Comparing Methods to Measure Air Emissions from Commercial Compost Facilities

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List of Abbreviations

atm	atmosphere
CFM	cubic feet per minute
C/N	carbon to nitrogen ratio
CO2	carbon dioxide
DMS	dimethyl sulfide
DMDS	dimethyl disulfide
GC	gas chromatography
GC-MS	gas chromatography mass spectrometry
ID	inside diameter
LPM	liters per minute
SLPM	standard liters per minute
mmol	millimole
mTorr	millitorr
m/z	mass to charge ratio
N_2	nitrogen gas
N_2O	nitrous oxide
OD	outside diameter
ppbv	parts per billion by volume
ppmv	parts per million by volume
ppmC	parts per million by carbon
PSD	prevention of significant deterioration
psia	pounds per square inch absolute
PTE	potential to emit
PTR-MS	proton transfer reaction mass spectrometry
sccm	standard cubic centimeters per minute
SLPM	standard liters per minute
TMA	trimethylamine
UHP	ultra high purity
USEPA	United States Environmental Protection Agency
VOC	volatile organic compound
WSU	Washington State University

Abstract

This study was motivated by the need to better understand volatile organic compound (VOC) emission factors to inform questions relating to air emissions permitting of commercial composting facilities in Washington State. This has become a more pressing issue as policies encouraging diversion of urban food and green waste from landfills to composting facilities are pursued, with the simultaneous risk that these same facilities may be subject to more costly and complicated air permitting applications as they expand their facilities to meet demand. Volatile organic compound emissions rates were successfully measured from the active phase of a negatively aerated 160-ton pile at the WSU Compost Facility with feedstocks consisting of manure and livestock bedding (straw, etc.). Emission rates through the negative aeration duct were 5.47 lbs per wet ton, while those from the surface averaged 0.084 lbs per wet ton, for a combined emission factor of 5.55 lbs VOCs per wet ton of compost. The small percentage (1.5%) of fugitive emissions from the surface suggests that negative aeration systems, such as the one at WSU, have a high potential to control VOC emissions if biofilters downstream of the duct can be operated efficiently. The very low emission rates at the end of active composting imply that fugitive VOC emissions from the stabilization and curing phases might also be very low (less than 1% of emissions during the active phase). SCAQMD Method 25.3 is a standard analysis method approved in California for emissions testing from combustion sources that has also been used to measure compost emissions. If emissions from this experiment are expressed in terms of mass carbon emitted, (the same units employed by SCAQMD Method 25.3), the results would be less than half the previously mentioned VOC mass emission rate (2.6 lbs carbon (C) per wet ton versus 5.4 lbs VOCs per wet ton). This is lower than the emissions factor of 5.71 lbs C per wet ton used by San Joaquin Valley Air Pollution Control District for windrow green waste composting, but larger than their value of 1.78 lbs C per wet ton for windrow manure composting.

Mass emission rates at the WSU Compost Facility through the duct were dominated by methanol (65%) followed by acetone (12%). Acetone is an USEPA exempt VOC and could therefore be discounted from the emission factor. If emission of methanol and other oxygenated compounds identified here are found to dominate emissions generally from Washington State compost facilities, then the Method 25.3 reporting of total VOC emissions as carbon mass would significantly underestimate VOC emission rates. Furthermore, the use of surface flux isolation chambers can cause problems for sampling water soluble organics. While surface flux isolation chamber sampling in combination with Method 25.3 has provided the initial baseline dataset for VOC emissions factors from windrows, this analysis methodology is less useful for sampling aerations duct exhaust and may be problematic for sampling from positively aerated piles. A partnership with stakeholders to develop more accurate, reliable, and cost effective VOC sampling and analysis methods is recommended. To that end, the following recommendations were provided in this chapter with regards to sampling compost emissions: limit surface flux sampling, if possible; improve surface sampling representativeness; test semi-continuous in-situ sampling of negative aeration ducts; develop speciated VOC emission factors independent of facility testing; and use total temporary enclosures for testing emissions from biofilters and positively aerated piles.

Introduction

Composting facilities in Washington State employ a range of composting methods ranging from turned windrows, mechanically aerated piles with positive, negative, or reversing aeration systems, and positively aerated piles covered with a microporous membrane material. The diversity of processing conditions poses some challenges in developing volatile organic compound (VOC) emission factors that could be broadly used in air emissions permitting. The purpose of this report is the comparison of two measurement methods for VOCs: gas chromatography mass spectrometry (GC-MS), used for testing emissions from samples collected in summa canisters, and proton transfer reaction mass spectrometry (PTR-MS) an *in-situ* analysis method suited for continuous emission testing. These techniques were applied at the Washington State University (WSU) compost facility and in lab-scale tests to determine best approaches for VOC sampling and emissions testing. WSU uses a negative aeration composting method and there is no documented method for testing this type of aeration process.

Our study is motivated by the need to better understand VOC emission factors to inform questions related to air emissions permitting in Washington State. These questions have become more pressing as policies encouraging diversion of urban food and green waste from landfills to composting facilities are pursued, with the simultaneous risk that these same facilities may be to more costly and complicated air permitting applications as they expand their facilities to meet demand. Understanding emission factors for the active composting phase and the efficiency of control technologies to reduce VOC emissions is the crux of the matter for air emissions permitting. The VOC emission factor, defined as pounds VOC emitted per wet ton of feedstock material, and the efficiency of control technologies utilized at the facility establish a facility's yearly emissions potential (potential to emit, PTE). The PTE value determines the course of the permitting process. If the PTE is greater than 100 tons / year the facility would be required to apply for a Title V air permit. This is a more complicated and expensive federally required permitting program administered by state and local air agencies. A tension now exists in Washington state between the policy of encouraging diversion of urban food and green waste from landfills to composting facilities, and potentially subjecting these same facilities to more costly and complicated air permitting applications as they expand their facilities to meet demand. There is a general need to better understand the green waste composting process as conducted in the state and determine the appropriate VOC emission factors. These factors are required for preconstruction permit programs for new, large facilities and for significant changes in capacity to current facilities that would warrant a Prevention of Significant Deterioration (PSD) permit, as well as for ongoing requirements for Title V air permitting.

A compost facility survey completed in Spring 2020 broadly determined the composting processes utilized for the Washington State's larger facilities (Jobson et al., 2020). Negative aeration in static piles was identified in the survey as the most commonly used process. Figure 1 illustrates a generic compost facility using a negative aeration system to highlight known VOC emission sources. In negative aeration ambient air is pulled through the pile by duct work beneath the pile and the air vented through a biofilter that destroys some fraction of the VOCs emitted from the piles. Emission of VOCs can occur from several points in this process as indicated by the red arrows in the figure. These points include the material feedstock piles, the active composting phase, stabilization / curing phases, and the biofilter. Feedstock material may be stockpiled for several days or more, either in an enclosed building or out in the open. The feedstock material is ground and mixed, adjusted for moisture content, then sent to the active composting stage where the majority of the decomposition occurs. After active composting, the material is stored for several more weeks as slow decomposition occurs before the material stabilizes and can be stockpiled for sale.

The active phase of composting is thought to be the major source of VOC emissions. In the active phase compost piles are aerated by mechanical air flow, such as negative or positive aeration systems, or are aerated by periodic turning of the pile in windrow systems. The active piles are required by regulation to be covered in a layer of finished compost or other materials to provide a thermal insulation cover to ensure that the pile is heated sufficiently to its outer surface. This covering can also act as a control technology for reducing VOC emissions from the pile surface. The active phase may last for three weeks, after which the piles are moved and spend time in a stabilization / curing phase. In this phase the piles are still biologically active but generate less heat and emit VOCs at a lower rate. These piles may or may not be aerated or turned depending on the facility operator, and this phase may last two to eight weeks.

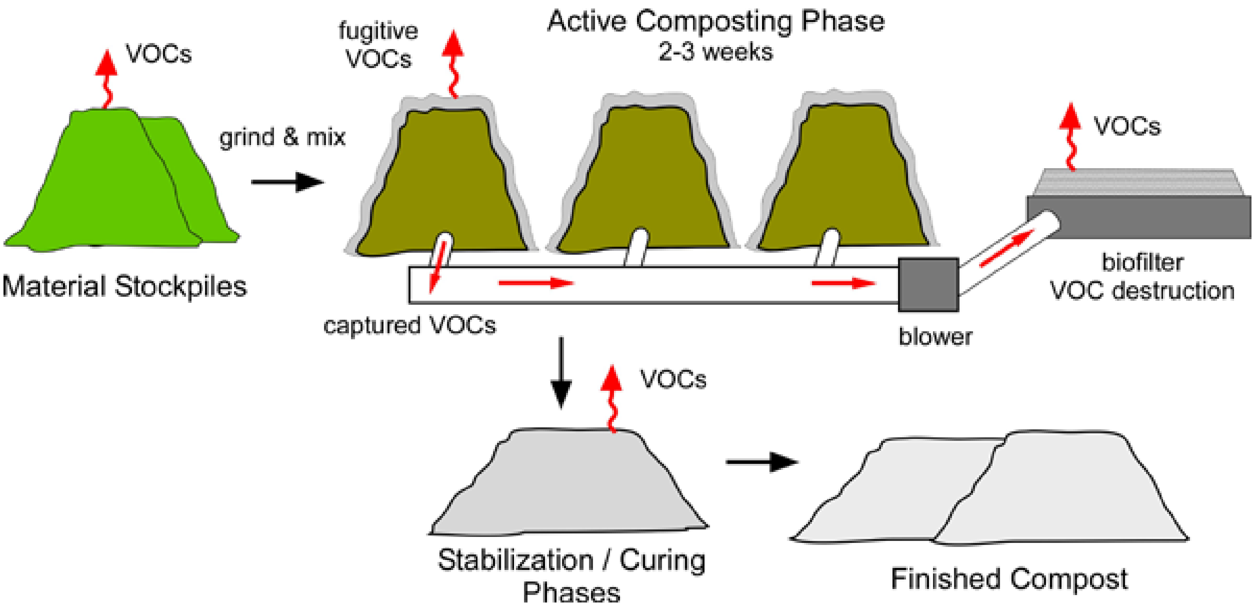

Figure 1: Schematic of VOC emission sources from a compost facility using negative aeration for active phase composting. VOC emissions are shown as red arrows.

Most of the work on measuring compost emission factors for air permitting needs has been conducted in California on windrow systems. These emission factors have been adopted by other air agencies for permitting windrow and ASP systems. It is not clear that ASP systems would emit VOCs at the same rate as window systems; the lack of ASP system emission data precludes such a comparison. For windrow systems, it has been estimated that 70% of the VOC mass is emitted during the active composting phase and 30% is emitted during the stabilization / curing phase (CIWMB, 2007). In the negative aeration system, the air pulled through the piles during the active phase is typically sent to a biofilter where the VOCs are consumed by microbes growing in some medium, typically wood chips. Biofilters have been documented to be efficient at removing VOCs and ammonia. This is an important control device in reducing facility VOC emissions for determining PTE. For negative aeration systems the proportion of fugitive VOCs emitted from the pile surface compared to the proportion pulled from the pile by the negative aeration flow has not been clearly established. Data may be available from site-specific testing reports but is generally not publicly available. At facilities using negative aeration with static pile systems, sampling of negative aeration ducts and measurement of biofilter destruction efficiency are the critical process points for VOC emission factor development.

There is limited data on VOC emissions factors from composting of municipal green waste and residential food waste useful for air permitting. These materials are major compost feedstocks for Washington State compost facilities (Jobson et al., 2020). The VOC emission factor represents the total amount emitted over the active and stabilization / curing phases of the composting process. The VOC emission factors that have been developed are based on emissions testing conducted in California from turned windrows and not ASP systems. Due to the limited nature of the underlying studies, it is possible that these emission factors may not adequately represent emissions from the types of composting processes and aeration types now being used in California and Washington. It is known that VOC emission rates are impacted by the conditions of the composting process and include material moisture level, oxygen levels, pH, carbon to nitrogen ratio (C/N), temperature, and nature of feedstock material (SJV, 2010; Sundberg, 2005). Variability in compost emission factors would be expected due to differences in process conditions and feedstock materials.

Table 1 lists green waste VOC emission factors from windrows with uncontrolled emissions determined in California studies. The studies listed in Table 1 were used to established emission factors for the San Joaquin Valley Air Pollution Control District in 2010 (SJV, 2010). The average from these four sites is 5.71 lbs VOC / wet ton compost. This emission rate represents uncontrolled emissions inherent to the windrow composting process. Efficiencies of any control technologies used are applied to this base rate, reducing the PTE. For example, the use of a finished compost layer cover over the windrow can significantly reduce fugitive VOC emissions (CIWMB, 2007). Washington State Department of Ecology and other air quality permitting jurisdictions in WA such as the Puget Sound Clean Air Agency (PSCAA) and elsewhere, such as Colorado (CDPHE, 2012), have adopted the San Joaquin Valley value of 5.71 lbs VOC / wet ton for uncontrolled VOC emissions if site specific data is lacking. VOC emission factors from material feedstock piles have been estimated to be on average 0.20 lbs VOC / wet ton per day (ARB, 2015).

Table 1: Green waste composting VOC emission factors from California studies (SJV, 2010)

Site	Active phase (lbs VOC / wet ton)
CIWMB (Modesto)	0.85
Site X	6.30
NorCal Jepson Prairie	5.65
Northern Recycling	10.03

Key issues in compost VOC emissions testing are the cost of testing and the inherent uncertainties and difficulties in the sampling and test methods. The standard method for measuring VOC emissions from surfaces employs a surface emission flux isolation chamber (USEPA, 1986). This is essentially a small dome placed on the pile surface that collects emissions from a relatively small surface area (0.13 m^2) compared to the total surface area of the pile. Obtaining a representative sample is a basic problem with this method and a number of locations on the pile surface are typically sampled over the course of the active composting phase. Air samples are collected from the chamber, and from the measured VOC concentrations a surface flux density (mg VOC hr^{-1} m^{-2}) can be calculated. The surface flux density can change significantly with time as the pile ages and from location to location on the pile surface. These spot measurements in time and location on the pile surface are used to determine the total VOC mass emitted given the pile surface area (Jobson and Khosravi, 2019). For the studies listed in Table 1, VOCs were sampled and quantified using a standard analysis method approved in California for emissions testing, SCAQMD Method 25.3. This method is similar in principle to USEPA Method 25. With this method, a total VOC value is determined from the sum of two separate samples collected from a surface flux isolation chamber: an air sample collected into an evacuated canister and a water filled impinger sample that collects water soluble VOCs not recoverable from canisters, such as organic acids. The canister sample is subsequently analyzed by gas chromatography for total nonmethane nonethane nonethene organic compounds. The water from the impinger is analyzed for total organic compounds using a commercial water quality analyzer. The results are combined to give a total VOC amount in units of ppmC (parts per million by carbon). The method does not quantify individual compounds that are emitted, nor does it determine total VOC mass emitted. The method measures carbon, as methane (CH_4) for the canister samples, and as carbon dioxide (CO_2) for the impinger sample, so the emission rates are based on amount of carbon emitted in the VOCs, but does not account for other elements like oxygen, hydrogen, or sulfur. A total VOC mass could be determined if the relative amounts of VOCs emitted were known (i.e., relative molar amounts of acetic acid, methanol, acetone, α-pinene, etc.). The GC-MS and PTR-MS techniques can be used to quantify individual compounds emitted to het this type of information. While some information is available for VOCs sampled into canisters from GC-MS analysis, no such information exists for the types of water-soluble VOCs collected in the impinger. A general lack of information on the types of VOCs emitted and how these vary with pile age and feedstock material prevents reporting emissions in terms of actual VOC mass emitted. Method 25.3 is discussed in more detail in the Appendix.

To provide a better accounting of VOC mass emitted, this study investigated the use of PTR-MS to measure VOCs. The PTR-MS instrument has the potential of being able to measure water-soluble VOCs emitted in composting such as alcohols, acids, and ketones. The PTR-MS instrument can be used in the field to sample directly from flux chambers and negative aeration ducts, thus eliminating the need for sample collection into water filled impinges and canisters. This would simplify the sampling and analysis of VOC emissions and provide an account of what compounds are emitted rather than total VOC carbon mass as reported by Method 25.3. Knowledge of the speciated emissions profile would be beneficial in developing VOC emissions factors for permitting. VOC emissions are regulated at the state and federal level because some are known to be toxic and thus potentially harmful to human health, and because they act as precursors in photochemical reactions that create other federally regulated pollutants such as ozone and particulate matter ($PM_{2.5}$). Some VOCs are exempt by the USEPA from the VOC category because they have low photochemical reactivity and thus do not participate in local ozone and $PM_{2.5}$ pollution and have low toxicity. Acetone is an exempt VOC and is commonly observed as a major compost emission, but the ability to discount emissions of acetone from composting facilities is not possible with methods that measure only total VOCs such as Method 25.3.

This report has two parts.

- The first part describes some laboratory-based composting experiments with feedstock material from the WSU facility, composed primarily of manure and animal bedding, and a trial with green waste feedstock from a commercial composter. Materials were composted in-vessel using 100-gallon containers with lids and positively aerated. The section describes the types of compounds emitted and what is measurable by PTR-MS and GC-MS.
- The second part describes results from emission testing at the WSU compost facility on a 160-ton negatively aerated uncovered pile. In this task a sampling approach was developed to continuously sample from the negative aeration duct using a PTR-MS instrument over the course of the active composting phase (25 days). VOC measurements were made once per minute, and from the measured concentrations and duct air flow rate a VOC mass emission rate was determined. This is the first report of continuous speciated VOC measurements from an aerated static pile (ASP) system. Canister samples were collected from the duct for comparison with the PTR-MS. Compost pile surface flux densities were also measured using flux isolation chambers. Chambers were sampled by the PTR-MS in addition to canister sample collection and analysis by GC-MS. The types of compounds emitted, VOC emission rates as a function of pile age, the relative proportion of fugitive surface emissions to duct emissions, and a total VOC emission factor for this ASP system are reported. The report concludes with some general recommendations for emissions sampling and testing methods based on results from this work and discussions held with various stakeholders, including technical experts at USEPA.

Methods and Materials

Analytical Methods

Proton Transfer Reaction Mass Spectrometry (PTR-MS)

Measurements of VOCs were made using a quadrupole type PTR-MS (Ionicon Analytik, Austria). The PTR-MS continuously measures VOCs by chemical ionization using a proton transfer reaction whereby H_3O^+ transfers a proton to an organic compound in the air sample (R) to create a positively charged organic ion (RH^+) that is detected by a mass spectrometer.

$$H_3O^+ + R \rightarrow H_2O + RH^+$$

The PTR-MS mass spectrum is thus interpreted as an M+1 mass spectrum where M represents the molecular mass of the VOC. The PTR-MS method is described in detail in the literature (Lindinger et al., 1998; de Gouw et al., 2006). The proton transfer reaction is fast for compounds with a proton affinity greater than that of water and thus the PTR-MS is principally used to measure these compounds. Many compounds reported from compost emissions can be measured using the PTR-MS (i.e., alcohols, ketones, aldehydes). The PTR-MS technique is not very sensitive to organic compounds that have proton affinities substantially less than water, notably ethylene and alkanes (~C_8 and smaller).

The advantage of this technique for compost emission sampling is that it uses a continuous *in-situ* (on-site) instrument that provides data in real time. A small air flow is continuously pulled into the PTR-MS instrument and the presence of organic gases in the air flow is continuously detected. In this project the mass spectrometer was programmed to measure ~40 VOCs of interest, and generated data for this list approximately once per minute. The *in-situ* continuous sampling and high time resolution measurements are a distinct advantage for study of emission processes that change with time such as VOC emissions from composting.

Field portability also means there is no air sample collection into canisters. Polar compounds such as acids, alcohols, aldehydes, and mercaptans can adsorb to canister surfaces and be lost to analysis. The PTR-MS technique can thus measure polar compounds which are not stable in canisters. The *in-situ* real time nature of the measurement also allows VOC data to be collected and viewed on site. Being able to visualize the data *on-site* was useful for the WSU compost facility surface flux sampling because it allowed for some quality assurance to be applied to the sampling. An example of this was noting how modest fogging of the flux chamber by humidity caused immediate loss of acetic acid. This real time observation is not possible with grab sample collection in canisters and analysis at an off-site lab.

Key compost emission compounds that the PTR-MS could measure are methanol, acetaldehyde, acetone, 2-butanone, monoterpenes, and perhaps acetic acid. These compounds have been noted to comprise a large fraction of VOC emissions from green waste composting (Jobson and Khosravi, 2019; Kummar et al., 2011). The PTR-MS instrument response is calibrated using external gas standards.

Gas Chromatography Mass Spectrometry (GC-MS)

Canisters samples were analyzed by gas chromatography mass spectrometry (GC-MS) at WSU following EPA Method TO-15 utilizing an Agilent GC-MS system (7890B GC and a 5977A mass spectrometer) coupled to Entech 7200 preconcentrator. This method provides identification and quantification of specific VOCs and thus provides a complete picture of what types of VOCs are emitted and their emission rates. This is important for air permitting as some VOCs may be exempt (such as acetone) or may be listed as toxic air pollutants (TAPs) by Washington State or as hazardous air pollutants (HAPs) by the USEPA (such as acetaldehyde). Measuring specific VOC emission rates is not possible by Method 25.3. An aliquot of air from the canister (50 to 300 mL depending on concentration of sample) was preconcentrated by the Entech 7200 system in a multistep procedure that involved water removal by cold trap dehydration at -40 °C, VOC preconcentration onto a Tenax TA trap cooled to -40 °C, and cryogenic focusing in an open tube trap. The method was suitable for trapping many hydrocarbons associated with compost emissions but was not able to preconcentrate C_2-C_3 alkanes and alkenes and the technique overall is not suitable for organic acids. While organic acids are known to be emitted in composting there is no data on emission of light hydrocarbons like ethene. Separation was done on a HP-624 column (length 60 m, diam 0.320 mm, film thickness 1.80 um) using constant flow of helium (He) carrier gas (1 ml/min). Quantification was done by integrating peak areas for the compound's quantification ion and applying response factors determined from calibration standards. Canister replicates were done every 4th or 5th sample as a QA/QC measure. The GC-MS/Entech system was also used to directly sample from the in-lab composting vessels.

