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Los Angeles

Application of Profile Methods to Evaluate and Mitigate
Air and Water Odor Problems

A dissertation submitted in partial satisfaction of the requirements
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Civil Engineering

by

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ABSTRACT OF THE DISSERTATION

Application of Profile Methods to Evaluate and Mitigate Air and Water Odor Problems

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Doctor of Philosophy in Civil Engineering

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Odor nuisance in both water and air can lead to public complaints and put pressure on municipal facilities. Odor profile method (OPM) and flavor profile analysis (FPA) present an option to evaluate and mitigate air and water problems, respectively. The OPM and the FPA enable consistent reporting of odor characteristics and intensities through the use of reference materials and standardized vocabulary for their definitions. Odor characteristics are indicative of responsible odorants while odor intensities are directly linked to odor sensorial impact on the receiving public. Moreover, odor intensity caused by a single odorant is found to be linear with the logarithmic value of its concentration, which is known as Weber-Fechner law. It can be used to determine an odorous compound's odor threshold concentration (OTC) and to understand odor persistency upon dilution as well as odor masking effects.

Two panels from California Air Resource Board (CARB) were trained to evaluate airborne odor using the OPM in order to examine whether OPM can be easily adopted by CARB and to determine the limitations of the method. It was found that with simple training for a week, both panels were able to accurately describe the characteristics and intensities of odor emissions from various types of facilities. Meanwhile, challenges for OPM application were identified including high variance of individual odor intensity values relative to panel average, loss of sensitivity using sampling bags and difficulty to characterize all odors within a mixture. As a result, analysis by a panel with multiple individuals, onsite OPM analysis and odor separation methods are warranted.

Dynamic olfactometry as a dilution-to-threshold method that was modified by the OPM to evaluate an air sample's odor characteristics and intensities with atmospheric dilution. The combination of OPM-modified dynamic olfactometry, sensory gas chromatography (SGC) and chemical analyses (gas chromatography/mass spectrometry (GC/MS) and specific chemical analysis (sulfur analyses) in this case) was used to evaluate an air odor treatment system for odor emissions from a sludge treatment, storage and truck loading process at a wastewater treatment facility. SGC could separate odorants within a mixture and then present them individually to a human analyst for OPM analysis. GC/MS with the same type of GC column as SGC could then assist the identification of odorants perceived by SGC based on mass spectra acquired at the same relative retention times. OPM-modified dynamic olfactometry revealed overall inefficiency of the treatment system based on high odor intensities of the characterized odors. The odor characteristics with dominant odor intensities were decaying vegetation, canned corn, manure and fecal. SGC and chemical analyses found methyl mercaptan (MeSH), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), p-cresol (p-C) and presently unknown to-be-identified fecal

odorants as primary odorants based on these odor characteristics. Measurement of their concentrations throughout the treatment system revealed a malfunctional GAC filter system as the primary reason for the odor treatment system's underperformance. The study proved the effectiveness of this unique combination of sensory and chemical analyses to evaluate air odor treatment systems. Future application of this methodology was strongly recommended.

FPA was used with SGC and GC/MS analysis to identify taste and odor (T&O) compounds in the drinking water sources for the Summit Water Treatment Plant (SWTP). An odor occurrence pattern was observed. Taste analysis was not conducted due to lack of final chlorination that was completed outside of the water treatment facility. FPA captured a moldy odor characteristic different from earthy/musty odor expected from the only two T&O compounds monitored, geosmin (GEO) and 2-methylisoborneol (2-MIB), by the facility. SGC and GC/MS full scan analysis identified 2-isopropyl-3-methoxypyrazine (IPMP) as also present at times that caused the moldy odor. IPMP originated from a different water source seasonally used. As a result, possible actions by SWTP for T&O mitigation targeting GEO and 2-MIB alone should include IPMP. Therefore, application of FPA and monitoring for IPMP was shown to be necessary to accurately evaluate T&O occurrences. This was critically important when the secondary water source was used in the fall and winter months.

Finally, the feasibility of SWTP water T&O mitigation using granular activated carbon (GAC) filters was evaluated for complete control of T&O occurrences. A column test targeting elevated levels of GEO, 2-MIB and IPMP at the same time was conducted with GAC preloaded with natural organic matter (NOM) and virgin GAC as comparison. It was found that both GAC filters could effectively remove GEO, 2-MIB and IPMP. This was surprising as NOM preloading with NOM did not severely decrease GAC capacities by direct competition and pore blockage.

While biodegradation of GEO and 2-MIB on GAC surface possibly counterbalanced the reduction of their adsorption, the reason for IPMP removal in spite of NOM preloading should be further investigated.

In conclusion, OPM and FPA can be easily adopted with simple training in a limited timeframe. Their application is essential for identification of all odorants causing nuisance with the help of SGC and the choice of appropriate chemical methods. It is clear that odor evaluation and mitigation should take all identified odorants into consideration to maximize odorant removal by appropriate air and water treatment methods.

The dissertation of Zhihang Yin is approved.

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List of Acronyms

D/T	Dilution-to-Threshold
T&O	Taste and Odor
OPM	Odor Profile Method
FPA	Flavor Profile Analysis
GEO	Geosmin
2-MIB	2-Methylisoborneol
CARB	California Air Resource Board
UPSIT	University of Pennsylvania Smell Identification Test
OC	Odor Concentration
OU	Odor Unit
MTBE	Methyl tert-Butyl Ether
DMS	Dimethyl Sulfide
DMDS	Dimethyl Disulfide
MMA	Methyl Methacrylate
IPMP	2-Isopropyl-3-Methoxypyrazine
MeSH	Methyl Mercaptan
FEP	Fluorinated Ethylene Propylene
SGC	Sensory Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
GAC	Granular Activated Carbon
p-C	p-Cresol
OTC	Odor Threshold Concentration

OCSan	Orange County Sanitation District
SKA	Skatole
IND	Indole
p-BFB	p-Bromofluorobenzene
4-EP	4-Ethylphenol
IBMP	2-Isobutyl-3-Methoxypyrazine
H ₂ S	Hydrogen Sulfide
TCA	2,4,6-Trichloroanisole
2,5-DMT	2,5-Dimethylthiophene
DMTS	Dimethyl Trisulfide
n-BA	n-Butyric Acid
TMP	2,3,5-Trimethylpyrazine
α-P	α-Pinene
MeOH	Methanol
EtOH	Ethyl Alcohol
1-BuOH	1-Butanol
NH ₃ •H ₂ O	Ammonium Hydroxide
H ₂ SO ₄	Sulfuric Acid
NaClO	Sodium Hypochlorite
NH ₃	Ammonia
COS	Carbonyl Sulfide
SIM	Selected Ion Monitoring
EtSH	Ethyl Mercaptan

CS ₂	Carbon Disulfide
iPSH	Isopropyl Mercaptan
tBSH	tert-Butyl Mercaptan
nPSH	n-Propyl Mercaptan
EMS	Ethyl Methyl Sulfide
T	Thiophene
iBSH	Isobutyl Mercaptan
DES	Diethyl Sulfide
nBSH	n-Butyl Mercaptan
3-MT	3-Methylthiophene
THT	Tetrahydrothiophene
2-ET	2-Ethylthiophene
DEDS	Diethyl Disulfide
sBSH	s-Butyl Mercaptan
RH	Relative Humidity
AC	Activated Carbon
MSIA	Methanesulfinic Acid
MSA	Methanesulfonic Acid
HClO	Hypochlorous Acid
OAV	Odor Activity Value
MDGC	Multi-dimensional Gas Chromatography
SWTP	Summit Water Treatment Plant
SWP	State Water Project

SPME	Solid-phase Microextraction
HPLC	High-performance Liquid Chromatography
NaHSO ₃	Sodium Bisulfite
NaCl	Sodium Chloride
iPOH	Isopropyl Alcohol
MCE	Mixed Cellulose Esters
DBP	Disinfection By-product
EI	Electron Ionization
SIS	Selected Ion Scan
RT	Retention Time
m/z	Mass to Charge Ratio
LOD	Limit of Detection
LOQ	Limit of Quantitation
S/N	Sound to Noise Ratio
LR	Linear Range
F820	FILTRASORB [®] 820
EBCT	Empty Bed Contact Time
DVB/CAR/PDMS	Divinylbenzene/Carboxen/Polydimethylsiloxane

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Yin, Z., Bader, T., Lee, L. F., McDaniels, G., & Suffet, M. (2024). *Training a Regulatory Team to Adopt Odor Profile Method for Airborne Malodor Evaluation*. Manuscript in preparation.

Yin, Z., Bader, T., Quinn, J., Vitko, T., & Suffet, M. (2024). *Sources of Error in Odor Intensity Values Determination by Odor Profile Method*. Manuscript in preparation.

CONFERENCE PRESENTATION

Bian, Y., Yin, Z. (presenter), & Suffet, M. (2022). *The use of an odor attribution study to evaluate the odors produced from landfill nuisance odor sources* [Slide show]. 2022 Air Quality Measurement Methods and Technology Conference, San Diego, CA, USA

Chapter 1

Introduction and Objectives

1.1. Introduction

The presence of odors in air and water can cause public complaints and pressure odor causing facilities to remove the odors (Zahraei et al., 2021; Wang et al., 2023). Current regulations for environmental odors often involve measurement of the number of dilution(s) by odorless background needed for an odorous sample to be barely perceptible and/or concentrations of specific odorants to determine compliance (Bokowa et al., 2021; US EPA, 2024; SAMRC and SAC, 2022; Kim and Park, 2021; European Committee for Standardization (CEN), no date). The number of dilution(s) is called dilution-to-threshold (D/T) value in air pollution (ASTM International, 2019) and threshold odor number (TON) in the field of water analysis (US EPA, 2024; CEN, no date). These methods do not include reporting of odor characteristics and their intensities. Odor intensities reflect the sensorial impact on the receiving public. Odor characteristics are indicators of responsible compounds (Burlingame et al., 2004). Meanwhile, there may be too many possible odorants present to be covered by the list of specific odorous compounds used by regulations. For example, Zahraei et al., (2021) compiled more than 60 taste and odor (T&O) compounds in water environment while Fisher et al., (2019) compiled 38 or more odorants from anaerobically digested and dewatered biosolids. Therefore, a sensory method to acquire more information from an odorous sample such as, odor characteristics and intensities are needed to provide guidance for chemical analysis.

The Odor Profile Method (OPM) is based upon the odor part of the flavor profile analysis (FPA) which is the standard method to analyze water taste and odor problems (APHA et al., 2023). The FPA enables consistent determination of odor characteristics and intensities through the use of reference materials. The reference materials develop a standardized vocabulary for definition of the odor character for panel training and guide chemical sample analysis. Thus the

common odor characteristics are the standardized vocabulary for the identification of the causative odorant chemicals. This information is usually compiled in the form of an odor wheel as exemplified by Figure 1.1. Therefore, an odor wheel can be used to select reference materials for panel training and to decide on possible causative odorants for chemical analysis based on perceived characteristics during sample analysis (Zhou, 2017). The odor intensity values are defined by sugar solutions at different concentrations. The odor intensity value caused by a single odorant is found to be linear with the logarithmic value of its concentration, which is known as the Weber-Fechner law (Fechner, 1860). Such relationship can be visualized by a Weber-Fechner curve (Figure 1.2).

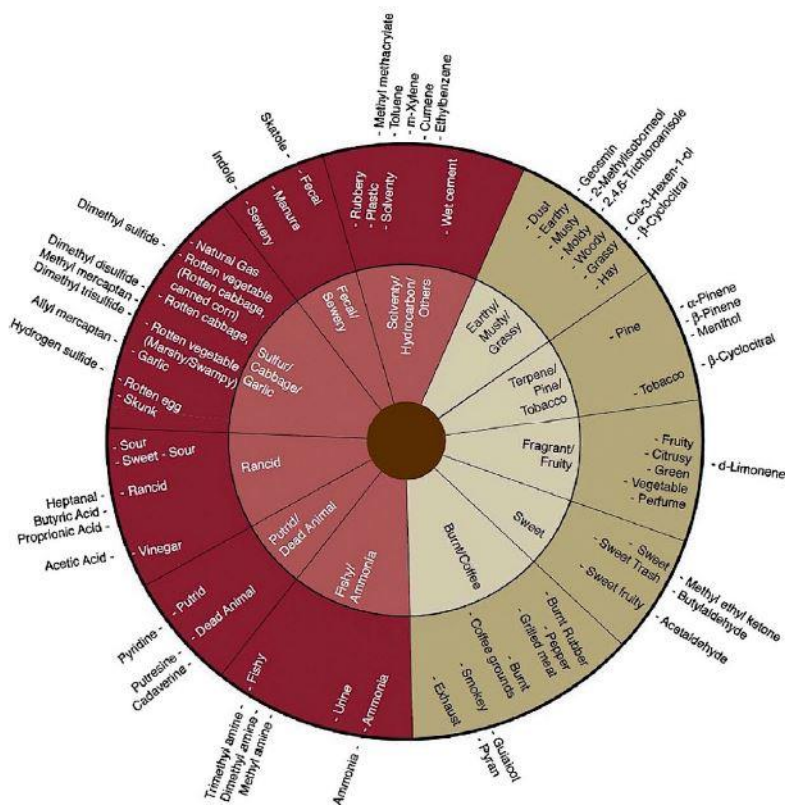


Figure 1.1. Landfill odor wheel (Bian et al., 2021).

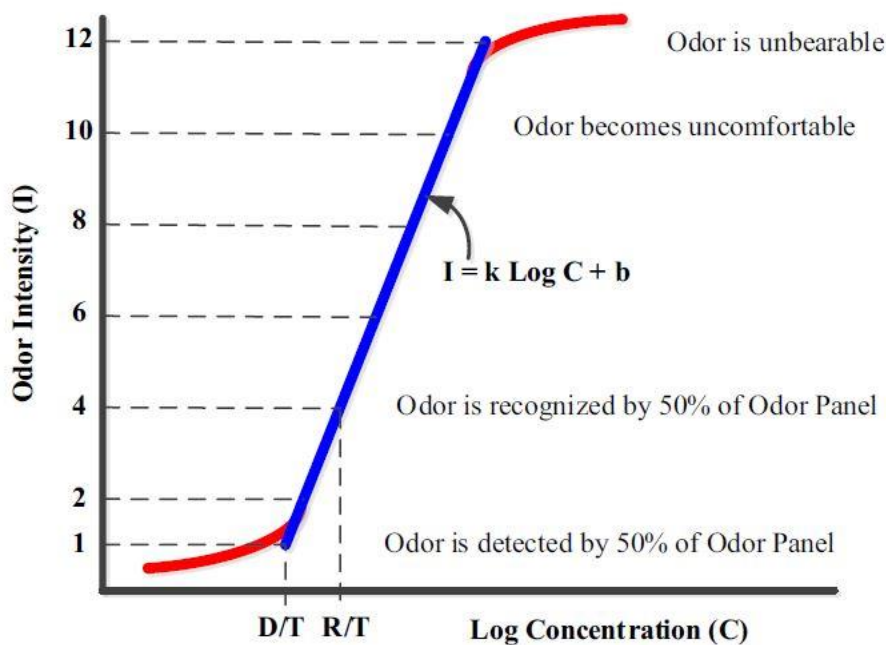


Figure 1.2. A Weber-Fechner curve (blue line) (Zhou et al., 2023).

Therefore, OPM could be a solution to the limitations of current regulatory approaches to evaluate odor impacts. The reported intensities better reflect odor sensorial nuisance while its reported characteristics can be the basis for identification of responsible odorants. However, while FPA is an overall standard method for water analysis (APHA et al., 2023), OPM is still not accepted as a standard method for air odor evaluation. This is in spite of its successful application in several case studies on airborne odors (Suffet et al., 2023; Curren et al., 2016; Vitko et al., 2022; Zhou et al., 2023; Lambert et al., 2000; Zhou et al., 2016; Burlingame, 1999; Suffet et al., 2009; Bian et al., 2021; Gao et al., 2022). Therefore, further application of OPM to case studies in air for odor evaluation and mitigation are needed to develop the standard method for air analysis of odors.

The occurrence of geosmin (GEO) and 2-methylisoborneol (2-MIB), the most prevalent T&O compounds in water (Devi et al., 2021), has been used exclusively to understand overall

T&O occurrences (Chislock et al., 2021; Goodling, 2021; Lee et al., 2020; Hooper, 2023; Franklin et al., 2023; Lee et al., 2023; Jeong Hwan et al., 2023; Howard, 2020; Hooper et al., 2023). Therefore, further application of FPA to water T&O problems is still needed.

1.2. Objectives

The overall objective of this dissertation was to apply the OPM and the FPA methods to evaluation of odor nuisance in both air and water assisted by instrumental methods, and to then use the complete understanding of odor nuisance for its mitigation.

In order to achieve the overall objective, specific objectives of research presented by this dissertation were to:

- 1) Evaluate the feasibility to adopt OPM with simple training and a limited timeframe,
- 2) Examine the ability of OPM assisted by instrumental methods to determine air odor nuisance and the odorous chemicals that caused the odor nuisance. This was completed by the evaluation of the performance of an existing odor reduction treatment system,
- 3) Evaluate the role of FPA in drinking water T&O occurrence attribution, evaluation and mitigation with the help of instrumental methods and
- 4) Compare the OPM and the FPA with mainstream odor measurement methods such as D/T and analysis of GEO and 2-MIB only.

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Chapter 2

Training a Regulatory Team to Adopt the Odor Profile Method for Evaluation of Atmospheric Malodors

2.1. Abstract

Members of California Air Resource Board (CARB) participated in the odor profile method (OPM) training program. OPM was initially developed for the flavor profile analysis (FPA) standard method that is widely used in drinking water taste and odor evaluations. It was found that pre-screening of potential trainees for anosmia cases with University of Pennsylvania Smell Identification Test (UPSIT) was effective and necessary. After a half-day training sessions every day for a week, a panel could be formed to provide accurate descriptions of air odor emissions from various facilities both in terms of odor characteristics and average intensity values at the fenceline. Meanwhile, challenges for OPM application were identified including high variance in individual intensity values relative to panel average, loss of sensitivity during laboratory analysis with sampling bags and perception of multiple odors within a mixture. Future studies are necessary to address the challenges. The successful application of OPM by a regulatory agency within a limited time frame using simple training in this study serves as important proof of feasibility that is essential for OPM to become a standard air analysis method like FPA for drinking water.

2.2. Introduction

The relationship between odor nuisances and health risks can be complicated because individual odorous compounds often occur below their hazard thresholds, yet the cumulative effects may bring risk to nearby receptors (Piccardo et al., 2022). As a result, some current air regulation policies are primarily centered around health risks and may not address odor nuisances unless regulated compounds happen to be odorous (Bokowa et al., 2021). The present regulations that consider sensorial effects rely heavily on dilution-to-threshold (D/T) values and/or concentrations of selected odorous compounds for malodor impact evaluation by direct

comparison with legal limits and/or by subsequent calculation of criteria like emission rates and separation distances (Brancher et al., 2017; Bokowa et al., 2021). Also known as odor concentration (OC), a D/T value is defined as the number of dilutions needed for a given sample to reach either the detection threshold or recognition threshold and it is described in terms of Odor Units (OUs) (ASTM, 2019).

Despite its common application, a D/T value of a certain odorous sample fails to convey important information for odor control, specifically the characteristics of odors indicating potential odor sources and responsible compound groups, as well as the intensities and acceptability of odors (Lambert et al., 2000). To further validate the point, Zhou et al., (2023) demonstrated different odor intensity reduction rates upon atmospheric dilution for different compounds upon dilution (Figure 2.1). Thus, a lower D/T value does not necessarily lead to a weaker odor if the primary odorant is different. Similarly, Vitko et al., (2022) observed disproportional reductions between D/T values and odor intensities after treatments. Hence, while a D/T value of a malodor source sample can be helpful for dispersion modelling that leads to important design control parameters, such as separation distance for a facility, its application to a receptor site as the main odor impact criteria, sometimes even as a surrogate for odor intensity itself as shown by Brancher et al., (2017) and Bokowa et al., (2021), can be misleading. As for concentrations of pre-selected odorous compounds, it is difficult to take all potential odorants into consideration. For example, Fisher et al., (2019) compiled more than 38 odorants belonging to at least 11 classes emitted from biosolids after anaerobic stabilization and/or dewatering. Therefore, two objectives need to be met for regulation criteria improvement. First, the D/T value alone should not be adopted to fully show malodor impact to a receptor from an odor source. Second, a technique to narrow down the list of possible primary odorants preferably

to a specific compound group should be adopted and validated. In this way, appropriate instrumental analysis can be applied to identify primary chemical causes of odor nuisances and proper compound concentration limits can be set up for the primary odorants to eliminate sensorial nuisance.

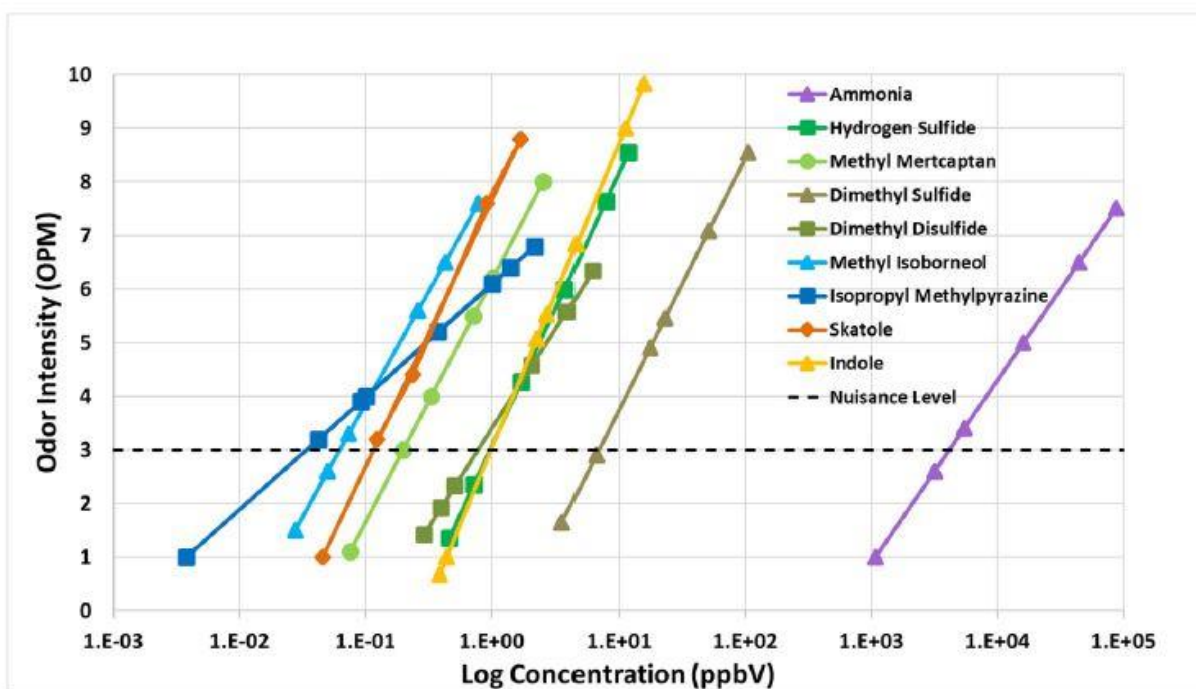


Figure 2.1. Different relationships between odor intensity and logarithmic value of compound concentration in air for different primary odorants identified in two wastewater facilities (Zhou et al., 2023).

To achieve the two objectives, determination of odor characters and intensities in air samples would be essential. However, their descriptions can be highly subjective unless references are applied for the process (Hawko et al., 2021). Flavor profile analysis (FPA) as Standard Method 2170 for water and wastewater examination (APHA, 2023) has been applied to describe the characteristics and intensities of tastes and odors in water samples as reviewed by Suffet et al., (2019). To ensure objective and consistent reporting, references containing standardized materials are used to define taste and odor characters while the intensity of each taste and odor

Thus far, OPM has not been selected as a standard method for air analysis, although many case studies with OPM applied have shown proof of concept (Suffet et al., 2023; Curren et al., 2016; Vitko et al., 2022; Zhou et al., 2023; Lambert et al., 2000; Zhou et al., 2016; Burlingame, 1999; Suffet et al., 2009; Bian et al., 2021; Gao et al., 2022). A possible way to accelerate the process is to introduce OPM to regulatory agencies with access to environmental samples. Once deemed effective in odor impact evaluation and attribution, OPM can then be applied by the agency much more frequently and broadly compared to current OPM adoption efforts largely limited in scope. Thanks to more experience in onsite environmental monitoring and environmental policy by air regulatory agencies, it can additionally help elaborate OPM protocol for air malodor, and eventually develop it into a standard method. However, a regulatory agency must be trained in a short period of time due to its already-existing obligations. Therefore, the objective of this study was to examine the ability of California Air Resource Board (CARB) as an air quality regulation agency to quickly master OPM and accurately apply it at various facilities.

2.3. Experimental Section

2.3.1. Chemicals and Materials

Reference materials for standardization of odor characters and intensities – Indole (99+%), methyl tert-butyl ether (MTBE) (99%), dimethyl sulfide (DMS) (99+%), dimethyl disulfide (DMDS) (99%), n-butyric acid (99+%), (+)-limonene (96%) and α -pinene (97%) stabilized with α -tocopherol were purchased from ThermoFisher Scientific (Waltham, MA, USA). 100 μ g/mL ($\pm$)-geosmin and 2-MIB solutions in methanol, cumene ($\geq 99.5\%$), n-octane ($\geq 99\%$) and cis-3-hexen-1-ol (98%) were purchased from Sigma-Aldrich Inc. (St. Louis, MO, USA). Guaiacol ($>98.0\%$), methyl methacrylate (MMA) ($>99.8\%$) stabilized with 6-tert-butyl-2,4-xyleneol and 2-

isopropyl-3-methoxypyrazine (IPMP) (>98.0%) were purchased from TCI America (Portland, OR, USA). 1-Butanol (ACS Reagent) was purchased from Baker Chemical Co. (Phillipsburg, NJ, USA). Sodium sulfide nonahydrate (98+%), molecular biology grade phenol (>95%) and pesticide grade ethyl acetate (>95%) were purchased from Fisher Scientific (Hanover Park, IL, USA). 1000 µg/mL methyl mercaptan (MeSH) solution in methanol was purchased from Chem Service, Inc. (West Chester, PA, USA). Cane sugar was purchased from Imperial-Savannah LP (Sugar Land, TX, USA).

Sampling and analysis supplies – 1 L fluorinated ethylene propylene (FEP) sampling bags were purchased from Jensen Inert Products (Coral Springs, FL, USA). Odorless water (Milli-Q water) for odor sample preparation was produced by a Milli-Q water purification system (Millipore-Sigma, USA) while flavorless distilled water for sugar solutions was purchased from Kroger Co. (Cincinnati, OH, USA). Disposable polycoated paper cups were purchased from Dart Container Corporation (Mason, MI, USA). All glassware was washed by Liqui-Nox[®] critical-cleaning liquid detergent (Jersey City, NJ, USA), hot tap water and Milli-Q water before use.

2.3.2. Panel Description

Two groups of volunteers participated in 2 separate OPM training events in order to satisfy potential future need for OPM analysis in both Northern California and Southern California. The 1st group was based in Sacramento, CA (panel S) and was made up of 13 volunteers at the beginning while the 2nd group was based in Riverside, CA (panel R) and was made up of 9 volunteers at the beginning. Before the initiation of training, all volunteers except for one in panel R were screened by University of Pennsylvania Smell Identification Test[®] (UPSIT[®]) purchased from Sonsonics International (Haddon Heights, NJ, USA) to make sure that all trainees did not suffer from severe microsmia or total anosmia.

2.3.3. Training Activities

All training activities were designed according to Standard Method 2170 (APHA, 2017). The latest version of the method (APHA, 2023) was still unavailable at the time. After sniffing 5~7 odor samples, the trainees were instructed to take a 30-minute break in an odorless room to avoid possible fatigue.

2.3.3.1. Odor Characteristic and Intensity Definition

The odor reference standards as summarized in Figure 2.2 were selected based upon the Standard Method 2170 (APHA, 2017) and additional odors identified in the past in air. After screening (Section 2.3.2), all qualified volunteers sniffed 20 odor references (Table 2.1) each containing a certain odorous compound and Milli-Q water for dilution purpose. The trainees recorded their best description of each reference before its odor characteristic in standardized vocabulary was revealed. Then, the participants were instructed to smell the 20 odor references again with the standardized vocabulary in mind until they were familiarized with all references. It was expected that both groups could characterize an odor consistently after the activity.

