INDOOR AIR MONITORING OF ETHANOL AND BENZENE IN A PILOT WINERY USING ACTIVE SAMPLING

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ABSTRACT

Indoor Air Monitoring of Ethanol and Benzene in a Pilot Winery Using Active Sampling

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Acute indoor concentrations of benzene and ethanol were evaluated in the California Polytechnic State University San Luis Obispo's pilot winery workroom. Air samples were collected during four different wine-making activities: fermentation, fermentation with Brix content testing, post-alcoholic fermentation pressing, and storage/finishing. Average workroom benzene concentrations ranged from 0.05 to 0.12 mg/m^3. Ethanol concentrations in the winery workroom varied with the activity, ranging from 0.9 to 12 mg/m^3. Pressing and fermentation with Brix content testing both led to higher indoor ethanol concentrations than fermentation without Brix content testing and storage/finishing.

Tracer gas decay air exchange tests were conducted to determine the air exchange rate of the winery workroom. A single-space mass-balance model was used to estimate the air exchange rate for the entire workroom. The calculated air exchange rates were correlated with wind speeds and wind direction to create a linear model estimating air exchange rates based on wind speed. These air exchange rates and the indoor concentrations of ethanol were used with the single-space mass-balance model to calculate an ethanol emission rate for each activity. Total estimated ethanol emissions for the four activities were 3.1 lbs. ethanol per 1000 gallons of wine produced.

Key words: volatile organic compound, ethanol, benzene, tracer gas decay, air exchange rate, indoor air quality, active sampling, thermal desorption, gas chromatography-mass spectrometry, winery

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TABLE OF CONTENTS

APPENDICES

LIST OF TABLES

LIST OF FIGURES

Figure Page

1. Introduction

This thesis project focused on two objectives:

1. Evaluate the indoor concentrations of ethanol and benzene in the Cal Poly pilot winery using active sampling.
2. Calculate ethanol emission rates within the winery workroom during the selected wine making activities.

Preliminary tracer gas decay air exchange tests were performed to determine the air exchange rate of the winery workroom. Then, the air exchange rates were used with wind data to create a model estimating the linear relationship between the workroom's air exchange rate and wind speed. A single-space mass-balance model of the winery workroom was used to estimate ethanol emissions using indoor ethanol concentrations.

Pilot winery workroom air samples were collected during four activities: fermentation with Brix content testing, fermentation without Brix content testing, pressing post-alcoholic fermentation, and finished wine storage. Air samples collected from each activity were analyzed using thermal desorption gas chromatography-mass spectrometry. Using measured ethanol concentrations and modeled air exchange rates, ethanol emission rates for each activity were calculated.

This study's intended purpose is to be a stepping stone for further research for indoor air quality monitoring and VOC emission monitoring for wineries. The findings in this study should not be interpreted as scalable for wineries larger than the Cal Poly pilot winery, as processes between small and large wineries vary. However, ethanol and other winery-emissions should be monitored at all sizes of production to determine how production methods influence emission rates and to ensure the safety of the workers and the environment.

2. Background Overview

To properly frame the context of this study, the following five essential questions will be addressed in this background:

1. What are volatile organic compounds, and how do they affect human health and indoor and outdoor air quality?
2. Why are winery indoor air quality and VOC emissions relevant to the environmental and anthropogenic health of California?
3. What scientific investigations have been conducted on winery indoor air quality and VOC emissions?
4. How are volatile organic compounds measured and quantified in environmental sampling?
5. What are the foundational concepts of the study of indoor air quality, and how do they relate to this study?

2.1 Volatile Organic Compounds in Indoor Air

Volatile organic compounds (VOCs) are a broad spectrum of carbon-based chemicals that are gaseous at room temperature (LBNL Indoor Environmental Group, 2018) (California Air Resources Board, 2009). Sources of indoor VOC emissions include paints, cleaning supplies, building materials, indoor smoking, cooking fuels, cosmetics, printers, carpets, and air fresheners (Wolkoff, Clausen, Jensen, Nielsen, & Wilkins, 1997) (Franco, Chairez, & Paznvak, 2012) (El-Hashemy & Ali, 2018). The label of VOC is broad, as chemicals that fall under this label come in a variety of structures. Alkanes, aromatics, terpenes, and halocarbons are the most prevalent in indoor air and are of research interest for their detrimental impact on human health (Zabiegala, Przyk, &

Przyjazny, 2000) (Sarwar, Corsia, & Kimura, 2002) (Khanchi, Hebbern, Zhu, & Cakmak, 2015). In the atmosphere, VOC emissions contribute to the greenhouse gas effect and play a critical role in the formation of photochemical smog.

2.1.1 Volatile Organic Compounds’ Effect on Human Health

The effect of VOCs on human health is a significant concern in indoor air quality. As previously stated, there are many sources indoors and outdoors that emit VOCs, making it important to understand how these chemicals affect human health. Previous studies have been conducted to determine if there are correlations between VOC exposure and adverse symptoms. For example, Aziz Khanchi et al. examined the relationship between indoor and outdoor VOC concentrations and cancer/non-cancer risk for residents in Windsor, Canada. This study concluded that VOC concentrations alone should not be relied on for determining cancer/non-cancer risk in people but should be taken into consideration for a more comprehensive evaluation (Khanchi, Hebbern, Zhu, & Cakmak, 2015). Another study by J.E. Colman Lerner et al. sought to characterize health risk in occupational settings in Buenos Aires, Argentina. The study determined that the use of VOC control technologies resulted in decreased indoor VOC concentrations, and suggested VOC’s role in increased cancer risk (Colman Lerner, Sanchez, Sambeth, & Porta, 2012).

Exposure is a critical health and safety concept. For this study, exposure will be defined as the physical contact between a person and the constituent of concern via skin or inhalation for a duration of time (Thatcher, et al., 2001). The correlation between adverse health effects and VOCs involves both exposure and toxicity: the more a subject is exposed to a VOC, the greater the likelihood of detrimental health effects due to its toxicity. VOCs such as benzene and styrene are commonly analyzed and sampled for, as they produce adverse effects on human health (Sundell, 2004) (Weschler, 2004) (Zhao, Cheng, Lin, & Cheng, 2016).

Adverse health effects have been categorized by OSHA into two categories: acute and chronic effects. Acute effects are those that occur rapidly due to short-term exposure, while chronic effects can appear after extended exposure (Occupational Safety and Health Administration, 2018). Examples of acute effects from VOC exposure include throat irritation, runny or burning nose, and headaches; chronic effects of long-term VOC exposure include increased cancer risk, decreased lung function, and increased respiratory morbidity (Colman Lerner, Sanchez, Sambeth, & Porta, 2012) (Wolkoff, Clausen, Jensen, Nielsen, & Wilkins, 1997) (Ravsoni, et al., 2017) (Zabiegala, Przyk, & Przyjazny, 2000). The severity of these effects is correlated to several factors, including the concentration of VOCs, length of exposure, and personal factors of the individual exposed.

While there is significant evidence suggesting exposure to VOCs is hazardous, the concentration of a single VOC or a sum concentration of all VOCs is not a direct measure of the safety of an indoor or outdoor environment. VOC concentrations must be considered with other factors such as relative toxicity of the compounds, temperature, relative humidity, and other environmental conditions. The study of VOC emissions is a critical aspect of assessing air quality, as it can affect humans in ways other than direct exposure (Sundell, 2004) (Wolkoff, Clausen, Jensen, Nielsen, & Wilkins, 1997) (Khanchi, Hebbern, Zhu, & Cakmak, 2015).

Benzene and ethanol were the VOCs analyzed in this study. Benzene is a VOC that is toxic to humans, damaging the immune system and bone marrow (Center for Disease Control and Prevention, 2018). However, it is not the by-product of wine making specifically: it is a VOC by-product of engine combustion. The pilot winery was located at the cross-roads of two heavy-traffic roads into the university and surrounded by four agricultural fields that were heavily used during sampling, raising concern for exposure of benzene in the winery workroom. Acute airborne exposure to ethanol causes similar health effects as ethanol ingestion, including eye irritation, headaches, vomiting, and unconsciousness (New Jersey Department of Public Health, 2016).

2.1.2 Volatile Organic Compounds and Indoor Chemical Reactions

Monitoring and control of VOCs (benzene, ethanol, etc.) are critical aspects of indoor health, but recent research suggests that there may be more to consider. In a review article, P. Wolkoff suggests that low concentrations of primary VOCs may not necessarily indicate low emission rates since indoor reactions may convert emitted VOCs to harmful secondary pollutants (Wolkoff, Clausen, Jensen, Nielsen, & Wilkins, 1997). Indoor environments are highly favorable for chemical reactions, particularly reactions involving ozone and VOCs (Weschler, 2004). Due to ozone's atmospheric prevalence and the generation of VOCs from natural and anthropogenic sources, these reactions are common in indoor environments (Sarwar, Corsia, & Kimura, 2002). The increased surface-to-volume ratio in an enclosed environment promotes O_3 and VOC interaction, resulting in the formation of hydroxyl (OH) radicals. OH radicals are potent oxidizers and will react with other VOCs to form alkyl and peroxy radicals (Wolkoff, Clausen, Jensen, Nielsen, & Wilkins, 1997) (Slominska, Konieczka, & Maniesnik, 2014). These secondary radicals have been shown react with the primary emitted VOCs and other constituents in the building via similar surface reactions, perpetuating the cycle of VOCs and ozone producing hydroxyl radicals. The radicals can cause physical irritation to building occupants through oxidation reactions with other airborne constituents, as well as interacting directly in the membranes of the eyes and nose (Weschler, 2004) (Sundell, 2004) (Wolkoff, Clausen, Jensen, Nielsen, & Wilkins, 1997).

Indoor chemical reactions between ozone and VOCs occur within minutes (Weschler, 2004). Thus, sampling strategies should evaluate the meaning behind certain VOC concentrations. It may be the case that low concentrations of primary reactants are measured, but products of these reactions could be increasing to an equilibrium state in the room. The idea of “the lamp-post effect” was asserted by J. Sundell. At night, it is difficult to see what is around if it isn’t illuminated by a lamp-post; similarly, scientists can only focus on what they are able to measure (i.e. under the “lamp-post”). Sundell suggests that although there is no direct association between measured VOC concentrations and health effects, the measurements aren’t without meaning. Researching efforts should be directed to further understand possible correlations between IAQ and human health by evaluating VOC reactants, products, and the risk they pose to the environment (Sundell, 2004).

