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UNIVERSITY OF CALIFORNIA

Los Angeles

The Identification, Analysis, and Treatment of Odor Nuisance Released
from Wastewater Treatment Plants

A dissertation submitted in partial satisfaction of the requirements

for the degree Doctor of Philosophy

in

Environmental Health Science

by

Yubin Zhou

2017

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2017

ABSTRACT OF THE DISSERTATION

The Identification, Analysis, and Treatment of Odor Nuisance Released
from Wastewater Treatment Plants

by

Yubin Zhou

Doctor of Philosophy in Environmental Health Science

University of California, Los Angeles, 2017

Professor Irwin H. Suffet, Chair

Odor nuisance has been a challenge to management of wastewater treatment plants (WWTPs) and endanger the relationship between these facilities and neighbors. A systematic methodology needs to be developed to understand and investigate odor nuisance from WWTPs, and provide practical solutions to solve the issue. The study of this methodology should include incorporation of both chemical and sensorial methods, optimization of sampling techniques, development of analytical methods, and understanding the masking effect in odorous mixtures.

Both sensorial and chemical methods should be applied to investigate odor nuisance from wastewater facilities. Using chemical analysis alone is not able to clarify the problem because there is a gap between the method reporting limit (MRL) and odor threshold concentration (OTC) of odorants. Sensorial methods, such as odor profile method (OPM) and Detection/Threshold

(D/T) method, should be used to bridge the gap. The OPM can determine the major odors presented and their intensities, and then narrow the major potential odorants to a manageable group. D/T determines the total odor and if there is an odor nuisance problem, while the OPM can define the odors and their intensities.

The losses of volatiles and odorants in sampling bags have been reported in literature. Thus, proper bag film is needed for both sensorial and chemical analysis. The stability of wastewater odorants samples in sampling bags of Tedlar (polyvinyl fluoride film) and Teflon FEP (fluorinated ethylene propylene film) was evaluated and compared. Quick losses of indole and skatole were found in Tedlar bag, with less than 5% left after 15 minutes due to adsorption on the bag wall, while skatole and indole showed over 75% recovery over 6 hours in Teflon bags. Thus, Teflon bags are required for the analysis of skatole and indole, which needs to occur within 6 hours of sample collection and also preferred for both chemical and sensory analysis due their lower background chemical and odorant contamination.

Sensory- gas chromatography (Sensory GC) and GC-mass spectroscopy (GC/MS) with the OPM can identify primary odor causing chemicals that are causing the odor nuisance. GC-MS was applied to investigate the chemical sources of fecal and musty odorants identified by the OPM. Skatole and indole were found to be the primary chemicals leading to fecal odor, due to its OC/OTC ratio that ranged from 2.8 to 22.5. 2-Methylisoborneol (MIB) and 2-isopropyl-3-methoxypyrazine (IPMP), that have been reported to cause musty odor in drinking water supplies, were identified as principal contributors to the musty nuisance odor at the WWTPs odor sources. The present ability of WWTP odor control treatment of these fecal odorants by different air pollution control methods was evaluated at different locations at two WWTPs by the OPM and

indole and skatole chemical analysis. Chemical scrubbing and biofiltration performed best in removing fecal odors among current control technologies.

The Concentration/OTC (C/OTC) ratio is a simple method to prioritize the odorants and employ both chemical and sensorial results to help eliminate them. The OTC of the nine “most detectable” odor characteristics by the OPM and D/T method and the odorants associated with these odors by the GC-MS and GC-Sensory Analyses at two WWTPs were determined based on Weber-Fechner curve. The Weber-Fechner Curve relates the Log of the Odor Intensity of each chemical causing the odor versus the Log of the Concentration of each odorant. The OTC of 2-isopropyl-3-methoxypyrazine (0.02 ng/L in air), methyl mercaptan (0.2 ng/L in air), 2-methylisoborneol (0.1 ng/L in air), and skatole (0.3 ng/L in air) were quite low. As dilution occurred, the intensities of both the fecal and the sulfur odors decreased. At the greater dilutions, musty odors appeared and the fecal and sulfur odors became undetectable. This is a masking of the odor, which is called “peeling the onion” effect.

This dissertation of Yubin Zhou is approved.

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2017

Table of Contents

| | |
|---|-------------|
| List of Tables | x |
| List of Figures | xii |
| List of Acronyms | xiv |
| Acknowledgements | xv |
| Biographical Sketch | xvii |
| Chapter 1: Introduction and Objectives | 1 |
| 1.1.Introduction | 2 |
| 1.2.Objective | 4 |
| 1.3.References | 6 |
| Chapter 2: Importance of Sensory Analysis and Odor Activity Values in the Determination of Odorants Causing Nuisances from Wastewater Treatment Plants | 8 |
| 2.1.Introduction | 9 |
| 2.2.Methods | 12 |
| 2.2.1. Sampling Locations | |
| 2.2.2. The D/T Method | |
| 2.2.3. The OPM Method | |
| 2.2.4. Chemical Analysis of Reduce Sulfides, Ammonia, and Amines | |
| 2.2.5. Instrument Analysis of Indole, Skatole, MIB and IPMP | |
| 2.3.Results | 16 |
| 2.3.1. Odor Analysis Gap | |
| 2.3.2. Major Odorants Defined by OPM | |
| 2.3.3. The Odorants Causing the Odors of Concern | |
| 2.3.4. Compare Sensorial and Chemical Results | |
| 2.3.5. Prioritize the Major Odorants | |
| 2.3.6. Dilution Threshold by OPM and D/T | |
| 2.4.Conclusions | 25 |
| 2.5.References | 26 |
| Chapter 3: Investigation of Losses of Odorants in the Tedlar and Teflon Sampling Bags | 29 |

| | |
|--|-----------|
| 3.1.Introduction | 30 |
| 3.2.Experimental | 31 |
| 3.2.1. Bag Material | |
| 3.2.2. Compounds and Concentrations of Concern as Nuisance Odorants | |
| 3.2.3. Quantification Methods | |
| 3.2.4. Investigation of Absorption by Tedlar and Teflon Bags | |
| 3.3.Results | 34 |
| 3.3.1. Background of Tedlar and Teflon Bags | |
| 3.3.2. Losses of Odorants in Tedlar Bags | |
| 3.3.3. Losses of Odorants in Teflon Bags | |
| 3.3.4. Absorption by Tedlar and Teflon Bags | |
| 3.4.Conclusions | 44 |
| 3.5.References | 46 |
| Chapter 4: Identification, Quantification and Treatment of Fecal Odors Released into the Air at two Wastewater Treatment Plants | 49 |
| 4.1.Introduction | 50 |
| 4.2.Methods | 52 |
| 4.2.1. Sample Locations | |
| 4.2.2. Sensory Evaluation by the Odor Profile Method (OPM) | |
| 4.2.3. Odor Threshold Concentrations (OTCs) | |
| 4.2.4. Quantitation | |
| 4.3.Results and Discussions | 56 |
| 4.3.1. Fecal Odor Nuisance | |
| 4.3.2. Odor Threshold Concentrations | |
| 4.3.3. Quantification of Indole and Skatole | |
| 4.3.4. Correlation between Odor Intensity and Concentration | |
| 4.3.5. The Effectiveness of Fecal Odor Treatment | |
| 4.4.Conclusions | 65 |
| 4.5.References | 67 |
| Chapter 5: Identification of Musty Odor Nuisance at Wastewater Treatment Plants | 71 |
| 5.1.Introduction | 72 |

| | |
|---|------------|
| 5.2.Methods | 76 |
| 5.2.1. Odor Profile Method | |
| 5.2.2. Solid Phase Microextraction and Gas Chromatography-Mass Spectrometry (GC-MS) | |
| 5.2.3. Odor Threshold Concentrations (OTCs) | |
| 5.2.4. Sampling Locations | |
| 5.3.Results and Discussion | 79 |
| 5.3.1. Odor Nuisances Determined by the OPM | |
| 5.3.2. Effectiveness of the Present Musty Odor Treatment Determined by OPM | |
| 5.3.3. Qualitative and Quantitative Analysis of Musty Odorants by GC-MS at the OCSD WWTPs | |
| 5.3.4. Odor Threshold Concentration of Musty Compounds in Air | |
| 5.4.Conclusions | 91 |
| 5.5.References | 93 |
| Chapter 6: Determination of Odor Threshold Concentration by Weber-Fechner Curves and the Peeling of an Onion Effect via Masking of Odors | 97 |
| 6.1.Introduction | 98 |
| 6.2.Methods | 102 |
| 6.2.1. Odor Panel Sensory Methods | |
| 6.2.2. Bag Material | |
| 6.2.3. Instrument Quantification of Indole and Skatole | |
| 6.2.4. Instrument Quantification of Musty Odorants | |
| 6.2.5. Instrument Quantification of Volatile Organic Sulfur Compounds | |
| 6.2.6. Instrument Quantification of Ammonia | |
| 6.3.Results and Discussion | 107 |
| 6.3.1. Odor Threshold Concentrations | |
| 6.3.2. Odor-Threshold Concentration by ASTM Method 679-04 | |
| 6.3.3. “Peeling the Onion” | |
| 6.4.Conclusions | 115 |
| 6.5.References | 116 |
| Chapter 7: Conclusions and Future Research | 115 |

| | |
|-----------------|-----|
| 7.1.Conclusions | 116 |
| 7.2.Future | 118 |

List of Tables

| | | |
|------------|--|-----|
| Table 2.1. | Flavor Profile Analysis Odor Intensity Strength Scale | 10 |
| Table 2.2. | Analytical Techniques for Reduced Sulfur, Ammonia and Amines | 15 |
| Table 2.3. | Odor character, MRL and OTC of Odorants at WWTPs | 17 |
| Table 2.4. | Average Intensity of 5 Samples from 5 locations at Plant 1 | 18 |
| Table 2.5. | Concentrations of Raw Odorants by Plant Process | 20 |
| Table 2.6. | C/OTC of Odorants by Plant Process | 23 |
| Table 2.7. | D/T Results for OPM and EN Method 13725 | 25 |
| Table 3.1. | Initial Compounds and Concentrations in the Sampling Bags | 32 |
| Table 4.1. | Standard Curve and Quality Parameters of Indole and Skatole | 55 |
| Table 4.2. | Odor Threshold Concentration Determination for Skatole (ng/L in Air) in Teflon Bags by an Expert Panel of 5 | 57 |
| Table 4.3. | Concentration of Indole and Skatole and OPM Results | 59 |
| Table 4.4. | Estimated Air Concentration of Indole and Skatole by Henry's Law | 60 |
| Table 5.1. | Average \pm the Standard Deviation of Four Odor Profile Method's Individual Odor Intensities of Earthy/Musty/Moldy Odor Group at Unit Operations at the OCSD WWTP by an Expert Panel | 86 |
| Table 5.2. | Concentration of MIB and IPMP and OPM Results for one sampling set | 89 |
| Table 5.3. | Comparison of Intensities of Musty Odors Detected by OPM and Calculated by Weber-Fechner Curves | 90 |
| Table 6.1. | Flavor Profile Analysis Intensity Scale used in the Odor Profile Method | 103 |
| Table 6.2. | Sampling and Analytical Techniques for Sulfur Compounds at OCSD WWTP | 102 |
| Table 6.3. | Linear Regression Results, OTCs, and Nuisance Levels of an Individual Odorant in Tedlar Bags Over a 6 Hour Time Period | 108 |
| Table 6.4. | Comparison of Odor Threshold Concentrations | 110 |

List of Figures

| | | |
|--------------|---|----|
| Figure 1.1 | Intensity Scale for Each Odor by Weber-Fechner Curve | 3 |
| Figure 2.1. | Waste Water Odor Wheel | 11 |
| Figure 2.2. | MRLs vs OTCs of Seven Odorants | 17 |
| Figure 2.3. | Comparing Total Reduced Sulfur (TRS) Compounds and D/T at Foul Air Discharge Points at OCSD Plant 1 | 21 |
| Figure 2.4. | Comparing Total Reduced Sulfur (TRS) Compounds and D/T at Foul Air Discharge Points at OCSD Plant 2 | 22 |
| Figure 3.1. | GC/MS Chromatography of Background in Tedlar Bags | 35 |
| Figure 3.2. | GC/MS Chromatography of Background in Teflon Bags | 35 |
| Figure 3.3. | The Losses of Hydrogen Sulfide in Tedlar Bags During 24 Hours | 36 |
| Figure 3.4. | The Losses of Ammonia in Tedlar Bags During 30 Hours | 36 |
| Figure 3.5. | The Losses of IPMP in Tedlar Bags During 30 Hours | 37 |
| Figure 3.6. | The Losses of MIB in Tedlar Bags During 30 Hour | 37 |
| Figure 3.7. | The Losses of Indole in Tedlar Bags During 30 Hours | 38 |
| Figure 3.8. | The Losses of Skatole in Tedlar Bags During 30 Hours | 39 |
| Figure 3.9. | The Losses of Hydrogen Sulfide in the Teflon Bags During 30 Hours | 40 |
| Figure 3.10. | Losses of IPMP in the Teflon Bags During 30 Hours | 41 |
| Figure 3.11. | The Losses of MIB in the Teflon Bags During 30 Hours | 41 |
| Figure 3.12. | Losses of Indole in Teflon Bags During 30 Hours | 42 |
| Figure 3.13. | The Losses of Skatole in the Teflon Bags During 30 Hours | 42 |
| Figure 3.14. | Percentage of Skatole Absorbed by Tedlar and Teflon bags | 43 |
| Figure 3.15. | Absorption Curve of Skatole by Tedlar Bags. | 44 |
| Figure 4.1. | Catabolic Pathway for Skatole | 51 |

| | | |
|-------------|--|-----|
| Figure 4.2. | Weber-Fechner Curve of Skatole Alone in Teflon bags | 60 |
| Figure 4.3. | Average Daily Intensity versus Log Concentration of Skatole | 61 |
| Figure 4.4. | Fecal Odors by OPM at "In" and "Out" of Treatments at Plant 1 | 62 |
| Figure 4.5. | Fecal Odors by OPM at "In" and "Out" of Treatments at Plant 2 | 63 |
| Figure 4.6. | Concentration of Indole and Skatole at Truck Loading at Plant 2 | 65 |
| Figure 5.1. | Intensity Scale for Each Odor by Weber-Fechner Curve | 76 |
| Figure 5.2. | Air Treatment of Musty Odor Intensities "In" vs. "Out" of Treatment Plant Processes at Plant 1 | 81 |
| Figure 5.3. | Air Treatment of Musty Odor Intensities "In" vs. "Out" of Treatment Plant Processes at Plant 2 | 84 |
| Figure 5.4. | The Weber-Fechner Curves of MIB and IPMP | 88 |
| Figure 6.1. | The Wastewater Odor Wheel | 100 |
| Figure 6.2. | Intensity Scale for Each Odor by Weber-Fechner Curve | 101 |
| Figure 6.3. | Weber-Fechner Curves for Individual Odor-Threshold Concentration Determination of an Odorant in Tedlar Bags except for indole and skatole which were determined in Teflon Bags | 109 |
| Figure 6.4. | OPM Results at the Activated Sludge Reactors at the OCSD WWTP | 113 |
| Figure 6.5. | OPM Results at the Truck Loading Locations | 114 |

List of Acronyms

| | |
|------------------|--------------------------------------|
| DMDS | Dimethyl Disulfide |
| DMS | Dimethyl Sulfide |
| FPA | Flavor Profile Analysis |
| GAC | Granular Activated Carbon |
| GC/MS | Gas chromatography/mass spectrometry |
| H ₂ S | Hydrogen Sulfide |
| IAA | Indoleacetic Acid |
| IPMP | 2-Isopropyl-3-methoxypyrazine |
| MIB | 2-Methylisoborneol |
| MIB | 2-Methylisoborneol |
| OAV | Odor Activity Value |
| OCSD | Orange County Sanitation District |
| OPM | Odor Profile Method |
| OTC | Odor Threshold Concentration |
| SPME | Solid Phase Micro-extraction |
| TCA | 2,4,6-Trichloroanisole |
| TRS | Total Reduced Sulfur |
| VOC | Volatile Organic Compound |
| VSC | Volatile Sulfur Compound |
| WWTP | Waste Water Treatment Plant |

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Biographical Sketch

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PUBLICATIONS

Zhou, Y., Hallis, S., Vitko, T., Suffet, I.H., 2016. Identification, Quantification and Treatment of Fecal Odors Released into the Air at two Wastewater Treatment Plants. *Journal of Environmental Management*, 180, 257-263.

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CONFERENCE PRESENTATIONS

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Chapter 1

Introduction and Objectives

1.1.Introduction

Complaints from neighbors around wastewater treatment plants (WWTPs) are mostly about the odors emitted from treatment facilities (Vitko et al., 2014). Odors are produced during different stages of the sewage treatment, especially in areas where sewage is stirred or splashed and where concentrated solids are squeezed or churned (Abraham, 2014). Odorous compounds are released into surrounding residential neighborhoods if the process areas are not properly covered, if there is no adequate negative pressure applied, and if the foul air is not adequately treated in scrubbers (Diaz et al., 2005). Air pollution from odors can lead to physiological stress, insomnia and irrational behavior according to Wilson et al., (1980).

Current treatments in most WWTPs are designed to remove toxic substances and meet the required standards. For example, the NIOSH exposure limit for H₂S is 15,000 ng/L while the odor threshold concentration (OTC) of H₂S is as low as 0.7 ng/L (Suffet and Rosenfeld, 2007). Thus, the lack of control on malodors will limit the reuse of treated sewage and worsen the relationship between WWTPs and citizens near the plant (Lin et al., 2001). The control of odor emissions has become one of the most important challenges in the wastewater treatment industry.

Knowing the most prevalent odorants at each of the sources is crucial in determining the treatment technology to be used in order to effectively control odors. All odorous chemicals must first be measured, characterized and then prioritized. Chemical analyses for key odorants have method reporting limits (MRLs) that are less sensitive than the human nose, thereby odorous compounds are not detected when in fact the odorants might still cause an odor nuisance. Thus, characterization of odors should be done both by chemical analysis and sensory methods.

The detection threshold of total odors is determined as the dilution factor needed so that 50% of the panelists begin sensing an odor. The dilution factor thus obtained is called “dilution to

threshold” or D/T (ASTM E679, 2011; EN13725, 2003; ASTM E544, 2010). The D/T method determines the dilution needed to reduce the total odor to a certain nuisance level. The characterization of the specific odors by the Odor Profile Method (OPM) (Burlingame, 1999; Burlingame, 2009) characterizes the odor into categories and defines each odor character on an intensity scale. The OPM also points out the possible compounds that may be responsible for the odors. The OPM helps determine what odors are present in that total odor and which odor is needed to target the treatment.

Odor prioritization helps define which are the major odors targeted for removal. The ratio of the concentration of a compound to its odor threshold (C/OTC), also known Odor Activity Value (OAV) (Patton and Josephson, 1957), provides a useful measure of which compounds in a mixture are likely to present the greatest odor nuisance. Using these relative ratios, rather than absolute concentrations, provides more meaningful information about which odorants pose an odor nuisance problem. The intensity of an odor obtained by the OPM is proportional to the logarithm (base 10) of the concentration of the odorant, based on Weber- Fechner law (Fechner, 1859). The OTC is defined as the concentration when intensity is 1 ($I=1$) on the Weber-Fechner curve (Figure 1.1) (Suffet et al., 1995).

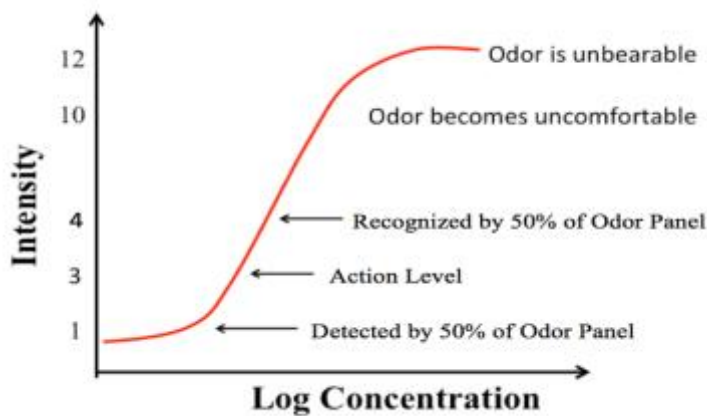


Figure 1.1. Intensity Scale for Each Odor by Weber-Fechner Curve

The losses of volatiles and odorants in sampling bags have been reported in literature (Hansen et al., 2011; Boeker et al., 2014). Boeker et al (2014) measured the fecal odorants indole and skatole at low concentration in Tedlar bags and found dramatic losses of these odorants. He determined that only about 5% remains of indole and skatole after initial losses due to adsorption to walls within a few minutes of sampling. Suitable sampling bags are needed to collect samples for the methods of D/T, the odor profile method (OPM), gas chromatography- mass spectroscopy (GC-MS) chemical analysis. This dissertation evaluated the stability of wastewater odorants samples in sampling bags of Tedlar (polyvinyl fluoride film) and Teflon FEP (fluorinated ethylene propylene film).

After the primary odor is removed, other odors become apparent and also need to be removed, which is called the “peeling the onion” effect. Predicting the nuisance of each layers of the onion becomes the challenge of odor control. For example, if the most prevalent odorants, such as reduced sulfide compounds, are removed, other odorous compounds will take the place and become the issue at a given location. Thus, odor treatment technologies should be designed to adequately remove both the primary and secondary odorous compounds.

1.2.Objectives

The goal of this dissertation was to establish a systematic methodology to investigate odor nuisances at WWTPs, and solve the analytical and sensorial issues needed to correctly evaluate odor problems. The specific objectives of this study were to:

- Fill the gap between MRLs and OTCs with sensorial methods, and develop a method to prioritize odorants by using C/OTC ratios.

- Determine and compare which type of sampling bag material represents the best option for simultaneous odorant sampling by D/T, the OPM, GC/MS chemical analysis and GC-Sensory Analysis.
- Identify the fecal odorant(s) in air, and relate fecal odors in air and their intensities measured by odor panels
- Observe if musty odor nuisance was present at the two WWTPs and evaluate the effect of current treatments of off-gases for removal of the musty odors after determining the chemical(s) causing the musty odors. Measure and understand what occurs during the dilution process of olfactometry, and investigate how odors are masked (layered in a mixture) and the persistence of odors by dilution.

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Chapter 2

Importance of Sensory Analysis and Odor Activity

Values in the Determination of Odorants Causing

Nuisances from Wastewater Treatment Plants

2.1.Introduction

Odorous compounds are released into surrounding residential neighborhoods by wastewater treatment plants (WWTPs) (e.g. Higgins et al., 2008). Odors are produced during these different stages of treatment (Lebrero et al., 2011). Due to population growth, WWTPs are in closer proximity to residential neighborhoods and businesses, resulting in a large increase in the number of public complaints about odor nuisance (Curren, 2014; Lebrero et al., 2011; Leson and Winer, 1991). Odorous emissions from WWTPs tend to consist of many individual odorous compounds that include reduced sulfur compounds, amines, and fatty acids (Adams et al., 2003; Hwang et al., 1994). Volatile sulfur compounds (VSCs), especially hydrogen sulfide (H₂S), are considered as the primary cause of odor emissions from anaerobic WWTPs (Fisher et al., 2016).

There are many different analytical chemistry methodologies to quantify known odorants that cause odors, e.g. hydrogen sulfide. Each methodology is dependent on the family of compounds being analyzed. Odor nuisances are difficult to evaluate solely on the basis of chemical analysis as 1) the odor must be characterized, 2) the intensity of each odor must be defined and 3) there may be a gap between the odor threshold concentration (OTC) of odorants and the chemical analysis method reporting limit (MRL). Odorants with concentration within the gap will cause malodor, but will not be reported by analytical methods. To effectively control odors, both sensory and chemical detection methods are needed to define the odor problem and then implement successful odor-removal technologies.

The public uses their noses to detect and complain about odors generated at locations such as WWTPs and other industries odorous emissions. The primary sensory methodology to determine odor nuisance is known as the dilution to threshold (D/T) method (ASTM E679, 2011; EN13725, 2003; ASTM E544, 2010). It uses dynamic olfactometry (St. Croix Sensory, Lakewood, MN) to

precisely dilute air samples to known ratios. An olfactometer is an air-dilution instrument that precisely dilutes a given odorous compound with pure air so that the exact concentration is known. This method determines, through successive dilutions, a factor at which the odor detection threshold occurs. The D/T ratio is a measure of the total odor from a source.