Table 2.1. Compositions of the odor references and their odor characteristics in standardized vocabulary used for both groups. (*Rotten egg odor was caused by hydrogen sulfide produced by equilibrium of sodium sulfide in water.)

#	Chemical Name	Odor Characteristic
1	Indole	Fecal
2	Cumene	Solvent
3	MTBE	Sweet Solvent
4	Geosmin	Earthy
5	2-MIB	Musty
6	cis-3-Hexen-1-ol	Grassy
7	DMS	Canned Corn
8	DMDS	Decaying Vegetation
9	Sodium Sulfide*	Rotten Egg
10	n-Butyric Acid	Rancid
11	1-Butanol	Alcohol
12	(+)-Limonene	Lemon
13	MMA	Plastic

14	Phenol	Medicinal
15	Ethyl Acetate	Sweet
16	Guaiacol	Smokey
17	Methyl Mercaptan	Natural Gas
18	α -Pinene	Pine
19	IPMP	Moldy
20	n-Octane	Hydrocarbon
*Rotten egg was caused by hydrogen sulfide produced by equilibrium in water.		

Intensity was standardized by a 7-point scale defined by cane sugar solutions as intensity references in distilled water at certain concentrations (Table 2.2). Compared to a potential alternative scale using n-butanol defined by ASTM Method E544-18 (ASTM, 2018), the 7-point sugar scale was found to be easier to administer in the field and less variable from one session to another (Curren et al., 2014). All trainees were told to take a sip of distilled water without sugar and then each sugar solution starting from the most dilute one. It was expected that trainees would be able to differentiate the change in intensity and give consistent rating for an odor after the activity. Interestingly, when the scale is applied, the odor intensity is usually proportional with the logarithmic value of odorant concentration, which is also known as Weber-Fechner law (Fechner, 1860). Such relationship was well-exemplified by Zhou et al., (2023) using Weber-Fechner curves (Figure 2.1).

Table 2.2. 7-point intensity scale standardized by cane sugar standards (APHA, 2017).

Intensity Value	Odor Strength	Sugar Solution Concentration (%)	Note
0	Odor Free	0	None
1	Threshold	Not Applicable	Detection Threshold
2	Very Weak	Not Applicable	Recognition Threshold
3	Action Level ¹	Not Applicable	The value of 3 is only a threshold for average intensity value, not for individual response. A higher average is expected to cause nuisance problems.
4	Weak	5	None

6	Weak-Moderate	Not Applicable	None
8	Moderate	10	Uncomfortable to Smell for Extended Periods ²
10	Moderate-Strong	Not Applicable	Very Uncomfortable to Smell for Extended Periods ²
12	Strong	12	Unbearable to Smell Even for Short Periods ²
¹ Vitko et al., (2022)			
² Zhou et al., (2023)			

During all subsequent training and analysis activities, all odor references and sugar solutions were available to the participants upon request. All samples for the subsequent training activities shown below were made of odorants specified in Table 2.1 for designated odors together with Milli-Q water or odorless air for dilution purpose.

2.3.3.2. Triangle Tests

Two types of triangle tests were conducted during the training process. During the sensitivity triangle test, the trainees were presented with 2 odorless samples together with an odorous sample. The trainees were instructed to pick out and characterize the only odorous sample out of the 3 to demonstrate their ability to detect an odor from odorless background. During the differentiation triangle test, the trainees were presented with 2 odorous samples with the same odor together with a sample with another odor. The trainees were instructed to pick out and characterize the sample with the different odor to show their ability to detect the difference in odor characteristics. The odors involved in each triangle test session are shown in Table 2.3. Session C was conducted to evaluate the effect of familiarization with test procedure during Session B on panel performance. Session D was conducted to examine the difference caused by change of media from water (Session A) to air.

Table 2.3. The odors applied in each triangle test session.

Test Session	Session A		Session B		Session C		Session D	
Test Name	Sensitivity Test #1	Sensitivity Test #2	Differentiation Test #1	Differentiation Test #2	Differentiation Test #1	Differentiation Test #2	Sensitivity Test (Air)* #1	Sensitivity Test (Air)* #2
Odor(s) Presented to Panel S	1 Canned Corn + 2 Odorless	1 Grassy + 2 Odorless	1 Rancid + 2 Solventy	1 Moldy + 2 Grassy	1 Fecal + 2 Alcohol	1 Medicinal + 2 Musty	1 Fecal + 2 Odorless	1 Canned Corn + 2 Odorless
Odor(s) Presented to Panel R	1 Canned Corn + 2 Odorless	1 Grassy + 2 Odorless	1 Rancid + 2 Solventy	1 Moldy + 2 Grassy	1 Fecal + 2 Alcohol	1 Medicinal + 2 Musty	Not Conducted	Not Conducted
*The samples were presented in 1L FEP sampling bags. An odorless sample contained 1L odorless air while an odorous sample was prepared by injection of the odorant specified in Table 1 into a 1L FEP bag full of odorless air and its subsequent evaporation. All other samples were prepared in Milli-Q water.								

2.3.3.2. Mixture Evaluation

As shown by previous studies, multiple odors are likely to co-exist in a single air sample (Zhou et al., 2023; Vitko et al., 2022; Curren et al., 2016; Lambert et al., 2000; Suffet et al., 2009; Bian et al., 2021; Gao et al., 2022). Therefore, both groups were presented with mixtures containing 2, 3, or 4 odors each so that the trainees could learn to identify individual odors within a mixture, and then characterize each. A detailed make-up of each mixture is shown in Table 2.4. Session #2 was scheduled after Session #1 to evaluate the effect of familiarization with test procedure during the 1st session on panel performance. Session #3 was conducted to examine the difference caused by change of media from water (Session #1 and Session #2) to air.

Table 2.4. Compositions of mixtures used for training.

Test Session	Session #1			Session #2			Session #3
Mixture	2 Odors	3 Odors	4 Odors	2 Odors	3 Odors	4 Odors	4 Odors (Air)*
Odor(s) Presented to Panel S	Fecal, Rancid	Canned Corn, Moldy, Rancid	Pine, Lemon, Earthy, Grassy	Not Conducted	Earthy, Moldy, Fecal	Rotten Egg, Canned Corn, Decaying Vegetation, Rancid	Canned Corn, Lemon Rancid, Fecal
Odor(s) Presented to Panel R	Fecal, Rancid	Canned Corn, Moldy, Rancid	Garlic, Earthy, Medicinal, Lemon	Musty, Lemon	Earthy, Moldy, Fecal	Canned Corn, Decaying Vegetation, Fecal, Rancid	Not Conducted
*The sample was prepared by injection of the odorants specified in Table 1 into a 1L FEP bag full of odorless air and their subsequent evaporation. All other samples were prepared in Milli-Q water.							

2.3.4. Performance Validation

After training specified by Section 2.3.3, the 2 panels went to various odor-emitting facilities and conducted OPM analysis at the fence line of each facility. Two types of OPM analysis, onsite analysis and laboratory analysis with sampling bags, were attempted in order to evaluate

potential differences in sensitivity. During onsite analysis, the panelists stood at the fenceline and took a sniff. As for laboratory analysis, the sample to be analyzed was transferred to a 1L FEP sampling bag using an in-house vacuum sampler and then transported to a laboratory where each participant opened the valve, squeezed the bag and took a sniff at the outlet within 6 hours after sampling. After sniffing, a panelist wrote down any odor characteristic(s) and intensity value(s) perceived before a discussion within the panel. When half or more of the panel detected a certain odor characteristic in a sample, the odor's presence was confirmed and its character, average intensity, and standard deviation were recorded. Details regarding the facilities analyzed are compiled in Table 2.5.

Table 2.5. Facilities analyzed for performance validation and any related observation.

Panel	Sample Name	Note
Panel S	Rendering Facility (Morning)	Trucks carrying dead animals were observed at the entrance.
	Rendering Facility (Afternoon)	No truck was present.
	Trash Transfer Station	None
	Organic Fertilizer Plant	None
	Landfill	None
	Sewage Treatment Plant	None
Panel R	Trash Transfer Station	Trucks carrying trash were observed at the entrance.
	Sewage Treatment Plant	A truck entered the entrance with unknown load.
	Cattle Farm #1	Cattle were denser and closer to the fenceline compared to cattle farm #2.
	Cattle Farm #2	None

Validation of panel performance was achieved by comparing confirmed odor characteristics and their panel average intensities to the nature of facility operations and results of previous studies on similar facilities. Finally, an attempt to cross-check panel S laboratory analysis results with laboratory analysis of the same samples by an experienced UCLA panel was made, but it failed due to low odor sensitivities of caused by sampling bags (Section 2.4.4.2).

2.4. Results

2.4.1. Screening by University of Pennsylvania Smell Identification Test® (UPSIT®)

According to criteria set by Doty, (1995), most volunteers from both groups were found to suffer from mild microsmia, while a single case of total anosmia was identified (Table 2.6). As a result, the individual dropped out before training initiation. Therefore, anosmia screening of potential trainees for OPM using UPSIT® was effective and necessary. Despite absence from screening, a participant demonstrated average performance during subsequent training and validation processes so was considered a part of panel R. Finally, 2 volunteers from panel R did not participate in any of the following activities, though they passed the screening process, due to limited availability. It showed the challenge brought by existing obligations during training at a regulatory agency.

Table 2.6. UPSIT® screening results.

Panel	Normosmia Case(s)	Mild Microsmia Case(s)	Moderate Microsmia Case(s)	Severe Microsmia Case(s)	Total Anosmia Case(s)	Total
Panel S	0	12	1	0	0	13
Panel R	2	5	0	0	1	8*

*One volunteer did not take UPSIT due to limited availability.

2.4.2. Odor References and Triangle Tests

Without standardized vocabulary for odor characteristics, both groups gave multiple descriptions for each of the 20 odor references in Table 2.1. As a result, few matched the vocabulary in Table 2.1 (Figure 2.3). Thus, definitions of odor characteristics expected in the field shared by a panel and their familiarization were found to be essential before training and/or OPM analysis. Otherwise, with vastly diverse descriptions, calculation of average intensity values and/or standard deviations would be impossible.

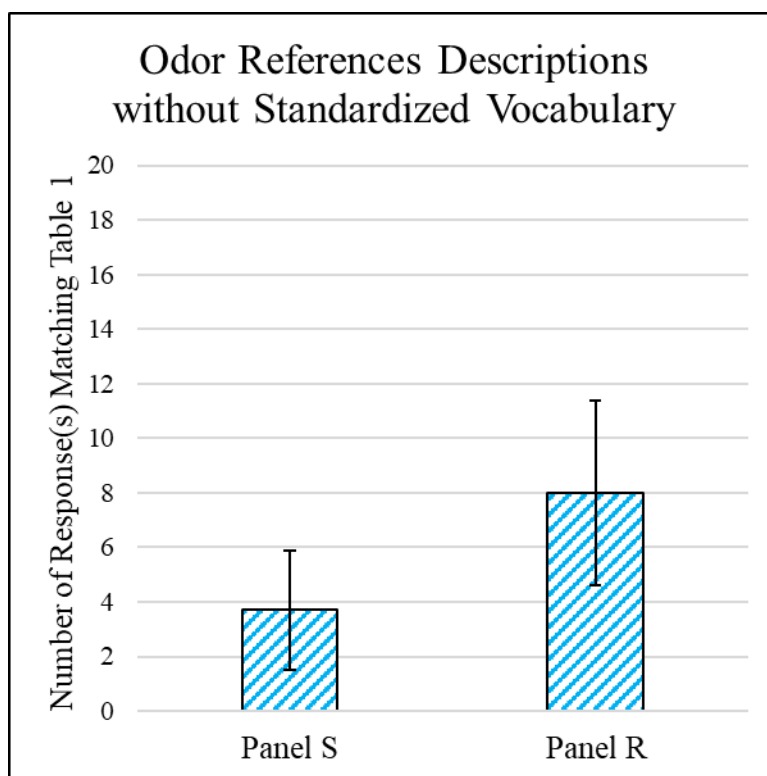


Figure 2.3. Average number of characters that matched the definition in Table 2.1. (13 trainees from panel S and 6 from panel R took part.)

Both groups demonstrated their ability to differentiate an odor from odorless background and from another odor with a different characteristic during triangle tests (Figure 2.4). It could serve to prove UPSIT[®] effectiveness. Besides, change of media from water to air (Session D) did not affect the ability of panel S to distinguish an odor from the odorless background. Finally, familiarization with triangle test procedure did not improve either panel's differentiation between 2 odor characteristics as shown by Figure 2.4B.

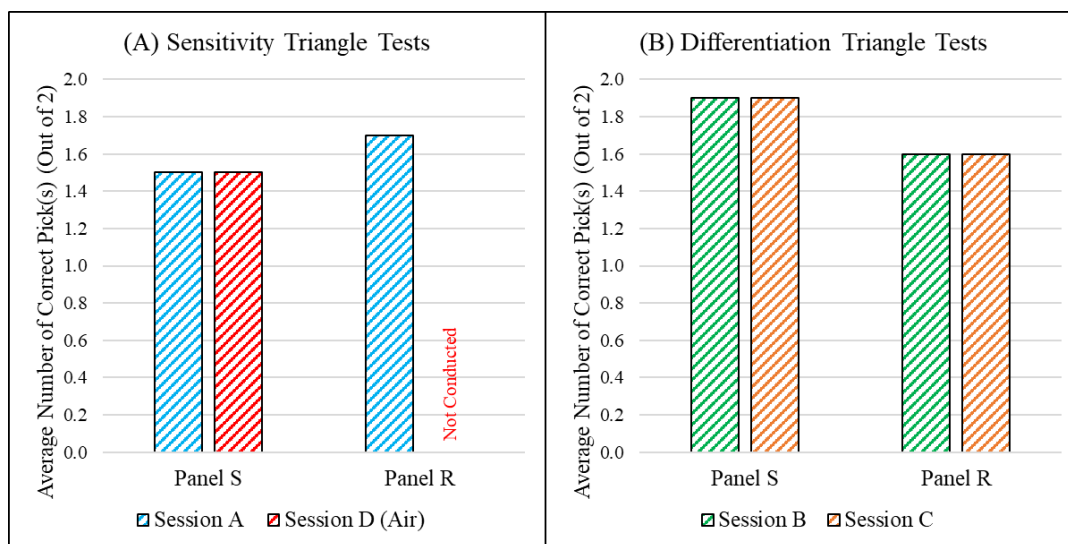


Figure 2.4. Sensitivity triangle tests (A) and differentiation triangle tests (B) results. 11 trainees from panel S took part in all sessions while 5 from panel R took part in Session B and Session C (6 in Session A). 2 volunteers from panel S permanently dropped out due to scheduling issues.

2.4.3. Odor Perception in Mixtures

Most trainees from both panels could not perceive all odor characteristics within a mixture containing 2, 3 or 4 different odors. As a result, on average the percentage of identified odor characteristics never exceeded 75% (Figure 2.5). Moreover, the change of media from water to air did not seem to affect the performance of panel S to analyze a mixture of 4 odors as shown in Sessions #1~#3, Figure 2.5C. Finally, familiarization with test procedure significantly improved Panel R's perception of a mixture of 4 odors (Sessions #1 and #2, Figure 2.5C), which was different from the analysis of a single odor (Figure 2.4) or a simpler mixture (Figure 2.5A and Figure 2.5B).

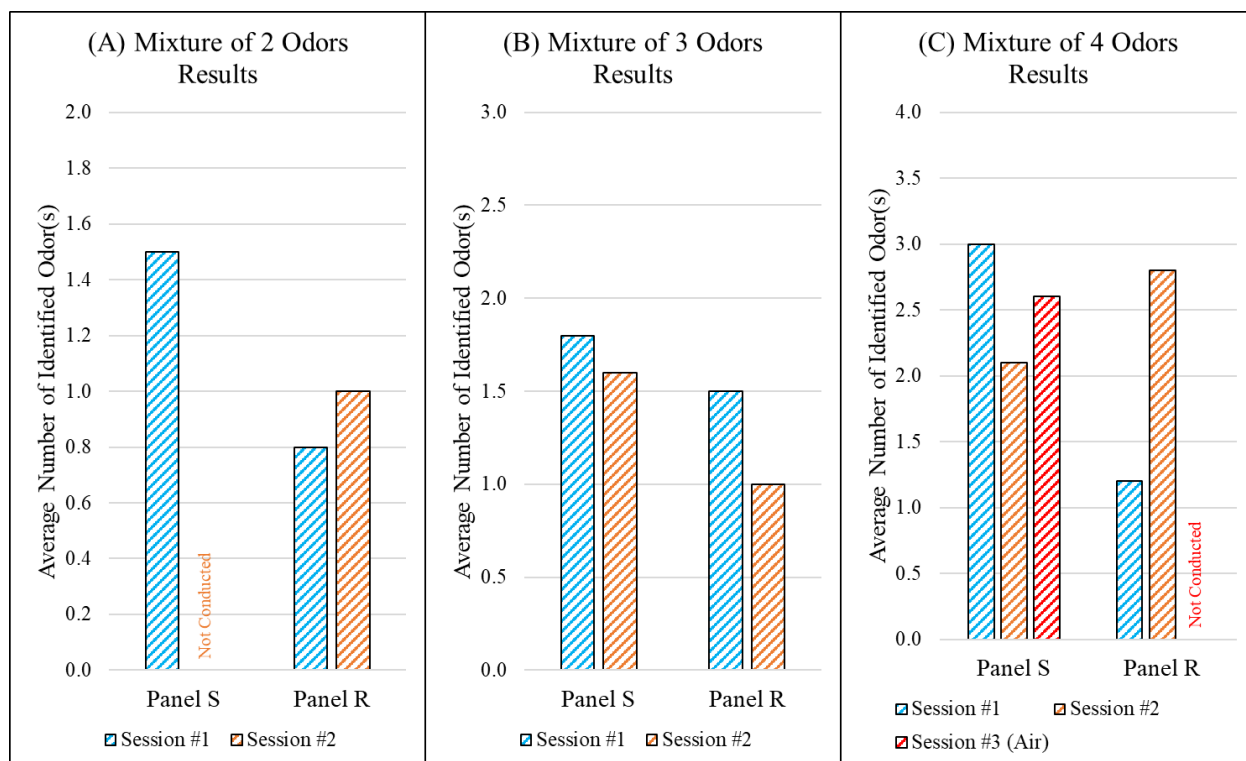


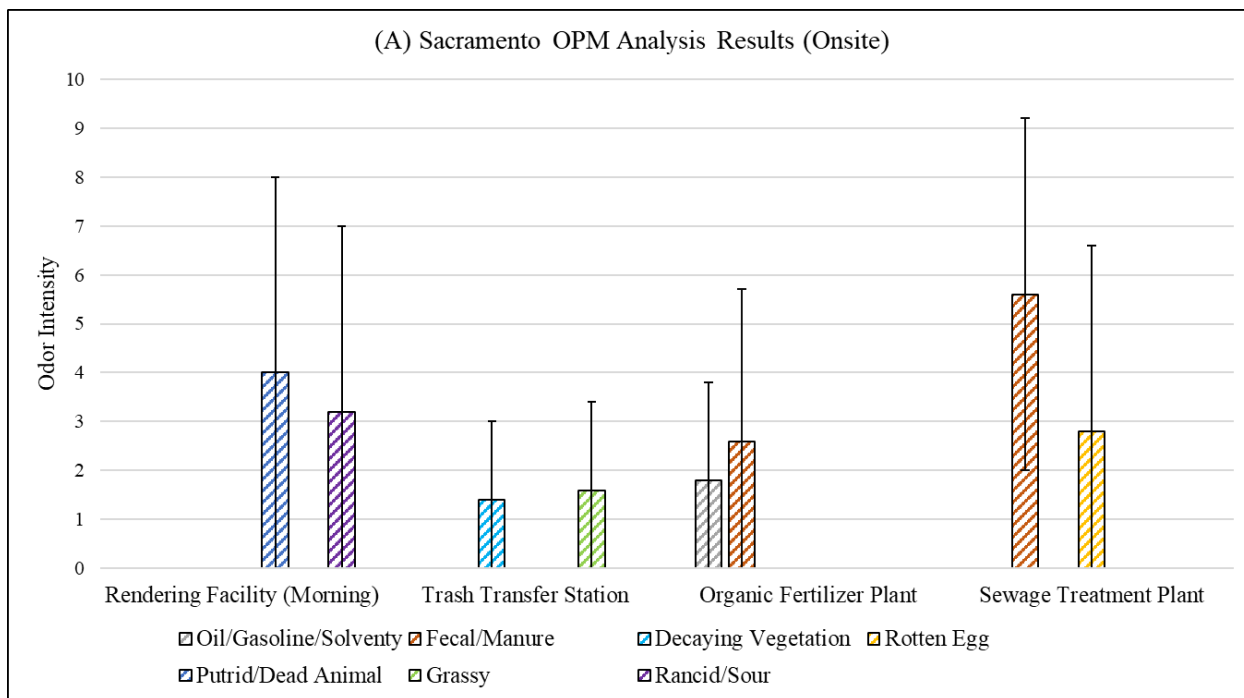
Figure 2.5. Average number of identified odor characteristic(s) from a mixture with 2 (A), 3 (B) or 4 (C) odors. 11 trainees from panel S participated in all sessions while 6 and 5 from panel R took part in Session #1 and Session #2, respectively.

2.4.4. Performance Validation by OPM Analysis of Facilities

2.4.4.1. Fenceline Analysis

Figure 2.6 shows the average odor intensity values and corresponding standard deviations of confirmed odor characteristics by both panels at the fenceline of various facilities. No odor was confirmed at a Sacramento Rendering Company in the afternoon and the landfill at the fenceline by panel S. Perception of decaying vegetation, rancid and exhaust odors in trash transfer stations is consistent with odors detected by Curren et al., (2016) at a trash transfer station. The grassy odor confirmed at the trash transfer station in Sacramento might have been caused by the nature of waste received pending further investigation. Similarly, fecal and/or rotten egg odors were reported by Bian, (2021), Zhou et al., (2023), Vitko et al., (2022), Zhou et al., (2016) and Gao et

al., (2022), supporting observations of both panels at sewage treatment plants. Detection of chlorine was not expected at the fence line of a sewage treatment plant, but it might have been related to the load of the truck described in Table 2.5 and/or variations of the chlorination process at the plant. Despite lack of previous OPM analysis, the odor characteristics confirmed at the organic fertilizer company (fecal/manure and oil/gasoline/solventy), rendering facility (putrid/dead animal and rancid/sour) and cattle farms (fecal/manure and grassy) were consistent with the nature of the facilities' operations. It should be noted that putrid/dead animal used as a descriptor during OPM analysis was not one of the odor characteristics the panels were familiarized with (Table 2.1). Panel S could quickly distinguish this particular odor from all odor characteristics in Table 2.1 thanks to the application of odor references and then agreed upon the vocabulary by discussion.



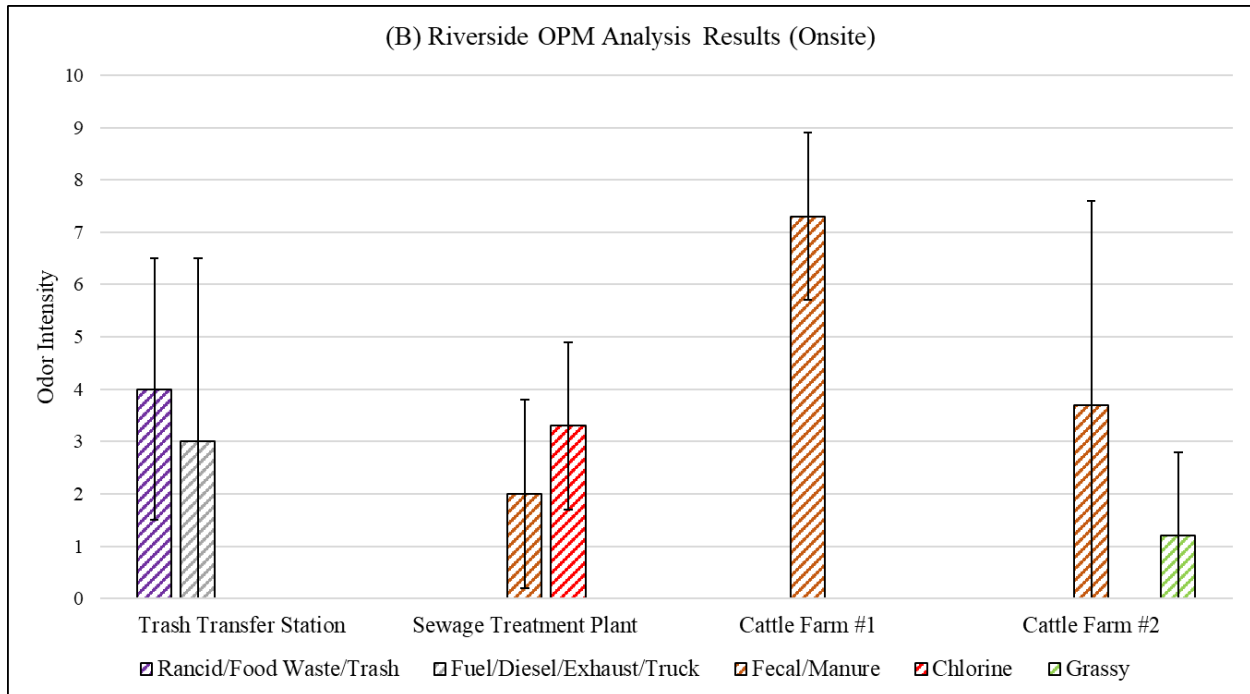


Figure 2.6. Onsite OPM analysis results for panel S (A) and panel R (B). 10 and 6 panelists took part from panel S and panel R, respectively. The standard deviations of the odor intensity values are indicated by the error bars.

As for odor intensities, it should be noted that high variance of individual odor intensity values relative to the panel average odor intensity was present in most cases. However, both panels were still able to report different panel average intensity values that correspond with changes in facility operations. Specifically, panel S reported putrid/dead animal and rancid/sour odor characteristics with average intensities of 4.0 and 3.2, respectively, at the fenceline of the rendering facility (Figure 2.6A) at the same time when trucks carrying dead animals were at the nearby entrance. Meanwhile, neither odor was confirmed by the majority of the panel in the afternoon when there was no truck with dead animals at the entrance and all operations were enclosed. In other words, the average intensities dropped to 0 for both odor characteristics. Similarly, panel R gave a higher intensity value for the fecal/manure odor characteristic from

cattle farm #1 with visibly denser cattle population situated closer to the fenceline compared to cattle farm #2.

In conclusion, after a week's simple training, both panels could accurately characterize odors produced by various facilities and react to variations in facility operations by reporting different odor intensities that changed accordingly.

2.4.4.2. Loss of Sensitivity during Laboratory Analysis

Compared to onsite OPM analysis (Session 2.4.4.1), few odors were confirmed from the same samples by sniffing from the outlet of FEP sampling bags. The only 2 facilities where odor characteristics were confirmed during laboratory analysis using sampling bags are shown in Figure 2.7 and their intensities are compared to those reported onsite. While odor characteristics perceived in both ways matched, the average intensities given by bag analysis were significantly lower compared to sniffing onsite. Therefore, there was a loss of sensitivity issue with the use of FEP sampling bags for OPM analysis.