2.1.3 Volatile Organic Compounds in Outdoor Air

The formation of photochemical smog is the result of a complex series of reactions between nitrous oxides, ozone, and emitted VOCs (Slominska, Konieczka, & Maniesnik, 2014) (Figure 1). VOC emission sources include traffic emissions, gasoline evaporation, industrial emissions, and solvent usage (near-road schools, isomeric analysis, fate). Additionally, indoor chemical reactions resulting in the formation of alkyl, peroxy, and hydroxyl radicals can be ventilated to the outdoor air and contribute to the formation tropospheric ozone (Slominska, Konieczka, & Maniesnik, 2014). Nitrogen dioxide is energized by solar irradiation, triggering a reaction with existing oxygen in the atmosphere to form ozone. This ozone is part of photochemical smog's composition, but also plays a role in the radicalization of VOCs in the atmosphere (Shan, et al., 2007). Once the VOCs are oxidized, they will react with nitrogen dioxide in the atmosphere to form peroxyacyl nitrates (PAN) and aldehydes, another component of photochemical smog. Nitric acid is another major component of photochemical smog, formed by the reaction between water vapor in the air and nitrogen dioxide (Miller & Hackett, 2011). The wine making season is from early August to late October. This timeframe has the hottest and sunniest weather California experiences: sunlight and heat are two major driving forces for the formation of photochemical smog (California Air Resources Board Ozone, 2016). Thus, VOC emissions from wineries have the potential to increase the formation of photochemical during the wine making season.

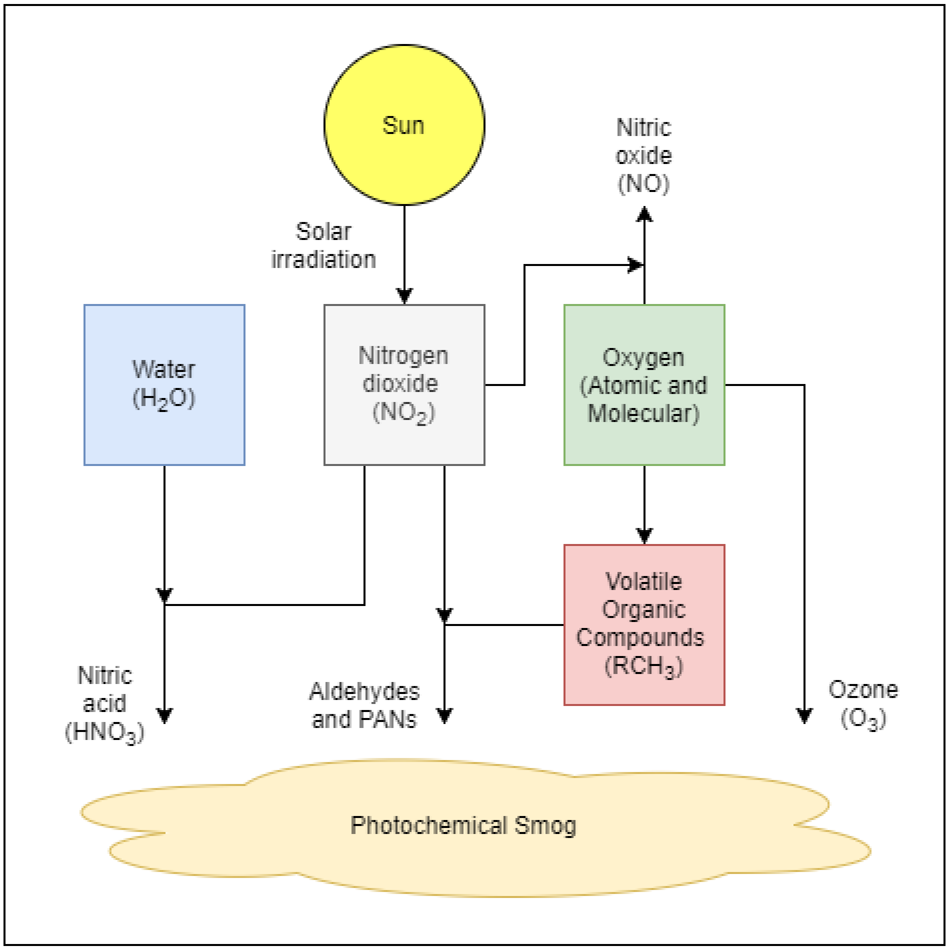


Figure 1. Summary of photochemical smog formation

For an individual building, the emissions of a given VOC are dependent on the equipment and processes inside. Office equipment such as printers, air purifiers, and paints/solvents contribute to the VOC profile within a building (Caselli, de Gennaro, Saracino, & Tutino, 2009). To maintain safe concentrations, OSHA has set maximum occupational exposure limits (OEL) for key VOCs (Table 1) (Occupational Safety and Health Administration, 2018) (Occupational Safety and Health Administration, 2018). While the atmospheric profile does not consist of only indoor sources, the emission of VOCs and their derivatives from multiple building sources increases the formation of photochemical smog when combined with outdoor emissions (e.g. cars and industrial processes).

Table 1. OSHA and Cal/OSHA regulatory limits

Substance	OSHA 8-hour TWA (ppm)	Cal/OSHA 8-hour TWA (ppm)
Benzene	10	1
Ethyl alcohol	1000	1000

2.2 Winery Indoor Air Quality and Outdoor Emissions

California is the largest producer of wine in the United States, responsible for 81% of the country's production in 2018 (Wine Institute, 2017). Approximately 4 million tons of grapes were grown and crushed in 2018, with 241 million cases sold in the United States (Wine Institute, 2017). This large-scale production of wine has attracted the attention of air quality regulatory agencies such as the USEPA, the California Air Resources Board (CARB), and local bodies such as the San Joaquin Air Pollution Control District and the Santa Barbara Air Pollution Control District (APCD). The San Joaquin and Santa Barbara APCDs are responsible for regulating their respective counties that collectively contribute 70% of California's wine production (Wine Institute, 2019). The largest emissions from wine production are ethanol and carbon dioxide (CO_2) (Midwest Research Institute, 1995). Ethanol is a volatile organic compound (VOC) that contributes to the formation of photochemical smog when emitted into the atmosphere and is monitored by the APCDs. Indoor concentrations are regulated by OSHA.

2.3 Previous Research on VOC Monitoring in Wineries

The presence of hazardous VOCs in wine-production facilities is an understudied aspect of indoor air quality. Historically, the main concerns for winery facilities have been CO_2 and ethanol, as both are generated in large quantities during fermentation and crush (Midwest Research Institute, 1995). However, advances in occupational health monitoring and increased regulations call for a more comprehensive look at the composition of indoor air quality at wineries. A study conducted by Daniel Sanjuan-Herrarez et al. evaluated hazardous VOC concentrations in a Spanish winery, using diffusive sampling to measure long-term exposure (Sanjuan-Herraez, de la Osa, Pastor, & de la Guardia, 2014). These concentrations were compared to those outlined by the registration, evaluation, authorization, and restriction of chemical substances (REACH) European standards and were determined to meet the REACH standards (Table 2).

Because of the minimal amount of research conducted on indoor air quality at wineries, other indoor environments and conditions were reviewed for VOC concentrations as a source of comparison. Three different settings were reviewed: building construction, near-road schools, and an indoor VOC concentration and VOC emission model for a generic indoor space.

Building construction is a process that uses many VOC-emitting products. A study conducted by Weihui Liang et al. determined that paints, flooring, and wall formation are all contributors to VOC emissions during apartment building construction (Table 2) (Liang, Wang, Yang, & Yang, 2014). A study by Zabiegala et al. was conducted to determine ambient indoor concentrations after the construction process of an apartment, rather than during construction (Zabiegala, Przyk, & Przyjazny, 2000). P. Wolkoff et al. determined that building materials will continually emit VOCs that make up the material’s composition, causing unwanted emissions that can be potentially harmful to building occupants (Wolkoff, 1990).

The winery workroom in this study is located near a busy road in the university, seeing constant commuting traffic throughout the day. A study conducted by Amit U. Raysoni et al. analyzed hazardous VOC concentrations in four elementary schools near busy roads in El Paso, Texas. The study concluded that there was a significant correlation between outdoor BTEX concentrations and heavy traffic, as well as a corresponding increase for indoor BTEX concentrations (Table 2) (Ravsoni, et al., 2017).

Table 2. Review of average ethanol and BTEX concentrations from different indoor environments

Study*	Ethanol (μg/m^3)	Benzene (μg/m^3)	Toluene (μg /m^3)	Ethylbenzene (μg /m^3)	m-,o-,p-Xylene (μg /m^3)
Air monitoring in wineries	-	0.1	0.3	0.1	0.1
Interior Construction	-	79.2	361.1	127.6	41.5
Hydroxyl - Sawar	188.4	0.4	1.1	0.2	0.2
Evaluation of IAQ	-	0.5	53.7	95.4	339.2
Near Road Schools	-	0.7	2.9	0.6	0.9

*References in descending order: (Sanjuan-Herraez, de la Osa, Pastor, & de la Guardia, 2014) (Liang, Wang, Yang, & Yang, 2014) (Sarwar, Corsia, & Kimura, 2002) (Zabiegala, Przyk, & Przyjazny, 2000) (Ravsoni, et al., 2017).

Golam Sarwar et al. estimated the indoor concentration of hydroxyl (OH) radicals with the use of an indoor air quality model that utilized the SAPRC-99 atmospheric chemistry model to replicate indoor reactions (Sarwar, Corsia, & Kimura, 2002). This model calculated the emission rate of select VOCs with an air exchange rate of 0.53 hr^{-1} (Table 3).

Table 3. Emission rates of select VOC compounds from emission model (Sarwar, Corsia, & Kimura, 2002)

Compound	Emission Rate (mg/min)
Ethanol	0.555
Benzene	0.035
Toluene	0.133
Ethylbenzene	0.026
Xylene	0.022

2.4 Introduction to Sampling Methods and EPA Method TO-17

Two sampling methods were considered for this study: active and passive sampling. Active sampling involves the use of a pump to actively collect a volume of air, while passive sampling utilizes diffusion to sorb contaminants onto a media. This study focused on the short-term exposure of wine crush participants to VOCs during the wine crush and fermentation processes. As previously mentioned in Section 2.1.1, acute effects occur due to short-term exposure. Thus, an active sampling strategy was employed to determine short-term exposure of the participants to VOCs throughout the wine crush. Active sampling is often used for acute exposure periods because of its ability to sample for contaminants in a shorter amount of time than passive sampling, which is utilized to determine an average concentration over a longer period (Goodman, et al., 2017). Additionally, the active sampling strategy avoids burdening the winery workroom with equipment for an extended period, as the crush and fermentation season lasts up to 90 days (Midwest Research Institute, 1995) (Storm, 1997). In addition, the various stages and activities in the wine making process have different emission profiles which requires short term sampling to determine appropriate activity related emission rates. The sampling strategy employed also allowed for sample collection representative of a long-term mixture of different operation and weather conditions.

