PROTON TRANSFER REACTION TIME OF FLIGHT MASS SPECTROMETRY COMPENDIUM TEST REPORT
ODOR ATTRIBUTION STUDY (OAS) RFP# 2019-004
BAY AREA AIR QUALITY MANAGEMENT DISTRICT
OAS (3 FACILITIES)
SAN FRANCISCO, CALIFORNIA

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REVIEW AND CERTIFICATION

All work, calculations, and other activities and tasks performed and presented in this document were carried out by me or under my direction and supervision. I hereby certify that, to the best of my knowledge, Montrose operated in conformance with the requirements of the Montrose Quality Management System and ASTM D7036-04 during this test project.

Signature:  Date: 7/1/2022

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EXECUTIVE SUMMARY

Montrose Air Quality Services, LLC (Montrose) was retained by the Bay Area Air Quality Management District, San Francisco, California (BAAQMD), in collaboration with Jacobs Engineering Group (Jacobs), to conduct an odor assessment and attribution screening program at and around multiple odor sources located near the southern end of the San Francisco Bay Area, including the City of Milpitas, California. The testing was performed in three phases; Fall Event (October 2020), Winter Event (March 2021), and Spring Event (May 2021). The events consisted of analysis of source odor bags collected by Jacobs Engineering. Onsite testing was conducted with the Proton Transfer Time of Flight Mass Spectrometer (PTR-TOF MS) during the May 2021 Spring Event.

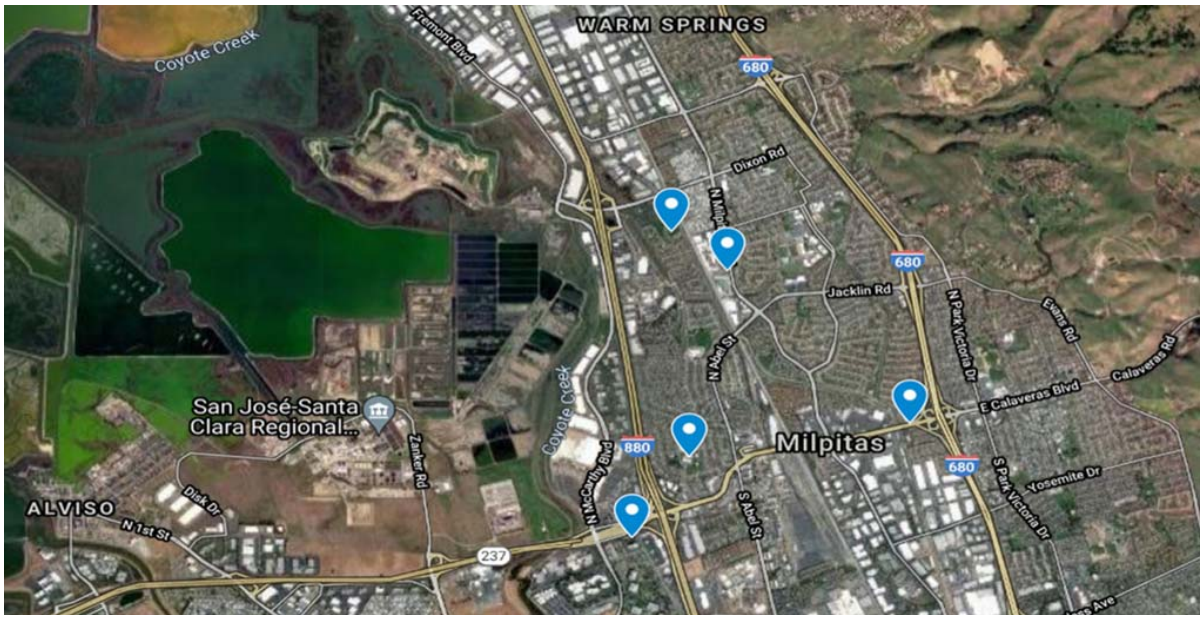
Air monitoring was accomplished in real-time at various locations using a mobile monitoring van to detect the presence of specific VOCs and odorous compounds. The mobile monitoring van contains the equipment necessary to identify and quantitate individual VOCs present in ambient air to ultra-low concentrations. This equipment measures and reports concentrations of select VOCs at sub-parts per billion (ppb) levels as quickly as one measurement per second. The mobile monitoring van surveyed the source “fingerprint” areas surrounding the City of Milpitas, and was also stationed overnight at separate locations to provide a complete upwind and downwind survey of the areas that reported numerous odor complaints in the past. During the nine-day on-site sampling program, over 202 hours of data were collected, which represents over 727,000 individual data measurements. Meteorological conditions and Global Positioning System (GPS) data were also collected and reported in real time. These data points were used to determine upwind and downwind sampling locations. Key findings from this study effort include:

- Unique “facility fingerprints” detected by PTR-MS agreed with Jacobs odor characterization and quantification results.
- Unique “chemical fingerprint” distinct to each odor source were found and those results were independently confirmed via principle component analysis (PCA).
- This study confirms that odorous air samples taken in the nearby community and analyzed by PTR-TOF MS and PCA modeling can be a valid technique to identify which facility (or which facilities) was/were the source(s) of the odors.

1.0 INTRODUCTION

Montrose was retained by the BAAQMD to conduct an odor assessment and characterization study in the Milpitas California area. This was a multi-phase study that was conducted over three separate sampling periods. Air samples were taken from multiple facilities in the Fall of 2020, Winter of 2021, and Spring of 2021 by Jacobs Engineering personnel, and were sent to Montrose for analysis by PTR-TOF MS. On site PTR-TOF MS sampling was also conducted during the Spring 2021 campaign during a two-week period. During this two-week period in the Spring of 2021, the Montrose PTR mobile platform fingerprinted each of the three facilities and the marine estuary. The fingerprints contain over 350 individual compound measurements at ppt to ppm levels. The community was then sampled overnight for several nights to capture transient plumes that may contain odorous compounds. The community data was then compared via Principle Component Analysis (PCA) to the facility fingerprints. The multivariate PCA data demonstrated that the plumes captured in the overnight studies originated from the Newby landfill working face with a 95% confidence level and at a 5% confidence level from the ZWED facility. This indicates that statistically, the Newby landfill working face was the primary source of the captured plumes in the community.

FIGURE 1-1
MAP OF HIGH-VOLUME ODOR COMPLAINTS FOR THE CITY OF MILPITAS CALIFORNIA



Odor issues have persisted in Milpitas, CA neighborhoods for years despite past collaboration from the air district, local organizations, industry, and community. Since 2019, Montrose Environmental Group has been engaged with the Bay Area Air Quality Management District (BAAQMD) on a study utilizing science-based methods to pinpoint the origin of offending odors derived from the composition, strength, and characterization of aromata in the Milpitas California area which could be originating from one of the various processes at a nearby facilities or through a natural occurrence, being close to a tidal estuary. The main suspected sources of odor include: Newby Island Resource Recovery Park (NIRRP), the San Jose-Santa Clara Regional Wastewater

Facility (RWF), and the Zero Waste Energy Development Company (ZWED). The five areas within the city of Milpitas, California that have the highest density of odor complaints from residential complaint logs is detailed in Figure 1-1.

After a pause due to the pandemic, Montrose has been using new technologies to help identify and quantify over 500 compounds at ultra-low concentrations, and gather data over a period of time to capture seasonal and operational changes in the nearby industries. Montrose has utilized the latest ultra-low detection technology, mobile platforms equipped with an ultra-high-resolution PTR-TOF MS, GPS and Meteorological ("MET") stations, geometric mapping algorithms for triangulation, and deep data gathering for multi-variate analysis (MVA).

The following sections provide discussion of the Montrose analytical work and how that product, and the Jacobs work product, complement each other for the purpose of meeting the overall study's goals and objectives. It should be noted that there is a distinguishing difference between the Jacobs and Montrose efforts, namely that Jacobs' efforts focused on odor characterization and quantification, while Montrose's efforts focused on collective chemical compound identification to generate "chemical fingerprints" of the odors emitted from the dominant odor sources followed by the collection of plumes in the community for a multivariate analysis of the community plumes to the chemical fenceline fingerprints to determine odor allocation. Correlations are determined from the principle component analysis (PCA) of unique compounds identified at the fenceline of facilities and ratios of compounds also found within the fenceline fingerprint. The community plumes are then compared mathematically and statistically to determine correlations to a particular facility or overlap of plumes from multiple facilities. The possible sources in relation to the community are detailed in Figure 1-2.

Data was collected at the specific emissions points at three facilities and at specific processes located within each facility, giving them an individual odor "fingerprint. The recently completed data gathering process has generated over a terabyte of data that will be introduced into an MVA software owned by Sartorius, as well as a secondary software that can track individual odor plumes. The proprietary Montrose geometric algorithm triangulates various odor plumes, and in conjunction with the MVA fingerprint analysis, specific plumes and combinations of plumes may be identified that are contributing to the odor occurrences in Milpitas.

FIGURE 1-2
GEOGRAPHICAL LOCATIONS OF POSSIBLE SOURCES OF COMMUNITY ODORS HIGHLIGHTED BY ARROWS FROM THE CENTER OF MILPITAS, CALIFORNIA

1.1 TEST PROGRAM OBJECTIVES AND SCOPE

BAAQMD has retained Montrose for the purpose of conducting a compound identification and chemical ratio study to characterize plumes emitted from the three key facilities: NIRRP, RWF, and ZWED.

The objectives and scope of the study were as follows:

- Sample identification and quantification using the PTR-TOF MS mobile platform
- Conduct measurements at the ppt level in real time (1/sec)
- Identify as many individual and unique compounds emitted past the fenceline of each facility as possible
- Use the mobile PTR-TOF MS platform to conduct measurements at various locations at and around the key facilities, as well as downwind in the community, by stationing the platform and capturing plumes as they pass by with changing wind patterns. Mobile monitoring was also conducted as well to actively search for odor plumes by driving the mobile platform through the city of Milpitas.