Another sensory method is known as the odor profile method (OPM) (Burlingame, 1999). The OPM identifies all the different odor characters (how odors smell i.e. rotten eggs, rancid, fecal etc.) present in an undiluted sample and reports them as odor characteristics with an odor intensity for each particular odor character. The OPM uses the Wastewater Odor Wheel (Figure 2.1) to determine which standards to use in the training of panelists in order to determine the odor character descriptors for a sample and which chemicals to analysis that could be causing the odor. Odor intensity is based on a seven-point scale using sugar standards as references levels (APHA, 2012; Curren, 202) (Table 2.1). Table 2.1 is based upon the Weber-Fehner Curve (Fechner, 1859; Suffet et al., 1995)

| Point of the Scale | % Sugar in Water | Odor Strength | Expected Off-Site Odor Problems from Wastewater Plant Odors |
|---------------------------|-------------------------|---|--|
| 0 | 0 % | Odor free | None |
| 1 | Threshold | Very Few | |
| 2 | Very Weak | Unlikely Off-Site Complaints | |
| 3 | Recognizable | Action Level | |
| 4 | 5 % | Weak | Probable Off-Site Odors -Recognition of Odor Character- (Complaints Begin by Off-site Neighbors) |
| 6 | Weak-Moderate | Definite Off-Site Odors -Objection of Odors- (Complaints by Off-site Neighbors) | |
| 8 | 10 % | Moderate | Definite Off-Site Odor Complaints |
| 10 | Moderate-Strong | Definite Off-Site Odor Complaints | |
| 12 | 15 % | Very Strong | Definite Off-Site Odor Complaints |

Table 2.1. Flavor Profile Analysis Odor Intensity Strength Scale (APHA, 2012)

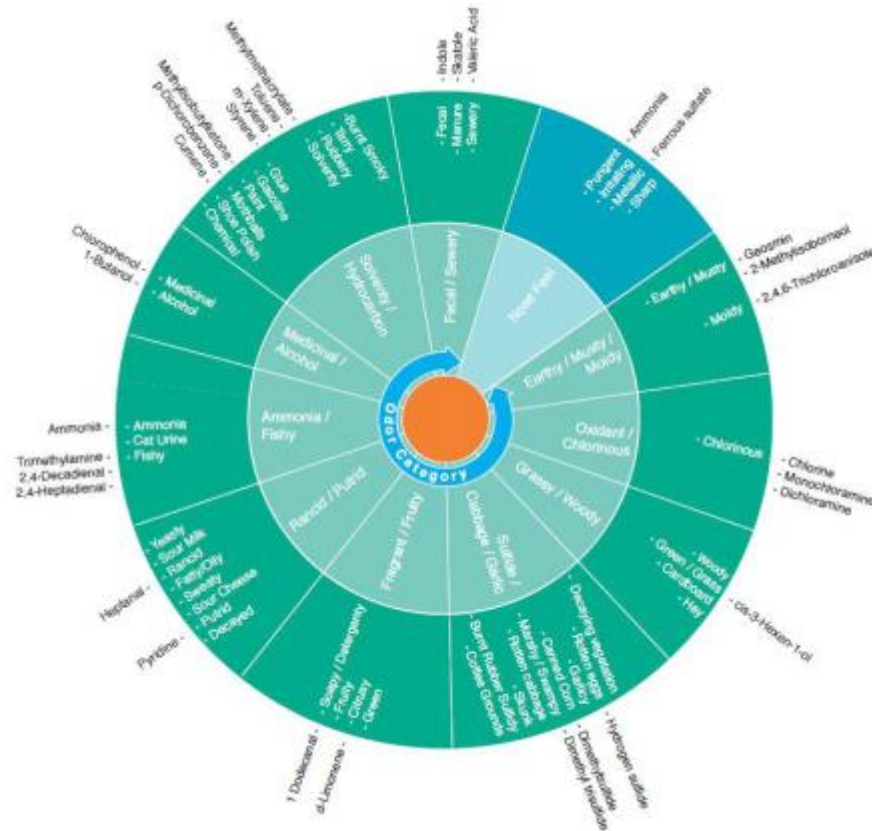


Figure 2.1. Waste water odor wheel

Odorant prioritization distinguishes the major odorants that need to be targeted for removal from the minor contributors. The major odorants are not only those present at the highest concentrations (C) but also those that have high concentration to the odor-threshold concentration (C/OTC) ratios. The higher the C/OTC ratios indicate the compounds that are likely to pose the odor nuisance, at a very low concentration.

The objectives of this study are to 1) evaluate the gap between chemical analysis reporting limits and OTCs, and thus, the necessity to employ sensory method; 2) to develop a method to determine the principal odorants possibly causing nuisances; 3) to offer a simple procedure to prioritize odorants by using C/OTC ratios; and 4) to compare the D/T method and the OPM.

2.2.Methods

2.2.1. Sample locations

The Orange County Sanitation District (OCSD), a special district of the County of Orange, California, serves a population of 2.5 million with its two municipal WWTPs. Plant 1 is located in the city of Fountain Valley and Plant 2 is in the city of Huntington Beach. Both have similar processes and serve as excellent examples of close proximity leading to odor nuisance management challenges.

Foul air samples were collected at all monitoring stations in both OCSD treatment plants using standardized methods (EPA, 1986). The foul air sources include wastehauler station, headworks scrubbers, primary scrubbers, trickling filter system, activated sludge, dissolved air flotation, dewatering, and truckloading. All foul air sources were sampled at existing positive pressure foul air collection ducts, except for those processes with open surfaces exposed to the atmosphere, such as: trickling filter media surface, trickling filter reactor basin, trickling filter mixed liquor channel, and activated sludge effluent channel, where a flux chamber was used.

2.2.2. The Dilution to Threshold ratio (D/T) method

Dynamic olfactometry was completed to determine the Dilution to Threshold ratio (D/T) using ASTM E679-04, EN 13725 and ASTM E544 (ASTM E679, 2011; EN13725, 2003; ASTM E544, 2010). D/T uses a trained human panel who are forced to choose between two blanks and a progressively less diluted odor sample to the point, where 50% of the panel begins to detect the total odor in the sample. The recognition threshold is where 50% of the panel begins to recognize the odor as having a particular character. This method determines, through successive dilutions, a factor at which the odor detection threshold occurs. The odor concentration at the detection threshold is defined as 1 ouE/m³, and the odor concentration is then expressed as multiples of this

unit. This method does not determine recognition odor(s) or their identified thresholds, nor does it measure the intensity of a potential annoyance. The final dataset typically only includes the data for the four or more panelists whose results are the most consistent with the overall panel's geometric mean value.

2.2.3. The OPM method

2.2.3.1. Training of panelists

Each panelist is taught to identify multiple odor characters presenting in a single sample and to rate their particular odor intensity as described by the odor wheel (Figure 2.1). Odor intensity uses the Flavor Profile Analysis method with sugar standards (APHA, 2012) using a seven-point odor intensity scale, as described by Table 2.1. Panelists are trained to distinguish odor mixtures and the intensity of each odorant. Panelists are presented with mixtures of 2, 3, and 4 odorants and are asked to identify the odor characteristics and the intensity of each odorant. With this process, an odor panel, composed of 4-8 individuals is trained to choose odors and appropriate intensities to analyze actual odor samples thereby able to identify complex odor mixtures in real life situations.

2.2.3.2. Calculation of intensity

For the odor characters reported by 50% or more of the panelists, OPM results are averages in odor character among the panelists expressed in units of intensity followed by the standard deviation. If an odor character was reported by fewer than 50% of the panelists, the odor was reported as an odor note without an intensity score and excluded from further analysis. The intensity ratings are proportional to the logarithm of the concentration of the odorant (Fechner,

1859; Suffet et al., 1995). As such, the apparently large standard deviation figures are not as critical as they would if they were on a linear scale for concentration.

At the odor threshold intensity of 1, an odor panelist can state that the odor is different than clean air. Only at an odor intensity of 4 can the panelist recognize odor characteristic. An average odor intensity of 3 is considered as an action level for drinking water plants to avoid odor nuisance complaints (Burlingame, 2004) (See Table 2.1). The use of the OPM and its relationship to the D/T method has been presented (Zhou et al., 2016a)

2.2.4. Chemical analysis of reduced sulfur, ammonia and amines

Samples were chemically analyzed for reduced sulfur, ammonia, amines, including methylamine, and volatile acids by ALS Laboratories (Simi Valley, CA). (Table 2.2)

| Odorant | Lowest Odor Threshold (ppbV) | Sampling Technique | Analytical Technique | Method Reporting Limit (ppbV) |
|--------------------|-------------------------------------|--|---|--------------------------------------|
| Acetic Acid | 1,019 | 1.0 L/min rate for 100 – 200 min. in sorbent tube. | TO-11A Method by GC/MS. | 9.2 - 4.6 |
| Butyric Acid | 0.33 | | | 0.76 - 0.38 |
| Propionic Acid | 27.77 | | | 0.9 - 0.45 |
| Isobutyl Mercaptan | 0.54 | Grab sample into 1 L Tedlar bag. | ASTM D5504 Method by Modified GC/SCD with sulfur chemiluminescence detection. | 5.0 |
| Ethyl Mercaptan | 0.013 | | | 5.0 |
| Methyl Mercaptan | 0.020 | | | 5.0 |
| Dimethyl Disulfide | 0.026 | | | 5.0 |
| Dimethyl Sulfide | 0.99 | | | 5.0 |
| Hydrogen Sulfide | 0.5 | | | 5.0 |
| Dimethyl Amine | 20.55 | 1.0 L/min rate for 100 – 200 min. in sorbent tube. | CAS 101/TO-17 Method by Modified GC/NPD | 5.6 - 2.8 |
| Ethyl Amine | 264 | | | 6.0 - 3.0 |
| Methyl Amine* | 19.89 | | | 0.0078 - 0.0039 |
| Trimethyl Amine | 0.33 | | | 4.1 - 2.1 |
| Ammonia | 38.28 | 0.5 L/min rate for 60 min. | OSHA ID-188/ID-164. | 0.26 |

Table 2.2. Analytical Techniques for reduced sulfur, ammonia and amines

2.2.5. Instrument Quantification of Indole, Skatole, 2-Methylisoborneol (MIB) and 2-Isopropyl-3-methoxypyrazine (IPMP)

Indole and skatole was extracted through a series of 3 impingers from a 10-L sample with 15 mL dichloromethane in each at flow of 0.5 L/min for 20 minutes. Then, the solution from the first two impingers were concentrated to 1 mL and measured by GC/MS (Zhou et al., 2016b).

A solid phase micro-extraction (SPME) method (Godayol et al., 2013) that was used to identify and quantify earthy/musty/moldy odorants. A SPME fiber of DVB/CAR/PDMS was injected into a 10-L sample bag and exposed for 20 minutes. The SPME fiber was injected onto a Varian 450 gas chromatograph (Varian Inc., Palo Alto, California) through an #1177 liquid-injector port (Zhou et al., 2017)

2.3.Results

2.3.1. Odor analysis gap

All odorants have a specific odor characters, analytical chemistry MRL, and OTC. Table 2.3 shows a typical list of odorants detected at WWTPs (Vitko et al., 2014). Note that the first six odorants in this list have their OTCs lower than their MRLs. Figure 2.2 compares these odorants that have OTCs lower than their MRLs. This illustrates how much odor information may be lost if one only relies on standard analytical results to describe odors. For example, the human nose is 10 times more sensitive than the lab method for hydrogen sulfide, but is 62 times more sensitive for methyl mercaptan, and 384 times more sensitive for ethyl mercaptan. This data shows an odor analysis gap by chemical analysis. Thus, sensory methods, such as D/T and OPM, are needed to help bridge the gap between chemical detection limits, nose characterization, and nose sensitivity.

| Odorant | Characteristic | MRL (ppbV)* | OTC (ppbV)** |
|---------------------|---------------------|-------------|--------------|
| Dimethyl Disulfide | Rotten garlic | 2.5 | 0.2 |
| Dimethyl Sulfide | Canned Corn | 5.0 | 3.0 |
| Ethyl Mercaptan | Rotten cabbage | 5.0 | 0.013 |
| Hydrogen Sulfide | Rotten eggs | 5.0 | 0.5 |
| Methyl Mercaptan | Rotten vegetable | 5.0 | 0.08 |
| Trimethylamine | Pungent, Fishy | 2.1 | 0.33 |
| Ammonia | Pungent, Irritating | 0.26 | 1,000 |
| Acetic Acid | Vinegar | 4.0 | 1,019 |
| Butyric Acid | Rancid | 0.3 | 0.33 |
| Valeric Acid | Sweat | 0.3 | 0.62 |
| Acetone | Solvent | 5.5 | 19,798 |
| Carbon disulfide | Ether-like | 8.0 | 7.81 |
| Methyl Ethyl Ketone | Butterscotch | 4.9 | 250 |
| Tetrahydrofuran | Solvent | 3.8 | 2,502 |
| Toluene | Solvent | 3.0 | 2,131 |

Table 2.3. Odor character, MRL and OTC of Odorants at WWTPs

*ASTM 55-04

** Ruth, 1986; Zhou et al., 2016a.

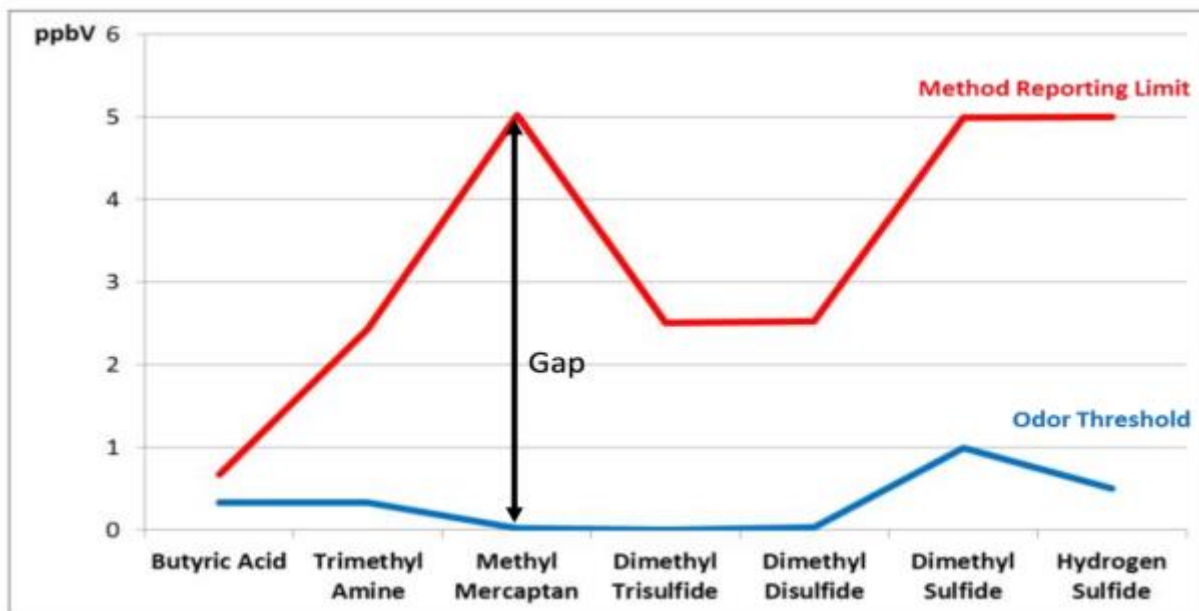


Figure 2.2. MRLs vs OTCs of seven odorants

2.3.2. Major odors defined by OPM

Table 2.4 shows the OPM results of 5 exemplary locations at Plant 1. As an intensity of 3 corresponds to an odor that the public from off-site would most certainly begin to complain about, there would be odor nuisance from all these locations (Suffet et al., 2008). The OPM identified that the major odors of concern are the sulfur group (rotten egg/vegetable/garlic), fecal group and the earthy/musty group. The rotten vegetable odors and fecal odors were the dominant odors at almost all the locations. The fecal odors can pose an off-site problem at all locations as the odor intensities were all above 3.

The musty odors and the garlic odors were the secondary odors at these locations. Because the rotten vegetable and fecal odors were too strong, the perception of secondary odors may be masked. It has recently been shown that when the primary odors are removed by treatment, the secondary odors may become the major odors and lead to a new odor nuisance (Zhou et al., 2016a). Thus, the musty odors and the garlic odors were considered as the major odors though their intensities were not over 3.

| Odor Profile Method (Character) | Pretreated Trunklines & Bin Loading Bldg. | Bar Screens & Grit Chambers | Primaries | Wastehauler Station | Truck Loading |
|--|--|--|------------------|----------------------------|----------------------|
| Rotten vegetable | 4.0±3.2 | 4.0±3.2 | 3.2±3.0 | 1.5±2.4 | 6.7±4.4 |
| Rotten Garlic | 0.7±1.9 | 0.5±1.5 | 0.4±1.2 | 1.7±2.8 | 1.6±3.1 |
| Earthy/Musty/Moldy | 1.3±2.0 | 1.2±1.7 | 0.8±1.5 | 0.4±1.1 | 3.4±3.2 |
| Fecal/Sewery/Manure/Rubbery | 5.2±1.9 | 4.0±2.9 | 4.1±2.7 | 4.4±3.1 | 7.4±3.7 |

Table 2.4. Average Intensity of 5 Samples from 5 locations at Plant 1

2.3.3. The odorants causing the odors of concern

The wastewater odor wheel not only shows each type of odor character, but also shows some of the major chemicals that could cause the particular odor character (Figure 2.1). For example, the presence of rotten vegetable odors indicates the occurrence of reduced sulfur compounds. Thus, based on the major odors detected by the OPM, the potential odorants causing the odors of concern can be found on the wastewater odor wheel:

- Rotten Egg: hydrogen sulfide (H₂S):
- Rotten Vegetable: methyl mercaptan (MM), dimethyl sulfide (DMS), dimethyl trisulfide (DMTS):
- Garlic: dimethyl disulfide (DMDS);
- Musty: 2-Methyl Isoborneol (MIB), 2-Isopropyl-3-Methoxypyrazine (IPMP), Geosmin;
- Fecal; skatole: indole.

The outcomes above helped narrow down the large number of odorants identified to a manageable number of odorants. It saved much time in targeting the correct odorants with the assistance of the OPM.

Table 2.5 shows the analytical results of 5 locations from each treatment plants. In terms of concentration, H₂S was dominant at 5 locations and the concentrations were much higher than those of other odorants. This is consistent with the assumption that H₂S is the major odorant emitted at WWTPs and that it is present at high concentrations (Iranpour et al., 2005; Lasaridi et al., 2010). Thus, most odor-elimination systems used in WWTPs currently are designed based on hydrogen sulfide (H₂S) removal. Meanwhile, high concentrations of DMS were observed at Trickling Filters and Truckloading at Plant 1. MM presented significantly high concentrations at Headworks and Truckloading at Plant 1, and Trickling Filters Plant 2. The concentration of ammonia at Truckloading of Plant 1 was as high as 7900 ppbV. However, the concentrations of

musty and fecal odorants were minor compared to other compounds. Thus, the major odors should come from reduced sulfur compounds and ammonia based on the chemical analysis results.

| Odorant | MM | H ₂ S | DMDS | DMS | NH ₃ | MIB | IPMP | Skatole | Indole |
|--|-------------|------------------|--------|-------------|-----------------|-------|-------|---------|--------|
| Odor | Rotten Veg. | Rotten Egg | Garlic | Rotten Veg. | Ammonia | Musty | Musty | Fecal | Fecal |
| Plant 1 (Concentration in ppbV) | | | | | | | | | |
| Headworks | 330 | 4,800 | 26 | 35 | | | 0.29 | | |
| Trickling Filters | 16 | 15 | 34 | 450 | 0.14 | | | | |
| Activated Sludge | 12 | 8.2 | 7 | 0.27 | | 0.36 | 0.06 | | |
| Dewatering | 13 | 3,300 | | | 1.6 | 0.25 | 0.08 | | |
| Truckloading | 390 | 52 | 27 | 520 | 7,900 | | | 1.4 | 0.75 |
| Plant 2 (Concentration in ppbV) | | | | | | | | | |
| Trickling Filters | 230 | 2,300 | 12 | 160 | | 0.19 | 0.28 | | |
| TF Reactors | 41 | 30 | | | | 0.32 | | | |
| TF Mixed Liquor | 28 | 13 | 1,500 | | | 0.41 | | | |
| DAFTs | 110 | 370 | 61 | | | | 0.09 | 0.30 | |
| Dewatering | 32 | 2,800 | | | | | | 0.39 | |

Table 2.5. Concentrations of Raw Odorants by Plant Process

Note: Reduced sulfur compounds and ammonia were measured on the same sampling date. MIB, IPMP, skatole and indole were measured on another sampling date.

2.3.4. Comparison of sensory and chemical results

Based on the chemical analysis results, the major odors should be rotten vegetable odors from reduced sulfur compounds and fishy odors from ammonia. However, this is not consistent with the OPM results. As shown in Table 2.4, fecal odors were the strongest odors at all locations. Rotten vegetable odors were also primary odors at these locations, but there were no rotten eggs and fishy odors reported. Though H₂S and ammonia presented in very high concentrations, they apparently do not cause odor nuisances, which was controversial to the traditional assumption.

Meanwhile, fecal odorants were the primary odorants although they were detected at much lower concentration levels.

When comparing the chemical analysis results with the D/T results, there were also discrepancies found. The total reduced sulfide (TRS) concentrations and D/T results are presented in Figure 2.3 for Plant 1 and Figure 2.4 for Plant 2. The thick black line indicates the D/T level above which complaints can be expected. There was no correlation observed between the total reduced sulfide concentrations and D/T result. The TRS concentration was over 2700 ppbV at AS discharge channel of Plant 2, but the D/T was below the nuisance level. At Trickling Filter #C out of Plant 2, the TRS concentration was only around 400 ppbV, but the D/T exceeded the nuisance threshold. High concentration of TRS did not necessarily cause an odor problem, while locations with little TRS may still have odor issues.

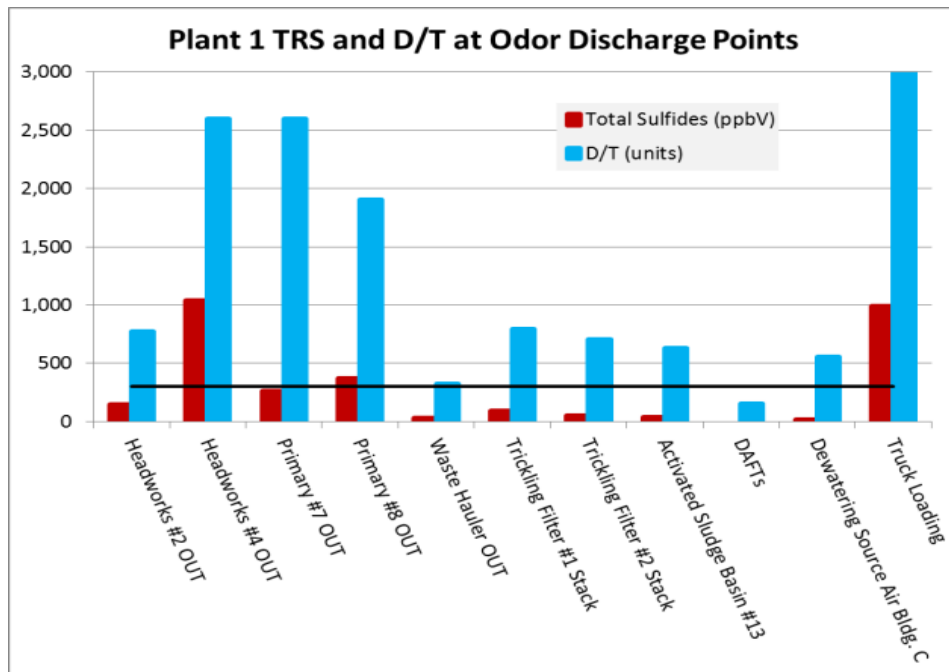


Figure 2.3. Comparing Total Reduced Sulfur (TRS) Compounds and D/T at Foul Air Discharge Points at OCSD Plant 1

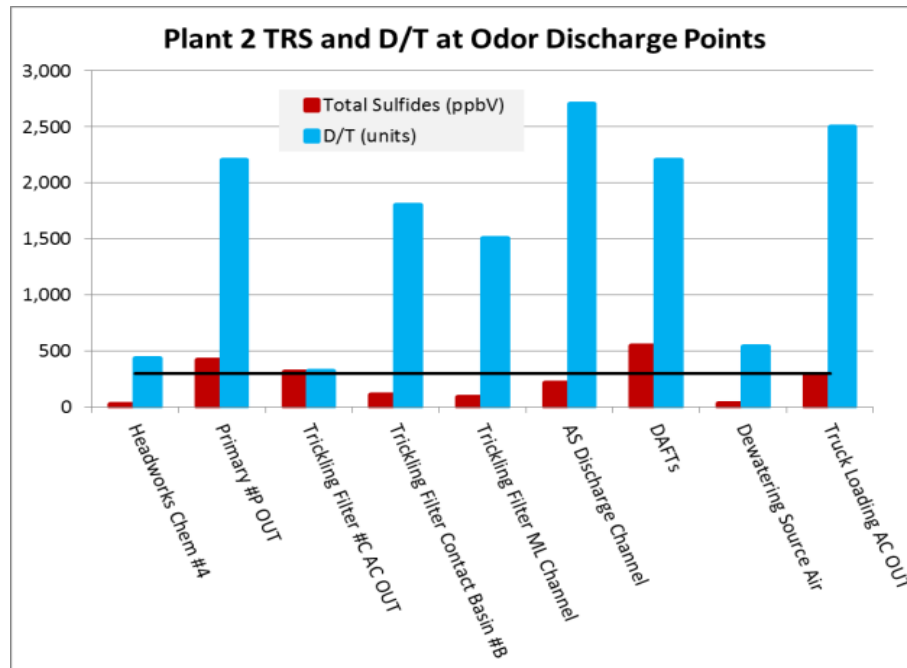


Figure 2.4. Comparing Total Reduced Sulfur (TRS) Compounds and D/T at Foul Air Discharge Points at OCSD Plant 2

One possible cause of the inconsistencies between chemical method and sensorial method is that some odorants have method reporting limits above the odor thresholds, which is the gap shown the Figure 2.2. Therefore, a substantial portion of the perceived odors may be reduced sulfur compounds that are below the method reporting limit yet still well above the OTC. More importantly, the composition of odors was different at each location, so the odors may be due to odorants other than reduced sulfur compounds. These chemicals may be at very low concentration level or even below the MRL, but OPM fills the detection gap between lab method reporting limit and odor threshold. The fecal odorants, indole and skatole, and the musty odorants, MIB and IPMP, are also important odorants causing odor nuisance, as qualified by OPM at many sites.

2.3.5. Prioritize the major odorants

A simple procedure to prioritize odorants is to convert the results in C/OTC of all odorants and compare one another, and the odorant with the highest C/OTC becomes the most important. The C/OTC ratio is known as the Odor Activity Value (OAV) (Patton and Josephson, 1957). C/OTC ratios present the odor data in a normalized form, which allows one to compare the results among all of the odorants present and rank them in order of importance. The major odorants obtained by this method must agree with the sensorial method.

Table 2.6 shows the same results in terms of the ratio between C/OTC. There are stronger and more persistent odorants even at low concentrations, such as IPMP and MIB, than other odorants. The OAVs of MM were higher than those of H₂S, though the concentrations of MM were much lower. MM became the most important sulfur odorant instead of H₂S. Ammonia did not lead to any odor issue due to its high OTC. Otherwise, IPMP and skatole became major odorants because of their very low OTCs. Above all, only those odorants with very low OTCs take preponderance over how concentrated these are being emitted. To determine OAVs is a useful way to understand which compounds are likely to cause an odor nuisance.

| Odorant | MM | H ₂ S | DMDS | DMS | NH ₃ | MIB | IPMP | Skatole | Indole |
|---|----------------|------------------|--------------|----------------|-----------------|---------------|---------------|--------------|-------------|
| Odor | Rotten Vege | Rotten Egg | Garlic | Rotten Vege | Amm- onia | Musty | Musty | Fecal | Fecal |
| Odor Threshold Concentration | 0.08 ppbV | 0.50 ppbV | 0.20 ppbV | 3.0 ppbV | 1,000 ppbV | 0.020 ppbV | 0.004 ppbV | 0.04 ppbV | 0.5 ppbV |
| Plant 1 (Ratio) | | | | | | | | | |
| Headworks | 4,125 | 9,600 | 130 | 12 | | | 77 | | |
| Trickling Filters | 200 | 30 | 11 | 0.4 | | | | | |
| Activated Sludge | 150 | 16 | 2 | 14 | | 17 | 18 | | |
| Dewatering | 26 | 3.3 | | | | 12 | 20 | | |
| Truckloading | 4,875 | 104 | 135 | 173 | 7.9 | | | 23 | 0.8 |
| Plant 2 (Ratio) | | | | | | | | | |
| Trickling Filters | 2,875 | 4,600 | 60 | 53 | | 9 | 98 | | |
| TF Reactors | 512 | 10 | | | | 16 | | | |
| TF Mixed Liquor | 350 | 4 | 1.5 | | | 20 | | | |
| DAFTs | 1,375 | 740 | 20 | 2.0 | | | 25 | 4.9 | |
| Dewatering | 64 | 2.8 | | | | | | 6.4 | 3.5 |

Table 2.6. C/OTC of Odorants by Plant Process

Note: Reduced sulfur compounds and ammonia were measured on the same sampling date. MIB, IPMP, skatole and indole were measure on another sampling date.