The canisters were cleaned using an Entech Model 3100D canister cleaning system. This model can hold 8 canisters and the oven temperature is controlled by software which enables heated and unheated cleaning cycles. Canisters are initially pressurized to 10 pounds per square inch absolute (psia) with humidified ultrahigh purity (UHP) N_2 (nitrogen gas) for 10 minutes and then evacuated: 2 cycles at room temperature followed by 3 cycles with the canisters heated to 75 °C. After this 5th cycle the canisters were evacuated under heat (75 °C) to < 50 millitorr (mTorr) pressure for 5 hours. Selected canisters were tested for cleanliness immediately after the cleaning procedure by filling them with UHP N_2 and analyzing a 400 mL sample. None of the target VOCs appeared in these cleaning blank samples, illustrating the cleaning procedure was very effective in removing traces of the sample from the canister.

Key compost emission compounds that the GC-MS could measure are C_2-C_4 alcohols (i.e., ethanol, propanol), C_2-C_6 aldehydes (i.e., acetaldehyde, propanal, isovaleraldehyde), C_3-C_6 ketones (i.e., acetone, 2-butanone), monoterpenes, dimethylsulfide (DMS), dimethyl disulfide (DMDS). These compounds have been noted to be important components of VOC emissions from green waste composting (Jobson and Khosravi, 2019; Kummar et al., 2011). The GC-MS instrument response is calibrated using external gas standards.

Calibration of PTR-MS and GC-MS

Calibration of the GC-MS and PTR-MS instruments using the same calibration gas standards was an important experimental protocol in order to isolate potential discrepancies to the principle of measurement. The PTR-MS and GC-MS response to various VOCs was determined by three calibration methods. For most VOCs, multi-component compressed gas standards (Apel-Reimer Environmental, Florida) were used. One such standard contained the following gases: propene, methanol, acetonitrile, acetaldehyde, acetone, isoprene, methacrolein, benzene, toluene, p-xylene, 1,2,4-trimethylbenzene, α-pinene, and 1,2,4,5-tetramethylbenzene. This gas standard was dynamically diluted in hydrocarbon free air (zero grade air) air at 50% relative humidity and used to calibrate both the GC-MS and PTR-MS. The other compressed gas standard contained monoterpene compounds: α-pinene, β-pinene, camphene, limonene, 3-carene, α-phellandrene, and terpinolene, and was used to calibrate the GC-MS. Instrument response factors for formaldehyde, acetic acid, hydrogen sulfide, and dimethyl sulfide was determined from permeation tubes (Kin-Tek) diluted into a 50% relative humidity zero grade air (hydrocarbon free) gas stream.

In addition, response factors were also determined from 15 millimole (mmol) solutions of water-soluble compounds by dynamically diluting them using a syringe pump (Harvard Scientific) into a heated air flow (Gueneron et al., 2015). This established response factors for 2-butanone, 2,3-butadione, ethanol, i-propanol, and dimethyl disulfide. The approach was validated against the compressed gas standards for methanol, acetone, and acetonitrile. This new calibration method was developed for this project recognizing that most of the VOCs emitted from compost are oxygenated, polar compounds, for which it is difficult to obtain compressed gas standards from commercial suppliers (since such compounds are not stable in cylinders). Permeation tubes are used for such compounds, but this approach can be expensive. A permeation tube is needed for each compound requiring calibration, an expense in terms of time needed to perform the individual compound calibrations and in the cost of purchasing the permeation tubes. The aqueous phase standards prepared from neat chemicals (Sigma-Aldrich) can be multicomponent, so that 4-6 compounds were made up in one solution, and thus one test gas mixture can be used to obtain response factors for many compounds. In this approach, the syringe pump infuses the solution at a known rate (30 µL / hr) into a heated 1 standard liter per minute (SLPM) flow of air at 50% relative humidity. The liquid evaporates and mixes with the air flow to produce a test gas mixture at a known mixing ratio. The resulting VOC mixing ratio in the test gas stream can be varied by changing the infusion rate or the diluting air flow rate. This approach worked well for calibrating both the PTR-MS and GC-MS.

In-Vessel Composting

Five in-vessel composting trials were conducted in the lab to examine VOC emissions from the WSU stock material and material from a commercial composter. The WSU Covid-19 lockdown in 2020 meant that little food waste from on campus dining halls was being composted at WSU. Thus, trials 1-4 used WSU feedstock material which was mostly manure and animal bedding with wood chips and straw. For trial 2 extra water was added to determine if ‘wet’ compost behaved differently. A squeeze test for this material wrung water from it, so moisture levels were much higher than the ~60% optimum the facility targets. Trial 5 used compost feedstock material from a commercial operator. It contained a significant amount of woody material and residential green waste and food waste. It was used as is, as dug out from a freshly ground stock material pile.

Figure 2 shows a schematic of the in-vessel composting set-up. Approximately 380 lbs of material was placed into a 100-gal polypropylene container (48 in tall by 26 in diameter). The material sat on a stainless-steel screen that was supported about 2 in off the bottom of the container. Into this gap air was metered using a rotomoter to supply a steady positive aeration flow of dry air at 5 liters per minute (LPM), yielding an aeration flow of 0.40 cubic feet per minute (CFM) / yd^3 of feedstock material. From our composting facility survey, commercial facilities used a much higher aeration flow when it was reported, 2 to 5 CFM / yd^3. Our tank appears to be more efficiently aerated given its small size relative to commercial piles, as compost temperature reached 70 to 80 °C in the first few days. Trial 1 used a combination of intermittent and continuous aeration. Intermittent aeration caused a significant spike in headspace VOC concentrations, presumably a result of sweeping the pore space of accumulated VOCs. For ease of analysis continuous aeration was used for the other trials.

The container was wrapped in R3 insulating foil to help maintain composting temperatures. Type K thermocouple probes were inserted through airtight fittings to record compost temperature in two locations: at the bottom (7 inches above the aeration zone) and middle of the pile (16 inches above the bottom probe level). Probes were inserted into the approximate center of the container. Headspace air temperature was also monitored. Temperatures were logged using Azeotech Daqfactory software and a Campbell CR1000 data logger.

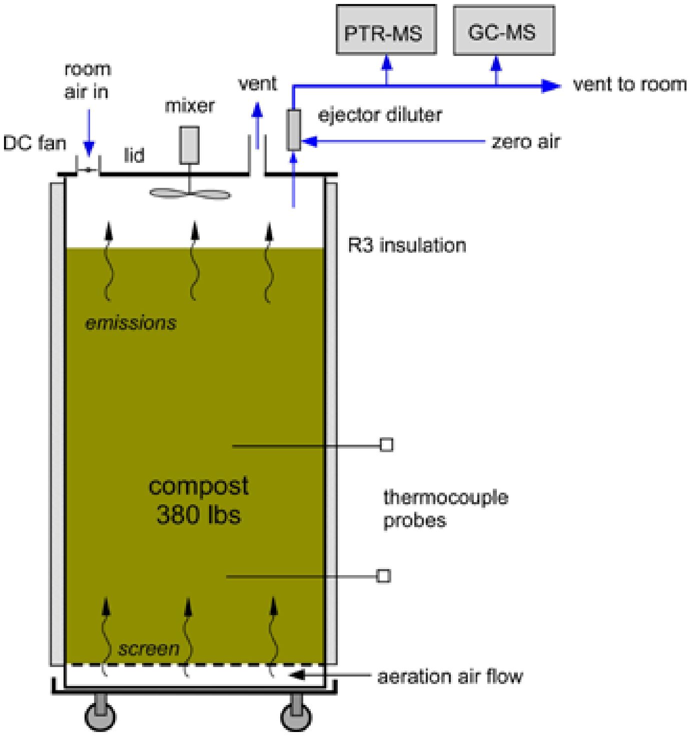

Figure 2: Air sampling from the in-vessel composting trial showing use of an ejector diluter to pull an air sample flow from the headspace and dilute it with clean dry air.

The container lid enclosed about a 50-L headspace volume from which air samples were continuously extracted for analysis by PTR-MS, GC-MS, and other instruments including a methane / carbon dioxide (CO_2) analyzer (Los Gatos UGGA). A small DC fan was fitted into an opening in the lid. This fan provided continuous room air flow air flow through the headspace. The flow rate could be set by the voltage applied to the fan. For all trials the air flow rate was set at 60 LPM, yielding an air change rate of ~1.2 volumes per minute. This ensured headspace concentrations came into rapid equilibrium with emission rate changes. A mixing fan stirred the headspace air to ensure emissions were well mixed with the 60 LPM air flow throughout the headspace. Air was vented out a 1-in diameter pipe fitted to the lid, and vented emissions were captured by a laboratory exhaust snorkel.

Different air sampling approaches were used to overcome issues with water vapor condensation in air sampling lines. As the pile heated a large volume of water vapor was emitted that condensed on the vessel lid and in air sampling lines. Handling water vapor is a basic challenge with compost emission sampling with flux isolation chambers. For trials 1-4, air from the vessel headspace was pulled at 8 LPM by a diaphragm pump. For the first two trials, the headspace air immediately passed through a 2-L PFA container which allowed air to cool and water vapor to condense and collect at the bottom of the container. This prevented condensed water from flowing into sample lines and into instruments. The container was emptied and dried each day. Some fraction of water-soluble gases such as acids and alcohols will dissolve into the water and be lost from the sample stream. To better reduce the occurrence of condensed water in sample lines, a dry air flow was added to the sample flow for trials 3 and 4. This was done by adding a dilution tee to the sample line inside the tank head space. Dry air (zero grade air) was added to the sample flow at a known rate by a mass flow controller. While this approach reduced the sample humidity it was a somewhat clumsy. The best configuration for handling the high humidity air sample was to use an ejector dilutor. This was done in trial 5 and adopted for sampling the negative aeration duct at the WSU facility. In this approach a continuous flow of dry air (controlled by a mass flow controller) goes to the ejector diluter venturi, creating a low-pressure zone that pulls a sample air flow out of the head space of the vessel. The sample air flow is determined by the length and internal diameter of the tubing attached to the ejector diluter's low-pressure side. The sample flow rate was measured periodically using a primary standard air flow calibrator (Synsidyne Gilbrator). In this approach the air sample is diluted and efficiently mixed with dry zero grade air, lowering the humidity and preventing condensation and subsequent loss of water-soluble gases in samples lines. The ejector diluter body and sample tubing could also be heated to prevent condensation in the small diameter sample tubing (1/16-in outside diameter [OD] x 0.020-in inside diameter [ID]). The flow from the ejector diluter exited through 3/8-in PFA tubing towards the analytical instruments and was vented into the room. The PTR-MS and GC-MS subsampled from this flow. For the other trials, the GC-MS/Entech system directly sampled from the vessel headspace using an 8-ft length of 1/8-in electropolished stainless steel heated to ~70 °C. Canister samples for trails 1-5 were collected by attaching a 1-ft length of 0.25-in PFA tube to the canister and inserting the tube into the headspace through the vent port on the lid. The evacuated canister was slowly opened to collect a sample. Fogging of the sample line frequently occurred. Canisters were typically analyzed one to two days after collection.

For trials 1-4, the air sample was pulled from the head space using a diaphragm pump and the PTR-MS and methane / CO_2 analyzer subsampled from this flow. These instruments also sampled room air every 10 minutes for an hour. The difference between room air concentrations and headspace concentrations was attributed to compost emissions. Room air concentrations of VOCs were very low compared to the headspace concentrations and this was a minimal correction.

VOC Emission Measurements at the WSU Compost Facility

Emissions from a 160-ton negatively aerated compost pile (zone 10) at the WSU compost facility were measured from July 31 to Aug 24, 2020. Surface flux densities of VOCs were measured from the pile surface using Washington State Department of Ecology's surface flux isolation chambers. Mass emission rates through the negative aeration duct were also measured.

The pile took 3 days to construct, with the first half built on July 29 and the second half completed at noon on July 31. An instrumented van operated by the Laboratory for Atmospheric Research housed the PTR-MS and other instruments was moved to the zone and parked alongside the pile towards the push wall. A picture of the van parked alongside the pile is shown in Figure 3. The van was powered from two 30 A electrical outlets installed on site for this project. The van was equipped with a weather station to measure ambient air temperature, wind speed and direction, air pressure, and relative humidity. PTR-MS measurements began ~3 PM on July 31, roughly 3 hours after the operator finished building the pile. The pile was removed on Aug 24.

Figure 3: Surface flux isolation chamber at sampling location #1 with instrumented van in background.

The volume of the pile was estimated to be 260 yd^3 based on measured pile dimensions (length 75 feet, height 8.5 feet, base width 18.6 feet, ridge width 3.5 feet). The WSU facility uses this value and an initial stockpile material density of 1,200 lbs yd^{-3} to determine initial pile mass. Given this density and volume, the initial wet mass of the pile was 160 tons. Negative aeration was supplied by single pipe comprised of three nested plastic pipes running the length of the pile at the base. The pile sat on asphalt. The aeration duct exited the pile through a 4-ft high concentrate push wall (ecology blocks) and entered the main aeration plenum as an 8-in diameter plastic pipe. Air flow from the zone was controlled by a butterfly valve on the 8-in pipe through the automated computer-controlled aeration system (Green Mountain Technology, WA). The air flow during the first week was ~500 CFM, yielding an estimated air flow-to-pile volume ratio of 1.8 CFM / yd^3. Note the pile surface was not covered with a finished compost layer so fugitive surface emissions were uncontrolled.

Emission measurements involved continuous sampling by the PTR-MS instrument from the 8-in negative aeration duct and surface flux sampling from three locations on the top of the pile using the surface flux isolation chambers. A schematic of the pile and sampling locations is shown in Figure 4. Wooden planks were placed on the pile surface to act as walkways and prevent compaction and disturbance of the surface around the flux chambers. Chambers sampled from the exact location each time, as indicated by a surface ring depression made by the chamber. The weather during the sampling period was typical for Pullman at this time of year with no rain and daytime temperatures often >90 °F (> 30 °C). Air temperature, dew point, pressure, and wind speed measured at the site are shown in Figure 5.

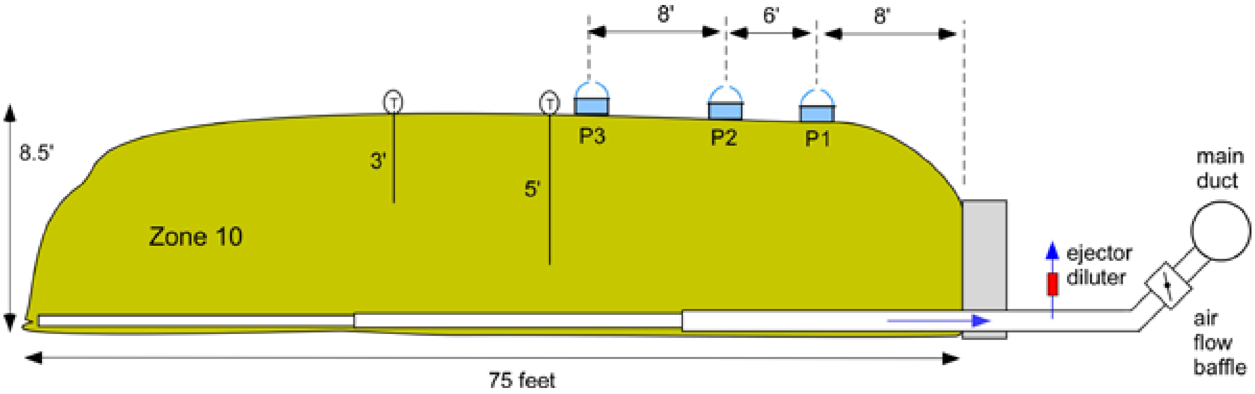

Figure 4: Sketch of surface flux sampling locations on pile ridge (P1, P2, P3). Pile was 75 feet long and ~ 8.5 feet high. Estimated initial mass was 160 tons. The bottom temperature probe (T) was 5 feet long and located beside sampling location P3. Air flow in the negative aeration duct was sampled using an ejector diluter at the position indicated as the duct exited the push wall.

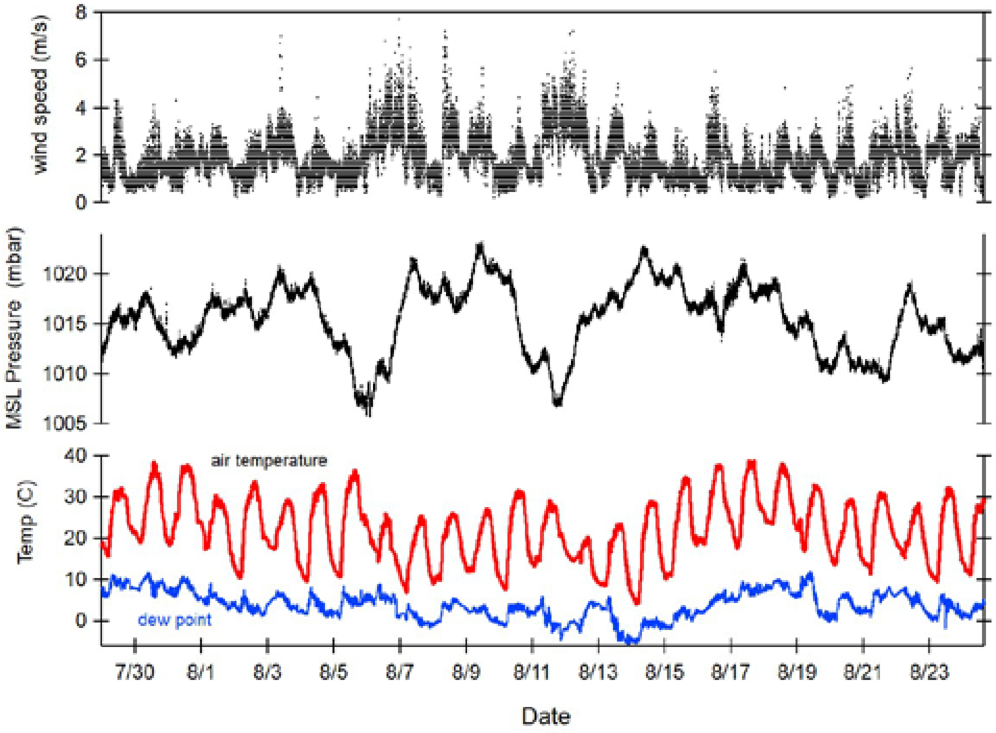

Figure 5: Measured weather conditions at the WSU compost facility during the sampling period.

Negative Aeration Duct Sampling

Air sampling of the aeration duct flow was done using an ejector diluter attached to a stainless-steel Swagelok compression port fitted to the 8-in duct. The ejector diluter caused the air sample to be continuously pulled from the duct and diluted with clean dry air to reduce water vapor concentrations to levels below the ambient dew point. The outlet of the ejector diluter was connected to ~20 feet of 3/8-in PFA tubing that went back to the van. This air flow was subsampled by the PTR-MS, a methane / CO_2 analyzer, and a nitrous oxide (N_2O) analyzer. The N_2O analyzer failed on the first day of sampling and no N_2O data was obtained in the experiment. A water trap was placed inside the van to collect any condensed water vapor before it reached the instrumentation. The trap was inspected each morning and emptied of any water. Dew point temperatures did fall low enough on several mornings that condensation in the sample line occurred and water was collected in the trap. Clean dry air was supplied to the ejector diluter from a zero-air generator (Teledyne) located in the van. Air flow was controlled by a mass flow controller at 18.5 SLPM. The sample line for the low-pressure side of the ejector diluter was a 12 cm length of 1/16-in OD x 0.020-in ID glass coated stainless steel tubing (Restek Inc.). The sample flow was measured at the beginning and end of the experiment to determine the sample dilution factor. The measured dilution factor was 28.9.

Figure 6: Ejector diluter on the negative aeration duct. Smaller diameter tubing is the zero air supply from the van. Larger ID tubing extending vertically is the sample air flow out to the van instrumentation. Wires seen at the bottom of the ejector diluter power resistive heating wires heating the body and the 1/16-in sample tube projecting into the duct.

To prevent sample loss and potential condensation in the 1/16-in sampling tube, the tube and ejector diluter were heated to 70 °C using a resistive heating wire. The sample line was insulated with glass wool and inserted into 1/2-in diameter stainless pipe. A silicon rubber plug sealed the end of the pipe around the 1/16" sampling tube with ~0.25 in of the sampling tube protruding from the end. The ½-in sleeve was then inserted into the duct through a ½-in through bore Swagelok compression fitting. The sample inlet was positioned vertically about 3-in from the duct wall, roughly the center of the duct. The ejector diluter body was insulated with glass wool and wrapped in aluminum foil to shield against the weather. A photograph of the assembly is shown in Figure 6.

Duct air velocity, air temperature, and absolute pressure were periodically measured in order to calculate the duct air flow rate (m^3 hr^{-1}) and to convert VOC mixing ratios into concentration units from which emission rates could be calculated. A mini vane anemometer (Dwyer VT-300) was used to measure duct air velocity by inserting the probe through a port in the aeration pipe. Flow measurements were taken across the diameter of the pipe. A weak air velocity gradient was noted, with slightly lower flow nearer the pipe walls. Standing water was evident in the bottom of the pipe. Given the small difference in air velocity across the diameter of the pipe, air flow measured at the center of the pipe was used to determine the volumetric air flow rate for calculating mass emission rates. A thermocouple wire (Omega) was used to measure air temperature at the center of the pipe. The absolute air pressure in the duct and ambient air pressure was measured by a pressure transducer (Druck DP705) with a pressure resolution of 0.1 Torr. The pressure transducer was connected to compression fitting port that was added to the duct for this purpose. When not in use, the port was capped to prevent air leakage. Measured values of duct air velocity, pressure, and air temperature are shown in Figure 7.

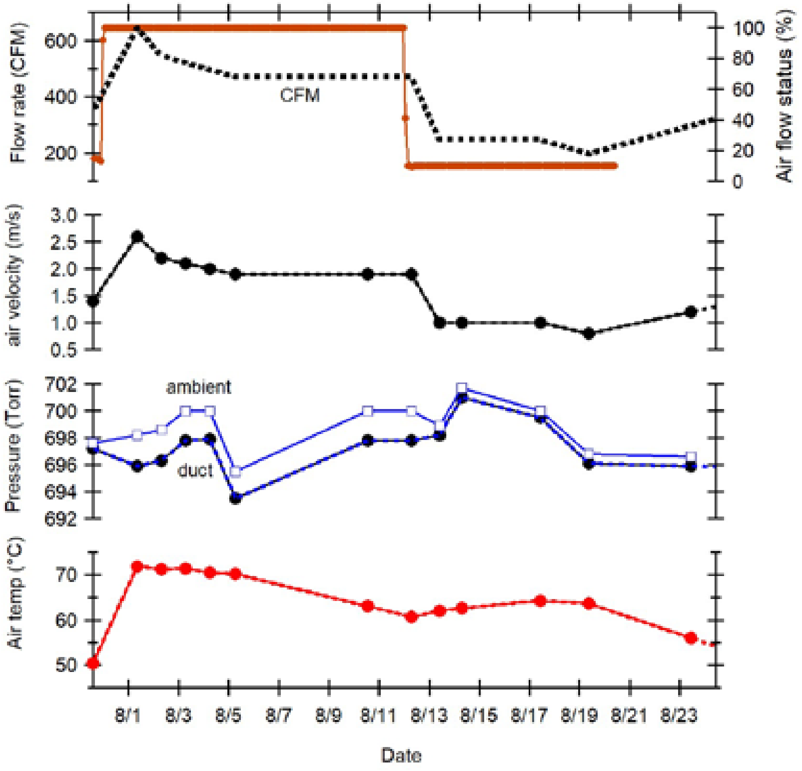

Figure 7: Measurements of duct air temperature, absolute pressure, and flow velocity at zone 10. Air flow rate was determined from velocity measurements and duct inner diameter. Data were linearly interpolated to yield hourly values. Air flow status is a metric recorded by the aeration control system.