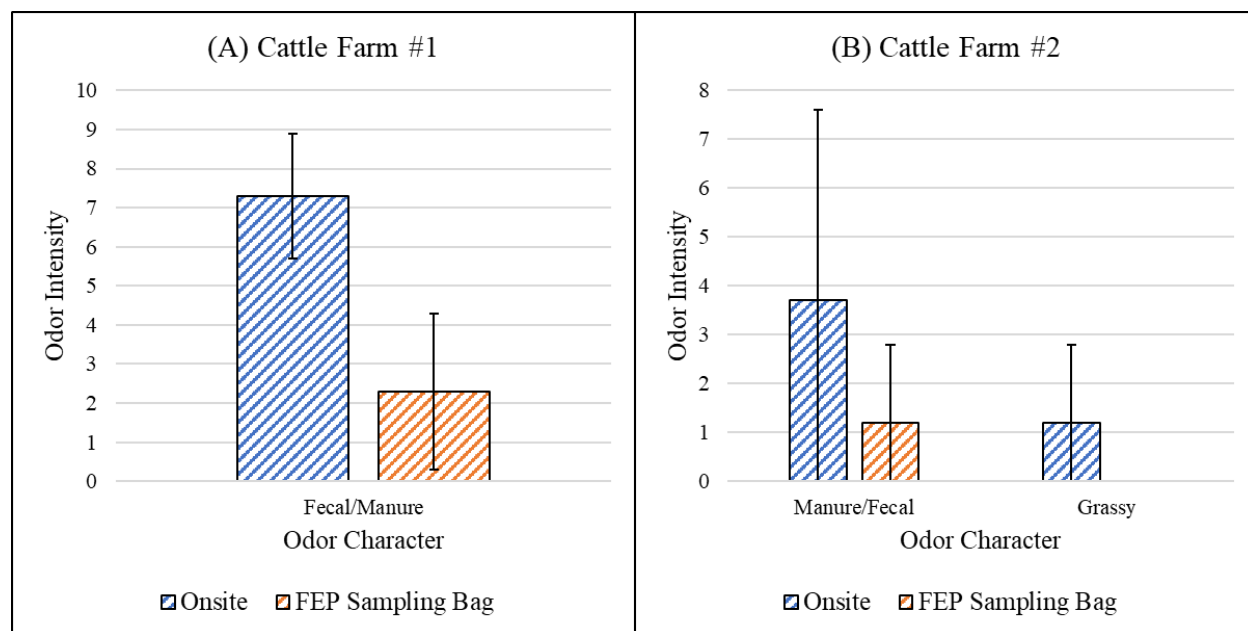


Figure 2.7. Intensities reported by bag analysis compared to those onsite at facility fenceline. No odor characteristic was confirmed by bag OPM analysis in Sacramento or

any other facility in Riverside listed in Table 2.5. 10 and 6 panelists took part in both onsite and bag analyses from panel S and panel R, respectively.

2.5. Discussion

2.5.1. Perception of Odor Mixtures

The results in Section 2.4.3 where both panels were limited in their abilities to characterize all odors in a mixture are consistent with the review by Laing and Jinks, (2001) where it was found that humans could rarely identify more than 3 odors in a mixture regardless of training, experience, method, and odorants. This restraint presents a challenge to airborne malodor analysis due to expectation of co-existing odors in a single sample based on previous studies (Zhou et al., 2023; Vitko et al., 2022; Curren et al., 2016; Lambert et al., 2000; Suffet et al., 2009; Bian et al., 2021; Gao et al., 2022). More importantly, due to difference in odor detection thresholds and odor intensity reduction rates upon dilution, an odorous compound may be masked by the smell of another odorant initially at the emission source, but its odor could still be detected after dilution by air at downwind locations. The phenomenon is known as “peeling of an onion effect” and was discussed by Zhou et al., (2023) (Figure 2.8) and Suffet et al., (2023). Combined with the limited number of odors a person can identify, it is possible for a facility to mistakenly choose the wrong target compound for malodor mitigation efforts even with OPM applied at the source. Similarly, odor attribution by odor characteristic comparison between receptor site and potential sources might also fail because of odor characteristic change by “peeling of an onion effect” during atmospheric dilution before source odor emission reaches the receiving communities.

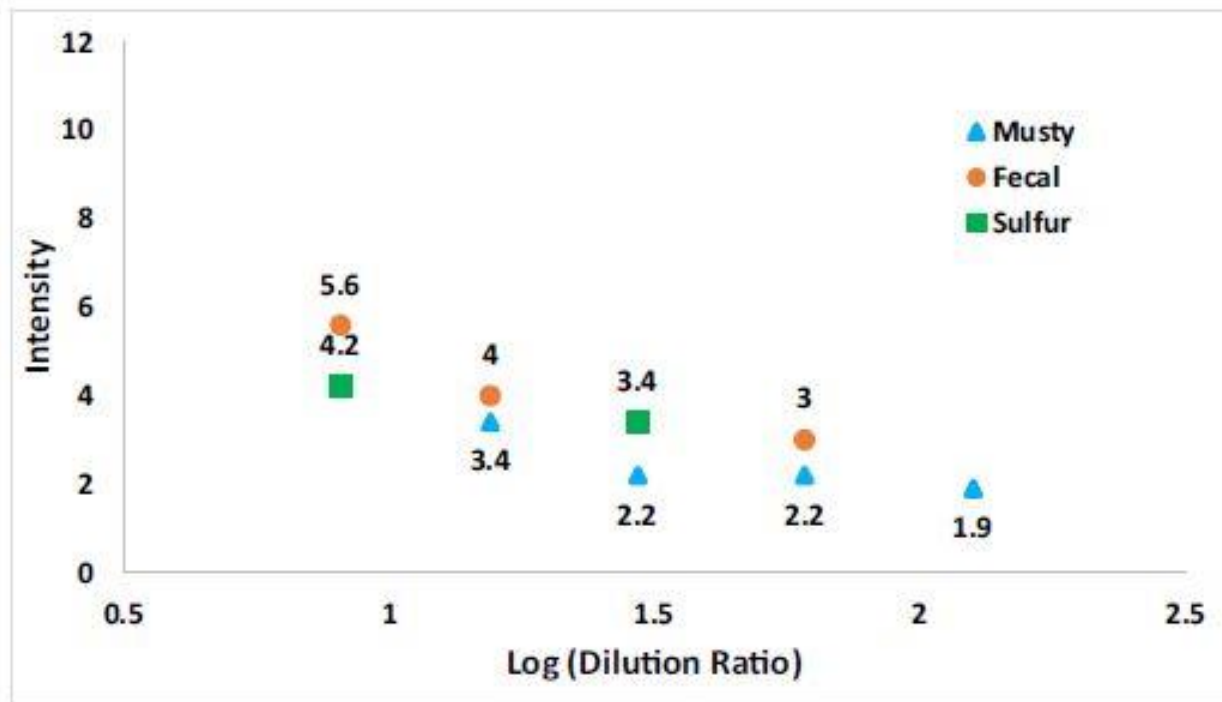


Figure 2.8. An example of “peeling of an onion effect” at activated sludge reactors where only fecal and sulfur odors were perceived initially, yet musty odor gradually became dominant with increasing dilution by odorless air using an olfactometer (Zhou et al., 2023).

To overcome the limitation, training on olfactometer operation should be conducted in the future. An olfactometer dilutes a given air sample at pre-set dilution ratios and presents the diluted flow to a panel for sensory analysis. It was used by Zhou et al., (2023) and Bian, (2021) to dilute odor emission source samples at various dilution ratios and conduct OPM analysis on the diluted flows to understand potential downwind malodor profiles and eventually bridge the gap between source odor characteristics and those at receptor locations.

2.5.2. High Variance in Individual Odor Intensity Values

The high standard deviation of odor intensity values across panelists compared to panel average odor intensity value shown by large error bars in Figure 2.6 are consistent with the finding of Curren et al., (2014). However, Curren et al., (2014) also noted less variance of panel average odor intensities across sessions. It should be able to explain why panel average odor

intensity can be used for Weber-Fechner curve fitting as exemplified by Figure 2.1 and for odor nuisance intensity threshold determination (Yu et al., 2014; Suffet et al., 2004) in spite of largely different odor intensity values from one panelist to another. Therefore, both panels should be able to refer to panel average odor intensity values to determine if perceived odors could become nuisances to the public by comparison with odor nuisance threshold value. Future research should compare panel average odor intensity with public complaint data at the same location to prove this point. Once proven, OPM can be used to examine compliance by odor emission sources.

2.5.3. Loss of Sensitivity with Sampling Bag Use

The lower odor intensities reported by laboratory analysis using FEP sampling bags compared to onsite analysis with direct sniffing shown by Figure 2.7 might have been caused by the narrow outlet tube attached to the FEP sampling bag valve (Figure 2.9). As a result, the sample flow out of the bag was restricted and quickly diluted by surrounding air before sniffed by panelists. On the contrary, the Erlenmeyer flask neck involved in Standard Method 2170 for water and wastewater examination (APHA, 2023) is usually wide enough for sniffing to take place without severe dilution. Since sniffing from sampling bags has been used for OPM analysis of environmental samples (Vitko et al., 2022; Zhou et al., 2016) and D/T value determination in some jurisdictions (Brancher et al., 2017), the cause of lower odor sensitivities and potential remedies should be further investigated. A good starter is to modify the valve of the FEP sampling bag to ensure higher sample flow rate during panel sniffing from bag outlet.

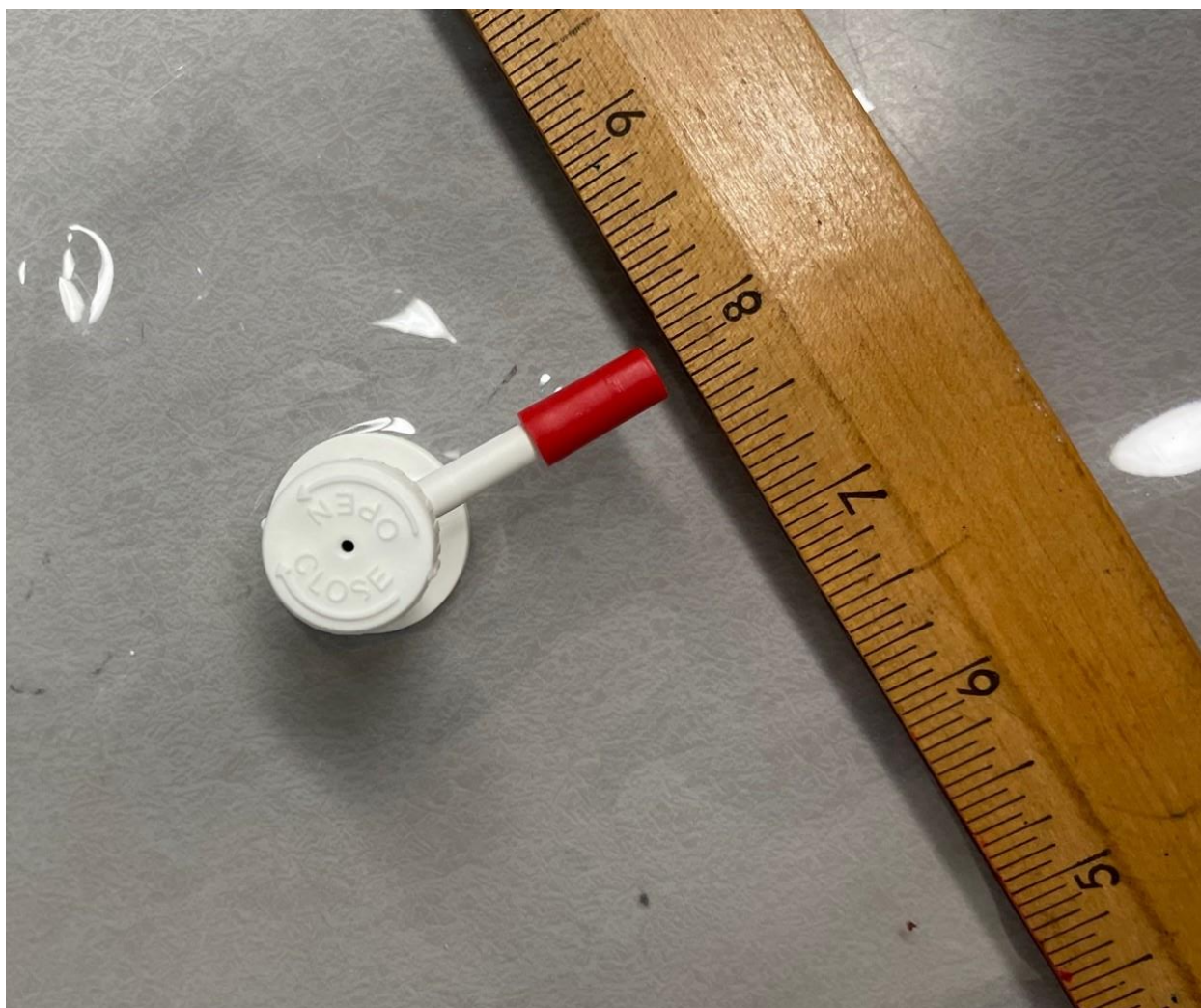


Figure 2.9. The valve and outlet tube with a red cap for the FEP sampling bags. The ruler next to the valve was in unit inch.

2.5.4. Implications

2 panels from CARB as a regulatory agency were trained on OPM analysis of air samples quickly in order to accelerate application and maturation of OPM as an airborne malodor analysis method. It was found that within a week, a panel could be formed and properly analyze common odor-emitting facilities using simple training procedure. However, challenges of significant dropout rates during training processes due to existing obligations of participants, as well as possible cases of anosmia, were noted. Therefore, a large group of volunteers together

with screening by UPSIT[®] before training would be essential for a successful outcome. In addition, limitations observed during odor mixture analyses warranted combination of OPM with dynamic olfactometry so that any initially masked odor at the source capable of causing nuisance downwind due to “peeling of an onion effect” (Section 2.5.1) could be revealed by dilutions of the olfactometer. Future training of the panels should involve familiarization with dynamic olfactometry together with OPM. Besides, additional odor references, especially for putrid/dead animal odor observed by panel S, should be determined and included in the inventory (Table 2.1). Moreover, the practice of sniffing from a sampling bag should be further investigated, especially in terms of odor sensitivities. Before its completion, it will be necessary to conduct OPM analysis of air onsite or in a way that does not involve sample flow restriction and dilution by air as a result. Finally, the consistency of panel average odor intensity values across sessions should be verified for the panels so that CARB could use the panel average to determine regulatory compliance.

As cumulation of the study’s findings, a handbook detailing OPM training and application procedure is in the works by coordination with CARB in the hopes that it will become the groundwork for a standard method in the future. However, its success will depend on the aforementioned improvements, including olfactometer operation and additional odor references. Also, discussion of OPM’s role in air malodor regulations should occur to further clarify the value of OPM in air monitoring. The study well validated a panel’s ability to characterize odors and give varying intensities consistent with operational changes of emission sources. Odor characteristics can be used to indicate possible compounds causing odor nuisance and thus proper chemical analysis methods (Burlingame et al., 2004). Meanwhile, odor intensities, especially the panel average values, can be used to determine regulatory compliance by

comparison with odor nuisance threshold. Moreover, regional primary odorant concentration limits may be established by construction of their Weber-Fechner curves and calculation of concentration values corresponding to a nuisance intensity level, also known as action level (Table 2.2), set by correlation with local complaint record. The practice has been proven effective in drinking water treatment (Yu et al., 2014; Suffet et al., 2004) and the action level of 3 has been directly applied to air treatment (Vitko et al., 2022). For example, in the study by Zhou et al., (2023), the action level of 3 was adopted so the intersection between each primary odorant's Weber-Fechner curve and $y=3$ should correspond with the odorant's concentration limit to avoid odor nuisance (Figure 2.1). However, interactions between odorants inside air samples affecting their odor intensities should be taken into account when calculating concentration limits using a pre-set action intensity level. Upon determination of concentration limits for primary odorants in a specific case, the regulation loop will be finally closed, and OPM as a first-step to decide sensorial impact of odor emissions, compounds of interest and their concentration limits will be widely applied.

2.6. Conclusion

A proof-of-concept for an idea to introduce OPM for air analysis to a regulation agency so that OPM can be frequently used in various settings to quickly mature the method was partially completed. A large pool of volunteers at the beginning to account for potential dropouts during training due to anosmia screening with UPSIT® and other already-existing obligations was essential for successful training. While the panels demonstrated an ability to quickly use the OPM for satisfactory analysis of various facilities with simple training for only a week, additional training on olfactometer, more odor references, further evaluation of panel average odor intensity values' consistency and better sampling bag valve design will be needed for its

final adoption by the agency. Hopefully, the experience gained so far, together with future training and investigations will enable further use of the OPM for better evaluation of odorous sites.

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Chapter 3

A Unique Combination of Sensory and Chemical Analyses for Air Odor Treatment System Evaluation Demonstrated by A Case Study

3.1. Abstract

In a case study, an odor treatment system for sludge odors at a wastewater treatment facility was evaluated using a unique combination of dynamic olfactometry modified by odor profile method (OPM), sensory gas chromatography (SGC) and chemical analyses (gas chromatography/mass spectrometry (GC/MS) and sulfur analyses in this case). The system consists of bleach scrubbers followed by granular activated carbon (GAC) filters. OPM-modified dynamic olfactometry revealed the treatment system's overall inefficiency based upon high effluent odor intensities that persisted with atmospheric dilution. It also characterized odors with dominant intensities as decaying vegetation, canned corn, manure and fecal. These characteristics helped pinpoint methyl mercaptan (MeSH), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), p-cresol (p-C) and to-be-identified fecal odorants as primary causes of the odor nuisance using SGC and chemical analyses. Finally, higher concentrations of these primary odorants after GAC filters were noted as the primary reason for system inefficiency while limited removal of MeSH, DMS and DMDS by bleach scrubbers was identified as a secondary problem. The case study proved the ability of this unique combination of sensory and chemical methods to evaluate an odor treatment system. It also showcased this unique combination's edge over mainstream odor measurement methods – dilution-to-threshold (D/T) measurement and chemical analysis of common odorous compounds. Specifically, using odor characteristics and intensities, this methodology could better assess odor sensorial impact and identify primary odorants. Therefore, future application of this unique combination of sensory and chemical analyses to other odor treatment systems is strongly suggested.

3.2. Introduction

The performance of any odor treatment system depends upon the sensorial impacts brought by the final effluent on nearby communities. Current odor measurement methods often involve dilution-to-threshold (D/T) value determination and chemical analysis targeting common odorants (Wang et al., 2023). Unfortunately, the D/T value measurement process does not involve description of odor characteristics and intensities. Both are important components of the sensorial effects caused by odor emissions. As for chemical analysis, odorous compounds have different odor characteristics and various odor threshold concentration (OTC) values that may be several orders of magnitude apart (Ruth, 1986). Besides, many odorants can be perceived by the human nose at levels not detectable by chemical analysis (Zhou et al., 2023). Moreover, synergistic and antagonistic effects on odor perception might exist in a mixture of multiple odorants (Hayes et al., 2023; Suffet et al., 2023). Finally, there may be too many compounds possibly causing odor nuisances to be exhaustively covered by chemical analysis without any means to narrow down the initial list of target compounds. For example, Fisher et al., (2019) compiled 38 or more odorants identified by previous studies from anaerobically digested and dewatered wastewater sludge. Similarly, Duan et al., (2021) summarized 63 common compounds other than methane and carbon dioxide in landfill emissions where the vast majority of these chemicals were odorous. The compounds in both cases belong to multiple chemical classes such as sulfur, nitrogenous, terpene and oxygenated groups and would be best analyzed by different methods. Therefore, translation of the concentration values of only detected odorous compounds into overall sensorial impact on the receiving public is impossible. In conclusion, an alternative sensory method to D/T value measurement is needed. It should be able to acquire more information from an odorous sample such as odor characteristics and intensities in order to better

understand the sensorial effects. The sensory method should also improve chemical analysis by assistance with target compound selection and interpretation of results.

Based upon the flavor profile analysis (FPA) for taste and odor analysis in water (APHA et al., 2023), the odor profile method (OPM) offers a valuable option for sensory analysis by utilization of pre-trained human panelists to describe odor characteristics and intensity values using a standardized vocabulary (Zhou et al., 2023). First, odor characteristics are defined by specific compounds as odor references. Secondly, a set of taste standards like sugar solutions at different concentrations are used to standardize an odor intensity scale. For a specific setting such as sludge processing, an odor wheel (Figure 3.1) is often used to summarize odor characteristics and known causative compounds to facilitate odor panel training and sample analysis. The intensity of an odor caused by a single odorant is usually linear with the logarithmic value of its concentration as defined by the Weber-Fechner law (Fechner, 1860). Weber-Fechner curves exemplified by Figure 3.2 can be used to describe the relationship and they have been used to estimate OTCs of odorants (Zhou et al., 2023) and to understand odor masking effects (Suffet et al., 2023). Such standardization efforts enable consistency in odor descriptions across different individuals and panels.

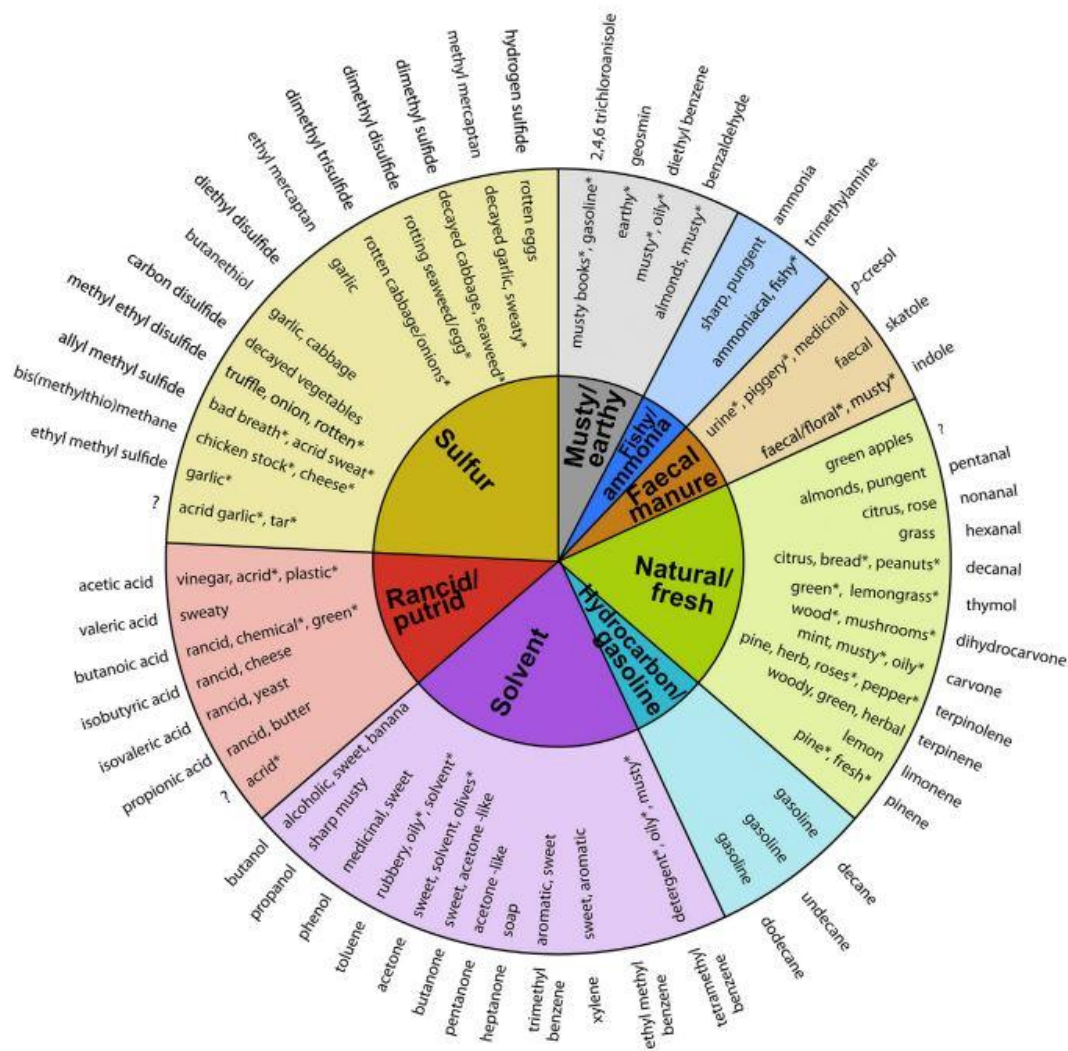


Figure 3.1. Biosolid processing odor wheel (Fisher et al., 2018).

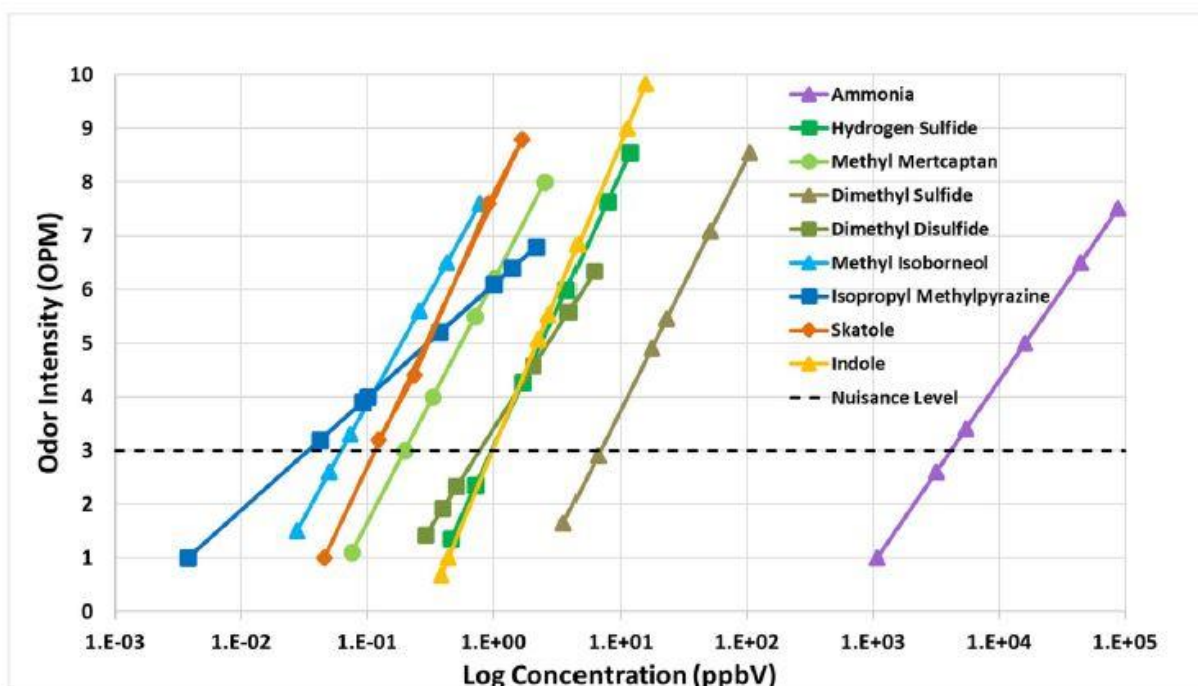


Figure 3.2. Weber-Fechner curves of several odorous compounds in air (Zhou et al., 2023).

Another challenge in odor impact evaluation is to account for atmospheric dilution before the emission reaches the public downwind from an odor source. This can lead to lower odor intensity values and even changes in perceived odor characteristics due to concentration-dependent masking effects between different odorants (Zhou et al., 2023; Suffet et al., 2023). Consequently, odor characteristics and their intensities reported by OPM analysis at an odor source do not necessarily reflect those perceived by the public downwind as exemplified by Figure 3.3. Despite its failure to determine odor characters or intensities, traditional dynamic olfactometry used for D/T value measurement does enable sensory analysis of diluted air samples (ASTM, 2019). Zhou et al., (2023) proposed and applied a modified dynamic olfactometry method where the odor sample was diluted at multiple ratios by odorless air using an olfactometer and then presented to a panel that reported perceived odor characteristics and intensity values at each

dilution level by the OPM. Thus, the evolution of odor characters and intensities with downwind atmospheric dilution after emission from source could begin to be properly evaluated.

