading sulfur containing

aminoacids. CS<sub>2</sub> emissions from soil have been described previously (Banwart and Bremmer, 1975; Watts, 2000).



**Figure 5.3** VOC's concentration from a) soil incorporation and; b) surface application of THAD biosolids.

#### 5.4.3 Electronic Nose Pattern Recognition

Linear discriminant analysis performed better than principal component analysis when attempting to create clear classes for the treatments tested, including the untreated samples and

the soil (blank) accounting for 90 to 98% of the total variance with two components. Figure 5.4 shows the patterns created for days 0, 2, 7 and 22. Four groups can be considered for the purpose of analysis: control (untreated sample), soil, THAD biosolids (mix and SA) and alkaline stabilized biosolids (5%, 15% and 25%). At day 0, the four groups can be distinguish with individual treatments also separated from each other with the exception of 5 and 15%. This is in agreement with the VOSC's and TMA concentrations where most of the treatments had different odorant profiles.

The pattern created by day 2 (Figure 5.4b) shows that 5% CaO approached the group of THAD. A possible explanation is the increase in DMS rather than MT in the 5% lime (Figure 5.2) to a concentration similar to that of CS<sub>2</sub> in the THAD biosolids for the same day. The response of the sensors in the PEN3 would be having a higher response to the sulfide functional group instead of the thiol group thus giving similar fingerprint for these classes. The pattern obtained by day 7 showed that the similarity between 5% CaO and THAD biosolids was no longer there. In addition, the classes for both application techniques of THAD biosolids overlapped suggesting that the treatments cannot longer be differentiated, which is confirmed by the odorant profiles in Figure 5.3.

Finally, THAD biosolids cannot be differentiated from the blank suggesting that the odor characteristics of these applications is that of the natural soil. This is not the case for the alkaline stabilized biosolids where the odorant profiles are still distinguishable by the PEN3.

Overall, the two-dimensional plot displaying the classes included in the pattern reduced its plane over time suggesting that all treatments approached the odorant characteristics of that of the natural soil. It is important to mention the limitations of the PEN3 observed in Chapter 3. Including data from additional tests could add variability to the treatments to the point where the

differences cannot be accounted for. In addition, electronic nose sensors can exhibit drift in response due to changing environmental conditions and over time (Romain and Nicolas, 2009), making the application of an electronic nose for field monitoring of odors from biosolids quite challenging.