2.3.6. Dilution Threshold by OPM and D/T

The D/T can be calculated as the dilution ratio when intensity equals 1 by OPM. The D/T results of OPM and EN 13725 Method (European Committee for Standardization, 2003) are compared in Table 2.7 using standards. The D/T results by OPM were all higher than the D/T results by EN Method 13725 for the sulfide and musty standards. Only, the fecal and ammonia standards are correlated. The EN 13725 method showed a much lower D/T ratio by 2-10 times for the sulfide and musty standards. This may be explained by the differences between the methods. The EN 13725 Method, selects only 4 panelists to calculate the D/T while the D/T results by OPM represent the overall result from a panel consisting of 10-14 and follows odor intensity of each odorant. The use of the D/T ratio by the EN 13725 method does not represent correctly the sulfide or musty odorants.

Therefore, D/T is a measure of the total odor in a sample and provide good information. However, this approach does not give sufficient information about what the specific odors are within the total odor. Thus, the D/T olfactory method may not be helpful for foul air treatment design and abatement of targeted odors. Results from the OPM provide the necessary information to fill in the gap between the detectability limitations of chemical analyses and the sensitivity of the human nose. The OPM for evaluation of mixtures and treatment design is recommended.

| Samples | | OPM | EN 13725 |
|-----------|------------------|--------|----------|
| | | D/T | D/T |
| Standards | H ₂ S | 1,100 | 490 |
| | DMS | 11,000 | 5,100 |
| | DMDS | 15,000 | 5,500 |
| | MIB | 2,500 | 860 |
| | IPMP | 22,000 | 2,500 |
| | Skatole | 330 | 160 |
| | Indole | 350 | 180 |
| | Ammonia | 570 | 510 |

Table 2.7. D/T Results for OPM and EN Method 13725

2.4. Conclusions

- There is a gap between the MRL and OTC of some common odorants, within which there is still odor nuisance while there is no chemical concentration reported. Sensorial method needs to be used to bridge the gap between chemical analysis and human nose.
- OPM characterizes the major odors and narrows the potential odorants to a manageable range.
- The chemical analysis results alone cannot determine the major odorants, as the results are not consistent with D/T and OPM.
- OAV (C/OTC) is a simple procedure to prioritize the odorants detected and combine the chemical and sensorial results.
- The dilution to threshold ratio obtained by OPM and D/T are not consistent. D/T presents the total odor and determines if there is odor issue, but it fails to point out the odors causing the problem. OPM should be used to analyze odorous mixture and target the odorants for treatment.

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Chapter 3

Investigation of Losses of Odorants in the Tedlar and Teflon Sampling Bags

3.1.Introduction

Controlling nuisance odors is an ongoing challenge for wastewater treatment plants that strive to be good neighbors with their surrounding residents (Wilson et al., 1980). The Wastewater Odor Wheel aids the identification of odors (Burlingame, 1999; Burlingame et al., 2004; Suffet and Rosenfeld, 2007; Burlingame, 2009). The study of odor nuisance at Wastewater Treatment Plants (WWTPs) requires a suitable sampling bag to collect samples at one time for the methods of olfactometry (EN 13725, 2003; ASTM 679-04, 2011), the odor profile method (OPM) (Burlingame, 2009; Burlingame, 1999) and GC/MS chemical analysis (Zhou et al., 2016).

Air sampling bags have been widely used in environmental studies to investigate the odor nuisance from factories, refineries, wastewater treatment plants, and landfills. Commonly used bag film includes Tedlar, Teflon, Nylon and Flexfoil. Tedlar (polyvinyl fluoride film) air sampling bag is the “classic bag” for volatile organic chemicals (VOCs) referenced in many EPA methods (TO-15, 1999). Tedlar bags show good stability for carbon monoxide, carbon dioxide, methane, VOCs, and some sulfur compounds, including hydrogen sulfide (Coyne et al., 2011). The sample hold time for analysis in the Tedlar bag varies by method and chemicals. The recommended hold time for sulfur compounds, including reactive sulfur compounds, such as hydrogen sulfide and methyl mercaptan, is 24 hours by ASTM D5504 (2012). Atmospheric and natural gases, such as CO, CO₂, CH₄ and C₂-C₅ Hydrocarbons can be held in the Tedlar bags for up to 3 days (ASTM D1946, 2014 and ASTM D1945 2015). The hold time to analysis for VOCs is also up to 3 days (Modified TO-15, 1999). The Tedlar bag seems to present very good stability for most compounds within 24 hours.

However, Posner and Woodfin (1986) recommended storage of air in Tedlar bags to less than 4 hours. Significant losses in odorant concentration were observed with 0.5 h (Trabue et al.,

2006). Boeker et al. (2014) determined that only about 5% remains of indole and skatole after initial losses due to adsorption to walls within a few minutes of sampling. Hansen et al. (2011) also demonstrated that the concentrations of indoles decreased by 50 to >99% during the 24 hours of storage in Tedlar bags. This issue applies to sulfur compounds as well but with lower losses. Mochalski et al. observed good storage recoveries (>90%) of volatile sulfur compounds (VSCs) during 6h but a significant drop of H₂S (65%) and COS (80%) after 24h. The recoveries of volatile fatty acid were less 40% after 1h storage in Tedlar bags (Parker et al., 2010).

The Teflon FEP (fluorinated ethylene propylene film) is the most chemically inert bag material. The recommended hold time in the Teflon FEP bags is up to 24 hours for some VOCs and low molecular weight gases due to possible permeation through the bag film (SKC, 2011).

The specific objective of this study was to determine and compare which type of sampling bag material represents the best option for simultaneous odorant sampling of the most important odorant nuisances found at WWTPs. The odorants found of prime concern as odor nuisances were tested; hydrogen sulfide (rotten eggs odor) to represent sulfur odorants, ammonia, indole and skatole (fecal odor), and 2-methylisborneol (MIB), and 2-isopropyl-3-methoxypyrazine (IPMP) (musty odors).

3.2.Experimental

3.2.1. Bag Material

Tedlar (polyvinyl fluoride film) sampling bags were provided by OCSD and purchase from SKC Inc. (Pittsburgh, PA, USA). Teflon FEP (polyvinyl fluoride film) sampling bags were purchased from Jensen Inert Products (Coral Springs, FL, USA).

3.2.2. Compounds and Concentrations of Concern as Nuisance Odorants

Five sampling bags were made each time for the test of losses at room temperature (21.0 °C). The relative humidity in the bag was set at 80%. Both H₂S and ammonia were introduced into the bags from gas cylinders using a fixed flow valve. MIB, IPMP, indole and skatole were introduced into the bags by syringe injection of chemical solutions in methanol. The concentration of the compounds introduced are shown in Table 3.1. Because the concentration level showed a great influence on the loss patterns of VOCs (Kim and Kim, 2012), the concentrations used represent the high concentrations found in previous studies (Vitko et al., 2014). The Odor Threshold Odor Concentrations (OTC) represent the wide range of OTCs reported in the literature (Nagata, 2003; Amoore, 1983; Sala et al., 2004; Ruth, 1986). The 5 bags were measured after 15 minutes, 3 hours, 6 hours, 24 hours and 30 hours to determine the loss of odorants. Both Tedlar and Teflon bags were tested in triplicate.

| Compound | Initial Concentration(C) (ppbV) | Odor Theshold Concentration (OTC) (ppbV) | C/OTC (unitless) | Method Reporting Limit (MRL) (ppbV) |
|------------------|--|---|-----------------------------|--|
| H ₂ S | 2,000 | 0.4-8.1 | 250-5,000 | 100 |
| Ammonia | 1,500 | 40-5,800 | 0.3-38 | 2,000 |
| MIB | 8.0 | 0.013-0.07 | 110-620 | 0.04 |
| IPMP | 7.3 | 0.0008-0.008 | 910-9,100 | 0.1 |
| Indole | 10.3 | 0.3-1.4 | 7-34 | 0.25 |
| Skatole | 9.6 | 0.00008-0.06 | 160-120,000 | 0.15 |

Table 3.1. Initial Compounds and Concentrations in the Sampling Bags

3.2.3. Quantification Methods

3.2.3.1. Musty and Fecal Odorants

A solid phase micro-extraction (SPME) (Godayol et al., 2013) was injected into a 10-L sample bag and exposed for 20 minutes. The SPME fiber was injected onto a Varian 450 gas chromatograph (Varian Inc., Palo Alto, California) through an #1177 liquid-injector port at 250 °C followed by a Varian 220 mass spectrometer (SGE Analytical Science, Austin, Texas) with 99.9999% helium as the carrier gas. The gas chromatograph was equipped with an Agilent DB-5MS column (length 60 m, inner diameter 0.25 mm, film thickness 0.25 µm) and held at an initial temperature of 35 °C with a hold of 5 mins, then with a ramp of 5.0 °C/min to 150 °C and then 15 °C/min to 250 °C. The carrier-gas flow rate was 1.0 mL/min through the column. The ion-trap mass spectrometer monitored the primary range of m/z units of IPMP (123-125, 136-138, and 150-153 m/z from 22.20 to 22.70 minutes), MIB (94-96 and 106-109 m/z from 25.50 to 26.10 minutes), indole (89-91 and 116-119 m/z from 28.40 to 29.00 minutes) and skatole (129-132 m/z from 30.40 to 30.90 minutes). The ion-trap mass spectrometer monitored the primary range of m/z units of MIB (56-58, 70-72 and 84-86 m/z from 14.50 to 17.00 minutes) and IPMP (108-110, 123-125, 136-138, and 150-153 m/z from 14.40 to 15.00 minutes). The recovery of this method was over 90% and the recovery was not calculated in the final results.

3.2.3.2.H₂S and Ammonia

H₂S was measure by an OdaLog[®] H₂S gas monitor with a working range of 100 to 2,000 ppbV (accuracy 10%). Ammonia was measured by ToxiRAE Pro ammonia monitor with a working range of 2 to 50 ppmV (accuracy 10%).

3.2.4. Investigation of Absorption by Tedlar and Teflon Bags

Five 10-L bags of skatole at different concentration levels were made of both Tedlar and Teflon bags. Then each bag was cut and a piece of 20cm*20cm bag film were extracted by 20 ml

Dichloromethane. The solution was concentrated to 1 ml by Kuderna–Danish Evaporator with a surface nitrogen flow. One microliter (μL) of solution was injected onto a Varian 450 GC (Varian Inc., Palo Alto, California) with a Varian 220 MS to measure the concentration of skatole. The recovery of the process was 66% and all the data were corrected by the recovery.

3.3. Results

3.3.1. Background of Tedlar and Teflon Bags

Figure 3.1 and Figure 3.2 showed the GC/MS results of background outgassing from Tedlar and Teflon bags. A large amount of phenol (retention time – 9.5 min) was detected by GC/MS from an air blank Tedlar bag (Figure 3.1). The phenol detected also contributed to a medicinal odor as the background for the sensory test by Tedlar bags by the OPM. The compounds commonly detected from a new Tedlar bags include methylene chloride, toluene, acetone, ethanol, 2-propanol, phenol, and dimethylacetamide (Eurofins, US, 2014). Elevated levels of phenol, acetic acid, and N, N-Dimethylacetamide were detected after 30-min storage of pure air in Tedlar bags (Trabue et al., 2006; Parker et al., 2010).

The Teflon bag has the lowest chemical impurities among commonly used air sampling bags (Koziel et al., 2005). The Teflon FEP bag air blank provides a much cleaner background for chemical analysis (Figure 3.2) without any major compounds detected by GC/MS. There was no emission of contaminants detected even after 48h (Mochalski et al., 2009). Very low VOCs and sulfur background was detected by the manufacturers (SKC, 2011). There were no odor notes reported by OPM panels from a new Teflon bag.

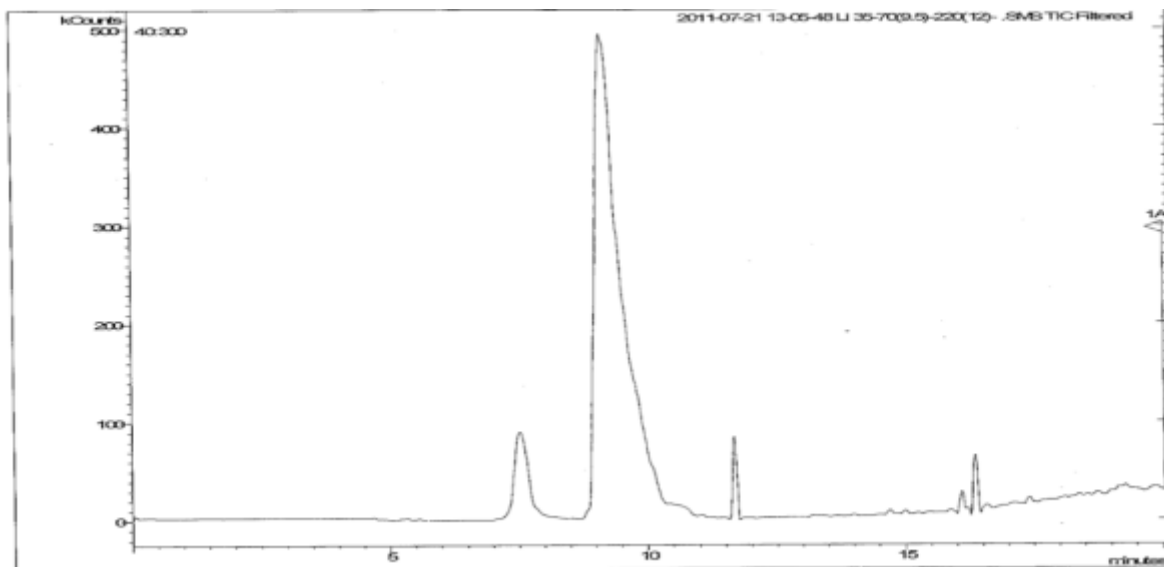


Figure 3.1. GC/MS Chromatography of Background in Tedlar Bags

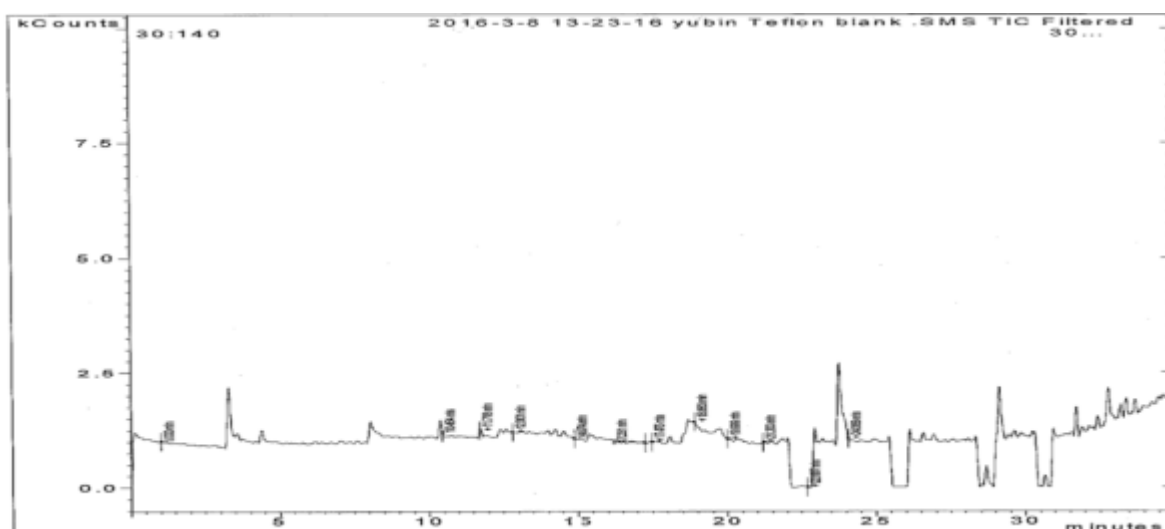


Figure 3.2. GC/MS Chromatography of Background in Teflon Bags

3.3.2. Losses of Odorants in Tedlar Bags

Figures 3.3 to 3.8 show the percentage remaining of each odorant stored during 30 hours in Tedlar bags. Each point is the average of 3 tests, and the standard deviations of the 3 tests were shown as error bars. Hydrogen sulfide and ammonia demonstrated good stability in Tedlar bags. The hydrogen sulfide exhibited an initial loss of 15% that remained constant over the 24 hours (Figure 3.3). However, only 65% hydrogen sulfide remained after 24h due to Mochalski et al.

(2009). Ammonia displayed no loss initially, only a 7% loss at both 3 and 6 hours, and 20% loss by 30 hours, all of which indicate reasonable stability in Tedlar bags (Figure 3.4). However, the 24-hour recovery of ammonia in the Tedlar bag was determined to be 62% in the literature (Coyne et al., 2011) again with actual samples with microorganisms present in the sampling bag

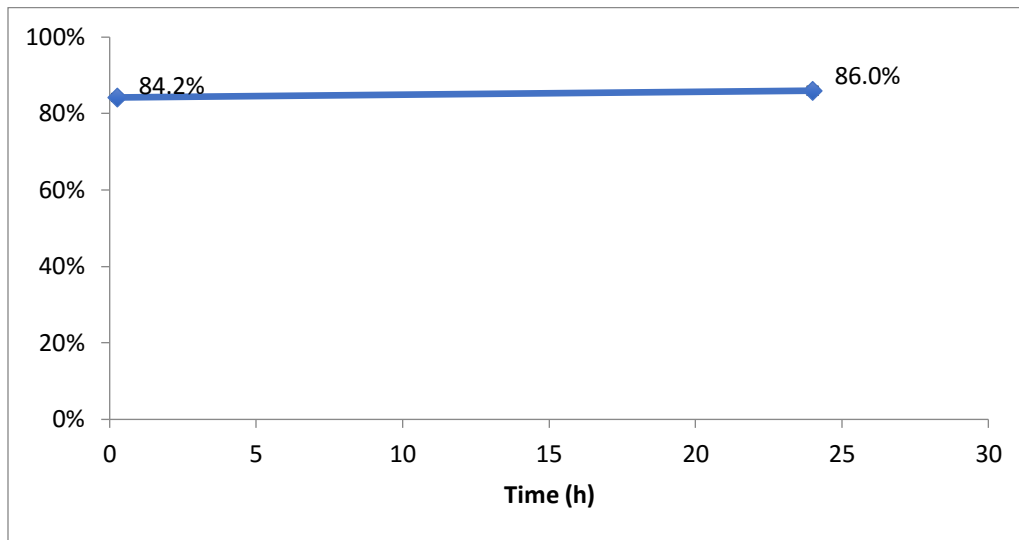


Figure 3.3. The Losses of Hydrogen Sulfide in Tedlar Bags During 24 Hours
Note: error bars are within the squares shown

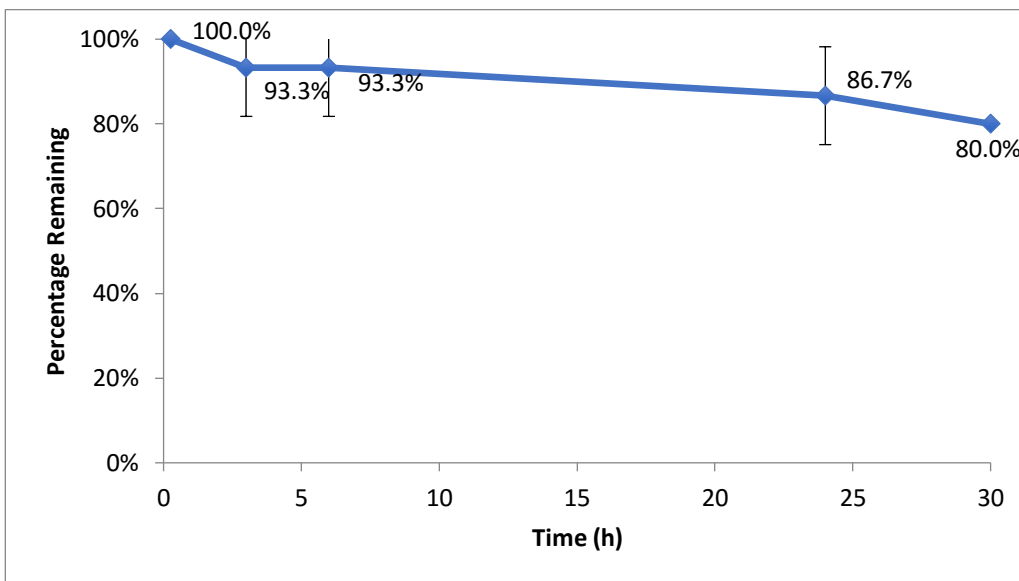


Figure 3.4. The Losses of Ammonia in Tedlar Bags During 30 Hours

Musty odorants, MIB and IPMP, were very stable in the Tedlar bags during 30 hours (Figures 3.5 and 3.6). The variation in concentration was within 5%. Thus, there were no appreciable losses of musty odorants, MIB and IPMP in the Tedlar bags.

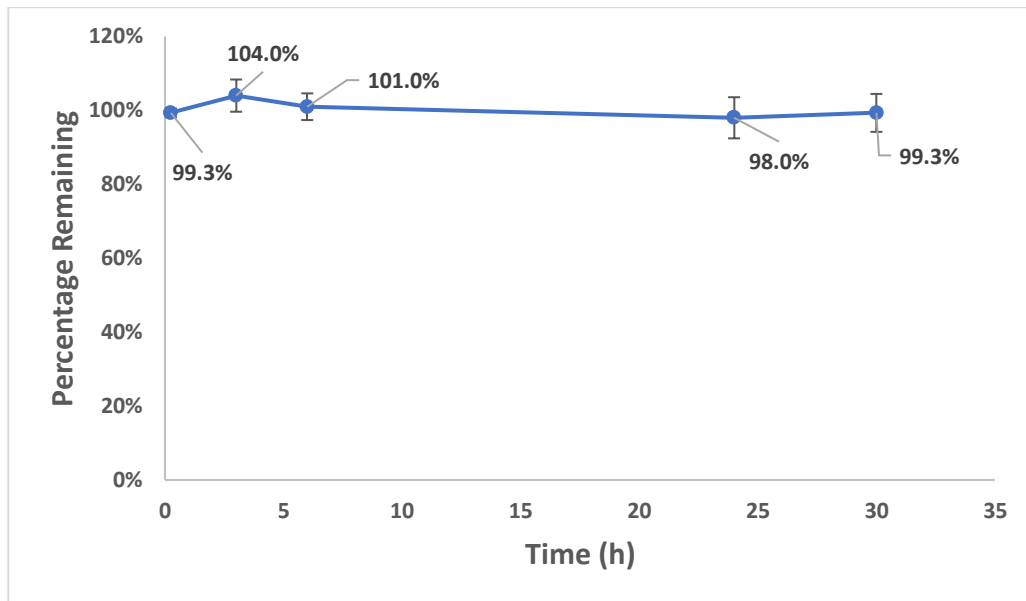


Figure 3.5. The Losses of IPMP in Tedlar Bags During 30 Hours

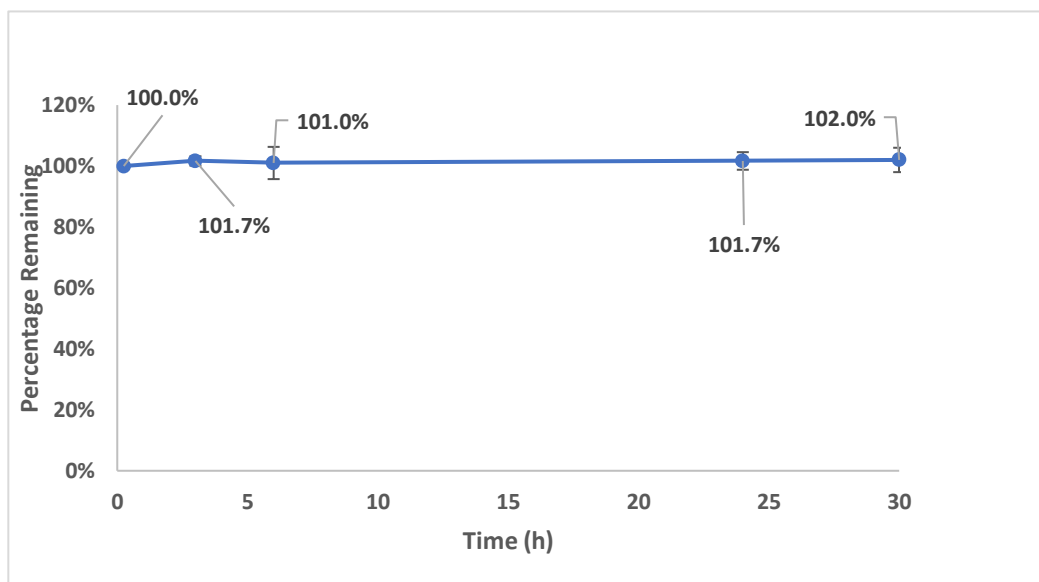


Figure 3.6. The Losses of MIB in Tedlar Bags During 30 Hour

Figure 3.7 and 3.8 show more than a 90% loss of indole and skatole, were observed after 15 mins. These results are similar to those of Boeker et al. (2014) and Hansen et al. (2011). Only 8.5% of indole and 9.8% of skatole remained after 15 mins. The indole concentration became relatively stable after the initial loss (decreasing from 8.5% to 6.9% after 30 hours). The skatole continued to decrease in concentration after the initial loss (from 9.8% to 2.8% after 30 hours). Such rapid losses within 15 minutes could be due to quick adsorption by the bag material. Loss may result from adsorption or from the reactions between skatole or indole and H₂S, ammonia and/or water vapor that are present at 200:1 concentration ratios to indole and skatole. Meanwhile, compounds with higher molecular weight showed quicker losses in Tedlar sampling bags (Kim and Kim, 2012).