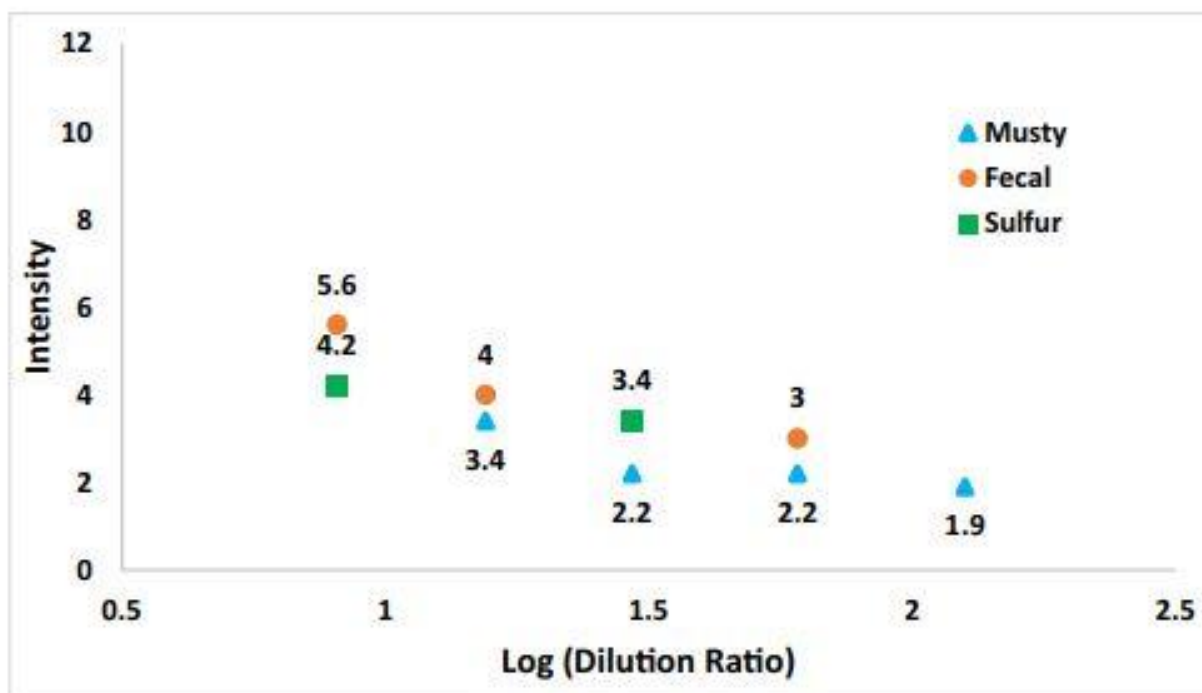


Figure 3.3. Changes in odor characters and intensities when an air sample collected from Orange County Sanitation District aeration tanks was diluted (Zhou et al., 2023). The fecal and sulfur odors masked the musty odor with limited dilution. However, as dilution progressed, the musty odor appeared and became dominant due to the slower reduction of its intensity with dilution compared to fecal and sulfur odors.

Moreover, the OPM-modified dynamic olfactometry can be combined with chemical analysis. In this way, perceived odor characteristics and intensities can be directly related to the presence of detected odorous compounds and their concentrations, respectively. Odor characteristics reported by OPM in a consistent manner are indicative of their possible chemical causes and thus helpful with the selection of proper chemical analysis methods (Burlingame et al., 2004). Hence, the list of target odorous compounds can be narrowed down from the large number of all chemicals possibly present to a specific group of compounds to analyze. As a result, the most suitable analytical chemical methods can be chosen to understand odor impacts.

For example, if only a sulfur odor is reported by the OPM from a sludge sample and its dilutions by the olfactometer, sulfur compounds should be analyzed as suspected primary chemicals causing the odor nuisance. This is indicated on the Biosolid Processing Odor Wheel (Figure 3.1). Therefore, despite the large number of odorants expected from sludge samples shown by Fisher et al., (2019), the adoption of sulfur analysis method like ASTM D 5504-201 (ASTM International, 2020) alone should be sufficient for chemical analysis of this sample. Since the chemical analysis is exhaustive with the help of OPM-modified dynamic olfactometry, the concentrations of target compounds before and after a treatment system can be used to demonstrate odor reduction performance on the molecular level. In this example of the sludge sample, if any treatment is attempted on its emissions, the reduction of sulfur compounds should be followed for evaluation of its performance as they are the primary causes of the odor nuisance. Finally, because the rates of odor intensity reduction with decreasing odorant concentration may be different from one odorous compound to another (as shown by the different slopes of the Weber-Fechner curves in Figure 3.2), the odor intensity values reported by OPM consistently should be the ultimate deciding factor in the overall performance of the treatment system. Therefore, in the sludge example, if the intensity of sulfur odor in sludge emissions after treatment and during dilution by odorless air is still higher than the nuisance threshold (See Section 3.4.1), the treatment is inefficient even when the removal rate of sulfur compounds is high.

Sensory gas chromatography (SGC) can be used to streamline the identification of compounds as primary causes of odor nuisance based on odor characteristics reported by OPM-modified dynamic olfactometry. During SGC analysis, a human panelist can apply the OPM to individual compounds separated by a GC column through a sniffing port (Hayes et al., 2023).

Thus, the odor characteristic of each odorant present in a sample can be evaluated individually and the contribution of each compound to the overall odor qualities of the sample can be better understood. When SGC is applied in parallel with GC coupled with mass spectrometry (GC/MS), the compounds responsible for the odor nuisance of a sample can be identified. Therefore, in the sludge example, after the sulfur odor is reported by OPM-modified dynamic olfactometry, SGC and GC/MS full scan analysis can be applied to the sample. If a sulfur odor is eluted from the GC column only once at a specific relative retention time and a compound is identified by the GC/MS system at the same relative retention time, this would be the primary cause of the overall sulfur odor of the sample. Thus, SGC combined with GC/MS narrows down the target compound list even further compared to the odor wheel. As a result, subsequent chemical analysis for odor treatment system performance evaluation can be further simplified.

This paper will demonstrate a case study where the combination of OPM-modified dynamic olfactometry, SGC and chemical analyses were applied to evaluate an odor treatment system. The odor treatment system was established at an Orange County Sanitation District (OCSan) wastewater treatment plant (Fountain Valley, CA, USA) after the identification of its sludge dewatering and truck loading processes as major odor sources by Zhou, (2017). Specifically, an intensive fecal odor caused by skatole (SKA) and indole (IND) and musty odor linked to 2-methylisoborneol (2-MIB) and 2-isopropyl-3-methoxypyrazine (IPMP) were emitted by both processes. A strong rotten vegetable odor was also produced by the truck loading process due to high levels of methyl mercaptan (MeSH), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS). The wastewater odor treatment system includes a first stage of 3 parallel bleach chemical scrubbers followed by a second stage of 2 parallel granular activated carbon (GAC) filters to treat collected emissions from sludge storage, thickening, chemical conditioning,

dewatering and truck loading processes. The techniques of both stages have been widely used in wastewater treatment plants (Ren et al., 2019). Bleach scrubbers have been found to be effective in removal of hydrogen sulfide (H_2S) (Petre et al., 2007; Wang et al., 2024; Couvert et al., 2008; Sanchez et al., 2006), MeSH (Petre et al., 2007; Wang et al., 2024; Couvert et al., 2008; Sanchez et al., 2006), DMS (Petre et al., 2007) and DMDS (Hentz Jr et al., 1992; Petre et al., 2007) while GAC filters could significantly lower the levels of SKA, IND, 2-MIB, IPMP and MeSH (Vitko et al., 2024). However, public complaints about malodors persisted after system installation. The case study serves as a proof of concept for the ability of this unique combination of sensory and chemical analyses to 1) evaluate the overall efficiency of the system, 2) identify primary odorous compounds as system performance indicators, and 3) analyze performance of each stage to locate system problems. It also offered an opportunity to compare this unique combination to mainstream odor evaluation methods including D/T value measurement and chemical analysis of common odorants with regard to accurate sensorial impact assessment and effective identification of primary chemical causes.

3.3. Experimental Section

3.3.1. Chemicals and Materials

Geosmin (GEO) (98.0%+) and 2-MIB (98.0%+) were acquired from FUJIFILM Wako Chemicals U.S.A. Corporation (Richmond, VA, USA). p-Bromofluorobenzene (p-BFB) (>98.0%), 4-ethylphenol (4-EP) (97.0+%) and IPMP (>98.0%) were purchased from TCI America (Portland, OR, USA). 2-Isobutyl-3-methoxypyrazine (IBMP) (95%), 2,4,6-trichloroanisole (TCA) (97%) and 2,5-dimethylthiophene (2,5-DMT) were obtained from Aaron Chemicals (San Diego, CA, USA). DMS (99+%), DMDS (99%), dimethyl trisulfide (DMTS) (98+%), n-butyric acid (n-BA) (99+%), IND (99+%), SKA (99%), 2,3,5-trimethylpyrazine

(TMP) (99%) and α -pinene (α -P) (97%) stabilized with α -tocopherol were supplied by ThermoFisher Scientific (Waltham, MA, USA). p-Cresol (p-C) (99%) and water (suitable for HPLC) was purchased from Sigma-Aldrich Inc. (St. Louis, MO, USA). 1000 μ g/L MeSH solution in methanol (MeOH) was acquired from Chem Service, Inc. (West Chester, PA, USA). Ethyl alcohol (EtOH) (95%) was supplied by Pharmco Products, Inc. (Brookfield, CT, USA). 1-Butanol (1-BuOH) (ACS Reagent) was provided by Baker Chemical Co. (Phillipsburg, NJ, USA). HPLC-grade MeOH ($\geq 99.9\%$), sodium sulfide nonahydrate (98+%) and ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$) (Certified ACS Plus) were purchased from Fisher Scientific (Hanover Park, IL, USA). 1 L and 10 L fluorinated ethylene propylene (FEP) sampling bags were acquired from Jensen Inert Products (Coral Springs, FL, USA). An extra-large Vac-U-Chamber air sampler was supplied by SKC, Inc. (Eighty Four, PA, USA).

3.3.2. Odor Treatment System Evaluated – Overview

The details of the odor treatment system evaluated and sampling locations are shown in Figure 3.4. Emissions from sludge storage, thickening, chemical conditioning, dewatering and truck loading processes were combined and then equally split into 3 parallel bleach scrubbers each with 3 chambers. Chamber #1 was initially reserved for ammonia (NH_3) removal using sulfuric acid (H_2SO_4) solution but no scrubbing was conducted at the time of this study due to low NH_3 concentration. Sodium hypochlorite (NaClO) solution with a pH value of ~ 7.9 was used as the scrubbing solution in both chambers #2 and #3 to oxidize H_2S and other sulfur compounds present in sludge emissions. The effluent of the scrubbers was combined and split into 2 GAC filters with 4 mm pelletized, CTC 60 coal-based carbon (Karbonous, Inc., City of Industry, CA, USA).

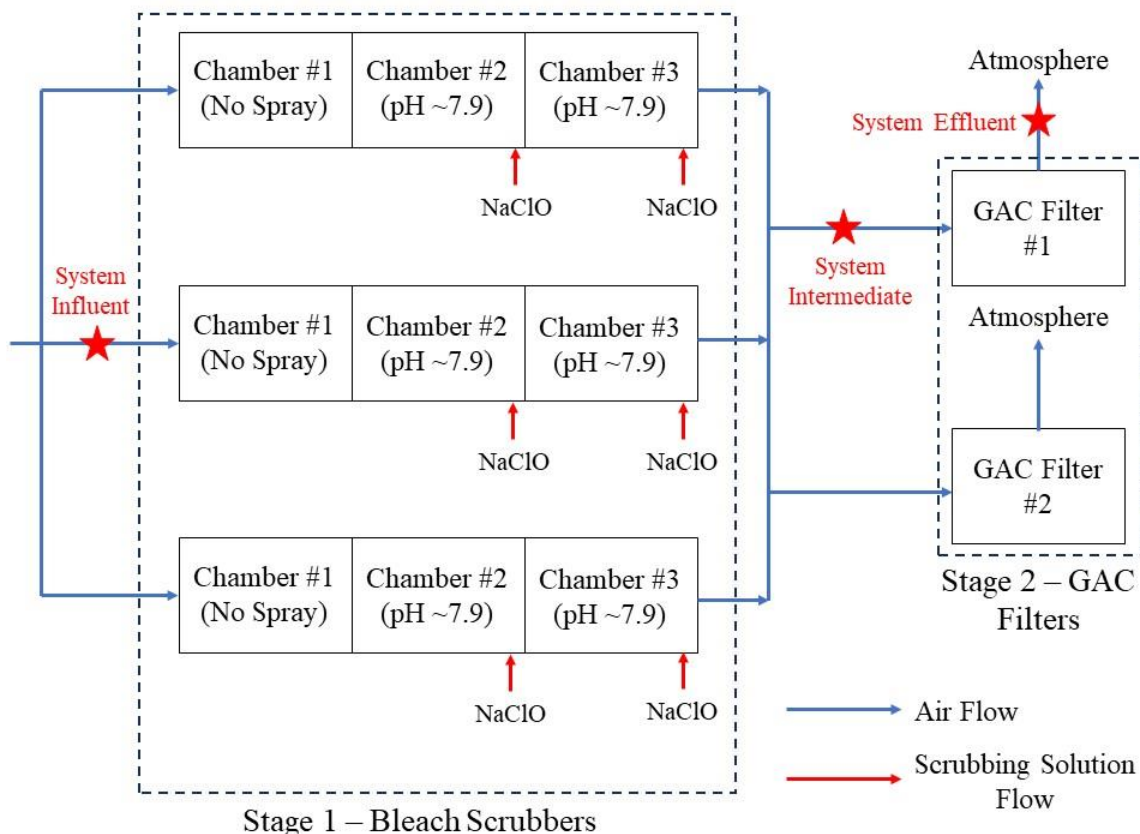


Figure 3.4. Sludge malodor control system flowchart and sampling locations (marked by red stars). Note that chamber #1 in each bleach scrubber was not in use at the time of this study.

3.3.3. Sampling, Delivery and Storage

In total, 4 sampling events were completed in 2 stages. The first stage of the 2 events took place on 10/12/2023 and 10/19/2023 in order to examine the overall efficiency of the 2-stage odor treatment system and to identify compounds that were primary causes of odor nuisance. Therefore, samples were only taken from system influent and effluent points. Due to overall system inefficiency (Section 3.4.1), the other stage of 2 events were conducted on 02/12/2024 and 03/04/2024 to evaluate the odor removal efficiency of each stage separately to locate the problem leading to the underperformance identified in stage 1. System influent, intermediate and effluent points were all sampled. Samples were collected from each location for OPM-modified

dynamic olfactometry, sulfur compounds analysis, SGC analysis, GC/MS full scan analysis and GC/MS selected ion monitoring (SIM) during all 4 events.

For OPM-modified dynamic olfactometry, SGC analysis, GC/MS full scan analysis and GC/MS SIM, a 10L sample was taken for each analysis at each location using a pristine 10 L FEP sampling bag and an extra-large Vac-U-Chamber air sampler. Meanwhile, for sulfur compounds analysis, a 1 L sample was taken at each location with a pristine 1 L FEP sampling bag and the same sampler. Teflon was chosen for all tubing involved in the sampling process to minimize compound loss by sorption. All samples were delivered overnight to the corresponding laboratories and were analyzed within 36 hours of sampling.

3.3.4. OPM-Modified Dynamic Olfactometry

3.3.4.1. OPM Panel Training

Before training the odor panel, all candidates were screened for anosmia by the University of Pennsylvania Smell Identification Test[®] (UPSIT[®]) (Sensonics International, Haddon Heights, NJ, USA). Individuals with severe microsmia or total anosmia were excluded from the sensory panel.

Panelists were trained by Standard Method 2170 B (APHA et al., 2023) modified for wastewater facility evaluations. Specifically, odor references were presented to panelists for standardization of odor characteristics. Sugar solutions at different concentrations were presented to define the intensity scale (Table 3.1). Perceptions of the standards were repeated until panelists could characterize random odor references and their mixtures correctly. Additional odor references were included in panel training to better represent odors expected from wastewater facilities. H₂S, IND and p-C were adopted as references for rotten egg, fecal and manure odors,

respectively. All references were available to panelists during OPM-modified dynamic olfactometry analysis.

Table 3.1. Odor intensity scale used for OPM (Zhou, 2017).

Odor Intensity Value	Sugar Solution Concentration (%)	Odor Strength	Expected Off-Site Odor Problems from Wastewater Plant Odors
0	0	Odor free	None
1	Solution not used	Threshold	Very few
2	Solution not used	Very weak	Unlikely off-site complaints
3*	Solution not used	Recognizable	Action level
4	5	Weak	Probable off-Site odors, recognition of odor character (complaints begin by off-site neighbors)
6	Solution not used	Weak-moderate	Definite off-site odors, objection of odors (complaints by off-site neighbors)
8	10	Moderate	Definite off-site odor complaints
10	Solution not used	Moderate-strong	Definite off-site odor complaints
12	15	Very strong	Definite off-site odor complaints
* The intensity value of 3 was not for individual reporting. It was a threshold to be compared with panel average odor intensity values to determine if odor nuisance could occur.			

3.3.4.2. Sample Analysis

The method of Zhou et al., (2023) was modified and applied for this study. Before analysis, an AC'SCENT® international olfactometer (St. Croix Sensory, Inc., Lake Elmo, MN, USA) was flushed with the sample for 30 seconds to minimize odorant loss by adsorption onto tubing during later analysis. The olfactometer was designed to dilute a sample at preset ratios by odorless air. After the flushing, each panelist conducted triangular forced-choice tests starting from the most dilute level. The panelists were presented with 3 choices at each level. Two of the choices were odorless air while the third choice was the diluted sample. Each panelist was instructed to pick out the diluted sample from the choices. If the selection was correct and an odor was perceived, the odor's character and intensity value were reported. Total air flow at the sniffing port was kept constant at 20 L/min. Since the olfactometer could not deliver an undiluted

sample to the panel, odor characterization of the original samples was achieved by sniffing directly at the sampling locations during sample collection. All panels consisted of 4 or more panelists. The odor was considered confirmed if half or more of the panel reported an odor character from a sample at a certain dilution level. The odor character and the average intensity of each confirmed odor were recorded. Odors perceived by fewer than half of the panelists were regarded as “odor notes” of less concern and were reported without intensity values to be aware of their possible presence in subsequent samples.

The application of olfactometer is subject to possible contamination by odorant adsorption to system surface and subsequent carryover to the next analysis (Burton et al., 2019). In this study, after a sample was analyzed, the system was purged with saturated 1-BuOH vapor, saturated EtOH vapor and odorless air for 16, 16 and 32 minutes, respectively. The sample intake tube and filter were replaced after each sample analysis or system purge by solvent vapor. No filter was attached during air purges to avoid adsorption of residual alcohol vapors to the filter. After the purges, the panel conducted a blank analysis. The air and/or vapor purges were repeated if necessary.

3.3.5. GC Analyses

3.3.5.1. Sample Extraction

A 1 cm-long Stableflex 50/30 μm DVB/CAR/PDMS solid-phase microextraction (SPME) fiber was introduced into the 10 L FEP sampling bag and then exposed to the sample of interest for 20 min in order to extract the volatile compounds including odorants. The SPME fiber was previously conditioned at 270°C for 30 min to remove impurities. If the extraction was for compound quantitation by GC/MS SIM, 0.5 μL 0.1 g/L p-BFB solution in MeOH was injected into the sample as internal standard 30 min before introduction of SPME fiber.

3.3.5.2. Compound Separation by GC

After extraction, the SPME fiber was swiftly injected into a Varian 450-GC system (Varian, Inc., Walnut Creek, CA, USA) through a 1177 split/splitless capillary injector. Extracted volatile compounds were desorbed from the SPME fiber at 260°C for 15 min and then introduced into a 60 m DB-5MS GC column (diameter – 0.25 mm, film thickness – 0.25 µm) (Agilent Technologies, Santa Clara, CA, USA) for separation. The injector split vent was off for the first minute to maximize compound introduction into the GC column and on with a split ratio of 100 during the rest of the run to limit peak tailing effects. 99.9999% helium (Airgas, Inc., Radnor, PA, USA) was used as the carrier gas. Column flow rate was 1 mL/min. Column oven temperature was held at 50.0°C for 2 min before rising to 260.0°C at a rate of 8.0°C/min, where it was maintained for 1.75 min. The total run time was 30 min.

3.3.5.3. GC/MS SIM

GC/MS SIM was used to identify and quantify compounds from a sample. The GC-eluted compounds were ionized in the mass spectrometer by electrons at 70 eV. Major ions produced by target compounds were monitored (scan frequency – 1 Hz) during their elution windows determined by standards. An isolation window of 3.0 (m/z) was applied for each ion monitored. The Varian 220-MS system (Varian, Inc., Walnut Creek, CA, USA) temperature setpoints were 150°C, 40°C and 270°C for ion trap, manifold and transfer line, respectively. Among the target compounds, IPMP, 2-MIB, SKA and IND were selected due to prior identification at the OCSan facility (Zhou et al., 2023). TMP, IBMP and GEO were selected due to similar structures with previously found compounds at OCSan facility as well as their presence in wastewater and/or biosolid processes (Zeman and Koch, 1981; Ventura et al., 2010; Zhu et al., 2023). TCA was selected due to its reported prevalence in dewatered sludge (Barczak et al., 2019). During the

first two sampling events, the presence of DMTS and p-C were noticed by SGC analysis (Section 3.4.1). Thus, they were included in GC/MS SIM of the other 2 events. 4-EP was added to the target chemical list for the last 2 events because of its similarity with p-C and its reported production during wastewater treatment (Shan et al., 2015; Garcia-Mancha et al., 2012). Table 3.2 shows the details of the target compounds.

Table 3.2. Target compounds for GC/MS SIM.

Compound Name	Ions Monitored (m/z)	OTC (ppb _v) ^{a,b,c}	Odor Character(s)	LOD (ppb _v)	LOQ (ppb _v)	LR (ppb _v)
DMTS*	126**, 79, 64, 111	1.18 ¹	Garlic ^{8,e}	0.2	0.4	0.3~100
TMP	122**, 81, 54, 53, 123	6.5~37.4 ²	Roasted ⁹	0.05	0.1	0.05~25
p-C*	107**, 108, 77, 79	0.0044~0.054 ^{3,4}	Manure ¹⁰	0.1	0.3	0.1~100
IPMP	137**, 152, 124, 138, 109	0.0038~0.004 ^{5,6,7}	Moldy ^{11,e}	0.004	0.01	0.005~10
4-EP*	107**, 122, 77, 108	0.086 ^d	Manure ^e	0.05	0.2	0.1~10
IBMP	124**, 94, 151, 81, 95	2.9E-4~0.0019 ^{1,2}	Moldy ^e	0.08	0.2	0.1~1
2-MIB	95**, 107, 108, 110, 135	0.020~0.026 ^{5,6,7}	Earthy/Musty ^{8,e,f}	0.1	0.4	0.5~2
IND	117**, 90, 89, 63, 118	0.44~1.0 ^{5,6,7}	Fecal ^e	0.08	0.2	0.1~1
TCA	195**, 197, 210, 212, 167***	0.016 ^d	Moldy ^{8,e}	0.4	1.3	3.5~15
SKA	130**, 131, 77, 103, 65***	0.018~0.055 ^{5,6,7}	Fecal ^{12,e}	0.1	0.5	0.1~2
GEO	112**, 55, 111, 67, 69	6.5E-3~0.066 ²	Earthy/Musty ^{8,e,f}	5	16	15~150

^a OTC values reported by Zhou et al., (2023); Zhou, (2017); Vitko et al., (2022) and/or measured by Method ASTM E679-19 (ASTM International, 2019) were preferred due to the same sample delivery and panel training methods as this study.

^b OTC value ranges reported by Ruth, (1986) and/or Gemert, (2003) were adopted if their higher limits are within 100 times their respective lower limits.

^c OTC values from other references were adopted for compounds uncovered by sources in a and b.

^d The OTC value was measured by Method ASTM E679-19 (ASTM International, 2019).

^e The odor character was confirmed by the panel in this study.

^f The OPM panel in this study could hardly differentiate between earthy and musty odor characteristics.

¹ Ruth, (1986).

² Gemert, (2003).

³ Nagata, (2003).

⁴ Chappuis et al., (2015).

⁵ Zhou et al., (2023).

⁶ Zhou, (2017).

⁷ Vitko et al., (2022).

⁸ Suffet et al., (2019).

⁹ Wagner et al., (1999).

¹⁰ Trabue et al., (2011).

¹¹ Yin et al., (2024).

¹² Suffet et al., (2009).

LOD – Limit of detection. Defined by a signal to noise ratio (S/N) of 3.

LOQ – Limit of quantitation. Defined by a S/N of 10.

LR – Linear range.

* Compounds were only quantitated in samples taken on 02/12/2024 and 03/04/2024.

** Ions were used to quantitate their respective compounds.

*** Ions were only monitored for samples taken on 10/12/2023 and 10/19/2023. They were not monitored for samples taken on 02/12/2024 and 03/04/2024 to observe additional target compounds.

3.3.5.4. SGC and GC/MS Full Scan Analysis

Despite prior knowledge of odorants produced at the OCSan facility (Zhou et al., 2023), changes in chemical profiles of sludge emissions were possible. Therefore, SGC combined with GC/MS full scan analysis was conducted in order to identify previously uncovered odorants. The sniffing port and the Varian 220-MS system were connected with two independent parallel 60 m DB-5MS GC columns (diameter – 0.25 mm, film thickness – 0.25 μ m). Parallel columns can potentially increase sensitivities of both GC analyses compared to application of the same column with a splitter to 2 sensors (Hayes et al., 2023).

For SGC, separated odorants from the GC column (Section 3.3.5.2) were combined with humidified air to prevent sensory fatigue and then presented to an analyst who reported elution time, odor character and intensity of each odorant. In this way, odorants in a sample could be characterized individually. Their retention times in SGC system and odor characters could be basis for their identification when compared to purchased standards.

For GC/MS full scan analysis, separated compounds from the GC column (Section 3.3.5.2) were ionized by electrons at 70 eV. All ions with m/z from 41 to 260 were monitored (scan frequency – 1 Hz). The MS system temperature setpoints were 150°C, 40°C and 270°C for ion trap, manifold and transfer line, respectively. The GC/MS system retention times of odorants in a sample and their mass spectra could be additional basis for their identification when compared to purchased standards.

3.3.6. Sulfur Analysis

Samples taken on 10/12/2023 were delivered to AtmAA, Inc. (Calabasas, CA, USA) for sulfur analysis by SCAQMD Method 307-91 (SCAQMD, 1994). All other samples were delivered to ALS Environmental (Simi Valley, CA, USA) for sulfur analysis by ASTM D 5504-20 (ASTM International, 2020). The target compounds of sulfur analysis and method sensitivities are summarized in Table 3.3. Among the analytes for sulfur analysis, H₂S, MeSH, DMS and DMDS were previously identified at OCSan facility (Zhou et al., 2023). Other target compounds were analyzed for possible changes in chemical profiles of sludge emissions leading to presence of other sulfur chemicals.

Table 3.3. Target compounds for sulfur analysis.

Compound Name	OTC (ppb _v) ^{a,b,c}	Odor Character(s)	MRL for Samples Taken on 10/12/2023 (ppb _v)	MRL for Other Samples (ppb _v)
H ₂ S	0.5~0.59 ^{1,2}	Rotten Egg ^{9,c}	80	5.0
Carbonyl Sulfide (COS)	56.1~100.1 ³	Pungent, Rotten Egg ¹⁰	80 (100*)	5.0
MeSH	0.07~0.08 ^{1,2,4}	Decaying Vegetation ^c	80	5.0
Ethyl Mercaptan (EtSH)	2E-06 ⁴	Garlic ⁸	80	5.0
DMS	2.5~3.0 ^{1,2,4}	Canned Corn (Low Concentration), Decaying Vegetation (High Concentration) ^{9,c}	80	5.0
Carbon Disulfide (CS ₂)	7.7~210 ^{5,6,7}	Disagreeable Sweet ⁸	80	2.5

Isopropyl Mercaptan (iPSH)	0.0060 ⁵	Skunk ¹¹	80	5.0
tert-Butyl Mercaptan (tBSH)	0.024~1.9 ³	Skunk ¹²	80	5.0
n-Propyl Mercaptan (nPSH)	0.013~0.064 ^{5,6}	Onion ¹³	80	5.0
Ethyl Methyl Sulfide (EMS)	6.95~39.17 ³	Cabbage ¹⁴	NA	5.0
Thiophene (T)	0.74 ⁸	Aromatic ⁸	NA	5.0
Isobutyl Mercaptan (iBSH)	0.53 ⁸	Onion ¹³	80	5.0
Diethyl Sulfide (DES)	3.12~4.72 ⁸	Foul, Garlic ⁸	NA	5.0
n-Butyl Mercaptan (nBSH)	0.52~1.07 ⁸	Milky ¹³	NA	5.0
DMDS	0.2~0.31 ^{1,2,4}	Decaying Vegetation ^{9,e}	80	2.5
3-Methylthiophene (3-MT)	Not Found	Fatty, Winey ¹⁵	NA	5.0
Tetrahydrothiophene (THT)	0.62 ⁵	Cabbage ¹⁶	80	5.0
2,5-DMT	Not Found	Solventy, Sweet Solvent, Sweaty, Rancid ^e	NA	5.0
2-Ethylthiophene (2-ET)	Not Found	Styrene ¹⁷	NA	5.0
Diethyl Disulfide (DEDS)	3.84 ⁸	Onion ¹³	NA	2.5
s-Butyl Mercaptan (sBSH)	0.030 ⁵	Skunk ¹⁸	80	5.0

^a OTC values reported by Zhou et al., (2023); Zhou, (2017); Vitko et al., (2022) and/or measured by Method ASTM E679-19 (ASTM International, 2019) were preferred due to the same sample delivery and panel training methods as this study.