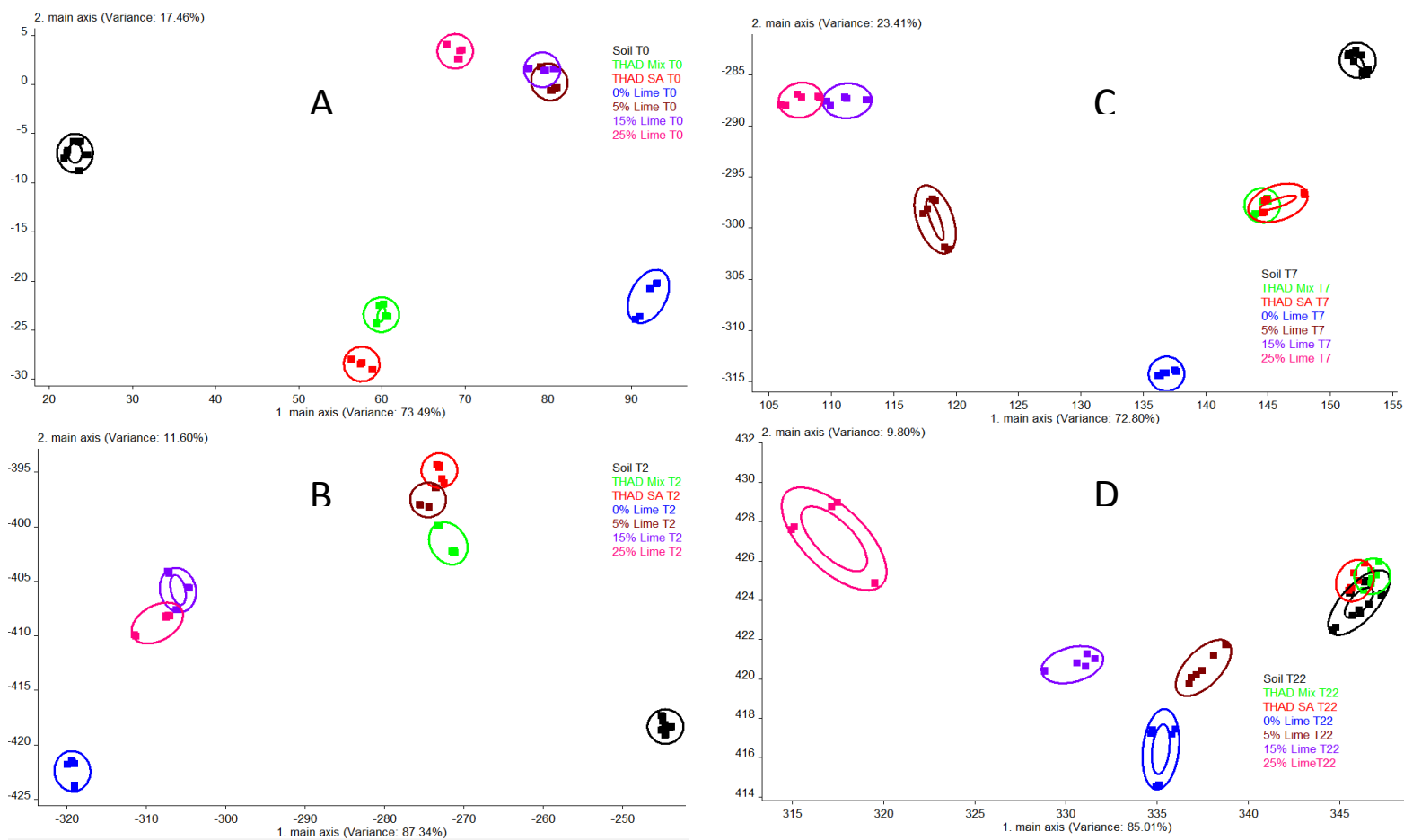
## **5.5 Conclusions**

Field application of alkaline stabilized and THAD biosolids was simulated to evaluate the characteristics of key odorants over time. Under-dosed of alkaline stabilized biosolids showed a spike in VOSC's whereas properly dosed biosolids did not, with low concentrations by day 1. No difference in the application technique of THAD on the behavior of the odorants was clear. Comparing THAD with alkaline stabilized biosolids, the former presented higher VOSC's at day 0 but the latter presented TMA which has been seen as a more unpleasant character for biosolids odors.

The electronic nose was able to distinguish treatment conditions after field application and over time. Extended testing time would ultimately show no difference in classes (treatments) approaching the characteristics of the soil used as blank. The limitations of the electronic nose technologies for environmental applications where treatment variability as well as environmental conditions highly impact the overall performance of this technology.

## **5.6 Acknowledgements**

Funding support was received from DC Water and Sewer Authority. In addition, a scholarship from the National Council for Science and Technology (CONACyT, Mexico) was awarded to Mr. Romero-Flores for graduate studies. In kind support from ARS-USDA is also greatly appreciated.



**Figure 5.4** Linear Discriminant Analysis applied to all treatments at a) day 0, b) day 2, c) day 7 and, d) day 22

## **Chapter 6. Conclusions and future work**

### **6.1 Conclusions**

State-of-the-art technology in combination with the scientific method have been applied to gain a better understanding on the characteristics of biosolids from an odor perspective as well as on the novel application of electronic noses for biosolids production monitoring. Several conclusions have been presented in Chapter 3 through Chapter 5 and can be summarized as follow:

1. An analytical method was developed in this study for the quantification of volatile organic sulfur compounds, the main odorants found in water and resource recovery utilities, with the sensibility below odor threshold. This tool allowed to evaluate the performance of the electronic nose tested in this study, the PEN3. In combination with olfactometry measurements, this method helped to successfully characterize odors from biosolids and to support the evaluation of odor prevention and control strategies.
2. Despite that by applying Linear Discriminant Analysis to the data collected by electronic nose, it was possible to discriminate between lime dosages for alkaline stabilized biosolids when a single sample was tested, limitations in pattern recognition and unknown samples classification appeared when the entire larger data set was included. The low specificity of the sensor in the PEN3 in addition to the intrinsic variability of the biosolids treatment process didn't allow for more precise and accurate results. Therefore, transitioning from laboratory scale testing to full scale training and deployment of an

electronic nose requires intensive investigation and further work is required to assure that sensor array technology is suitable for this type of application where environmental conditions and process variability are important parameters that may affect overall performance of an electronic nose. This work exposed the need for a different and more sensitive sensor array for the monitoring of alkaline stabilized biosolids production process.

3. Thermal hydrolysis-anaerobic digested biosolids (THAD) and alkaline stabilized biosolids reported similar odor concentration measured as dilution to threshold and recognition threshold. However, the fishy odor given by TMA emissions due to the increase in pH resulted in more offensive and unpleasant odors, measured as hedonic tone, when compared to THAD.
4. The presence of furan and three methylated homologues in TH-AD biosolids was reported for the first time proposing that these compounds are produced during thermal hydrolysis process however, additional research is needed to fully describe the formation of these compounds and their potential correlation with odor characteristics in biosolids.
5. Over a 28 days period of storage in air tight containers, THAD biosolids showed an increase in dilution to threshold but no correlation was found with the target organic reduced sulfur compounds suggesting that other not-targeted chemicals are being produced while further stabilization is occurring during storage. This increase in odors was not observed in alkaline stabilized biosolids.



6. Field application simulations showed the importance of achieving the proper alkali dose in alkaline stabilized biosolids to control odorant release in the field. No difference in the application technique of THAD on the behavior of the odorants was clear. Comparing THAD with alkaline stabilized biosolids, the former presented higher VOSC's at day 0 but the latter presented TMA which has been seen as a more unpleasant character for biosolids odors. Gradual decline in measured odorant from THAD was observed falling below the odor threshold by day 5. The electronic nose was able to distinguish treatment conditions after field application and over time. Extended testing time would ultimately show no difference in classes approaching the characteristics of the soil used as blank.