The 1999 EPA Compendium Method TO-17: *Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes* guidelines were used for developing the sampling and analysis strategies of VOCs in the winery workroom air. TO-17 calls for the use of sorbent tubes with analysis using gas chromatography via thermal desorption for gas chromatography-mass spectrometry (GC-MS) analysis (Center for Environmental Research Information Office of Research and Development, 1999). Thermal desorption is an ideal choice for GC-MS analysis when coupled with sorbent tubes, proving to be effective and resource-efficient. The process of thermal desorption coupled with GC-MS creates few waste products and can reuse most of its supplies. There are no solvents or reagents used during thermal desorption, decreasing the likelihood of analysis interference in the gas chromatograph (Sanjuan-Herraez, de la Osa, Pastor, & de la Guardia, 2014) (Zhang, Zhao, Xu, Wang, & Miao, 2010). The results of analysis using thermal desorption are comparable to solid-phase micro-extraction (SPME), and thermal desorption aids analysis by removing unnecessary tails in the results (Zhang, Zhao, Xu, Wang, & Miao, 2010). Thermal desorption also allows for the reuse of the sorbent tubes: each tube is decontaminated of analytes, also known as “conditioned,” each time it is inserted into the thermal desorber for GC-MS analysis. This is convenient if resources for sampling materials are limited, as sampling runs can be completed as soon as the initial tubes are analyzed. The TO-17 methodology was ideal for this study: guidelines for use of active sampling along with sorbent tubes helped ensure the quality of the data collected. Concentrations for all measured constituents were compared to OSHA and Cal/OSHA regulatory limits to ensure compliance (Occupational Safety and Health Administration, 2018).

2.5 Introduction to the Study of Indoor Air Quality

Indoor air quality is a field of research that is extremely important as humans now spend as much as 90% of their day inside (Sundell, 2004). The well-being of people is affected by the composition of the indoor air (Sanjuan-Herraez, de la Osa, Pastor, & de la Guardia, 2014) (Sundell, 2004). The study of indoor air quality aims to understand the factors that make an indoor environment a comfortable and healthy place for individuals to work or live.

2.5.1 Ventilation and Air Exchange Rate

To maintain a thermally controlled environment, building designers and engineers can manipulate the indoor climate through ventilation. Ventilation systems rely on mechanical ventilation to control factors such as temperature and indoor concentrations of anthropogenic and natural constituents. Mechanical ventilation consists of a system of exhaust fans to move air from the outside-in and from inside-out via ductwork infrastructure; it is often accompanied by additional mechanisms like filters and condensate coils to help facilitate the comfortable environment desired by the inhabitants (Thatcher, et al., 2001).

Conversely, natural ventilation is the flow of air through open windows, doors, or any other intentional opening to the outdoor environment. Natural ventilation is predominantly determined by two factors: the size of the openings and the outdoor weather conditions. Unlike mechanical ventilation, natural ventilation has no controls over what air enters the building: this poses a potential threat to the inhabitants if dangerous levels of chemicals or particulate matter are close to the building (Thatcher, et al., 2001).

A third factor affecting the air exchange rate is infiltration. Infiltration is the flow of air through small cracks and openings common in all buildings. Unlike natural ventilation, it is not designed into the construction of the building, but rather a result of it. Infiltration air flow rates are determined by the pressure differential between the interior and exterior sides of the opening (Thatcher, et al., 2001).

The combination of mechanical ventilation, natural ventilation, and infiltration in concert is quantified as the air exchange rate (AER). Measured in units of hour^{-1}, AERs are a measure of the number of times the volume of air in a space is exchanged with outdoor air in one hour. AERs are critical in determining the mass-balance of chemicals and airborne constituents for an indoor environment (Thatcher, et al., 2001) (El-Hashemy & Ali, 2018). AERs are a versatile measure of a building's ventilation, as building size does not affect the units of this measurement.

Air exchange tests are utilized to approximate the AER of a space and are a critical tool for HVAC engineers to evaluate indoor comfort. Recommended air exchange guidelines are set by the American Society of Heating, Refrigeration, and Air Conditioning Engineers (ASHRAE), depending on the nature of the indoor space. ASHRAE Standard 62 is the primary guideline for designing ventilation systems for commercial and residential buildings and is published to aid HVAC engineers create a safe and comfortable space for the building inhabitants (Storm, 1997).

AERs are often readily available for recently built buildings, with design parameters set into an automated control system. However, older buildings without an automated HVAC system require further testing to determine an AER.

2.5.2 Defining Boundaries and Mass Balance Model

An important concept in the study of indoor air quality is that of the building shell: the building shell is the defined boundary line between the interior of the building and the outdoor environment that the building is located in. To understand the make-up of the indoor air, the building shell is critical for creating a mass-balance model.

Once the boundary is established, the make-up of the inside air can be estimated through a mass-balance equation. By including various terms to describe the composition of the indoor air, this change is described as:

$$\frac{\Delta C_o * V}{\Delta t} = \mathrm{OutdoorSourceEntry} - \mathrm{VentilatedOutside} - \mathrm{MassRemoval} + \mathrm{IndoorMassGeneration} \quad (2.1)$$

C_0 = compound concentration

V = volume of room

t = elapsed time

The outdoor source entry term describes outdoor contaminants that are introduced into the indoor air via ventilation or infiltration. Ventilation rates will affect the concentration of the constituent being expelled. Mass removal is the combination of indoor chemical reactions and physical capture technologies, both of which vary based on the agent of concern and indoor concentrations. Filters and scrubbers are a common way to physically capture particulate matter and compounds such as ethanol (Santa Barbara Air Pollution Control District, 2018). Generally, indoor chemical reaction rates will differ based on site conditions and quantities of the reactants, making estimates difficult to accurately estimate (Sarwar, Corsia, & Kimura, 2002) (Wolkoff, Clausen, Jensen, Nielsen, & Wilkins, 1997). To determine the profile of the indoor air quality, mass generation sources are important to identify and quantify. Indoor air pollution is generated by many sources, which vary between different indoor spaces within a building (Burge, 2004).

2.6 VOCs Selected for Study

This study focused on two VOCs: ethanol and benzene. Ethanol has been identified as the most dominant VOC in winery air, due to its emission from fermentation (Midwest Research Institute, 1995). Ethanol has been approved by the EPA as an environmentally-friendly alternative for fuel and a substitute for many household chemicals (United States Environmental Protection Agency, 2018). But recently, there has been controversy over the impact that ethanol emissions have on the environment. An EPA report released in late June 2018 emphasized that there have been negative environmental impacts associated with the increase of ethanol emissions during the bio-fuel manufacturing process, including contribution to the greenhouse gas inventory as well as formation of tropospheric ozone (United States Environmental Protection Agency, 2018) (Yassaa, Brancaleoni, Frattoni, & Ciccioli, 2006) (Semadeni, 1994). Ethanol has also been a regulated VOC in California since 2005, particularly in counties that have large-scale wine production (San Joaquin Air Pollution Control District, 2005).

Benzene is part of a group of VOCs referred to as BTEX, which is comprised of benzene, toluene, ethylbenzene, and xylene (El-Hashemy & Ali, 2018) (Sanjuan-Herraez, de la Osa, Pastor, & de la Guardia, 2014) (Slominska, Konieczka, & Maniesnik, 2014) (Chen, Zhou, & Qi, 2008). Acute effects of short-term exposure to BTEX are headaches, dizziness, and mental confusion. Long-term exposure to BTEX has been linked with increased cancer risk as well as disruption to the endocrine system (Khanchi, Hebbern, Zhu, & Cakmak, 2015) (El-Hashemy & Ali, 2018) (Ravsoni, et al., 2017). BTEX is a critical group of aromatic compounds to sample for because of its increasing prevalence in the outdoor and indoor air. Common outdoor sources of BTEX include vehicle emissions, industrial emissions, and gasoline evaporation (Goodman, et al., 2017) (Slominska, Konieczka, & Maniesnik, 2014) (Ravsoni, et al., 2017). Air fresheners, various cleaning products, and adhesives have been cited as some of the indoor sources of BTEX (El-Hashemy & Ali, 2018) (Khanchi, Hebbern, Zhu, & Cakmak, 2015) (Bari, Kindzierski, Wheeler, Heroux, & Wallace, 2015).

Only ethanol and CO_2 are produced directly from vinification: benzene is not a byproduct of wine-making. However, benzene is commonly found in air that experiences high vehicle activity (Ravsoni, et al., 2017) (Sanjuan-Herraez, de la Osa, Pastor, & de la Guardia, 2014) (Slominska, Konieczka, & Maniesnik, 2014). Because the winery workroom in this study is located near a busy road, popular parking lot, and agricultural fields, engine combustion emissions have been identified as a potential hazard to the indoor air of the winery workroom. Thus, benzene was chosen as the indicator compound for engine combustion emissions inside of the winery workroom.

2.7 Vinification Process Overview

Wine is an alcoholic beverage consisting of fermented sugars from fruit juice most commonly made with grapes. Wine production, also known as vinification, is a multi-stepped process (Figure 2) (Midwest Research Institute, 1995). This section will focus on:

1. Identifying critical steps in the wine-making process.
2. Determining an estimate of California wineries' contribution to VOC emissions.

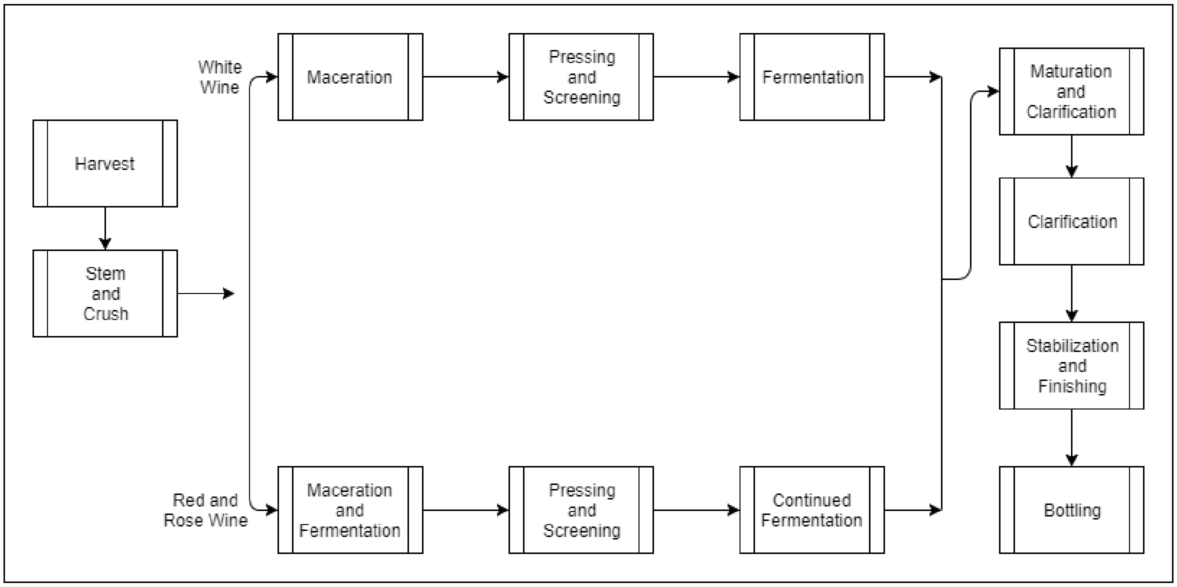


Figure 2. Basic vinification flowchart for red and white wines.