VOC concentrations ($mg\ m^{-3}$) were calculated from the measured molar mixing ratios using the following equation:

$$\text{mg m}^{-3} = \text{molar fraction x (P/RT) x MW x 1000 L m}^{-3} \text{ x 1000 mg g}^{-1}$$

where P is the duct air pressure (atm), R is the universal gas constant (0.08206 L atm mol^{-1} K^{-1}) and T is the duct air temperature (K), MW is the molecular weight of the VOC (g mol^{-1}). Duct air temperature and pressure were measured periodically, and data linearly interpolated to yield estimates over the entire period.

The VOC mass emission rate (g hr^{-1}) through the duct was determined by multiplying the duct VOC concentration by the duct air flow rate. The air flow rate was calculated from the measured air velocity and cross-sectional area of the inner pipe. The duct air velocity was measured periodically, and the data linearly interpolated to yield an estimate of the air flow rate (m^3 hr^{-1}) over the entire time period. The mass emission rate is given by

$$\text{g hr}^{-1} = 10^{-3} \text{ x C x F}$$

where C is the VOC concentration (mg m^{-3}), and F is the duct air flow rate (m^3 hr^{-1}).

Surface Flux Sampling

Sampling from the pile surface was done using two surface flux isolation chambers according to established EPA methodology (EPA, 1986). Three different locations were sampled on the pile ridge as illustrated in the schematic shown in Figure 4. Each chamber sampled a 0.13 m^2 surface area of the pile. The chambers consisted of a stainless steel ring to which a Plexiglas dome was fixed with an airtight O-ring seal as illustrated in Figure 8. A 0.75-in hole in the dome center vented the chamber and allowed the chamber pressure to be in equilibrium with local air pressure. The chambers were swept with clean dry air at 8 SLPM provided by a zero air generator in the van. To this air flow was added a 20 standard cubic centimeters per minute (sccm) flow of a tracer gas that was measured by the PTR-MS and GC-MS. Typically, helium is used as the tracer but for this work benzene was used as a tracer gas since it could both be detected by the GC and PTR-MS methods, is not water-soluble, has low abundance in Pullman ambient air, and is not emitted in significant quantities from the WSU material (as observed in lab experiments). This allowed for *in-situ* analysis of the chamber conditions to determine if steady state conditions were achieved and examine the extent of chamber dilution caused by wind. Tests were conducted with this tracer to ensure that it was not lost to the pile surface due to adsorption.

The chamber was continuously sampled by the PTR-MS by pulling a 1 SLPM flow to the van through ¼-in PFA tubing. After chamber concentrations had reached a steady state condition, as determined by visual inspection of the real time PTR-MS data displayed on the instrument screen in the van, a canister sample was collected from the chamber. This was done by connecting a length of ¼-in PFA tubing to an evacuated 6-L SUMMA canister and inserting the tube through the vent port in the dome so that the tubing end was in line with the PTR-MS sampling line. The canister was slowly filled over the course of 10 minutes. After canister filling the air temperature in the chamber was recorded with a handheld thermocouple gauge. Duplicate samples were collected by filling a second canister immediately after the first sample was collected. After sampling, the chambers were rinsed with distilled water and dried. Blank samples were also collected by placing a clean chamber on a sheet of aluminum foil and sweeping chamber with the 8 SLPM of zero air flow as done for sampling. This was done on-top of the push wall rather than the top of the pile for convenience. There was no evidence of sample carry over or contamination of the chambers from the blank samples. Can sampling metadata are listed in Table A2 of the Appendix.

Figure 8: Flux chamber sampling at PI. Left photo shows chamber on July 31. Right photo is same chamber on August 2 showing condensation on the Plexiglas dome. Clean zero air flow with added tracer was supplied to the flux chamber at 8 SLPM from a zero-air generator in the van. A 1 SLPM air flow from the chamber was pulled back to the van via ¼" PFA tubing for continuous analysis by PTR-MS. Canister sampled through ¼" PFA tubing through chamber top. Aluminum foil was sometimes used to shield the chamber opening from wind.

The emission rates of the measured VOCs were determined from the measured molar mixing ratio, the sweep air flow rate through the chamber (8 SLPM), the tracer dilution correction factor that accounts for dilution of the chamber by wind, and the surface area sampled (0.13 m^2). Measured mixing ratios were converted to concentrations ($\mu g\ m^{-3}$) using standard air temperature and pressure conditions (1 atm, 273 K) since the sweep air flow was controlled at standard conditions. VOC flux density ($\mu g\ m^{-2}\ min^{-1}$) was calculated

$$\text{flux density} = C \times Fs \times DF \ / \ As$$

where *C* is the concentration, *Fs* is the constant sweep air flow rate, and *DF* is the dilution factor determined from the measured tracer concentration in the chamber and the concentration in the sweep air, and *As* is the 0.13 m^2 surface area enclosed by the chamber.

Wind diluted the sample by as much as a factor of six on windy days. To mitigate wind dilution an aluminum foil wind block was used to shield the chamber opening and this provided some relief. To further reduce the impact of wind, measurements were typically done in the early morning when wind speeds were light. Figure 9 illustrates chamber data collected by the PTR-MS for the tracer and for methanol and illustrates the impact of wind on chamber concentrations. Tracer abundance in the chamber was compared to the tracer values measured in the sweep air flow (red dashed line in the figure) to determine the dilution factor. For position #1 little dilution by wind was observed on this day. Wind speeds were light during this time of day (06:30) measured at 1.1±0.2 m s^{-1} at the weather station on the van. However significant dilution by wind occurred when sampling at position #2 due to higher winds at 2.2 ± 0.23 m s^{-1} at that time (07:30). The dilution correction factor for position #2 was a 2.1. Dilution factors greater than 10 have been listed for sampling done by Washington State Department of Ecology and testing reports examined from California facilities. The assumption made in applying these dilution correction factors is that the diluting ambient air is free of VOCs. This is perhaps a poor assumption when sampling at a compost facility where the ambient air concentrations of VOCs would be elevated by the facility emissions. For example, methanol is generally the most abundant VOC in ambient air and in Pullman ambient air mixing ratios of 5 parts per billion by volume (ppbv) were noted. Thus, even with no surface emissions of methanol from the pile, wind dilution of the chamber would cause methanol to be measured and counted as a pile emission. When VOC surface emission rates become low as the pile ages, accounting for ambient concentrations in the diluting wind might be an important consideration in facility sampling.

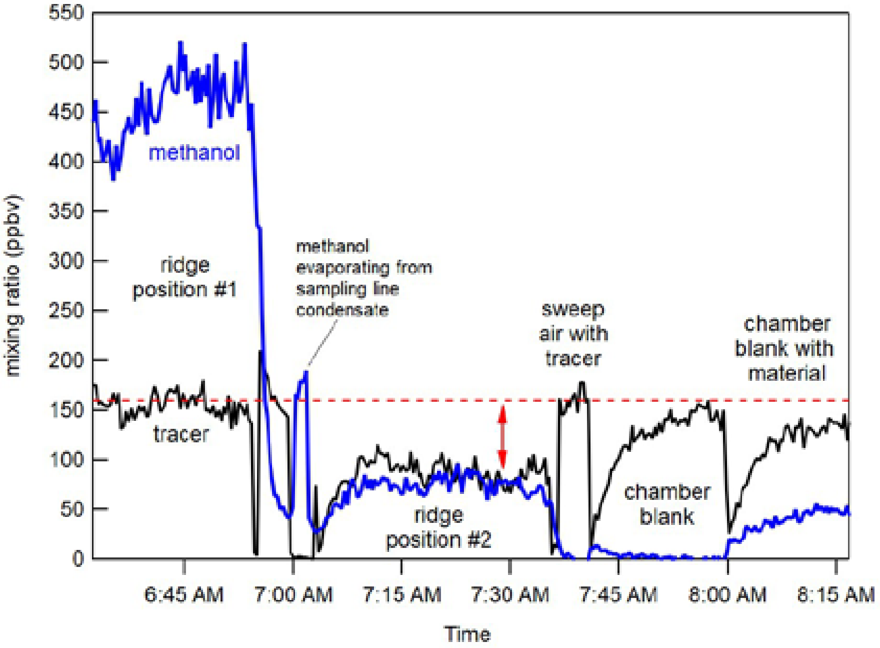

Figure 9: Time series of PTR-MS measurements from the flux isolation chambers performed on Aug 1 showing methanol and dilution tracer mixing ratios. Dashed red line is except tracer abundance. Lower values indicate dilution of chamber by wind. Higher wind speeds resulted in more dilution.

Another sampling issue is shown in the figure where a methanol spike occurred when purging the sampling lines with dry air after sampling at position #1. The chamber air was somewhat humid and warm with a temperature of 29 °C compared the 24 °C air temperature. While no condensation (fogging) of the plexiglass chamber surface occurred, some condensation must have occurred in the ¼-in PFA tubing leading to the PTR-MS. This condensation causes soluble gases to be lost, or partially lost in the case of methanol, and is recovered when the condensate evaporates. For some compounds such as acetic acid only a little bit of fogging of the chamber was required to cause sudden decreases in chamber concentrations.

The last point to be made from this figure is the observation of significant methanol emissions from a couple of handfuls of compost material collected from the pile surface. This material was placed inside the chamber following a sample blank. There was enough material to cover the aluminum foil bottom of the chamber blank to about a 0.5 cm depth. Blanks tests were performed by placing the chamber on plywood board on the push wall, and this location tended to be out of the wind compared to the pile ridge so tracer abundance is typically higher. Given the methanol concentration and dilution factor compared to position #2, the methanol flux from the handful of material was ~40% of that measured position #2. This suggests that emissions from the immediate surface material may be a significant portion surface flux for methanol and other compounds present in this test, notably acetaldehyde, acetone, and acetic acid.

Figure 10 illustrates fundamental problems with the surface flux chamber in measuring acetic acid. When fogging of the Plexiglas dome became evident there was an immediate decrease in concentration. For position #1 sampling this was observed, and enough fogging occurred in the chamber and sample lines that no acetic acid was measurable by the time the canister was to be collected. This compound would be trapped in the impinger sampling of Method 25.3 as it is very water-soluble. The less soluble acetone and monoterpenes compounds were not impacted by chamber fogging. Afterwards the chambers are rinsed with DI water and dried and the sample line is connected to the sweep air supply by a tee fitting. Pulling clean dry air through the sample tube dries it out, and eventually a large spike of acetic acid appears as the last of the condensed water evaporates. A spike in mass to charge ratio (*m/z)* 47 also typically occurred when this happened, suggesting that formic acid is also present in the emissions along with ethanol. Ethanol and formic acid are both detected at *m/z* 47. Ethanol was observed in the GC-MS analysis of the canisters, but formic acid is not recoverable from canisters, nor can acids

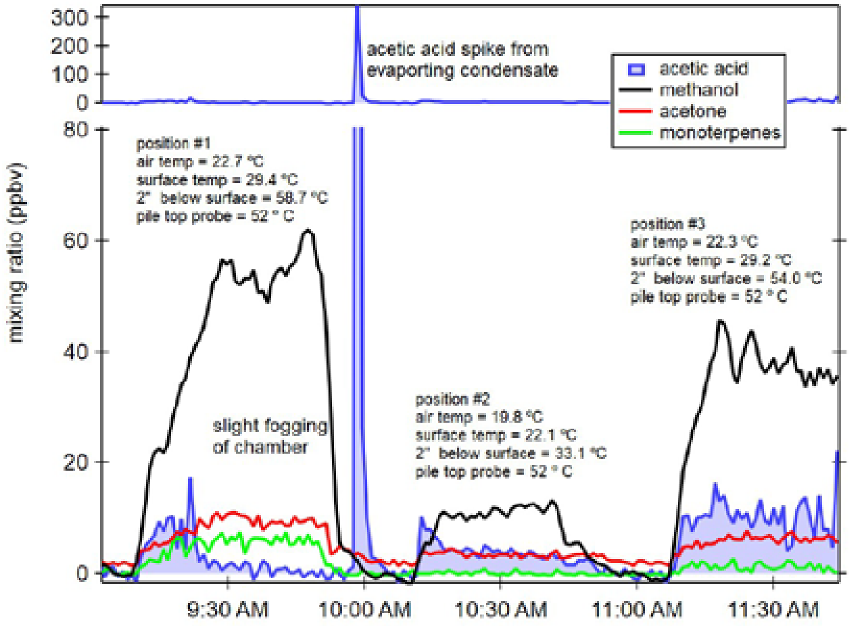

Figure 10: Time series of PTR-MS measurements from the flux isolation chambers performed on Aug 12 showing loss of acetic acid to chamber fogging.

be chromatographed by our analytical method. Ethanol and formic acid have very different PTR-MS response factors. Given the uncertainty of how to attribute this ion signal, and the generally small signal seen for the chamber sampling, *m/z* 47 was not included in the chamber surface flux density calculations. Given the duct had standing water in it, it was assumed the *m/z* 47 signal was primarily due to ethanol for the duct measurements.

Results and Discussion

Lab Composting

Lab composting was conducted to better understand what VOCs are emitted from composting, to test the PTR-MS instrument, to test different air sampling methods. An example of the data collected from in-vessel composting is illustrated in Figure 11, showing data from trial 4 (WSU feedstock of manure and bedding). Data were collected as 1-minute averages from the temperature probes and the methane/CO_2 analyzer. The PTR-MS data was averaged to 1-minute intervals. As was typically observed in these in-vessel composting experiments, temperatures quickly climbed to 70 to 80 °C over the first couple of days then slowly decreased. There was an initial significant emission of methane and VOCs for the first couple of days before VOC emissions rapidly dropped to near room air levels after 3 or 4 days. Carbon dioxide and methane continued to be emitted from the pile after VOC emissions had ceased, indicating the pile was still biologically active. Typically, the experiment was run for 5-7 days until VOC abundance in the headspace was insignificant for most compounds.

The figure shows the alternation in the methane and carbon dioxide data between head space sampling (high concentrations) and room air sampling (low concentrations). For this trial the room air concentration of methane was 1.8 parts per million by volume (ppmv), compared to 4.9 ppmv in the headspace measured after 3 days of composting. Carbon dioxide was strongly elevated in the head space, reaching a high of ~2% by volume, before dwindling to about 0.4% after 3 days, roughly 10x greater than room air abundance of 410 ppmv. In this trial monoterpenes (principally α-pinene), acetone, 2-butanone and methanol were the most abundant compounds emitted. The different compounds displayed different emission profiles with time. For example, methanol displayed a large initial emission that went to near zero as the pile heated, then displayed a small secondary maximum a couple day later as the pile started to cool. Monoterpenes on the other hand displayed highest emissions when the pile was hot and fell rapidly as the pile cooled.

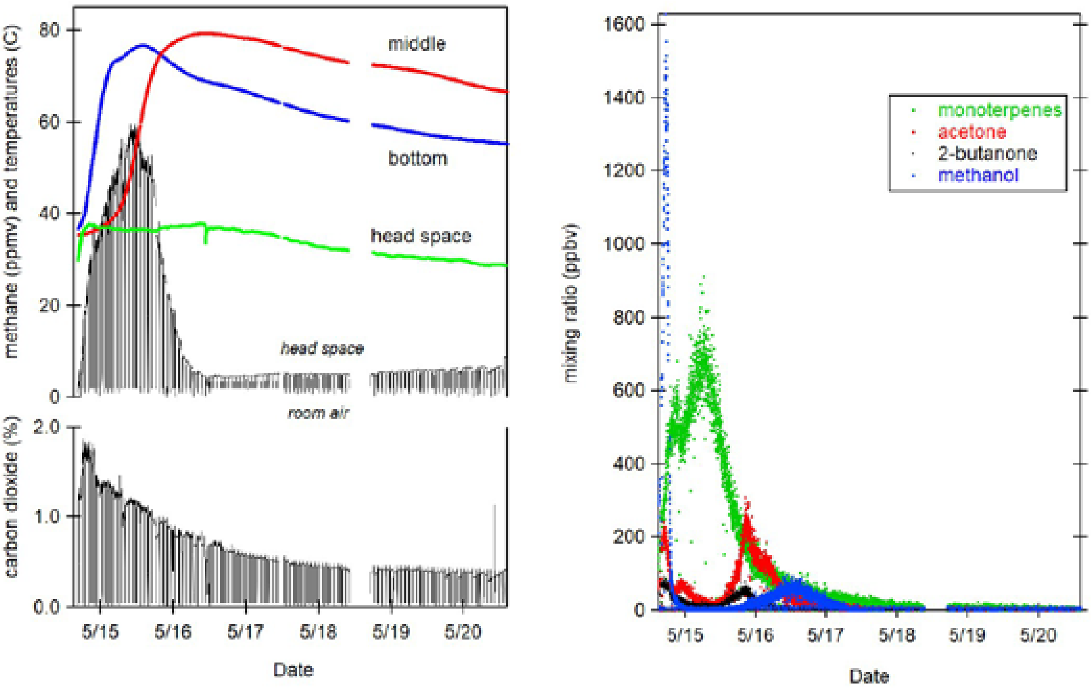

Figure 11: Time series from trial 4 with WSU feedstock material, showing the temperature of the headspace (green trace) and pile (red and blue traces), along with headspace abundance of methane and CO_2 and selected most abundant VOCs as measured by PTR-MS. Crenulations in the methane and CO_2 data reflect the alternate sampling between tank headspace and room air.

Figure 12 shows a similar time series from trial 3 (WSU feedstocks). Emissions of some VOCs, including methanol, were much greater for trial 3 than for trail 4, and the bulk of the emission occurred in the first few days. The reason for the difference in the magnitude of methanol emission between trials 3 and 4 is not clear. The methanol emission profile was similar between the trails with the occurrence of a secondary maximum after the methane emissions peak. The methanol data illustrate a basic air sampling problem using surface flux enclosures for hot and humid compost. The methanol data show that for the periods before and after the methanol emission peak, the room air abundance (~5 ppbv) was greater than the headspace abundance. Since room air flows into the headspace, headspace air should be as large or greater than the room air abundance. This situation likely indicates that methanol entering the vessel from the room air flow, and potentially emitted from the compost, was being dissolved into water vapor condensed on the wet surfaces of the vessel (wet lid and sides, and potentially wet compost surface). Monoterpenes have a much lower solubility in water, and they appear not to be affected. This has important implications for the data quality of surface flux chambers where hot humid air emitted from the piles causes condensation in the chambers as noted in Figure 10.

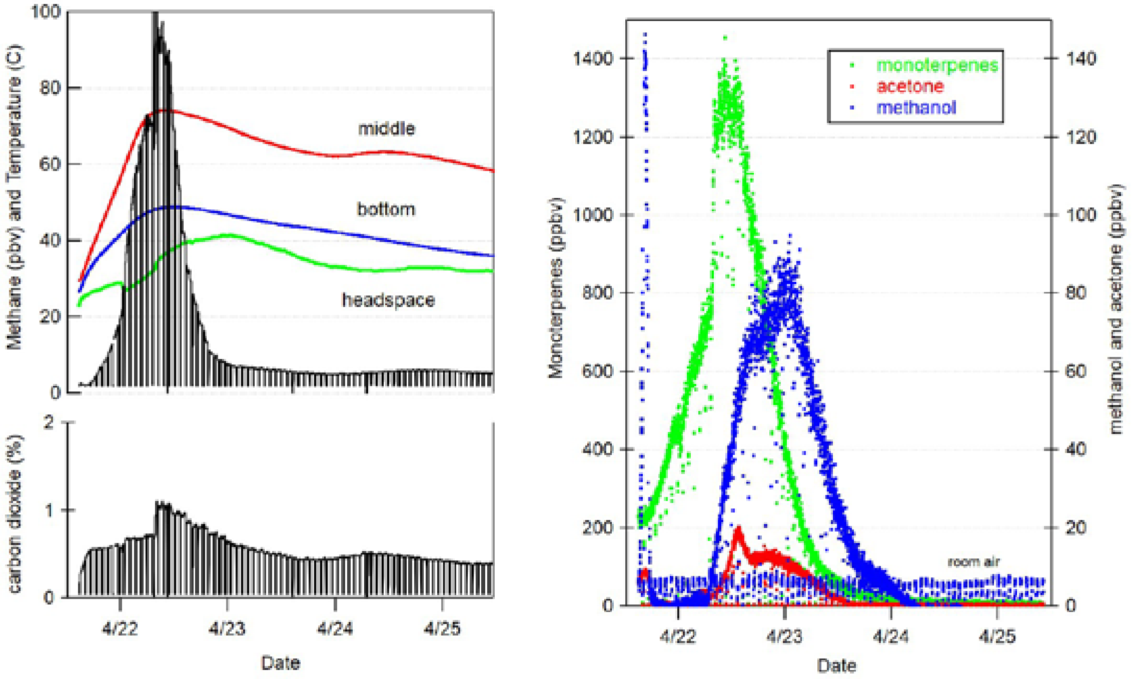

Figure 12: Time series from trial 3 with WSU feedstock material, showing headspace and pile temperatures, along with headspace abundance of methane, CO_2, and selected VOCs as measured by PTR-MS. Methanol in room air (~ 5 ppbv) is greater than headspace abundance before and after the methanol peak, indicating loss of methanol to wet surfaces in the vessel.

Figure 13 shows a timeseries from trial 2. In this experiment the feedstock material was much wetter, a squeeze test produced dripping water. Emission of methane and some VOCs, notably methanol, 2-butanone and acetone, were much higher than in other trials. This suggests that the magnitude and relative abundance of the VOCs emitted will be a function of compost process conditions. This wet material emitted a series of C_3-C_9 ketones as identified by GC-MS. The emissions of larger ketones may be a useful emissions signature of overly wet composting conditions.