The results from this work helped to expand the knowledge and deepened the understanding on the odor characteristics of biosolids produced by a process new to the United States and that, although this technology has been used in Europe for several years now, little attention had been paid to the odor profiles from a scientific perspective. In doing so, it is clear that additional research needs to be developed in order to address the new questions that arose from these conclusions. In addition, the methods developed in this work may well be of support in other areas of the water and resource recovery field. Some of this opportunities are described below.

## **6.2 Future work on odor characterization from biosolids**

Alkaline stabilized biosolids have been described in literature and their incorporation in this study has been with the purpose of comparison with THAD biosolids only. This project was the first attempt of odor characterization of THAD biosolids utilizing simultaneously sensory measurements and chemical analysis. In addition, normal handling of biosolids was simulated for storage and field application with several questions yet to be answered.

1. What are the mechanisms of furan and methylated homologues production in THAD biosolids?
2. What are the implications of furan and methylated homologues for the odor characteristics of biosolids?
3. What are the implications of furan and methylated homologues in biosolids for the human health and the environment?
4. What are the main compounds causing the increase of odors in THAD biosolids under storage conditions?
5. How can these odor causing compounds be inhibit or controlled?

These research questions need to be answer in order to increase the quality of THAD biosolids and to avoid any potential environmental risk due to the presence of furans. For the quantification of furans, the analytical instrumentation employed in this research can be used since it showed good chromatographic resolution and peak shape to allow for the development of a calibration curve. The compounds causing the increase in odor concentrations from THAD biosolids in storage need to be assessed

with sensory measurement along with chemical analysis. A first approach can be to evaluate the behavior of hydrogen sulfide with more suitable analytical tools than the ones used in this study. In addition, ammonia and methane emissions could be affecting the odor characteristics as well, given the anaerobic conditions.

### **6.3 Future work on odors in activated sludge**

Odor emission from activated sludge (AS) has become an important challenge for resource recovery facilities due to its large emission surface area, high cost and off-gas treatment. Despite odor production and emission have been mostly studied for sewer lines and biosolids management, only little is known about the mechanisms of production and emission of odorous compounds from secondary reactors.

Volatile organic sulfur compounds (VOSC's) have been found to be the main group of chemicals emitted from AS process that relate to odor problems (Kim et.al. 2002). Sekyiamah *et.al.* (2008) studied the emission profile showing that dimethyl disulfide (DMDS) and dimethyl sulfide (DMS) were the main compounds being emitted suggesting that 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 methyl mercaptan, a key odorant, to DMDS and thus lacking of the accuracy needed to evaluate strategies for odor prevention and control. During an odor control master plan for Blue Plains Advanced Wastewater Treatment Plant (AWTP) (Data not published, 2012), it was found that methyl mercaptan accounted for up to 96% of total reduced sulfur compounds and showed a strong correlation with olfactometry measurements.

There is a need for evaluating the impact of new processes on the emission of odorous compounds. With the intensification of resource recovery in wastewater treatment plants, technologies and processes are being developed and implemented to redirect carbon from secondary treatment to the solids stream to increase energy production potential. High-rate activated sludge (HRAS), for example, aims for carbon sorption in the aerobic tanks rather than oxidizing it. This approach, however, may involve the need for longer retention times in the clarifiers and can thus potentially result in higher VOSC's production.

The method for quantification of VOSC's developed in this study may be used to evaluate the impact of activated sludge operation on the emission of odorous compounds. Research questions are proposed:

1. What are the VOSC's being produced and emitted from the secondary aeration process?
2. What are the mechanism by which VOSC's are produced?
3. What are the conditions that inhibit or reduce their emission rate?
4. How does a high rate process affects the production and emission of VOSC's?

Some of the work related to this topic has begun in collaboration with the Department of Research and Development at DC Water with the goal of providing insights on the operation of activated sludge systems to inhibit the formation of VOSC's.

## Appendices

### Appendix A. Sampling port for untreated sludge



Figure A.1. Untreated sludge sample collected after preliminary dewatering.