2.7.1 Harvest

Harvest is the process of collecting grapes from their vines and transporting them for stemming and crushing. Because of the grape’s delicate skin and body, sulfite compounds are used to prevent the growth of mold or bacteria on the grapes during transportation between the fields and the processing facility (Midwest Research Institute, 1995). The harvest season is from August to October (Robinson, 2006).

2.7.2 Stem and Crush

Stemming and crushing grapes immediately after harvest is commonly practiced to prevent the growth of bacteria and mold. Stemming involves the removal of leaves, stems, and other residual plant matter from the grape bodies. During crush, the grape’s juices are extracted from the grape body via physical processes like pressing and centrifugal forces (Storm, 1997). Typically, both the stemming and crushing process are handled in the same step utilizing a crusher-stemmer (Storm, 1997) (Midwest Research Institute, 1995).

2.7.3 Maceration

Maceration is the biological and physical degradation of grape solids, yielding a mixture of solid and liquid grape matter called “must.” Red and white wines have different kinds of must: red wine must includes all solid and liquid grape matter, while white wine must only consists of the juice that is separated from the solids. Maceration time and treatment will vary depending on the type of wine to be produced and the flavor profile that is being pursued (Midwest Research Institute, 1995).

2.7.4 Fermentation

There are two types of fermentation: alcoholic fermentation and malolactic fermentation. Malolactic fermentation is a secondary fermentation used to reduce the acidity of the fermented juice. In alcoholic fermentation, sugars such as fructose and glucose are processed by yeast cultures to form C_2H_5OH (ethanol) and CO_2 (Walker & Stewart, 2016).

$$\mathrm{C_6H_{12}O_6} \rightarrow \mathrm{2C_2H_5OH} + \mathrm{2CO_2} \tag{2.2}$$

Alcoholic fermentation is initiated with the addition of yeast cultures into the must. Common fermentation vessels include wooden, plastic, or metal barrels and tanks. Fermentation is an exothermic process, requiring constant temperature monitoring and control as yeast culture death in the batch will completely disrupt the fermentation process. Fermentation monitoring also includes the measurement of Brix content (°B): one-degree Brix is equal to 1 gram of sucrose per 100 grams of solution. Initial Brix content is a key parameter because fermentation stops once the sugar content of the fermenting juice is zero. As with maceration, red and white wines fermentation techniques differ. Red wines are fermented at higher temperatures than white wines, 25°-

28°C and 8-15°C, respectively. Brix content also varies between reds and whites, with reds fermenting at 23 °B initial and whites at 20 °B initial (Storm, 1997) (Midwest Research Institute, 1995).

According to G.M. Walker et al., the stoichiometric conversion of glucose to ethanol is 180 grams of glucose to 92 grams of ethanol and 88 grams of CO_2. In common practice, G.M. Walker estimates that yields are at most 90% of the theoretical yield, as some carbon that would be released as CO_2 is instead consumed to produce more yeast biomass (Walker & Stewart, 2016). As glucose reserves in the must and juices decreases throughout fermentation, ethanol and CO_2 production also decreases.

2.7.5 Pressing

During fermentation, additional juice from the must is extracted during the pressing stage. There are typically two phases to this step. First, the must rests so that its juices can be collected passively. Afterward, the remaining juices in the must are extracted through active pressing. This pressing can be performed by rollers or by gas compression against a perforated screen (Walker & Stewart, 2016) (Midwest Research Institute, 1995).

2.7.6 Maturation

Prior to bottling, wine profiles are adjusted through a series of changes to their major characteristics: acidity, sweetness, alcohol content, and color adjustment. In this step, wines can be blended with other varieties to change the flavor profile. Physicochemical or biological processes are also applied during maturation to manage acidity via precipitation of VOCs such as tartaric acid (Midwest Research Institute, 1995).

2.7.7 Clarification

Clarification is the process of removing sediment from the wine. Wine sediment is the combination of yeast and bacteria cells, grape matter, and precipitated matter from the maturation step. This is a critical step, as sediment will spoil the wine if it is not completely removed during the clarification phase. Clarification can be performed by decantation between multiple vessels or by centrifugal force (Midwest Research Institute, 1995).

2.7.8 Stabilization and Finishing

Prior to the bottling phase, the producer will prevent sediment accumulation and taste change through stabilization. Common stabilization techniques include clarification and filtration, as well as aging. Aging allows for organic compounds in the wine to break down, altering the aroma, color, and taste of the wine. Finishing is often associated with stabilization, but similar to clarification in that chemical agents are added to further precipitate sediment from the wine. The precipitated sediment will be filtered from the wine before bottling in a final clarification/filtration step (Midwest Research Institute, 1995).

2.7.9 Bottling

Excessive oxidation in wine can ruin the aroma and taste, so extra precautions are taken during bottling to minimize contact between the finished wine and the atmosphere. Disinfectants such as sulfur dioxide and fluid transfer via siphon or vacuum pump can help minimize oxidation potential (Midwest Research Institute, 1995).

2.7.10 Effects of Winery Size on Vinification Process

The Santa Barbara APCD identified three general classifications of wineries: boutique/small wineries, industrial sized wineries, and wine refineries (Goldman, 2018). This scale is based on three determining factors: size of fermentation tanks, VOC emissions, and greenhouse gas emissions. The boutique/small wineries will operate most differently than the industrial sized wineries and the wine refineries. Boutique/small wineries generally will not have expensive monitoring or operational equipment to make their wine. Instead they will opt for smaller scale fermentation tanks, blending tanks, and simpler wine-monitoring methods during fermentation (Goldman, 2018) (Storm, 1997). An example operational difference between a boutique/small winery and an industrial sized winery would be the method of testing Brix content. A boutique/small winery may check each fermentation tank individually for the sugar content, opening and closing the tank for each test. An industrial sized winery or larger would have electronic equipment to monitor Brix content to monitor sugar content within their stainless-steel fermentation tanks: the tanks would not be opened at any point during fermentation to prevent any possibility of spoilage or loss of ethanol. The Cal Poly pilot winery was classified as a boutique/small winery because its estimated total tankage volume for production is small relative to recorded tankage industrial sized wineries or wine refineries (Table 4) (Goldman, 2018).

Table 4. Select Winery Classifications

Winery Classification	Winery	Estimated Total Tankage (gallons)
Boutique/Small	Cal Poly Pilot Winery	1,300
Industrial Sized Winery	Central Coast Wine Services	564,000
Wine Refinery	E&J Gallo	4,200,000

2.8. California Wine Production and Air Quality

As Californian wine production flourished in the late 20th century, the EPA assessed the impact of winery emissions on human and environmental health. A review of winery emissions was conducted and compiled in 1995. It was comprised of two parts: assessment of the potential for emissions in each step of the wine making process and evaluating previous research on winery emissions (Midwest Research Institute, 1995). Ethanol and CO_2 were identified as the two compounds most emitted during wine production (Midwest Research Institute, 1995) (Williams & Boulton, 1983). The fermentation phase was identified as the step with the most ethanol and CO_2 emissions. The EPA evaluated several emission factor models for ethanol. A 1983 journal article by R. Boulton and L. Williams proposed a computer model to estimate the ethanol emissions from fermentation; this model was determined by the EPA to be a reasonable estimate of fermentative ethanol loss (Williams & Boulton, 1983) (Midwest Research Institute, 1995). The study produced two emission factors that are used by CARB and local APCDS today: 2.5 lbs. ethanol/1000 gallons white wine produced, and 6.2 lbs. ethanol/1000 gallons red wine produced (California Air Resources Board, 2005). These emission factors were used with crush data collected by the United States Department of Agriculture (USDA) for the 2017 California wine season to calculate the total ethanol emissions (Table 5) (United States Department of Agriculture, 2018). The USDA's grape crush tonnage was multiplied by a factor of 150 gallons of wine production per ton of grapes crushed to calculate the total gallons of wine produced in 2017 (Gerling, 2011).

Table 5. Calculated Ethanol Emissions from 2017 California Wine Season

	Wine Production (gallons)	Calculated Ethanol Emissions (lb.)
Red	337,239,000	2,091,000
White	264,814,000	662,000

Total Ethanol Emissions (lb.)	2,753,000

2.8.1 Wine Emissions Compared to Other ROG Sources

The CARB and USEPA maintain databases of different sources and their emissions through an emissions inventory. These inventories include field data for each source and create an emission rate profile of different constituents such as hydrocarbons, particulate matter, CO2, and nitrous oxides (California Air Resources Board, 2016). The CARB further distinguishes hydrocarbon emissions as one of two groups: total organic gases (TOG) and reactive organic gases (ROG) (California Air Resources Board, 2009). The CARB defined the terms VOC and ROG as interchangeable. The ROG category includes all TOGs except carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, ammonium carbonate, and a list of other compounds determined to be non-reactive by the CARB and the EPA (California Air Resources Board, 2009). The difference between reactive and non-reactive organic gases is that ROGs contribute to the formation of photochemical smog because of their photochemical reactivity. Ethanol is included in the hydrocarbon and ROG category for its photoreactive properties (Alvim, et al., 2018) (California Air Resources Board, 2009).

Winery emissions represent approximately 0.9% of all VOC emissions in California during the fermentation season, based on a comparison to previously published CARB emissions inventory literature on source VOC emissions (Table 6) (California Air Resources Board, 2016). The ethanol emissions calculated from Table 5 were averaged over 91 days, which is the wine grape harvest season from August 1st to October 31st. Because wine is not fermented year-round, the harvest time frame was assumed to be done concurrently with wine fermentation (Midwest Research Institute, 1995) (Robinson, 2006).

Table 6. Comparison of Select Source Emissions of VOCs

Selected Emission Sources	VOC Emissions (tons per day)	% of Total Emissions
Winery Fermentation (2017)	15	0.9%
Electric Utilities	3	0.2%
Light Duty Passenger Vehicles	158	9.3%
Landfills	16	1.0%
Oil and Gas Production	31	1.8%
Off Road Equipment	119	7.0%
Architectural Solvent Evaporation	72	4.3%

Total Statewide	1688

2.9 Winery Emissions Control and Regulations

At the federal, state, and local level of government, the United States has taken efforts to protect the environment. Air quality regulatory agencies have made effort to evaluate the impact that sources of emissions have on people and their surroundings. This section covers the following topics:

1. The history of federal, state, and local levels of air quality regulatory bodies.
2. The impact that environmental regulation has had on the wine industry.
3. How the wine industry has directed efforts towards sustainability and improving environmental health.