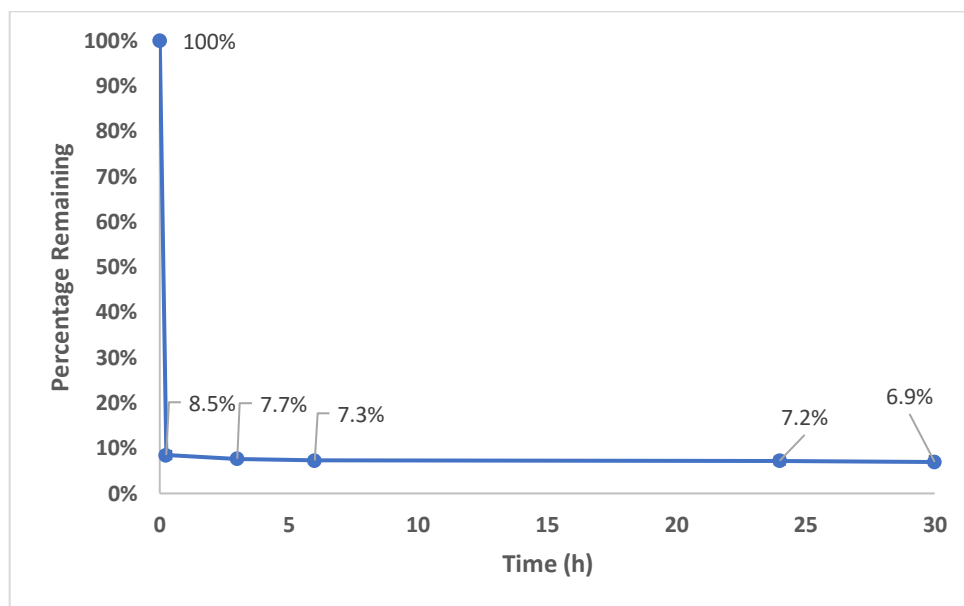


Figure 3.7. The Losses of Indole in Tedlar Bags During 30 Hours

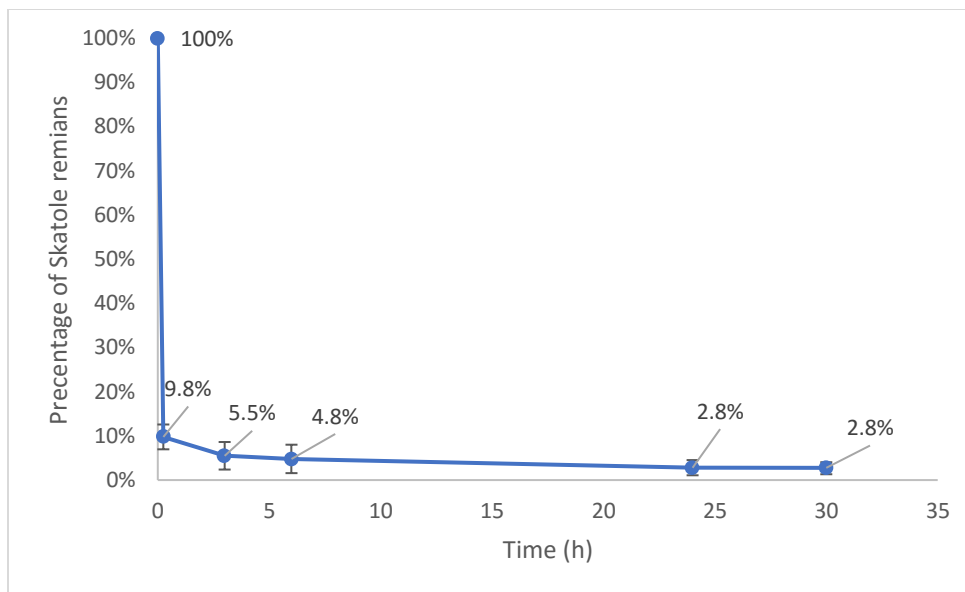


Figure 3.8. The Losses of Skatole in Tedlar Bags During 30 Hours

3.3.3. Losses of Odorants in Teflon Bags

Figures 3.9 to 3.13 show the percentage remaining of each odorant during 30 hours in Teflon FEP bags. Each point is the average of 3 tests and the standard deviations of the 3 tests are showed as error bars. Figure 3.9 shows less than 15% loss of H₂S at 15 minutes, which remained constant through the 30-hour duration. The recovery of hydrogen sulfide after 24 hours was 72.2% in spiked samples in air as reported by Coyne et al. (2011). The results are close considering the accuracy and variation of the analytical method.

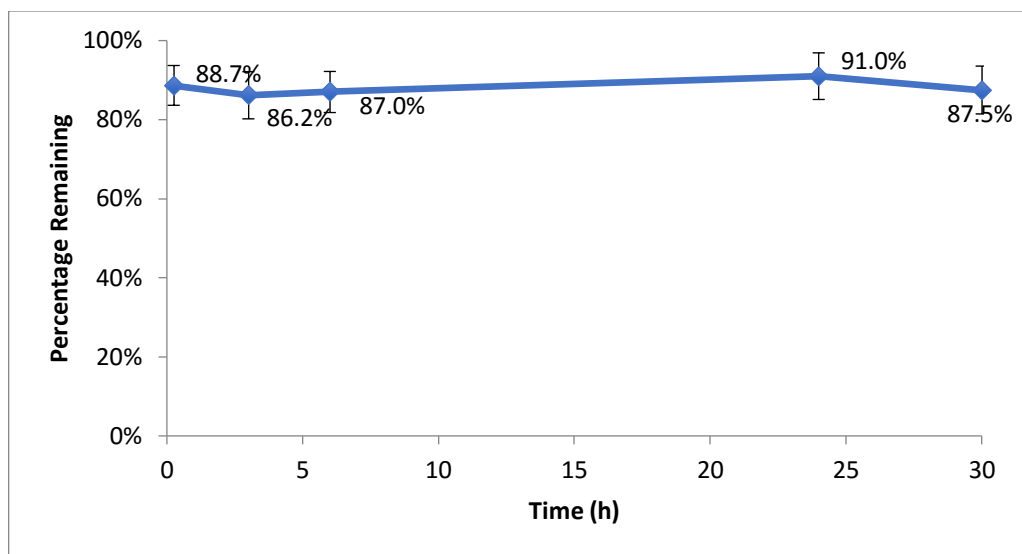


Figure 3.9. The Losses of Hydrogen Sulfide in the Teflon Bags During 30 Hours

Musty odorants, MIB and IPMP, were very stable in the Teflon bags during 6 hours (Figure 3.10 and 3.11). There were about 10% losses for both MIB and IPMP observed after 24 hours. The variation of concentration was within 5%. Thus, there was no appreciable losses of musty odorants, MIB and IPMP, in the Teflon bags over 6 hours.

Figures 3.12 showed less than 5% loss of indole at 6 hours followed by slow loss to about 60% of original concentration after 30 hours. Figure 3.13 showed less than 10% loss of skatole at 3 hours followed by slow loss to about 30% of original concentration after 30 hours. Skatole clearly is the limiting odorant requiring quick Olfactometry, OPM and GC/MS analysis within 6 hours of sample collection. Loss may result from adsorption or from the reactions between skatole or indole and H₂S, ammonia and/or water vapor that are present at 200:1 concentration ratios to indole and skatole. Overall, indole (Figure 3.12) is almost as unstable as skatole (Figure 3.13) in Teflon™ bags. Thus, 6 hours should be the maximum storage time from sampling for OPM, Olfactometry or chemical analysis.

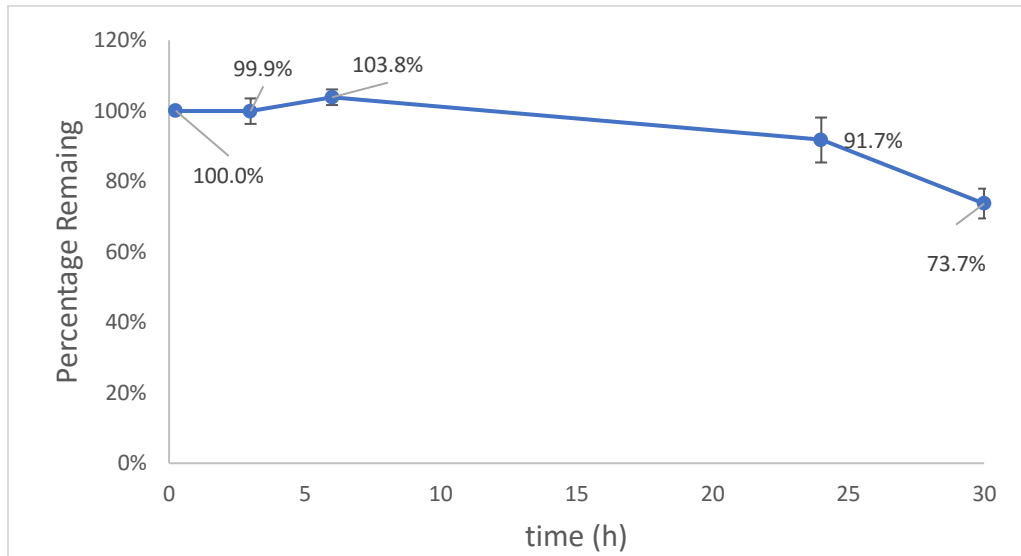


Figure 3.10. Losses of IPMP in the Teflon Bags During 30 Hours

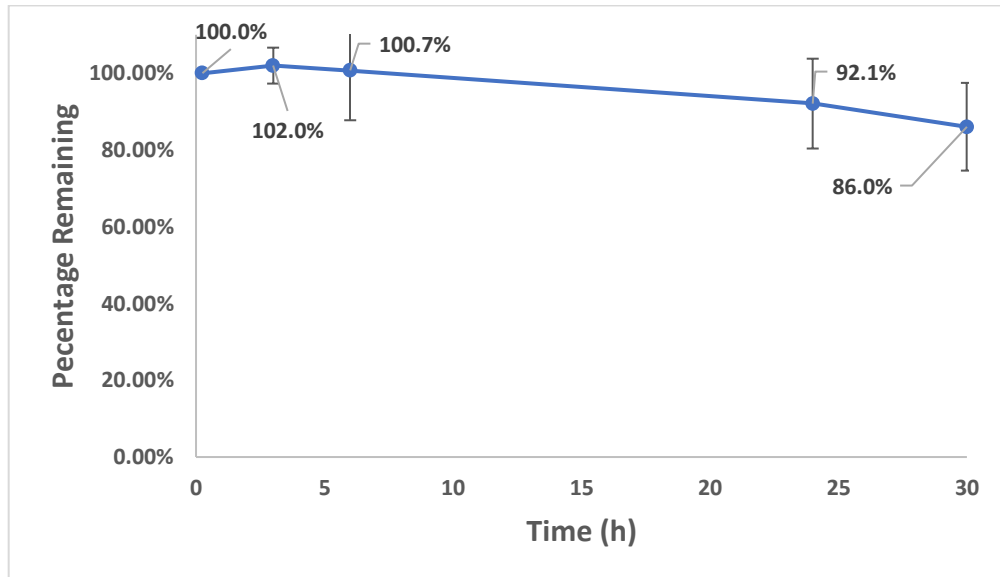


Figure 3.11. The Losses of MIB in the Teflon Bags During 30 Hours

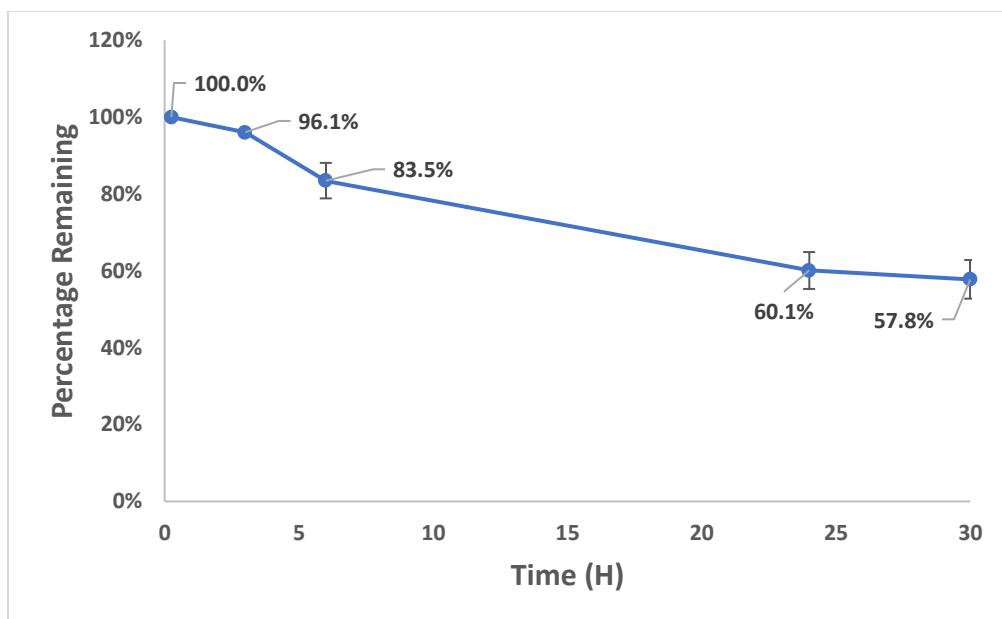


Figure 3.12. Losses of Indole in Teflon Bags During 30 Hours

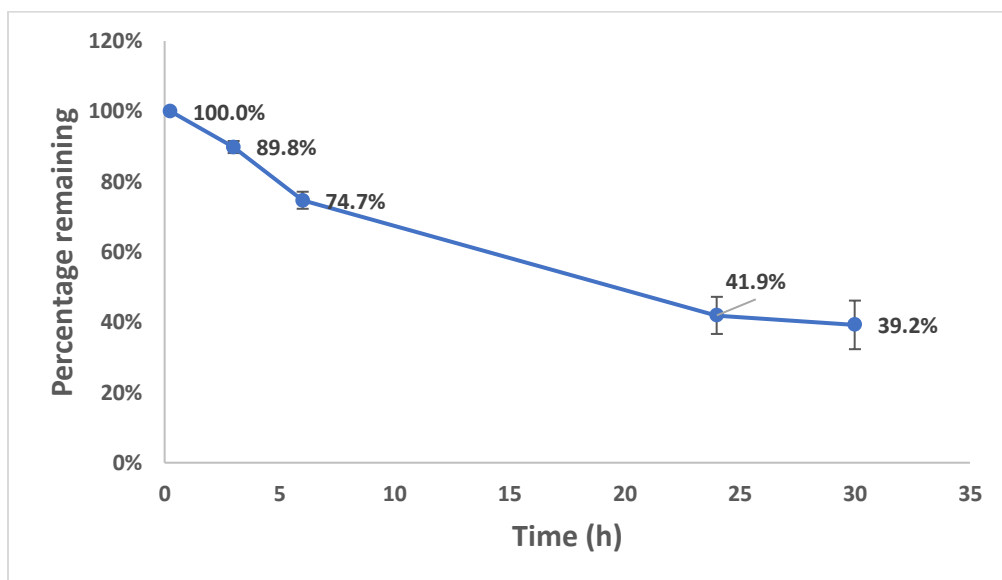


Figure 3.13. The Losses of Skatole in the Teflon Bags During 30 Hours

3.3.4. Adsorption by Tedlar and Teflon bags

An adsorption test was conducted to investigate the major reason of loss skatole in sampling bags. As shown in Figure 3.14, there was no adsorption by Teflon bags observed until the initial air concentration reached as high as 10,000 ng/L in air. It showed very good stability of skatole

in Teflon bags. However, the percentages of skatole absorbed by Tedlar bags were over 90% at various concentration levels while the percentage decreased to 83.8% when the initial concentration was at the high end. Thus, the absorption by bag film is the major reason for the loss of skatole in Tedlar bags, compared to humidity and reaction with other chemicals.

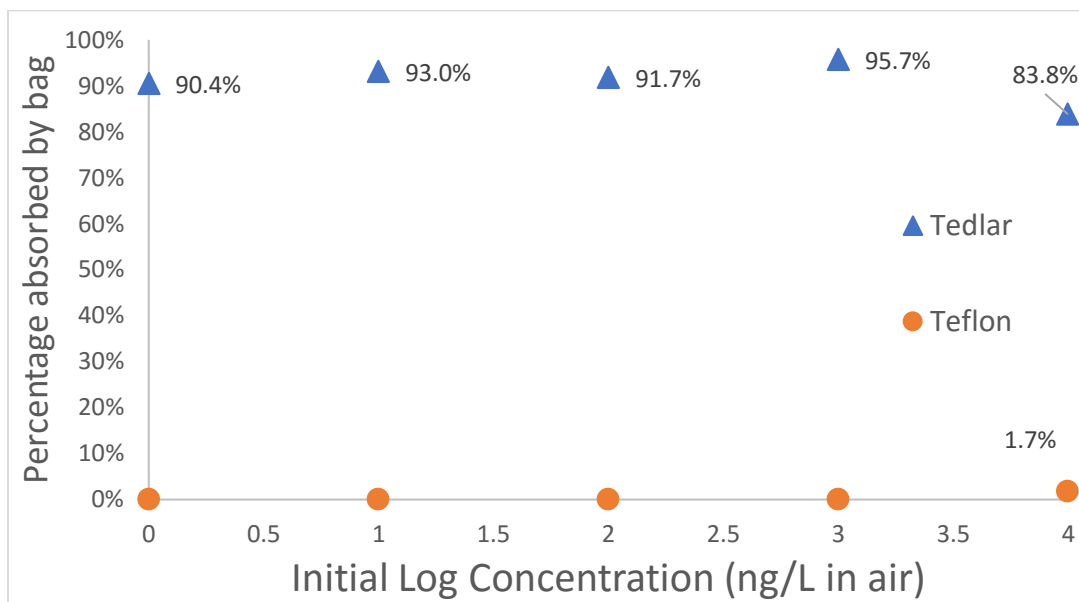


Figure 3.14. Percentage of Skatole Absorbed by Tedlar and Teflon bags

Figure 3.15 shows the absorption curve of skatole by Tedlar bags. The amount of skatole absorbed by per cm² of Tedlar film increased as the remaining concentration of skatole in air increased, which meant Tedlar bags would not be saturated within the concentration range and could absorb most of skatole in air. Thus, no matter what concentration level of skatole to be investigated, Tedlar bags are not suitable for both chemical and sensorial analysis.

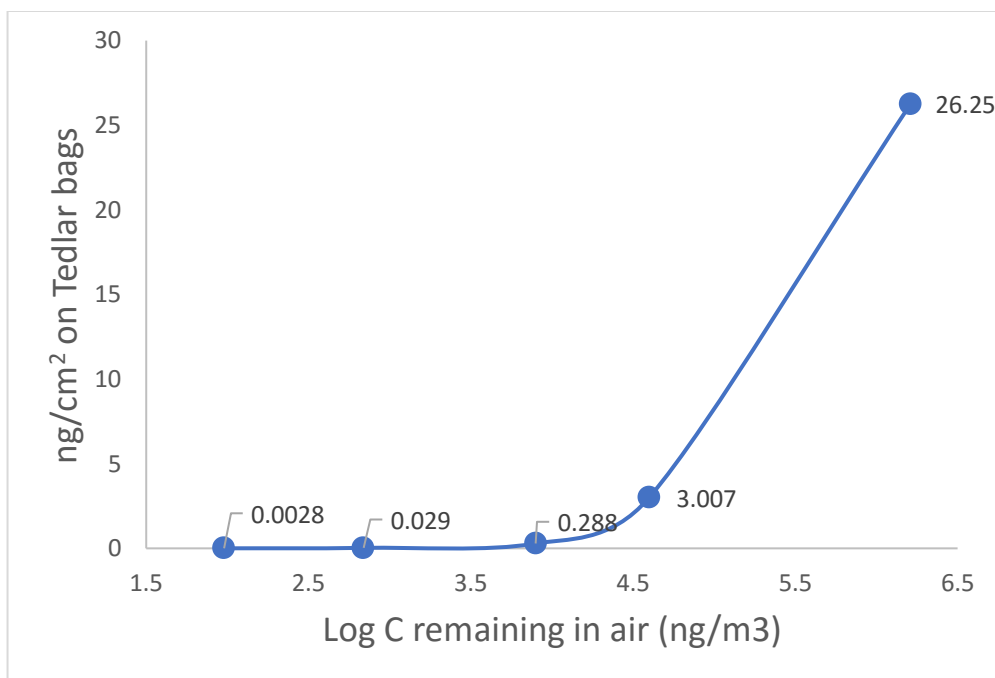


Figure 3.15. Absorption Curve of Skatole by Tedlar bags

3.4. Conclusions

- Hydrogen sulfide, IPMP and MIB, were stable in both Teflon and Tedlar bags.
- Ammonia was stable in Tedlar bags, especially during the first 6 hours.
- Indole and skatole were unstable in the Tedlar bags, with large initial losses of 95% observed over 15 minutes. Therefore, Tedlar is not a suitable bag material for samples containing indole and skatole.
- There was no absorption of skatole by Teflon bags observed while Tedlar bags could absorb over 90% of skatole and would not be saturated by skatole even at high concentration level.
- Teflon bags are required for the analysis of skatole and indole, which needs to occur within 6 hours of sample collection.
- Teflon bags are also preferred for both chemical and sensory analysis due their lower background chemical and odorant contamination.

- Overall, Teflon bags should be used for simultaneous sample collection for OPM, Olfactometry and GC/MS chemical tests instead of Tedlar bags.

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Chapter 4

Identification, Quantification and Treatment of Fecal Odors Released into the Air at two Wastewater Treatment Plants

4.1.Introduction

Odororous compounds can be released into surrounding residential neighborhoods by wastewater treatment plants (WWTPs), causing an odor nuisance. Release of odors is typically associated with improperly covered process areas, insufficient negative pressure, and inadequately treated foul air. Insufficient control of malodors may impact the reuse of treated sewage and worsen the relationship between WWTPs and surrounding communities (Lin et al., 2001). The control of odororous emissions has become a major challenge in the wastewater treatment industry.

In order to control odors, it is necessary to have a consistent language for their definition and an understanding of the possible chemical compounds responsible. The Wastewater Odor Wheel and the odor profile method (OPM) (Burlingame, 1999; Burlingame et al., 2004; Suffet and Rosenfeld, 2007; Burlingame, 2009) were developed to categorize typical wastewater odors and their intensities by odor panels as well as to help identify the chemicals that define those odors characteristics by chemical analysis techniques.

Indole (fecal/rubbery odor) and skatole (fecal/manure odor) are typical fecal odor-causing compounds (Lebrero et al., 2011). The odor threshold concentrations (OTC) of indole in water was reported as 0.1-14 $\mu\text{g/L}$ (Lasaridi et al., 2010) and the (OTC) of skatole in water was reported as 1 $\mu\text{g/L}$ (Malleret et al., 2001). However, the OTC of skatole in air has been reported as low as 0.004 ng/L in air (0.75 pptV) (Ruth, 1986). A very low method detection limit is required for analytical techniques to detect these compounds in air, which makes air analysis challenging.

Indole and skatole in aqueous phase have been reported in aqueous influent and primary effluent of WWTP to be from 430-700 $\mu\text{g/L}$ in a literature review by Hwang et al., (1995).

Godayol et al. (2011) detected indole at 90 µg/L and skatole at 10 µg/L from wastewater influent. Islam et al. (1998) detected indole at concentrations between 6 to 61.8 µg/L and skatole at 4.83 µg/L in the aqueous phase from a sludge treatment process. However, there are only a few studies that deal directly with their presence and control in air. A solid phase microextraction (SPME) coupled to GC-MS method was developed to detect indole and skatole in air samples from WWTPs (Godayol et al., 2013; Razote et al., 2002). However, indole and skatole were not detected in air samples from the influent, biologic treatment and sludge pretreatment areas of the WWTP with a working range from 0.8 to 40 ng/L in air (Godayol et al., 2013). The understanding of fecal odors in the air escaping from WWTPs is critical to the development of air treatment methods to control these compounds to enable the modeling of the impact of the odor at the plant fence line and in the surrounding communities.

Indole and skatole are formed biochemically by anaerobic degradation of the amino acid tryptophan (Yakoyama et al., 1979). The primary metabolite of tryptophan is indole. Skatole were found to be produced from tryptophan and indoleacetic acid (IAA) in intestinal tract, rumen, and swine manure (Yakoyama et al., 1977; Whitehead et al., 2008). IAA is formed by deamination of tryptophan and subsequently decarboxylated to skatole (Figure 4.1). The production of skatole is associated with low-GC gram-positive bacteria, including the *Clostridium*, and *Bacteroides* (Cook et al., 2007).

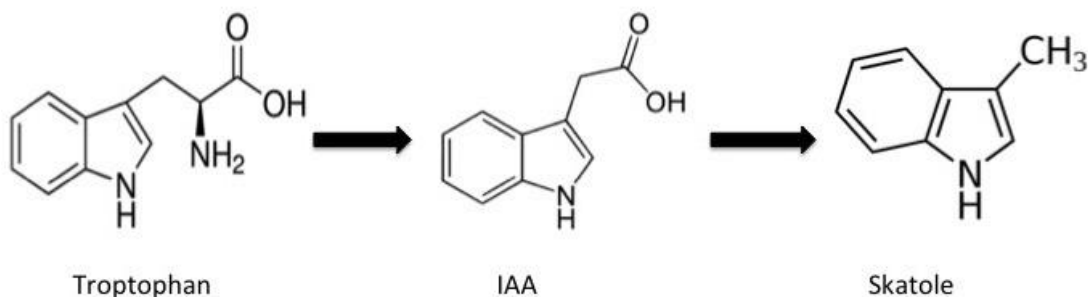


Figure 4.1. Catabolic Pathway for Skatole

The first objective of this study was to relate fecal wastewater odors in air and their intensities measured by odor panels and identify the fecal odorant(s), in air by GC-MS. A second objective was to measure the OTCs of fecal odor causing compounds and try to determine a correlation between the odor intensity and concentration of these fecal odorants. This study was part of the Orange County Sanitation District's Odor Control Master Plan for 2014. The OCSD project's objective was to characterize the odors from different wastewater treatment processes and quantify suspected chemicals. The results will be used in future studies to design odor control technologies for the nuisance odors.

4.2. Experimental

4.2.1. Sample Locations

Initially, air samples were collected for the Odor Profile Method (Curren et al., 2014; Vitko et al., 2014, Abraham, 2014) analysis at 16 stations at Plant 1 from August to September, 2013 and 16 stations at Plant 2 from October to November, 2013 at the Orange County Sanitation District WWTPs in 10 Liter Tedlar Bags for qualitative identification. Subsequently, Teflon Bags were used for quantitation as it was reported that Tedlar Bags adsorbed Skatole and Teflon Bags did not over the sample to analysis time of 6 hours (Boeker et al., 2014; Zhou et al., 2016).