^b OTC value ranges reported by Ruth, (1986) and/or Gemert, (2003) were adopted if their higher limits are within 100 times their respective lower limits.

^c OTC values from other references were adopted for compounds uncovered by sources in a and b.

^e The odor character was confirmed by the panel in this study.

¹ Zhou, (2017).

² Vitko et al., (2022).

³ Gemert, (2003).

⁵ Nagata, (2003).

⁶ Rosenfeld et al., (2007).

⁷ Amoore and Hautala, (1983).

⁸ Ruth, (1986).

⁹ Suffet et al., (2019).

¹⁰ Barczak et al., (2022).

¹¹ National Library of Medicine, (n.d.b).

¹² National Library of Medicine, (n.d.c).

¹³ Burdack-Freitag et al., (2009).

¹⁴ National Library of Medicine, (n.d.a).

¹⁵ The Good Scents Company, (n.d.c).

¹⁶ The Good Scents Company, (n.d.a).

¹⁷The Good Scents Company, (n.d.b).

¹⁸National Library of Medicine, (n.d.d).

MRL – Method reporting limit.

NA – Not analyzed.

* The MRL value of 100 ppb_v only applied to influent sample taken on 10/12/2023.

3.4. Results

3.4.1. Overall Efficiency and Primary Odorants

In this section, the combination of OPM-modified dynamic olfactometry, SGC and chemical analyses successfully identified the overall inefficiency of the odor treatment system. It also pinpointed compounds as primary causes of odor nuisance so their concentrations would later be tracked throughout the system by chemical analysis to locate any problem leading to the underperformance of the treatment system.

The data from OPM-modified dynamic olfactometry during the 2 sampling events in 2023 are summarized in Figure 3.5 in the form of dilution curves. Dilution curves show evolution of odor intensity value for each confirmed odor character with dilution by an odorless background. Since the relationship between odorant concentration and odor intensity is logarithmic, a logarithmic scale was chosen for the dilution ratio defined by volume of diluted mixture over volume of original sample. An average intensity value of 3 was considered the nuisance threshold and adopted in previous studies of OCSan facility malodors (Zhou et al., 2023; Zhou et al., 2016; Suffet et al., 2023; Vitko et al., 2022).

The nuisance threshold was not exceeded by any odor character perceived in system effluent sampled on 10/12/2023 at any dilution ratio (Figure 3.5A2). Therefore, overall system performance on 10/12/2023 was satisfactory. By contrast, a decaying vegetation odor in system effluent on 10/19/2023 (Figure 3.5B2) was not significantly decreased compared to system influent (Figure 3.5B1) and a manure odor remained intensive. As a result, a dilution ratio of

126.2 ($\log_{10}$ value – 2.1) was needed for both decaying vegetation and manure odor intensity values to be lowered to the nuisance threshold of 3. Thus, the treatment system underperformed on 10/19/2023 and downwind public complaints were possible. Further investigation into each stage separately to identify reasons for insufficient odor reduction was determined to be necessary.

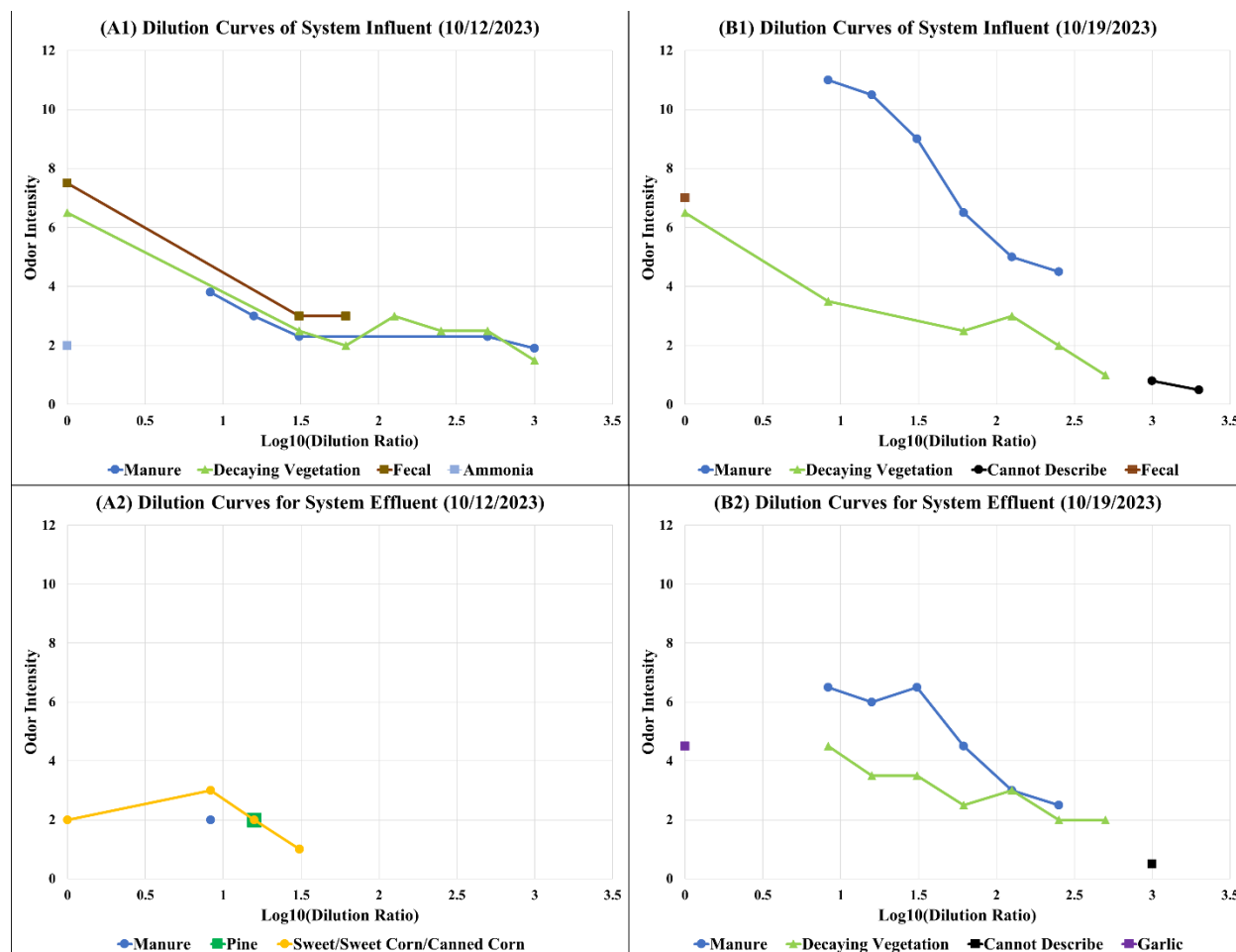


Figure 3.5. Dilution curves of system influent (1) and system effluent (2) samples collected on 10/12/2023 (A) and 10/19/2023 (B). Note that undiluted samples ($\log_{10}(\text{dilution ratio}) = 0$) were analyzed by direct sniffing at the sampling locations during sample collection because the olfactometer could not present samples without mixture with odorless air.

The persistent decaying vegetation odor in system effluent on 10/19/2023 was consistent with high effluent concentrations of MeSH, DMS and DMDS compared to their OTCs on that

day (Table 3.4). However, no target compound quantitated could explain the perception of manure odor in all samples. While GC/MS full scan analysis failed to identify any manure odorant of interest due to co-elution with background compounds, the manure odor was perceived during SGC analysis of system influent sampled on 10/19/2023. The elution time of manure odor (14.7 min) matched the retention time of the manure odor of the p-C standard at 14.6 min. Similarly, an odor was noticed during SGC analysis of system effluent sampled on 10/19/2023. Though the odor was too weak to be characterized, its elution time (12.6 min) perfectly matched that of purchased DMTS (12.6 min), a known garlic odorant (Suffet et al., 2019). Meanwhile, the garlic odor was confirmed by panel in the same sample without dilution (Figure 3.5B2). It should be noted that the panelists were able to distinguish a garlic odor from a decaying vegetation odor because a different odor reference was used for each character during panel training. Garlic and decaying vegetation characters were defined by DMTS and DMDS, respectively. The panelists were also able to differentiate between manure and fecal odors defined by p-C and IND, respectively, during panel training. Therefore, presence of p-C and DMTS was identified. Both chemicals together with 4-EP became additional target compounds for quantitation by GC/MS SIM during later sampling events.

Table 3.4. Quantitation results for system influent (In.) and effluent (Ef.) samples taken on 10/12/2023 and 10/19/2023. Target compounds (Table 3.2 and Table 3.3) undetected in all samples are not shown.

Compound Name	Odor Character(s) ^a	OTC (ppb _v) ^a	Compound Concentration (ppb _v)			
			10/12/2023		10/19/2023	
			In.	Ef.	In.	Ef.
H ₂ S	Rotten Egg	0.5~0.59	4980	ND	2000	400
COS	Pungent, Rotten Egg	56.1~100.1	ND	ND	12	10
DMS	Canned Corn (Low Concentration), Decaying Vegetation (High Concentration)	2.5~3.0	490	ND	3200	85
MeSH	Decaying Vegetation	0.07~0.08	690	ND	1100	180
DMDS	Decaying Vegetation	0.2~0.31	ND	ND	180	92

nPSH	Onion	0.013~0.064	ND	ND	6.6	ND
iPSH	Skunk	0.006	ND	ND	6.2	ND
tBSH	Skunk	0.024~1.9	ND	ND	6.0	ND
CS ₂	Disagreeable Sweet	7.7~210	ND	ND	23	6
SKA	Fecal	0.018~0.055	<0.5	<0.5	0.5	ND
IND	Fecal	0.44~1.0	0.6	0.4	>1	0.4
GEO	Earthy/Musty	0.0065~0.066	16.6	<16	ND	ND
2-MIB	Earthy/Musty	0.020~0.026	>2	<0.5	>2	>2
IBMP	Moldy	0.00029~0.0019	ND	0.3	ND	ND
TCA	Moldy	0.016	9.6	6.8	<3.5	<3.5
^a See Table 3.2 and Table 3.3 for sources of the odor characters and OTC values. ND – Not detected.						

Among the odorants detected by chemical analyses and/or SGC, specifically MeSH, DMS, DMDS and p-C directly determined overall treatment system performance because they were responsible for decaying vegetation, canned corn and manure odors. One or more of these odors were dominant in all 4 samples by maintaining their odor intensities throughout the dilution process. As a result, system underperformance on 10/19/2023 was mainly caused by insufficient removal of MeSH, DMS, DMDS and p-C as the primary causes of odor nuisance. Thus, the concentration profiles of these compounds throughout the system were given particular attention during the following 2 sampling events.

It was also observed that SKA and IND caused significant fecal odor in system influent. This was especially true on 10/12/2023 when the fecal odor even persisted after dilution as shown on Figure 3.5A1. Nevertheless, the chemicals were removed by the treatment system efficiently as no fecal odor was perceived in system effluent on both days. However, their concentration profiles were still considered important during later sampling because any increase of SKA and IND production could make fecal a dominant odor in the system effluent and thus make the 2 compounds primary odorants. Likewise, the significance of DMTS depended on whether garlic odor could become dominant in diluted system effluent samples later due to sufficient increase in DMTS formation. By contrast, despite high concentrations compared to OTC values in one or

more of the 4 samples, the rotten egg odor of H₂S and the earthy/musty/moldy odors of GEO, 2-MIB, IBMP and TCA were the least concerning as they were not perceived in any sample. Their absence might have been the result of masking and/or blending effects between odorants discussed by Zhou et al., (2023). The hypothesis would require further investigation after the system is improved to remove the primary odorants – MeSH, DMS, DMDS and p-C.

3.4.2. Stage by Stage Investigation

In this section, the unique combination of sensory and chemical analyses determined the problems leading to overall system inefficiency through assessment of primary odorants' removal by each stage of the odor treatment system. OPM-modified dynamic olfactometry served to verify conclusions based on quantitation of primary odorants while SGC analysis was conducted to identify any additional odorants of interest. Quantitation results for the 2 sampling events in 2024 are shown in Table 3.5.

Table 3.5. Quantitation results for system influent (In.), intermediate (Int.) and effluent (Ef.) samples taken on 02/12/2024 and 03/14/2024. Target compounds (Table 3.2 and Table 3.3) undetected in all samples are not shown.

Compound Name	Odor Character(s) ^a	OTC (ppb _v) ^a	Compound Concentration (ppb _v)					
			02/12/2024			03/04/2024		
			In.	Int.	Ef.	In.	Int.	Ef.
H ₂ S	Rotten Egg	0.5~0.59	450	36	6.3	800	86	200
COS	Pungent, Rotten Egg	56.1~100.1	ND	ND	5.7	ND	ND	ND
DMS	Canned Corn (Low Concentration), Decaying Vegetation (High Concentration)	2.5~3.0	930	34	330	450	110	750
MeSH	Decaying Vegetation	0.07~0.08	680	240	36	480	97	190
DMDS	Decaying Vegetation	0.2~0.31	140	72	210	57	15	120
DMTS	Garlic	1.18	13.3	6.5	6.3	3.9	5.2	8.9
CS ₂	Disagreeable Sweet	7.7~210	ND	ND	3.1	ND	ND	ND
IND	Fecal	0.44~1.0	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
p-C	Manure	0.0044~0.054	1.9	0.3	0.5	1.5	<0.3	0.5
2-MIB	Earthy/Musty	0.020~0.026	>2	>2	>2	>2	>2	>2
TCA	Moldy	0.016	ND	ND	ND	<3.5	<3.5	<3.5
^a See Table 3.2 and Table 3.3 for sources of the OTC values. ND – Not detected.								

3.4.2.1. Additional Primary Odorants

Fecal odor became one of the dominant odors in all 6 samples in terms of odor intensity values throughout OPM-modified dynamic olfactometry dilution (Figure 3.6). However, concentrations of IND were lower than its OTC value in all samples while SKA was not detected at all. Though SKA's limit of detection (0.1 ppb_v) was higher than its OTC (0.018~0.055 ppb_v) (Table 3.2), the difference could not account for perception of fecal odor in all samples except for system effluent collected on 02/12/2024 with a dilution ratio of 316.2 (log₁₀ value – 2.5). Therefore, compounds other than SKA and IND caused the fecal odor during the 2 sampling events. Fecal odor was eluted and perceived at 20.8 min and 26.6 min during SGC analysis of system intermediate and effluent samples collected on 03/04/2024, respectively. Neither perception could be attributed to IND and SKA that had different elution times. Unfortunately, no retention time for any fecal compound other than IND and SKA in the SGC system was available for comparison. Moreover, GC/MS full scan of system intermediate sample failed to identify any fecal compound of interest probably due to co-elution with other chemicals. As for system effluent, GC/MS full scan analysis was not conducted due to sampling bag leakage. The to-be-identified fecal odorants were considered primary odorants alongside MeSH, DMS, DMDS and p-C. Meanwhile, garlic odor failed to gain dominance in any diluted sample. Thus, DMTS was considered less important for system evaluation similar to H₂S, 2-MIB and TCA.

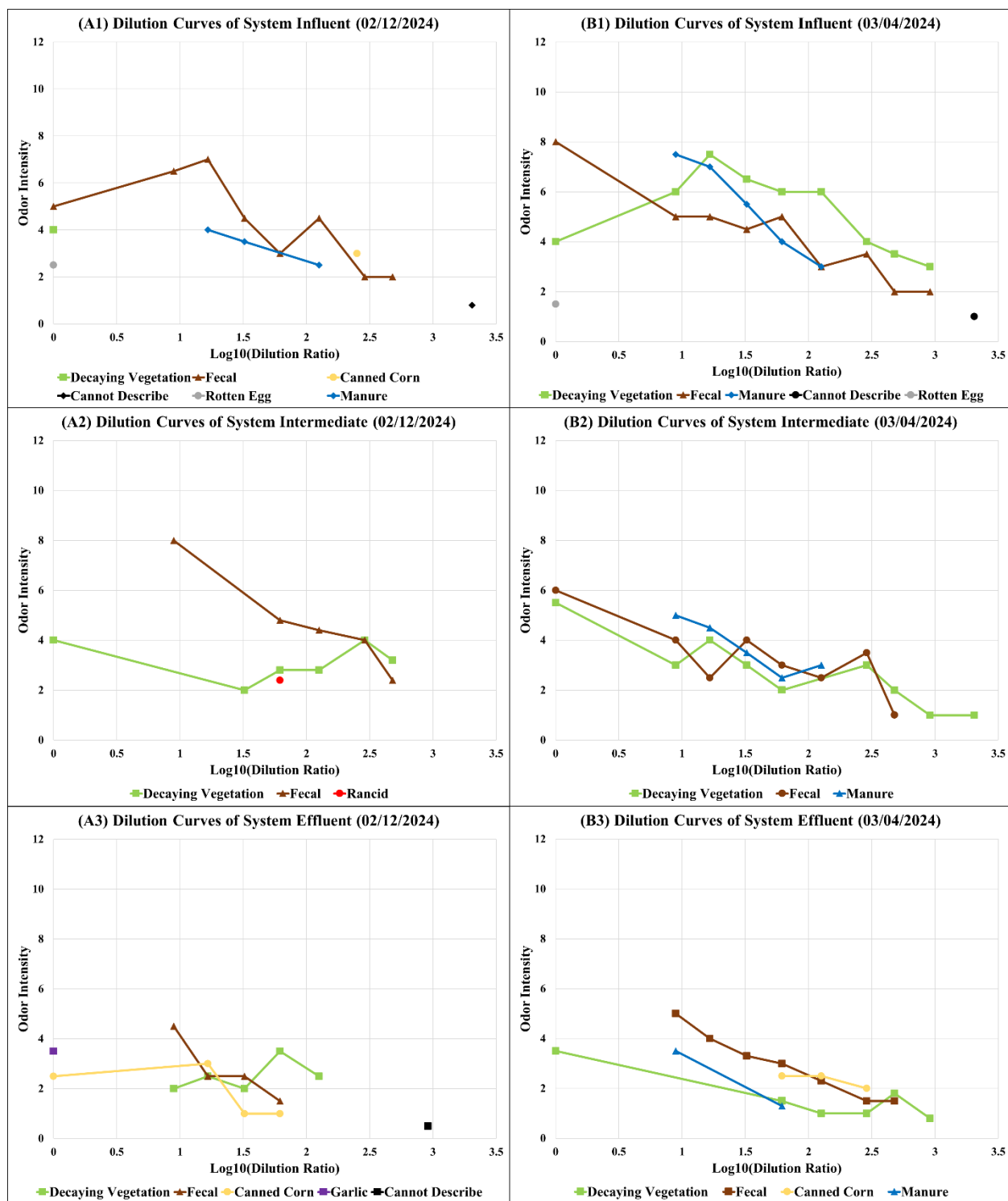


Figure 3.6. Dilution curves of system influent (1), intermediate (2) and effluent (3) samples collected on 02/12/2024 (A) and 03/04/2024 (B). Note that undiluted samples ($\log_{10}(\text{dilution ratio}) = 0$) were analyzed by direct sniffing at the sampling locations during sample collection because the olfactometer could not present samples without mixture with odorless air.

3.4.2.2. Bleach Scrubbers (1st Stage)

After the 1st stage treatment by bleach scrubbers, p-C and all sulfur compounds detected in system influent were reduced except for DMTS on 03/04/2024. The removal was consistent with lower decaying vegetation and manure odor intensities in system intermediate on 03/04/2024 throughout dilution by the OPM-modified dynamic olfactometry (Figure 3.6B2) compared to system influent on that day (Figure 3.6B1). The removal of fecal compounds in the 1st stage was highly likely since fecal odors were also weakened after the scrubbers on 03/04/2024. However, decaying vegetation and fecal odors became more intense during dilution of system intermediate sample by OPM-modified dynamic olfactometry on 02/12/2024 (Figure 3.6A2) compared to system influent as shown by Figure 3.6A1. The inconsistency was possibly the result of manure and canned corn odors elimination by the scrubbers and thus subsequent unmasking of decaying vegetation and fecal odors. Therefore, the performance of the bleach scrubbers as the 1st stage was considered to be somewhat satisfactory because the odorant load to the GAC filters as the 2nd stage was significantly reduced. However, the reduction was uneven for different sulfur compounds. Compared to H₂S removal rates after scrubbers (92% on 02/12/2024, 89% on 03/04/2024), those of MeSH (65% on 02/12/2024, 80% on 03/04/2024), DMDS (49% on 02/12/2024, 74% on 03/04/2024) and DMTS (51% on 02/12/2024, -33% on 03/04/2024) were significantly lower on both days. Despite a satisfactory removal rate of 96% on 02/12/2024, only 76% of the DMS in system influent was removed by bleach scrubbers on 03/04/2024. As discussed in Section 3.4.1, removal of MeSH, DMS and DMDS was more important compared to H₂S due to dominance of decaying vegetation and canned corn odors over rotten egg odor in all samples. As a result, performance of the 1st stage needs further improvement.

3.4.2.3. GAC Filters (2nd Stage)

By contrast, concentrations of DMS, DMDS and p-C increased after the 2nd stage (system effluent) compared to system intermediate on 02/12/2024. It counterbalanced the removal of MeSH and led to appearance of the canned corn odor as well as insufficient reduction of the decaying vegetation odor in system effluent (Figure 3.6A3) compared to system intermediate (Figure 3.6A2). As a result, a dilution ratio between 61.7 ($\log_{10}$ value – 1.79) and 126.2 ($\log_{10}$ value – 2.1) was needed to lower odor intensities to the nuisance threshold of 3. Meanwhile, the fecal odor was weakened by GAC treatment on 02/12/2024 so the responsible compounds were possibly removed during the process. On 03/04/2024, concentrations of DMS, MeSH, DMDS and p-C increased after GAC treatment. Consequently, canned corn odor not found in system intermediate appeared while manure and decaying vegetation odors persisted in system effluent. At the same time, the fecal odor was slightly enhanced by GAC treatment on 03/04/2024 (Figure 3.6B2 and Figure 3.6B3) and partially masked the decaying vegetation and manure odors. Thus, concentrations of the to-be-identified fecal compounds possibly rose after the GAC filters. A dilution ratio of 61.7 ($\log_{10}$ value – 1.79) was needed to lower the odor intensities to 3.

In conclusion, the sludge malodor treatment system underperformance was primarily caused by a malfunctional GAC 2nd stage. Specifically, odorants causing canned corn, decaying vegetation, manure and/or fecal odors exited the GAC filters at higher concentrations leading to limited reduction or even enhancement of malodors in system effluent. Meanwhile, the less than perfect performance of bleach scrubbers (1st stage) could be considered a secondary reason for system underperformance.

3.5. Discussion

3.5.1. Reasons for Malfunctional GAC Filters (Primary Problem)

Significant amount of condensed water was noticed in the system effluent duct during sampling, thus moisture adsorption by GAC and subsequent condensation on its surface were suspected. As a result, on 03/04/2024, relative humidity (RH) values of system influent, intermediate and effluent were measured and found to be 56%, 80% and 53%, respectively. Therefore, additional moisture was introduced into the air flow during bleach scrubbing (1st stage) and GAC (2nd stage) retained much of the water. The elevated humidity level in GAC influent was also present in previous studies on odor treatment by GAC filters for emissions from trickling filters and incoming trunklines of the other OCSan wastewater treatment facility (Huntington Beach, CA) as discussed by Vitko et al., (2024). Increase of DMS and DMDS concentrations after GAC filters was also observed. Besides, it was also noted that the GAC filters were likely aerobic due to continuous introduction of sludge truck loading area air into the odor treatment system. This should be confirmed in future studies.

Menon, (1995) reported that the presence of water in GAC lowered its capacity for compounds with limited solubilities such as ethyl acetate. Therefore, the adsorption capacity of the GAC filters in this study for MeSH, DMS, DMDS, p-C and fecal compounds may have been restricted by the large amount of retained water. As a result, they were prone to desorption from GAC upon competition with other compounds. On top of possible desorption of odorants, chemical and/or microbiological processes may also have contributed to the higher odorant concentrations observed after the GAC filters. For example, MeSH on activated carbon (AC) surface could be oxidized to DMDS (Bashkova et al., 2002; Bashkova et al., 2005) which could then be oxidized to methanesulfinic acid (MSIA) and then to methanesulfonic acid (MSA)

(Bashkova et al., 2002). The processes may have led to the increase in DMDS concentration after the GAC filters in this study (Table 3.5). Moreover, DMS could be aerobically formed by microorganism via methylation of H_2S (Li et al., 2023) and MeSH (Li et al., 2023; Carrión et al., 2015; Carrión et al., 2017). Similarly, p-C could be produced from toluene that has been found in sludge emissions (Fisher et al., 2019) by oxic microbiological metabolism (García-Peña et al., 2005; Whited and Gibson, 1991; Weber et al., 1995) and hydroxyl radicals (Van Buren et al., 2020). However, future research is needed to see if these reactions involving DMS and p-C formation can take place on AC surface. If so, these processes may have contributed to the higher concentrations of DMS and p-C after the GAC filters in this study (Table 3.5).

3.5.2. Reasons for Underperformance by Bleach Scrubbers (Secondary Problem)

The bleach scrubbers as the 1st stage of the odor treatment system lowered the concentrations of MeSH, DMS, DMDS, p-C and possibly the unidentified fecal compounds. However, their performance was not perfect, especially for MeSH, DMS and DMDS removal when compared to H_2S (Section 3.4.2.2). Sanchez et al., (2006) reported similar lower removal rate for MeSH compared to H_2S in caustic-bleach scrubbers and attributed the difference to a higher pK_a value for MeSH impeding its dissociation. On the contrary, Hentz Jr et al., (1992) recommended a lower pH value for removal of DMDS that does not dissociate in water by bleach scrubbing due to production of hypochlorous acid (HClO) as a stronger oxidant. The pH value of the NaClO scrubbing solution in this study was ~ 7.9 which was between the pK_a value of 9 for MeSH and the pK_{a1} value of 7 for H_2S (Sanchez et al., 2006). Therefore, the dissociation of H_2S in the NaClO scrubbing solution was likely facilitated while that of MeSH was possibly hindered, leading to the better removal of H_2S compared to MeSH. The pH value of the NaClO scrubbing solution (~ 7.9) was also higher than the optimal value of 6.5 recommended for DMDS removal

by Hentz Jr et al., (1992). It could explain the insufficient removal of DMDS and future research should examine whether the pH value of the NaClO scrubbing solution is also too high for DMS removal as well.

3.5.3. Implication

This case study serves as a proof of concept for an effective methodology to evaluate an odor treatment system suspected of underperformance. Odor intensity values determined by OPM-modified dynamic olfactometry compared to nuisance threshold can quickly determine the overall system performance. Meanwhile, odor characters and intensities obtained during OPM-modified dynamic olfactometry analysis can be basis for prioritization of compounds detected by SGC and chemical analyses. After that, prioritized compounds (primary odorants) can be quantitated throughout the system in order to identify locations of insufficient removal stage by stage. Reasons for underperformance can be proposed in the end based on the occurrences and properties of primary odorants like solubilities, reactivities and pH-dependent dissociations in this study.