### Appendix B. Schematic of analytical instrumentation

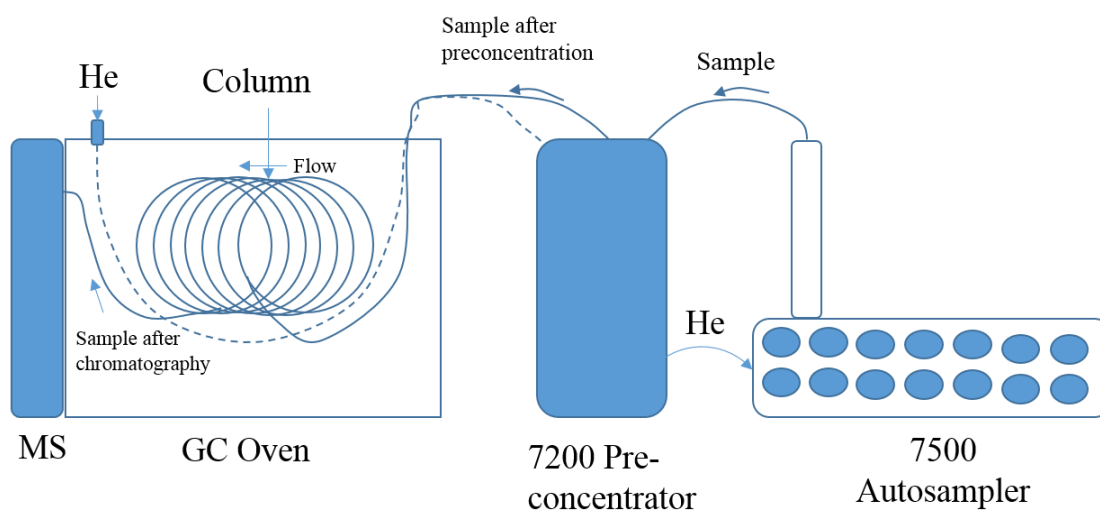


Figure B.1 Components of the analytical system

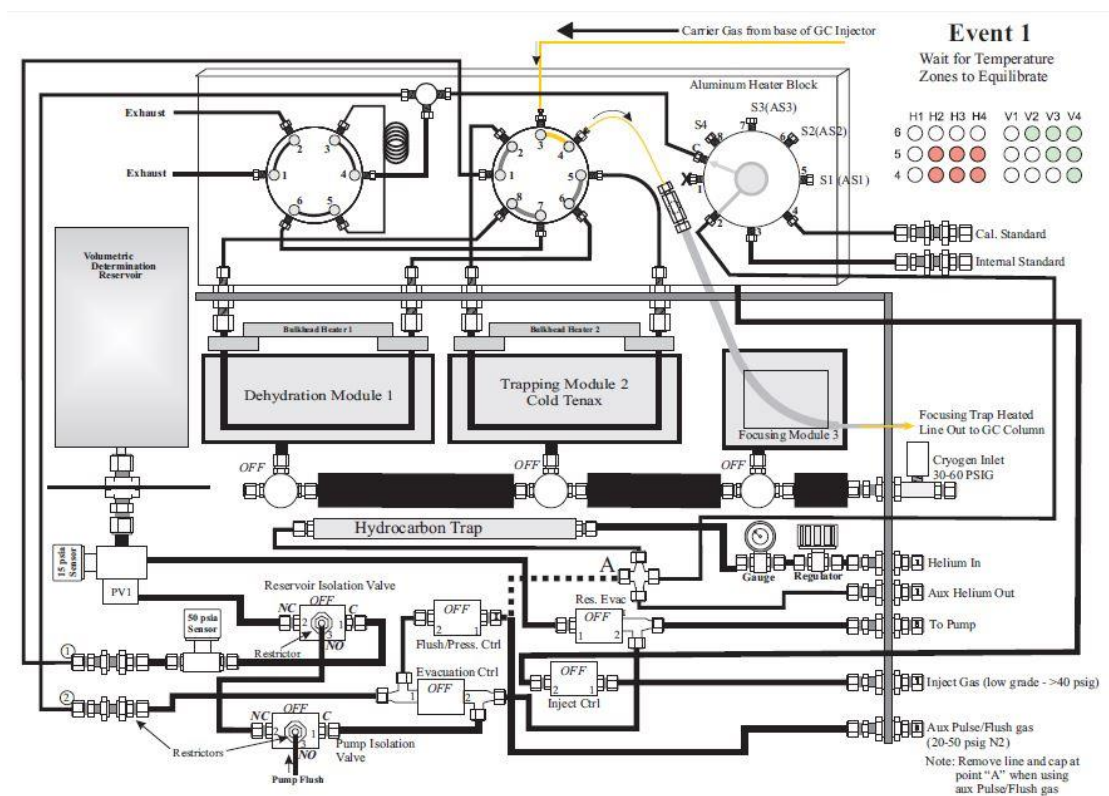


Figure B.2 7200 model preconcentrator. Source: Entech Instruments 2014.

## Appendix C. Calibration curve

Table C.1 Volumes and concentration for trimethylamine

Standad concentration (ppb)	Volume injected (mL)	Final concentration A (ppb)	Final concentration B (ppb)
5000	10	100	5000
5000	25	250	12500
5000	50	500	25000
5000	75	750	37500
5000	100	1000	50000
5000	200	2000	100000

**A** Based on a 500 mL sample injection.

**B** Based on a 10 mL sample injection

Table C.2 Volumes and concentration for sulfur compounds standard and DMDS standard

<b>Standard concentration (ppb)</b>	<b>Volume injected (mL)</b>	<b>Final concentration A (ppb)</b>	<b>Final concentration B (ppb)</b>
5000	35	350	<b>17500</b>
5000	30	300	15000
5000	25	250	12500
5000	20	200	10000
5000	15	150	7500
5000	10	100	5000
250	400	200	10000
250	200	100	5000
250	100	50	2500
250	50	25	1250
250	25	12.5	625
250	15	7.5	375
250	10	5	250
250	400	200	10000
25	200	10	500
25	100	5	250
25	50	2.5	125
25	25	1.25	62.5
25	15	0.75	37.5
25	10	0.5	25
25	5	<b>0.25</b>	12.5