The partnership and collaboration between Jacobs and Montrose for this study has been invaluable in that the two firms provide unique skill sets and expertise that complement each other. These include the following:

Jacobs Expertise:

- Extensive experience in odor characterization and mitigation
- Highly qualified professional staff with deep relevant experience assigned to the project
- Versed in public engagement and communication of results

Montrose Expertise:

- Ability to identify a wide range of individual chemical compounds at ppt levels in real time
- Expertise in chemical analysis and degradation pathways in conjunction with the implementation and use of a mobile platform allowing real-time measurements at and around the key facilities and within communities
- Through partnership with Sartorius, ability to perform a multivariate SIMCA Principal Component Analysis (PCA) on the data to differentiate “fingerprint” compounds from each key facility
- Quality control and assurance expertise for metrology studies

2.0 MOBILE PLATFORM SAMPLING PROGRAM

2.1 MOBILE MONITORING VAN AIR SAMPLING DESCRIPTION

The mobile monitoring van is a Mercedes 2500 Sprinter Van outfitted with the equipment necessary to identify and quantitate individual analytes present in ambient air to ultra-low concentrations. The mobile monitoring van is equipped with an Ionicon Model 6000-X2 proton transfer time-of-flight mass spectrometer (PTR-TOF MS). This instrument provides concentrations of select VOCs at sub-parts per billion (ppb) levels for many of the compounds and as quickly as one measurement per second. Detection limits are target compound specific, so many compounds were measured at the ppt level and others at the ppb levels. The mobile monitoring van is outfitted with an external sampling system, which transports ambient air from outside of the van into the PTR-TOF MS sample inlet for immediate real-time analysis. The entire sampling system is comprised of Teflon or Teflon-coated materials, which ensures the lowest amount of sample loss due to surface absorption of analyte molecules. The mobile monitoring van incorporates a high-precision global positioning system (GPS), a sonic anemometer to measure wind direction and wind velocity, and a multitude of other incorporated meteorological (MET) sensors as shown in Figure 2-1.

The following elements are included in the Montrose mobile platform:

- Ionicon PTR-TOF MS Model 6000-X2 real time analyzer
- Agilent 5890 GC for speciated PTR-TOF MS results
- MKS 2030D and Optically Enhanced Starboost^{TM} MKS FTIR for single digit parts per billion (ppb) formaldehyde
- Computerized Environics NIST traceable gas dilution system (10000:1) dilution
- Teledyne Zero Air Generator with Act. Charcoal Scrubber
- Integrated sampling system
- Columbia Weather Systems Magellan MX 500 geographic positioning system (GPS)/Meteorological Station equipped with a sonic 3D anemometer with automatic self-alignment of wind direction for movement compensation
- Integrated generator and voltage line cleaners with uninterruptable power supply
- Heated sampling line with heated probe and filtration system (100 feet) plus Snorkel

FIGURE 2-1
MONTROSE MOBILE SAMPLING PLATFORM

2.2 PROTON TRANSFER TIME OF FLIGHT MASS SPECTROMETRY DESCRIPTION

PTR-TOF MS technology uses gas phase hydronium reagent ions that are produced in an ion source. A PTR-TOF MS instrument consists of an ion source that is directly connected to a drift tube. The ion products from the drift tube are coalesced and focused into the time of flight mass spectrometer through a series of electromagnetic field focusing lens directly to the mass analyzing system (TOF mass spectrometer). The key PTR-MS components are illustrated in Figure 2-2. See Appendix A of this report for specific PTR-TOF MS operating conditions.

FIGURE2-2
PTR-TOF MS ILLUSTRATION

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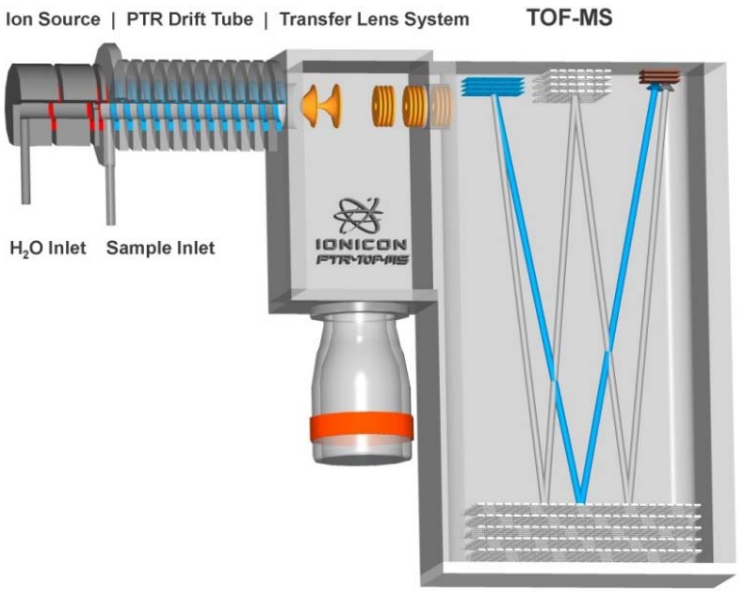


The use of proton transfer spectrometry allows for many advantages over traditional electron impact mass spectrometry that is typically employed in mobile monitoring platforms. Hundreds of VOCs can be detected simultaneously and in real time, with no sample preparation. The ambient gaseous sample is directly examined. Other advantages include low fragmentation – only a small amount of energy is transferred during the ionization process (compared to e.g. electron ionization), therefore fragmentation is suppressed and the obtained mass spectra are easily interpretable. Commercially available PTR-TOF MS instruments have a response time of about 100 milliseconds and reach a detection limit in the single digit ppt or lower, depending on the compound sensitivity which is dependent upon ion generation efficiency when mixed with the reagent gas.

3.0 SAMPLING PROGRAM TEST RESULTS

3.1 SAMPLE EVENTS

The level of engagement varied for the different sample events. Each sample event in which Montrose participated is described in the following subsections.

3.1.1 Sample Event No. 1 – Fall 2020

Jacobs collected multiple bag samples at the three key facilities and shipped them overnight to Montrose for analysis using PTR-TOF MS. Samples were collected October 19-21, 2020. The purpose of this approach was to pre-determine which individual compounds might be present at each sampling location, and to build a library of odorous compounds prior to the future onsite sample event.

The following sources were sampled and analyzed to perform an initial PTR-TOF MS scan to identify the wide range of individual compounds and specific markers of these odor sources:

- ZWED Interior Space (sample ID no. M102)
- RWF Primary Clarifier Effluent Weir Collection Box (sample ID no. M201)
- NIRRP Composting Piles (sample ID no. M301)
- NIRRP Landfill Working Face (sample ID no. M302)
- NIRRP Dried Biosolids (sample ID no. M303)
- NIRRP MRF Ambient Inside (sample ID no. M402)

3.1.2 Sample Event No. 2 – Winter 2021

Jacobs collected multiple bag samples at the three key facilities and shipped them overnight to Montrose for analysis using PTR-TOF MS. Samples were collected March 3, 2021. The purpose of this sampling event was to validate previous findings and provide additional data sets for the odorous compounds database.

The following sources were sampled and analyzed to perform an initial PTR-TOF MS scan to identify the wide range of individual compounds and specific markers of these odor sources:

- Upwind of key facilities (sample ID no. M-02)
- RWF Primaries (sample ID no. M-03)
- RWF Bioreactors (sample ID no. M-04)
- ZWED Interior Space (sample ID no. M-01)
- ZWED Biofilter (sample ID no. M-06)
- NIRRP Landfill Working Face (sample ID no. M-05)

3.1.3 Sample Event No. 3 – Spring 2021

Jacobs collected multiple bag samples at the three key facilities and delivered them overnight to Montrose for their analysis using PTR-TOF MS. The sampling was conducted on May 18-20, 2021, in conjunction with the onsite PTR-TOF MS sampling event. The purpose of this approach was for Montrose to validate previous findings and provide additional data sets.

The following sources were sampled and analyzed to identify the wide range of individual compounds and specific markers of these odor sources:

- RWF East Primaries (sample ID no. 5-18 East Primaries)
- RWF Bioreactors (sample ID no. 5-18 Bioreactor Aerobic)
- RWF Bioreactors (sample ID no. 5-18 Bioreactor Mixing Zone)
- RWF Lagoon (sample ID no. 5-18 Lagoon)
- ZWED Interior Space (sample ID no. 5-17 ZWED Interior)
- NIRRP Landfill Gas (sample ID no. 5-19 Landfill Gas)
- NIRRP Landfill Working Face (sample ID no. 5-19 Landfill Working Face)
- NIRRP Composting Pile (sample ID no. 5-19 NIRRP Composting Pile)

For this sample event, the mobile platform was transported to the vicinity for in-situ analysis.

A brief description of the onsite activities follows:

- The mobile testing platform arrived on May 12, 2021, and was set up to prepare for real-time monitoring. A power supply issue with the PTR-TOF MS occurred that caused slightly lower sensitivity than normally obtained. A new power supply was ordered and was installed in the field before testing began.
- BAAQMD decided that they would send any automatic odor complaint notifications received directly to Montrose so there could be a rapid placement of the mobile testing platform in response. Prior to Montrose's arrival, BAAQMD had been receiving multiple nighttime complaints. Most odor complaints originated in the area enclosed between Dixon Landing Road, California Circle, and Milmont Drive (closest neighborhood to NIRRP) or near the intersection of Jacklin Road and North Milpitas Boulevard. Any odor complaints were to be reported to Montrose and the Jacobs Team 2 (field survey team) for rapid response and measurements at the affected location. Unfortunately, during the Spring 2021 sampling event, no odors complaints were received.