The Orange County Sanitation District (OCSD), a special district of the County of Orange, California, has a service area of 463 sq. miles containing 587 miles of sewers and serving a population of 2.5 million in two municipal wastewater treatment plants: Plant 1 located in the city of Fountain Valley has an average daily influent of 95 MGD and Plant 2 in the city of

Huntington Beach has an average daily influent of 112 MGD. Both plants are adjacent to residential areas that occasionally become affected by odors.

The treatment facilities were sampled before and after treatment to determine their effectiveness in reducing particular odorants (Vitko et al., 2014). There was a knowledge gap regarding fecal compounds. Thus, a goal of the OCSD project included the quantitation of compounds responsible for all odors including the fecal odor that comprised part of the total odor at the plant measured by Olfactometry. For quantitation of fecal odors, locations with high fecal odor intensities were sampled with Teflon bags and immediately delivered and analyzed within a maximum of 6 hours.

4.2.2. Sensory Evaluation by the Odor Profile Method (OPM)

The OPM was used as the sensory evaluation of gas samples at UCLA by a trained odor panel. OPM is a modification of Standard Method 2170: the Flavor Profile Analysis Method (FPA) (APHA et al., 2012). The FPA Method has been used in the drinking water industry since 1980's to characterize odor sources and identify analytical methods to understand odor problems (Suffet et al., 1988). The only difference is that the sampling bag is opened to smell the air sample for the OPM whereas the headspace over the water is smelled for the FPA method.

The panelists were taught to identify multiple odor characters and their respective intensities in a single sample. The odor intensity was evaluated using the FPA Method's seven-point odor intensity scale which has been shown to be equivalent to the butanol air odor intensity scale (Curren et al., 2014). Weber observed that increased stimuli is relative to the previous amount experience and his student, Fechner, described this relationship through the following formula:

$$I = k \text{ Log } C/C_0$$

where intensity (I) is proportional to the logarithm (base 10) of the concentration (C) relative to a previous concentration (C₀) (Suffet et al., 1995).

The average and standard deviation of intensity was calculated if 50% or more of panelists reported that odor character. If an odor character was reported by less than 50% of the panelists, the odor was reported as odor note without an intensity. Based upon the knowledge of the drinking water industry, an intensity of 4 was used to indicate where 50 % of the general public could recognize the odor (Suffet et al., 2008). Thus, an odor intensity of 3 was suggested as the odor nuisance level where that more sensitive neighbors may start to complain.

4.2.3. Odor Threshold Concentrations (OTCs)

The Odor Threshold Concentration (OTC) is at an odor intensity level of 1 on the Weber Fechner Curve where 50% of the panelists could state that a sample was different from odorless air. The OTCs of skatole and indole were determined by ASTM Method 679 (2011), a multiple forced choice sample presentation triangle test in an ascending concentration series by an AC'SCENT olfactometer by St. Croix Sensory Inc. (Stillwater, MN). Trained panelists, from 3 age groups (18-29, 30-48, and 49-65), detected the presence or absence of a given odorous compound. A set consisting of one odorous sample and two blank samples was presented to the panelist each time. The panelist was forced to choose which of the three samples was different from the other two. For each panelist, the geometric mean of the last concentration missed and the first after which all guesses are correct was calculated as the individual OTC. Then the log geometric mean of individual thresholds of the panelists was calculated as the OTC of the panel.

4.2.4. Quantitation

A Liquid-Gas Impinger System with Selective Ion GC-MS analysis was developed to quantify indole and skatole in air samples from WWTPs processes. A 10-liter bag of sample was pumped through three impingers with 15 mL dichloromethane in each. The solvent in the impingers was concentrated to 1 mL at 40°C in a micro Kuderna–Danish Evaporator with a surface nitrogen flow. One microliter (μL) of solution was injected onto a Varian 450 GC (Varian Inc., Palo Alto, California) with a Varian 220 MS, using 99.9999% Helium as the carrier gas. The column used was an Agilent DB-5MS column (length 60 m, ID of 0.25 mm ID, film thickness of 0.25 μm). The temperature program used was: initial temperature of 65°C with a ramp of 9.5°C /min to 160 °C and then 12°C /min to 240°C. The flow of carrier gas was 1.0 mL/min through the GC column. The Ion Trap monitored the primary range of m/z units of indole and skatole. These were the m/z units of 62-64, 89-91 and 116-119 m/z from 12.00 to 13.00 min, 76-78, 102-104, 129-132 m/z from 13.00 to 14.50 min.

The minimum detection limit (MDL) in solvent and in air and the analytical parameters of indole and skatole are shown in Table 5.1. The recovery of method was 73-78%. The MDL was determined to be 8 $\mu\text{g/L}$ in solvent and 0.8 ng/L in air as the gas volume is 10 L and the final solvent volume is 1 mL. In contrast, the MDL of Godayol et al. (2013) SPME method is 0.8 ng/L in air for indole and 1.0 ng/L in air for skatole.

| Chemical | MDL ($\mu\text{g/L}$ in solvent) | MDL (ng/L in air) | Linearity (R^2) | Recovery | Working range ($\mu\text{g/L}$ in solvent) | Working range (ng/L in air) |
|----------|-----------------------------------|-----------------------------|---------------------|---------------|---|---------------------------------------|
| Skatole | 10 | 0.8 | 0.995 | 78 \pm 4.4% | 8-200 | 0.8-20 |
| Indole | 10 | 0.8 | 0.983 | 73 \pm 5.6% | 8-200 | 0.8-20 |

Table 4.1. Standard Curve and Quality Parameters of Indole and Skatole

4.3.Results and Discussion

4.3.1. Fecal Odor Nuisance

Odor characters from the OPM are sometimes grouped together into broader categories to better characterize the odorants. In this study, the groups of rotten vegetable/canned corn/sulfide/rotten garlic (Rotten Vegetable group), musty/earthy/moldy (Musty group), and fecal/sewery/manure/rubbery (Fecal group) were used for simplifying interpretation of results and the chemical analysis selection.

In the initial study with Tedlar Bags, fecal odors were reported at all 32 sites tested by the OPM at both WWTPs and they were the dominating odors at most locations. The intensities of fecal odors were higher than an intensity (I) of 6 at locations such as Dewatering and Truck Loading at Plant 1. Considering the average fecal odor intensities reported by OPM panels at the outlets of treatment facilities and at sites without treatment, an off-site nuisance is probable due to fecal odors at Dewatering (Intensity (I) = 6.3) and Truck Loading (I= 7.3) at Plant 1, and the outlets of Trunkline (I= 3.4), Headworks (I= 3.4) and Truck Loading (I= 3.4), Dissolved Air Flotation Treatments (DAFTs) (I= 3.6) and Dewatering (I= 3.2) at Plant 2. These data are qualitative at best as the Tedlar Bags do adsorb over 90 % of Skatole instantly (Boeker et al., 2014). However, the residual fecal odorants (skatole, indole and maybe other odorants) in the air of the bag in equilibrium with the adsorbed fecal odorants was sufficient to qualitatively define differences of the fecal odor by the analysis by the OPM panelists.

4.3.2. Odor Threshold Concentrations

Table 4.2 show the results of OTC determination for skatole and indole. The odor threshold of indole was determined to be 5.02 ng/L in air (1.04 ppbV) and the odor threshold of skatole was

determined to be 0.327 ng/L in air (60 pptV) in Teflon Bags. The odor threshold for skatole was within the range in the literature (ranging from 0.074 pptV to 60 pptV) (Ruth, 1986; Nagata, 2003). The odor threshold for indole was near the values in the literature (1.4 ppbV) (Nagata, 2003). Table 4.2 shows the boxes in yellow where for each panelist, the geometric mean of the last concentration missed and the first after which all guesses are correct was calculated as the individual OTC from Teflon Bags. Then the geometric mean of individual thresholds of the panelists was calculated as the OTC of the panel (bottom line - far right box of Table 4.2).

| Panel | | | Concentration (ng/L in air) | | | | | | | | OTC (ng/L in air) |
|----------|-----|--------------|-----------------------------|-------|-------|------|------|------|------|------|-------------------------|
| Panelist | Sex | Age group | 0.149 | 0.290 | 0.675 | 1.30 | 2.61 | 4.99 | 9.32 | 19.7 | |
| 611 | M | 18-29 | O | O | X | X | X | X | X | X | 0.442 |
| 612 | M | 18-29 | O | X | X | X | X | X | X | X | 0.208 |
| 614 | M | 30-48 | O | X | X | X | X | X | X | X | 0.208 |
| 613 | M | 49-65 | O | O | X | X | X | X | X | X | 0.442 |
| 500 | M | 30-48 | O | O | X | X | X | X | X | X | 0.442 |
| Panel | | | | | | | | | | | 0.327 |

Table 4.2. Odor Threshold Concentration Determination for Skatole (ng/L in Air) in Teflon Bags by an Expert Panel of 5

Note: M = male; F = female X= correct response; O= incorrect response

The odor threshold concentration of a chemical can vary across orders of magnitude, as shown in the literature. The inconsistency mainly results from the individual differences in sensitivity of panel members and their training, as well as the methodologies used. The wide range of odor thresholds indicates a large variability in detection of different panelists. Thus, the OTC is considered as a guideline and should not be used as a specific limit to prevent odor nuisances from occurring.

4.3.3. Quantification of Indole and Skatole

Five sites with high fecal odor intensities were sampled with Tedlar bags for skatole and indole in June 2014: Truck Loading (Plant 1), Dewatering (Plant 1), Trickling Filter #C In (Plant 2), Truck Loading In (Plant 2), and Truck Loading Out (Plant 2). Indole and skatole were detected in all five locations. The chromatographic response of indole and skatole are both highest at the Truck Loading at Plant 1. However, the potential losses of indole and skatole were reported in the Tedlar sampling bags (Boeker et al., 2014; Zhou et al., 2016). Thus, a new sampling was conducted and analyzed with Teflon FEP sampling bags in April 2016. The concentrations of indole and skatole and the intensities of the OPM of fecal odors at five locations at both OCSD Plants are shown in Table 4.3. The odor concentration to odor threshold concentration (C/OTC) ratios in air are also included for indole and skatole based on the OTCs measured in this study. The OPM values of fecal odors at the Truck Loading at Plant 1 and both the inlet of Dewatering Scrubbers in Plant 2 were higher than the odor nuisance Level of 3, which would likely lead to offsite complaints for fecal odor.

Fecal odors indicate the presence of compounds such as indole and skatole, thus the concentrations of these compounds were evaluated in air samples (Hwang et al., 1995). The only other study to evaluate the concentration of these compounds in air, Godayol et al (2013), did not detect indole and skatole in gaseous samples from WWTPs. A novel finding in this study is based upon an analytical method with a method detection limit of 1 ng/L that is below the OTC of indole and slightly above the OTC of skatole. The concentrations of indole and skatole are both highest at the Truck Loading at Plant 1. The OC/OTC ratios of indole vary from 0.19 to 0.79 while the C/OTC ratios of skatole vary from 2.8 to 22.5. In this case, skatole may be the major chemical leading to fecal odor, whereas indole is unlikely to be contributing greatly to the odor as it was generally found at less than its OTC. Other related odorous fecal compounds may

also be present, but these were not observed by GC-MS in this study. Further Investigation for other fecal odors are in progress.

| Location | Skatole | | Indole | | OPM-Fecal odor intensity |
|---------------------------|-----------------|-------|-----------------|-------|--------------------------|
| | C (ng/L in air) | C/OTC | C (ng/L in air) | C/OTC | |
| P2 Activated Sludge | / | / | 0.94±0.09 | 0.19 | 1.5±1.9 |
| P2 Dewatering Scrubber In | 2.09±0.17 | 6.4 | / | / | 3.5±2.5 |
| P2 DAFT In | 1.60±0.19 | 4.9 | / | / | Note |
| P2 DAFT Out | 0.92±0.14 | 2.8 | / | / | Note |
| P1 Truck Loading | 7.35±0.92 | 22.5 | 3.96±0.67 | 0.79 | 6.0±1.4 |

Table 4.3. Concentration of Indole and Skatole and OPM Results

Estimated air concentrations of indole and skatole based upon the aqueous influent of wastewater and the Henry's law constant of these compounds from several studies are presented in Table 4.4. The estimated concentrations are lower than the concentrations found in air samples at OCSD. Thus, skatole and indole may present more of an odor nuisance than indicated by the estimated values from the liquid phase. It is noted that the Henry's law constants are determined in a closed system and wastewater systems are an open system. This appears to lead to different air concentrations in reality versus the theoretical calculated concentration. Thus, air measurements are necessary to evaluate indole and skatole in the gas phase at a location to observe general wastewater odor emissions.

| | Concentration range in wastewater ($\mu\text{g/L}$) * | Henry's Law Constant** | Estimated Concentration in air (ng/L) |
|---------|---|------------------------|--|
| Indole | 90-570 | 2.5×10^{-6} | 0.23-1.4 |
| Skatole | 10-700 | 2.4×10^{-6} | 0.024-1.75 |

Table 4.4. Estimated Air Concentration of Indole and Skatole by Henry's Law

* Hwang et al., 1995; Godayol et al., 2011.

**Greenman et al., 2005.

4.3.4. Correlation between Odor Intensity and Concentration

Odor intensity is linearly related to the log concentration of a given chemical from intensity 0-12 as can be demonstrated by the Weber-Fechner law (Suffet et al., 1995; Greenman et al., 2005). A Weber-Fechner curve of intensities of the fecal odors versus the log concentrations of skatole was shown in Figure 4.2. The Weber-Fechner law for skatole alone followed the Weber-Fechner law (log intensity is proportional to log concentration). The Weber Fechner Law was not followed by the fecal odor when there was a mixture of fecal odorants and other odorant types (Figure 4.3).

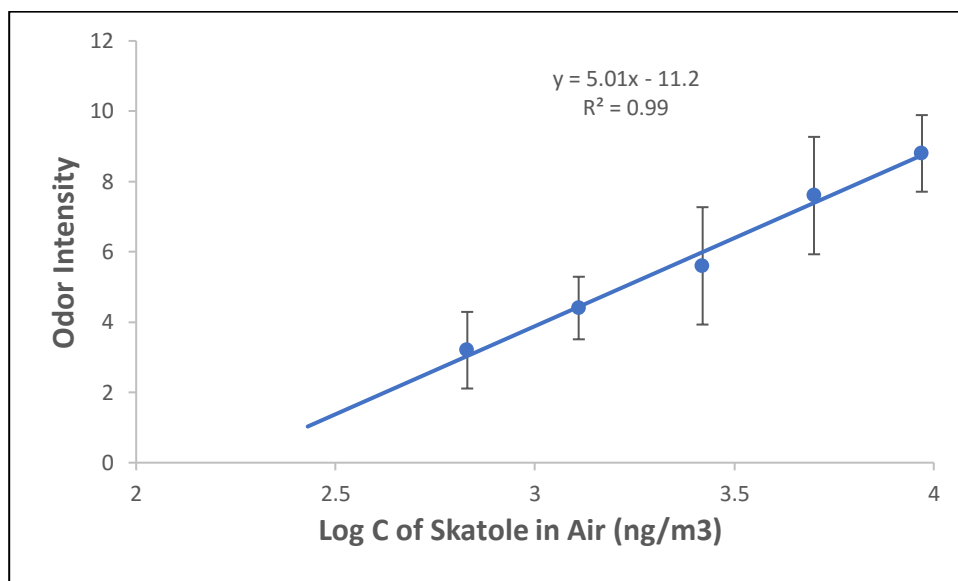


Figure 4.2. Weber-Fechner Curve of Skatole Alone in Teflon bags

The linear correlation of concentration to odor intensity appears to be very difficult to establish in real samples because there can be masking effects and difficulty in characterizing intensities of more than two odorants. This may result from the interference of other odors (antagonism), such as the strong Rotten Vegetable odors, which make the panel unable to quantify fecal odor intensities accurately. Most of the samples in this study had at least three odor characters reported and are clearly complex as shown by GC/MS analysis. Meanwhile, other compounds, which cause fecal odors, may be responsible for some portion of the fecal odors. Additionally, to see a proper Weber-Fechner curve, the concentrations would need to cover several orders of magnitude as they are on a log scale and this makes establishment of a correlation more difficult.

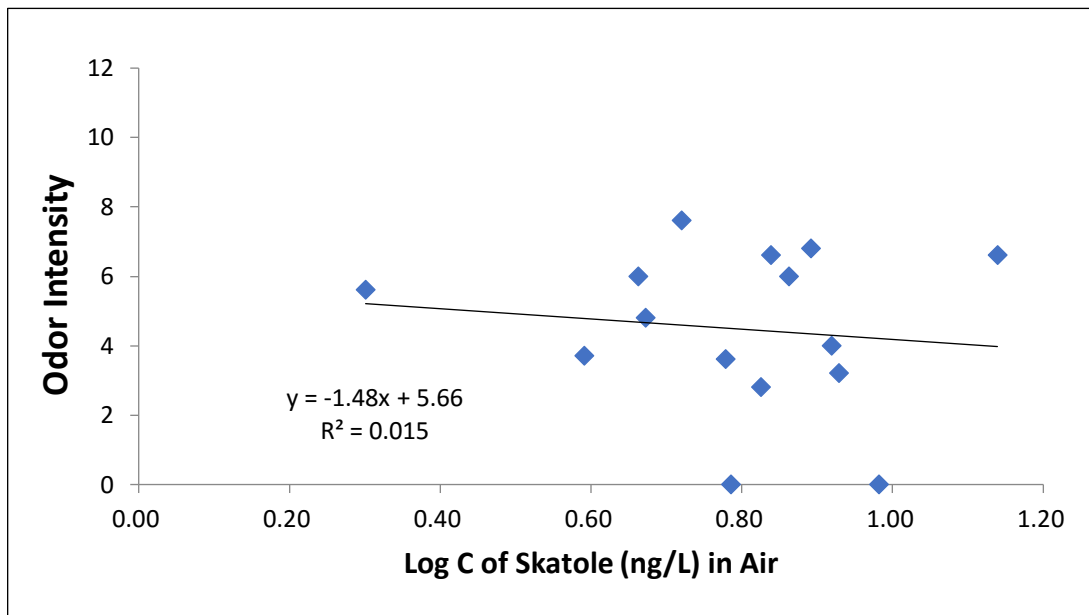


Figure 4.3. Average Daily Intensity versus Log Concentration of Skatole

4.3.5. The Effectiveness of Fecal Odor Treatment

OCS&D in 2013 has four different odor treatment technologies that were evaluated: biofilters (natural media), biotowers (biotrickling filters with synthetic media), packed bed chemical scrubbers, and activated carbon filters (Vitko eat al., 2014). However, the current air odor control at the majority of WWTPs is mainly focused on hydrogen sulfide and occasionally other sulfide compounds (Iranpour et al., 2005). As can be seen in Figure 4.4, all the fecal OPM intensities of outlets measured in Tedlar bags are removed to a level under an intensity of 3 in Plant 1. In Plant 2, although fecal odors can be removed partially, the outlet intensities of Trunkline, Headworks and Truck Loading odors are still higher than an OPM intensity of 3 (Figure 4.5). Thus, fecal odor may lead to offsite nuisance at these locations after treatment. These are initial qualitative based analysis because of the adsorption of skatole on Tedlar Bags.

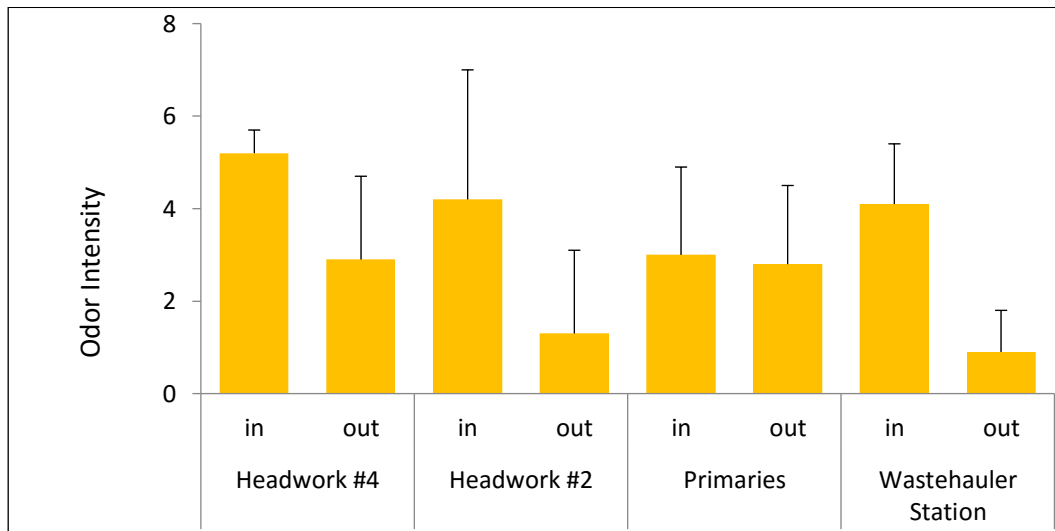


Figure 4.4. Fecal Odors by OPM at "In" and "Out" of Treatments at Plant 1

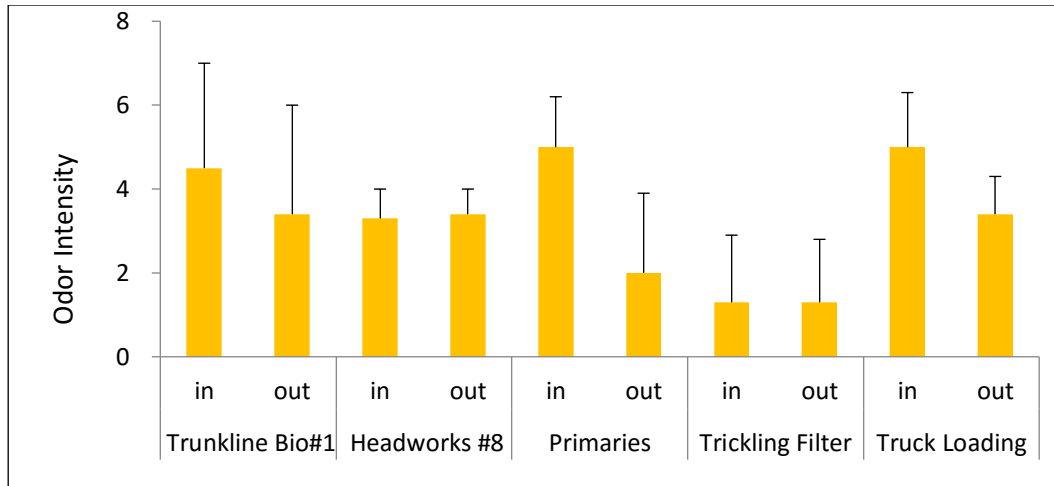


Figure 4.5. Fecal Odors by OPM at "In" and "Out" of Treatments at Plant 2.

The headworks and the primary treatment facilities at Plant 1 use chemical scrubbers (bleach and caustic) to treat hydrogen sulfide. At Plant 2, bioscrubber towers are used prior to chemical treatment at the headworks. Fecal odorants may be removed with increased water solubility by oxidation of skatole and indole by chlorine to amines (Henry et al., 1980). This mechanism needs further quantitative study to understand if some fecal odor removal is due to this mechanism at the WWTPs.

At Plant 1, Headworks Chemical Scrubber #4 removed fecal odors in the range of 50% of OPM intensity. Headworks Chemical Scrubbers #2 removed fecal odors in the range of 70 % of the OPM intensity. OPM fecal odor intensities were slightly removed by primary chemical scrubbers. In Plant 2, Primary scrubbers removed fecal odors in the range of 60% of OPM intensity. The scrubber technology for removal of indole and skatole along with the fecal odor evaluations needs careful study to optimize it while maintaining the removal of reduced sulfur compounds.

In the literature, biofilters have provided higher removal of volatile organic chemicals (VOCs) than biotowers. Biofilters removed 52-99% of VOCs whereas biotowers only removed 39% of

VOCs in previous studies (Easter et al., 2005). Also, the literature shows more than 80% of sulfur and nitrogen containing odorants can be removed by an aerated biofilter (Chen et al., 2001).

The OPM intensity of the fecal odor was removed in the range of 80% by the biofilter at the Wastehauler in Plant 1. In Plant 2, biotowers are used at several locations including Trunkline Biological Scrubbers #1 and Headworks Biological Scrubbers #8. The biological scrubbers are less targeted to hydrogen sulfide than the chemical scrubbers used at the Headworks at Plant 1. However, Trunkline Biological Scrubbers #1 reduced OPM fecal odors intensity in the range of 25% only.

In a study, skatole and indole in flushed manure were removed totally by anoxic biological nitrogen treatment (Loughrin et al., 2006) as an alternative biological process. The relationship of bio-removal processes, particularly biofiltration of skatole and indole versus OPM fecal intensities needs to be studied in the future for optimal fecal odor removal.

The adsorption capacity and removal efficiency of sulfur compounds by activated carbon are much higher than those of nitrogen compounds, probably due to the ionization and breakthrough of nitrogen compounds. Activated carbon reduced sulfur containing odors effectively at the Trickling Filter but failed to remove fecal odors as determined by OPM fecal odor intensity. Figure 4.4 shows that fecal odors are removed in the range of 30% of OPM intensities by activated carbon at the Truck Loading. The removal of the chemicals indole and skatole at the Truck Loading are shown in Figure 4.6. Both the concentrations of indole and skatole are higher at the outlet. This strongly suggests that breakthrough of the carbon bed by these chemicals had occurred and competitive desorption by more adsorbent chemicals was occurring. Thus, the optimization of removal of these compounds by activated carbon needs complete evaluation.