**A** Based on a 500 mL sample injection.

**B** Based on a 10 mL sample injection

## Appendix D Simulation of field application



Figure D.1 Samples during field application



## Bibliography

- Ariunbaatar, J., Panico, A., Esposito, G., Pirozzi, F., Lens, P. (2014). *Applied Energy*. 123 143-159,
- Banwart, W.L., and Bremner, J.M. (1975). Formation of Volatile Sulfur Compounds by Microbial Decomposition of Sulfur-Containing Amino Acids in Soils. *Soil Biol. Biochem.*, 7, 359.
- Beecher, N., Crawford, K., Goldstein, N, Kester, G., Lona-Batura M., Dziezyk, E. (2007); *National Biosolids Regulation, Quality, End Use & Disposal Survey*. North East Biosolids and Residuals Association. Tamworth, NH: North East Biosolids and Residuals Association.
- Bingham, E.; Cohrssen, B.; Powell, C.H.; (2001). *Patty's Toxicology Volumes 1-9* 5th ed. John Wiley & Sons. New York, N.Y. p. V7 p.690
- Boeker, P. (2014). On 'Electronic Nose' methodology, *Sens. Actuators B Chem.*, 204, pp. 2–17
- Bonnin C., Laborie A. and Paillard H. (1990) Odor nuisances created by sludge treatment: problems and solutions. *Water Sci. Technol.* 22, 65-74.
- Boon A. G. (1995) Septicity in sewers: causes, consequences and containment. *Water Sci. Technol.* 31, 237-253.
- Bourgeois, W., and Stuetz, R.M. (2002). Use of a chemical sensor array for detecting industrial pollutants in wastewater. *Water Research* 36, 4505–4512.
- Brezmes, J. Llobet, E. Vilanova, X. Saiz, G. Correig. X. (2000). Fruit ripeness monitoring using an electronic nose. *Sens. Actuators B, Chem.*, 69, pp. 223–229.

- Bright D.A. and Healey, N. (2005) Contaminant risks from biosolids land application: Contemporary organic contaminant levels in digested sewage sludge from five treatment plants in Greater Vancouver, British Columbia. *Environmental Pollution*. Volume 126, Issue 1, November 2003, Pages 39–49.
- Carlsson, M., Lagerkvist, A., Morgan-Sagastume, F. (2012). The effects of substrate pre-treatment on anaerobic digestion systems: a review. *Waste Manage.* (Oxford), 32 (2012), pp. 1634–1650.
- Chen, Y., Higgins, M., Maas, S., Murthy, S. Toffey, W. and Foster, D. (2005) Roles of methanogens on volatile organic sulfur compound production in anaerobically digested wastewater biosolids *Water Science & Technology* Vol 52 No 1-2 pp 67–72.
- Chang, J.-S., M. Abu-Orf, and S.K. Dentel. 2005. Alkylamine odors from degradation of flocculant polymers in sludge. *Water Res.* 39:3369–3375.
- Cheng, K.L.; Zhu, D.-M. On Calibration of pH Meters. (2005) *Sensors*, 5, 209-219.
- De Maesschalck, Roy; Jouan-Rimbaud, Delphine; and Massart, Désiré L. (2000); The Mahalanobis distance. *Chemometrics and Intelligent Laboratory Systems* 50:1–18.
- Delgado-Rodríguez, M. Ruiz-Montoya, M. Giraldez, I. Lopez, R. Madejon, E. Diaz, M.J. (2012) Use of electronic nose and GC-MS in detection and monitoring some VOC. *Atmospheric Environment* 51; 278-285.
- Devos, M., Patte, F., Rouault, J., Laffort, P., Van Gemert, L., (1990). *Standardized Human Olfactory Thresholds*. IRI Press at Oxford University Press, New York.
- EPA (1995). *The standards for the use or disposal of sewage sludge*. 40CFR Part 503. Washington D.C.: EPA.

- EPA. (2000). *Biosolids technology fact sheet: Land application of biosolids*. EPA 832-F-00-64. United States Environmental Protection Agency, Washington, D.C.
- Feng, T., Zhuangb H, Ran Yec, Zhengyu Jin, Xueming Xu, Zhengjun Xie. (2011) Analysis of volatile compounds of Mesona Blumes gum/rice extrudates via GC–MS and electronic nose. *Sensors and Actuators B, Chem.*, 160, 964– 973
- Freeman, J.W. (1991). The Physiology of Perception. *Sci. Am.* 264, 78-85.
- Gabriel, S., Vilalai, S., Arispe, S., Kim, H., McConnell, L., Torrents, A., Peot, C., Ramirez, M. (2005): Prediction of dimethyl disulfide levels from biosolids using statistical modeling. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering*, 40:11, 2009-2025.
- Ghasemi-Varnamkhasti, M., Mohtasebi, S.S., Siadat, M., Balasubramanian, S., (2009). Meat quality assessment by electronic nose (machine olfaction technology). *Sensors* 9, 6058–6083.
- Harkness N. (1980) Chemistry of septicity. *Effluent Water Treatment J.* 20, 16-23.
- Harper W. (2001).The Strengths and Weaknesses of the Electronic Nose. *Adv Exp Med Biol.* ; 488:59-71.
- Higgins, M.J., D.P. Yarosz, Y.C. Chen, S.N. Murthy, N. Maas, J. Cooney, D. Glindemann. (2003). Mechanisms of Volatile Sulfur and Odor Production in Digested Biosolids. *Proceedings of Water Env. Federation and AWWA Annual Biosolids and Residuals Conference*. 2003, Baltimore.
- Higgins, M. J.; Yarosz, D. P.; Chen, Y. C.; Murthy, S. N.; Maas, N.; Cooney, J.; Glindemann, D.; Novak, J. T. (2006). Cycling of Volatile Organic Sulfur Compounds in