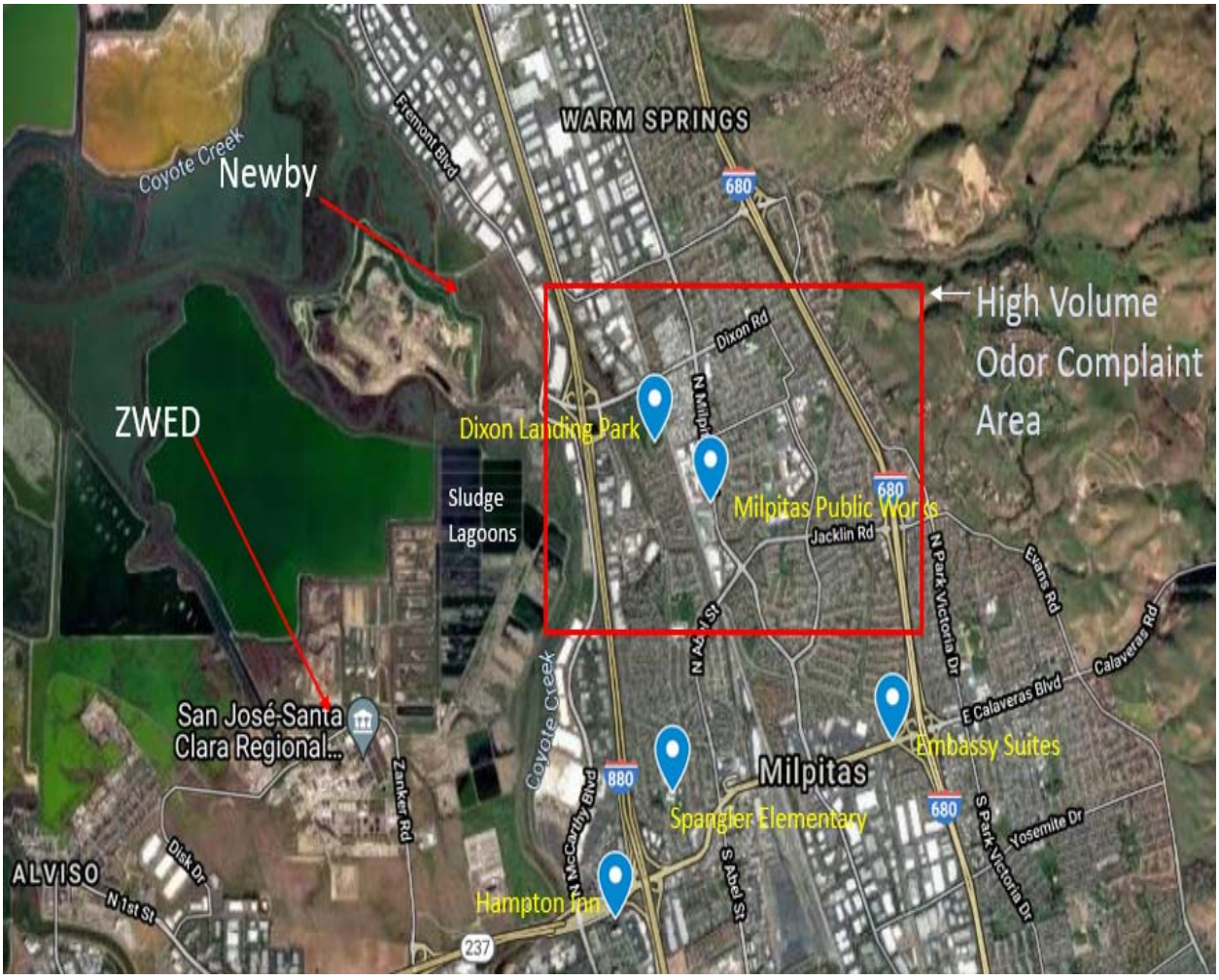
The following sources and areas were analyzed by Montrose's mobile platform during Sample Event No. 3:

- Control Upwind
- Estuary High Tide
- Estuary Low Tide
- ZWED, along the fenceline and downwind of biofilters/roll-up door

- San Jose RWF, continuous sensing of all primary and secondary tanks (e.g. aeration basins, secondary clarifiers, sludge lagoons, and drying beds)
- Downwind of Recycling center next door to ZWED
- NIRRP, including composting facility, landfill, and MRF
- Odor complaint address in Milpitas
- Fremont town office park (Dixon Landing Park)
- Milpitas elementary school (Anthony Spangler School)
- Milpitas High School
- Milpitas Hampton Inn parking lot (overnight continuous)
- Milpitas Public Works parking lot (overnight continuous)

The map of analysis areas is shown in Figure 3-1.

FIGURE 3-1
SELECTED SPRING 2021 SAMPLING EVENT TESTING LOCATIONS



3.2 PROCESS TEST RESULTS

3.2.1 Results of PTR-TOF MS Analyses

The PTR-TOF MS results revealed unique individual compounds associated with specific facilities/sources. Appendix A contains the tabular results of all of the bag samples presented in this report. Due to the extremely large number of individual compounds found during this study, it is not possible to summarize the results in the text of the report. This contains each constituent determined, and the concentration of each constituent measured. In each analysis, the mass spectra results were screened against a library of known compounds obtained from the NIST Mass Spectrum standard library and the ChemSpider Mass Spectrum library. This list was accumulated from the analytical results of all of the samples analyzed during the entirety of the test program. Additional compounds were added as a result of extensive literature searches of known odor causing compounds. All possible attempts were made to accurately determine the composition of all compounds detected by the MS; however, there were instances when it was not possible to determine the origins of all peaks detected, e.g. water cluster compounds, fragments and dissociation products. See Appendix B of this report for the specific operating conditions of the PTR-TOF MS used to obtain the test results. Appendix C contains fingerprint data not presented in the report, and data used for the PCA analysis.

Figures 3-2 through 3-11 provide graphical details that illustrate compound mass versus concentration that was detected in each sample. Note that in all figures, the “x” axis represents m/z values, which is compound mass divided by charge. In most cases, the charge is essentially 1, thus the m/z value can be considered as mass (amu).

FIGURE 3-2
CHEMICAL FINGERPRINT OF THE AIR UPWIND OF
THE MAIN ODOR-EMITTING FACILITIES
(WINTER 2021 SAMPLE EVENT)

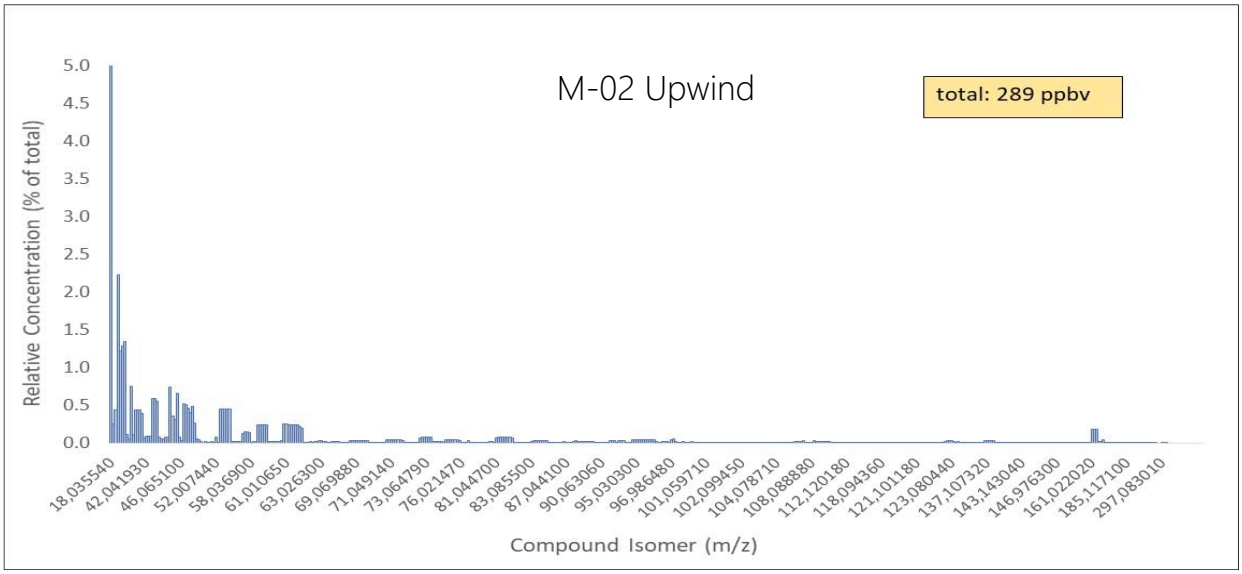


FIGURE 3-3
CHEMICAL FINGERPRINT OF THE AIR INSIDE THE ZWED FACILITY
(FALL 2020 SAMPLE EVENT)