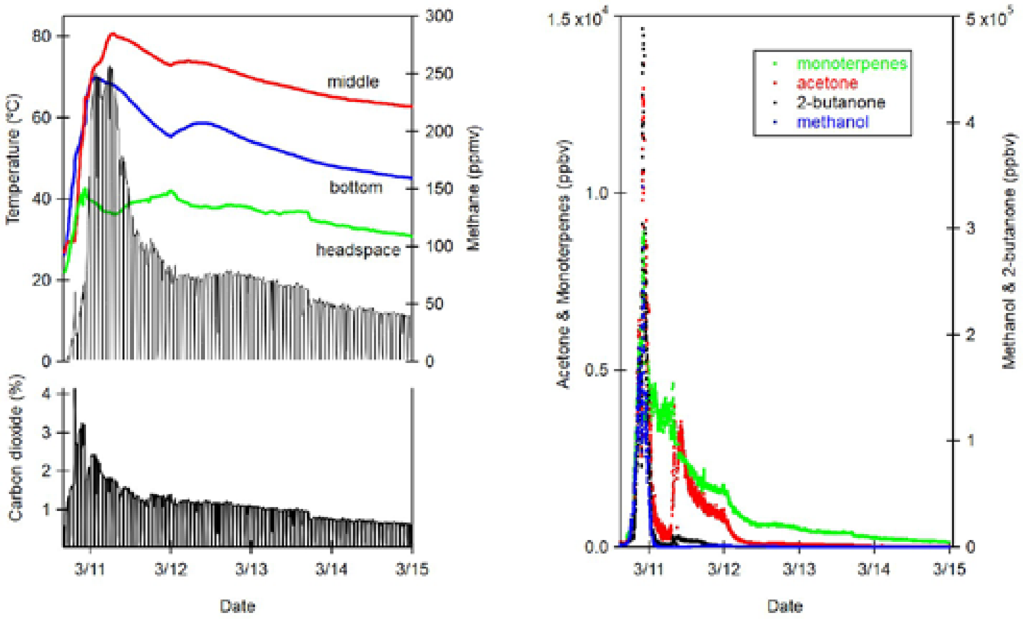

Figure 13: Time series from trial 2 with WSU feedstock material, showing headspace and pile temperatures, along with head space abundance of methane, CO_2, and selected VOCs as measured by PTR-MS. Pile was very wet and VOC and methane emissions were much larger.

PTR-MS mass scans provided a means of establishing the dominant VOCs emitted in the composting process. These scans were compared to GC-MS sampling to identify compounds where possible. A list of attributions of VOCs to ion signals is found in Appendix Table A.1. Figure 14 shows a PTR-MS mass scan where instrument response is plotted against ion mass to charge ratio (*m/z*) for the trial 3 experiment. The figure compares WSU feedstock material to green waste material composting from a commercial composter. Green waste was tested to see if significantly different types of compound were emitted compared to the manure-based compost from WSU. Data shown are when emissions were at a maximum (~day 2) to illustrate the types of compounds emitted. Ion signals have been color coded in the figure to illustrate similar types of compounds (i.e., ketone ion signals are red). The attribution of the ion signal to a specific VOC is noted in the figures. Comparison to GC-MS analysis confirms that monoterpenes, camphor, acetone, 2-butanone, dimethylsulfide (DMS), dimethyl disulfide (DMDS), and acetaldehyde were present in the samples. Monoterpenes fragment to produce a strong ion signal at *m/z* 81 as well as the expected mass at *m/z* 137 so both these ions are color coded green as well as camphor at *m/z* 153.

Clear differences in the types of compounds emitted and their relative abundance are evident in Figure 14. From the green waste material methanol (*m/z* 33) and acetic acid (*m/z* 61) had the largest emissions. Green waste / foodwaste compost emissions of VOC reported from Washington facilities using USEPA methods TO-15 and TO-11 analyses of VOC from samples collected from surface flux chambers were dominated by light alcohols (ethanol and methanol), ketones (acetone and 2-butanone), and monoterpenes (α-pinene and limonene) with minor contributions from DMS and acetaldehyde (Jobson & Khosravi, 2019). Missing from that analysis were measurements of organic acids. Our measurements from in-vessel composting are

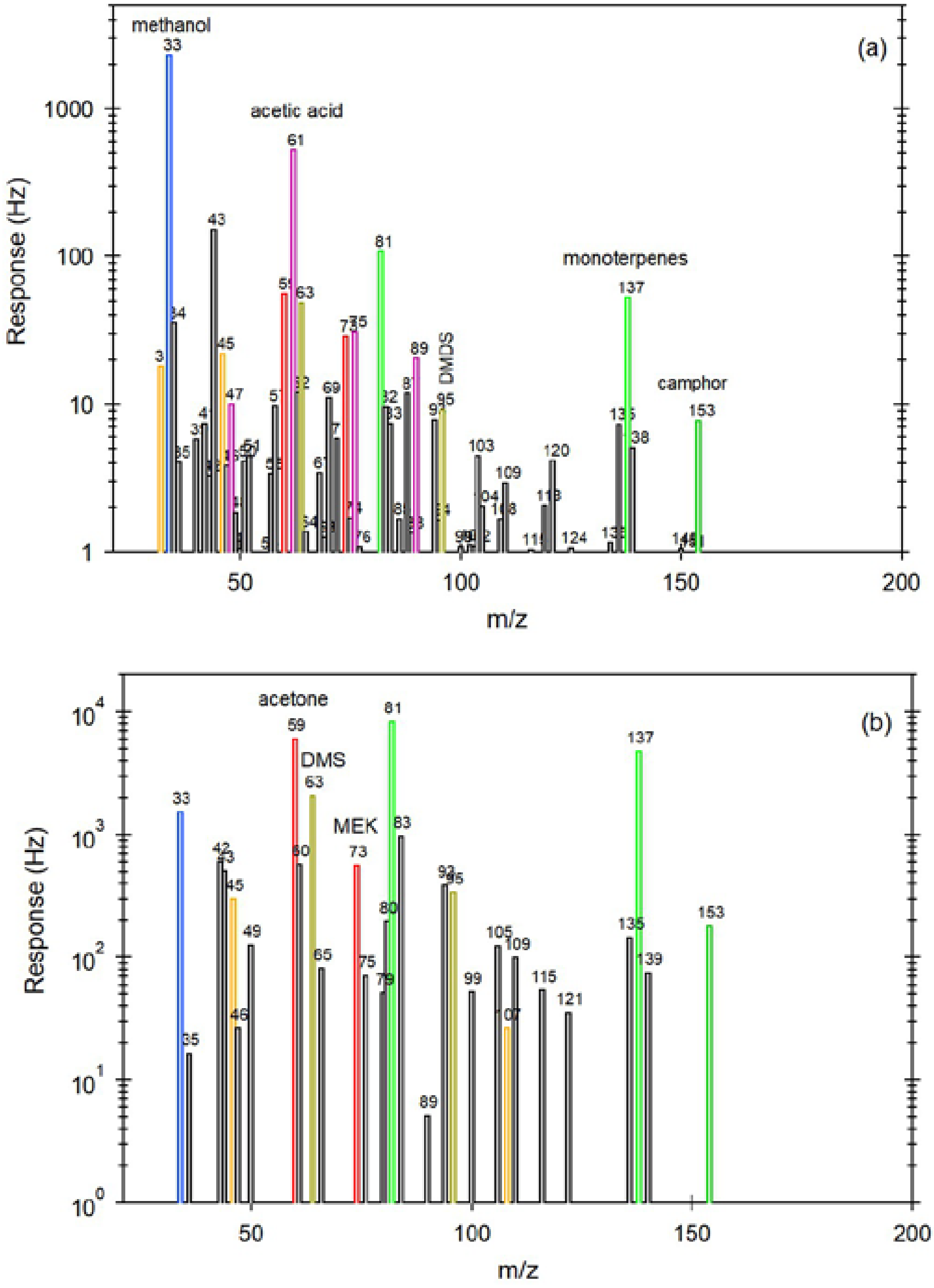

Figure 14: Comparison of PTR-MS mass scans for day 2 of composting showing (a) green waste material from a commercial facility (trial 5), and (b) WSU facility material (trial 3). Numbers above bars are the ion mass to charge ratio (*m/z*). Color coding: green for monoterpenes and camphor, red for ketones, orange for aldehydes, pink for acids, brown DMS and DMDS, blue for methanol. Methanol and acetic acid emissions were much greater for the green waste material.

consistent with those results. Neither ethanol nor i-propanol was observed as a major emission from the WSU or commercial green waste material. Kummar et al. (2011) reported i-propanol as the dominant VOC emission (42.3%) for a green waste windrow composting facility in San Joaquin Valley (CA), followed by ethanol (18%), methanol (12.8%), and acetic acid (5.9%). While there are general differences in the relative amounts of the various VOCs emitted between the Kummar study and those observed with our in-vessel composting and for Washington compost facilities (Jobson & Khosravi 2019), there is general agreement that water-soluble oxygenated organics (such as alcohols, ketones and acids) can have the highest mass emission rates and thus dominate the total VOC surface flux. The importance of water-soluble compounds like methanol and acetic acid underscore the need for sound sampling procedures to prevent losses to condensed water in surface flux chambers.

Figure 15 shows a PTR-MS bar scan from the zone 10 negative aeration duct when the WSU ASP system was being tested. Shown is data from day 2 when VOC emission rates were high. The material being composted was the same as the in-vessel lab trials consisting of manure, animal bedding, and wood chips. VOC emissions from the ASP system appear in different proportions than what was observed with the in-vessel lab trails. Methanol is clearly the most abundant VOC, followed by acetone and acetaldehyde. Monoterpenes had a diminished importance compared to the in-vessel results. The negative aeration duct samples had a different relative VOC composition than the in-vessel composting samples. The differences observed suggest that in-vessel small scale lab composting may not be a reliable model for actual facility emissions. It will likely be difficult to reproduce facility conditions in a large pile (pH, O_2, moisture, temperature) with small scale lab experiments. However, the basic conclusion that water-soluble oxygenated VOCs are important constituents of compost emissions holds. The role of water-soluble organics in determining compost VOC emission rates has important implications for use of Method 25.3 and surface flux sampling.

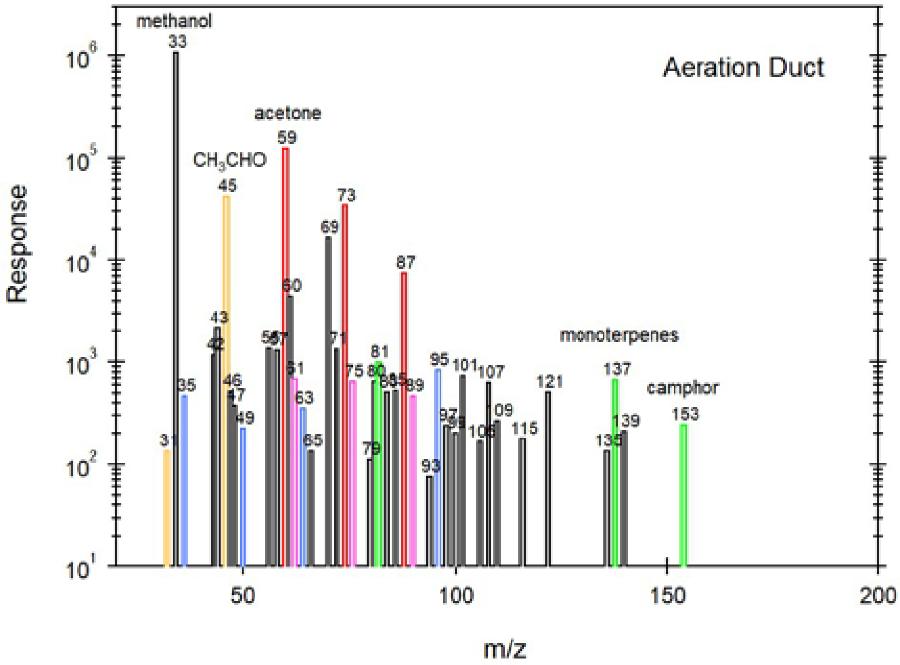

Figure 15: PTR-MS bar scan of negative aeration duct at the WSU compost facility on day 2. Emissions were dominated by methanol (m/z = 33), acetaldehyde (m/z = 45), acetone (m/z = 59) and 2-butanone + 2-methylbutanal (m/z 73).

Comparison Between PTR-MS and GC-MS

The PTR-MS was compared to the GC-MS for the emission sampling done at the WSU compost facility. There was generally good agreement in results from the PTR-MS and canister samples measured with GC-MS for the most abundant VOCs. Figures 16 to 21 show the comparison for the most abundant VOCs measured by both techniques. The regression plots show the 1:1 line with ± 20% shading reflecting a subjective threshold of good agreement for VOC measurements. In general acetaldehyde and acetone agreed well. For 2-butanone, the PTR-MS yielded higher values by approximately a factor of three. This is likely due to interfering compounds identified in the GC-MS analysis such as 2-methylpropanal (same mass) and 2-methylbutanal which fragment upon protonation to yield the *m/z* 73 ion. Our interpretation here is that the *m/z* 73 ion is tracking 2-butanone and 2-methylpropanal emissions and those of larger organics that fragment to mass 73 and thus is still useful for emissions testing. The factor of three off-set appears to apply over the whole composting period.

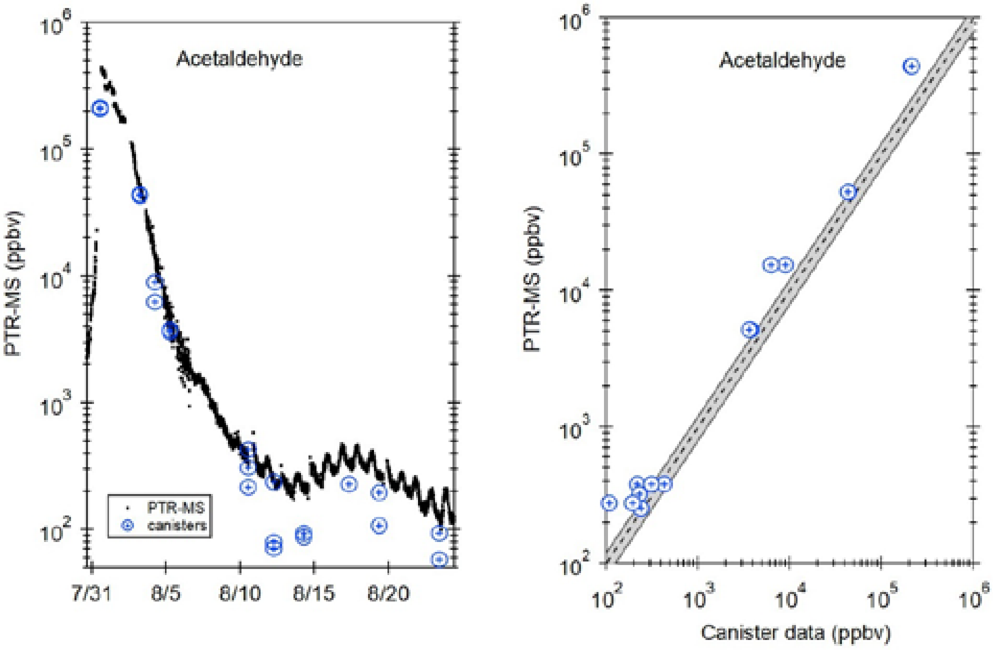

Figure 16: Comparison of acetaldehyde mixing ratios measured from the Zone 10 negative aeration duct at the WSU compost facility by the PTR-MS and canisters analyzed by GC-MS. Dashed line is the 1:1 line with ± 20% shading. Cans collected on July 31 had no corresponding PTR-MS vales at that time, so PTR-MS data taken 3 hours later was used.

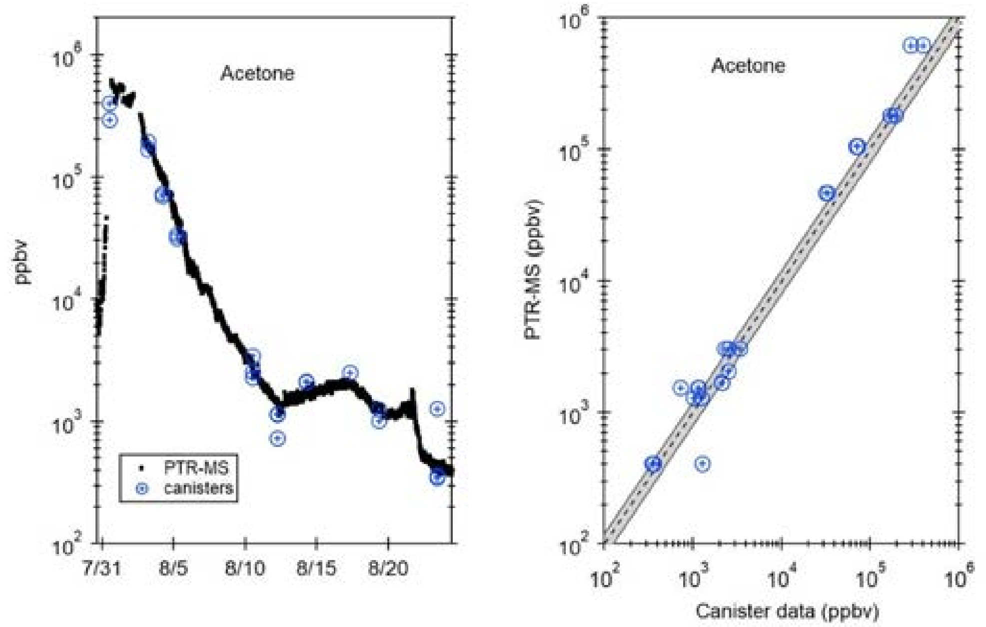

Figure 17: Comparison of acetone mixing ratios measured from the Zone 10 negative aeration duct at the WSU compost facility by the PTR-MS and canisters analyzed by GC-MS. Dashed line is the 1:1 line with ± 20% shading. Cans collected on July 31 had no corresponding PTR-MS values at that time, so PTR-MS data taken 3 hours later was used.

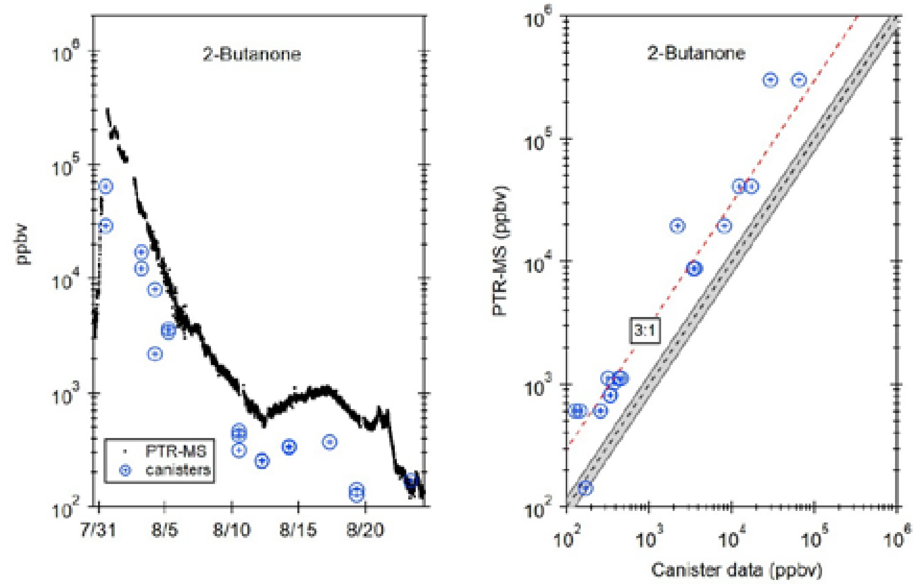

Figure 18: Comparison of 2-butanone mixing ratios measured from the Zone 10 negative aeration duct at the WSU compost facility by the PTR-MS and canisters analyzed by GC-MS. Dashed line with shading is the 1:1 line ± 20%. Red dashed line is the 3:1 line. Cans collected on July 31 had no corresponding PTR-MS values at that time, so PTR-MS data taken 3 hours later was used.

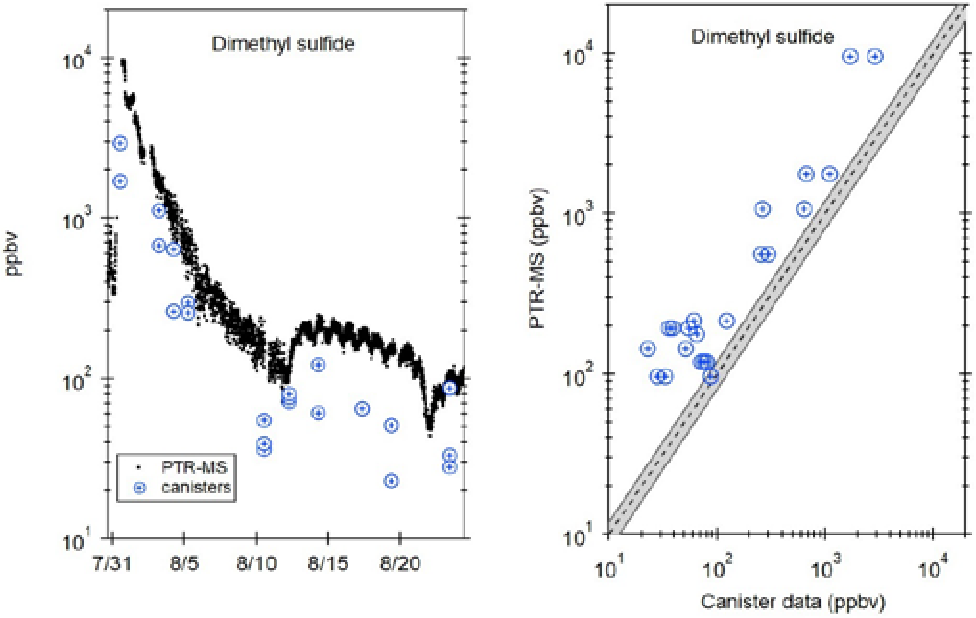

Figure 19: Comparison of dimethyl sulfide (DMS) mixing ratios measured from the Zone 10 negative aeration duct at the WSU compost facility by the PTR-MS and canisters analyzed by GC-MS. Dashed line is the 1:1 line with ± 20% shading. Cans collected on July 31 had no corresponding PTR-MS values at that time, so PTR-MS data taken 3 hours later was used.