- Anaerobically Digested Biosolids and its Implications for Odors. *Water Environ. Res.*, 78, 243–252.
- Higgins, M.J., Chen, Y., Novak, J.T., Glindemann, D.E., Forbes, R., Erdal, Z., Witherspoon, J., Mcewen, D., Murthy, S.N., Hargreaves, R. and Adams, G. (2008). A multi-plant study to understand the chemicals and process parameters associated with biosolids odors. *Environ. Eng.: Appl. Res. Pract.* 5: 1-13.
- Hofman T. Characterization of the Chemical Structure of Novel Colored Maillard Reaction Products from Furan-2-carboxaldehyde and Amino Acids. *J. Agric. Food Chem.*, 1998, 46 (3), pp 932–940
- Huang, Q. (2011) Utilizing Raman Microscopy to Identify Sources of PM10 Downwind of Agricultural Operations. *Master's Thesis*. Retrieved from UMCP HBK Maryland Room Maryland Thesis. Call number LD3231.M70m 2011 HuangQ.
- Iranpour, R. Cox, H.J., Kearney, K.H., Clark, A.B., Pincince, A, Daigger, G.T. Regulation for biosolids land application in US and European Union. *Journal of Residuals Science and Technology*. Vol. 1, No.4. October 2004.
- Janpengpen, A; Baecher, G; Kim, H; Peot, C; Ramirez, M. (2007). Real-time monitoring and forecasting of odor after dewatering in wastewater treatment. *Proceedings of the Water Environment Federation, WEFTEC: Session 41 Through Session 50*, Pp. 3556-3561(6).
- Jones, K.C., and A. Sewart. 1997. Dioxins and furans in sewage sludges: A review of their occurrence and possible sources in sludge and of their environmental fate and behavior, and significance in sludge-amended systems. *Crit. Rev. Environ. Sci. Technol.* 27:1–85.

- Johnson, D.E., (1998). *Chapter 5: Principal Component Analysis*, in Johnson, D.E., Applied multivariate methods for data analysts, Brooks/Cole Publishing Company, Pacific Grove, CA, USA, pp. 93-97.
- Kasirga, E.; Peot, C.; Higgins, M; Odor Characteristics of CAMBI and Lime Stabilized Biosolids A Case Study Blue Plains AWTP, DC Water. *Sustainable Biosolids Technologies Workshop*. Virginia Beach, VA – September 10, 2012.
- Kim, H., Murthy, S.N., Peot, C., Ramirez, M. and Strawn, M. McConnell, L.L. (2001). Examination of mechanisms for odor compound generation during lime stabilization. *Proceedings of the Water Environment Federation*, WEFTEC: 2001.
- Kim, H.; Murthy, S.; McConnell, L.L.; Peot, C.; Ramirez, M.; Strawn, M. (2002). Characterization of wastewater and solids odor using solid phase microextraction at a large wastewater treatment plant. *Water Sci. Technol.*, 46 (10), 9–16.
- Kim, H., S. Murthy, C. Peot, M. Ramirez, M. Strawn, C.-H. Park, and L. McConnell. 2003. Examination of mechanisms for odor compound generation during lime stabilization. *Water Environ. Res.* 75:121–125.
- Knobloch, H. Turner, C. Spooner, A. Chambers, M. (2009). Methodological variation in headspace analysis of liquid samples using electronic nose. *Sensors and Actuators B, Chem.* 139 (2009) 353–360.
- Kuhn, E. P. and Suflita, J. M. (1989), Microbial degradation of nitrogen, oxygen and sulfur heterocyclic compounds under anaerobic conditions: Studies with aquifer samples. *Environmental Toxicology and Chemistry*, 8: 1149–1158