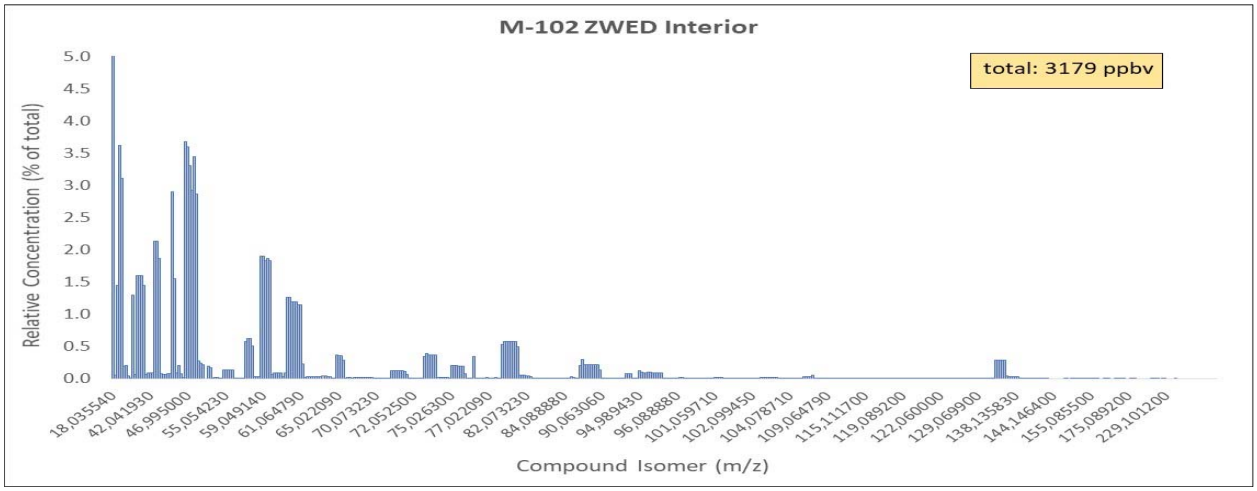


FIGURE 3-4
CHEMICAL FINGERPRINT OF THE AIR EMITTED AT THE BIOFILTER ZWED FACILITY
(WINTER 2021 SAMPLE EVENT)

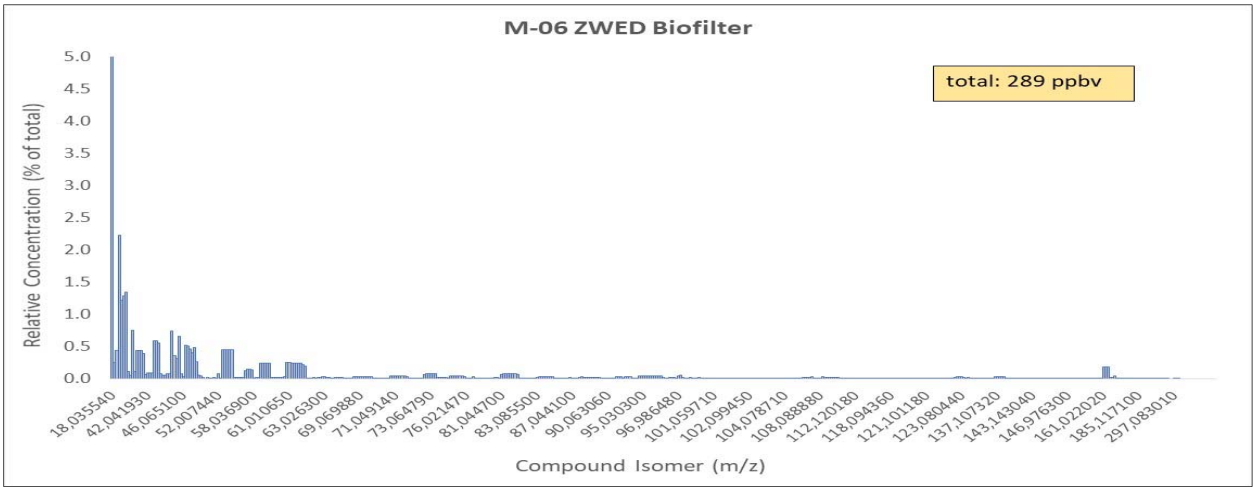


FIGURE 3-5
CHEMICAL FINGERPRINT OF THE AIR EMITTED FROM A PRIMARY CLARIFIER AT THE RWF FACILITY
(FALL 2020 SAMPLE EVENT)

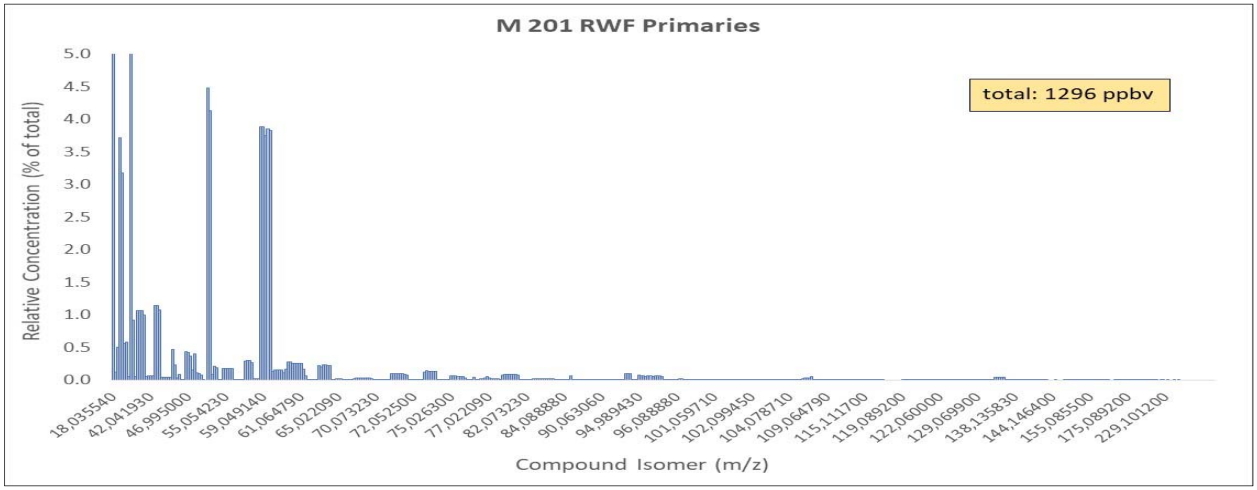


FIGURE 3-6
CHEMICAL FINGERPRINT OF THE AIR EMITTED FROM A BIOREACTOR AT THE RWF FACILITY
(WINTER 2021 SAMPLE EVENT)

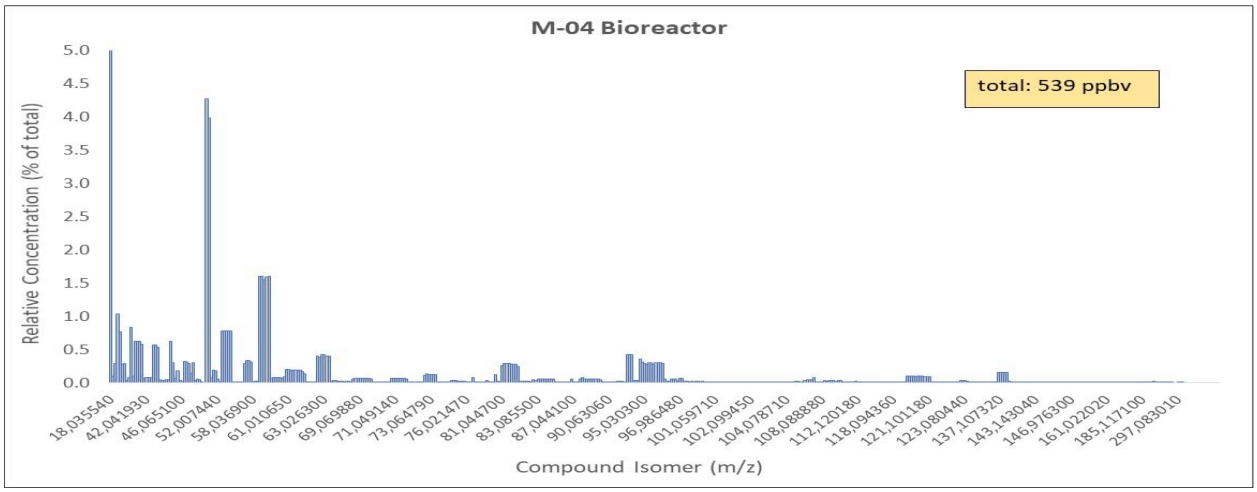


FIGURE 3-7
CHEMICAL FINGERPRINT OF THE AIR DOWNSTREAM OF THE LAGOONS AT THE RWF FACILITY
(SPRING 2021 SAMPLE EVENT)

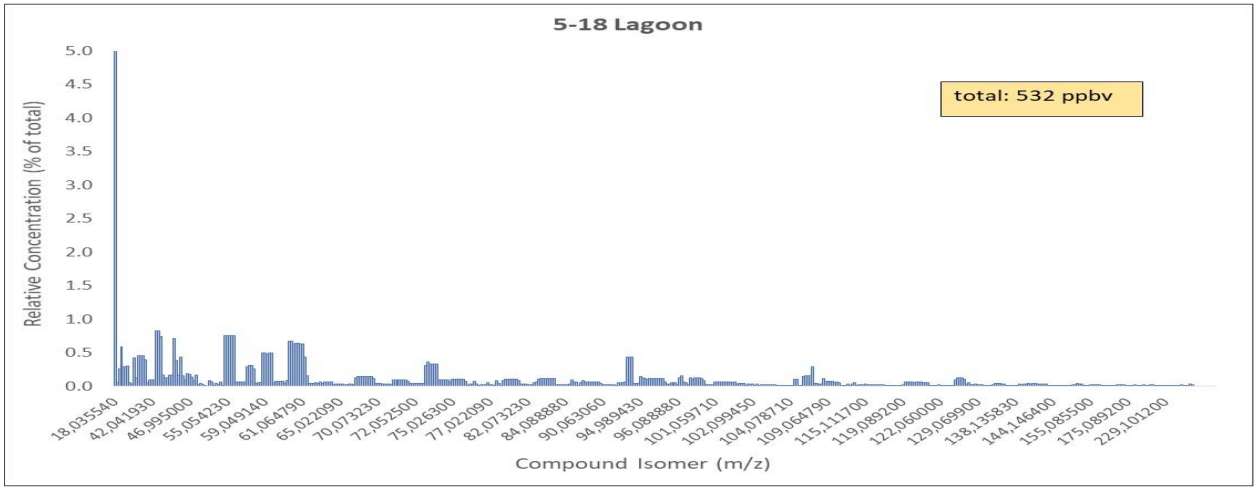


FIGURE 3-8
CHEMICAL FINGERPRINT OF THE AIR DOWNWIND OF THE LANDFILL AT THE NIRRP FACILITY
(FALL 2020 SAMPLE EVENT)