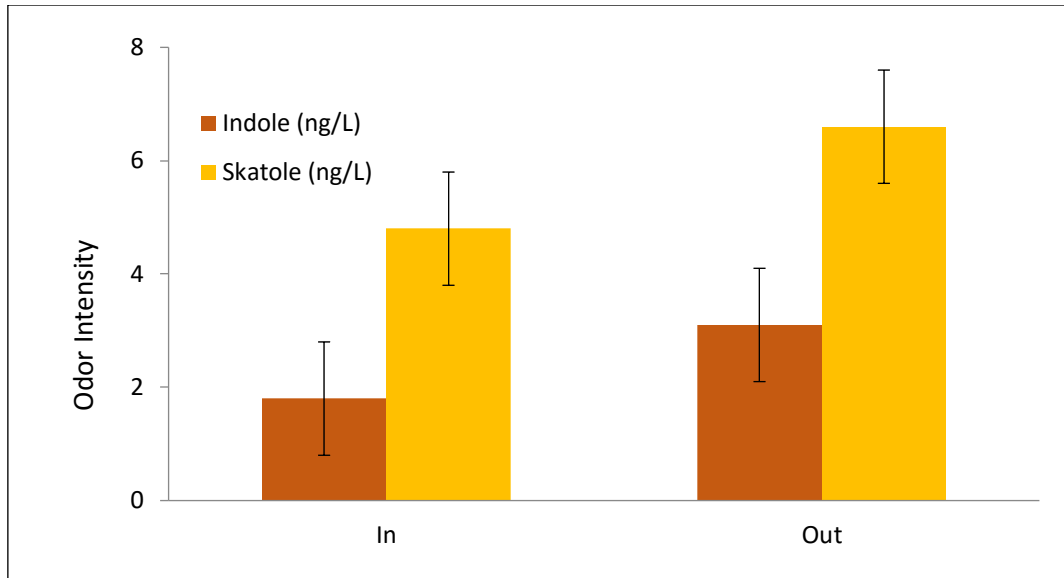


Figure 4.6. Concentration of Indole and Skatole at Truck Loading at Plant 2

Future research needs to be completed to determine the best methods of control for fecal odors and odorant compounds by all the unit processes discussed. Anoxic biofiltration and ozonation may be appropriate treatments for fecal odors and should also be studied (Alfonsin et al., 2015). For example, ozonation could be a chemical oxidation pretreatment method before chemical scrubbers to deal with fecal odors. The removal of sulfur containing compounds by ozonation has been shown to be faster than that of nitrogen compounds (Hwang et al., 1994). However, nitrogen-containing compounds may optimize removal when the ozone dosage is increased.

4.4.Conclusions

- Fecal odors were found to be dominant odors in both OCSD plants by Odor Profile Method and can lead to off-site nuisance due to their high intensities.

- The odor threshold of skatole is 0.327 ng/L (60 pptV) and the odor threshold of indole is 5.02 ng/L (1.05 ppbV) for our trained panelists.
- Skatole as identified as the major fecal odorant due to its high OC/OTC ratio, from 2.8 to 22.5, at two WWTPs.
- Qualitatively, chemical scrubbers and biofilters performed best in removing fecal odors among current control technologies used for air odor nuisance control at two WWTPs.
- Anoxic biofiltration and ozonation may be appropriate treatments for fecal odors and need further study.

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Chapter 5

Identification of Musty Odor Nuisance at Wastewater Treatment Plants

5.1.Introduction

Complaints from neighbors around wastewater treatment plants (WWTPs) are primarily about the odors emitted from treatment processes. Usually complaints are from anaerobic treatment processes (Hwang et al., 1995). Volatile sulfur compounds (VSCs), especially hydrogen sulfide (H_2S), are considered as the primary cause of odor emissions from anaerobic WWTPs (Fisher et al., 2016). Typical odors from VSCs are rotten eggs (hydrogen sulfides) (Van Langenhove et al., 1985; Zarra et al., 2008) and rotten vegetable (methyl sulfides) (Zarra et al., 2008). Therefore, in many odor studies at WWTPs, the control of hydrogen sulfide is a surrogate for odor control (Fisher et al., 2016). However, other volatile organic compounds (VOCs) can also contribute to the odor emissions, but have been paid little attention. For example, Zhou et al., (2016) reported the fecal odor as a major odor from WWTPs. Two fecal odorants indole and skatole were identified as chemicals that were present that have very low odor threshold concentrations (OTCs) at these WWTPs. When these chemicals were removed, the fecal odor dissipated.

In order to control odors, it is necessary to have a consistent language for their definition and an understanding of the possible chemical compounds responsible. The Wastewater Odor Wheel and the odor profile method (OPM) (Burlingame, 1999; Burlingame et al., 2004; Suffet and Rosenfeld, 2007; Burlingame, 2009) were developed to categorize potential wastewater odors and their intensities by odor panels as well as to help identify the chemical odorants that define those odors characteristics by chemical analysis methods.

Specific chemical causing odor nuisances can be evaluated by the ratio of the concentration of the odorants divided by its odor threshold concentration (OTC) of the offending compound, the so-called Odor Activity Value (OAV) (Feilberg et al., 2010). The OTC is the odorant concentration where 50% of an odor panel can identify a difference of odor for a chemical vs.

odorless air. The Weber-Fechner curves which relates the OTC in air to the odor intensity of a chemical concentration in air must be defined to evaluate the odor nuisance. Weber observed that increased stimuli is relative to the previous amount experience and his student, Fechner (1859) described this relationship that has been used by Greenman et al., (2005); Munoz et al., (2010); and Suffet et al., (1995). The intensity of an odor characteristic is a measure of its odor strength, which is related to the log of its concentration via the Weber-Fechner law Eq. (1):

$$I = k \text{Log}(C/C_0) \quad (1)$$

The intensity (I) is proportional to the logarithm (base 10) of the concentration (C) relative to a previous concentration (C₀). This has previously been demonstrated for the fecal odorant skatole (Zhou et al., 2016).

An initial study of the nuisance odors at 32 WWTP process locations at the two Orange County Sanitation District (OCSD) WWTPs in Southern California indicate that musty/moldy/earthy (musty group) odors identified by the Wastewater Wheel were actually present in odors released (Vitko et al., 2014). Musty odors have been detected by residents near the WWTPs studied (Vitko, 2014). These odor types from studies at natural and drinking water locations occur from aerobic sites (Mackay *et al.*, 2008, Yu *et al.*, 2014; Joe *et al.*, 2007). These types of odors have not been reported as an odor nuisance from WWTPs to the best of our knowledge.

Musty/earthy odors are the most common descriptors for odor complaints in the drinking water industry from aerobic natural water locations (Suffet et al 2017). Trans-1,10-dimethyl-trans-9-decalol (geosmin), an earthy odor, 2-methylisoborneol (MIB), a musty odor, 2-isopropyl-3-methoxypyrazine (IPMP), an earthy/musty odor and 2,3,6-trichloroanisole (TCA), a musty/moldy/cork odor are primarily considered to cause earthy/musty/moldy type odors as

highlighted in the Drinking Water Taste and Odor Wheel (Suffet et al., 2017). For example, the major source of MIB in drinking water is primarily from the metabolism and biodegradation of algae, such as, cyanobacteria (Izaguirre et al., 1982) and IPMP has been detected as a result of the metabolism of Algae (Peter et al., 2009). Musty nuisance odors have also been found in wine (Ortega et al., 2001), indoor air (Ömür-Özbeket et al., 2011) and pulp mill waste (Ferguson et al., 1995), but little attention has been given to the earthy/musty/moldy odors at WWTPs. The Wastewater Odor Wheel notes musty/earthy odors as a possibility, but without identification of a specific chemical (Burlingame, 1999; Burlingame et al., 2004; Suffet and Rosenfeld, 2007; Burlingame, 2009). Recently, MIB has been detected in the effluent water of municipal wastewater, with a concentration of up to 30 ng/L (Agus et al., 2012). It was not identified in the air from different WWTP processes.

The OTC of the known earthy/musty/moldy odors in drinking water have been determined. At about 20 °C, the OTC of MIB in water is reported ranging from 5 to 15 ng/L as generally compiled by Mallevalle and Suffet (1987) and Suffet *et al.* (1995a). A recent study (Yu *et al.*, 2014) found a wide variation in MIB odor sensitivity between eight different drinking waters using Flavor Profile Analysis (FPA)-trained odor panels in China. The OTCs in water ranged from 7 to 20 ng/L for samples at 45 °C. The OTC in water was determined by FPA to be 2.1 ng/L for MIB at 45 °C in USA studies in Philadelphia PA and at the Metropolitan Water District of Southern California (Mackey *et al.*, 2008). Drinking water consumers usually complain when the levels of MIB reach 10 ng/L (Suffet et al., 2008). The OTC of MIB in air varies from 0.013-0.07 ppbV and the OTC of IPMP in air varies from 0.0008 to 0.008 ppbV as reported in literature (Ömür-Özbeket et al., 2011; Sala et al., 2004). Thus, it was strongly suspected these odorants would be odor nuisance in air at the ppbV level.

The objectives of this study were: 1) to observe if the earthy/musty/moldy odor nuisance was present at the two WWTPs of the OCSD by odor panel analysis, 2) to evaluate the effect of current treatments of off-gases for removal of the earthy/musty/moldy odors by odor panel analysis, 3) to determine the chemical(s) causing the earthy/musty/moldy odor nuisance, if present at the two WWTPs, 4) to determine the OTCs of the odorants by Weber-Fechner curves and 5) to determine the earthy/musty/ moldy chemical odorants found at different WWTP sources.

5.2.Methods

5.2.1. Odor Profile Method

As there is no instrument that can simulate the human nose to identify odor character, an odor panel was used. The odor panel used the Odor Profile Method (OPM) with the Wastewater Odor Wheel to describe odor characters and the FPA Intensity Scale for each odorant to report odor intensity (Burlingame, 1999; Curren et al., 2014). The OPM is based upon the FPA Standard Method #2170, (APHA, 2011) that is used as sensory panel methods in drinking water odor control studies (Suffet et al., 1987). A minimum of 4 trained panelists were used to analyze air samples at UCLA as well as 14 consumer panelists at OCSD.

For each odor character, the OPM method develops an odor intensity that is related to log concentration of the odorous chemical. The odor intensity scale has 7 points from 1 to 12; 1 (threshold), 2, 4 (recognition), 6, 8, 10, and 12. At the odor threshold intensity of 1, an odor panelist can state that the odor is different than clean air. Only at an odor intensity of 4 can the panelist recognize odor characteristic. An average odor intensity of 3 is considered as an action level for drinking water plants to avoid odor nuisance complaints (Burlingame, 2004). Thus, a

calculated average panel odor threshold of 3 was used as an action level warning to the WWTP that an odor nuisance can occur from a particular type of odor.

Thus, no odor is defined as an intensity of 0 and the OTC is defined as the concentration when intensity is 1 (I=1) on the Weber-Fechner curve (Figure 5.1). The OTC is formally described as the point where 50% of a population (minimum of 4 panelist) can define a difference between pure air and air containing an odorant. The odor recognition threshold is where 50% of an odor panel can define the type of odor from the odor wheel.

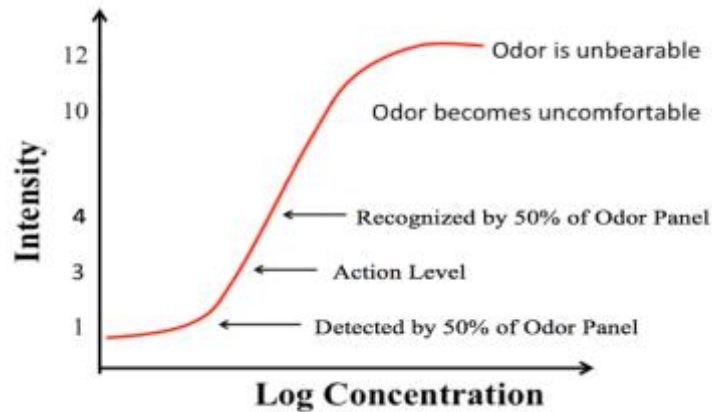


Figure 5.1. Intensity Scale for Each Odor by Weber-Fechner Curve

5.2.2. Solid Phase Microextraction and Gas Chromatography-Mass Spectrometry (GC-MS)

A solid phase micro-extraction (SPME) method (Godayol et al., 2013) that was used to identify and quantify Skatole and Indole (Zhou et al., 2016) as odor nuisances at WWTPs was adapted for analysis of earthy/musty/moldy odorants. A SPME fiber of DVB/CAR/PDMS was injected into a 10-L sample bag and exposed for 20 minutes. The SPME fiber was injected onto a Varian 450 gas chromatograph (Varian Inc., Palo Alto, California) through an #1177 liquid-injector port at 250 °C followed by a Varian 220 mass spectrometer (SGE Analytical Science,

Austin, Texas) with 99.9999% helium as the carrier gas. The gas chromatograph was equipped with an Agilent DB-5MS column (length 60 m, inner diameter 0.25 mm, film thickness 0.25 μm) and held at an initial temperature of 65 $^{\circ}\text{C}$ with a ramp of 9.5 $^{\circ}\text{C}/\text{min}$ to 160 $^{\circ}\text{C}$ and then 12 $^{\circ}\text{C}/\text{min}$ to 240 $^{\circ}\text{C}$. The carrier-gas flow rate was 1.0 mL/min through the column. The ion-trap mass spectrometer used selective ion monitoring for the primary range of m/z units of all earthy/musty odorants found in drinking water. For example, for MIB (56-58, 70-72 and 84-86 m/z from 14.50 to 17.00 minutes) and IPMP (108-110, 123-125, 136-138, and 150-153 m/z from 14.40 to 15.00 minutes) were used. The detection limit for MIB was 0.4 ng/L in air. The detection limit for IPMP was 0.4 ng/L in air. The SPME recovery for MIB and IPMP were 92% for MIB and 90% for IPMP. The concentrations measured in field samples were not corrected for recovery.

5.2.3. Odor Threshold Concentration (OTC)

The OTCs of odorants in this study were determined by trained odor panelists by the OPM (Burlingame, 1999) using the ASTM Method 679-04 (2011), a forced choice triangle test in an ascending concentration series with dilutions made by an AC'SCENT olfactometer (St. Croix Sensory, Lakewood, MN). An olfactometer is an air-dilution instrument that precisely dilutes a given odorous compound with pure air so that the exact concentration is known. The bag with odorants was then attached to an olfactometer, which delivered dilutions at known ratios to panelists. The panelists were forced to choose between two blanks and an odorous sample in the triangle test. The panelists were then asked to provide an odor-intensity rating for each dilution using the OPM scale. OTCs were then calculated by plotting the average odor intensity of at least 4 panelists for a given concentration versus the logarithm (base 10) of the concentration (in

ng/m³), performing a least-squared linear regression, and calculating the concentration that would give an intensity of 1 (threshold) using the linear equation.

5.2.4. Sampling Locations

Samples were collected at 16 locations at the OCSD WWTPs in 2013. Plant 1 is located in Fountain Valley, CA and Plant 2 in Huntington Beach, CA. The sampling locations studied were from:

Plant 1

headwork scrubbers, primary scrubbers, waste hauler biofilter, trickling filters, activated sludge, dewatering, and truck loading facilities; and at

Plant 2

trunkline scrubber, primaries scrubber, headwork scrubber, trickling filter scrubber, trickling filter contact basin, trickling filter mixed liquor channel, activated sludge discharge channel, dewatering and truck loading scrubber.

Air samples were collected at existing positive pressure air collection ducts in 10 L Tedlar or Teflon Bags, except for those processes with open surfaces exposed to the atmosphere, such as: activated sludge discharge channel, trickling filter media surface, trickling filter reactor basin, and trickling filter mixed liquor channel, where a flux chamber with sweep gas was used to fill the bags (EPA 1986). [EPA/600/8-86/008 M.R. Kienbusch, Radian Corp. "Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber" February 1986.] Where the WWTP process area foul air was treated with a scrubber, sampling was done before (IN) and after (OUT) the scrubber unit.

5.3.Results and Discussion

5.3.1.Odor Nuisances Determined by the OPM

The OPM determined many nuisance odors at the 32 WWTP locations at the 2 OCSD WWTPs. In order to better characterize the odors identified at OCSD, odors were grouped into 4 broader categories in this study (Vitko et al., 2014):

Rotten vegetable/canned corn/sulfide (rotten vegetable group),

Rotten garlic (rotten garlic group),

Musty/moldy/earthy (musty group),

Fecal/sewery/manure/rubbery (fecal group)

This general nomenclature is based on the Wastewater Odor Wheel (Burlingame, 1994). Since an average odor intensity of 3 was considered as an action level for drinking water plants to avoid odor nuisance complaints (Burlingame, 2004), it was used as guideline for odor nuisances in this study as defined by the Weber-Fechner Curve (Figure 5.1).

Objective 1 was to observe if the earthy/musty/moldy odor nuisance was present at the two OCSD WWTPs by odor panel analysis. Table 5.1 showed that the musty odor group was reported by the OPM at over half of the locations in both WWTPs. The intensities by the OPM of musty odors at Plant 2 were higher than those at Plant 1. The OPM values that are reported are the average of 4 –10L grab samples taken in the morning at each location on different days from August to October in 2013. Thus, the average and standard deviation shows the variability of the OPM data at each location. The rotten vegetable and fecal odor groups were dominant at all locations at both plants, but musty odors were detected as part of the OPM odor characteristics. It should be noted that for clarity, other odors were present but are not shown on Table 5.1. Thus,

these musty group odor intensity values are minimum values as masking of the musty odors could occur from the rotten garlic, rotten vegetable and fecal odorants.

The OPM results indicate the highest intensities of musty odors were primarily from aerobic secondary wastewater biological treatments unit operations, such as activated sludge and trickling filters. Musty odors of near an Intensity of 3 are likely to pose off-site nuisance from the unit operations of Dewatering (Intensity = 2.9) and Trickling Filter (Intensity = 3.3) at Plant 1 and Trickling Filter Contact Basin (Intensity = 4.8) and the Activated Sludge Discharge Channel (Intensity = 4.5) as well as the Trickling Filter Mixed Liquor Channel (Intensity = 4.5) at Plant 2.

5.3.2. Effectiveness of the Present Musty Odor Treatment Determined by OPM

Objective 2 was to evaluate the effect of current treatments of off-gases for removal of the earthy/musty/moldy odors by odor panel analysis, Four different odor treatment technologies were in use at OCSD: biofilters (natural media), bioscrubbers (biotrickling filters with synthetic media), packed bed chemical scrubbers with caustic and/or bleach and activated carbon filters (Vitko et al., 2014). The present efficiencies of these treatment technologies after a long time of service were evaluated by comparing the inlet and outlet intensities of musty odors based upon the data of Table 5.1, that reports OPM panel analysis values as the average of 4 samples taken at each location. Thus, the average and standard deviation shows the variability of the OPM data at each location. The rotten vegetable and fecal odor groups were dominant at all locations at both plants, but musty odors were detected as part of the OPM odor characteristics.

The input and output of 4 treatment processes were investigated in Plant 1. Figure 5.2 shows that the 3 primary chemical scrubbers, that were operated in the caustic/bleach mode (at pH = 8-9) at the time, performed best for musty odor control, removing up to 44% of the OPM odor

intensity. This is surprising since it is generally accepted that chlorine does not oxidize musty odorants as MIB and geosmin under water treatment conditions (Srinivasan et al., 2011). Thus, it is hypothesized that 1) dissolution in water is the primary mechanism of removal of the musty chemicals or 2) this data may indicate masking of the inlet odor by high concentrations of fecal and rotten vegetable odors that would make the inlet odor lower than it is chemically whereas the outlet odor would not be as strongly masked as the fecal and rotten vegetable odors are decreased. The mechanism for removal of musty odorants on a true chemical basis in the chemical scrubbers should be investigated.

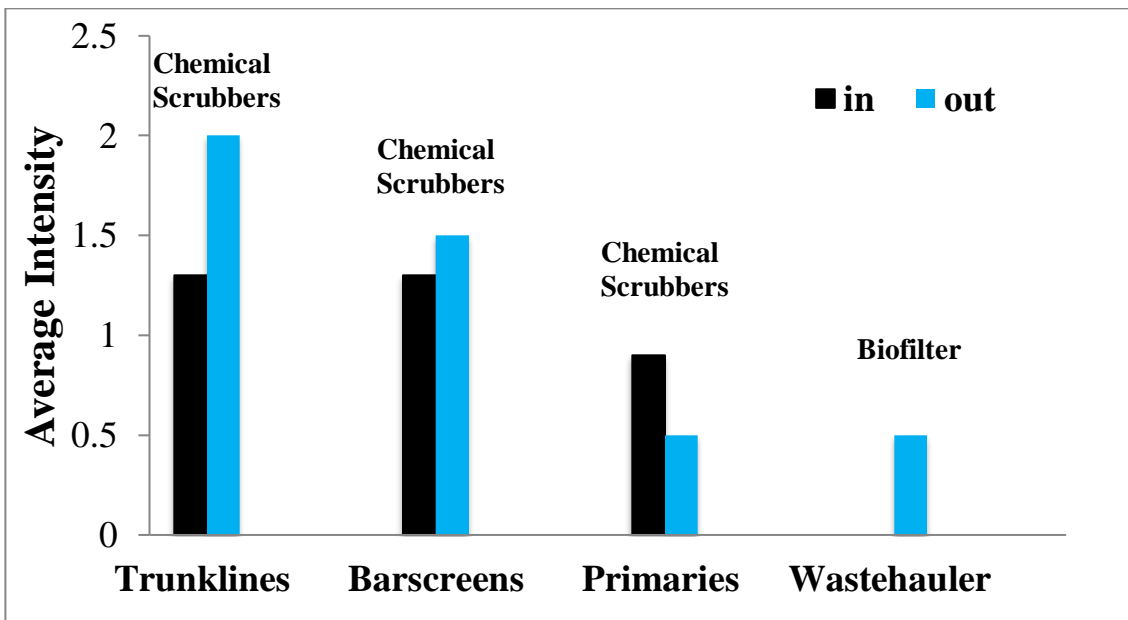


Figure 5.2. Air Treatment of Musty Odor Intensities "In" vs. "Out" of Treatment Plant Processes at Plant 1

Figure 5.2 shows that the biological treatment technologies of a biofilter, operating at the Plant 1 Wastehauler Station actually created musty odors. The general findings in water treatment technology was that biological treatment do not remove musty odors (Srinivasan et al., 2011). Thus, the second hypothesis above for chemical treatment probably explains the result,

i.e. masking of the inlet odor by high concentrations of fecal and rotten vegetable odors would make the inlet odor lower than it is chemically whereas the outlet odor would not be as strongly masked as the fecal and rotten vegetable odors are decreased. The mechanism for removal of musty odorants by biological treatment should be investigated.

In Plant 2, there are 5 plant processes that undergo treatment, using Chemical Scrubbers, Bioscrubbers, or Granular Activated Carbon (GAC) filters. The present efficiencies of these treatment technologies after a long time of service were evaluated by comparing the inlet and outlet intensities of musty odors based upon the data of Table 5.1, that reports OPM panel analysis values as the average of 4 samples taken at each location. Thus, the average and standard deviation shows the variability of the OPM data at each location. The rotten vegetable and fecal odor groups were dominant at all locations at both plants, but musty odors were detected as part of the OPM odor characteristics.

Figure 5.3 shows that based upon the OPM intensities, all treatments can remove part of the musty odor. The musty odors were removed 100% at Primary Chemical Scrubbers. This is similar to Plant 1 and remains surprising since it is generally accepted that chlorine does not oxidize MIB 1 under water treatment conditions (Srinivasan et al., 2011). Thus, it is again hypothesized as for Plant 1 that 1) dissolution in water is the primary mechanism of removal of MIB or 2) this data may indicate masking of the inlet odor by high concentrations of fecal and rotten vegetable odors would make the inlet odor appear lower than it is chemically whereas the outlet odor would be as strongly masked as the fecal and rotten vegetable odors are decreased. Again, the mechanism for removal of MIB in chemical scrubbers is not known and should be investigated.

In Plant 2, the Bioscrubber at the Trunckline remove 38% of the musty odor intensities. The general findings in water treatment technology was that biological treatment do not remove musty odors (Srinivasan et al., 2011). This result was surprising. No explanation can be developed for this to occur at this time. More studies are needed.

GAC columns are widely used on taste and odor control for musty odorants as MIB and geosmin in drinking water (Suffet et al., 1995, Bruce et al., 2002). GAC filters at the Trickling Filter removed 65% of the musty odors while only 29% were removed by the GAC columns at the Truck Loading Facilities. The GAC systems at these locations in Plant 2 did not completely remove the musty odors. The probable reasons were that the GAC may have been partial blinded by excess water and or the GAC may have been saturated and desorbing odorants. Knowledge of the history of the musty input chemicals and competing chemicals in these column is not sufficient to understand the reason for the low removal by these GAC filters.