Current odor evaluation relies heavily on determination of dilution to threshold (D/T) value by traditional dynamic olfactometry or triangle odor bag method and chemical analysis for common odorants (Wang et al., 2023). However, such approach leaves out odor characters at source and downwind locations as important information on possibly responsible odorants. Moreover, D/T values do not necessarily indicate the absolute odor strength (intensity) that is more directly linked to sensorial impacts on receiving public. For example, following the calculation specified by Method ASTM E679-19 (ASTM International, 2019), the D/T value of system intermediate sample taken on 02/12/2024 was 970.9 and it was lower than system effluent sample's D/T value of 1189.9. Nonetheless, the system intermediate sample (Figure

3.6A2) produced mostly higher odor intensities throughout dilution by the olfactometer than the system effluent sample (Figure 3.6A3). Specifically, a dilution ratio of 477.3~906.5 was needed to lower odor intensities produced by system intermediate sample taken on 02/12/2024 to the nuisance threshold of 3. By comparison, a dilution ratio of only 61.2~126.2 was needed for system effluent sample. As a result, system intermediate on 02/12/2024 had higher potential to create odor nuisance to downwind communities due to higher odor intensities in spite of a lower D/T value compared to system effluent. Since odor intensity reduction rates upon dilution were different from one odorant to another as exemplified by Figure 3.2, it is possible for a sample to have an odor that is both weak in terms of intensity and persistent in terms of dilution. In conclusion, OPM-modified dynamic olfactometry is superior to D/T value measurement because it extracts more information from a sample and enables more accurate understanding of its sensorial impacts.

As for chemical analysis for common odorants, high occurrence frequencies do not guarantee major contribution to overall odor nuisance by an odorous compound. For example, 2-MIB were found in all samples throughout the study. Yet, its earthy/musty odor character was not confirmed by the panel in any sample. While the application of odor activity value (OAV) defined by ratio of an odorant's concentration over its OTC to prioritize detected odorants and identify major contributors (Laor et al., 2014) should be acknowledged, a higher OAV of a compound does not always result in its more involvement in odor nuisance perception. For instance, based on quantitation results and OTC values in Table 3.5, the OAV of p-C in system influent on 03/04/2024 was 27.8~340.9, significantly lower than the H₂S's OAV of 1355.9~1600. Yet, the rotten egg odor produced by H₂S with a higher OAV than p-C was much weaker than the manure odor caused by p-C in terms of odor intensities (Figure 3.6B1). Interactions between odorants

like addition, synergy, antagonism and masking exist and are not fully understood (Wang et al., 2023). Therefore, any attempt to evaluate an odor treatment system must be checked by OPM's odor characterization so that odorants can be prioritized based on their true sensorial effects and removal of compounds that really matter can be studied.

Future application of this methodology in other case studies involving other odor treatment systems is warranted due to the ability of this unique combination of sensory and chemical methods over mainstream odor evaluation methods. In this way, the method can be further improved. For example, the challenge in odorant identification due to co-elution during GC/MS full scan analysis observed in this study may be overcome by improved compound separation by chromatography. A potential candidate is the application of multi-dimensional GC (MDGC). Compared to a single GC before a detector used in this study, MDGC using heart-cut is able to achieve better separation of compounds (Hayes et al., 2023). However, whether MDGC can result in better identification of odorants should be tested in future case studies.

3.6. Conclusion

OPM-modified dynamic olfactometry, SGC and chemical analyses (GC/MS and sulfur analyses) were combined and applied to evaluation of a 2-stage odor treatment system suspected of underperformance. Overall system performance was found to be unsatisfactory due to odor intensities exceeding nuisance threshold. Decaying vegetation, canned corn, fecal and manure odors were found to be main odors in this study. The characters led to the discovery of MeSH, DMS, DMDS, p-C and to-be-identified fecal compounds as primary chemical causes of odor nuisance. By quantitation of these primary odorants stage by stage, odorant desorption and/or production within GAC filters was found to be the primary cause of system inefficiency while the less than perfect performance of bleach scrubbers was a secondary cause. The methodology

proved to be effective in odor treatment system evaluation. More importantly, this unique combination of sensory and chemical methods was also proved to be superior to traditional odor evaluation methods including D/T value measurement and chemical analysis of common odorants. Specifically, this methodology was able to report odor characteristics, to understand odor nuisance more accurately using odor intensities and to prioritize odorants more effectively. Thus, this approach should be further applied to other case studies involving odor treatment systems in the future.

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Chapter 4

Drinking Water Taste and Odor Pattern Requires the Use of Flavor Profile Monitoring

4.1. Abstract

Taste and odor (T&O) events in Summit Water Treatment Plant (SWTP) water was once attributed to only the California State Water Project (SWP) supply via Silverwood Lake due to its high geosmin (GEO) and 2-methylisoborneol (2-MIB) concentrations mainly in summer and fall seasons. However, after application of flavor profile analysis (FPA) a recurring odor other than earthy/musty expected from GEO and 2-MIB was noticed. The odor was characterized as moldy and 2-isopropyl-3-methoxypyrazine (IPMP) was identified as its cause by gas chromatography/mass spectrometry (GC/MS) and Sensory GC methods. Later monitoring showed that IPMP and its moldy odor mainly originated from Lytle Creek supply that was a second water source for SWTP during fall and winter. As a result, previous conclusions on spatial and temporal (summer and fall seasons) patterns of T&O events required further investigation. For the same reason, IPMP was selected together with GEO and 2-MIB as target compounds in a subsequent granular activated carbon (GAC) feasibility study. The case study serves as a precaution against targeting GEO and 2-MIB only for drinking water T&O investigation and mitigation efforts in spite of the apparent popularity of such approach. Instead, complete understanding of drinking water T&O patterns requires using the FPA method. The nose knows.

4.2. Introduction

Geosmin (GEO) and 2-methylisoborneol (2-MIB) are earthy/musty compounds often caused by algal or cyanobacterial blooms and they are the most commonly targeted biogenic drinking water taste and odor (T&O) chemicals by regulations, monitoring and studies due to their omnipresence and low odor threshold concentrations (OTCs) (Paulino et al., 2023). By comparison, other biogenic T&O compounds rarely receive the same attention by water utilities

(Zhu et al., 2022). For example, this monitoring approach was adopted to evaluate T&O occurrences in the Summit Water Treatment Plant (SWTP) (Rialto, CA, USA) source water from California State Water Project (SWP) supply via Silverwood Lake and the Lytle Creek water supply. It was concluded that SWTP T&O issues were mainly brought by SWP supply due to high GEO and 2-MIB concentrations in Silverwood Lake in summer and fall (Figure 4.1). By contrast, Lytle Creek supply was deemed superior with less GEO and 2-MIB. Together with the fact that the Lytle Creek supply was more limited in summer and fall due to drought, T&O events were expected mostly during the two seasons. However, sole GEO and 2-MIB analysis could lead to unexpected and unexplained T&O events resulted from other T&O compounds (Zhu et al., 2022). Therefore, conclusions regarding T&O occurrences in SWTP sources could be incomplete. This would then lead to a flawed feasibility study planned by SWTP to upgrade the plant for T&O removal using granular activated carbon (GAC) filters. As a result, this study was initiated in order to identify all T&O compounds and evaluate T&O occurrences in a comprehensive manner before the GAC feasibility study.

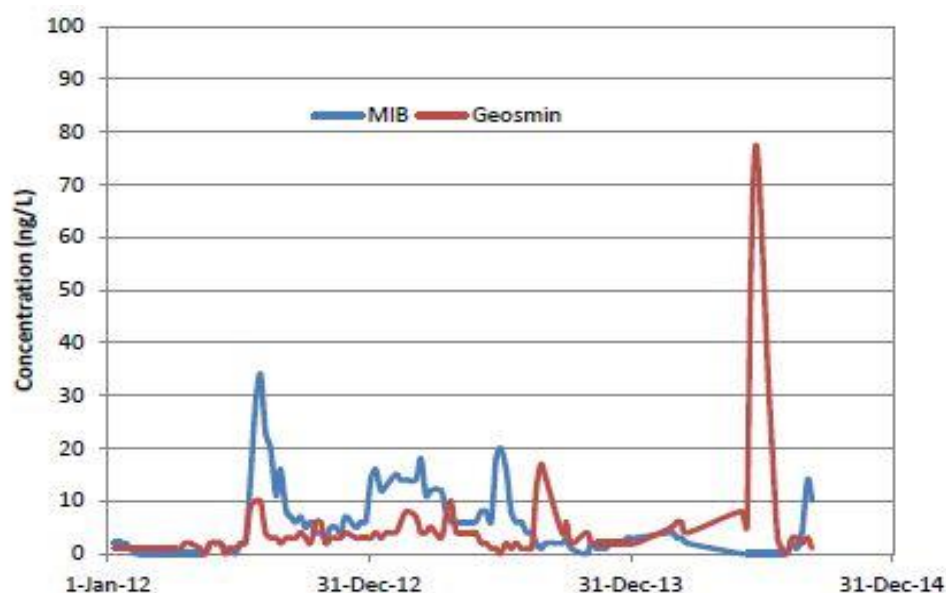


Figure 4.1. GEO and 2-MIB monitoring data in Silverwood Lake during 2012~2014.

The vast number of potential T&O compounds in drinking water and their often extremely low OTCs as exemplified by Zahraei et al., (2021) present overwhelming challenges to monitor all T&O compounds with chemical analysis only. On the other hand, sensory analysis like flavor profile analysis (FPA) enables comprehensive T&O impacts evaluation regardless of responsible compounds. As an accepted standard method, FPA determines T&O characters defined by specific standards as well as intensity values using a scale standardized by taste standards at multiple concentrations (APHA et al., 2023). Common T&O characteristics and their responsible compounds in a specific setting such as drinking water are often summarized by a T&O wheel (Figure 4.2) to facilitate panel training and sample analysis. As for intensity values, the odor intensity value caused by a single compound has been shown to be linear with the logarithmic value of odorant concentration, known as Weber-Fechner law (Fechner, 1860). Weber-Fechner curves are often used to illustrate the relationship (Figure 4.3). The standardization efforts result in better consistency across individuals and panels that evaluate the same sample. As a result, changes of T&O characters and intensities in water over time that indicate shifts in T&O compounds' compositions and concentrations can be used to direct monitoring, treatment and regulation efforts. Hence, FPA was applied to SWTP water to better understand T&O occurrences and test previous conclusions based solely on GEO and 2-MIB monitoring.

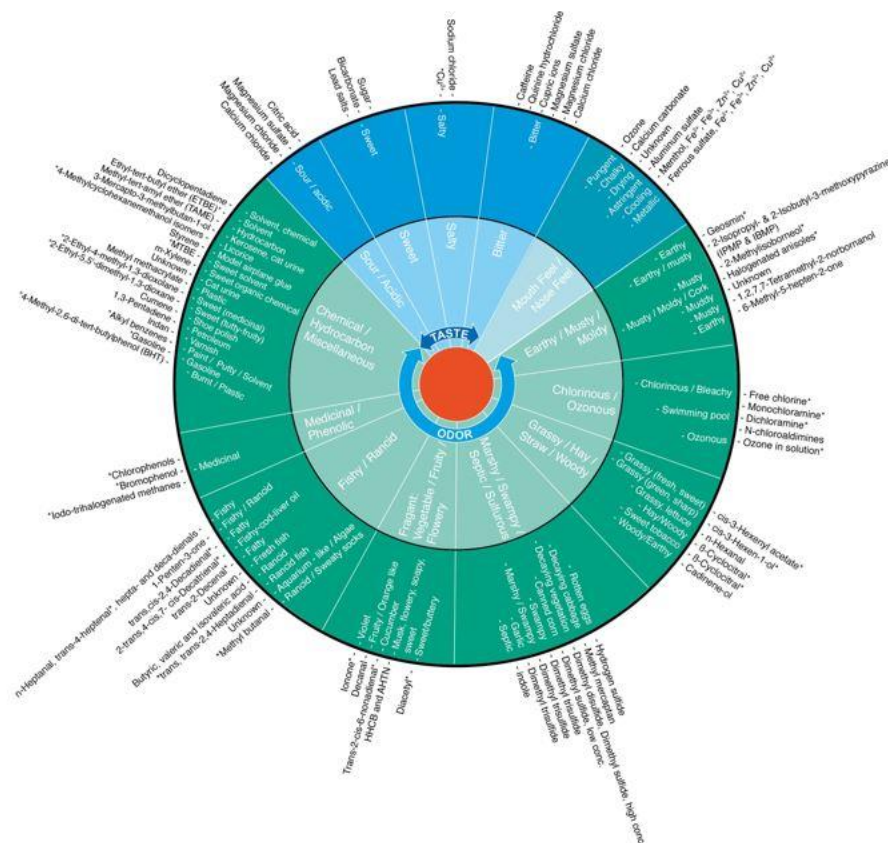


Figure 4.2. Drinking water T&O wheel (Suffet et al., 2019).

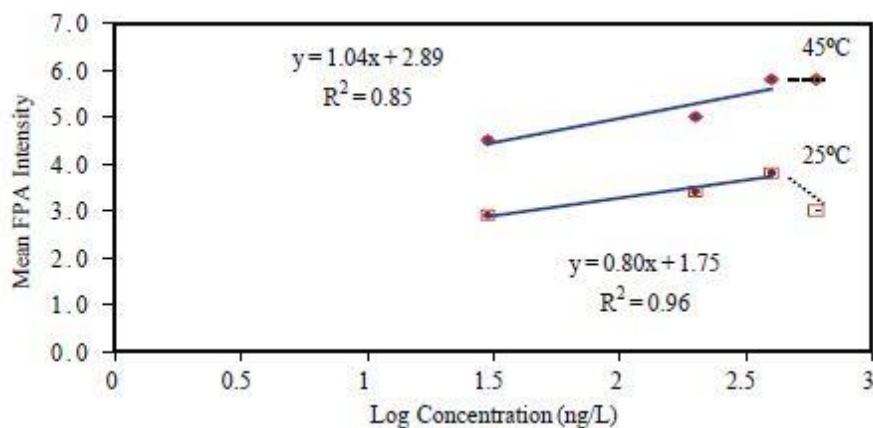


Figure 4.3. Weber-Fechner curves for (±)-GEO in water at 25°C and 45°C (Whelton and Dietrich, 2004). Note that odor intensity was linear with logarithmic value of (±)-GEO concentration at both temperatures.

Finally, in order to identify T&O compounds other than GEO and 2-MIB in SWTP water, gas chromatography/mass spectrometry (GC/MS) combined with Sensory GC analysis was applied

in this study. Sensory GC separates odorous compounds within a mixture with the GC column and then presents the odorants to a human panelist so that the odorants can be sensorially characterized one by one while parallel GC/MS analysis reveals the identities of perceived compounds (Hayes et al., 2023). In this way, odors identified by FPA can be attributed to compounds detected by GC/MS analysis with matching characters perceived by Sensory GC. Moreover, the presence of an odorant within a mixture can be discovered even if its odor was masked by other odors from the sample during the FPA.

4.3. Methods

4.3.1. Chemicals and Materials

100 µg/mL (±)-GEO and 2-MIB methanol (MeOH) solutions and water (suitable for high-performance liquid chromatography (HPLC)) were purchased from Sigma-Aldrich Inc. (St. Louis, MO, USA). p-Bromofluorobenzene (p-BFB) (>98.0%), sodium omadine (>97.0%) and 2-isopropyl-3-methoxypyrazine (IPMP) (>98.0%) were obtained from TCI America (Portland, OR, USA). HPLC-grade MeOH ($\geq 99.9\%$), sodium bisulfite (NaHSO_3) ($\geq 58.5\%$) and sodium chloride (NaCl) ($\geq 99.0\%$) were purchased from Fisher Scientific (Hanover Park, IL, USA). 70% isopropyl alcohol (iPOH) solution was purchased from Kroger Co. (Cincinnati, OH, USA). The water suitable for HPLC was only intended for Sensory GC humidifier refills (Section 4.3.5.2). In other cases, water produced by a Milli-Q water purification system (Millipore-Sigma, Burlington, MA, USA) was used and was referred to as Milli-Q water.

Mixed cellulose esters (MCE) membrane filters (pore size – 0.22 µm) were obtained from Millipore-Sigma (Burlington, MA, USA). Teflon-faced silicone septa of 22 mm, 1 cm Stableflex™ 50/30 µm DVB/CAR/PDMS solid-phase microextraction (SPME) fiber assemblies and their manual holders were purchased from Supelco (Bellefonte, PA, USA). Teflon-coated

octagon magnetic stirrer bars of $5/8 \times 5/16$ ” were bought from VWR International, LLC (Radnor, PA, USA).

Prior to use, all 1 L amber glass bottles with Teflon-lined caps were washed by Liqui-Nox[®] critical-cleaning liquid detergent (Jersey City, NJ, USA), tap water and Milli-Q water. All magnetic stirrer bars, 65 mL amber glass sample vials together with their caps were rinsed by HPLC-grade MeOH, tap water and Milli-Q water and all 250 mL Erlenmeyer flasks as well as watch glasses were rinsed by 70% iPOH solution, tap water and Milli-Q water.

4.3.2. Water Utility Overview

The SWTP has a conventional filtration water treatment process that includes prechlorination, coagulation, multi-zone flocculation, clarification, rapid sand filtration and then chlorination. It receives water from SWP supply via Silverwood Lake and/or Lytle Creek supply. Though Lytle Creek supply was deemed more preferable due to lower GEO, 2-MIB and disinfection by-products (DBPs) precursors levels, its availability is limited in drier summer and fall seasons. Therefore, the SWP supply is dominant in SWTP influent during these months (Table 4.1).

Table 4.1. Source water composition for SWTP during the course of the study.

Period		07/2022~11/2022	11/2022~12/2022	01/2023
Source Water Composition (%)	Silverwood Lake	92	85	0
	Lytle Creek	8	15	100

4.3.3. Sampling, Delivery and Storage

Clarified water before rapid sand filtration was sampled from 07/25/2022 to 01/09/2023. The sampling frequency was twice a week during 07/25/2022~08/14/2022. For the rest of the study, sampling was conducted weekly. SWTP filtration effluent was also sampled weekly during 10/17/2022~01/09/2023 in the hope that it better represented the product water distributed to the

consumers. However, findings from SWTP filtration effluent were limited due to high residual chlorine concentration (See Section 4.3.4.2). During the week of 08/22/2022 and that of 11/28/2022, no sample was collected due to limited staff availability. During sample collection, a 1 L and a 65 mL amber glass bottles with Teflon-faced cap-liners were used to hold original sample and preserved sample using 90 μ L 3.2% sodium omadine solution, respectively, with minimal headspace. All samples were sent to UCLA overnight in a cooler box with ice bags. Upon receipt, the samples were filtered through 0.22 μ m MCE filters and then stored in the dark at $\sim$ 4°C until analysis.

4.3.4. Flavor Profile Analysis (FPA)

4.3.4.1. Panelists Screening and Training

Before training, all candidates for the panel were screened by University of Pennsylvania Smell Identification Test[®] (UPSIT[®]) (Sensonics International, Haddon Heights, NJ, USA). Potential Panelists with severe microsmia or total anosmia were excluded from the sensory panel.

All panelists were trained according to Standard Method 2170 B (APHA et al., 2017). Specifically, odor reference standards and intensity scale defined by sugar solutions in the method were applied to standardize panelists' description of an odor's character and its intensity value, respectively. Vocabulary modifications were made to the original method based on panel consensus during training. The odor characters for GEO, 2-MIB and IPMP were set as earthy, musty and moldy, respectively. Trainees familiarized with the standards until they were able to give correct and reproducible characterization of random odor references. All references were available upon request during FPA of a sample.

4.3.4.2. Sample Analyses

FPA was applied to every delivered sample without preservative within 48 hours after its filtration by MCE filters according to Standard Method 2170 B (APHA et al., 2017). Specifically, 50 mL sample was added to a 250 mL Erlenmeyer flask. Then the flask was covered by a watch glass and heated to 45°C before panel analysis. Though a panel was supposed to consist of 4 or 5 panelists, a few samples were processed by a smaller panel due to limited personnel availability. Each analyst was reminded not to apply any perfume on the day of analysis and not to eat or drink at least 30 minutes before sample evaluation. If an odor character was reported by half or more of the panel from a sample, the odor was considered confirmed. Its character and average intensity value were recorded. When an odor was perceived by fewer than half of all examiners, the odor was only regarded as an “odor note” and recorded as such for reference without an intensity value. Taste analysis was not conducted because the samples were deemed undrinkable without adequate disinfection at the points of sampling.

Strong chlorine odor was noticed in SWTP filtration effluent samples due to chlorination applied right after filters. As a result, other odors were masked in most cases. Therefore, clarified water before filtration was chosen for T&O occurrence monitoring. Nevertheless, in cases odors other than chlorine were detected (Section 4.4.2), the results were recorded for reference.

4.3.5. GC/MS and Sensory GC Methods

4.3.5.1. Sample Extraction

Headspace SPME specified by Standard Method 6040D (APHA et al., 2017) was modified and applied to all clarified water samples in the study. For GC/MS analysis, 5.0 µL 500 µg/L p-BFB MeOH solution was added to each sample before extraction as the internal standard. Meanwhile, no internal standard was applied for Sensory GC method. 2-Isobutyl-3-

methoxypyrazine (IBMP) and IPMP were previously detected in drinking water samples (Zahraei et al., 2021). Therefore, they were not adopted as internal standard and surrogate as per Standard Method 6040D (APHA et al., 2017). The StableFlex™ 1 cm 50/30 µm DVB/CAR/PDMS SPME fiber used in the study was previously conditioned at 270°C for 30 minutes. Sample volume, headspace volume, temperature, extraction time, stirring speed and NaCl addition were 45 mL, 20 mL, 65.0±1.0°C, 35 minutes, 180±10 rpm and 15.00 g, respectively. Unpreserved samples were extracted and analyzed by GC methods within a week after filtration. However, due to the time-consuming nature of headspace SPME and GC processes, a few samples preserved by sodium omadine were extracted within a month after their filtration in case of a backlog. SWTP filtration effluent collected on 10/25/2022 was extracted in the same manner (Section 4.4.2) except that 2.0 µL 145 g/L NaHSO₃ solution was injected into the sample before extraction as a dechlorination agent.

4.3.5.2. GC/MS Full Scan with Parallel Sensory GC Analysis

After headspace SPME, compounds sorbed to the SPME fiber were introduced into one of the 2 parallel 60 m DB-5MS GC columns (diameter – 0.25 mm, film thickness – 0.25 µm) (Agilent Technologies, Santa Clara, CA, USA) within a Varian 450-GC system (Varian, Inc., Walnut Creek, CA, USA) through a 1177 split/splitless capillary injector. 99.9999% helium (Airgas, Inc., Radnor, PA, USA) was used as the carrier gas. The injector temperature was 260°C, extracted compounds desorption time was 15 min and the split vent was off for the first minute after injection before turned on with a split ratio of 100 to minimize peak tailing. Column flow rate was 1 mL/min while the column oven temperature was held at 50.0°C for 2 min after injection before raised at a rate of 8.0°C/min to 260.0°C where it was held for 1.75 min.

For GC/MS full scan analysis, eluted compounds from the GC column were introduced into a Varian 220-MS system (Varian, Inc., Walnut Creek, CA, USA) where electron ionization (EI) at 70 eV was applied. Then, the produced ions with mass to charge ratio (m/z) within 41~260 were scanned at a frequency of 1 Hz. MS system temperature setpoints were trap - 150°C, manifold - 40°C and transfer line - 270°C. As for Sensory GC analysis, odorous compounds separated by the other GC column were combined with humidified air for odor fatigue prevention and then presented to a human analyst at a sniffing port. Elution time of each odorant, its odor character and peak intensity value were recorded. Odorant identification was achieved by matching its retention times (RTs) in both GC/MS and Sensory GC systems, its odor character at sniffing port and its mass spectrum obtained by MS system with those of purchased standard chemical.

4.3.5.3. GC/MS Selected Ion Monitoring (SIM)

GC/MS SIM was used to quantitate known odorants in every clarified water sample where an odor was confirmed by FPA. The procedure was the same with GC/MS full scan analysis except that the ions produced by EI were analyzed under selected ion scan (SIS) mode during the elution windows of compounds for quantitation (Table 4.2).

Table 4.2. Details of Selected Ion Monitoring for compound quantitation.

Compound Quantified	Elution Window (min) ¹	Ions Monitored (m/z) ²	Samples Analyzed
p-BFB (Internal Standard)	9.50~11.00	174.0 ³ , 95.0, 176.0, 75.0, 50.0	All Sampled Analyzed
IPMP	13.00~14.00	137.0 ³ , 152.0, 124.0, 138.0, 109.0	Samples Taken on and after 11/01/2022 ⁴
2-MIB	15.50~16.50	95.0 ³ , 93.0, 107.0, 108.0, 135.0	All Sampled Analyzed
GEO	19.00~20.50	112.0 ³ , 126.0	All Sampled Analyzed
¹ SIS was applied during the elution windows. Full scan mode specified by Section 4.3.5.2. was used for the rest of the 30min analysis. ² An isolation window of 3.0 (m/z) was adopted for each ion monitored under SIS mode. ³ Primary ions whose peak areas were used for quantitation. ⁴ IPMP was quantitated only after its discovery in SWTP filtration effluent on 10/25/2022 (Section 4.4.3).			

External calibration was conducted for compound quantitation using standard samples containing GEO, 2-MIB and IPMP at different levels. The linear range, limit of detection (LOD) and limit of quantitation (LOQ) for each analyte is shown in Table 4.3.

Table 4.3. Linear ranges, detection and quantitation limits of analytes.

Analyte	Linear Range (ng/L)	Limit of Detection (LOD) ¹ (ng/L)	Limit of Quantitation (LOQ) ² (ng/L)
IPMP	0.5~120 ³	0.5	1.5
2-MIB	2.5~120 ³	3.3	8.6
GEO	0.5~120 ³	0.2	0.5
¹ LOD was defined by a signal to noise ratio (S/N) of 3. ² LOQ was defined by a S/N of 10. ³ The upper limits of the linear ranges may have been higher than 120 ng/L but the determined linear ranges were sufficient for the study.			

4.4. Results

4.4.1. GEO and 2-MIB Occurrence

The occurrence of the earthy/musty odors expected from GEO and 2-MIB in clarified water are shown in Figure 4.4. 2-MIB was not detected by GC/MS SIM throughout the study so it is not included in Figure 4.4. Both GEO concentration and earthy/musty odor intensity were higher in summer before their gradual decline throughout fall and winter months. Since the ratio of SWP supply water via Silverwood Lake in SWTP influent was the highest in summer (Table 4.1), results shown by Figure 4.4 are consistent with pre-study conclusions that SWTP T&O problems were mostly attributed to Silverwood Lake water and were expected mainly in summer and fall months. However, this deduction relied on the assumption that no recurring odorant other than GEO and 2-MIB was present.

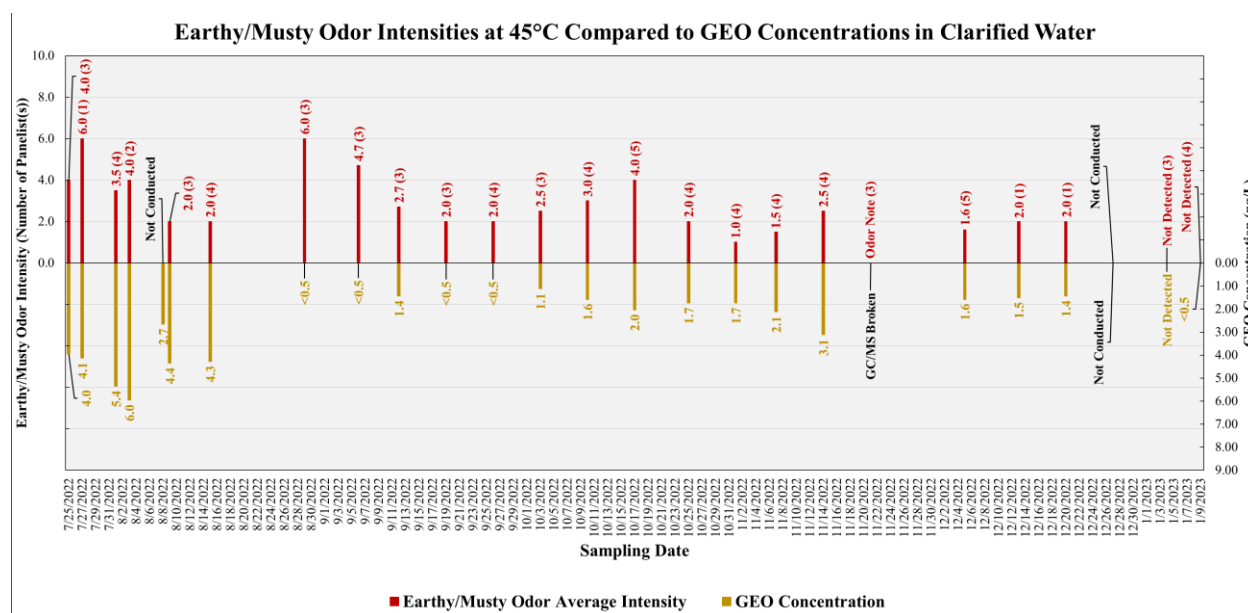


Figure 4.4. Average intensity of earthy/musty odor expected from GEO and/or 2-MIB at 45°C (number of panelist(s) present) (upper half) and GEO concentration (lower half) in clarified water samples. 2-MIB was not detected by GC/MS SIM throughout the study. Some scheduled analyses were not conducted due to unavailable, missing and/or broken bottles during sampling, delivery and/or analysis.