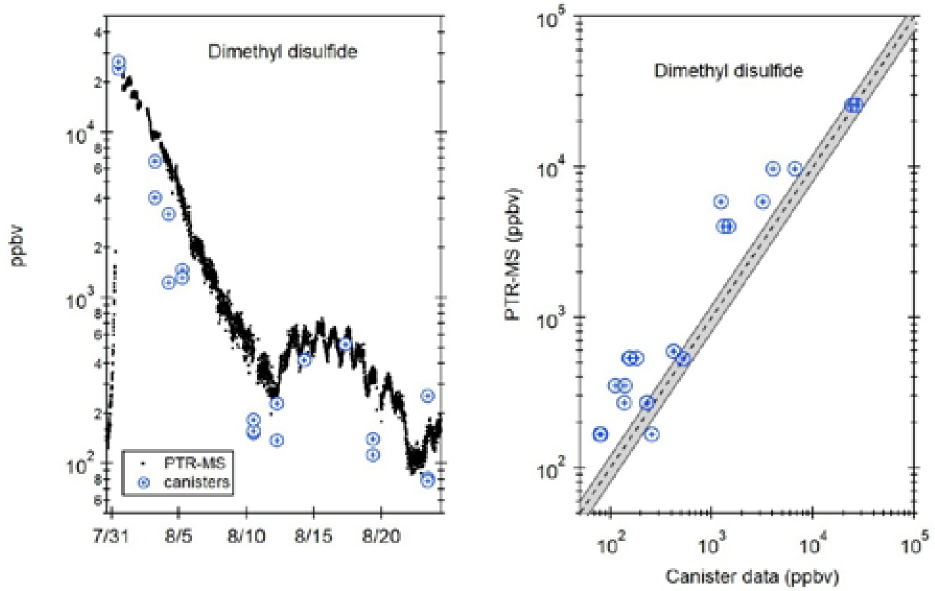

Figure 20: Comparison of dimethyl disulfide (DMDS) mixing ratios measured from the Zone 10 negative aeration duct at the WSU compost facility by the PTR-MS and canisters analyzed by GC-MS. Dashed line is the 1:1 line with ± 20% shading. Cans collected on July 31 had no corresponding PTR-MS values at that time, so PTR-MS data taken 3 hours later was used.

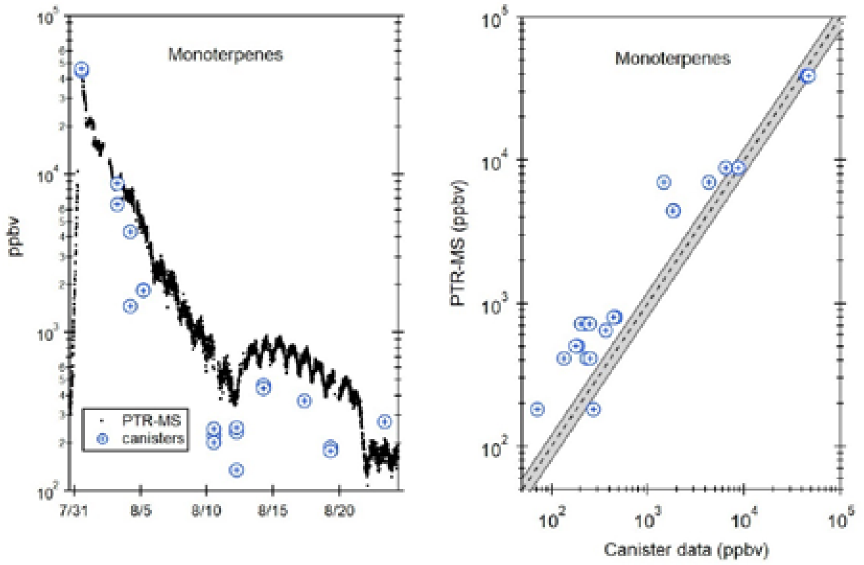

Figure 21: Comparison of total monoterpene mixing ratios measured from the Zone 10 negative aeration duct at the WSU compost facility by the PTR-MS and canisters analyzed by GC-MS. Dashed line is the 1:1 line with ± 20% shading. Cans collected on July 31 had no corresponding PTR-MS vales at that time, so PTR-MS data taken 3 hours later was used.

Figure 22 shows chromatograms from GC-MS analysis of duct air samples collected in canisters. The figure shows the initial presence of several aldehydes, notably acetaldehyde, 2-methylpropanal, 2-methylbutanal, 3-methylbutanal (isovaleraldehdye), and benzaldehyde. The abundance of the C_5 aldehydes relative to acetone decreased rapidly with pile age. The figure also shows the presence of two alcohols: ethanol and 3-methyl-1-butanol. Dimethyl disulfide co-eluted with the C_5 alcohol and these appear in the figure as a merged peak. Iso-propanol was not observed as has been reported from California testing (Kumar et al., 2015) and our method could not analyze for methanol. The dominant ketones were acetone, 2-butanone, acetophenone, and camphor. The dominant monoterpenes in order of abundance were: α-pinene, β-pinene, limonene, 3-carene, and β-myrcene. What is notable from the figure is that only a few compounds comprise most of the VOCs measurable from canisters and these compounds are not typically quantified in standard TO-15 analysis reporting. Most of these compounds are not considered stable in canisters and other methods and/or sampling devices would be used to quantify them. Short turnaround times between sampling and analysis helps, and perhaps the high concentrations of ammonia in the canisters serves a role in passivating canister surfaces to limit adsorption losses.

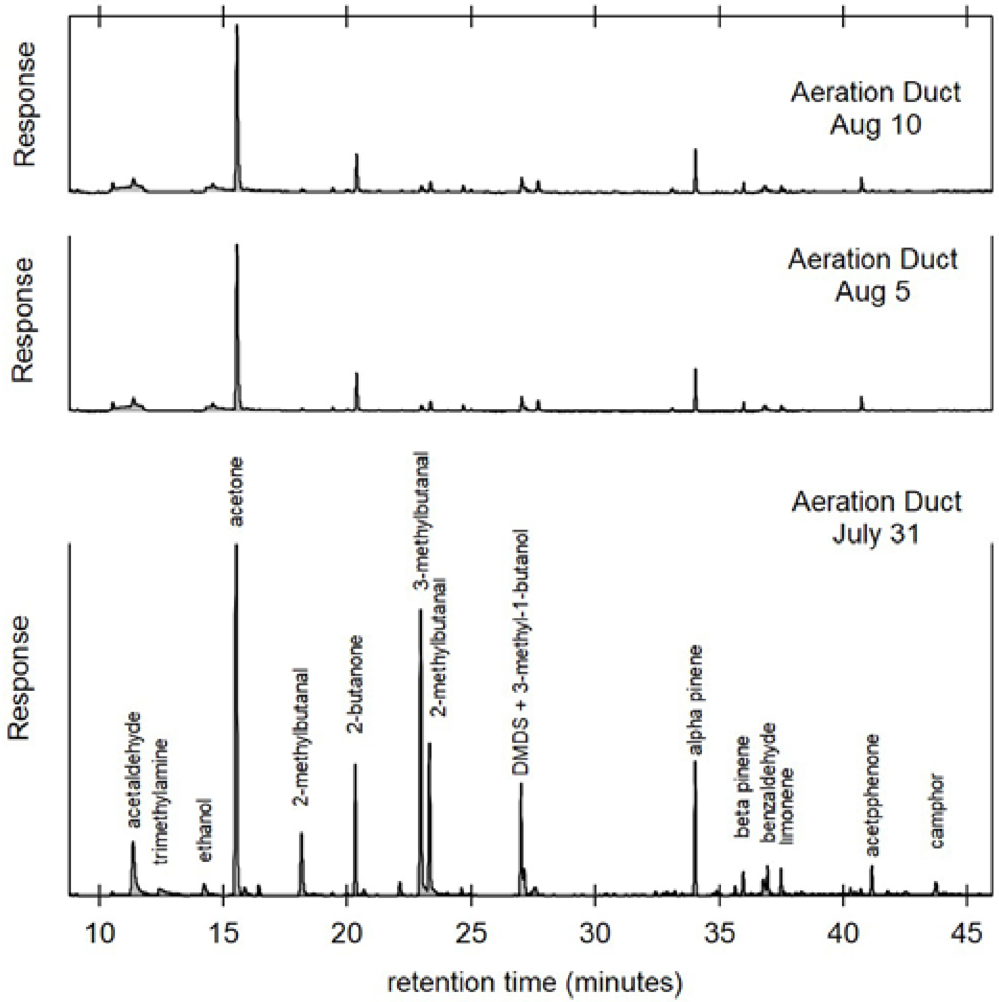

Figure 22: GC-MS chromatograms from duct samples collected on different days as the pile aged, illustrating major VOCs identified in the air samples and change in relative emission rates.

The level of agreement for the sulfur compounds dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) is shown in Figure 14 and 15. The PTR-MS measurements were about a factor of two larger than the canister data. There is a larger amount of scatter in the data and the stability of these compounds in canisters is likely variable between canisters and a cause of some of this discrepancy and scatter between methods. It is not known if there are positive inferences from other VOCs for PTR-MS analysis of these compounds.

For the total abundance of monoterpenes, the level of agreement shown in Figure 16 was good for high concentrations observed at the beginning and was fair for the lower concentrations measured towards the end of the composting period. The level of agreement would be expected to be good if α-pinene dominates the monoterpene mixture, since the PTR-MS is calibrated to this particular compound. GC-MS analysis indicates that α-pinene was 56% of total monoterpene abundance, a fraction that did not change over the composting period.

For the flux isolation chamber samples, measured mixing ratios were much lower than the duct and varied over a smaller concentration range. The comparison of the chamber samples is shown in Figure 23 for four compounds measured in highest abundance including the dilution tracer benzene. In general, there was more scatter and the PTR-MS reported higher mixing ratios. For monoterpenes, the PTR-MS was consistently higher by approximately a factor of three. This may be due to loss of these compounds in the canister, though based on experience this seems like more loss than would be expected due to canister surface adsorption effects. Even the dilution tracer displayed significant differences, which would not be expected from canister storage effects. Acetone displayed significant scatter for the chamber samples but not for the duct samples. The more volatile compounds, acetaldehyde and acetone, had better agreement than less volatile benzene and monoterpenes. A possible cause for these differences is ammonia (NH_3). Ammonia sampled into the canister may be causing trouble with the VOC trapping efficiency in the GC-MS sample preconcentrator. This may be due to competitive adsorption effects impacting the preconcentrator's ability to capture VOCs (ppbv levels) onto the cooled Tenax trap due to adsorption of much greater concentration of NH_3 (ppmv levels). The relative amount of NH_3 to VOCs in the duct is likely much lower than the chambers due to standing water in the negative aeration pipe and duct, into which NH_3 would dissolve, and very high VOC concentrations in the duct compared to the surface flux chambers. This is something that will have to be examined with test gas mixtures made in the lab. This may be an issue isolated to this particular preconcentrator design and the preconcentration parameters used. Given the uncertainties with the preconcentrator, the PTR-MS data was used for calculating surface emission rates.

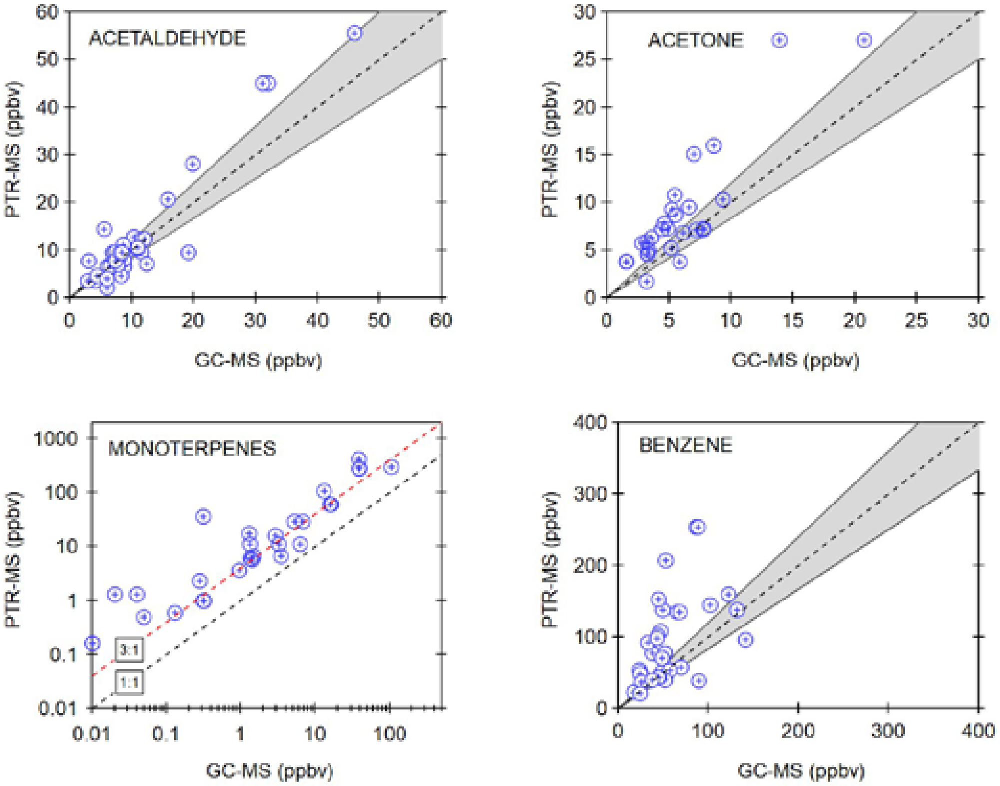

Figure 23: Comparison of PTR-MS measurements from the surface flux isolation chambers and GC-MS results for four compounds. Dashed line is the 1:1 line and shading represents ±20% about the line.

WSU Facility Emissions Testing

Dust Emissions

The emission rates of the most abundant VOCs measured in the negative aeration duct by the PTR-MS are shown in Figure 24 over the 26-day active composting phase. The temperature from the pile top temperature probe (3-ft depth) is also shown. Temperature data are missing for the last few days. The most abundant VOC was methanol followed by acetone. VOC emission rates peaked on day 2 when pile temperatures were highest. Methanol emission rates went from 2 grams hr^{-1} upon the start of sampling on July 31 to 4,500 grams hr^{-1} (9.9 lbs hr^{-1}) at peak emission about 38 hours later. Emission rates for all VOCs rapidly dropped after their peak as the pile cooled. A week later emission rates were a factor of 10 or more lower than the initial peak. This implies that accurate source emission testing must resolve the rapid increase and decrease suggested by this profile. By the end of the active composting phase, VOC emission rates were 2 to 3 orders of magnitude lower. For example, methanol emission rates were 3 grams hr^{-1} at the end of active composting compared to the peak of 4,500 grams hr^{-1}.

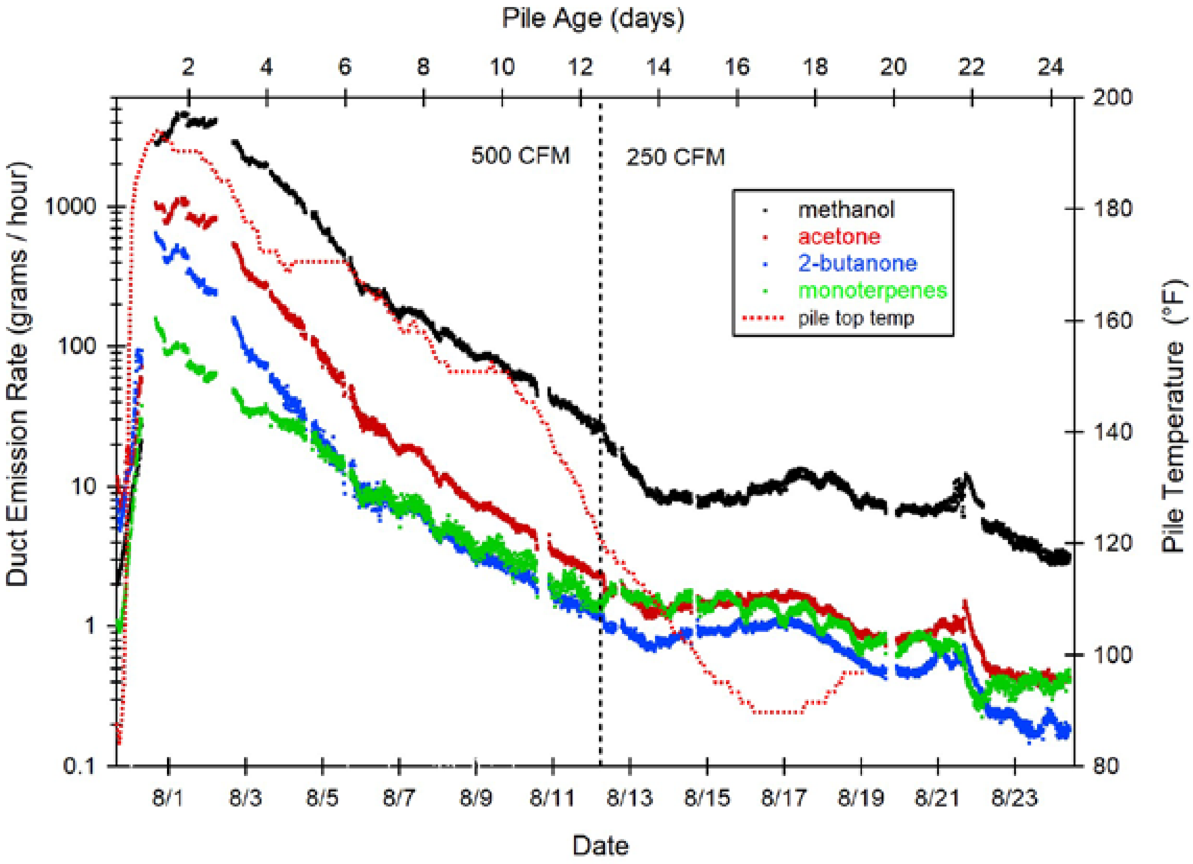

Figure 24: VOC emission rates measured in the negative aeration duct versus pile age. Shown are 10-minute averages for some of the most abundant compounds measured.

The sum total of the measured VOC emission rates are shown in Figure 25. This total was calculated from the VOCs listed in Table 2. Given the pile initial mass of 160 wet tons, Table 2 lists the total amount emitted in pounds and the corresponding emission factors in units of lbs VOC / wet ton for the WSU feedstock material. The total amount of VOC emitted through the duct was 855 lbs. The total emission factor through the duct was 5.47 lbs VOC / wet ton. Methanol represented 65% of the total VOC mass emitted. Emission of oxygenated compounds were 92% of the measured VOC mass emitted. Acetone, an exempt VOC, was 12% of total emissions. After 130 hours (5.4 days), 90% of the total VOC mass emitted through the duct had been emitted.

The large temporal change in VOC emissions rates from this negatively aerated system highlights an issue of how frequently to conduct emissions sampling. Work in California on windrows emissions typically followed a sampling schedule where at most 3 surface flux samples were collected in the first week [Jobson & Khosravi, 2019]. The more active composting of covered aerated static pile systems suggests the need for more frequent sampling during the first week to accurately capture the rapid increase and decrease of emissions.

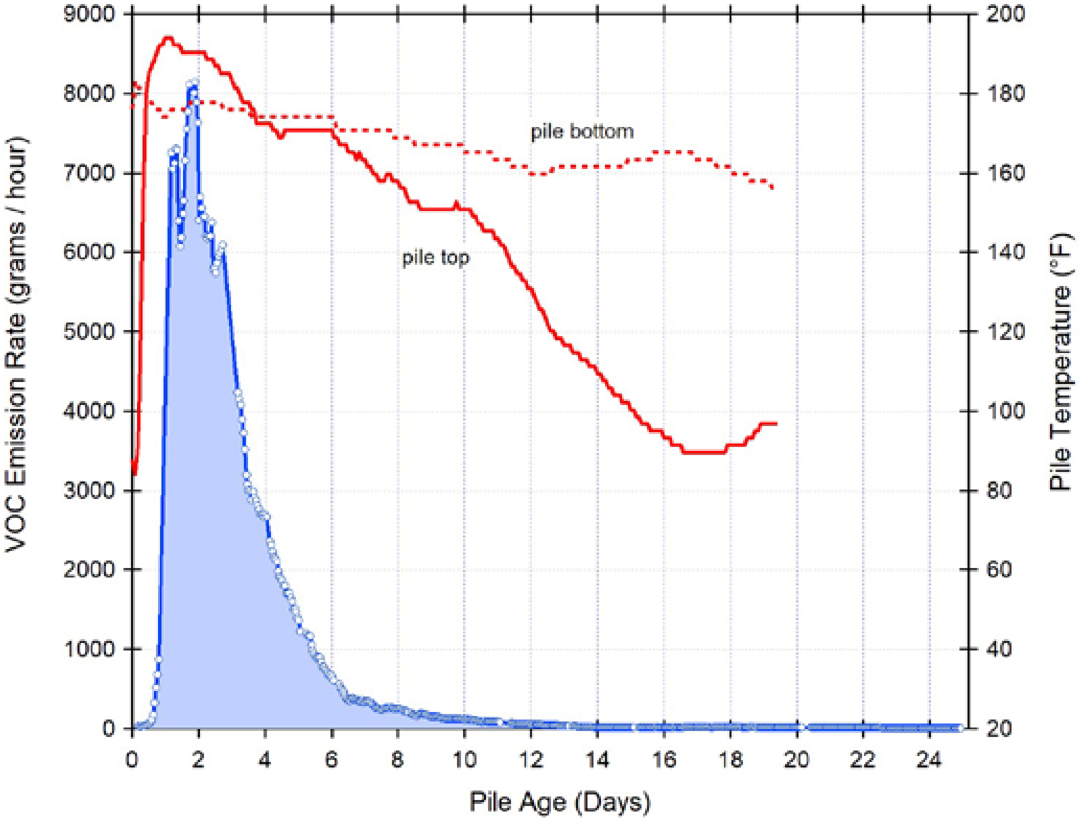

Figure 25: Sum of VOC mass emission rates measured in the negative aeration duct versus pile age. Shown are 1-hour averaged data. Ninety percent of the total VOC mass was emitted in the first 130 hours.