2.9.1 History of Indoor/Outdoor Air Quality Regulation in the United States

The United States has established several levels of regulatory bodies to propose and enforce industrial, occupational, and residential IAQ standards. The United States Environmental Protection Agency (USEPA) was established through the signing of the *Reorganization Plan No. 3 of 1970* (United States Environmental Protection Agency, 2018). Since its creation, the USEPA has been charged with creating and governing programs and laws to ensure the protection and preservation of environmental health. However, the USEPA has more responsibility than just air quality regulation: they are also responsible for other facets of environmental health such as water quality and the use of manufacturing and processing chemicals. There are 10 regional offices for overseeing sponsored programs within designated regions of the United States. Each regional office oversees the enforcement of federal regulations alongside the state and local agencies (United States Environmental Protection Agency, 2018).

President Nixon also signed the *Williams-Steiger Occupational Safety and Health Act of 1970* that same year (Occupational Safety and Health Administration, 2018). This act created the Occupational Health and Safety Administration (OSHA) and the National Institute of Occupational Safety and Health (NIOSH). Since their creation, OSHA and NIOSH have utilized their research to identify new hazardous compounds and modify existing exposure limits to keep workers safe. Exposure limits for a given chemical compound are identified as the permissible exposure limit (PEL), a maximum allowable concentration for worker exposure to a pollutant (Occupational Safety and Health Administration, 2018).

The EPA and OSHA are both federal programs, setting baseline laws and limits for the state and local agencies to adhere to. However, California has the authority to create its own environmental regulations that are more stringent than those set forth by the federal agencies. Three years after the creation of OSHA, the state of California's Department of Industrial Relations passed *The California Occupational Health and Safety Act of 1973* (State of California Department of Industrial Relations, 2016). This allowed California to pass stricter limits on exposure and worker's rights than were administered by the federal OSHA at the time. Cal/OSHA is governed through California's Department of Industrial Relations and is responsible for the well-being of occupational workers throughout the state (State of California Department of Industrial Relations, 2016).

At the state level, educational programs can be more intimately tailored to inform residents of potential indoor and outdoor air pollutants. The California Air Resources Board (CARB) was established in 1967, when Governor Ronald Regan signed the Mulford-Carrell Act to unite the Bureau of Air Sanitation and the Motor Vehicle Pollution Control Board (California Air Resources Board, 2018). Today, CARB's primary focus is on transportation emissions and "protecting the public from the harmful effects of air pollution and developing programs and actions to fight climate change" (California Air Resources Board, 2018). The CARB has also created the Indoor Air Quality and Personal Exposure Assessment Program, aiming to improve public health through awareness and education. The California Department of Public Health (Cal DPH) is another state agency that works with CARB to teach about the relationship between environmental and personal health. Cal DPH created the Environmental Health

Laboratory Branch, the first state-level IAQ health program in the United States. Cal DPH offers programs and information on potential indoor and outdoor air quality hazards that are faced by the residents and workers of California (California Department of Public Health, 2018).

With the establishment of the CARB, the state also created local air districts to aid in the regulation and monitoring of stationary emission sources (California Air Resources Board, 2018). There are 35 unique air pollution control districts (APCD) and air quality management districts (AQMD) throughout California that differ only in name. Both APCDs and AQMDs are responsible for enforcement of federal, state, and local air quality regulations within their respective basins.

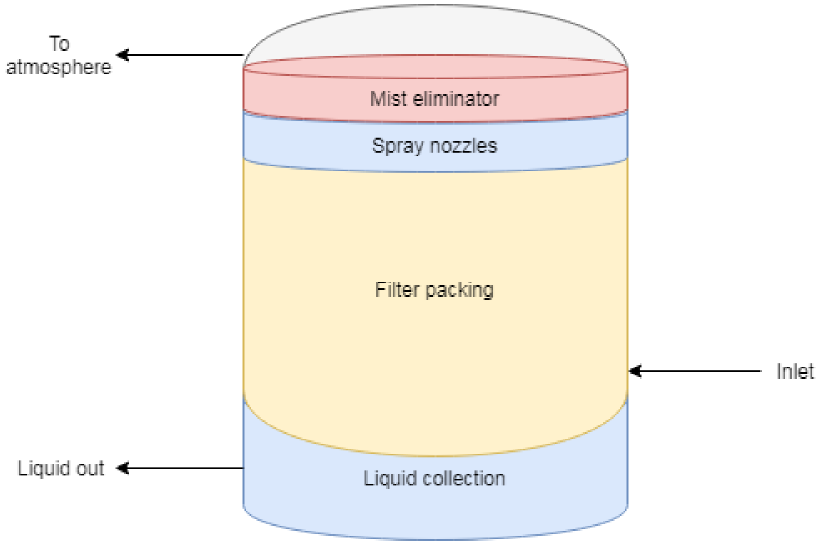
In short, these regulatory bodies all play a role in air quality regulations and monitoring: the occupational bodies (e.g. OSHA and Cal/OSHA) are more concerned with indoor/occupational air quality, while environmental health-based agencies (e.g. USEPA, CARB, and the APCDs/AQMDs) focus on emission sources and their effect on air quality.

2.9.2 Winery Emission Regulation

Early research on the environmental impact of wine production was conducted primarily through the EPA and CARB. As previously stated, the EPA has conducted an emissions inventory for production of different types of wine and brandy, publishing this information for regulatory agencies to use for their emissions calculations. Since then, the CARB has produced an emissions factors model for wine production (California Air Resources Board, 2005). These resources are used by the APCDs and AQMDs, along with information provided by the wineries, to create permits to construct and operate winery equipment. These permits pertain to fermentation emissions, boilers, and generator engines (Santa Barbara County Air Pollution Control District, 2019).

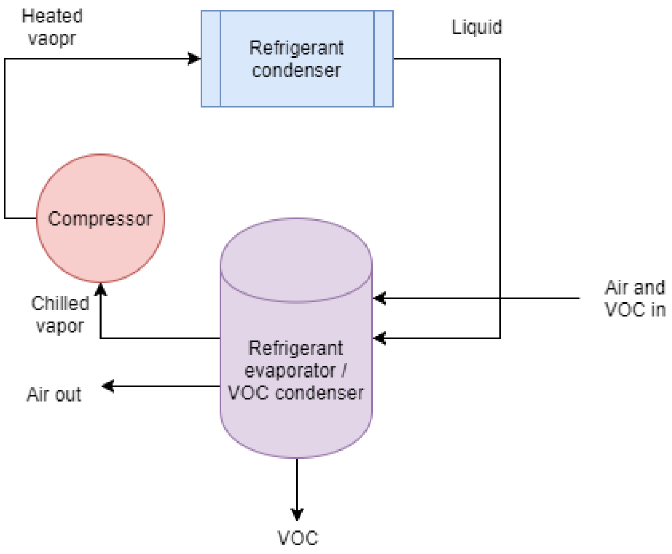
2.9.3 Best Available Control Technologies

The APCDs and AQMDs will call for the implementation of best available control technologies (BACT) to mitigate emissions of GHGs or VOCs (Santa Barbara Air Pollution Control District, 2018). Examples of BACT for winery emissions include the use of wet scrubbers and chiller condensers to mitigate the emissions of VOCs (i.e. ethanol) during fermentation. Because of ethanol's high solubility in water, water-based capture methods are ideal. The two most commonly used technologies are wet scrubbers and chiller condensers. A wet scrubber is a control device that forces gas through either a spray or collection of water, stripping the VOCs out of the air and retaining them in the water for further treatment (Figure 3) (United States Environmental Protection Agency, 2003) (Cooper & Alley, 2011). Chiller condensers decrease the temperature of the VOC-laden air down to its dewpoint, where the air condenses into water and is collected for VOC treatment (Figure 4) (United States Environmental Protection Agency, 2001) (Cooper & Alley, 2011). Both technologies are currently applied to large fermentation tanks as supplementary piping connected to the top of enclosed fermentation tanks.



Adapted from *Air Pollution Control: A Design Approach*

Figure 3. Basic flow diagram of a wet scrubber



Adapted from EPA 2001 technical bulletin on refrigerated condensers for VOC emissions control

Figure 4. Basic flow diagram of a chiller condenser

2.9.4 History of Winery Emission Regulations in California

In December 2005, the San Joaquin Valley APCD approved of the state's first winery emissions control regulation for large-scale wineries through Winery Rule 4694. Winery Rule 4694 was the first of its kind in California: no other APCD nor AQMD had previously established regulations specifically for the wine industry. This new rule aimed to curb ethanol emissions from the fermentation and storage of wine in facilities with an annual ethanol fermentation emission rate of 10 tons or greater. Rule 4694 called for a minimum 35% reduction in emissions through any combination of three options: onsite emissions controls, capture of ethanol emissions from non-winery sites, or payments to district-funded mitigation efforts (San Joaquin Air Pollution Control District, 2005) (Bustillo, 2005).

Since the creation of Rule 4964, other APCDs and AQMDs in California have adopted similar regulations for their wineries. Santa Barbara County APCD (SBAPCD) is another forerunner in creating and overseeing winery emission regulation. On April 26, 2017, Central Coast Wine Services (CCWS) filed for a permit to authorize modifications in their wine production facilities for expanding production. The SBAPCD approved of the permit but called for the continued use of BACT on the new fermentation tanks being used in their facilities. This use of BACT became a heavily debated topic between the SBAPCD and CCWS. The core issue was whether CCWS's current use of the ethanol control technologies constituted as "achieved in practice," i.e. an established BACT precedent for other wineries to follow. If it was determined to be "achieved in practice," then CCWS would have to implement new control measures on their larger fermentation tanks. As for future wineries that apply for similar permits from other APCDs/AQMDs, they would also have to adhere to the same BACT requirements as CCWS (Santa Barbara County Air Pollution Control District, 2018) (Todorov, 2018).

The dispute ended in a settlement June 2018, creating a new requirement for BACT on indoor fermentation tanks more than 30,000 gallons (Todorov, 2018) (Santa Barbara County Air Pollution Control District, 2018). This is a potentially landmark case for wineries across the state of California: the new requirement for control technologies now applies to mid-sized wineries and larger, increasing operating costs for wine producers with indoor fermentation tanks larger than 30,000 gallons. These operating costs may also affect the price of the wine that is produced by these mid-sized wineries, affecting overall production and profits.

The sentiment towards ethanol capture among wine producers has remained the same since the establishment of Rule 4694 in 2005: wine makers are willing to contribute towards cleaner air, but do not believe that the implementation of ethanol control devices is the best method (Bustillo, 2005). Many wine makers argue that the potential loss of ethanol and other VOCs that constitute wine aroma will result in a poorer quality product (Storm, 1997). Additionally, ethanol has been determined by the EPA as a chemical of low concern, determining that it is a safe ingredient to humans and the environment (United States Environmental Protection Agency, 2018). Because of its comparatively low emission levels and ethanol’s safe ingredient designation, mitigation requirements have been fought against by wine producers since the publication of the 1995 emissions study and continues to be a topic of debate (Todorov, 2018) (Storm, 1997).