- Lakhwinder S. Hundal, Albert Cox, Thomas C. Granato and Zainul Abedin (2008) Levels of Dioxins in Soil and Corn Tissues after 30 Years of Biosolids Application. *Journal of Environmental Quality*. 2008 37: 4: 1497-1500.
- Laor, Y.; Ozer, Y.; Ravid, U.; Hanan, A.; Orenstein, P. 2010, Methodological aspects of sample collection for dynamic olfactometry. *Chem. Eng. Trans.* 23, 55-60.
- Laor Yael, Moshe Naor, Uzi Ravid, Pinchas Fine, Ilan Halachmi, Yona Chen, and Rima Baybikov. (2011). Odorants and Malodors Associated with Land Application of Biosolids Stabilized with Lime and Coal Fly Ash. *J. Environ. Qual.* 40:1405 – 1415.
- Lebrero, R., Lynne Bouchy, Richard Stuetz & Raúl Muñoz (2011): Odor assessment and management in wastewater treatment plants: a review. *Critical Reviews in Environmental Science and Technology*, 41:10, 915-950.
- Liu, X. Cheng, S. Liu, H. Sha, H. Zhang, D. Ning, H. (2012) A survey on gas sensing technology. *Sensors*, 12, pp. 9635–9665.
- Loutfi, A. Coradeschi, S. Mani, G.K. Shankar, P. J. Rayappan. B.B. (2015). Electronic noses for food quality: a review. *Journal of Food Engineering*, 144 pp. 103–111
- Lu, Q., He, Z., Stoffella, P. Land application of biosolids in the USA: A review. *Applied and Environmental Soil Science*. Volume 2012, Article ID 201462, 11 pages.
- Miller, J.D., Novak, J.T., Knowkce, W.R. Pruden, A. Elevation of antibiotic resistance genes at cold temperatures: implications for winter storage of sludge and biosolids. *Lett Appl Microbiol*, 2015 Dec: 59 (6): 587-93.
- Mottram DS. Flavour formation in meat and meat products: a review. *Food Chem.* 1998;62:415–424.

- Muller, C.D., Park, C., Verma, N., Novak, J.T. (2007). The influence of anaerobic digestion on centrifugally dewatered biosolids odors. *Oral Presentation and Conference Proceeding*, Water Environment Federation 21<sup>st</sup> Annual Residuals Biosolids Management Conference, Denver, Co.
- Murthy, S. Higgins, M. Chen, Y. Novak, J. Wilson, C. Riffat, R. Aynur, S. (2009). Impacts of enhanced digestion processes on biosolids quality parameters: odors and indicators. *Proceedings, WEFTEC Conference 2009*.
- Navab-Daneshmand, T. Enayet, S., Gehr, R., Frigon, D. (2014) Bacterial pathogen indicator regrowth and reduced Sulphur compounds' emissions during storage of electro-dewatered biosolids. *Chemosphere*. 113 109-115.
- Novak, J. T.; Glindmann, D.; Murthy, S. N.; Gerwin, S.; Peot, C. (2002) Mechanisms For Generation and Control of Trimethyl Amine and Dimethyl Disulfide from Lime Stabilized Biosolids. *Proceedings of the Water Environment Federation Odors and Toxic Air Emissions Conference*, Albuquerque, New Mexico, April 29–30; Water Environment Federation: Alexandria, Virginia.
- Novak, J. T.; Adams, G.; Card, T.; Chen, Y. C.; Erdal, Z.; Forbes, R. H. Jr.; Glindemann, D.; Hargreaves, J. R.; Hentz, L.; Higgins, M. J.; et al. (2006) Odor Generation Patterns from Anaerobically Digested Biosolids. *Water Environ. Res.*, 76, 2699–2702.
- Oberg, L.G., R. Anderson, and C. Rappe. 1992. De novo formation of hepta- and octa-CDDs from pentachlorophenols in municipal sewage sludge. *Organohalogen Comp.* 9:351–354.

- Obreza, T.A., and O'Connor, G.A. (2003). *The basics of biosolids application to land in Florida*. University of Florida: Florida Cooperative Extension Service, Institute of Food and Agricultural Science.
- O'Dette, Robert G. Biosolids recycling: will it be sustainable in the 21<sup>st</sup> century? (2002) Proceedings of the Water Environment Federation, WEFTEC 2002: Session 1 through Session 10, pp. 309-337(29).
- O'Neil, M.J. (ed). (2006). *The Merck Index – An Encyclopedia of Chemicals, Drugs and Biologicals*. Whitehouse Station, NJ: Merck and Co., Inc., p. 1668.
- Otto, M. (1999). Chemometrics—Statistics and Computer Application in *Analytical Chemistry*, Wiley-VCH, Weinheim, 1999.
- Perrin D.D; (1972). *Dissociation constants of organic bases in aqueous solution*. IUPAC Chemical Data Series: Suppl. 1972. Butterworth, London.
- Ram, S. Majumder, P. Chaudhuri, S. Chanda, S. C. Santra, A. Chakraborty & M. Sudarshan (2015). A Review on Air Pollution Monitoring and Management Using Plants with Special Reference to Foliar Dust Adsorption and Physiological Stress Responses. *Critical Reviews in Environmental Science and Technology*, 45:23, 2489-2522, DOI:10.1080/10643389.2015.1046775.
- Romain, AC. Nicolas, J Long term stability of metal oxide-based gas sensors for e-nose environmental applications: an overview. (2010). *Sens. Actuators B: Chem.*, 146, pp. 502–506
- Rosenfeld, P., (1999) "Characterization, Quantification, and Control of Odor Emissions from Biosolids Application to Forest Soil." *Ph.D. Dissertation*. University of Washington, Seattle, WA.1999.