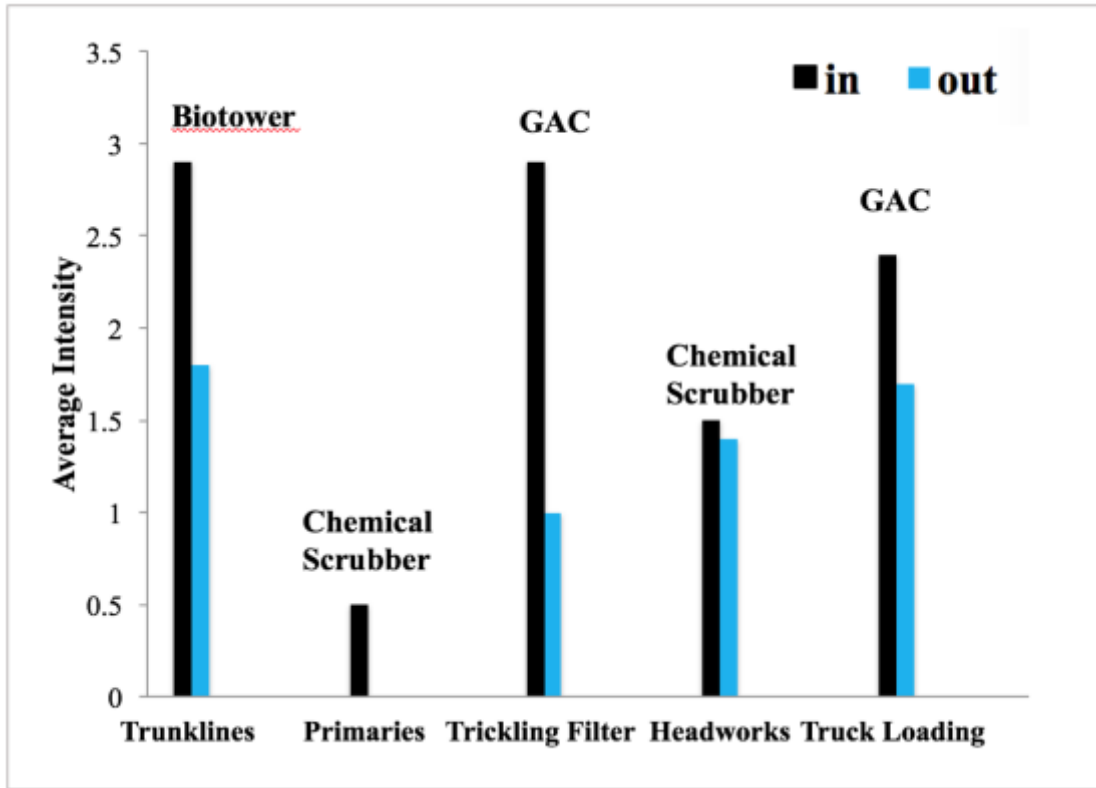


Figure 5.3. Air Treatment of Musty Odor Intensities "In" vs. "Out" of Treatment Plant Processes at Plant 2

Thus, the current air treatment technologies of off-gases from WWTP processes as presently used at OCSD do not remove musty odors efficiently. The ability of the current foul air treatment technologies to remove the musty odors seemed to relate more to odor loading of the GAC columns rather than specifically to the removal of musty odors. Musty odorants can be removed efficiently by activated carbon filtration at drinking water treatment plants (Suffet et al., 1995). WWTPs do not currently treat musty odors in any targeted manner. GAC systems from start-up should be evaluated for musty odorants with the chemical matrix of the process to determine the useful efficiency of these systems. Advanced oxidation technologies using hydroxyl radical chemistry (e.g. ozone and UV-peroxide) have been found to be effective in removing musty odorants from water (Suffet et al., 1995; Jung et al., 2004) and should be tested also as an

alternative musty odorant removal method in air treatment systems of off-gases from WWTP process.

| | | | | | | | | | | |
|--|---|-----------------------------------|------------------|------------------|--------------------------------|-------------------------------|---------|------------------------------------|---------------|-----------------|
| Plant 1 | Pretreated Trunklines & Bin Loading Bldg. | Bar-screens & Grit Chamber | Primaryes | Waste-Hauler | Trickling Filter | Activated Sludge | DAFTs | Dewatering | Truck Loading | |
| | | | | | | | | | | Chemical |
| Earthy/ Musty/ Moldy Odor Group | 1.3±1.9 (in) | 1.3±1.2 (in) | 0.9±1.5 (in) | 0 | 3.3±0.6 | 2.8±1.8 | 2.7±1.1 | 2.9±1.7 | 2.2±2.3 | |
| | 2.0±1.2 (out) | 1.5±1.5 (out) | 0.5±0.8 (out) | 0.5±1.0 (out) | | | | | | |
| Plant 2 | Trunklines | Pretreated Trunklines & Headworks | Primaryes | Trickling Filter | Trickling Filter Contact Basin | Trickling Filter Mixed Liquor | DAFTs | Activated Sludge Discharge Channel | Dewatering | Truck Loading |
| | | | | | | | | | | |
| Earthy/ Musty/ Moldy Odors | 2.9±1.1 (in) | 1.5±1.8 (in) | 0.5±1.0 (in) | 2.9±2.5 (in) | 4.8±0.9 | 4.5±1.5 | 1.4±1.6 | 4.5±1.2 | 1.1±1.3 | 2.4±1.8 (in) |
| | 1.8±1.4 (out) | 1.4±1.1 (out) | 0 | 1.0±1.2 (out) | | | | | | |

Table 5.1. Average ± the Standard Deviation of Four Odor Profile Method's Individual Odor Intensities of Earthy/Musty/Moldy Odor Group at Unit Operations at the OCSO WWTP by an Expert Panel.

5.3.3. Qualitative and Quantitative Analysis of Musty Odorants by GC-MS at the OCSD WWTPs

GC/MS scans of the samples from each OCSD location were evaluated for the four primary known earthy, musty and moldy odorants known: MIB, IPMP, Geosmin and TCA. MIB (musty) was detected at 6 locations at Plant 1 and Plant 2 and IPMP (musty) were detected at 6 locations at Plant 1 and Plant 2. There was no detection of other earthy/musty/moldy odorants, such as Geosmin or TCA in the samples. The concentrations of MIB and IPMP in air samples were quantified by GC-MS. The concentrations of MIB and IPMP and the intensities of the OPM of musty odors at 9 locations at both OCSD Plants are shown in Table 5.2. The concentration of MIB at Activated Sludge (2.5 ng/L) was the highest at Plant 1 and the concentrations at Mixed Liquor (2.8 ng/L) were the highest at Plant 2. The concentration of IPMP at the inlet of Headworks (1.8 ng/L) was the highest at Plant 1 and the concentrations at Trickling Filters (2.4 ng/L) were the highest at Plant 2.

5.3.4. Odor Threshold Concentration of Musty Compounds in Air

The OTCs of MIB and IPMP in air samples were measured using the Olfactometer (Figure 5.4). The odor threshold of MIB was found to be 0.1 ng/L (0.02 ppbV). The odor threshold of IPMP was found to be 0.02 ng/L (0.004 ppbV).

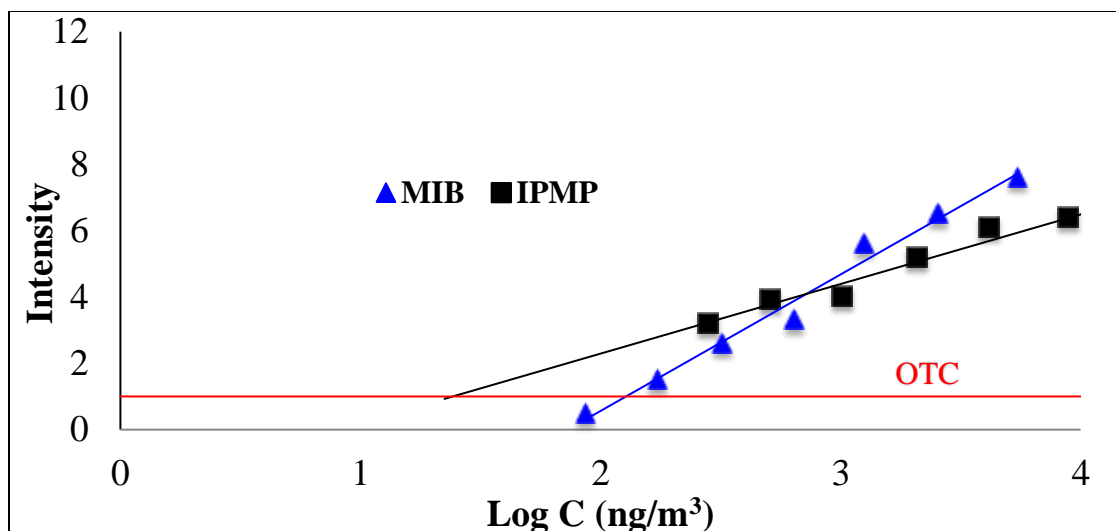


Figure 5.4. The Weber-Fechner Curves of MIB and IPMP

The OTC of MIB in air was reported as 0.09-0.47 ng/L in air (Ömür-Özbeket et al., 2011). The OTC of IPMP was reported as 0.005-0.05 ng/L in air (Sala et al., 2004). Both the OTCs of MIB and IPMP measured in this study were within the range of literature values in air. The difference between the literature and the results reported here may be due to the sensitivity of panel members, the methodologies used, the number, age, and sex of the panelists (Curren et al., 2014). The wide range of odor thresholds in the literature indicates variability in odor detection of different individual panelists. OTCs provide important information on the identification of the source of the odors as well as the importance of its odor nuisance potential.

The OPM values of musty odors at the Activated Sludge and Dewatering at Plant 1 and the Trickling Filter Reactor A in Plant 2 were higher than 3, which could lead to offsite complaints for musty group odors from these sites alone. Whenever there were musty odors reported by the OPM, there were MIB or IPMP detected by the GC-MS. This indicates a conclusive confirmation that MIB and IPMP would be the major musty odorants released from WWTPs.

Table 5.2 shows the importance of the odor nuisance potential by the ratio of the odor concentration to odor threshold concentration (C/OTC), i.e. the OAV in air. The OAV ratios are included for MIB and IPMP based on the OTCs measured in this study. The concentrations of MIB detected were higher than the concentrations of IPMP. However, the OAV ratio of IPMP (17-98) were higher the OAV ratio of MIB (4-20) due to the very lower OTC of IPMP. In this case, IPMP may contribute more to musty odors. However, both MIB and IPMP can likely lead to a musty odor nuisance off-site.

| April 2016 Location | IPMP | | MIB | | Site OPM |
|------------------------------------|--------------------|----------------|--------------------|----------------|-------------|
| | C (ng/L in air) | OAV = C/OTC | C (ng/L in air) | OAV = C/OTC | |
| P2 Trickling Filter | 2.4±0.1 | 98 | 1.3±0.2 | 9 | 3.0 |
| P2 Trickling Filter (Reactor A) | | | 2.2±0.4 | 16 | 5.0 |
| P2 Mixed Liquor West | | | 2.8±0.3 | 20 | 2.0 |
| P1 Headworks Inlet #1 | 1.8±0.1 | 77 | | | Note |
| P1 Activated Sludge #5 | 0.4±0.0 | 17 | 2.5±0.3 | 18 | 3.5 |
| P1 Dewatering | 0.5±0.1 | 20 | 1.7±0.3 | 12 | 3.5 |
| P1 Daft Inlet | 0.4±0.0 | 17 | | | 1.5 |
| P2 Daft In | 0.6±0.4 | 25 | | | 1.0 |
| P2 Trickling Filter #1 | | | 0.6±0.0 | 4 | 2.8 |

Table 5.2. Concentration of MIB and IPMP and OPM Results for one sampling set

The concentrations of MIB and IPMP were used to calculate the expected musty odor intensities, using the Weber-Fechner curve in Figure 5.4. Table 5.3 shows the comparison of

intensities of musty odors detected by OPM and calculated by Weber-Fechner Curves. The detected intensities were all lower than the expected values calculated from the concentration of either MIB or IPMP. The difference was most obvious at P1 Headworks Inlet, where strong fecal and rotten vegetable odors were shown. This strongly indicates that a masking effect for the OPM would occur where high fecal and rotten vegetable odors occur. The mechanism of masking effect of musty odors by the dominated odors needs to be investigated in future research. Therefore, if musty type odors are found by the OPM by odor panels, a chemical analysis for the musty odorants MIB and IPMP must be completed to evaluate the true effect of a musty odor nuisance off-site by the ratio of (C/OTC), i.e. the OAV in air at different WWTP sources.

| Apr-16 | Detected OPM | Calculated Musty Intensity | |
|--|-------------------------|---------------------------------------|------------|
| | | IPMP | MIB |
| Location | | | |
| P2 Trickling Filter | 3.0 | 5.2 | 5.0 |
| P2 Trickling Filter (Reactor A) | 5.0 | | 5.9 |
| P2 Mixed Liquor West | 2.0 | | 6.4 |
| P1 Headworks Inlet #1 | Note | 4.9 | |
| P1 Activated Sludge #5 | 3.5 | 3.6 | 6.2 |
| P1 Dewatering | 3.5 | 3.8 | 5.5 |
| P1 Daft Inlet | 1.5 | 3.6 | |
| P2 Daft In | 1.0 | 3.9 | |
| P2 Trickling Filter #1 | 2.8 | | 3.6 |

Table 5.3. Comparison of Intensities of Musty Odors Detected by OPM and Calculated by Weber-Fechner Curves

5.4. Conclusions

- Musty odors have been detected by residents near the WWTPs studied. Musty type odors (Musty/moldy/earthy) were observed as odor nuisance at the two WWTPs of the OCSD by odor panel analysis.
- The musty odor was not removed by present foul air treatment devices from the WWTP unit operations, as determined by odor panel analysis. The biological treatment methods that were in use at OCSD did not remove musty odors well. GAC current treatment technologies of off-gasses from WWT processes as used at OCSD do not remove musty odors efficiently. GAC saturation and desorption is hypothesized to be the primary cause of the problem with present GAC columns. The wet scrubbers performed best to remove musty odors among current control technologies. Probably, dissolution in water is the primary mechanism of removal of the musty chemicals.
- The odorous chemicals MIB and IPMP were determined as two primary chemicals that cause the musty odor nuisance from WWTP unit operations. The OC/OTC (OAV value) data for MIB and IPMP confirm that musty odor group could lead to off-site nuisance at WWTPs.
- The OTCs of the musty odorants of MIB and IPMP were determined by the Weber-Fechner curve. The odor threshold of MIB is 0.1 ng/L and the odor threshold of IPMP is 0.02 ng/L for our untrained panelists. These values are within the range of other OTC determined for these compounds in air.
- Rotten vegetable and fecal odors apparently mask odor panels identification by the OPM of the true intensity of musty odors. When rotten vegetable and fecal odors are removed efficiently, musty odors may become major odor issues at WWTP locations as musty odorant

have very low OTCs and may have OAV ratios sufficient to be an off-site odor nuisance. Thus, if an odor panel identifies musty odors, a chemical analysis is needed to determine removal efficiency.

- The ratio of the odor concentration to odor threshold concentration in air were determined at specific locations at the OCSD Plants and large OAV figures indicate potential off-site odor nuisance.

5.5.References

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Chapter 6

Determination of Odor Threshold Concentration by Weber-Fechner Curves and the Peeling of an Onion Effect via Masking of Odors

6.6. Introduction

Most odor abatement systems used in Wastewater Treatment Plants (WWTPs) are designed based on hydrogen sulfide (H₂S) removal. It is assumed that H₂S is the major odorant emitted and that it presents itself at high concentrations (Iranpour et al., 2005; Lasaridi et al., 2010). However, recent tests of foul air scrubbing systems at Orange County Sanitation District (OCSD) WWTPs showed that although the chemical analyses confirmed acceptable performance by the H₂S-removal systems, the total odor intensities measured by Dilution to Threshold (D/T) remained high (Vitko et al., 2014). Also, the Odor Profile Method (OPM) odor panel method (Burlingame, 2009; Burlingame, 1999) which measures the individual odorant types determined by the Wastewater (WW) Odor Wheel (Burlingame, 1999; Burlingame et al., 2004; Suffet and Rosenfeld, 2007; Burlingame, 2009) and the intensities of these odorant types remained high as measured by the Weber-Fechner Curve (Fechner, 1859) as described by Suffet et al., (1995).

Odorant prioritization distinguishes the major odorants that need to be targeted for removal from the minor contributors. The “most detectable” odorants are not only those present at the highest concentrations (C) but also those that have higher frequency of appearance and high concentration to the odor threshold concentration (C/OTC) ratios. The C/OTC ratio is also known as the odor activity value (Patton and Josephson, 1957). Higher C/OTC ratios indicate the “most detectable” odorants, or the compounds that are likely to pose the highest odor nuisance at a given location (Vitko et al., 2016a). Nine chemicals were found to be the “most detectable” odorants from the process areas of the two OCSD plants defined by the Wastewater Odor Wheel (Vitko et al., 2016a):

- Hydrogen sulfide (H₂S) (sulfur group)
- Methyl mercaptan (MM) (sulfur group)

- Dimethyl sulfide (DMS) (sulfur group)
- Dimethyl disulfide (DMDS) (sulfur group)
- 2-Methylisoborneol (MIB) (musty group)
- 2-Isopropyl-3-methoxypyrazine (IPMP) (musty group)
- Indole (fecal group)
- Skatole (fecal group)
- Ammonia (ammonia group)

Unfortunately, OTCs that have been determined in the literature vary widely depending upon how they are measured, the type of sampling method used, e.g. bags or adsorption tubes, etc, the conditions in the environment during the odor assessment, the age and gender of the odor panel participants, and the level of training of these panelists. Accurate determination of OTCs is required for accurate odorant prioritization. The best approach for a study is to determine the OTCs with the same panel who will be completing the olfactometry and other odor panel approaches, such as the OPM.

Sensory methods help bridge the gap between chemical detection limits, nose characterization of odorant type, and nose sensitivity measured by intensity. The OPM, and D/T methods are based upon the ASTM Odor Threshold Method 679-04 (2011) and the EN 13725 (European Committee for Standardization Method, 2003). In this study, the AC'SCENT® International Olfactometer User Manual (2005) was used. The OPM uses the Wastewater Odor Wheel (Figure 6.1) to train and determine the odor character descriptors for a sample (Burlingame, 1999; Burlingame et al., 2004; Suffet and Rosenfeld, 2007; Burlingame, 2009).

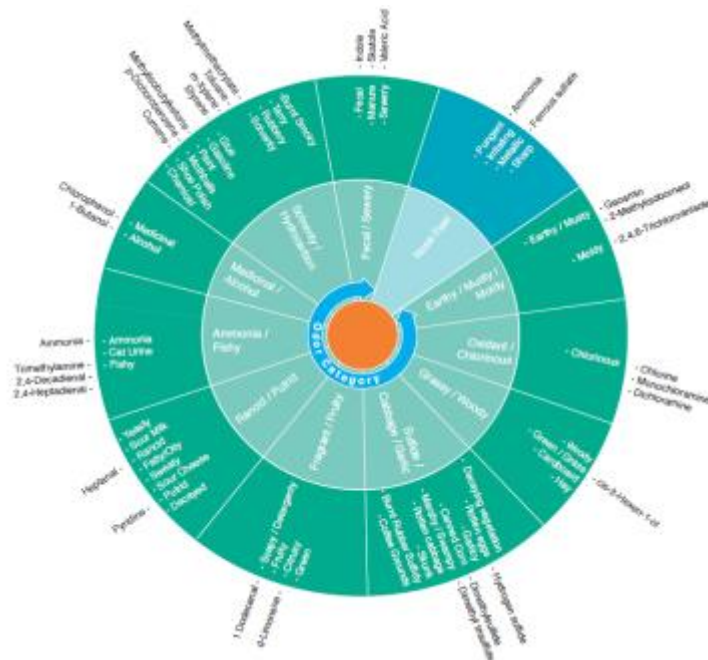


Figure 6.1. The Wastewater Odor Wheel

The second part of the OPM is to determine the intensity of each odorant described by the odor panel. This requires the use of an intensity scale utilizing the Weber- Fechner Law described in Suffet et al., (1995). Weber observed that increased stimuli is relative to the previous amount experience and his student, Fechner (1859), described this relationship through the following formula:

$$I = k \text{ Log } C/C_0$$

where intensity (I) is proportional to the logarithm (base 10) of the concentration (C) relative to a previous concentration (C₀).

The OTC is defined as the concentration when intensity is 1 (I=1) on the Weber-Fechner curve (Figure 6.2). The OTC is formally described as the point where 50% of a population (minimum of 4 panelist) can define a difference between pure air and air containing an odorant. The Weber-Fechner intensity scale for each odorant is 0, 1 (OTC), 2, 4 (Odor Recognition Concentration, [ORC]), 6, 8, 10, and 12. The ORC is formally described as the point where 50%

of a population can define the odorant type. The Action Level for an odor nuisance is suggested to be set at the intensity of 3 to ensure action is taken before 50% of the general population recognizes the odor.

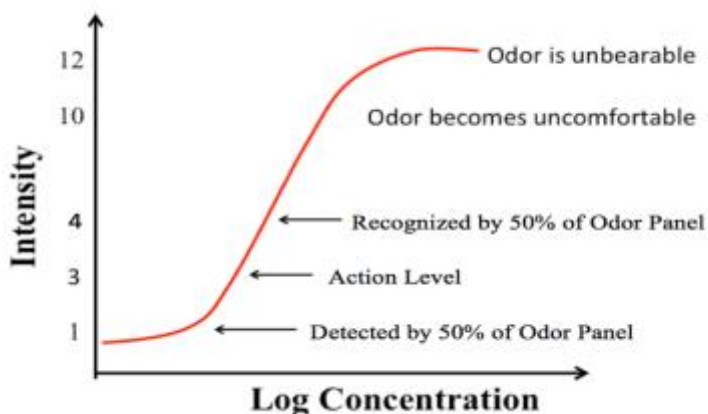


Figure 6.2. Intensity Scale for Each Odor by Weber-Fechner Curve

The actual presence of these compounds, however, even when high C/OTC ratios occur, may not elicit the anticipated OPM intensities when the air samples contain mixtures of compounds. Sensory perceptions cannot be predicted accurately from chemical data alone. The odors from multiple odorants may blend or produce an integrated odor (Lawless, 1999), mask each other (antagonism) and by dilution unmasks other odors. This dilution effect can be viewed as “peeling an onion”, i.e. when one high concentration odorant is removed, another takes its place and then dominates. In other words, after the primary odor is removed, other odors become apparent and subsequently need to be controlled as odor nuisances. Predicting the nuisance level of each layer of the “onion” is the broader challenge of odor control (Vitko et al., 2016b).

The objective of this study was to measure and understand what occurs during the dilution process of olfactometry to the nine “most detectable” odorants with an odor panel by the OPM and olfactometry method. The second objective was to investigate how odors are layered in a

mixture and the persistence of odors by dilution. Once reliable OTCs have been determined, odor treatment technologies can be targeted to remove those compounds with high C/OTC values.

6.2.METHODS

6.2.1. Odor Panel Sensory Methods

The sensory method used to determine OTCs in this study was a combination of the OPM (Burlingame, 1999; Burlingame, 2009), the ASTM Method 679-04 (ASTM, 2011), EN13725 (European Committee for Standardization, 2003), and The AC'SCENT® International Olfactometer User Manual (2005) (St. Croix Sensory, Lakewood, MN). The Wastewater Odor Wheel (Figure 6.1) was used to standardize the odor character descriptors during training and analysis for the OPM. In this study, the following simplified groups were used to streamline the interpretation of results and selection of chemical-analysis methods for the OPM (Vitko et. al. 2016a):

- Rotten eggs/rotten vegetable/canned corn/sulfide/rotten garlic (sulfur group)
- Musty/earthy/moldy (musty group)
- Fecal/sewery/manure/rubbery (fecal group)

The OPM was completed at OCSD by a consumer panel of 12-14 members with minimum training. OPM is a modification of Standard Method 2170: the Flavor Profile Analysis Method (FPA) (APHA et al., 2012). The panelists were taught to identify multiple odor characters and their respective intensities in a single sample based upon the wastewater Odor Wheel (Figure 6.1). The OPM panelists learned how to associate the intensity of each odor using a surrogate sugar-solution scale used for the FPA Method (APHA, et al. 2012) (Table 6.1). It should be

noted that the sugar standard has been shown to be easier to use and equivalent to the ASTM Method E544 (2004) butanol intensity scale for air samples (Curren et al., 2014).

| Intensity Scale | Intensity Description | Concentration of Sugar in Water |
|-----------------|-----------------------|---------------------------------|
| 0 | Odor-Free | 0% |
| 1 | Threshold (OTC) | |
| 2 | Very Weak | |
| 4 | Weak (ORC) | 5% |
| 6 | Weak-Moderate | |
| 8 | Moderate | 10% |
| 10 | Moderate-Strong | |
| 12 | Very Strong | 15% |

Table 6.1. Flavor Profile Analysis Intensity Scale used in the Odor Profile Method

An olfactometer is an air-dilution instrument that precisely dilutes a given odorous compound with pure air so that the exact concentration is known. This study used a known concentration of a given compound in liquid, which was introduced into a sampling bag of known volume and allowed to evaporate therein. The bag was then attached to an olfactometer (St. Croix Sensory, Lakewood, MN), which delivered dilutions at known ratios to panelists. OTCs were determined by triangular forced choice sample-presentation in ascending concentration series according to ASTM Method 679-04 (ASTM, 2011). Each panelist was forced to choose between two blanks and an odorous sample. The panelists must select one of the three presentations they observed. Meanwhile the panelists were asked to provide an odor-intensity rating for each dilution using the OPM Weber-Fechner scale (Table 6.1), which uses the FPA scale defined above (APHA et al., 2012).

For the FPA and OPM, if the panelist made the correct choice in the triangular forced choice test, the intensity and odor character reported for this dilution level was recorded. When a

panelist made a wrong choice, the odorous sample was not distinguished from the blanks, then a 0 was assigned to intensity. If an odor character was reported by fewer than 50% of the panelists, the odor was reported as an odor note without an intensity score and excluded from further analysis. For the odor characters reported by 50% or more of the panelists, individual panelist's identification errors were assigned an intensity score of 0. OTCs were then calculated by plotting the average odor intensity for a given concentration versus the logarithm (base 10) of the concentration (in ng/m³), performing a least-squared linear regression, and calculating the concentration that would give an intensity of 1 (threshold) using the linear equation.

6.2.2. Bag Material

The OTCs of H₂S, MM, DMS, DMDS, ammonia, MIB, and IPMP were measured in Tedlar sampling bags from SKC Inc. (Pittsburgh, PA, USA) as there is no significant loss of these compounds in Tedlar bags within 6 hours (Zhou et al., 2016). The OTCs of indole and skatole and air samples from OCSD were measured in Teflon FEP sampling bags from Jensen Inert Products (Coral Springs, FL, USA) because there were significant losses of fecal odorants in Tedlar bags within minutes (Zhou et al., 2016; Hansen et al., 2011; Boeker et al., 2014).

6.2.3. Instrument Quantification of Indole and Skatole

A 10-L sample was pulled through a series of 3 impingers with 15 mL dichloromethane in each at flow of 0.5 L/min for 20 minutes. Indole and skatole were detected by GC/MS in the solutions from the first two impingers but not from the third. Accordingly, the solutions from the first two impingers were transferred to 10-mL Kuderna–Danish concentrator tubes and inserted

into a Kontes tube heater (Kontes Corporation, Vineland, New Jersey) to concentrate each sample to 1 mL at 40 °C under a very low surface flow of nitrogen.

One microliter (μL) of solution was injected onto a Varian 450 gas chromatograph (Varian Inc., Palo Alto, California) through an #1177 liquid-injector port followed by a Varian 220 mass spectrometer (SGE Analytical Science, Austin, Texas) with 99.9999% helium as the carrier gas. The gas chromatograph was equipped with an Agilent DB-5MS column (length 60 m, inner diameter 0.25 mm, film thickness 0.25 μm) and held at an initial temperature of 65 °C with a ramp of 9.5 °C/min to 160 °C and then 12 °C/min to 240 °C. The carrier-gas flow rate was 1.0 mL/min through the column. The ion-trap mass spectrometer monitored the primary range of m/z units of indole (62-64, 89-91 and 116-119 m/z from 12.00 to 13.00 minutes) and skatole (76-78, 102-104, 129-132 m/z from 13.00 to 14.50 minutes). Sampling to analysis time was 6 hours.

6.2.4. Instrument Quantification of Musty Odorants

From a prepared or sampled Tedlar bag, a 100-mL air sample was collected by ground glass syringe and injected into a gas-adsorbent trap/heat-desorption system (designed by Randy Cook, Lotus Instruments, Long Beach, California). The trap was made out of five layers: 60/80 mesh glass beads, Carbopack C, Carbopack B, Carbosieve 569 and Carbosieve 1003. During collection the trap was maintained at 35 °C and to initiate injection was rapidly heated to 270 °C. The purged sample entered the same gas chromatograph/mass spectrometer described above. The gas chromatograph was held at an initial 40 °C with a ramp of 8 °C/min to 88 °C, 10 °C/min to 100 °C, 6 °C/min to 156 °C, and 10 °C/min to 240 °C with a hold time of 0.73 min. The carrier-gas flow rate was 1.0 mL/min through the column. The ion-trap MS was monitored from 45-300 m/z. The ion-trap mass spectrometer monitored the primary range of m/z units of MIB (56-58,

70-72 and 84-86 m/z from 14.50 to 17.00 minutes) and IPMP (108-110, 123-125, 136-138, and 150-153 m/z from 14.40 to 15.00 minutes). Sampling to analysis time was 6 hours.