3. Experimental Methods

The experimental methods for determining VOC concentrations within the winery workspace and ethanol emission rates are explained in this section. A preliminary carbon dioxide (CO_2) tracer-gas experiment was deployed to determine the indoor air exchange rate of the winery workroom, which was used to estimate ethanol emission rates from the indoor concentrations. Air samples were collected from within the workroom during different activity periods using active sampling and sorbent tubes. These samples were analyzed using thermal desorption gas chromatography-mass spectrometry (GC-MS) methods adapted from similar indoor VOC monitoring studies to determine the indoor concentration of VOC contaminants inside of the winery workroom.

3.1 Tracer Gas Air Exchange Test Theory

An air exchange rate (AER) test can be conducted through several different methods: blower door test, duct blaster test, flow hood test, and the tracer gas decay test (Hancock, Norton, & Hendron). This study utilized the tracer gas decay test for its ease of implementation and affordability.

The tracer gas test relies on two assumptions:

1. The concentration of the tracer gas is well mixed inside of the system.
2. There are no sources, reactions, or losses in the system.

The mass balance equation referenced in Section 2.5.2 was modified to fit this tracer gas decay study approximation. Applying the two assumptions to the mass balance equation, the equation can be simplified:

$$\frac{\Delta C_o * V}{\Delta t} = \text{Outdoor Source Generation} - \text{Ventilated Outside} \tag{3.1}$$

C_0 = initial concentrations of constituent, ppm

V = Volume of building space

t = time

The “Outdoor Source Generation” and “Ventilated Outside” terms were simplified to be the concentration of the tracer gas entering or leaving the building multiplied by the flowrate of air entering and exiting the indoor space:

$$\frac{\Delta C_o * V}{\Delta t} = C_{enter} * Q_{enter} - C_{exit} * Q_{exit} \tag{3.2}$$

Q_{enter} = entering air volumetric flow rate, $\frac{\text{Volume}}{\text{Time}}$

Q_{exit} = exiting air volumetric flow rate, $\frac{\text{Volume}}{\text{Time}}$

C_{enter} = entering air concentration of constituent

C_{exit} = exiting air concentration of constituent

For a well-mixed system with no sources or losses in the building space, the previous equation is integrated to become:

$$C_t = C_0 * e^{-\lambda t} + C_{enter} * \left(1 - e^{-\lambda t}\right) \tag{3.3}$$

C_t = concentration at time t

C_0 = initial concentration at time t = 0

C_{enter} = concentration of contaminant in entering air

t = time

λ = time^{-1}

Equation 3.3 is the non-ideal tracer gas decay equation. To simplify the calculations, an ideal tracer gas could be used. An ideal gas is one that does not occur naturally in the environment of the test, i.e. C_{enter} will be zero.

The non-ideal tracer gas equation was used with tracer gas test data with the initial parameters C_0 and C_{enter} measured. Then, an estimated λ was used, comparing the estimated C_t values with field-measured concentrations C_t. The estimated λ was determined so that the modeled concentrations from the non-ideal tracer gas equation were approximately equal to the measured concentrations. An average AER was calculated from 4 tests.

3.1.2 Tracer Gas Decay Air Exchange Test Method Design

For this study, CO_2 was the chosen tracer gas for its accessibility and affordability (Cui, Cohen, Stabat, & Marchio, 2015) (You, et al., 2012). The CO_2 was injected into the winery workroom instantaneously via gas bags and allowed to mix inside of the winery workroom for 5 minutes, achieving maximum concentrations of 2,500 ppm; this concentration allowed a long enough decay period to determine the AER. Gas bags were filled with 30 ft^3 of 99% purity CO_2 and were placed at 5-foot elevations inside of the room. 12 gas bags were used, placing four equally-distanced rows of three bags from the north to the south end of the room. Preliminary background CO_2 level concentration tests yielded average concentrations ranging from 468 ppm to 582 ppm. All windows and doors into the space were kept closed during the mixing period. After 5 minutes of mixing, the doors and windows in the space were opened to simulate the conditions that the workroom is usually operated in when workers are present. Entry into the building was restricted during the test so that inadvertent mixing inside of the workroom was mitigated and no human produced CO_2 during the test. After a 15-minute measurement period, the space was allowed to air out any remaining CO_2 inside of the room.

CO_2 data was collected using two Fluke 975 Indoor Air Quality Meters, set at 3 feet and 8 feet above the floor at the south and center of the room, respectively (Figure 5). Placing meters near the roll-up door at the northern end of the room yielded CO_2 concentration drops that were too rapid for analysis using the tracer gas decay equation, indicating that they were primarily measuring outdoor air blowing past the sensor. While this is an important consideration for a model that includes multiple spaces with differing AERs, the model used in this study focused on a single space assumption. The tracer gas decay testing was conducted two weeks prior to the anticipated crush and fermentation period during September 2018 to simulate anticipated weather conditions: wind speed and wind direction have been shown to play a role in a building’s AER (Hancock, Norton, & Hendron). Thus, testing the AER during crush and fermentation anticipated weather conditions allowed for a more relevant estimate of the winery workroom’s AER. AER measurements could not be made during the VOC sampling period because CO_2 generation by workers and the fermentation process would interfere with the tracer gas decay.

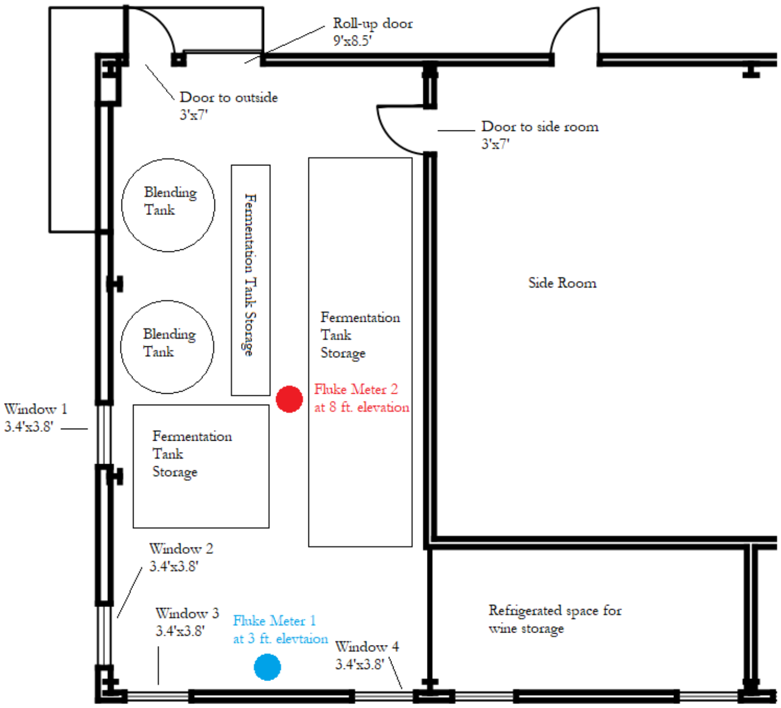


Figure 5. Basic layout of the winery workroom showing locations of Fluke 975 meters measuring CO_2 Concentrations

3.1.3 Determination of AER

Because CO_2 was used as the tracer gas in this air exchange test, non-zero outdoor CO_2 concentrations meant that the ideal gas assumption could not be made. Outdoor background CO_2 measurements were taken before each test to determine the C_{enter} term. The declining tracer gas concentration was modeled using the AER which created the best line of fit for the data (Figure 6). The average AER from the four testing periods was 8.9 ± 1.9 hr^{-1}. Winery ventilation is governed by the ASHRAE published standards 62, calling for a minimum ventilation rate of 20 cubic feet per minute (cfm) per person (Storm, Winery Utilities). This winery workroom has a volume of 9000 cubic feet; when multiplied by the average AER of 8.9 hr^{-1}, the average ventilation rate was 1,335 cfm. This ventilation rate is acceptable for the operations that take place within the workroom, which hosts up to 15 students and professors at a time performing their vinification duties. Typical ventilation rates for a winery mechanical workroom are 3 to 12 hr^{-1} (Winery Utilities).

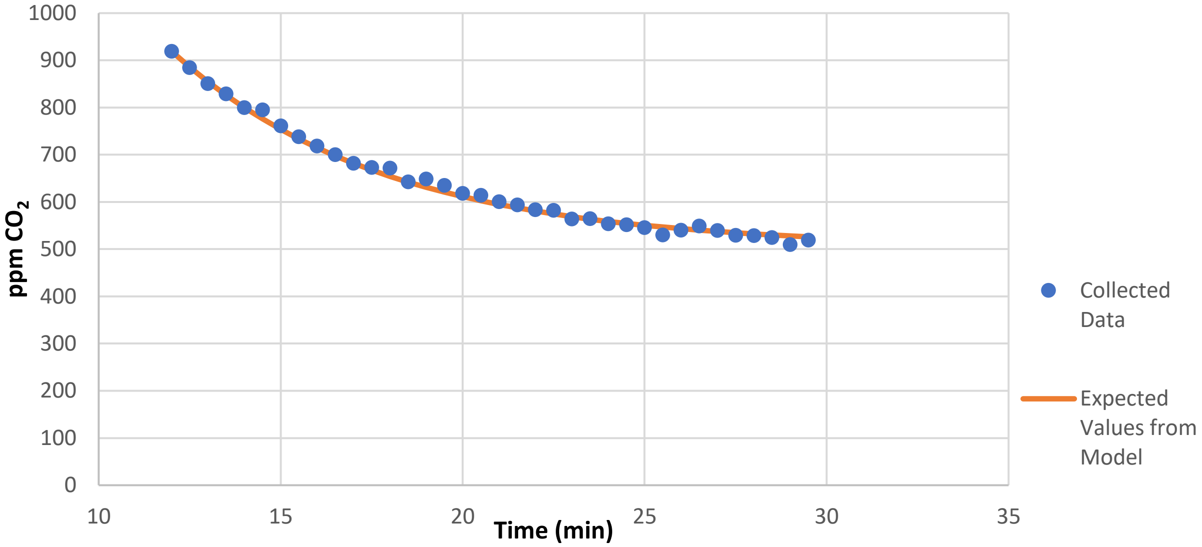


Figure 6. Tracer gas decay modeling for data collected from 9-7-2018 plotted using an AER of 10.2 hr^{-1}

3.2 Sampling Methods

Sampling methods followed the protocol outlined in EPA Method TO-17. Twenty sorbent tubes (Stainless Steel Thermal Desorption Tubes Anasorb GCB1/Carbosieve S-II) were used in total for the sampling procedures. Two method blanks, two trip blanks, and two field blanks were implemented for quality assurance monitoring during sample handling. The remaining fourteen sorbent tubes were used for collecting air samples at the workroom.