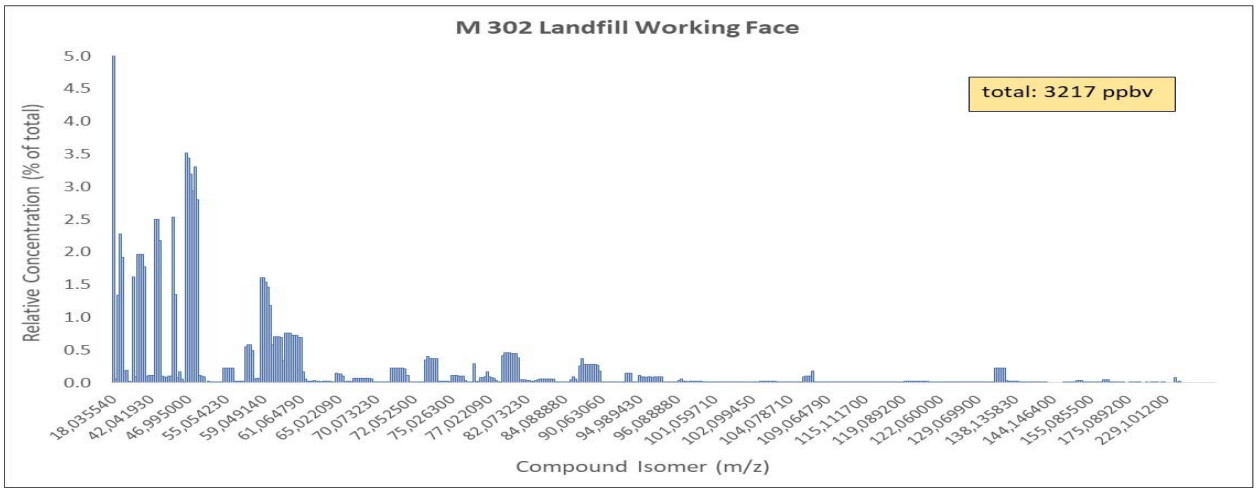


FIGURE 3-9
CHEMICAL FINGERPRINT OF THE AIR EMITTED FROM A COMPOST PILE AT THE NIRRP FACILITY
(SPRING 2021 SAMPLE EVENT)

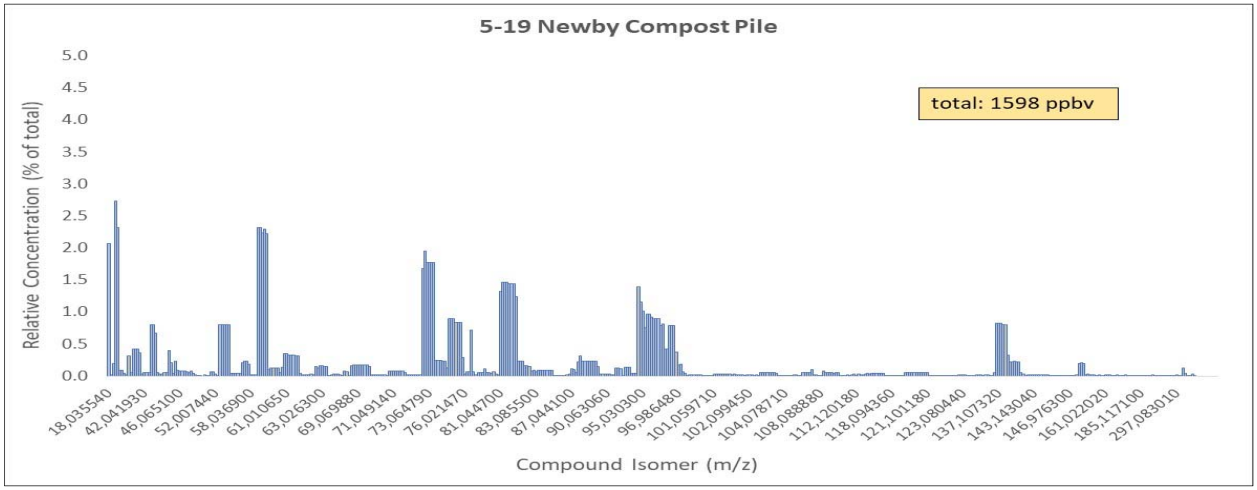


FIGURE 3-10
CHEMICAL FINGERPRINT OF THE AIR INSIDE THE MRF AT THE NIRRP FACILITY
(FALL 2020 SAMPLE EVENT)

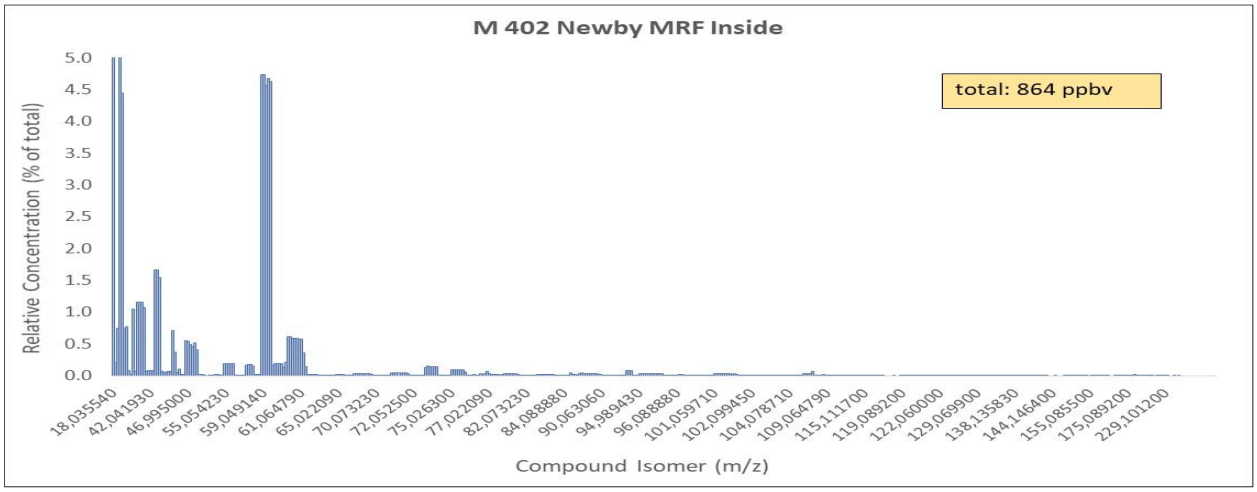
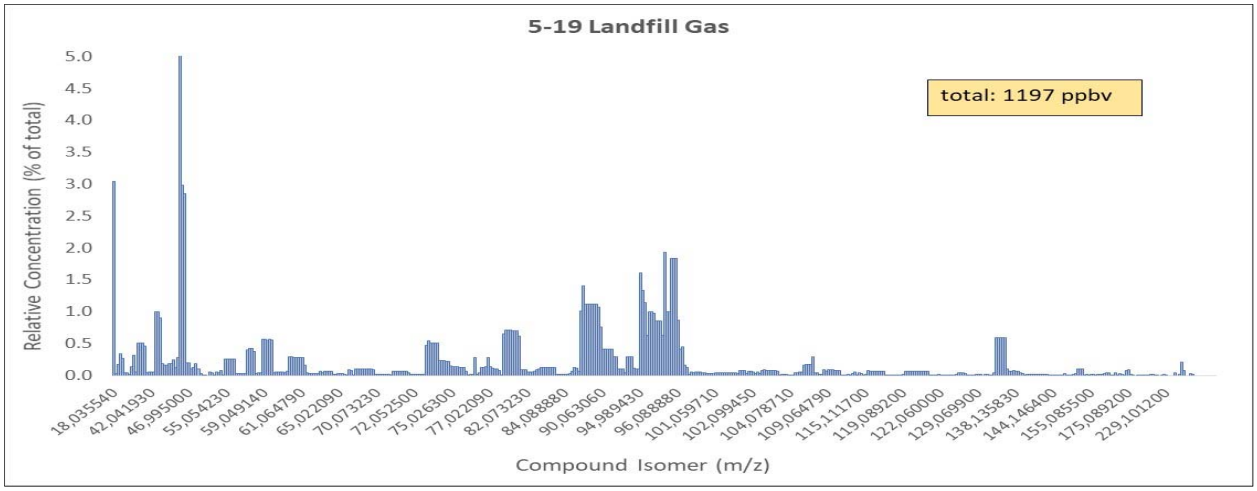


FIGURE 3-11
CHEMICAL FINGERPRINT OF THE LANDFILL GAS AT THE NIRRP FACILITY
(SPRING 2021 SAMPLE EVENT)



These results of the PTR-TOF MS bag analyses confirm the findings by the field assessors that the three main odor emitting facilities each have a relatively unique odor character.