- Rosenfeld, P.E., C.L. Henry, R. Dills, and R.B. Harrison. (2001). Comparison of odor emissions from three different biosolids applied to forest soil. *Water Air Soil Pollut.* 127:173–191.
- Serjeant, E.P., Dempsey B.; (1979) *Ionisation Constants of Organic Acids in Aqueous Solution. International Union of Pure and Applied Chemistry (IUPAC). IUPAC Chemical Data Series No. 23, 1979. New York, New York: Pergamon Press, Inc., p. 989.*
- Senante, E., Vivola, L., Alric, G., and Commet, M. (2008, October). Composting process monitoring based on RQ BOX electronic nose measurement. Paper *Presented at the 3rd IWA International Conference On Odour And VOC*. Barcelona, Spain.
- Singh, R.P. and Agrawal, M. (2008). Potential benefits and risks of land application of sewage sludge. *Waste Management*, 28, 347-358.
- Sironi, S. Capelli, L. C´entola Paolo, Del Rosso, R. (2007a) Development of a system for the continuous monitoring of odours from a composting plant: Focus on training, data processing and results validation methods. *Sensors and Actuators B, Chem.* 124 336–346.
- Sironi, S. Capelli, L. C´entola Paolo, Del Rosso, R., Il Grande, M. (2007b). Continuous monitoring of odours from a composting plant using electronic noses. *Waste Management.* 27, 389–397.
- Sironi, S. Capelli, L. C´entola Paolo, Del Rosso, R., Il Grande, M. (2008). Electronic noses for the continuous monitoring of odours from a wastewater treatment plant at specific receptors: Focus on training methods. *Sensors and Actuators B, Chem.* 131, 53–62.

- Sohn, J.-H., Pioggia, G., Craig, I.P., Stuetz, R.M., and Atzeni, M.G. (2009). Identifying major contributing sources to odour annoyance using a non-specific gas sensor array. *Biosystem Engineering*. 102, 305–312.
- Stockwell, C. E., Veres, P. R., Williams, J., and Yokelson, R. J.: Characterization of biomass burning emissions from cooking fires, peat, crop residue, and other fuels with high-resolution proton-transfer-reaction time-of-flight mass spectrometry, *Atmos. Chem. Phys.*, 15, 845-865, doi:10.5194/acp-15-845-2015, 2015.
- Stuetz, R. M., Engin, G., and Fenner, R. A. (1999). Sewage odour measurements using a sensory panel and an electronic nose. *Water Science and Technology*. 38, 331–335.
- Stuetz, R.M., Fenner, R.A., and Engin, G. (1999b). Assessment of odours from sewage treatment works by an electronic nose, H<sub>2</sub>S analysis and olfactometry. *Water Research*. 33, 453–461.
- Strube, A. Guth, H. Buettner, A. (2009) Identification of a medicinal off-flavor in mineral water. *Water Research*, Volume 43, Issue 20, December 2009, Pages 5216–5224.
- Trabue, S. L.; Anhalt, J. C. ; Zahn, J. A. 2007. Bias of tedlar bags in the measurement of agricultural odorants. *Journal of Environmental Quality*; 35, 5; 1668-1677
- Trabue, S., Scoggin, K., Mitloehner, F., Li, H., Burns, R., and H. Xin, (2008a): Field sampling method for quantifying volatile sulfur compounds from animal feeding operations. *Atmos. Environ.* 42, 3332-3341.
- Trabue, S. Scoggin, K. Burns, H. Xin, R. 2008b. Field sampling method for quantifying odorants in humid environments. *Environ. Sci. Technol.*, 42 (10), 3745-3750
- Trabue, S. Scoggin, K. McConnell, L. Maghirang, R. Razote, E. Hatfield, J. 2011. Identifying and tracking key odorants from cattle feedlots. *Atmos Environ*; 45(25):4243-4251.

- Villanueva, F., Barnes, I., Monedero, E., Salgado, S., Gomez, M.V., Martin, P. Primary product distribution from the Cl-atom initiated atmospheric degradation of furan: environmental implications. *Atmospheric Environment* 41 (2007) 8796-8810.
- Vincent A. and Hobson J. (1998). *Odour control*. CIWEM Monographs on Best Practice No. 2, Chartered Institution of Water and Environmental Management, Terence Dalton Publishing, London.
- Vranová J., Ciesarová Z. (2009): Furan in food – a review. *Czech J. Food Sci.*, 27: 1–10.
- Watts, S. The mass budgets of carbonyl sulfide, dimethyl sulfide, carbon disulfide and hydrogen sulfide. *Atmospheric Environment*. Volume 34, Issue 5, January 2000, Pages 761–779
- Young P. J. (1984) Odours from effluent and waste treatment. *Effluent Water Treatment J.* 24, 189-195.
- Zeynep K. Erdal, Robert H. Forbes Jr., Jay Witherspoon, Greg Adams, Ron Hargreaves, Rob Morton, John Novak & Matthew Higgins (2008): Recent findings on biosolids cake odor reduction. Results of WERF phase 3 biosolids odor research. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering*, 43:13, 1575-1580.