It should be noted that discrepancies between strong earthy/musty odor and low GEO concentration existed in 08/2022 and 09/2022. Presence of 2-MIB in samples may have played a role due to its relatively high LOD of 3.3 ng/L by GC/MS SIM compared to its reported OTC values of 1.2 ng/L and 1.3 ng/L at 45°C by Piriou et al., (2009). If it was the case, FPA demonstrated superior sensitivity compared to GC/MS SIM for earthy/musty events monitoring.

4.4.2. IPMP Identification

A moldy odor was confirmed by a panel of 4 with an average intensity of 4.0 in SWTP filtration effluent sample collected on 10/25/2022. It was clearly distinguished from earthy/musty odor by GEO and/or 2-MIB due to available odor references for the panel (Section 4.3.4.1). In order to identify the compound responsible for the moldy odor, GC/MS full scan analysis and parallel Sensory GC were conducted on the sample. The moldy odor was perceived by Sensory

GC analysis and its elution time matched that of purchased IPMP, a moldy odorous compound. In addition, a peak was noted in GC/MS full scan chromatogram (Figure 4.5). Its elution time and mass spectrum matched those of purchased IPMP as well. Therefore, presence of IPMP causing moldy odor in SWTP water was confirmed.

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Overlaid Chromatogram Plots

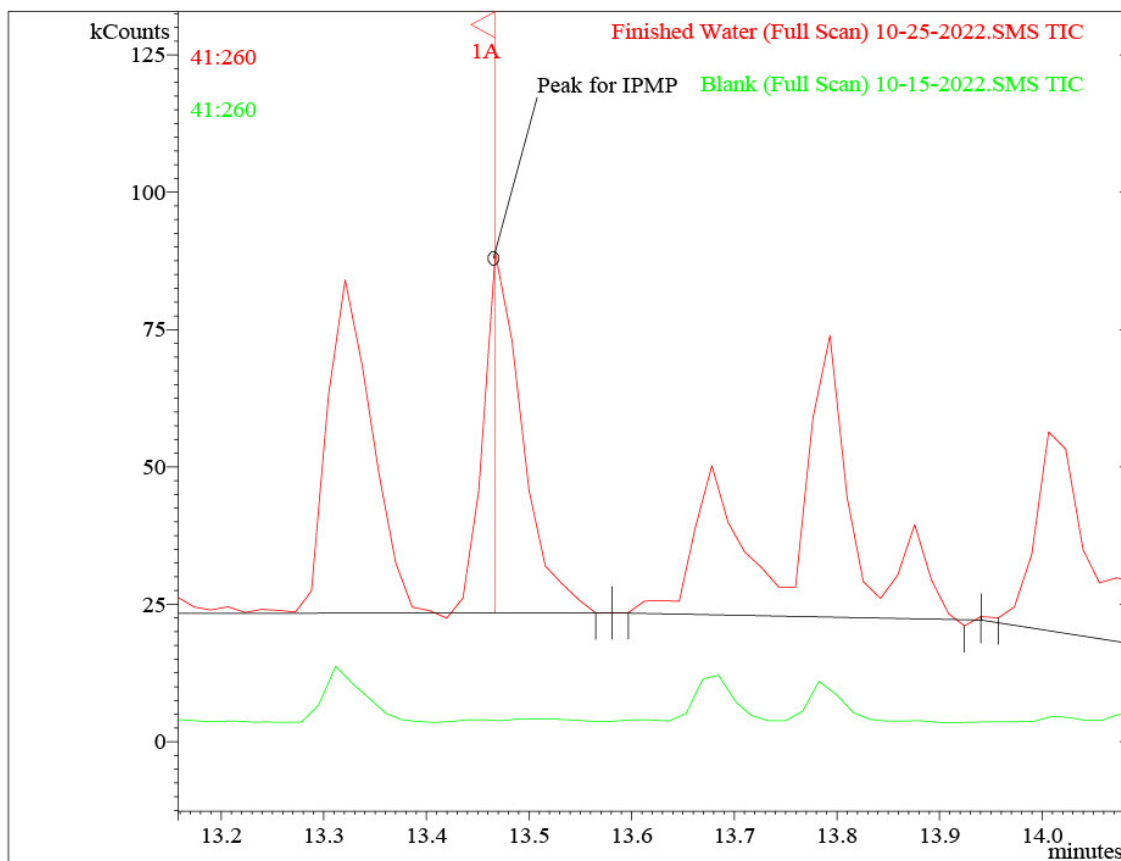


Figure 4.5. Peak of IPMP in GC/MS full scan chromatogram for SWTP filtration effluent (red) sampled on 10/25/2022. The chromatogram was overlaid with that acquired from GC/MS full scan analysis of Milli-Q water as background reference (green).

At this point, an odorous compound other than GEO and 2-MIB was found. Validation of pre-study conclusions on T&O spatial (Silverwood Lake) and temporal (summer and fall) distribution hinged on occurrence pattern of IPMP compared to GEO and 2-MIB.

4.4.3. IPMP Occurrence

Beginning 11/01/2022, GC/MS SIM was modified to include IPMP quantitation (Table 4.2). Before then, IPMP was not quantitated because its presence was unknown until 10/25/2022. IPMP concentration since 11/01/2022 and average intensity of moldy odor expected from IPMP throughout the study in clarified water are shown in Figure 4.6. FPA clearly showed a higher sensitivity toward IPMP than GC/MS SIM, leading to moldy smell confirmation with average intensity of 1.5 on both 11/07/2022 and 01/09/2023 without IPMP instrumental detection. The discrepancy is consistent with an extremely low OTC of 0.2 ng/L at 40°C previously reported for IPMP by Young et al., (1996) compared to its LOD of 0.5 ng/L by GC/MS SIM (Table 4.3).

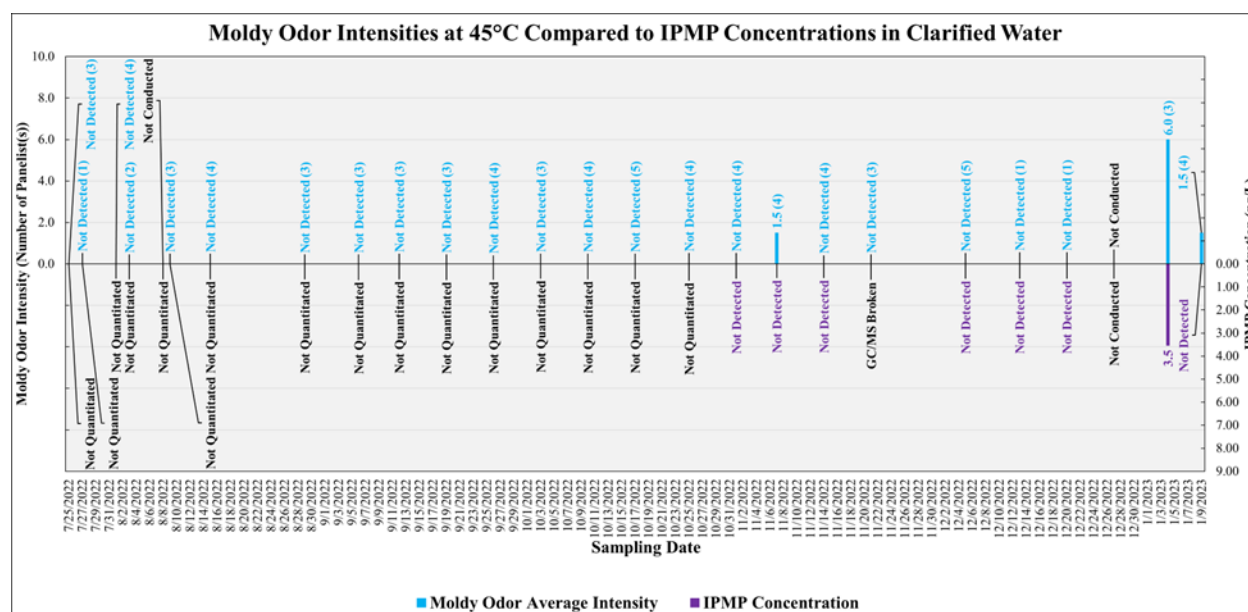


Figure 4.6. Average intensity of moldy odor expected from IPMP at 45°C (number of panelist(s) present) (upper half) and IPMP concentration (lower half) in clarified water samples. IPMP quantitation by GC/MS SIM was not conducted on samples taken before 11/01/2022. Some scheduled analyses were not conducted due to unavailable, missing and/or broken bottles during sampling, delivery and/or analysis.

Moldy odor caused by IPMP was absent throughout the summer before its occasional appearance in fall and winter months. Because IPMP was not quantitated before 11/01/2022, it

was still possible that IPMP occurred in summer but its moldy odor could have been masked by stronger earthy/musty odor. To test the hypothesis, IPMP perception by Sensory GC was referred to as shown in Figure 4.7. The odorants within the samples were first separated before their presentation to the analyst. Therefore, the absence of the moldy odor of IPMP could no longer be explained by interference from other compounds. In addition, Sensory GC was more sensitive toward IPMP than GC/MS SIM because IPMP was perceived by Sensory GC in samples where GC/MS SIM results were negative (11/07/2022, 11/14/2022, 12/05/2022 and 12/20/2022).

Sensory GC results clearly showed that IPMP was absent in summer before its frequent occurrence in fall and winter. During fall months, moldy odor by IPMP was covered up by other odors from time to time (11/14/2022, 12/05/2022 and 12/20/2022) but the masking effect wore off in winter due to lower GEO and 2-MIB levels. The appearance of IPMP coincided with periods with higher percentage of Lytle Creek supply in SWTP influent (Table 4.1). Thus, Lytle Creek supply was the apparent main IPMP contributor rather than SWP supply via Silverwood Lake.

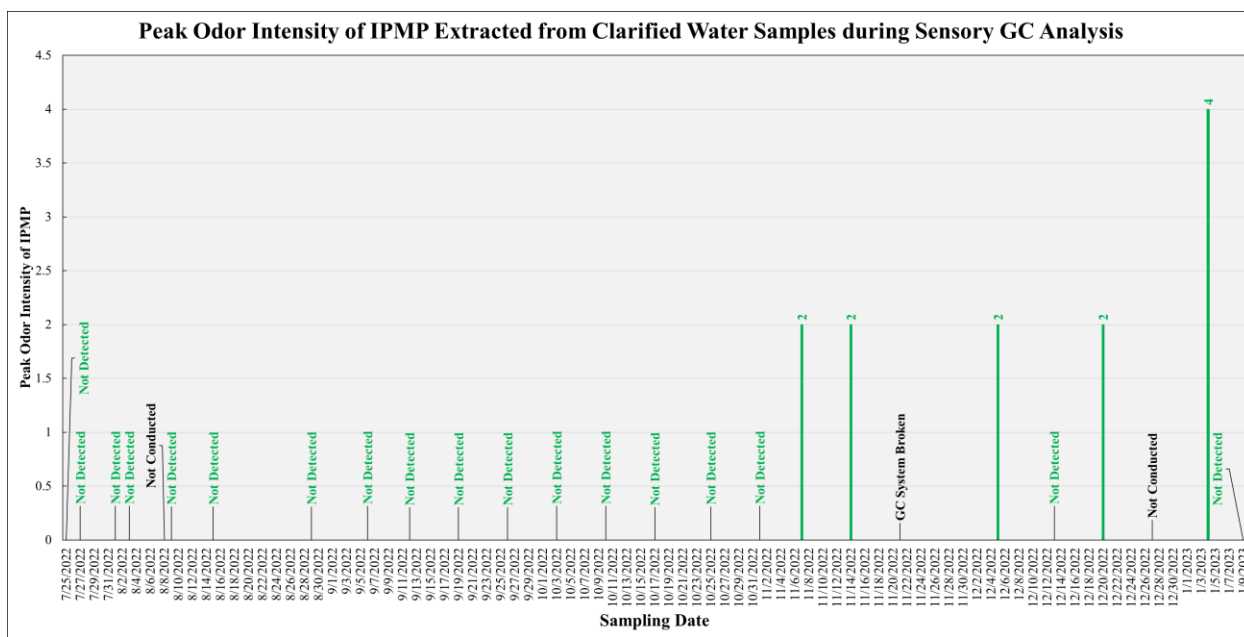


Figure 4.7. Perceptions of IPMP by Sensory GC analysis of clarified water samples. Note that IPMP was considered detected by Sensory GC when moldy odor was perceived at the sniffing port and its elution time matched that of purchased IPMP compound. Some scheduled analyses were not conducted due to unavailable, missing and/or broken bottles during sampling, delivery and/or analysis.

In conclusion, IPMP was found as another recurring odorant and its spatial and temporal patterns were different from those of GEO and 2-MIB. As a result, pre-study conclusions regarding T&O occurrence were questionable. In addition, later feasibility study of GAC filtration would need to take IPMP removal into consideration just like GEO and 2-MIB.

4.5. Discussion

4.5.1. Source of IPMP

GEO and 2-MIB originate from a wide range of sources including algae, cyanobacteria, actinomycetes and fungi (Zahraei et al., 2021). By contrast, IPMP is produced by soil organisms like actinomycetes (Khiari et al., 1997). Cotsaris et al., (1995) reported IPMP appearance from algae *A. formosa* but attributed its production to fungi or bacteria sorbed to the algal cells. As a result, IPMP occurrence seems related to sediment disturbance (Zhang et al., 2016).

Discharge rate of Lytle Creek throughout the study is shown in Figure 4.8. Every incident of IPMP detection by Sensory GC (Figure 4.7) and/or perception of its moldy odor by FPA (Figure 4.6) was preceded by a sudden surge and drop of creek flow rate several days earlier. Meanwhile, absence of IPMP in summer coincided with stable and low Lytle Creek discharge rate. Therefore, IPMP occurrence was most probably caused by abrupt change in Lytle Creek flow and subsequent sediment disturbance. Future study should examine the hypothesis by long-term monitoring of Lytle Creek IPMP concentration, turbidity and flow rate in order to see if sharp fluctuation of creek flow always leads to increase in both turbidity (sediment disturbance) and

IPMP level. If so, Lytle Creek flow rate data may provide early warning to SWTP as the recipient to remove IPMP in its influent.

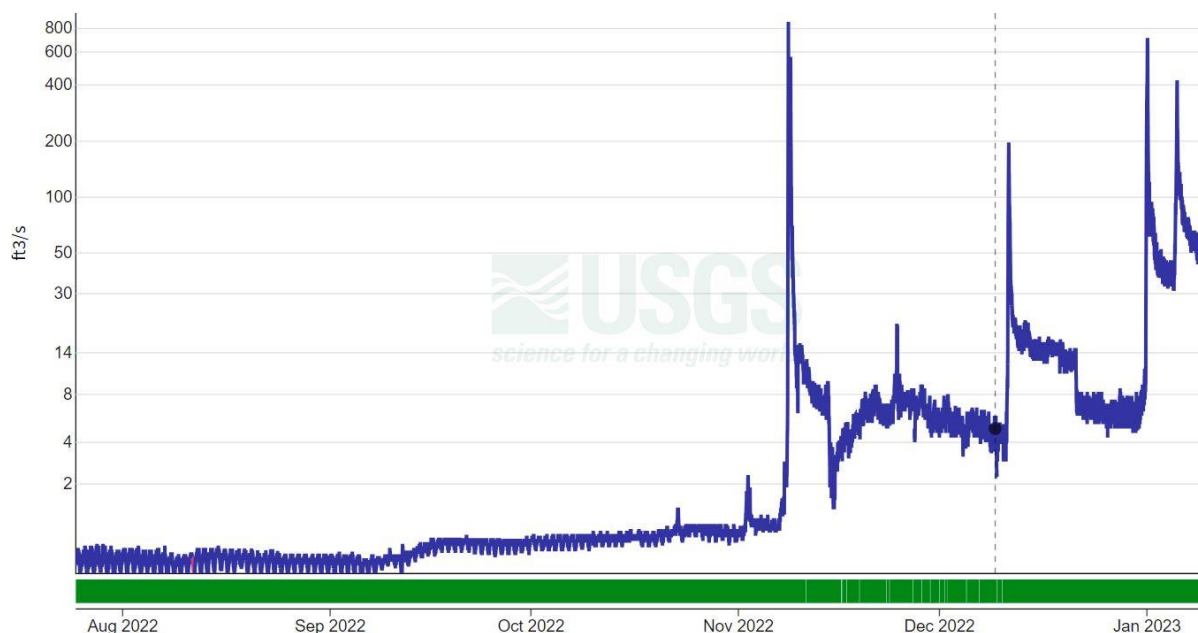


Figure 4.8. Discharge rate of Lytle Creek from 07/25/2022 to 01/09/2022 (USGS, 2022a).

4.5.2. Implications

GEO and 2-MIB are the most common T&O compounds in water worldwide (Devi et al., 2021). Thus, their occurrence in water sources have been exclusively evaluated in order to understand T&O events (Chislock et al., 2021; Goodling, 2021; Lee et al., 2020; Hooper, 2023; Franklin et al., 2023; Lee et al., 2023; Jeong Hwan et al., 2023; Howard, 2020; Hooper et al., 2023). However, their prevalence does not necessarily rule out importance of other T&O compounds. Before this study, historical GEO and 2-MIB data led to belief that SWP supply via Silverwood Lake was the primary T&O source for SWTP and events mainly took place in summer and winter. However, application of FPA to clarified water successfully captured the presence of moldy odor that could not be attributed to earthy/musty GEO and 2-MIB. Analysis by GC/MS combined with Sensory GC identified IPMP as the culprit. More importantly, later

monitoring found that IPMP and its moldy odor were formed in Lytle Creek supply instead of SWP supply and their occurrence took place in fall and winter. Therefore, previous conclusions that T&O events originated from SWP supply in summer and fall were no longer certain.

At the time of the study, a plan to control T&O problems in SWTP water using GAC filtration was under consideration. Without knowledge of IPMP's presence and patterns, mistakes might be made in future T&O mitigation efforts. To begin with, removal of T&O compounds from SWTP water would be deemed unnecessary in winter and spring due to absence of GEO and 2-MIB even though IPMP may occur, which might lead to overly optimistic cost projection. Moreover, once Lytle Creek supply becomes abundant, treatment for T&O compounds might cease. Instead, more Lytle Creek water would simply be introduced into SWTP as a cheap intervention because of its lower GEO and 2-MIB concentrations. In fact, Lytle Creek flow rate after the sampling period (07/25/2022~01/09/2023) turned out to be much higher regardless of seasons (Figure 4.9). Unaware of IPMP compound, SWTP may have chosen to aggressively increase Lytle Creek supply in summer and fall of 2023 to lower T&O intensities by dilution. Yet, Lytle Creek flow rate in summer of 2023 was not as stable as in summer of 2022 so IPMP might have been produced by sediment disturbance and then led to unexplained public complaints in summer of 2023. Thanks to the discovery of IPMP, Lytle Creek supply's T&O potential was brought to attention for the first time and the compound was included in the target compound list for later evaluation of GAC filters to removal T&O compounds.

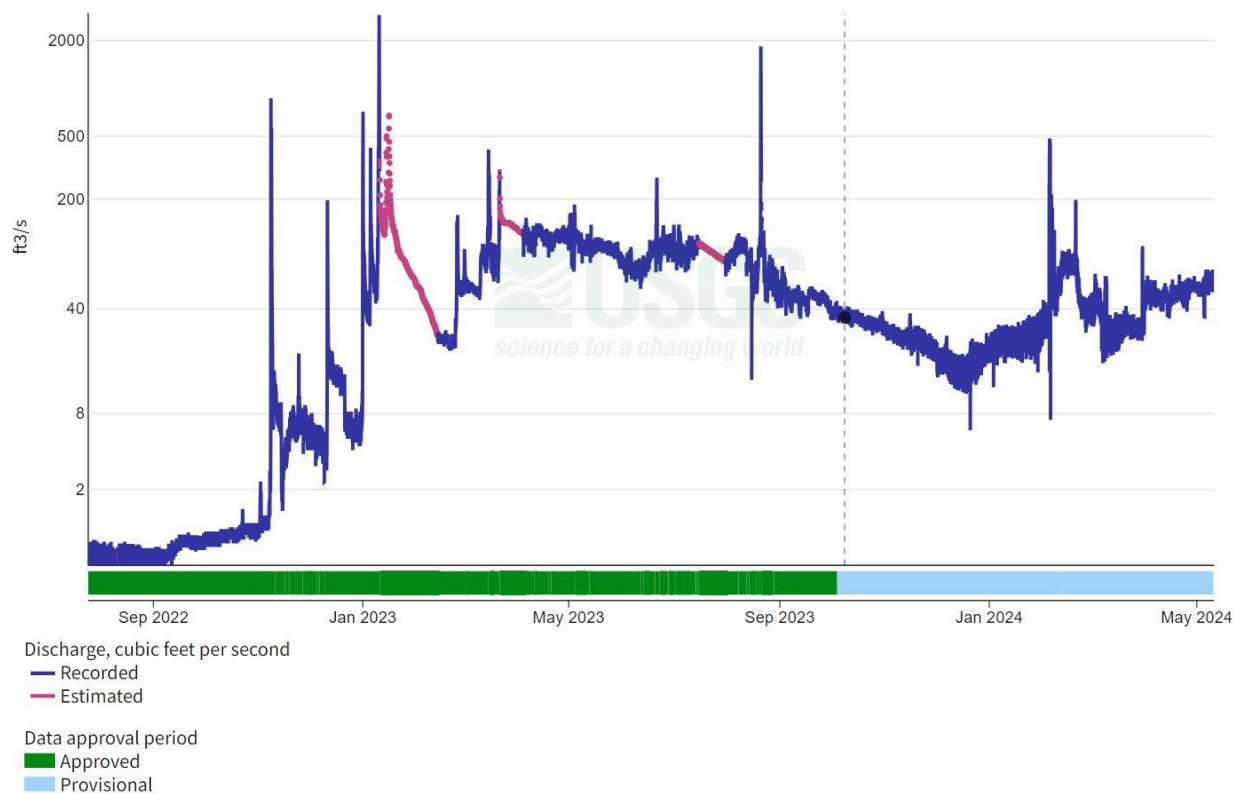


Figure 4.9. Lytle Creek discharge rate both during and after the sampling period (07/25/2022~01/09/2023) (USGS, 2022b).

Similarly, water utilities that have analyzed only GEO and 2-MIB in order to evaluate T&O occurrence should re-examine their conclusions regarding T&O spatial and temporal patterns before any mitigation attempt. T&O compounds other than GEO and 2-MIB should be identified and monitored, especially if the compounds are recurring with a pattern different from GEO and 2-MIB. FPA and GC/MS with parallel Sensory GC analysis are proposed in this study for a complete odor evaluation. Another option to find and track all T&O compounds is the use of simultaneous instrumental analysis of multiple odorous chemicals as exemplified by Bao et al., (1999) and Pochiraju et al., (2021). However, there is no guarantee that the compounds of interest for a specific utility can be exhaustively covered by such analysis. In comparison, any T&O compound missed by instrumental analysis like GC/MS method can be quickly noticed by

either an unexplained odor character perceived by FPA or detection of a smell at Sensory GC sniffing port with a character and elution time unmatched by currently monitored analytes. Moreover, FPA often possesses superior sensitivity compared to instrumental analysis as demonstrated for 2-MIB (Section 4.4.1) and IPMP (Section 4.4.3) in this study. Therefore, the methodology of this study is still more preferable for T&O occurrence assessment beyond GEO and 2-MIB.

4.6. Conclusion

In this study, application of FPA, GC/MS and Sensory GC analysis successfully revealed the presence of recurring IPMP in SWTP water. While GEO and 2-MIB mainly originated from Silverwood Lake during summer and fall seasons, IPMP was found to occur in Lytle Creek in fall and winter. The difference in occurrence patterns showed pre-study conclusions about T&O occurrence pattern based only on GEO and 2-MIB data was not reality. Such incomprehensive conclusions could lead to ineffective odor mitigation efforts by SWTP using GAC filters. The study should raise awareness of T&O compounds other than GEO and 2-MIB, their role in drinking water T&O issues and the ability of FPA to draw attention to their presence. The prevalence of targeting only GEO and 2-MIB may lead to misunderstanding of T&O occurrence, inefficient treatment and unexplained public complaints.

4.7. References

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Chapter 5

Drinking Water Odor Mitigation with Granular Activated Carbon Preloaded with Natural Organic Matter

5.1. Abstract

Drinking water taste and odor (T&O) occurrences are usually sporadic events. Moreover, pre-exposure to natural organic matter (NOM) in source water has been reported to lower granular activated carbon's (GAC's) capacity for target compounds via pore blockage. As a result, performance of T&O control by GAC filters was evaluated in a case study with pore blockage accounted for using a bench-scale column test. GAC preloaded with NOM from clarified surface source water and virgin GAC were loaded onto 2 separate columns. Elevated levels of geosmin (GEO) with earthy odor, 2-methylisoborneol (2-MIB) with musty odor and 2-isopropyl-3-methoxypyrazine (IPMP) with moldy odor were then introduced simultaneously as a simulated T&O event. Preloaded GAC showed lower capacity for GEO and 2-MIB compared to virgin GAC but surprisingly not for IPMP. The effluent concentrations of GEO, 2-MIB and IPMP were still low throughout the test despite NOM interference which was possibly counterbalanced by biodegradation. Therefore, the application of GAC was deemed feasible for this water supply. Future areas of study were suggested in order to better understand the effects of preloaded NOM on GAC's ability to removal T&O compounds, especially IPMP due to lack of research on this T&O compound.

5.2. Introduction

San Gabriel Valley Water Company's (SGVWC's) Summit Water Treatment Plant (SWTP) in Rialto, CA receives water from 2 surface water sources – Silverwood Lake and Lytle Creek. It is developing an upgrade of their water treatment plant including taste and odor (T&O) mitigation. A T&O attribution study by Yin et al., (2024) revealed geosmin (GEO), 2-methylisoborneol (2-MIB) and 2-isopropyl-3-methoxypyrazine (IPMP) as recurring T&O compounds of interest in SWTP influent. GEO and 2-MIB originated from Silverwood Lake while IPMP was formed in

Lytle Creek. Since both Silverwood Lake and Lytle Creek were sources for SWTP, concentrations of GEO, 2-MIB and IPMP could peak at the same time in the combined influent water to be treated. Therefore, a feasibility study of granular activated carbon (GAC) filters simultaneously targeting GEO, 2-MIB and IPMP was conducted using bench-scale column tests.

Application of GAC to odor mitigation has been shown to be subject to competition with natural organic matter (NOM) via direct adsorption site competition and pore blockage as reviewed by Paulino et al., (2023). Due to the possibility of pore restriction by NOM, the sequence of contact between NOM and target T&O compounds might affect GAC's performance. For example, GAC preloaded with NOM has been found with lower capacity for 2-MIB (Ho and Newcombe, 2010; Kim, 2007). As for GEO, studies have shown that longer NOM pre-exposure period can reduce its removal by GAC filters (Huang et al., 2021; Huang et al., 2019; Yuan et al., 2020). However, Doederer et al., (2018) reported little difference in GEO removal between preloaded GAC and virgin GAC due to biodegradation of GEO on preloaded GAC. Therefore, the effect of NOM pre-exposure on GEO removal by GAC is uncertain and should be evaluated in a case-by-case manner. While Velten, (2008) reported lower capacity of preloaded GAC for IPMP compared to virgin GAC, the study was limited in scope because it only involved a single water source for NOM supply. Finally, no study has been reported on removal of GEO, 2-MIB and IPMP by preloaded GAC at the same time. Since T&O episodes mostly occur in a sporadic pattern (Suffet et al., 1996), pre-exposure of GAC filters to NOM should be expected and taken into account in any feasibility study.