Table 2: WSU feedstock VOC emission rates from the negative aeration duct

Compound	m/z	Total mass emitted (lbs)	Cumulative amount of total (%)	Emission factor (lbs VOC / wet ton)	Emission factor (lbs C / wet ton)
methanol	33	554	64.8	3.54	1.33
acetone	59	105	12.3	0.67	0.50
C_5 aldehydes	87	52.5	6.1	0.34	0.19
2-butanone + 2-methylpropanal	73	41.2	4.8	0.26	0.17
acetaldehyde	45	35.8	4.2	0.23	0.13
trimethylamine (TMA)	60	14.7	1.7	0.094	0.057
monoterpenes	137	13.4	1.6	0.086	0.076
H_2S	35	9.66	1.1	0.062	0.0000
DMDS	95	8.35	1.0	0.053	0.0135
ethanol / formic acid	47	4.95	0.6	0.032	0.0167
camphor	153	4.82	0.4	0.031	0.0245
pyridine	80	3.15	0.4	0.020	0.0152
benzaldehyde	107	2.61	0.3	0.017	0.0135
acetic acid	61	1.60	0.2	0.010	0.0040
DMS	63	1.33	0.2	0.0085	0.0033
acetonitrile	42	1.09	0.1	0.0070	0.0041
dimethylamine	46	0.55	0.06	0.0035	0.0019
CH_3SH	49	0.37	0.04	0.0024	0.0006
Total		855		5.47	2.55

Table 2 lists VOC emission rates as the actual mass emitted and are different from what is report in SCAQMD Method 25.3. As noted previously in the introduction, Method 25.3 counts carbon. Table 2 also lists the emissions as lbs C / wet ton so that these data can be more directly compared with Method 25.3 reporting. Reporting only carbon mass emitted significantly reduces the mass emitted as the mass of oxygen and other atoms are not counted. For example, methanol mass is only 37.5% C. The measured methanol mass emission rate of 3.54 lbs VOC / wet ton was multiplied by this mass fraction to get the Method 25.3 equivalent rate of 1.33 lbs C / wet ton. The total duct emission rate was 2.55 lbs C / wet ton, about half the actual VOC mass emission rate. Reconciling the actual VOC mass emission rate from compost facilities is something that has not been specifically addressed in the emissions factor development work from California. If emission of methanol and other oxygenated compounds identified here are found to dominate emissions generally from Washington State compost facilities, then Method 25.3 reporting of total VOC emissions as carbon mass would significantly undercount VOC mass emission rates.

The are other ways to report mass emission from the total VOC determination of Method 25.3. Sometimes mass is reported as methane equivalents or as hexane equivalents. Hexane equivalents is the USEPA default reporting method if there is no knowledge of the chemical composition of the sample. Reporting as methane or hexane equivalents increases the mass emission rate by 33% and 20% respectively. To report mass emissions in terms of another chemical constituent the carbon mass is multiplied by a factor calculated from the ratio of the molar mass of the compound to the molar mass of carbon in the compound. This conversion is described in detail in the Appendix.

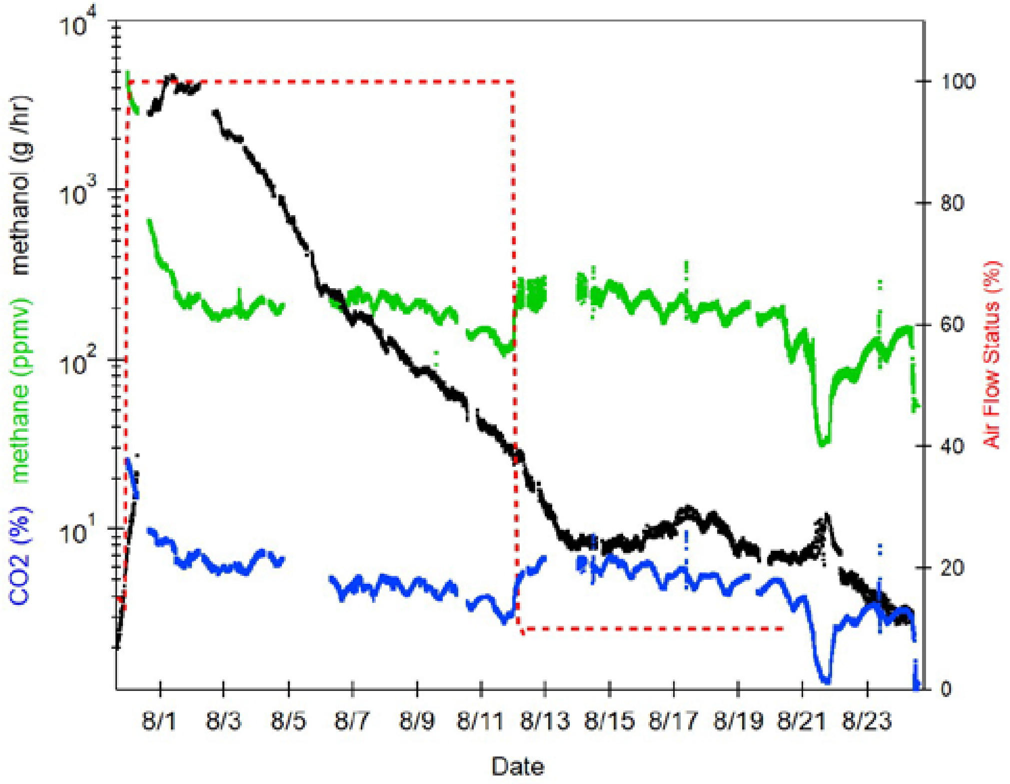

Figure 26: Measured negative aeration duct mixing ratios of methane and CO2 along with methanol mass emission rate (g hr-1). Methane and CO2 abundance did not vary significantly over the course of the active composting phase in contrast to VOCs. Shown are 1-minute averaged data for methane and CO2, and 10-minute averaged data for methanol.

The amount of methane and CO_2 in the duct were also measured. These data are shown in Figure 26 as mixing ratios compared to the methanol mass emission rate. Methane and CO_2 were initially high during the first several hours and mixing ratios dropped as the pile was aerated and pile top temperatures increased. CO_2 and methane abundance in the duct did not change significantly over the active phase. While VOC emissions were very low by the end of the active aeration phase, CO_2 and methane were still abundant, implying the pile was still biologically active.

An explanation for these initially elevated levels CH_4 and CO_2 is that the front half of the pile, built on July 29, had begun composting under naturally ventilated conditions like a windrow, and this generated VOCs, methane, and CO_2 vapors. These vapors were extracted from the pile interior upon initiation of aeration on July 31. At the start of the aeration and VOC measurements, the bottom probe temperature in the front half of the pile was already at 180 °F, indicating active composting had already begun. This initial data from July 31 also had a different VOC composition. Ketone and aldehyde abundances relative to methanol were much larger on July 31 as illustrated in Figure 27. It is interesting that methanol emissions were relatively low compared to other VOCs from this time, but increased rapidly as the pile became aerated to dominate the VOC mass flux through the duct. The observation suggests that aerated systems may have higher emission rates of methanol than more poorly aerated windrow systems. This observation needs to be verified, as it indicates the aeration process may impact the types of VOCs emitted, an important point for air permitting.

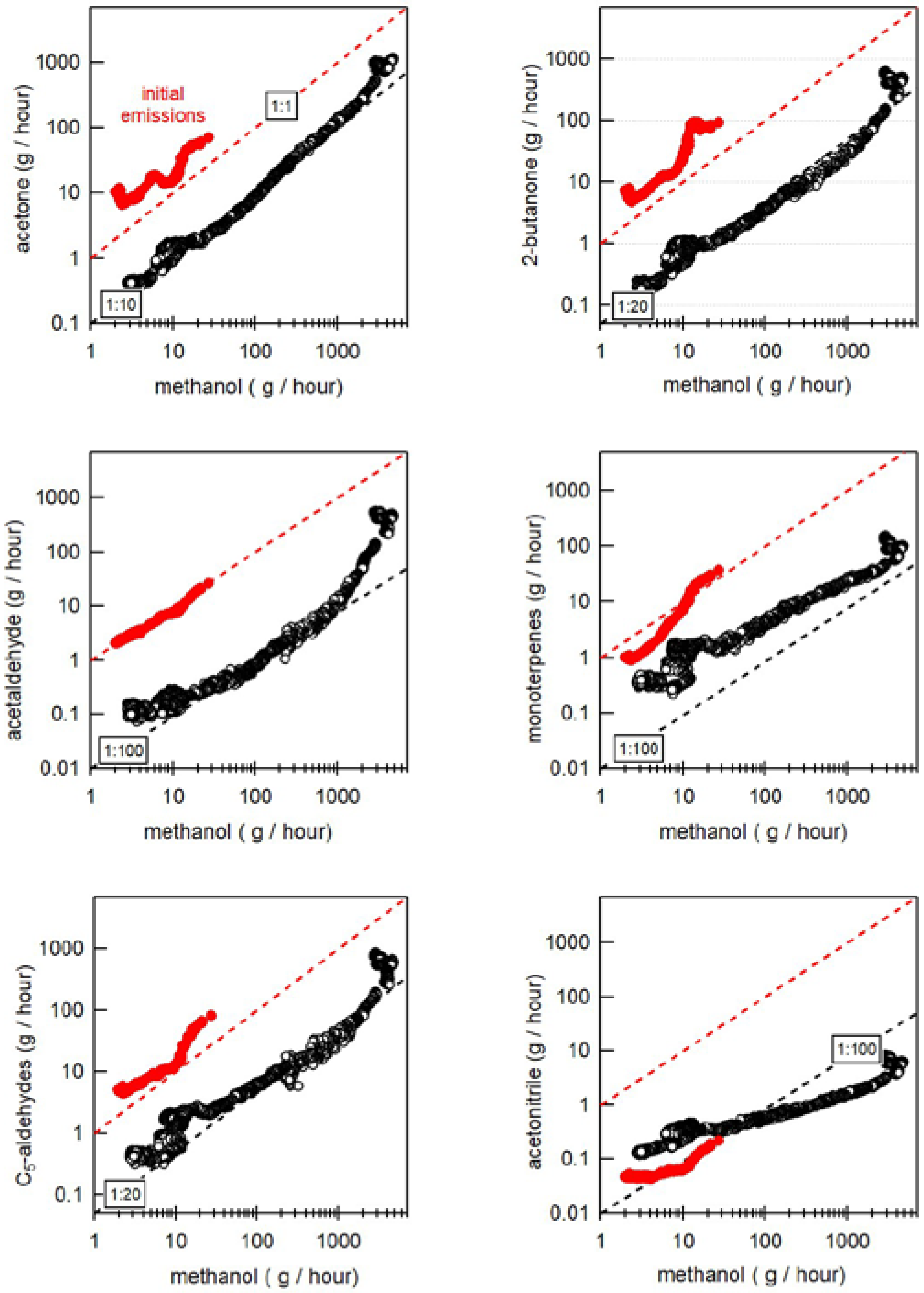

Figure 27: Correlations of selected VOC emission rates versus methanol. Dashed lines indicate relative amounts. Red dashed line is the 1:1 line. Initial pile emissions from July 31 are shown as red symbols. Methanol emissions increased significantly compared to other VOCs as the pile became aerated. Shown are 10-minute averaged data.

Surface Emissions

Surface emissions were determined on 10 different days: July 31, Aug 1, 2, 3, 4, 5, 10, 12, 14, and 19. July 31 is considered day 1. Surface emission rates were determined from PTR-MS measurements. The relative abundance of VOCs observed in the flux chambers were somewhat different than those measured in the duct. Initially, surface emissions were dominated by trimethylamine (TMA), though this was not the dominant VOC emission in the duct. Surface emission rates rapidly declined over the first week. Figure 28 shows example chromatograms from the GC-MS analysis of the canister samples collected on July 31, Aug 5, and Aug 10 from position #1. While many VOCs were detected in the July 31 sample, including a large amount of TMA, VOC abundance rapidly dropped as evident by the near absence of chromatographic peaks of comparable size to the benzene tracer peak for the Aug 5 and 10 samples. In the July 31 sample, the benzene tracer peak is small compared to the much higher concentrations of other VOCs such as acetone, 2-butanone, and DMDS.

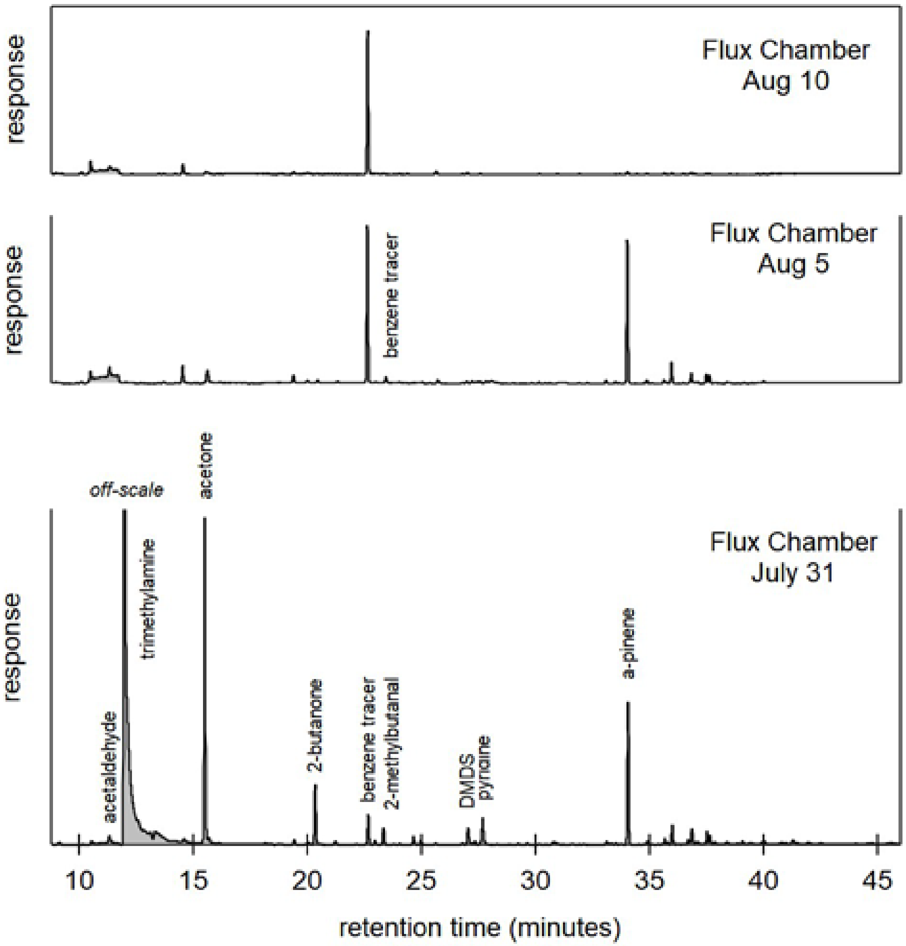

Figure 28: Chromatograms from canisters collected from the flux isolation chamber on three different days from position #1, showing identified compounds and how their abundance changes with respect to the sweep gas tracer benzene. For each sample, the benzene concentration is approximately the same. VOC concentrations are high on July31, dwarfing the sweep gas benzene signal, compared to the very low concentrations on Aug 10, and near absence of VOCs compared to benzene.

Table 3 lists the measured surface flux density of the most abundant species measured by the PTR-MS at location P1. This position had the highest flux densities and was sampled on all days. Surface fluxes were elevated for all VOCs for the first day compared to subsequent days. It is not clear why this day had such high emission rates. This front half of the pile was first constructed on July 29 and surface emissions on this day may have been high compared to later days because it was still behaving like a naturally ventilated windrow. This unusual chamber sample is consistent with the different VOC ratios relative to methanol observed in the duct (Figure 27) and the initially very high methane and CO_2 observed in the duct (Figure 26) on this day.

Table 3: Speciated VOC surface flux density (mg m^{-2} hr^{-1}) measured at sampling location P1.

Date	July 31	Aug 1	Aug 2	Aug 3	Aug 4	Aug 5	Aug 10	Aug 12	Aug 14	Aug 19
Day	1	2	3	4	5	6	11	13	15	20
TMA	978	18.0	3.85	18.1	1.80	0.72	0.11	0.18	0.083	0.12
methanol	15.4	2.57	1.56	1.59	0.81	0.69	0.50	0.98	0.73	0.94
acetaldehyde	1.36	0.20	0.34	0.41	0.18	0.14	0.10	0.25	0.14	0.21
acetone	19.0	0.90	0.46	1.03	0.16	0.11	0.035	0.18	0.13	0.19
acetic acid	17.0	0.59	0.23	0.64	0.17	0.13	0.29	0.52	ND	0.52
2-butanone*	7.33	0.28	0.24	0.50	0.08	0.08	0.028	0.11	0.043	0.068
DMS	1.02	0.43	0.39	0.46	0.22	0.15	0.045	0.13	0.056	0.097
DMDS	7.49	0.70	0.76	1.53	0.32	0.26	0.01	ND	0.012	0.006
monoterpenes	46.2	6.61	6.53	9.00	3.08	2.06	0.19	0.36	0.22	0.18
camphor	21.4	1.99	2.43	5.53	0.95	0.56	0.056	0.077	0.13	0.067
H_2S	28.6	0.63	0.37	1.03	ND	0.11	ND	ND	ND	ND
acetonitrile	1.03	0.23	0.15	0.35	0.11	0.087	0.017	0.064	0.011	0.010
benzaldehyde	1.12	0.11	0.14	0.20	0.08	0.048	0.019	0.090	0.027	0.027
C_5-aldehydes	12.5	2.59	1.75	2.60	0.44	0.32	0.11	0.35	0.14	0.19
pyridine	17.3	1.05	1.04	1.90	0.42	0.27	0.074	0.037	0.12	0.12
Total	1175	36.9	20.2	44.9	8.82	5.74	1.58	3.33	1.84	2.75

* also includes 2-methylpropanal
ND = not detected

Figure 29 illustrates the measured VOC surface flux densities from location P1. For the first week surfaces fluxes were dominated by TMA and monoterpenes. After the first week surface fluxes were dominated by methanol with a surface flux density of ~1 mg m^{-2} hr^{-1}. Surface flux densities for other VOCs were significantly less than 1 mg m^{-2} hr^{-1} after the first week. The sharp decrease in surface emissions after the first week is consistent with the observed decline in duct emissions rates. The majority of fugitive VOC emissions occurred in the first week.

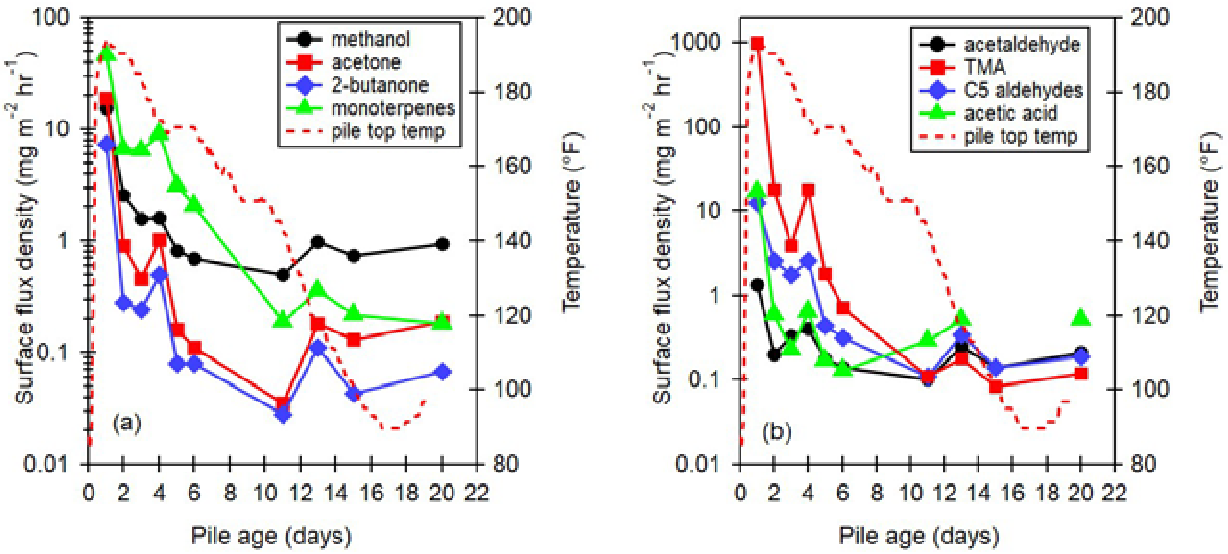

Figure 29: VOC surface flux density measured at located P1 and pile surface temperature at 3-foot depth. Plot on left shows methanol, acetone, 2-butanone, and monoterpenes. Plot on right shows TMA, acetaldehyde, C_5-aldehydes, and acetic acid. TMA initially dominated the surface flux.

From the measured VOC flux densities, a surface emission rate (g hr^{-1}) was calculated from the pile surface area. Previous studies from windrows have estimated that VOC emissions are greatest from the pile ridge (top) due to the rising heat flux from the pile (CARB, 2007). This may not be true for a negatively aerated pile so surface emission rates were determined from the surface area of the entire pile, estimated to be 200 m^2, compared to the 24.2 m^2 surface area of the pile ridge. The resulting surface emission rates determined from the three sampling locations are shown in Figure 30, using a 200 m^2 pile surface area. Flux densities varied somewhat between the sampling locations, yielding different values of the surface emission rate for the entire pile. Emission rates fell sharply from the first day peak, then leveled off so that the three sampling locations were reasonable similar for the last 10 days of composting. Position 2 consistently had the lowest surface flux densities. There is some indication that emission rates were increasing slightly toward the end of the composting period. However, these emission rates are very small compared the duct emissions and do not make a significant contribution to the overall pile emission factor.

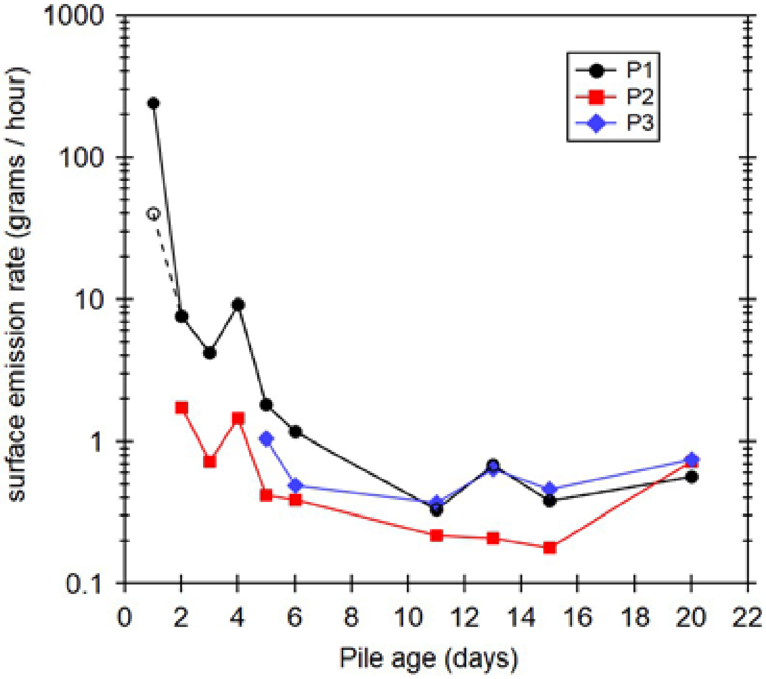

Figure 30: VOC pile surface emission rate (g hr^{-1}) calculated from measured flux densities at the three sampling locations, assuming uniform emissions from the entire pile surface. Open circle is the emission rate measured at P1 on day 1, excluding TMA.