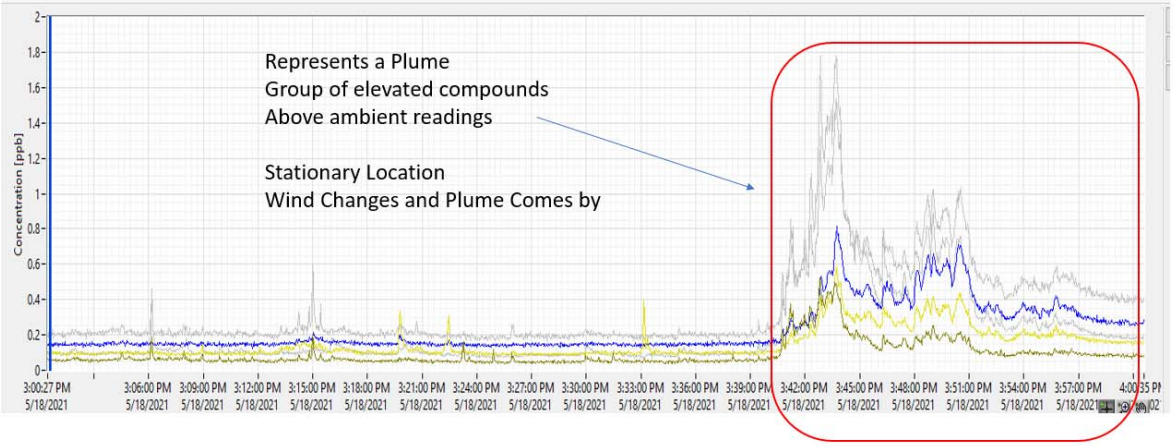
Additionally, compound types (functional groups) varied between facilities and typically fell into four categories:

1. Alcohols
2. Reduced Sulfurs
3. Amines
4. Ketones and Aldehydes (Carbonyls)

These groups of compounds vary dramatically in their ability to reach the community and in their odor thresholds (ability for human olfactory senses to detect). Polar volatile organic compounds (PVOC) compounds such as alcohols, ketones, and amines will not travel as far as other odorous compounds such as alkanes, alkenes, and heavier molecular weight compounds containing sulfur due to various mechanisms including association with water droplets and aerosol formation that tend to remove the compound from ambient air by scrubbing and deposition. Heavier compounds cannot be lofted as far by plumes and will also deposit onto the terrain due to gravitational forces as they conglomerate. It was noted that each facility has its share of common compounds but the ratio of unique classes of compounds such as more oxidized alcohols, carbonyls, and sulfur or sulfur/nitrogen compounds are what allow for specific facility assignment. The heavier the compound and the more oxidized compounds will tend to distribute themselves in deposition as a function of distance from the facility. Therefore, some facilities may tend to have more compounds reach farter into the community based on the classifications fo compounds in the plume. A few unique compounds also enabled the multivariate analysis software to correlate between facilities when community plumes were detected as shown in Figure 3-12 below. Note: the figure is a simplified representation of a plume detected in the community. There are only 4

example compounds represented graphically, in reality, the plume consisted of dozens of compounds detected with the PTR-TOF MS.

FIGURE 3-12
COMMUNITY PLUME EXAMPLE AS IT PASSES BY THE MOBILE PLATFORM



As discussed in Section 3 of the Jacobs Engineering report, on average, 2 field assessments were undertaken every 3 weeks on random days of the week and a random time of the day measured between November 2019 and July 2021 by trained Milpitas field assessors.

The odor character downwind of the odor emitting facilities were relatively unique and have predominantly been described by different field assessors as follows:

- RWF (and Main Lift Station): Sewage, Septic, Fecal, or Urine
- NIRRP Facility: Garbage, Sweet, or Rotten Vegetables
- ZWED Facility: Rancid, Putrid, Manure, Rotten Vegetables, or Pungent

Bag samples were also occasionally taken for lab odor analyses at UCLA by an odor panel trained to identify the multiple dominant odor characters in a single sample and their respective intensities at different dilutions (aka Odor Profile Method). Persistency curves were developed to understand how odor impacts the communities when traveling from the odor sources into the community. The results were consistent with the observations in the community during the field assessments. These observations were also consistent with the PTR-TOF MS results that showed each source has a definitive unique “chemical fingerprint” which can be used to qualitatively determine which source is emitting the particular odor being sampled.

3.2.2 Principal Component Analyses of the PTR-TOF MS Data Results

PCA is a statistical procedure that converts a set of observations of possibly correlated variables into a set of values of linearly uncorrelated variables called principal components. In simpler words, PCA is often used to simplify data, reduce noise, and find unmeasured “latent variables”. This means that PCA will help determine a reduced number of features that will represent the original dataset in a compressed way, capturing up to a certain portion of its variance depending on the number of new features that end up selecting. This transformation is defined in such a way that the first principal component has the largest possible variance (that is, accounts for as much

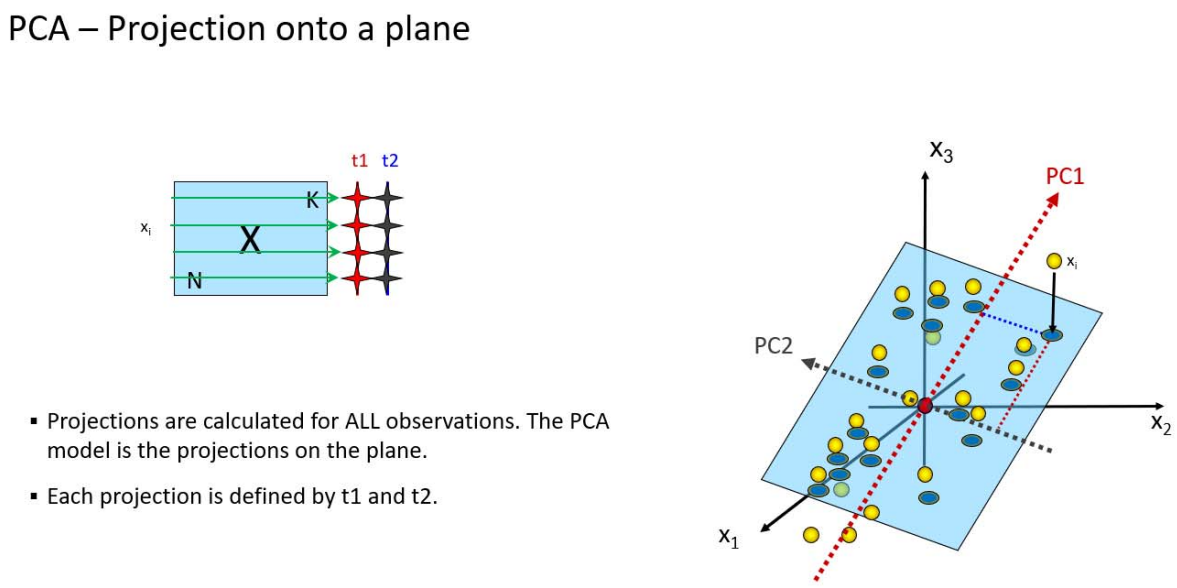
of the variability in the data as possible), and each succeeding component, in turn, has the highest possible variance possible [wiki]. This is accomplished by using a geometric array of variables and applying covariances and eigenvectors to reduce the matrix to its principle components that are unique to the data set.

PCA is used to reduce the dimensionality of large data sets by transforming a large set of variables into a smaller one that still contains most of the information in the large set. In essence, it correlates a group of compounds to all the possible compounds in a model. In this project, the MVA PCA measures how variables, such as ratios between certain compounds or specific unique compounds in a group of compounds (plume) correlate to all of the possible compounds in a model (facility plume fingerprint). Please note: The RWF is designated as the wastewater treatment plant (WWTP) in the PCA analysis section of the report. The PCA analysis was performed by data scientists employed by Sartorius North America, who owns the multivariate software package formally known as Umetrics.

PCA allows for fingerprinting each facility/source to generate a model to determine the uniqueness of that data set to compare to other similar data sets. Then, plumes that are measured in the community can be compared to the model to provide correlation, or to calculate the similarity or difference between the two sets of data.

The methodology used for the PCA analysis may be summed up in the following sequence of figures as shown in Figure 3-13.

FIGURE 3-13
REDUCTION OF A LARGE DATA SET TO TWO DIMENSIONS



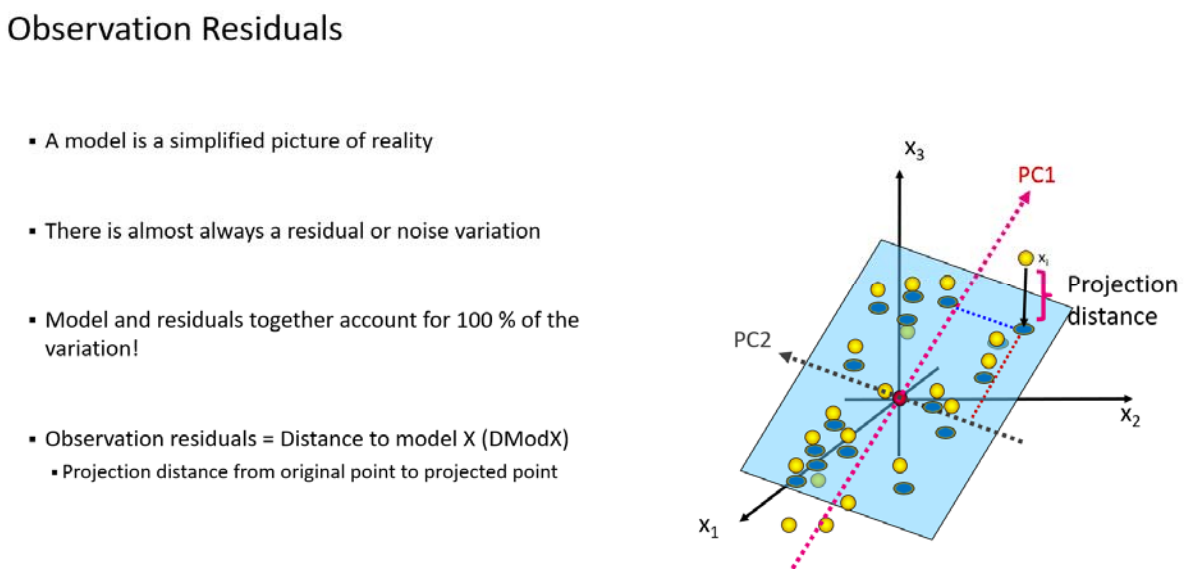
In the first step of the PCA analysis, a very large multi-dimensional data set is reduced to 2 dimensions. This projects all the observations onto a plane, which allows us to determine if there is any difference between the individual data sets. Each projection is now defined in terms of a 2-

dimensional plane. In order to perform a PCA, we first find the axis of greatest variation, which is basically the line of "best fit". This line is called the first principal component. Finally, we "project" our data points onto first principal component. Imagine the line of "best fit" as a ruler. Each data set's variation is represented by a colored dot with each new value equaling how far along the regression curve or line of best fit the resultant is.