Huang et al., (2019) proposed and validated a procedure to determine remaining capacities of existing plant GAC filters preloaded with NOM for GEO and 2-MIB adsorption by bench-scale column tests using GAC sampled from the filters. In this study, such methodology was modified

for feasibility evaluation of future full-scale GAC filters via a small column test using GAC taken from a pilot-scale filter near the end of its service life of 6 months and thus preloaded with NOM. Another small column with virgin GAC was used as comparison. In this way, GAC pore blockage by NOM in the worst case possible for the future full-scale filters was simulated and accounted for during later feasibility evaluation and actual GAC operation at the SWTP in the future. Also, this study added to the limited knowledge regarding removal of GEO, 2-MIB and IPMP by preloaded GAC by adoption of different source water and its NOM matrix compared to previous research and introduction of the target compounds together.

5.3. Experimental Section

5.3.1. Chemicals

GEO (98.0%+) and 2-MIB (98.0%+) were acquired from FUJIFILM Wako Chemicals USA Corporation (Richmond, VA, USA). p-Bromofluorobenzene (p-BFB) (>98.0%) and IPMP (>98.0%) were purchased from TCI America (Portland, OR, USA). HPLC-grade methanol (MeOH) ($\geq 99.9\%$) and sodium chloride (NaCl) ($\geq 99.0\%$) were purchased from Fisher Scientific (Hanover Park, IL, USA). Deionized water was produced by a Milli-Q water purification system (catalog number – ZFSQ115P4) (Millipore-Sigma, USA) and referred to as Milli-Q water in this study.

5.3.2. Preloaded and Virgin GACs

FILTRASORB[®] 820 (F820) GAC (Calgon Carbon Corporation, Moon Township, PA, USA) preloaded with NOM was taken from the top 30 cm of the GAC layer in a pilot F820 GAC/sand filter (diameter – 6 in., GAC layer depth – 60 in., sand layer depth – 6 in.) right after a backwash by insertion of a 1/2” polyvinyl chloride (PVC) column. Before GAC sampling, the pilot filter received clarified SWTP influent containing various levels of total organic carbon (TOC) (Figure

5.1) from 07/11/2022 to 01/17/2023 with occasional backwash using SWTP plant filter effluent whenever a terminal head loss of 10 ft. across the media was reached. The amount of NOM preloaded to the GAC is shown by the difference between influent and effluent TOC values. It is noted that the GAC was almost saturated by NOM after 11/11/2022 reflected by similar influent and effluent TOC values.

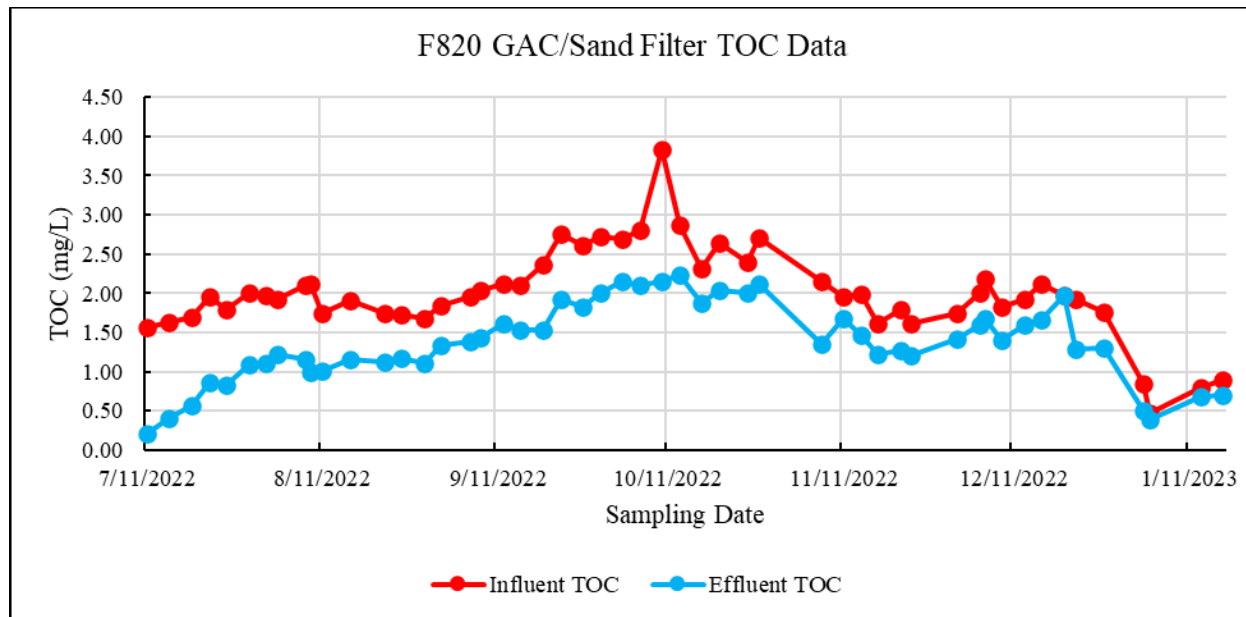


Figure 5.1. Influent TOC data for the F820 GAC/sand filter used to preload the GAC.

Thanks to the different densities, the GAC layer was sufficiently separated from the sand layer in the pilot filter throughout its operation in spite of the occasional backwash at intervals of 2~3 days. GEO, 2-MIB and IPMP were present in filter influent during the 6-month pilot study but their concentrations were very low (≤ 6.0 ng/L, < 3.3 ng/L and ≤ 3.5 ng/L for GEO, 2-MIB and IPMP, respectively) as reported by Yin et al., (2024). Empty bed contact time (EBCT) of the pilot filter was 8 minutes from 11/03/2022 to 12/31/2022 and 4.5 minutes during the rest of the study to 1/17/23. The 1/2" PVC column with the collected preloaded GAC (media depth – 30 cm) was used in the small column test (Section 5.3.3). In order to evaluate the difference caused

by prior NOM introduction, virgin F820 GAC rinsed by Milli-Q water to remove impurities was filled into another 1/2" PVC column with a media depth of 30 cm for comparison.

It should be noted that in a previous study, identical removal rates of GEO and 2-MIB by preloaded GAC collected at different depths of a full-scale GAC filter were achieved after operation for 7 weeks (Yuan et al., 2021). Similar constant capacities of preloaded GAC for trichloroethylene (Summers et al., 1989) and atrazine (Knappe et al., 1999) regardless of the depth within the GAC filter where the preloaded GAC was collected have also been reported after only weeks of NOM pre-exposure. In all cases, it was proposed that with sufficient NOM preloading, NOM fouling throughout the GAC filter eventually became uniform. As a result, removal of micropollutants by preloaded GAC collected at various depths of the filter became identical. Knappe et al., (1999) presented further evidence where the GAC filter was saturated with NOM shortly before constant removal of atrazine by preloaded GAC regardless of its depth within the GAC filter was found. Since the preloaded GAC mostly stopped NOM uptake due to exhaustion beginning 11/11/2022 (Figure 5.1), uniform NOM fouling layer throughout the GAC layer was likely formed at the time of GAC sampling. Therefore, the preloaded GAC collected from only the top 30 cm of the pilot filter's 60-inch GAC layer in this study was deemed representative of all preloaded GAC throughout the pilot filter regardless of its depth.

5.3.3. Bench-Scale GAC Column Test

The bench-scale GAC column test lasted for 14 days. The EBCTs of both GAC small columns were kept at 8 minutes throughout the test. Minimal headspace was allowed during sampling to prevent odorant loss through evaporation. During the first 9 days, clarified SWTP influent was spiked with GEO, 2-MIB and IPMP as target compounds to simulate a T&O episode before equally split and introduced into to the virgin GAC and preloaded GAC columns.

Daily samples were taken from the influent and effluent of each column and transported overnight to the laboratory in 250 mL amber glass bottles with Teflon-lined caps and ice packs. Column influent was sampled individually in order to evaluate mixing efficiency before the split of the spiked influent. As for the remaining 5 days, clarified SWTP influent was loaded into the 2 GAC columns without spiking to observe any desorption of target compounds from GAC columns as previously reported by Mackenzie et al., (2005). The test compounds were not spiked into clarified SWTP influent before column inlets during the remaining 5 days. Thus, the results from clarified SWTP influent alone were considered representative of both column influents. Daily samples of clarified SWTP influent and the effluents of both columns were delivered to the laboratory overnight in 250 mL amber glass bottles with Teflon-lined caps and ice packs for analysis. All 250 mL bottles and caps used for sampling were rinsed by MeOH, tap water, Milli-Q water and their designated samples prior to use.

5.3.4. Target Compound Quantitation

5.3.4.1. Sample Extraction

Upon receipt, in the laboratory, the samples were filtered through mixed cellulose esters (MCE) membrane filters with a pore size of 0.22 μm (Millipore-Sigma, Burlington, MA) and then stored in the dark at about 4°C. Within a week after filtration, headspace solid-phase microextraction (SPME) was applied to extract target compounds from each sample as described by Yin et al., (2024). In short, 45 mL filtered sample was mixed with 15.00 g of NaCl and 5.0 μL 500 $\mu\text{g/L}$ p-BFB (internal standard) in MeOH in a 65 mL amber glass sample vial sealed by a Teflon-faced silicone septum (Supelco, Bellefonte, PA, USA). The vial was heated to 65.0 $\pm$ 1.0°C by distilled water bath. Then, a StableFlexTM 1 cm 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) SPME fiber (Supelco,

Bellefonte, PA, USA) was exposed to the headspace for 35 min to extract volatiles with stirring at 180±10 rpm using a 5/8 × 5/16” Teflon-coated octagon magnetic stirrer bar (VWR International, LLC, Radnor, PA, USA). After 35 minutes, the fiber was retrieved and ready for analysis. Prior to use, all sample vials and stirrer bars were rinsed by MeOH, tap water and Milli-Q water. In addition, the SPME fiber was conditioned at 270°C for 30 min before use.

5.3.4.2. Gas Chromatography/Mass Spectrometry (GC/MS) by Selected Ion Monitoring (SIM)

GC/MS SIM as described by Yin et al., (2024) was completed. Briefly, after sample extraction, the SPME fiber was swiftly injected into a Varian 450-GC system coupled with a Varian 220-MS system (Varian, Inc., Walnut Creek, CA, USA) through a 1177 split/splitless capillary injector. The injector temperature was 260°C, analyte desorption time – 15 min, split vent – off during 0~1 min and on at ratio 100 during 1~30 min. A 60 m DB-5MS (diameter – 0.25 mm, film thickness - 0.25 µm) GC column (Agilent Technologies, Santa Clara, CA) was used with 99.9999% helium (Airgas, Inc., Radnor, PA, USA) as the carrier gas with a column flow rate of 1 mL/min. Column temperature was held at 50°C for 2 minutes and then raised at 8.0°C/min to 260 °C where it was kept constant for another 1.75 minutes. The MS system used electron ionization (EI) at 70 eV and its temperature setpoints were 150°C for trap, 40°C for manifold and 270°C for the transfer line. Ions produced by EI whose mass to charge ratio (m/z) values were specific to target compounds and p-BFB (internal standard) were analyzed under selected ion scan (SIS) mode (frequency – 1 Hz) at their elution windows (Table 5.1). Otherwise, full scan mode (frequency – 1 Hz) was used with a scanning range (m/z) of 41~260. External calibration was conducted and the results are shown in Table 5.2.

Table 5.1. Details of SIS Applied for Target Compounds and Internal Standard.

Compound	Elution Window (min)	Ions Monitored (m/z) ¹
p-BFB	9.50~11.00	174.0 ² , 95.0, 176.0, 75.0, 50.0
IPMP	13.00~14.00	137.0 ² , 152.0, 124.0, 138.0, 109.0

2-MIB	15.50~16.50	95.0 ² , 93.0, 107.0, 108.0, 135.0
GEO	19.00~20.50	112.0 ² , 126.0
¹ An isolation window of 3.0 (m/z) was adopted for each ion monitored under SIS mode.		
² Primary ions whose peak areas were used for quantitation.		

Table 5.2. Linear Ranges, Detection and Quantitation Limits of Analytes.

Target Compound	Linear Range (LR) ¹ (ng/L)	Limit of Detection (LOD) ² (ng/L)	Limit of Quantitation (LOQ) ³ (ng/L)
IPMP	0.5~120 ⁴	0.5	1.5
2-MIB	2.5~120 ⁴	3.3	8.6
GEO	0.5~120 ⁴	0.2	0.5
¹ LR between target compound concentration and peak area of target compound's primary ion to peak area of internal standard's (p-BFB's) primary ion (m/z – 174.0) ratio was determined for each analyte.			
² LOD was defined by a signal to noise ratio (S/N) of 3.			
³ LOQ was defined by a S/N of 10.			
⁴ The upper limits of the linear ranges may have been higher than 120 ng/L as external calibration was not conducted further.			

5.4. Results

Concentrations of GEO, 2-MIB and IPMP throughout the column test are presented in Figure 5.2. During the first 9 days, when spiking of target compounds was conducted, influent GEO, 2-MIB and IPMP concentrations showed limited differences between the virgin GAC column and the preloaded GAC column except for the IPMP inlet concentrations on day 9. The difference indicated insufficient IPMP mixing after it was spiked into the clarified SWTP influent before the flow split and its contact with both GAC columns. However, despite higher IPMP concentration in its influent, IPMP was not detected in preloaded GAC effluent throughout the study, which was consistent with virgin GAC effluent. Thus, the 6-month NOM preloading to the F820 GAC column did not affect its capacity for IPMP at all whether by direct competition or the pore blockage effect. GAC filtration was deemed feasible for IPMP removal without regulatory limit for reference since the LOD of IPMP (0.5 ng/L) was close to its reported odor threshold concentration (OTC) of 0.2 ng/L at 40°C (Young et al., 1996).

At the same time, higher levels of 2-MIB and GEO were found in the preloaded GAC effluent compared to virgin GAC effluent. Therefore, the 6-month pre-exposure to NOM lowered F820 GAC's capacity for GEO and 2-MIB. This proved the necessity to use GAC with prior NOM introduction in feasibility assessment of GAC application to account for any pore restriction effect. Nevertheless, concentrations of 2-MIB and GEO in preloaded GAC effluent never exceeded 10 ng/L. Thus, the performance of preloaded GAC was still satisfactory to the currently available regulatory limits of 10 ng/L (SAMRC and SAC, 2022) or 20 ng/L (Kim and Park, 2021) for GEO and 2-MIB in drinking water.

In conclusion, a F820 GAC filter could efficiently remove odorants from SWTP influent during a T&O episode near the end of its 6-month service life despite prior NOM loading and the pore restriction effect caused by it.

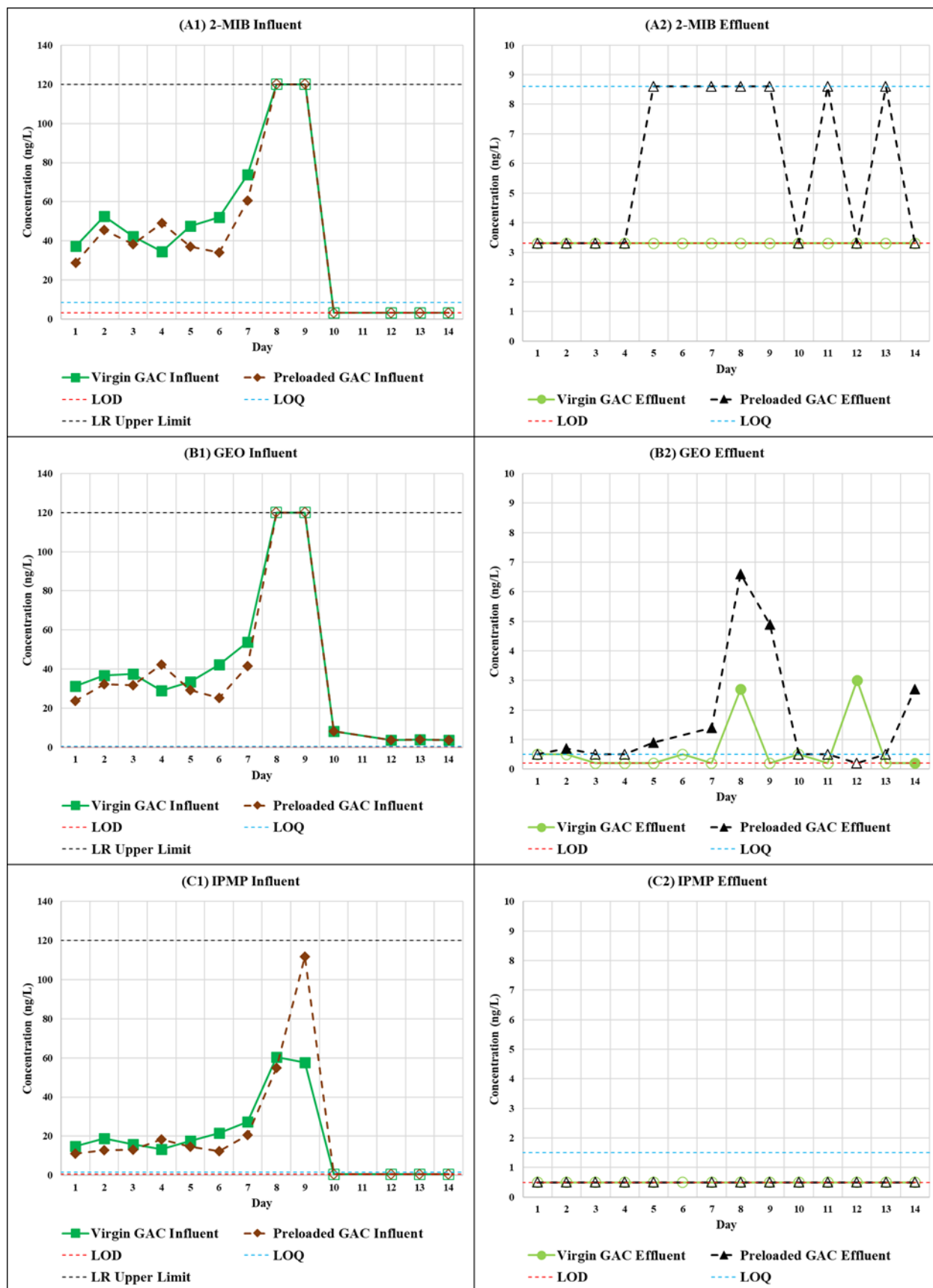


Figure 5.2. GEO (A), 2-MIB (B) and IPMP (C) concentrations in influent (1) and effluent (2) of each GAC column. Unfilled data points refer to concentration above LR (Linear Range) upper limit, below LOQ (analyte detected but not quantitated) or below LOD (analyte not detected) specified by Table 5.2. Clarified SWTP influent on day 11 (influent of both columns) and preloaded GAC column on day 6 were not analyzed due broken bottles during sample delivery.

5.5. Discussion

Prolonged NOM introduction into GAC prior to a T&O event has been shown to negatively affect GAC's ability to remove GEO and 2-MIB (Yuan et al., 2021). However, in this study, the GAC performance in GEO and 2-MIB removal remained satisfactory despite slight deterioration due to preloaded NOM. Biodegradation of GEO and 2-MIB in the biofilm formed on the surface of preloaded GAC as reviewed by Yuan and Hofmann, (2022) probably limited the reduction of their removal due to NOM interference. In comparison, IPMP adsorption was totally unchanged, even with a higher IPMP influent concentration compared to the control group with virgin GAC. A possible reason for the difference in the NOM effects is the higher polarity of IPMP than GEO and 2-MIB. In this case, IPMP might have shared fewer common adsorption sites on GAC surface with NOM than GEO or 2-MIB. This resulted in a weaker direct competition between IPMP and NOM. Also, the smaller molecule size and the flatter molecule shape of IPMP than GEO or 2-MIB may have made it more difficult for pore blockage to take place. It is also possible, that IPMP may have been more biodegradable within preloaded GAC column compared to GEO and 2-MIB. Although Velten, (2008) found no significant biodegradation of IPMP on preloaded GAC, the study involved only one surface water source to support formation of biofilm and preload NOM on GAC surface. Therefore, the finding may not be widely applicable compared to the extensive review by Yuan and Hofmann, (2022) regarding biodegradation of GEO and 2-MIB. To compare the biodegradation rates of GEO, 2-MIB and

IPMP, their removal rates by both preloaded GAC and sterilized preloaded GAC should be measured to determine the biodegradation rate of each compound using the difference due to sterilization. Finally, a lower influent concentration profile of IPMP than GEO and 2-MIB might have caused less severe competition with NOM. To evaluate the possibility, another column test using preloaded GAC with the same inlet molar concentration profiles of GEO, 2-MIB and IPMP should be conducted with virgin GAC as a control experiment.

It should be noted that the unchanged removal of IPMP despite NOM interference in this study is inconsistent with the finding by Velten, (2008) where a pilot GAC filter preloaded with NOM from lake water with a dissolved organic carbon (DOC) value of 1.1 ± 0.04 mg/L for 6 months (EBCT = 15.76 min) demonstrated lower IPMP removal rates compared with virgin GAC filter. However, a much higher IPMP influent concentration of $\sim 1,500$ ng/L was adopted by Velten, (2008) and it appears to be the reason behind a different outcome from this study.

Desorption of GEO and 2-MIB from GAC was observed from day 10 to day 14 when no spiking was applied to the clarified SWTP influent. This finding is consistent with 2-MIB desorption reported by Mackenzie et al., (2005) as shown in Figure 5.2 (day 10 to 14). Fortunately, desorption of GEO and 2-MIB were limited for both preloaded and virgin GACs and did not pose serious risk to drinking water quality in this case study. In contrast, no desorption of IPMP ever took place from both preloaded and virgin GACs. Such difference might have been the result of better IPMP affinities to GAC surface and/or lower IPMP influent concentration than GEO and 2-MIB. Further investigation of this situation can be developed using a small column test with identical inlet molar concentration profiles of GEO, 2-MIB and IPMP and sterilized preloaded GAC for comparison.

5.6. Conclusion

Adsorption of NOM by GAC prior to contact with GEO, 2-MIB and IPMP was found to reduce GAC's capacity for GEO and 2-MIB. Yet, the difference did not pose a risk to drinking water acceptability at levels lower than 10 ng/L for GEO and 2-MIB. Meanwhile, IPMP removal was not influenced at all. Therefore, the feasibility of the GAC filters planned for SWTP was acceptable. This study also added to existing knowledge regarding the effects of NOM pre-exposure on GAC removal of GEO, 2-MIB and IPMP, especially for their simultaneous removal. Finally, future studies were identified to better understand T&O mitigation by preloaded GAC. Specifically, same influent molar concentrations of GEO, 2-MIB and IPMP should be applied to future column tests. In this way, any discrepancies in their removal performance by preloaded GAC will be attributed to difference in their properties rather than their inlet concentrations. Besides, the possibility of IPMP biodegradation on preloaded GAC surface should be further investigated because currently available study is too limited in scope to be conclusive. If verified, IPMP biodegradation rate on preloaded GAC surface should be compared with those of GEO and 2-MIB.

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Chapter 6

Conclusions and Future Research

6.1. Conclusions

With simple training for a week, an air odor panel could be formed and provide accurate characterization of air odor emissions from various facilities by reporting odor characteristics and intensities consistent with previous studies on the same types of facility and/or the nature of facilities' operations. However, total anosmia and severe microsmia screening by UPSIT[®] method was found to be essential before the start of the training for successful application of OPM. Moreover, limitations of OPM were identified including lower sensitivity of laboratory OPM analysis with sampling bags, high standard deviation of individual odor intensity values relative to panel average and difficulty to characterize all odors within a mixture, especially for a mixture of 3 or 4 odor characteristics. Therefore, the combination of onsite OPM analysis, a panel with multiple individuals and instrumental methods for odor separation from each other such as using the dynamic olfactometry method are necessary for OPM evaluation of air odors.

In a case study involving an air odor treatment system for sludge related odors from a wastewater treatment plant, OPM combined with dynamic olfactometry revealed the overall inefficiency of a treatment system based upon high effluent odor intensities persistence with atmospheric dilution. Odor characteristics with dominant intensities reported by the method also became the basis for identification of primary odorants causing nuisance by SGC, GC/MS and sulfur analysis. Quantitation of these compounds (MeSH, DMDS, DMS – decaying vegetation odor; DMS – canned corn odor; p-C – manure odor and unidentified fecal odorants) before and after each treatment process within the system located malfunctional GAC filters as the root-cause of system underperformance. The case study proved the abilities of this unique combination of OPM-modified dynamic olfactometry, SGC and chemical analyses (GC/MS and sulfur analysis in this case) to evaluate the overall performance of an air odor treatment system.

The data determined the primary chemical causes of the odor nuisance and located the problems leading to system underperformance. It also showcased the superiority of this methodology over mainstream odor evaluation approaches including D/T measurement and chemical analysis of common odorants. This is because these methods had the ability to determine odor characteristics and intensities which could be indicators of odor sensorial impact and responsible odorants.

As for odors from a water supply, FPA was applied to drinking water at entering a Water Treatment Plant treating water from two different surface sources. FPA successfully captured the presence of an odorant not routinely monitored by the facility. SGC and GC/MS revealed its identity as 2-isopropyl-3-methoxypyrazine (IPMP). Compared with geosmin (GEO) and 2-methylisoborneol (2-MIB) monitored by the facility to represent overall T&O occurrence, IPMP was formed in a different surface water source with different seasonal patterns due to its different formation mechanism. As a result, the facility's understanding of overall T&O occurrence could now allow the facility to take actions for T&O mitigation targeting these odorants. The study showed the problem with sole monitoring of GEO and 2-MIB, which is the usual practice in water treatment for evaluation of overall T&O occurrence. Thus, the study showed the necessity to include FPA for T&O evaluations.

The complete understanding of T&O causes and patterns was acquired with the help of FPA and a bench-scale GAC column test targeting elevated concentrations of GEO, 2-MIB and IPMP at the same time was conducted. Although natural organic matter (NOM) preloading to GAC did lower its adsorption capacities for GEO and 2-MIB, the effect was likely counter-balanced by biodegradation of both compounds on the GAC surface. As a result, GEO and 2-MIB concentrations in column effluent were still deemed satisfactory. By comparison, IPMP removal

by GAC was not affected by NOM preloading at all and further investigation is needed to find out the reason why.

In conclusion, OPM and FPA are easily adoptable and essential for complete evaluation of odor occurrence and its chemical causes in both air and water with the assistance by instrumental methods enabling odor separation and/or chemical analysis. In turn, effective odor mitigation efforts should take all odorants present into consideration. Therefore, further use of FPA for water analysis and the application of OPM for air analysis are warranted for understanding environmental odors and their control.

6.2. Future Research

- Future studies should apply more effective compound separation methods by chromatography compared to GC/MS system such as Multi-dimensional GC systems, especially for source samples with very complex matrices such as wastewater and gaseous odor emission samples compared to ambient samples.
- Possible chemical and biological processes on GAC surface in both air and water should be investigated. Specifically, the origin and fate of each primary odorant in Chapter 2 on GAC surface during air treatment should be evaluated. Fate of IPMP on GAC surface in water treatment should also be studied.
- Improvements should be designed, tested and applied to the air odor treatment system specified in Chapter 2 based on the findings of this study. Specifically, GAC surface modification can be attempted to favor reactions depleting primary odorants. Moreover, pH adjustment of bleach scrubbing solution or adoption of a different scrubbing agent can also be tried to improve scrubber performance.

- OPM-modified dynamic olfactometry should be combined with atmospheric dispersion modelling to evaluate sensorial impact of an odor source with a significant distance from receiving public. Specifically, modelling should be able to determine dilution ratio of interest based on location, weather and topographic information of both the odor source and the receptor point. After that, the odor characteristics and intensities shown by the dilution curves at the dilution ratio of interest should determine the nuisance impact but field studies are needed for validation.

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