3.2.1 Sorbent Tube Preparation and Storage

Sorbent tube conditioning is an essential part of sorbent tube analysis. Conditioning was performed by heating the sorbent within the tube to temperatures up to 350 °C while an inert carrier gas flowed through the tube, purging any unwanted compounds that could interfere with subsequent analysis. For this study, sorbent tubes were conditioned and purged using the Markes Unity 2 thermal desorption unit. Tubes were initially conditioned at 350 °C for two hours at a helium gas flow rate of 100 mL per minute: this is in accordance with the TO-17 recommended guidelines for conditioning sorbent tubes with the Anasorb GCB1 sorbent (TO-17). In between samplings, tubes were conditioned for 30 minutes; this was performed so that background compounds sorbed onto the tubes were kept as low as possible (Jing Chen et. al, Study on Thermal Desorption). Once conditioned, sorbent tubes were capped, wrapped in aluminum foil, and placed in an opaque glass container. The container was stored in a refrigerator at 4 °C until the sorbent tubes were needed for sampling.

3.2.2 Pump Calibration

Low volume sampling pumps were used for the sample collection of winery workroom air: one SKC Pocket Pump Touch, two SKC Pocket Pumps, and one Byron model 10 sampling pump. A flowrate of 200 mL per minute was selected: this is the recommended maximum flowrate for sorbent tubes per TO-17 to prevent channeling within the sorbent medium. Flow rate calibrations were performed with the Gilian Gilibrator 2 calibration system. Per TO-17 methods recommendations, pre-sampling calibrations of the pumps incorporated the sorbent tubes in the calibrations set-up, allowing for accurate adjustments to the pump flow rate as required. The pumps were transported to and from the workroom via carrier bag.

3.2.3 Site Sampling Set Up

For the first sampling session, sampling pumps were placed at the two ends and center of the workroom. The workroom itself is used for educational purposes and hosts a variety of equipment and activities throughout the area. Pump 1 was placed adjacent to the roll-up door, which was always open during workroom operation and sampling. Pump 2 was placed in between two blending tanks that were not in use during any of the sampling periods, and across the room from where the fermentation tanks and basins are kept in the workroom. Near Pump 3, the open windows face towards an active road and parking lot. Cleaning equipment and supplies are also kept in shelving adjacent to the windows. Pumps were kept at an elevation of four feet, equal to the elevation of the fermentation tanks' openings and within the exposure elevation for building occupants.

After the first sampling session, a fourth sampling pump was obtained so that outdoor concentrations could be monitored as well. Sessions 2, 3, and 4 utilized the four-pump set-up to measure for indoor and outdoor air concentrations of the select VOCs (Figure 7). The indoor pump locations were not altered between each session.

For all four sampling sessions, sorbent tubes were distributed to each pump randomly until all 14 sampling tubes and 2 field blank tubes were distributed equally among the four sampling pumps. This allowed for multiple samples to be collected at each pump during the sampling session. Including site preparation, sampling, and site clean-up, the duration of each sampling session averaged 3 hours.

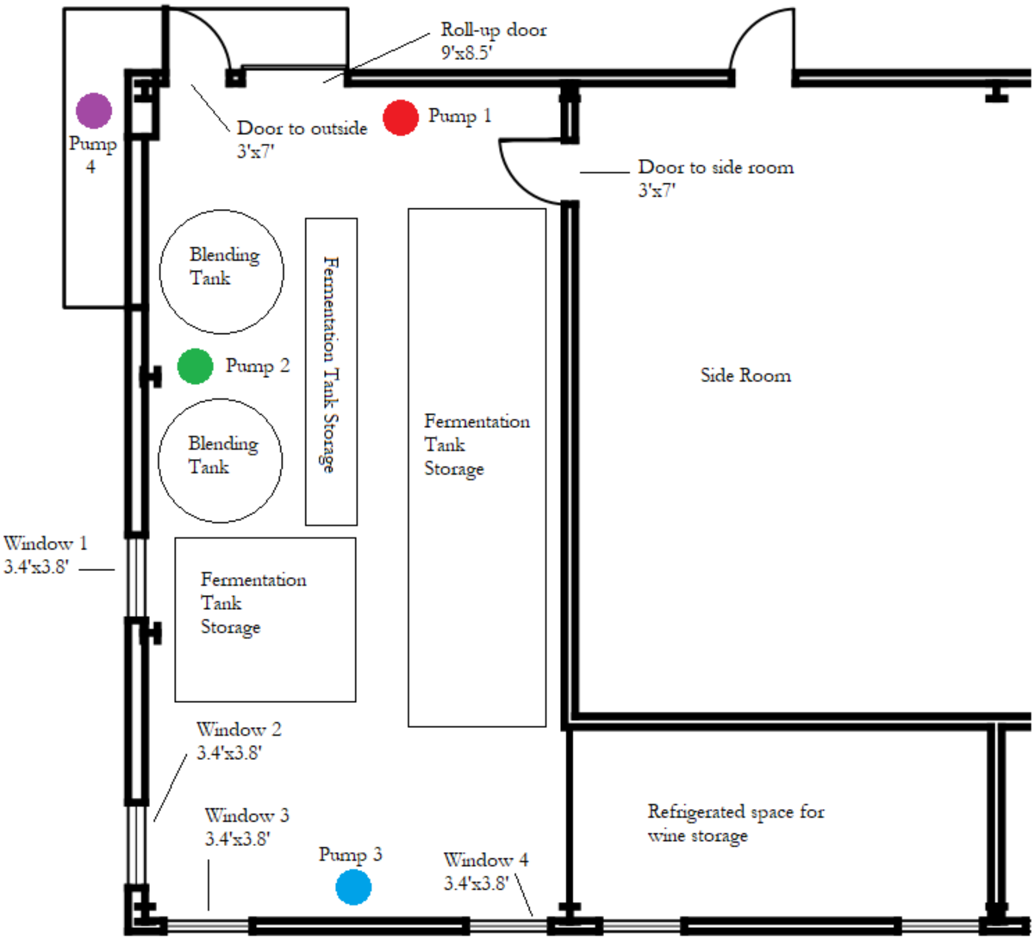


Figure 7. Pump locations in winery workroom for Session 2 on November 16, 2018; Session 3 on November 19, 2018; Session 4 on November 30, 2018. Pump 4 was not operational during Session 1.

The workroom is located on the corner of a busy road leading into the Cal Poly campus, an access road for agricultural equipment or commuters, and adjacent to a staff parking lot. Additionally, it is located in between four agricultural practice fields, which are used and maintained throughout the year (Figure 8).

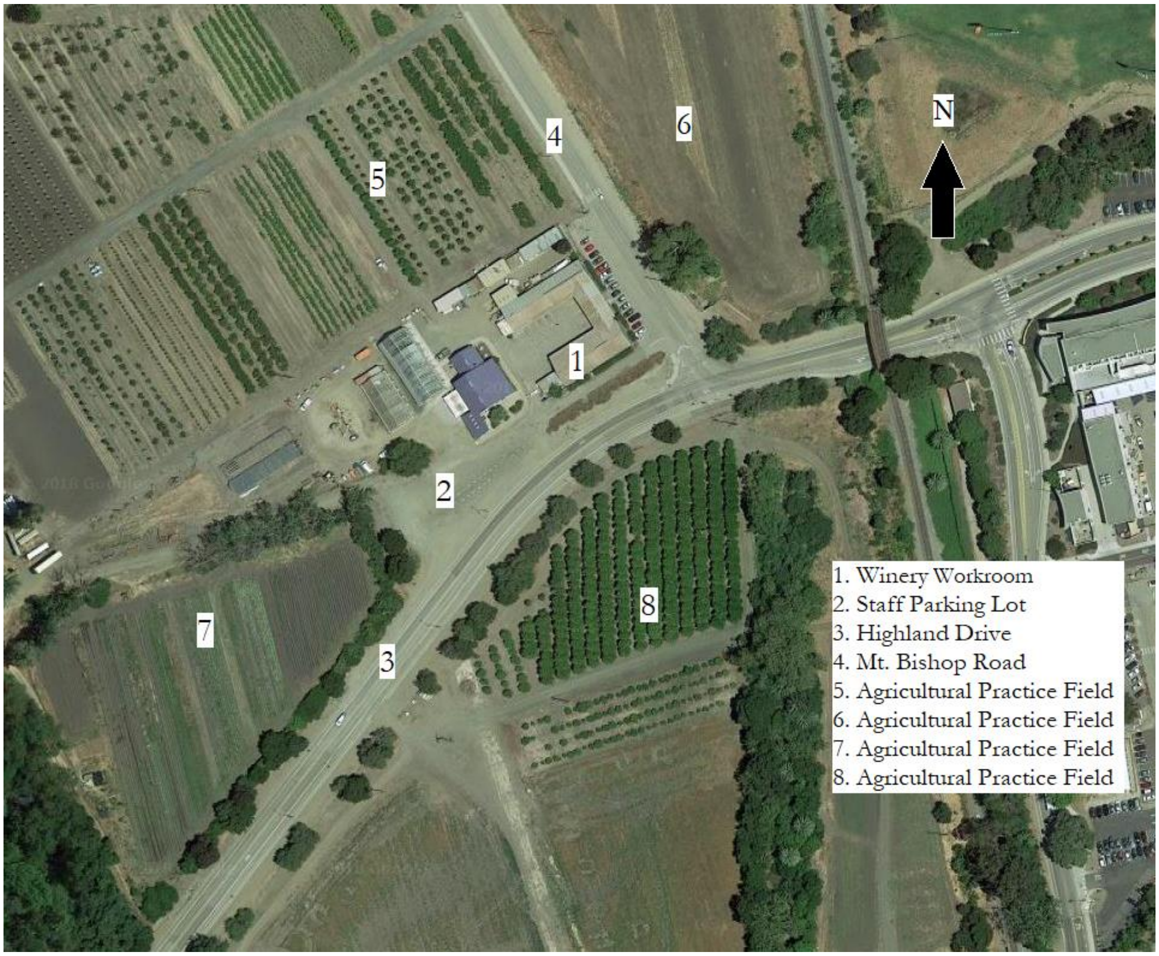


Figure 8. Site map of winery workroom and surrounding area (Google, n.d.)

3.3 Gas Chromatography-Mass Spectrometry Methods

Liquid standards of benzene, toluene, ethylbenzene, xylene, and ethanol were obtained from Millipore Sigma (Table 7). The method of injecting liquid calibration standards onto sorbent tubes followed the methods outlined in TO-17 Section 9.3 Liquid Standards (TO-17). Liquid standards were injected onto sorbent tubes via 5 µL micro-syringe injections. The sorbent tubes were then placed into the thermal desorber and purged using the thermal desorption GC-MS settings optimal for sample analysis (Tables 8, 9, 10) (Air Monitoring, Monitoring of VOCs, Newspapers, Development of Improved Methods). Thermal desorption GC-MS analysis of field samples was conducted using the same operating parameters used for liquid injection calibrations.