Pile emission rates for P1 are shown in Table 4, listing emissions for the ridge surface and emissions for the entire pile. Peak surface emissions for the entire pile went from 242 g hr^{-1} on July 31 (high emission rate of TMA) to 7.6 g hr^{-1} on Aug 1. These rates are small compared to over 7,000 g hr^{-1} for peak duct emission rates. Interpolating between measurements, it is estimated that the pile surface emitted 13.4 lbs VOC over the active phase, yielding an emissions factor of 0.084 lbs VOC / wet ton.

Table 4: Total VOC emission rate (g hr^{-1}) from the pile surface using P1 flux densities.

Date	July 31	Aug 1	Aug 2	Aug 3	Aug 4	Aug 5	Aug 10	Aug 12	Aug 14	Aug 19
Ridge	28.6	0.90	0.49	1.09	0.22	0.14	0.039	0.081	0.045	0.067
Entire pile surface	242	7.60	4.17	9.25	1.82	1.18	0.33	0.69	0.38	0.57

Given total emissions from the duct of 855 lbs, the pile surface emission rate was 1.5% of the duct emission rate. Most of the surface emissions came on the first day (88%) due to TMA. Excluding TMA from the first day, then only 3.6 lbs of VOCs were emitted, 0.04% of the duct emissions. These measurements indicate that the fugitive surface emissions are a small fraction of the total VOCs emitted from negatively aerated piles. Duct emissions are sent through a biofilter (Leson and Winer, 1991) which have demonstrated removal efficiencies of 70% for compost VOCs (Colon et al, 2009).

The total VOC pile surface emission rates are compared to the duct emission rates as a function of pile age in Figure 31. Emissions rates from the duct are at least an order of magnitude greater than surface emissions for most of the active composting period. The initial emission rates from the duct and pile surface were similar on the first day of sampling, July 31, but then quickly diverged as the pile became aerated. This indicates that the negative aeration system work well to reduce fugitive emissions from the pile surface. At the end of the active composting phase duct emissions rates were 4.5 g hr^{-1} (75% methanol) and pile surface emission rates were ~0.5 g hr^{-1}. The orders of magnitude decrease in VOC emission rates over the active phase suggests that VOC emissions from the stabilization and curing phases might be quite low in comparison to the active phase. If the total emission rate of 4.5 g hr^{-1} from the pile mass at the end of the active phase can be applied to the stabilization / curing phase, then the pile could emit another 3.2 kg (7.1 lbs) of VOCs over the next month. This is less than 1% of that emitted in active phase composting. The stabilization and curing phases for this facility are likely not significant VOC emission sources. If most of the negative aeration duct emissions can be destroyed in the biofilter, then negative aeration compost facilities may be able to capture most of the VOCs generated in the composting process.

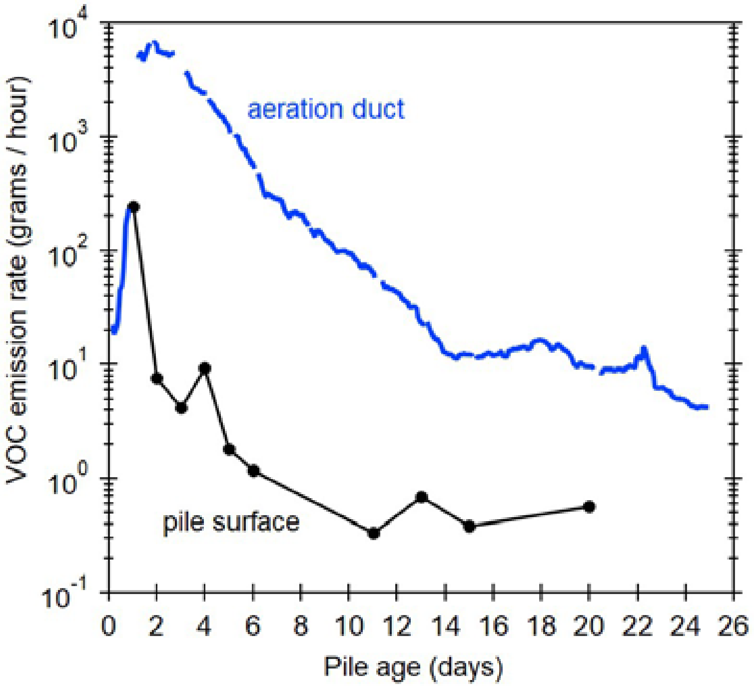

Figure 31: Comparison of total VOC emission rates from the pile surface and aeration duct.

Figure 32 compares the contribution of specific VOCs to the duct emission factor (lbs VOC / wet ton), as listed in Table 2, to the total VOC emission factor from the pile surface. The figure illustrates the diminutive amount of surface emissions compared to duct emissions. Total VOC mass from the duct was 5.47 lbs VOC / wet ton, compared to 0.084 lbs VOC / wet ton from the pile surface. Most of the VOC mass was emitted as methanol and acetone from the duct.

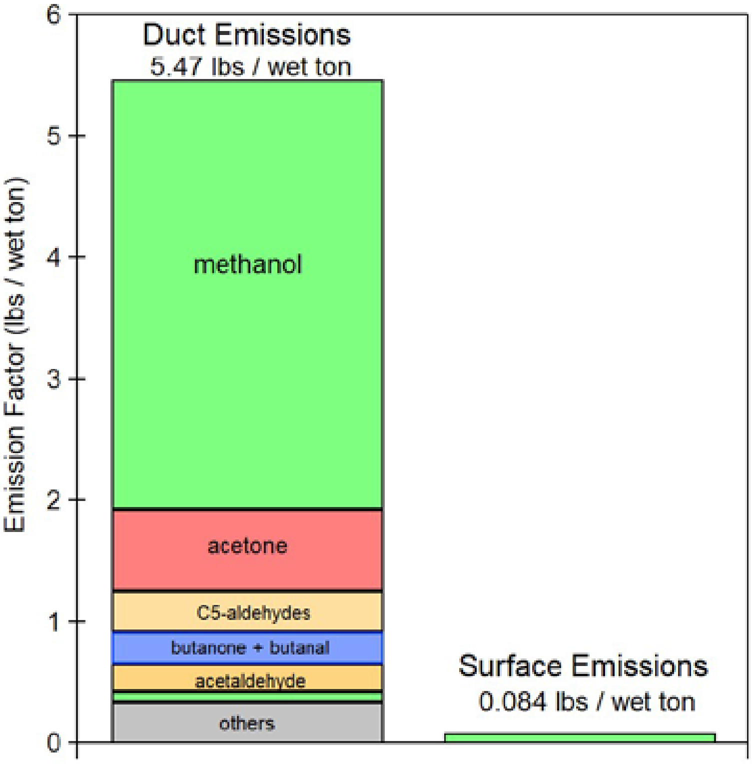

Figure 32: Summary of negatively aerated pile VOC emission factors for the duct and pile surface. Thin green band below acetaldehyde are monoterpenes. Values are actual mass and not carbon mass.

The principal finding from sampling emissions from the negatively aerated pile at WSU was that methanol dominated VOC emissions and that the fugitive VOC emissions from the uncovered pile surface were small compared to the duct. Methanol is not frequently listed as a dominant VOC emission in the composting emissions literature (Jobson & Khosravi, 2019). This can be attributed in part to VOC analysis methods used such as GC-MS (where methanol is difficult to measure) and air sample collection on adsorbents (where volatile methanol is difficult to trap). A related field of research to compost emissions is VOC emissions from decomposition of forest leaf litter were PTR-MS has been recently used as a VOC measurement technology. Methanol has long been observed to be a dominant VOC emission from abiotic and microbially assisted decomposition of forest leaf litter and soil emissions (Schink and Zeikus, 1980; Warneke et al. 1999; Gray et al. 2010; Ramirez et al., 2010). The microbiological decomposition of biopolymers (lignin, cellulose, hemicellulose) found in forest leaf litter typically yields methanol as the dominant emission, comprising 78% to 98% of VOC mass emitted (Gray et al. 2010). While the relative proportion of emitted VOCs can vary with litter type and perhaps microbial community composition, similar VOC compounds have been found in the emission profiles of many leaf litters: methanol, acetone, acetaldehyde, monoterpenes (Gray et al., 2010; Ramirez et al., 2010; Faiola et al., 2014). One source of methanol emissions is thought to be from the breakdown of pectin found in the cell walls of the non-woody parts of the plant (Schink and Zeikus, 1980; Mancussco et al., 2015). It makes some sense based on the leaf litter decomposition literature that methanol might be an expected emission from green waste composting. However, Seewald et al. (2010) noted that under anaerobic conditions emissions of methanol were low compared to other VOCs, but was a dominant emission under aerobic conditions in a soil emission study. Methanol emissions from composting may be dependent on oxygen levels in the pile. Windrows may be lower emitters of methanol than aerated piles because of lower oxygen levels in the pile.

The PTR-MS measurement method is useful for measuring methanol and other oxygenated compounds (acetaldehyde, acetone, acetic acid) emitted in composting; however this is not a standard EPA test method. The PTR-MS has been largely used as a research tool over the last 20 years since its initial development. Methanol can be quantified by whole air sample collection and analysis by gas chromatography with flame ionization detection (FID) as a standard EPA method (TO-12). There is no standard EPA method for analysis of organic acids in air. EPA TO-11a is used for aldehydes and ketones. Given the wide variety of VOCs emitted and the different analytical test methods needed to quantify them it makes sense to employ a standard total VOC test method, such as SCAQMD Method 25.3, to determine emission factors for compost facility permitting. This approach simplifies the analysis and associated costs. Speciation of VOC emissions will require test methods that can collectively quantify light alcohols, aldehydes, ketones, monoterpenes, and organic acids as noted in this study and in Kummar et al. (2011). The PTR-MS seems well suited to this purpose and has been widely used in leaf litter decomposition studies to measure methanol and other oxygenated organics. Speciated VOC emission profiles should be developed through a focused research effort on stock material type and aeration methods (windrow versus aerated static piles) used in Washington state.

From our experience using surface flux chambers over the last few years some general comments can be made about compost emissions sampling. One potential issue is that flux chambers fog and accumulate moisture on interior surfaces, preventing soluble gases from being accurately quantified as shown in Figure 10. This problem was encountered in this project with both in-vessel composting and surface emission testing on a negatively aerated pile. This would be a more acute problem for positively aerated piles and reversing aeration systems where hot humid air is vented through the pile surface. The colder the outdoor air temperature the worse this problem will be. An example of this situation is shown in Figure 33, a photograph of surface flux sampling performed at Lenz Enterprises in March 2018 by the Washington State Department of Ecology. The composting system utilized reversing aeration. On positive flow mode the vented water vapor from the pile surface condenses in the colder ambient air producing a fog and also heavy condensation in the surface flux sampling chamber. Condensation was heavy enough that the water beaded and was running down the Plexiglas dome. Some fraction of water-soluble gases such as alcohols, aldehydes, and organic acids would partition to the liquid water on the chamber surface. For this sampling condition, the accuracy in measuring emissions of water-soluble organics is doubtful. Verifying the veracity of the surface flux sampling approach and providing quality assurance guidelines for its use to ensure good results is something that is needed. I note again that for the green waste stock material examined in the lab composting experiment, methanol and acetic acid were the dominant VOC emissions (Figure 14), both very water-soluble compounds.

Figure 33: Surface flux sampling from a reversing aeration system conducted in March 2018 at Lenz Enterprises. The positive aeration condition is shown. Note water vapor vented from the pile is condensing in the colder ambient air and the heavy condensation in the surface flux isolation chamber where water is beading and running down the Plexiglas dome surface. (Photo: Doug Collins, WSU Puyallup)

For determining accurate VOC emission factors, the central issue is how much of the VOC emissions are water soluble compounds that can be potentially lost to the wet surface of flux isolation chambers. Some indication can be gleaned from Method 25.3 test results from compost emission testing reports. The impinger sample collects water soluble organics, the same compounds that can be lost to water condensed on the chamber surface. In examining VOC emission test reports from California compost facilities using SCAQMD Method 25.3, it was found that the carbon content of the impinger sample often determined the VOC emission rate, containing more than 50% of the carbon mass in many samples. These reports did not indicate how wet the surface flux chambers were. As an example, Figure 35 shows results from the Modesto, CA facility (CIWMB, 2007) to illustrate the importance of the impinger measurement. The top panel shows VOC concentrations from both the impinger and the canister sample co-collected from the ridge of a green waste windrow. The windrow did not have a finished compost later cover (uncontrolled emissions). On most days two samples were collected from different locations on the ridge. VOC concentrations were reported as ppmv CH_4. The top panel shows that the impinger concentrations were frequently greater than the canister sample. The bottom panel shows the fraction of carbon in the impinger sample. The fraction ranged from a high of 89% to a low of 23%, with an average of 51%. Water soluble organics were clearly important to the overall emission flux from the windrow and often dominated the flux on some days, in particular on days 1 and 2 when overall VOC emission rates were high. This test report and others examined indicate the importance of water-soluble organics to compost VOC emission factors. There is a high likelihood that these water-soluble compounds in the impinger would be lost to some extent to the wet surface of the flux isolation chamber. This loss has not been determined in the method evaluations of the surface flux chamber.

Figure 34 also shows significant variability in the water-soluble fraction, though it is hard to understand why the relative emission of water-soluble VOCs would change so much from day-to-day (compare day 3 to day 2), and location-to-location. This variability suggests a basic issue with chamber sampling and compound losses due to water vapor condensation in the chamber and sample lines. Improving surface sampling to avoid condensation in the flux chamber would likely improve the quality of data and reproducibility of surface flux sampling.

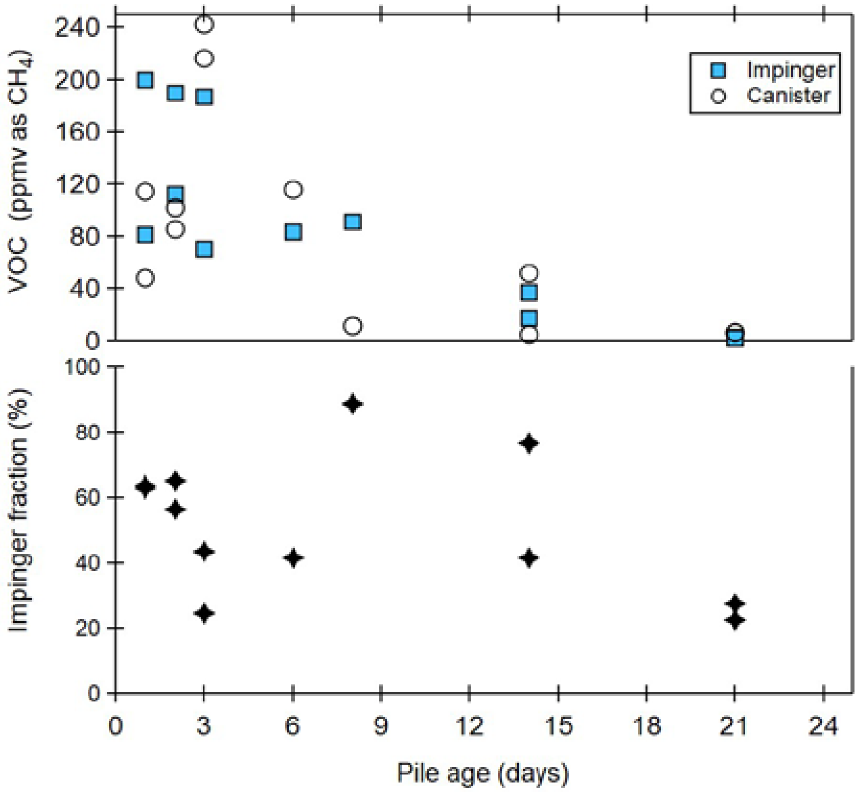

Figure 34: Compost emission testing report data from the Modesto, CA facility (CIWMB, 2007) illustrating the importance of VOCs collected in the impinger. Shown are data from surface sampling on the ridge of a green waste windrow without a compost cover layer. Top panel shows measured VOC concentrations as ppmv CH_4 in the impinger water (blue squares) and the canisters (open circles). Impinger concentrations were frequently much greater than the canister samples. Bottom panel shows the fraction of VOC carbon in the impinger sample.

Another issue with the surface flux sampling method is related to the ambient air dilution of the chamber by wind. Ambient air backgrounds are not subtracted from the chamber data. Blanks used in the method are sweep air blanks best suited for examining cross-over contamination of the chambers from a previous sample. From our experience and from the data listed in emission test reports reviewed (Jobson & Khosravi, 2019), it was often the case that the dilution correction factor for blanks were small compared to the samples. One potential reason for this is the blank measurements are performed on the ground (out of convenience) where it may be less exposed and thus less windy than the top of the pile. The fact that the flux isolation chamber samples are often extensively diluted by ambient air, by factors up to 10, means these samples are sometimes really measuring ambient air at the facility with some added VOCs from compost emissions. Air samples collected from flux chambers on top of piles may include exhaust emissions from heavy equipment operating nearby or simply polluted urban air. The lack of an ambient air correction of the chamber concentration has implications for air permit writers examining TO-15 test results or other speciated VOC analysis of the canister sample. TO-15 test results of compost emissions typically report a suite of hydrocarbons associated with urban air pollution as this is what the analysis method is designed to do: vehicle exhaust compounds and volatile chlorinated organics. While such compounds are stable in canisters and have well established analysis methodology (including commercially available calibration standards) they may have low relevance to compost emission factors. It is important to realize that low concentrations of VOCs measured in the flux chamber may not in fact have been emitted from the compost. Ambient air dilution of the flux chamber may explain the occurrence of benzene and naphthalene (air toxic compounds) and other fossil fuel type hydrocarbons in the testing reports previously examined (Jobson & Khosravi, 2019). Air permit writers should be circumspect about using TO-15 analysis of canister samples from flux chambers and attributing low concentrations of VOCs to compost emissions.

Conclusions & Recommendations

Volatile organic compound emissions rates were successfully measured from the active phase of a negatively aerated 160-ton pile at the WSU Compost Facility. Feedstock materials primarily consisted of manure and animal bedding that contained large amounts of straw and wood chips. VOC emissions rates through the duct were much larger than fugitive emissions from the uncovered pile surface. Emission rates through the duct were 5.47 lbs / wet ton, and from the surface 0.084 lbs / wet ton, for a combined emission factor of 5.55 lbs / wet ton. In terms of mass carbon emitted, as would be reported by SCAQMD Method 25.3, the emission rate is 2.6 lbs C / wet ton. This value is lower than the SJV recommendation of 5.71 lbs C / wet ton for windrow green waste composting, but higher than their 1.78 lbs C / wet ton for windrow composting with manure, biosolids, and poultry litter (SJV, 2010). The small fraction of fugitive emissions from the uncovered pile surface implies that negative aeration systems have a high potential to control VOC emissions if biofilters downstream of the duct can be operated efficiently. This should be encouraging news for composting facilities.

Mass emission rates through the duct were dominated by methanol (65%) followed by acetone (12%). Acetone is an USEPA exempt VOC and could be discounted from the emission factor. Ninety-two percent of the VOC mass emitted was oxygenated compounds. This is important for two reasons. The water solubility of these compounds means losses are likely in sampling from humid surface flux isolation chambers where water vapor has condensed on the chamber surface. The second is that the VOC mass can be significantly underestimated if total VOC methods such as SCAQMD method 25.3 are used without application of an appropriate correction factor to account for the mass of the VOC to mass of VOC carbon measured. VOC emission rates in the duct rapidly increased over the first 38 hours then rapidly decreased; 90% of the VOC mass was emitted in the first 130 hours (5.4 days). Accurate source emission testing for aerated static pile systems must sample the rapid increase and decrease in emissions suggested by this profile.

Our results can also speak to the potential for the stabilization / curing phase to emit VOCs. Given the VOC emission rate at the end of the active phase (4.5 g hr^{-1}) and applying this as a constant rate through the stabilization / curing phase, it is estimated another 7.1 lbs VOC could be emitted over the next 30 days, less than 1% emitted in the active phase. This ratio is much lower than the 30% recommended for windrow-based composting (CIWMB, 2007), indicating basic differences in material processing rates between windrow composting and aerated static pile systems.

VOC measurements made by the PTR-MS compared reasonably well with GC-MS measurements for the duct testing. Good agreement was observed for acetone and acetaldehyde. Methanol could not be quantified by our GC-MS system but this is an important compound to target; use of GC-FID as used in EPA method TO-12 would be a better approach for this compound. In general, the PTR-MS measured higher abundances of DMS, DMDS, and total monoterpenes. PTR-MS measurements of 2-butanone had interferences from 2-methylpropanal (same mass) and larger aldehydes that can fragment to yield the *m/z* 73 ion used to monitor the presence of 2-butanone. The PTR-MS proved useful for continuous monitoring and quantifying oxygenated VOCs, in particular methanol, and very polar compounds like acetic acid.

Measurements made from laboratory based in-vessel composting of green waste feedstock from a commercial facility showed that methanol and acetic acid were emitted in the highest amounts. Water-soluble organics appear to be the most important compounds emitted from both green waste and manure / animal bedding composting materials. Aerated static pile systems may have larger emissions of methanol than less oxygenated windrow systems.

Some general recommendations on compost emissions testing can be made following the experience gained in this project.

Recommendation #1: Limit surface flux sampling if possible

Surface emissions sampling with flux isolation chambers using Method 25.3 is fraught with potential problems and this motivates reducing its use. The small fraction of VOCs emitted from the negatively aerated pile surface has implications for the necessity of surface flux sampling for such systems. The very low emission rates at the end of active composting also imply that fugitive VOC emissions from the stabilization / curing phases might also be very low. This should be confirmed at another facility using negative aeration. If this finding is generally true, considerable expense and effort could be avoided by using a default fugitive emission fraction rather than performing surface flux sampling with flux isolation chambers. For windrow composting it will still be necessary to measure surface fluxes. Facilities using positive aeration must also measure surface emissions which is potentially problematic given the issues of water condensation in the flux chamber. For reversing systems, it may be sufficient to measure emission rates in the negative aeration duct and simply assume that same emission rate would apply under the same positive air flow.