To understand the PCA data sets, we can visually demonstrate the power of the matrix by projecting each dimensionality of the correlations between compounds and/or plumes by projecting onto a two-dimensional plane. This allows the user to visually identify how sets of variables contained within the data set correlate with each other. Distance is a function of correlation. The farther a group of variables is from another group of variables demonstrates increasing non-correlation between data sets. The data is further separated into quadrants which provide important information as to the overall distance of the data set from the overall mean of the data set. This allows the user to visually see how unique each data set (plume) is from another data set (community plume and facility plumes) with juxtaposed data sets in different quadrants having no correlation to another quadrant.

The second component of the PCA analysis is the calculation of the covariance matrix and the determination of the covariance between the pairwise means. The covariance matrix is a symmetric matrix with rows and columns equal to the number of dimensions in the data. It explains how the features or variables diverge from each other by calculating the covariance between the pairwise means. This is determined using Eigenvector values, and the corresponding Eigenvector values. The differences are the residuals, or variances between the principle component (model) and the set of data. First calculate the covariance matrix of the data, calculate the eigenvectors of the covariance matrix, and the principal components. The eigenvector with the largest eigenvalue is the first principal component, and the eigenvector with the smallest eigenvalue is the last principal component. A graphical representation of the calculations is presented in Figure 3-14.

FIGURE 3-14
COVARIANCE MATRIX AND RESIDUALS OF THE PCA

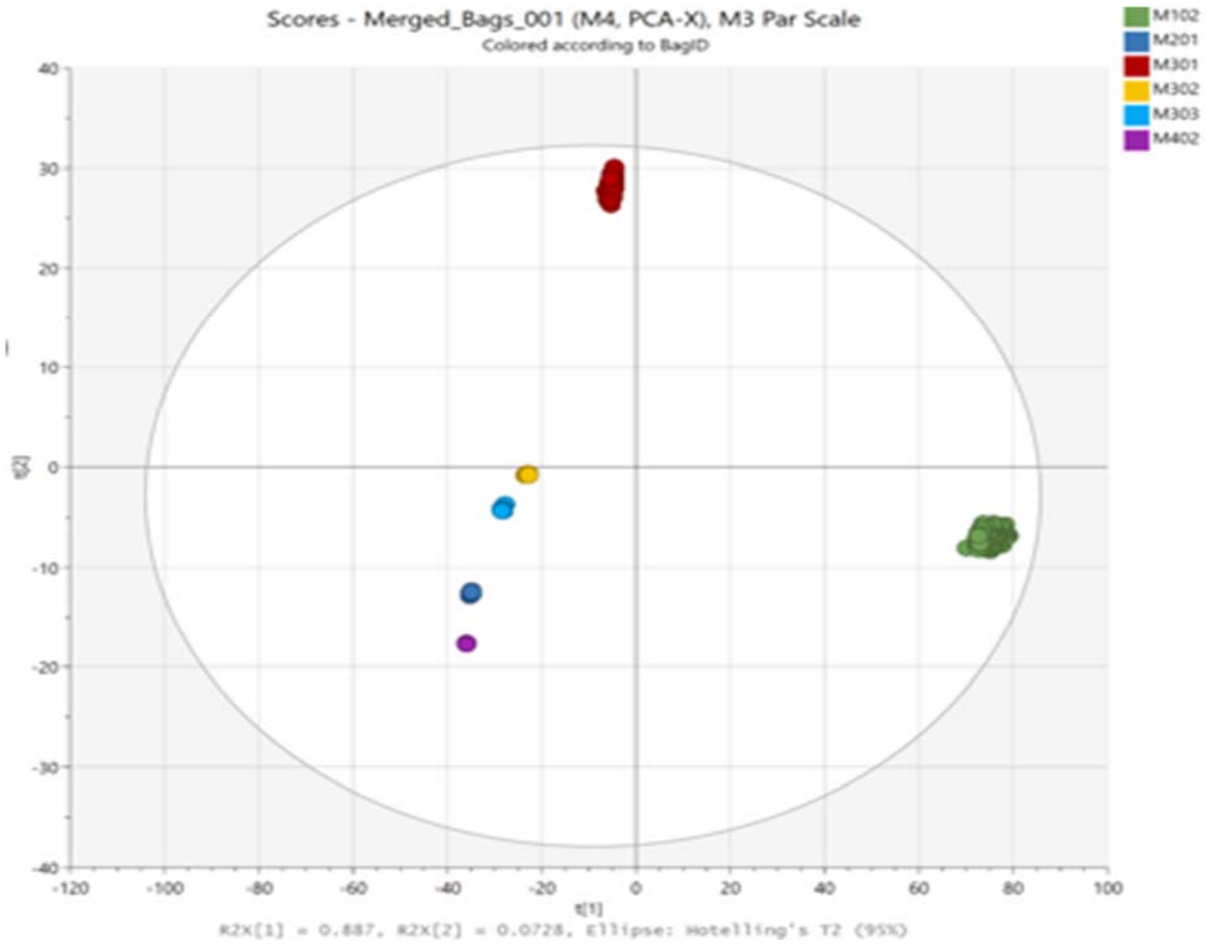


During the odor sampling analysis program, PTR-TOF MS results were sent to Sartorius North America for development of the PCA model. As more data were collected, the Soft Independent Model by Class Analogy (SIMCA) Method of PCA was determined to be the most efficient and accurate model for the odor fingerprint data. This PCA model is fit for each location and then new observations are projected. Classification is based on which model the observation is nearest in terms of Scores and DModX, both of which are mathematical evaluations of the resulting modeling. Figure 3-15 provides the PCA results as Scores correlation values between facilities/sources for several bag samples.

Note the following bag sample identification in Figure 3-15:

- M102 is ZWED Interior Space
- M201 is Primary Clarifier Effluent Weir Collection Box (RWF)
- M301 is Composting Piles (NIRRP)
- M302 is Landfill Working Face (NIRRP, with ZWED residuals)
- M303 is Dried Biosolids (NIRRP)
- M402 is MRF Interior (NIRRP)

FIGURE 3-15
PCA SIMCA SCORES DIFFERENTIATION BETWEEN BAG SAMPLES



As indicated in Figure 3-15, good differentiation exists between the sources, allowing for "fingerprinting." The results of this analysis indicate that there is a sufficient difference between the three major odor sources, and even between the different emission points within the major sources, to move forward with the modeling program. **Note:** This figure is a two-dimensional representation of a multi-dimensional graph. In this case, the actual graph represents a seven-dimensional fit of the data sets.

Figure 3-16 provides a summary of multiple individual PCA SIMCA Scores analyses of the bag samples. This demonstrates that each combined plume (or combined sources at a fenceline) at the fenceline would be unique and allow for fingerprinting and correlation of offsite odors to specific facilities, and can be further applied to individual sources within that facility. This is achieved by examining the grouping, or precision, of the different colored data sets. A tighter grouping demonstrates more unique plume compound characteristics.

3.2.3 Findings

The PCA results from several of the plumes captured in the community are depicted in the following section, as well as the bins of correlations attributed to each facility. The data are further broken down into the percent bins of a total individual analysis (each second) to its correlating facility plume at the fenceline.

Figure 3-17, shows the initial classification of compounds (over 520 individual species) to their initial facility. However, there are certain compounds within this group of 520+ compounds that are common to all or several facilities. This is denoted as the baseline noise. There was need to eliminate the effect the common compounds have on the correlations to facilities and focus the statistical analysis instead to unique compounds. Secondary focus was placed on the ratios of common compounds originating from facilities so that the analysis is more focused on speciation of the fingerprint compounds and the robustness of the model. The initial "cutoff" number, which is a ppt or ppb value, was varied to determine the effect on the model results. This is a bit subjective, but every geographic location has a common set of ambient compounds for that region based on many variables. The cutoff is necessary because as you eliminate compounds common to the geographic area and each facility, a stronger correlation will present itself as the commonality between plumes and ambient air is eliminated. This is a numerical factor that determines which results are included or discarded from inclusion of the model. As seen in Figure 3-17, the cutoff can affect the results of the binning. The cutoff value was determined by raising and lowering the concentration number and reviewing the correlations. If the correlations are poor, raising the cutoff will eliminate more common compounds, causing them to fall out of the model and make the other correlations stronger. The cutoff is not raised until only one facility is indicated, because the correlations are a percentage match to a facility fingerprint. This is why one facility is correlated at 95% confidence and the other one at 5% confidence. Statistically, there is a chance that the smaller correlation is the source of the plume but statistically, is not likely. A number that allows correlations to other facilities in much lower confidence percentages is necessary to prevent subjective bias of the data set.