6.2.5. Instrument Quantification of Volatile Organic Sulfur Compounds

Table 6.2 shows the compounds analyzed by ALS Laboratories (Simi Valley, CA). Sampling to analysis time was 24-30 hours. Table 6.2 shows the sampling and analytical techniques for sulfur compounds at OCSD WWTP.

| Odorant Type | Specific Compound | Odor Character by WW Odor Wheel | Method Reporting Limit (ng/L in air) | Analytical Technique | Sampling Technique |
|--------------------------|-------------------------------------|---------------------------------|--------------------------------------|---|------------------------------------|
| Reduced Sulfur Compounds | Methyl Mercaptan (MM) | Rotten Vegetable | 10.0 | ASTM D5504 Method by Modified GC with sulfur chemiluminescence detection. | Grab sample into a 1 L Tedlar bag. |
| | Dimethyl Disulfide (DMDS) | Rotten Garlic | 9.6 | | |
| | Dimethyl Sulfide (DMS) | Canned Corn | 12.5 | | |
| | Hydrogen Sulfide (H ₂ S) | Rotten Egg | 7.0 | | |
| | Dimethyl Trisulfide (DMTS) | Rotten Vegetable | 13.0 | | |

Table 6.2. Sampling and Analytical Techniques for Sulfur Compounds at OCSD WWTP

6.2.6. Instrument Quantification of Ammonia

The samples were prepared in 10 L Tedlar Bags and measured the same day. A 10-L sample was pulled through a series of 3 impingers with 15 mL 0.1M sulfuric acid in each at flow of 0.5 L/min for 20 minutes. The solution in first two impingers was transferred into a 100-mL

volumetric flask and diluted to 100 mL with 0.1M sulfuric acid. The third electrode did not have any ammonia present. An ammonium selective electrode system was used to measure the ammonia by the Standard Method 4500-NH₃ (APHA, 2012). The detection limit of this method is 15 µg/L in air.

6.3.Results and Discussion

6.3.1. Odor Threshold Concentrations

The OTCs for the 9 “most detectable” chemical odorants were determined using the OPM by 12-14 panelists. The Weber-Fechner curves for these 9 compounds are shown in Figure 6.3. Based upon the knowledge of using OPM in the drinking water industry, the same process was used to determine the concentrations associated with a nuisance intensity score of 3, which is the point at which more sensitive neighbors could recognize the odor and may start to complain (Suffet et al., 2008). This is an average value of the participants that are just below the general population’s ORC (intensity 4) and therefore was considered the Action Level (intensity 3). The OTCs and nuisance levels of the 9 compounds are given in Table 6.3.

The OTC of IPMP (0.02 ng/L in air) is the lowest among the 9 odorants. The OTCs of MM (0.2 ng/L in air), MIB (0.1 ng/L in air), and skatole (0.3 ng/L in air) are also quite low. Panelists were more sensitive to these odorants. Thus, even if high concentration of ammonia is detected, the ammonia odor is weak due to its high OTC. Meanwhile, there will be an odor nuisance caused by MM, MIB, IPMP and skatole at low concentration.

| Chemical | Linear Equation | R ² | OTC (Intensity Score 1) | | Nuisance (Intensity Score 3) | |
|------------------|-----------------|----------------|----------------------------|-------|---------------------------------|-------|
| | | | ng/L in air | ppb-v | ng/L in air | ppb-v |
| H ₂ S | y=5.1x-13 | 0.99 | 0.7 | 0.5 | 2 | 1 |
| MM | y=4.5x-8.7 | 0.99 | 0.2 | 0.08 | 0.4 | 0.2 |
| DMS | y=4.7x-17 | 0.99 | 8 | 3 | 20 | 8 |
| DMDS | y=3.7x-9.9 | 0.95 | 0.8 | 0.2 | 3 | 0.8 |
| MIB | y=4.2x-8.1 | 0.98 | 0.1 | 0.02 | 0.4 | 0.06 |
| IPMP | y=2.1x-1.9 | 0.96 | 0.02 | 0.004 | 0.2 | 0.04 |
| Skatole | y=5.0x-12 | 0.99 | 0.3 | 0.04 | 0.6 | 0.1 |
| Indole | y=5.7x-18 | 0.96 | 2 | 0.5 | 5 | 1 |
| Ammonia | y=3.4x-19 | 0.99 | 900 | 1000 | 3000 | 5000 |

Table 6. 3. Linear Regression Results, OTCs, and Nuisance Levels of an Individual Odorant in Tedlar Bags Over a 6 Hour Time Period

Figure 6.4 shows the slope of the regression line for IPMP is the lowest (most gradual), which indicates that IPMP is more persistent in air because its odor intensity decreases slowly with distance. In the mixture, musty odor from IPMP may show up later and lead to an off-site problem because IPMP is more persistent in air. Thus, even though musty odors maybe masked by strong fecal and sulfur odors at the WWTP, they can cause a problem at fence-line. The slopes for indole and skatole are higher (steeper), which indicates that their (fecal) odor intensities would decrease quicker with distance. Thus, the strong fecal odors reported on-site may not be problematic as both indole and skatole disappear quicker than other odorants. These conclusions should be verified by using the OPM method at different distances from the plant according to wind direction.

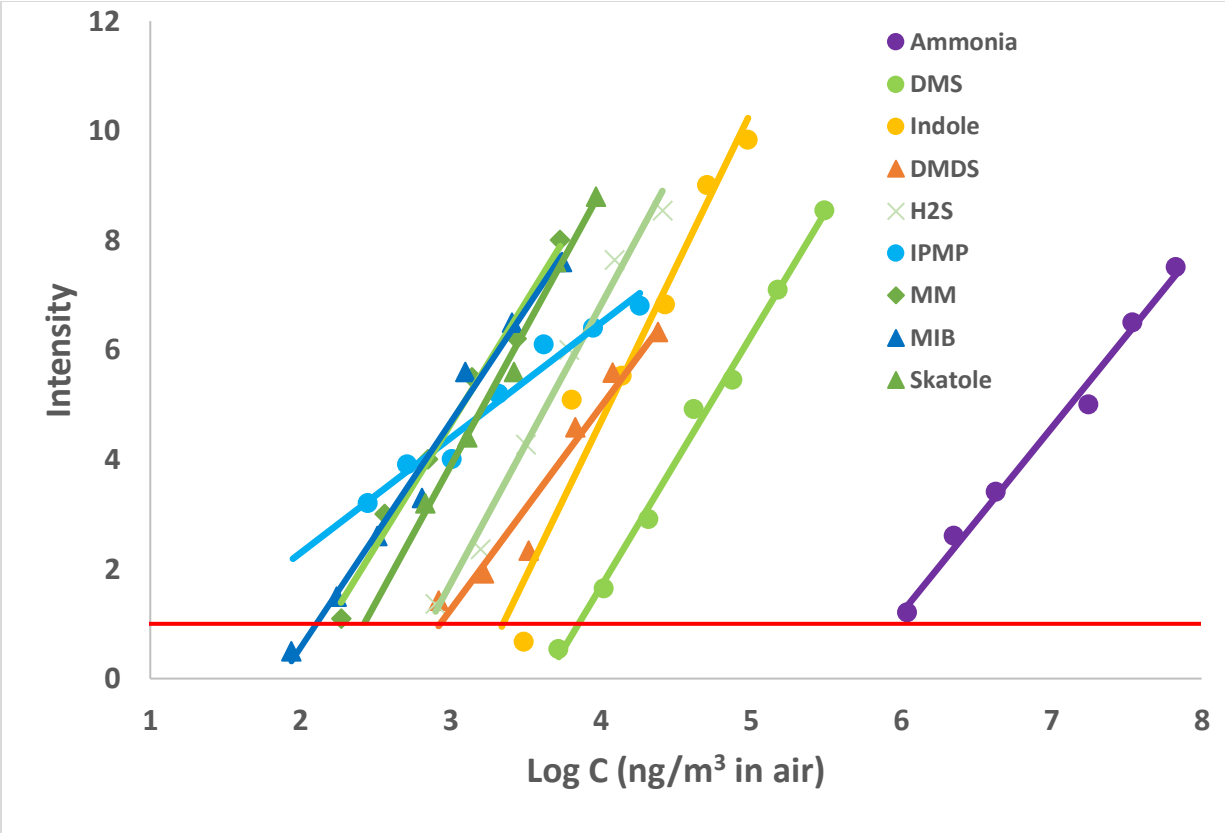


Figure 6.3. Weber-Fechner Curves for Individual Odor-Threshold Concentration Determination of an Odorant in Tedlar Bags except for indole and skatole which were determined in Teflon Bag

| Chemical | Determined OTCs | Reference OTCs |
|------------------|-----------------|----------------|
| | ng/L in air | ng/L in air |
| H ₂ S | 0.7 | 0.6-11 |
| MM | 0.2 | 0.04-3.2 |
| DMS | 8.0 | 2.5-12 |
| DMDS | 0.8 | 0.1-8.5 |
| MIB | 0.1 | 0.09-0.5 |
| IPMP | 0.002 | 0.005-0.05 |
| Skatole | 0.3 | 0.0004-0.3 |
| Indole | 2.0 | 1.4-6.7 |
| Ammonia | 900 | 28-4000 |

Table 6.4. Comparison of Odor Threshold Concentrations

NOTE: References OTCs - Combined data from Nagata, 2003; Rosenfeld et al., 2007; Amoore, 1983; Ömür-Özbeket et al., 2011; Sala et al., 2004; Ruth, 1986.

The wide range of odor thresholds indicates a large variability in detection by the odor panelists. This variability can be explained by the individual differences in sensitivity and ability to smell of panel members and their age, sex, training, as well as the methodologies used (Curren et al., 2014). The OTCs often spans orders of magnitude in the literature. The large range of OTC of skatole may be due the methodologies used in different studies. In this study, threshold was defined as where 50% of panelist can notice the odor. But some researchers set the threshold at the lowest concentration reported by a single panelist (Ruth, 1984).

Thus, the OTC should be considered a guideline at other locations rather than a specific limit to prevent odor nuisances from occurring at other locations. That said, OTCs still provide important information on the identification of the chemical source of malodors and for the prioritization of odorants for treatment (Vitko et al., 2016a).

6.3.2. Odor-Threshold Concentration by ASTM Method 679-04

In addition to OPM OTCs, the OTCs of the 9 odorants were also calculated using ASTM Method 679-04 (2011). For each panelist, the geometric mean of the last concentration missed and the first after which all guesses were correct was calculated as the individual's OTC. Then the geometric mean of individual OTCs of the panelists was calculated as the OTC for the entire panel. The 95% confidence interval of OTC was determined by ASTM method 679 (2011) to properly compare the results of the two methods.

As shown in Table 6.5, the OTCs of the 9 odorants by OPM and ASTM Method 679 -04 are virtually the same and well within an order of magnitude in the two cases where they deviate (indole and ammonia). More specifically, the OTCs for H₂S, MM, DMS, DMDS, MIB, IPMP, skatole, and ammonia from the OPM method all fell within the 95% confidence interval by ASTM Method 679-04. The OTC of indole by OPM, however, was below the lower limit of the 95% confidence interval by ASTM Method 679-04. This could be due to the standard deviations of the ASTM method being much lower than those of the OPM method, which results from the standard deviations from panel intensity calculation being avoided. Overall, the resulting OTCs from the two methods are highly comparable, thus either method can be used to determine OTCs accurately. This is the first time that such a comparison has been completed and shows that the OTCs by the OPM method are as valid as those by the ASTM Method 679-04, which is considered the “gold standard” for the determination of OTCs.

| Chemical | OPM | ASTM 679-04 | |
|------------------|---------------|---------------|-----------------|
| | OTC | OTC | 95% CI |
| | (ng/L in air) | (ng/L in air) | (ng/L in air) |
| H ₂ S | 0.72 | 0.84 | (0.50 - 1.40) |
| MM | 0.15 | 0.14 | (0.08 - 0.22) |
| DMS | 7.5 | 6.4 | (2.9 - 14.2) |
| DMDS | 0.85 | 1.2 | (0.54 - 2.4) |
| MIB | 0.14 | 0.18 | (0.08 - 0.43) |
| IPMP | 0.024 | 0.029 | (0.021 - 0.041) |
| Skatole | 0.3 | 0.3 | (0.20 - 0.50) |
| Indole | 2.3 | 5 | (2.7 - 9.44) |
| Ammonia | 880 | 620 | (300 - 1270) |

Table 6.5. Comparison of OTCs by OPM and ASTM Method 679-04

6.3.3. “Peeling the Onion”

High C/OTC ratios may not elicit the anticipated OPM intensities when the air samples contain mixtures of compounds. Sensory perceptions cannot be predicted accurately from chemical data alone. The odors from multiple odorants may mask, blend or produce an integrated odor. After the primary odor is removed, other odors become apparent and subsequently need to be controlled — “Peeling the Onion” effect via masking of odors.

An example of the “Peeling the Onion” effect is shown in Figure 6.4 completed by olfactometry and the OPM. Figure 6.4 shows that individual odors are layered in a mixture of odors and the mixture of odors change with dilution. The results are presented in a way to show the dilution with time of the odorants and the “peeling of the onion” of odorant concept (Vitko, et al., 2014). In fact, the data is presented opposite the way than the data was collected, i.e. in a descending sequence to illustrate the effect. The fecal and sulfur odors were initially prominent

(with no musty odors reported) at the foul air from an Activated Sludge reactor, as was reported at most other locations studied at OCSD WWTP. As dilution was completed, the intensities of both the fecal and the sulfur odors decreased (peeling the onion of odors) with the fecal odors disappearing first. At the greater dilutions, musty odors appeared and the sulfur odors became undetectable. At the greatest dilution, only musty odors were detectable. This indicates that fecal and sulfur odors may dominate on-site (close to the source) while musty odors may be the odor nuisance off-site (at the fence line).

This may be due to the low OTCs of musty odorants, MIB and IPMP. This shows that the musty odors are less detectable with the presence of other high odor intensities such as fecal and the S group of odors and these odors must be peeled away before the musty odor is detected. Also, that the musty odor of IPMP is more persistent than other odorants. The musty odors become noticeable when other odors disappear by dilution.

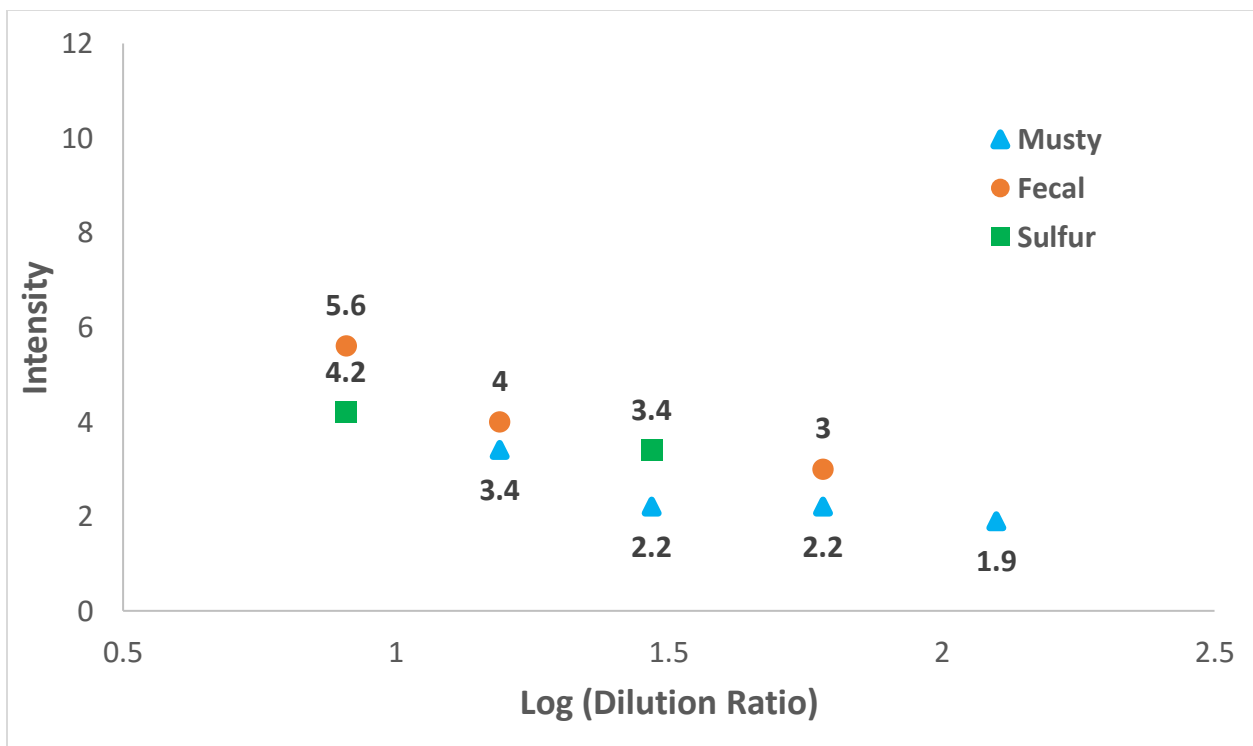


Figure 6.4. OPM Results at the Activated Sludge Reactors at the OCSD WWTP

Another peeling of the onion layered pattern occurred at the Truck Loading Locations at the OCSD, with a much stronger odor source (Figure 6.5). Initially, fecal (I=8.4) and sulfur odors (I=6) odors dominated with very high intensities. At this time, no other odors can be perceived due the masking effect of the strong fecal and sulfur odors. Fecal and sulfur odors decreased by increased dilution. Musty odors were reported once both the sulfur and fecal odor were decreased to a lower intensity by successive dilutions. This is consistent with the finding that IPMP and other musty chemical odors are very persistent in air and their odor intensities decrease slowly with distance, i.e., has a relatively flat slope (see Figure 6.3).

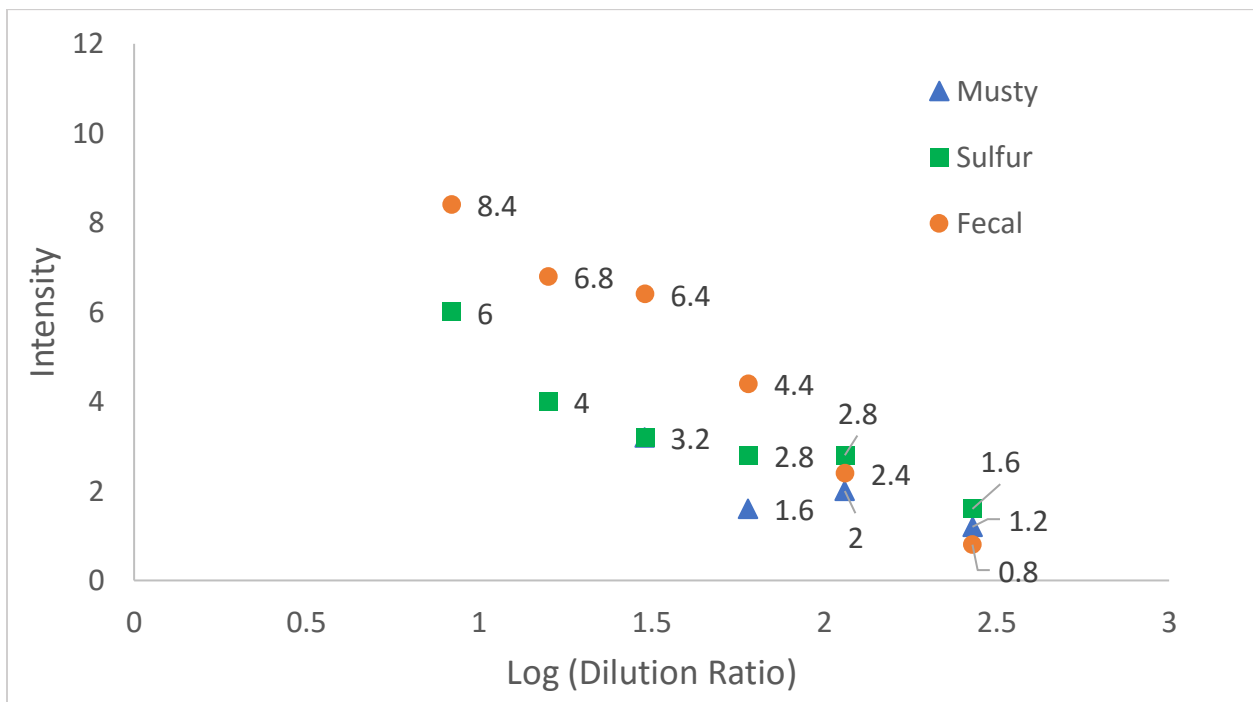


Figure 6.5. OPM Results at the Truck Loading Locations

The OPM can be used to evaluate odor treatment technologies along with Olfactometry. The D/T number by Olfactometry can be used as an indicator to identify if there is an odor problem and if the treatment has remove all the odors to a sufficiently low level. However, the OPM

method needs to be applied to determine the odorants causing the odor nuisance. Therefore, treatment can be designed based on the OPM and not Olfactometry. Meanwhile, the OPM method with Olfactometry can reveal the “peeling of the onion” effect to target the correct odors causing offsite nuisances.

6.4. Conclusions

- The OTCs of the 9 “most detectable” odorants at OCSD WWTPs were determined using the Weber-Fechner curves for H₂S, MM, DMS, DMDS, MIB, IPMP, skatole, indole, and ammonia.
- The OTC of IPMP (0.02 ng/L in air), MM (0.2 ng/L in air), MIB (0.1 ng/L in air), and skatole (0.3 ng/L in air) are quite low.
- The OTCs measured by the Weber-Fechner curves were within the literature range and 95% confidence interval of ASTM method 679-04.
- Odors mask each other and can be described by the “peeling an onion” concept. Due to the varying abilities of odors to persist with dilution (represented by distance from the source), the simple presence of odorants on-site, even with high concentrations or C/OTC ratios, may not necessarily lead to off-site odor problems.
- Musty odors, for example, may have relatively low intensities on-site if they are masked by other odors. However, once the primary odor is removed (i.e. after peeling of the fecal and sulfur odors), the musty odor can become apparent and could lead to an odor nuisance off-site.
- The OPM can be used to evaluate odor treatment technologies along with Olfactometry.

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Chapter 7

Conclusions and Future Research

7.1. Conclusions

In order to understand odor nuisance at WWTPs better, both sensorial and chemical analysis should be employed, because there is a gap between the method reporting limit (MRL) and odor threshold concentration (OTC) of odorants. Odorants with concentration within the gap will cause malodors, while there is no chemical concentration reported. Chemical analysis alone cannot determine the major odorants, as the result is not consistent with D/T and OPM. Sensorial method, such as odor profile method (OPM) and D/T method, should be used to bridge the gap between chemical analysis and human nose. OPM can determine the major odors presented, and then narrow the potential odorants to a manageable range. D/T and OPM should be used to investigate different aspects of an odor nuisance. D/T determines the total odor and if there is a problem presented while OPM can define the odors and odorants causing the issue, which provides useful information for treatment design.

An evaluation of stability of odorants in Tedlar and Teflon sampling bags was conducted. Hydrogen sulfide, IPMP and MIB, were stable in both Teflon and Tedlar bags. Quick losses of indole and skatole were found in Tedlar bag, with less than 5% left after 15 minutes, probably due to adsorption on the bag wall. Therefore, Tedlar is not a suitable bag material for samples containing indole and skatole. More than 75% of indole and skatole remained after 6 hours Teflon bags. Teflon bags are required for the analysis of skatole and indole, which needs to occur within 6 hours of sample collection. Thus, Teflon bags are better sampling bags for the same-day OPM and Olfactometry odor analysis and GC/MS chemical analysis.

The fecal and musty types of odors have not been quantitatively reported as an odor nuisance from WWTPs to the best of our knowledge. Skatole was found to be the primary chemical leading to fecal odor, due to its odor concentration to odor threshold concentration ratio that

ranged from 2.8 to 22.5. MIB and IPMP were identified as principal contributors to the musty odors. The OC/OTC data for MIB (4-20) and IPMP (17-98) confirm that musty odor group could lead to off-site nuisance at WWTPs. Qualitatively, chemical scrubbers and biofilters performed best in removing fecal odors among current control technologies used for air odor nuisance control at two WWTPs. Anoxic biofiltration and ozonation may be appropriate treatments for fecal odors and need further study.

The C/OTC ratio is a simple method to prioritize the odorants and employ both chemical and sensorial results. The OTC of IPMP (0.02 ng/L in air), MM (0.2 ng/L in air), MIB (0.1 ng/L in air), and skatole (0.3 ng/L in air) are quite low. The OTCs measures by the Weber-Fechner curves were within the range in the literature. The results were comparable with the odor threshold concentration measured by the ASTM 679-04.

Fecal and sulfur odors were initially prominent (with no musty odors reported). As dilution occurred, the intensities of both the fecal and the sulfur odors decreased. At the greater dilutions, musty odors appeared and the fecal and sulfur odors became undetectable (i.e. the “peeling the onion effect”). This occurs because of the masking of the musty odors by fecal and the sulfur odors. Rotten vegetable and fecal odors apparently mask odor panels identification by the OPM of the true intensity of musty odors. When rotten vegetable and fecal odors are removed efficiently, musty odors may become major odor issues off-site from WWTP locations as musty odorant have very low OTCs and may have OAV ratios sufficient to be an off-site odor nuisance. Thus, if an odor panel identifies musty odors, a chemical analysis is needed to determine removal efficiency.

7.2.Future Research

- Future Research is needed to establish a correlation between the OPM and D/T results to better understand these two sensorial methods, and employ them in the investigation of odor nuisance from WWTPs in the best manner.
- The OTCs of more odorants should be measured to establish a data base because C/OTC will be a commonly used method to prioritize the odorants. A standard reproducible accepted procedure by the industry is needed to be able to reproduce data.
- Future studies should develop more sensitive analytical methods to narrow the gap between MRLs and OTCs, and identify more odorants.
- Identification of other odorants causing fecal odors is needed because skatole and indole may not be the only contributors.
- Furthermore, the interaction between odors in a mixture should be investigated to provide a better understanding of the “Peeling the Onion” effect.