As discussed, an additional issue with the flux isolation chamber method is that there are no ambient air "blanks" used to correct chamber VOC concentrations for wind dilution. Test reports showing speciated VOC data from TO-15 analysis of canister samples may be reporting compounds not emitted from the compost but rather reflect compounds found in polluted ambient air that diluted the chamber. Air permit writers should be made aware of this basic issue.

Recommendation #2: Improve surface sampling representativeness

The second issue with surface sampling is the representativeness of the samples given the small size (0.13 m^2) of the surface flux isolation chambers typically used compared to the very large surface area of the compost pile. Recommendations from staff at the USEPA Measurement Technology Group included using a total temporary enclosure that could be built over the pile so that emissions from the whole pile could be captured and sampled (USEPA Method 204). This might be a prudent approach for sampling biofilters and for positively aerated piles. In both cases there is forced air flow coming up to the surface and flows may not be uniformly distributed across the surface due to local differences in under lying porosity. It is not clear how easy this would be to implement on a large positively aerated pile, but should be straightforward to implement on biofilters. Measurement of biofilter collection efficiency is very important for the emission permitting process but there are limited reports documenting performance with well-tested sampling protocols. The issue of water condensing on the enclosure surfaces could still be an issue for positively aerated piles but should be much less a problem for biofilter sampling where the air flow temperature and water vapor concentration are lower. It is recommended that a simple procedure for enclosure sampling of biofilters be worked out with facility owners. Construction materials for the enclosures should be carefully considered to ensure they have low VOC outgassing rates.

Recommendation #3: Test continuous *in-situ* duct sampling

Sampling from aeration ducts will be necessary to determine emissions rates from compost piles using negative or reversing aeration systems, and for upstream sampling ahead of the biofilter to establish its collection efficiency. A protocol needs to be established for doing this. The USEPA Measurement Technology Group recommended *in-situ* monitoring of ducts and avoiding use of canister sampling as many of the oxygenated compounds and other heteroatom compounds emitted in compost emissions are not stable in canisters. With Method 25.3 there is the need to determine the collection efficiency of the impinger for the high VOC concentrations in the duct.

Continuous measurements from the duct were relatively straightforward to implement using a heated ejector diluter. This allowed rapid dilution and mixing of the duct air sample with dry air to reduce the humidity and prevent sample line losses of water-soluble VOCs. For measuring the VOCs in this diluted air flow, consideration should be given to testing the commercially available semi-continuous total VOC monitors employing flame ionization detectors. Such VOC monitors use a similar measurement principle as described in USEPA

Method 25 (and SCAQMD 25.3) for analyzing VOCs recoverable from canisters. These instruments are available from a number of companies, where the market is continuous emissions monitoring (CEM) from stacks. While they are designed for the analysis of hydrocarbons found in fossil fuel combustion exhaust, modifications or a custom specification may allow for measuring the light alcohols, ketones, aldehydes and monoterpene compounds emitted from compost. It is not clear how well they would perform with organic acids. For pile emissions, getting enough data in the first week to really capture the exponential increase and decrease of VOC emission rates will be important for accurate emission factors. Automated, semi-continuous sampling with these *in-situ* monitors would allow for around the clock monitoring of ducts and temporary enclosures of piles and biofilters. A less labor-intensive sampling methodology would reduce labor costs for source testing.

Recommendation #4: Emission factor development independent of facility testing

A small scale (50 yd^3 pile size) two zone pilot plant is being constructed at WSU by Engineered Compost Systems (Seattle, WA) with funding from Environmental Research and Educational Foundation (EREF) to test VOC emissions as a function of process conditions such as aeration method. An opportunity exists to use this testing facility to help develop VOC emissions factors for green waste, food waste, biosolids composting in Washington State that does not involve specific facility testing. A key issue in air permitting has been the adoption of California emission factors based on windrow composting. Much of Washington state composting by the biggest facilities is not windrow composting but an aerated static pile process (Jobson et al., 2020). Windrow emission factors may not accurately reflect VOC emissions from aerated static piles, where better control of temperature and oxygen levels in the pile may decrease emission rates compared to windrows. This is something that should be determined experimentally with the pilot plant in side-by-side trails. The data would be extremely useful to the air emissions permitting process for the composting systems widely used in Washington state. The pilot plant could also be a test bed to develop enclosure sampling and *in-situ* duct sampling methods recommend by the USEPA Measurement Technology Group. A partnership with stakeholders (compost facility operators, air permit writers, equipment suppliers, air quality chemists) to guide development of more accurate, reliable, and cost-effective VOC sampling and analysis methods for the state is recommended.

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Appendix A: VOC Analysis Methods

PTR-MS

There are two factors that can complicate the interpretation of the PTR-MS mass spectrum. First are isobaric interferences, where multiple compounds share a common molecular weight and thus produce the same RH^+ ion. An example of this type of interference is between acetone (a ketone) and propanal and aldehyde, both with chemical formula C_3H_6O. For this project, an important isobaric interference is with the various structural isomers of monoterpene compounds, like α-pinene and limonene, both with chemical formula $C_{10}H_{16}$. Monoterpene compounds cannot be distinguished from one another and thus a total sum is reported. Secondly, the proton transfer reaction takes place in an ion drift tube and not all reactions lead to a simple M+1 mass ion. The ion drift tube has a DC electrical potential applied across its length to increase the ion kinetic energy. This extra kinetic energy is designed to break apart clusters that form between reagent ions and water vapor, yielding $H_3O^+{\bullet}H_2O$ for example. Such clustering also occurs with organic ions and would confuse interpretation of the mass spectrum. Clustering also diminishes instrument sensitivity by reducing the abundance of H_3O^+ in the drift tube. The electric field used in the measurement is a key technical description of the method. Drift tube electric field conditions are quantified in units of Townsends, which is the ratio of the drift tube electrical potential to the molecular number density of air inside the drift tube (E/N, $1\ \mathrm{Td}=10^{-17}\ \mathrm{V\ cm^2}$). This is typically reported as a Townsend number (Td). Typical values ranging between 120 to 150 Td are used. This study used 120 Td. A negative side effect of this additional kinetic energy is that proton transfer reactions with many compounds are dissociative. These dissociation reactions produce cations at lower molecular weights than the parent compound, so called fragment ions, confusing the interpretation of the mass spectrum as an M+1 mass spectrum. Fragment ions can cause positive interferences for some compounds. As an example, a well-known problem in urban air measurements is that ethylbenzene (C_8H_9) dissociates upon protonation to produce protonated benzene ($C_6H_6{\bullet}H^+$ at $m/z = 79$ amu). The dissociation problem is significantly reduced by operating the drift tube at a lower electric potential (i.e., 80 Td), and has been done in urban air quality studies to measure formaldehyde, but requires removal of water vapor and thus is a more technically difficult measurement to perform (Jobson and McCoskey, 2010).

The interpretation of the PTR-MS mass spectrum has been facilitated over the last 20 years by comparison to other measurement methods, such as GC-MS, which are better able to separate mixtures into individual components for identification. Co-sampling of pollution sources using both methods allows for the PTR-MS measurements to be more useful for air pollution monitoring and source sampling. Newer versions of this instrument use time-of-flight mass spectrometry that provides a higher mass resolution spectrum to better separate and identify compounds (chemical formula of ions) based on their exact mass. However, the basic problem of compound dissociation remains. From our experience with this project the major dissociation reactions to account for in compost emission are 1) monoterpenes, 2) pentanals, 3) pentanols, and 4) acetic acid and larger organic acids. These reactions and impacts are discussed below.

Monoterpenes

Monoterpenes dissociate upon protonation to yield an ion at *m/z* 81 along with the protonated parent molecule at *m/z* 137. The relative yield of *m/z* 81 ion depends on the monoterpene. The most abundant monoterpenes measured in the compost emission were a-pinene, b-pinene, limonene, and 3-carene. Thus, the presence of a strong *m/z* 81 signal and *m/z* 137 ion signal in the mass spectrum indicate the presence of monoterpenes.

Pentanals

GC-MS analysis of compost emissions from the WSU facility stock material and commercial facility green waste stock material identified emissions of the C_5 aldehydes 3-methylbutanal, also called isovaleraldehye, and 2-methylbutanal ($C_5H_{10}O$). Isovaleraldehyde is an expected emission from food materials through the breakdown of leucine. Protonation would produce an *M*+1 ion at *m/z* 87. As reported by Ionicon, dissociative protonation of isovaleraldehyde is significant, producing *m/z* 69 ion at 73% yields and the *m/z* 87 ion at only 10% yields. Yields of *m/z* 87 from 2-methylbutanal are higher at 49%, but also yields the *m/z* 73 fragment ion at 16% yields. The presence of 2-methylbutanal thus produces a positive interference for 2-butanone which is detected at its *M*+1 ion *m/z* 73.

Pentanols

It is known that proton transfer reactions to longer carbon chain alcohols results in loss of the protonated hydroxyl group and formation of fragment ion. An alcohol that had significant emissions from the WSU compost, as identified by GC-MS, was 3-methyl-1-butanol ($C_5H_{12}O$). As reported by Ionicon, dissociative protonation produces the fragment ion *m/z* 71 ($C_5H_{11}^+$) at 100% yield, and there is no response at the *M*+1 ion *m/z* 89. The *m/z* 71 ion is a common fragment ion from many compounds and not a useful marker for this compound.

Acids

The emission of organic acids such as acetic acid, propionic acid, butanoic acids, and pentatonic acids have been reported from compost emissions and have unpleasant odors. As reported by Ionicon, dissociative protonation of organic acids occurs to a varying extent. For acetic acid ($C_2H_4O_2$) only about 10% dissociates to produce the *m/z* 43 ion. This was confirmed for calibrations done for this compound in our lab. Thus, for acetic acid a strong signal should be observed at the *M*+1 ion at *m/z* 61 and should be quantifiable. For propionic acid ($C_3H_6O_2$) about there is ~50% yield at *M*+1 ion *m/z* 75, with the major fragment ion *m/z* 57 at 43% yield. For butanoic acid ($C_4H_8O_2$) there is ~40% yield at the *M*+1 ion *m/z* 89 and the major fragment ion is *m/z* 43 at ~40% yield. The pentatonic acids ($C_5H_{10}O_2$) valeric and isovaleric acids also produce strong *M*+1 signals, occurring at *m/z* 103. Pentanoic acids are common in foods and production of isovaleric acid can occur through microbial decomposition of the amino acid leucine. Capronic acid ($C_6H_{12}O_2$), found in animal fats and oils, produces a *M*+1 signal at m/z 117 in 43% yields. Compost emissions of these organic acids should be detectable by PTR-MS at their respective *M*+1 ions. All of these ions were observed in PTR-MS measurement of in vessel composting of the municipal green waste feed stock material, consistent with its different odor when compared to the WSU facility's manure-based feedstock material.

Table A.1: Attribution table of ions measured by PTR-MS and associated VOCs emitted from WSU facility compost material.

m/z	Compound	Formula
31	formaldehyde	$HCHO$
33	methanol	CH_3OH
35	hydrogen sulfide	H_2S
42	acetonitrile	CH_3CN
45	acetaldehyde	CH_3CHO
46	dimethylamine	C_2H_7N
47	ethanol	C_2H_6O
49	methylmercapton	CH_3SH
59	acetone + propanal	C_3H_6O
60	trimethylamine	$N(CH_3)_3$
61	acetic acid	$C_2H_4O_2$
63	dimethyl sulfide	$S(CH_3)_2$
73	2-butanone + C_5 pentanals	C_4H_8O
75	propionic acid	$C_3H_6O_2$
80	pyridine	C_5H_5N
87	pentanals	$C_5H_{10}O$
89	butanoic acid	$C_4H_8O_2$
95	dimethyl disulfide	$C_2H_6S_2$
107	benzaldehyde	C_7H_6O
137	monoterpenes (α-pinene + limonene)	$C_{10}H_{16}$
153	camphor	$C_{10}H_{16}O$

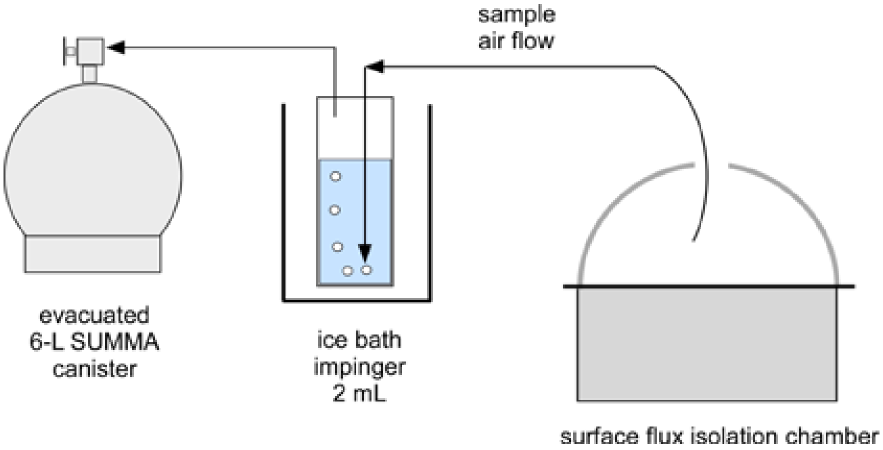
Table A.2: Canister meta data from surface flux sampling.

Date	Time (PDST)	Can #	Chamber air temp (°C)	Ambient air temp (°C)	Wind speed (m/s)	location	Dilution factor
July 31	16:49	6908	50.2	36 C	2.2	P1	1.1
Aug 1	07:00	6906	29.0	24.2	< 1	P1	1.0
Aug 1	08:30	6900	32.1	24.2	< 1	P2	1.8
Aug2	08:03	6905	31.8	23.7	0 – 0.3	P1	1.0
Aug 2	08:53	T3	32.9	26.7	0 – 0.3	P2	1.50
Aug 2	07:30	6898	ND	ND	ND	blank	1.03
Aug 3	07:42	T13	37.5	23.1	0.9 – 1.4	P1	1.04
Aug 3	08:23	6904	32.9	23.7	2 - 3	P2	2.80
Aug 4	08:00	6907	33.0	22.2	0 – 0.3	P1	1.28
Aug 4	08:10	T1	33.0	22.2	0 – 0.3	P1	1.30
Aug 4	09:19	6903	32.5	23.0	1 – 2	P2	2.10
Aug 4	10:07	T24	35.3	26.6	1 – 1.6	P3	1.96
Aug 5	07:50	T9	ND	ND	ND	P1	1.25
Aug 5	08:27	6901	ND	ND	ND	P2	1.65
Aug 5	10:00	6894	ND	ND	ND	P3	1.65
Aug 10	07:50	T11	20.1	19.4	0.5 -1.0	blank	1.0
Aug 10	08:23	T8	26.4	19.3	0.5 - 1.5	P1	1.3
Aug 10	11:56	T5	38.6	27.6	0.5 – 1.5	P2	2.2
Aug 10	13:19	6897	39.2	28.3	0.5 – 1.3	P3	2.6
Aug 12	09:44	6902	22.7	16.4	2 – 4.3	P1	3.4
Aug 12	10:29	T18	22.1	16.9	2 – 4.3	P2	5.0
Aug 12	11:28	T19	22.3	18.6	2 – 4.3	P3	6.1
Aug 14	08:30	T8	26.0	20.4	1 - 2	P1	1.94
Aug 14	09:25	T10	28.2	22.9	1 - 2	P2	2.61
Aug 14	10:22	T7	32.1	23.8	2 - 3	P3	3.78
Aug 19	09:52	T2	37.2	26.5	1 - 2	P1	2.0
Aug 19	12:03	T11	38	33.8	0.5 - 1	P2	2.55
Aug 19	12:24	T14	38	33.8	0.5 – 1	P2	2.55
Aug 19	14:12	T6	40.6	32.9	1.7 – 2.5	P3	3.55

*ND = no data

SCAQMD Method 25.3

This method titled "DETERMINATION OF LOW CONCENTRATION NON-METHANE NON-ETHANE ORGANIC COMPOUND EMISSIONS FROM CLEAN FUELED COMBUSTION SOURCES" is a modified version of USEPA method 25, used to determine total VOC emissions rates from combustion sources. Method 25.3 collects two samples, one into an evacuated canister for gas analysis, and one into water filled impinger for total dissolved organic carbon analysis. Air samples are collected from the flux isolation chamber using evacuated SUMMA canisters. VOCs that have low vapor pressures or are very polar are not recoverable from SUMMA canisters are collected in the impinger. Method 25.3 first samples air by bubbling the air flow through an impinger filled with ~2 mL of distilled water cooled in an ice bath. Water-soluble gases such as acids, aldehydes, and alcohols will dissolve in the impinger water and be trapped there (the collection efficiency is unknown), while less water-soluble gases pass through to the evacuated canister. The impinger also reduces the air humidity to prevent water collecting in the canister when sampling humid sources. The impinger and canister are connected in series, and the evacuated canister pulls the air sample at a slow flow rate from the source through the impinger and into the canister as shown below.



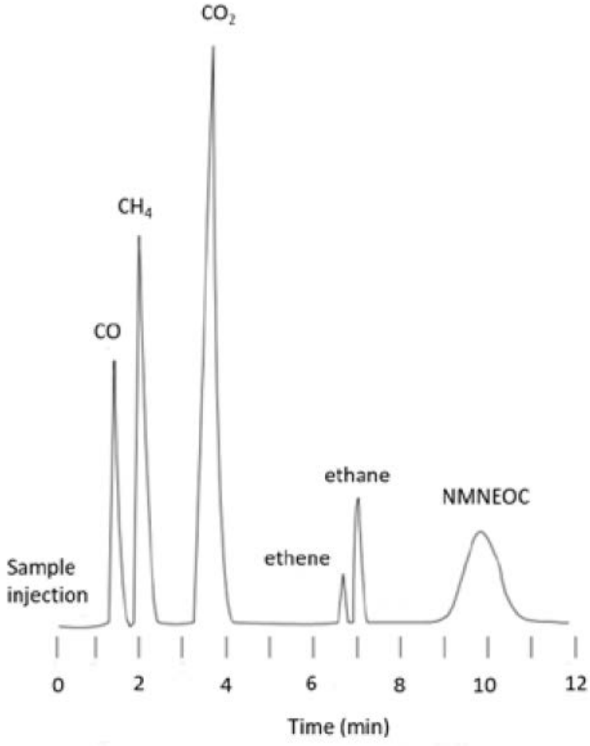
The impinger water is analyzed using a total dissolved organic carbon analyzer; these are readily available commercially and widely used for water quality analysis. In this analysis the organics are catalytically converted to CO_2 gas and the amount of CO_2 is measured by a non-dispersive infra-red analyzer, and results reported as ppmC or ppmV. The conversion between ppmV and ppmC is to multiply ppmV by the number of carbon atoms in the molecule.

ppmC = ppmV x number carbon atoms in the molecule

For CO_2 these units are equivalent since CO_2 contains 1 carbon atom. CO_2 is also soluble in water, and found in high concentrations in compost emissions. Thus, the CO_2 must be purged from the impinger before analysis. This can be done at the time of field sampling, the purge gas pulled through the impinger by the still partially evacuated sampling canister. An examination of some compost emission test reports show that the amount of carbon collected in the impinger can be 10 x the amount from the canister sample. There has been little analytical work to determine the types of VOCs in the impinger water. This method has not been evaluated for negative aeration duct sampling of compost systems where VOC concentrations may be very high. The method states it use is limited to trap concentrations less than 25 ppmC so this may be problematic for high concentration duct sampling.

One major difference between Method 25.3 and USEPA Method 25 is the use of a water filled impinger and analysis of the water sample by a TOC analyzer. In Method 25 a dry ice cooled condensate trap is used to remove organics that are not recoverable from canisters. The trap and canister are both analyzed by a total carbon analyzer described below. The use of a water filled impinger does simplify the sampling and analysis process and also allows for condensed water in the sample line to be flushed into the impinger for analysis.

The canister is analyzed on a custom gas chromatograph designed as a total carbon analyzer (TCA). In Method 25.3 the gas chromatograph separates the VOCs from other carbon containing gases such as CO_2, CO, and methane. Method 25.3 also removes ethane (C_2H_6), as this is an exempt VOC by the US EPA, and ethene (ethylene) as an unavoidable result of the chromatographic separation (ethene elutes before ethane). Ethene is a photochemically reactive VOC that contributes to ozone formation and a common fossil fuel exhaust compound, so it is somewhat strange this compound is excluded from a testing method originally designed for combustion sources. The resulting VOC that are measured are called non-methane non-ethane organic compounds (NMNEOC). An example chromatogram from the Method 25.3 description is shown below, illustrating the separation of methane, ethene, and ethane from the other VOCs.



After separation the NMNEOC are back flushed from the column and the flow sent to a high temperature oxidizer that catalytically converts the carbon atoms in the VOCs to CO_2. CO_2 is then reduced on another catalyst to methane and the methane is then detected by a flame ionization detector (FID). This two-step conversion process ensures all carbon in the NMNEOC portion is detected. It does not measure the heteroatoms in the VOCs such as oxygen, sulfur, or nitrogen. The measured methane detected is reported as ppmV which is equivalent to ppmC since methane has 1 carbon atom.

The respective analyses report molar fractional abundance of VOC carbon. The total VOC carbon emitted is the sum of the TOC and TCA analysis:

Total VOC (ppmC) = TOC analyses (ppmC) + TCA analyses (ppmC)

If there is no knowledge of the types of VOC compounds in the mixture, the method prescribes using hexane as a surrogate VOC to compute a concentration (mass / volume) from the measured total VOC mixing ratio. Using hexane (C_6H_{12}) as a surrogate, the VOC mass per measured carbon atom would be determined from the molecular weight of hexane divided by 6 carbon atoms per molecule of hexane:

hexane conversion factor = 86.18 g mol^{-1} / 6 C-atoms = 14.35 g / C-atom mol

Other surrogate hydrocarbons are used in compost emission reporting, notably methane. The mass conversion factor for methane would be

methane conversion factor = 16.04 g mol^{-1} / 1 C-atoms = 16.04 g / C-atom mol

If methanol is used as the surrogate the mass conversion factor would be:

methanol conversion factor = 32.04 g mol^{-1} / 1 C-atoms = 32.04 g / C-atom mol

The formula to convert the measured total VOC molar mixing ratios (ppmC) in a flux chamber sample to concentration (grams m^{-3}) using hexane as the surrogate VOC and assuming air pressure and temperature at standard conditions of 1-atm and 273 K is as follows:

$$g\,m^{-3} = ppmC \times 10^{-6} \times \left(\frac{1\,atm}{R \times 273\,K}\right) \times 14.35\,g\,Catom\,mol^{-1} \times 1000\,Lm^{-3}$$

where R is the universal gas constant (0.08206 L atm mol^{-1} K^{-1}).