FIGURE3-16
COMPARISON OF PCA RESULTS OF MULTIPLE BAGS FROM INDIVIDUAL SOURCES

FIGURE 3-17
INITIAL CLASSIFICATION RESULTS WITH DIFFERING CUTOFF VALUES

Misclassification Table for Model 9, 10, 11, 12

	1	2	3	4	5	6	7	8
1	M9, M10, M11, M12	Members	Correct	WWTP	Newby	ZWED	Estuary	No class (PModX+ <= 0)
2	WWTP	0	0%	0	0	0	0	0
3	Newby	0	0%	0	0	0	0	0
4	ZWED	0	0%	0	0	0	0	0
5	Estuary	0	0%	0	0	0	0	0
6	No class	3356		0	1656	1049	0	651
7	Total	3356	0%	0	1656	1049	0	651

2.00

Misclassification Table for Model 17, 18, 19, 20

	1	2	3	4	5	6	7	8
1	M17, M18, M19, M20	Members	Correct	WWTP	Newby	ZWED	Estuary	No class (PModX+ <= 0)
2	WWTP	0	0%	0	0	0	0	0
3	Newby	0	0%	0	0	0	0	0
4	ZWED	0	0%	0	0	0	0	0
5	Estuary	0	0%	0	0	0	0	0
6	No class	3356		2	2234	687	81	352
7	Total	3356	0%	2	2234	687	81	352

0.20

Misclassification Table for Model 13, 14, 15, 16

	1	2	3	4	5	6	7	8
1	M13, M14, M15, M16	Members	Correct	WWTP	Newby	ZWED	Estuary	No class (PModX+ <= 0)
2	WWTP	0	0%	0	0	0	0	0
3	Newby	0	0%	0	0	0	0	0
4	ZWED	0	0%	0	0	0	0	0
5	Estuary	0	0%	0	0	0	0	0
6	No class	3356		3	2680	51	98	524
7	Total	3356	0%	3	2680	51	98	524

0.50

Misclassification Table for Model 21, 22, 23, 24

	1	2	3	4	5	6	7	8
1	M21, M22, M23, M24	Members	Correct	WWTP	Newby	ZWED	Estuary	No class (PModX+ <= 0)
2	WWTP	0	0%	0	0	0	0	0
3	Newby	0	0%	0	0	0	0	0
4	ZWED	0	0%	0	0	0	0	0
5	Estuary	0	0%	0	0	0	0	0
6	No class	3356		201	1522	1483	138	12
7	Total	3356	0%	201	1522	1483	138	12

0.10

Misclassification Table for Model 25, 26, 27, 28

	1	2	3	4	5	6	7	8
1	M25, M26, M27, M28	Members	Correct	WWTP	Newby	ZWED	Estuary	No class (PModX+ <= 0)
2	WWTP	0	0%	0	0	0	0	0
3	Newby	0	0%	0	0	0	0	0
4	ZWED	0	0%	0	0	0	0	0
5	Estuary	0	0%	0	0	0	0	0
6	No class	3356		241	1698	1222	184	11
7	Total	3356	0%	241	1698	1222	184	11

0.05

The results showed that the lowest cutoff numbers had the lowest number of constituents not classified. The cutoff value of 2.0 was the “cleanest”, or excluded the most data points. This leads to future work of determining the exact cutoff value and what is an acceptable percentage of “No Classification” values. For this phase of the study, a cutoff value of 0.05 was used to include the majority of data points for the modeling. This value allows an accurate determination of the ratios of the components present, and then scored those ratios to identify the source.

In Figure 3-18, the baseline noise cutoff is expanded to eliminate common compounds that skew the correlations to multiple facilities, since facilities with the strongest correlations to the unique compounds and ratios of common compounds between facilities be determined. The analysis of the locations detailed in Figure 3-18 showed the highest correlation of compounds with those found in the Newby Island fingerprints.

Samples from the various locations in the Milpitas area were compared to the source model comprised of Primary and Secondary fingerprint constituents. The cutoff value used for this modeling was 0.05, as discussed above. The model determines the ratios of the components present, then scores those ratios to identify the source.

Figure 3-19 details a 21-hour stationary sampling event at a local hotel parking lot within the community. The binning results were calculated using the SIMCA PCA model developed from the fingerprint bags and fingerprint source previous testing. The 21-hour sampling results were then analyzed using the developed model. The binning results table shows that the measured plume did change during the course of the monitoring period. The percentage of binned compounds ranged from 89 to 100% over the duration of the monitoring period. This demonstrates that this model can provide accurate results over changing conditions and that the model can determine correlations between different attribution sources.

FIGURE 3-18
FACILITY ATTRIBUTION OF MEASURED PLUMES WITH BASELINE NOISE DIMINISHED

Spangler Middle	Members	Correct	WWTP	Newby	ZWED	Estuary	No class (PModX+ <= 0)
WWTP	0	0%	0	0	0	0	0
Newby	0	0%	0	0	0	0	0
ZWED	0	0%	0	0	0	0	0
Estuary	0	0%	0	0	0	0	0
No class	2173		0	1286	841	46	0
Total	2173	0%	0	1286	841	46	0
			0%	59%	39%	2%	0%

Dixon Landing	Members	Correct	WWTP	Newby	ZWED	Estuary	No class (PModX+ <= 0)
WWTP	0	0%	0	0	0	0	0
Newby	0	0%	0	0	0	0	0
ZWED	0	0%	0	0	0	0	0
Estuary	0	0%	0	0	0	0	0
No class	3939		0	3886	17	0	36
Total	3939	0%	0	3886	17	0	36
			0%	99%	0%	0%	1%

Embassy Suites	Members	Correct	WWTP	Newby	ZWED	Estuary	No class (PModX+ <= 0)
WWTP	0	0%	0	0	0	0	0
Newby	0	0%	0	0	0	0	0
ZWED	0	0%	0	0	0	0	0
Estuary	0	0%	0	0	0	0	0
No class	16701		0	16289	151	0	261
Total	16701	0%	0	16289	151	0	261
			0%	98%	1%	0%	2%

Milpitas PW	Members	Correct	WWTP	Newby	ZWED	Estuary	No class (PModX+ <= 0)
WWTP	0	0%	0	0	0	0	0
Newby	0	0%	0	0	0	0	0
ZWED	0	0%	0	0	0	0	0
Estuary	0	0%	0	0	0	0	0
No class	15736		0	14998	0	0	738
Total	15736	0%	0	14998	0	0	738
			0%	95%	0%	0%	5%

FIGURE 3-19
STATIONARY SAMPLING EVENT BINNING RESULTS

Hampton Inn 1430-2030	Samples	WWTP	Newby	ZWED	Estuary	No class
Total	10802	0	9652	1103	28	19
5/14/21		0%	89%	10%	0%	0%
Hampton Inn 2030-0230	Samples	WWTP	Newby	ZWED	Estuary	No class
Total	10803	0	9701	995	0	107
		0%	90%	9%	0%	1%
Hampton Inn 0230-0830	Samples	WWTP	Newby	ZWED	Estuary	No class
Total	10803	0	10783	6	0	14
5/15/21		0%	100%	0%	0%	0%
Hampton Inn 0830-1130	Samples	WWTP	Newby	ZWED	Estuary	No class
Total	5180	0	5067	93	0	20
		0%	98%	2%	0%	0%

3.2.3.1 Summary of Final Key Points of the Study

Key findings from the PTR-TOF MS and PCA analysis efforts include:

- **Unique "chemical fingerprint" distinct to each key odor source were found and confirmed via PCA. However, the plume must be speciated and analyzed by PTR-TOF MS to be used with the PCA model. The model is generated which allows for bags or SUMMA canisters to be collected from the community when odorous plumes exist. The speciated data may then be used to plug into the multivariate PCA model to identify which is the facility of origin.**
- **Unique "facility fingerprint" detected by PTR-MS agreed with Jacobs odor characterization and quantification results.**
- **This study confirms that odorous air samples taken in the nearby community and analyzed by PTR-TOF MS and PCA modeling can be a valid technique to identify which facility (or which facilities) the odors are originating from.**

It must be noted that the PTR-TOF MS does not distinguish between odorous and non-odorous or lower olfactory threshold compounds. Therefore, the data cannot state that the odorous complaints are due to these particular plumes that were measured within the community at this particular time. This is further complicated during these events because when these plumes were captured, there was no discernible odor and therefore, no odor complaints filed. The data analysis identified the source of the emissions measured in the community locations, however since there were no odor complaints/odors during that sampling event, the results do not state which facility is causing odor complaints. Odor attribution is discussed in the Jacobs report. The instrumental analysis used in this study does detect compounds below the odorous threshold of the human olfactory senses. Therefore, until the platform can be deployed during an actual odor complaint and then determine that the plume captured is the same odorous plume, one cannot state that an individual facility(ies) is the cause of the odor complaints. This data suggests that there were non-complaint plumes originating from different facilities that are reaching the community. These plumes can be detected by the PTR-TOF MS and correlated to the facility from which it originated.

3.3 POSSIBILITIES FOR FUTURE WORK

The results for the study confirm that Principal Component Analysis modeling is a valid technique for classification of odor plumes present in the South Bay area.

Future work needs to be confirmed and refined. Additional tasks are listed below:

- Collection and analysis of more "fingerprint" samples for model refinement and to check the ongoing validity of the current models.
- Refinement of reprocessing methods and model with the goal to remove known and unknown bias, with the ultimate goal to provide a robust, defendable model for the prediction of determination of the odor source. Random uncertainty (bias) may be reduced by repeating the collection and analysis of facility fingerprints to improve the model.
- Sampling during odor complaint periods is warranted. Non-odorous plumes were captured and analyzed during this project, and the facilities causing the

measured plumes were identified. However, no odors were detected during this event. An additional sampling event if timed to occur during an odor complaint period would identify which facility(ies) are the source of the odors.

APPENDIX A
TABULAR RESULTS
SEE ATTACHED
DVD-ROM DISK

APPENDIX B
PTR-TOF MS OPERATING CONDITIONS
SEE ATTACHED DVD-ROM DISK

APPENDIX C
FINGERPRINT AND PCA ANALYSIS DATA
SEE ATTACHED DVD-ROM DRIVE

APPENDIX D
SAMPLE LOCATION PICTURES
SEE ATTACHED DVD-ROM DRIVE

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