Table 7. VOC Compound Standards

Compound	Mass of Compound in 1 mL (µg)
Benzene	200
Toluene	200
Ethylbenzene	5000
M-Xylene	5000
O-Xylene	5000
P-Xylene	5000
Ethanol	2000

Table 8. Sorbent Tube Desorption Parameters

Purge time (trap in-line)	1 min
Desorption time	10 min
Desorption temperature	300 °C
Temperature of cold trap	-10 °C
Desorption flow	20 mL/min
Split flow	44 mL/min
Carrier gas pressure	15 psi

Table 9. Focusing Trap Desorption Parameters

Desorption time	3 min
Temperature of cold trap	300 °C
Split flow	44 mL/min
Temperature of transfer line	150 °C

Table 10. GC-MS Parameters

Carrier gas flow	1.7 mL/min
Oven start temperature	40 °C
Hold start temperature	9 min
Ramp temperature rate	20 °C/min
Ramp temperature finish	200 °C
Hold ramp temperature	2 min

4. Results and Discussion

Methods discussed in Section 3 were applied to calculate the air exchange rate (AER) of the winery workroom during VOC sampling. The indoor concentrations of ethanol and benzene during VOC sampling were estimated using GC-MS output readings and calibration curves. The AER and indoor concentrations were combined to determine emission rates from the workroom during each activity. Finally, typical activity durations for a hypothetical 14-day wine-making process were assumed to calculate an ethanol generation rate per 1000 gallons of wine produced.

4.1 Air Exchange Rate Determination

After the data from each tracer gas decay test were recorded and plotted, an AER for each test was estimated to best fit the decay of the CO_2 (Table 11). The average AER was 8.9 ± 1.9 hr^{-1}. Weather conditions for the tracer gas decay test days were analyzed to determine the relationship between windspeed, wind direction, and AER (Table 12). Weather reports indicated that wind blew from the west or northwest of the workroom during the tracer gas decay test days (Weather Underground, 2019). Additionally, the two days with the highest recorded wind speeds during testing also had the highest AER values. It was concluded that westerly and north-westerly wind direction and high wind speed are the two major contributors to the workroom's AER. The wind direction's

Table 11. Calculated AERs from Tracer Gas Decay Tests

Date	λ (hr^{-1})	Precision (±)
9/7/2018	10.2	1.2
9/9/2018	7.5	1.2
9/12/2018	10.8	1.2
9/13/2018	6.9	1.2

Average	8.9	1.9

Table 12. Calculated AERs and Wind Data

Date	Wind mph	AER	Direction
9/7/2018	18.4	10.2	NW
9/9/2018	9	7.5	W
9/12/2018	18.4	10.8	NW
9/13/2018	12.7	6.9	NW

contribution to AER seemed feasible, as the large roll-up door is located at the northern side of the winery workroom. Using these assumptions, a simple linear regression model was created to estimate the AER of the winery workroom on VOC sampling days (Figure 9). To determine the applicability of the model, weather conditions for VOC sampling and the tracer gas decay test sessions were compared. Weather reports confirm that the wind during VOC sampling days generally blew from the NW as well (Weather Underground, 2019). However, the wind speed on VOC sampling days were lower than those on the AER testing days: therefore, AERs for the VOC sampling days were extrapolated from the linear regression model to estimate an AER for the given VOC sampling day (Table 13).

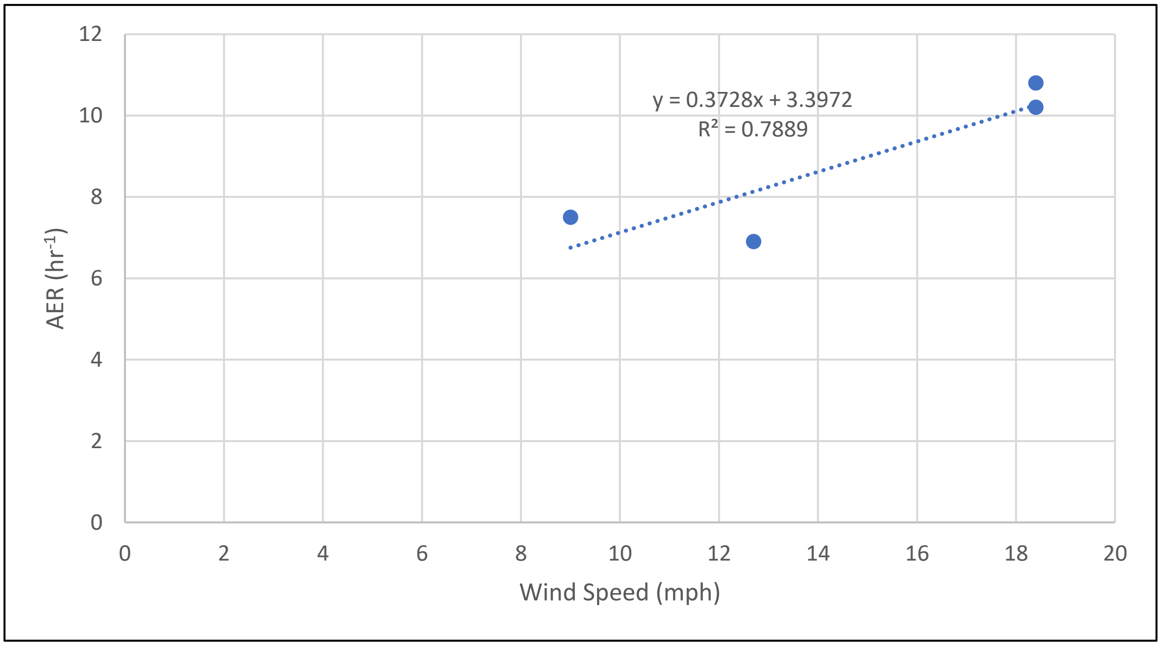


Figure 9. Air exchange rate (AER) vs. wind speed model for winery workroom

Table 13. VOC Sampling Date and Estimated AER

Date	Wind mph	AER	Direction
10/16/2018	7	6.0	NW
11/16/2018	7	6.0	NW
11/19/2018	3	5.3	-
11/30/2018	9	6.8	N

4.2 VOC Calibration Curves for GC-MS

To determine the indoor concentration of the selected VOCs in the winery workroom, a linear relationship was established between the GC-MS data output and the mass sorbed onto the sorbent tubes using a calibration curve: a linear regression model that established a mathematical relationship between the mass of the select VOC on the tube and abundance, the GC-MS's output measurement. Calibration curves were made for benzene (Figure 10) and ethanol (Figures 11 and 12). After initial calibration curves were created, GC-MS analysis determined that a single calibration curve for ethanol would not be feasible: recorded ethanol GC abundance values differed by as much as three orders of magnitude. To account for the wide range of ethanol abundance, two calibration curves were created, one for the lower concentrations and a second for the upper magnitudes of the range. Only one benzene calibration curve was created because field samples were all within the bounds of the curve. Calibration curve creation determined that the precision of the ethanol and benzene concentrations were ± 2 and 1 μg/m^3, respectively.

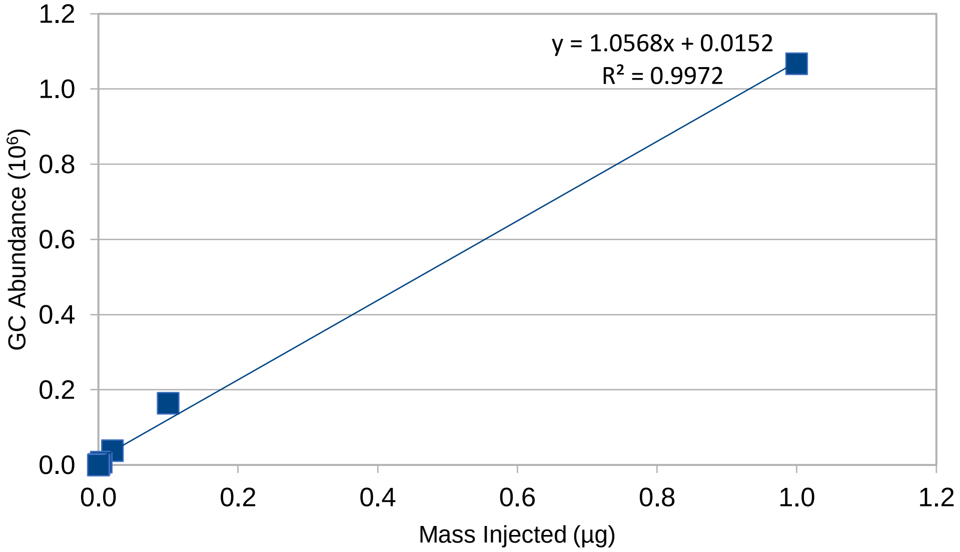


Figure 10. Benzene calibration curve

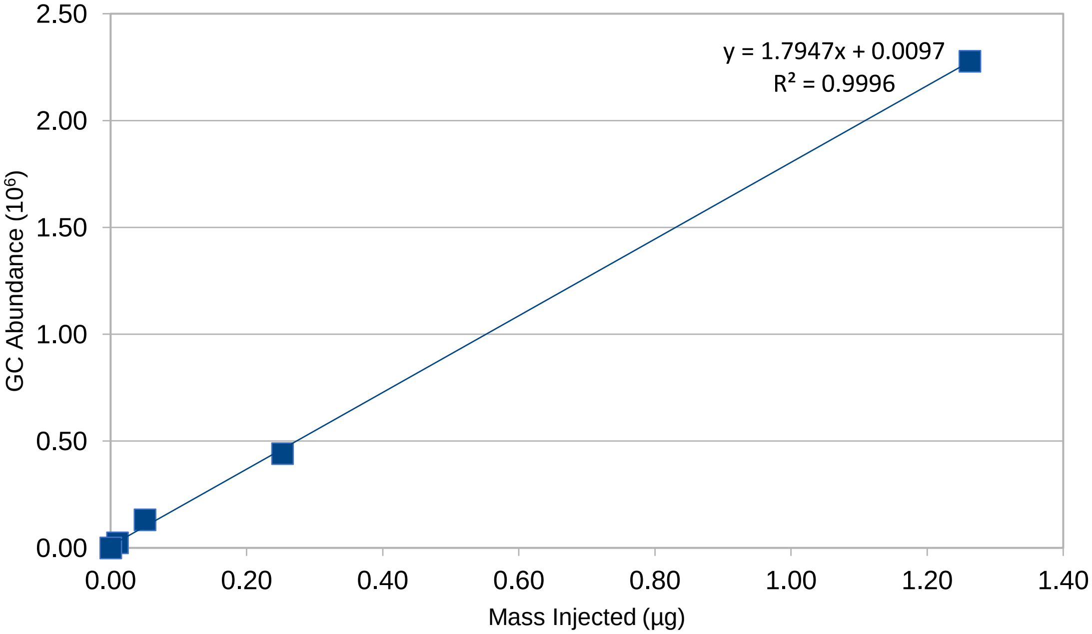


Figure 11. Upper range ethanol calibration curve

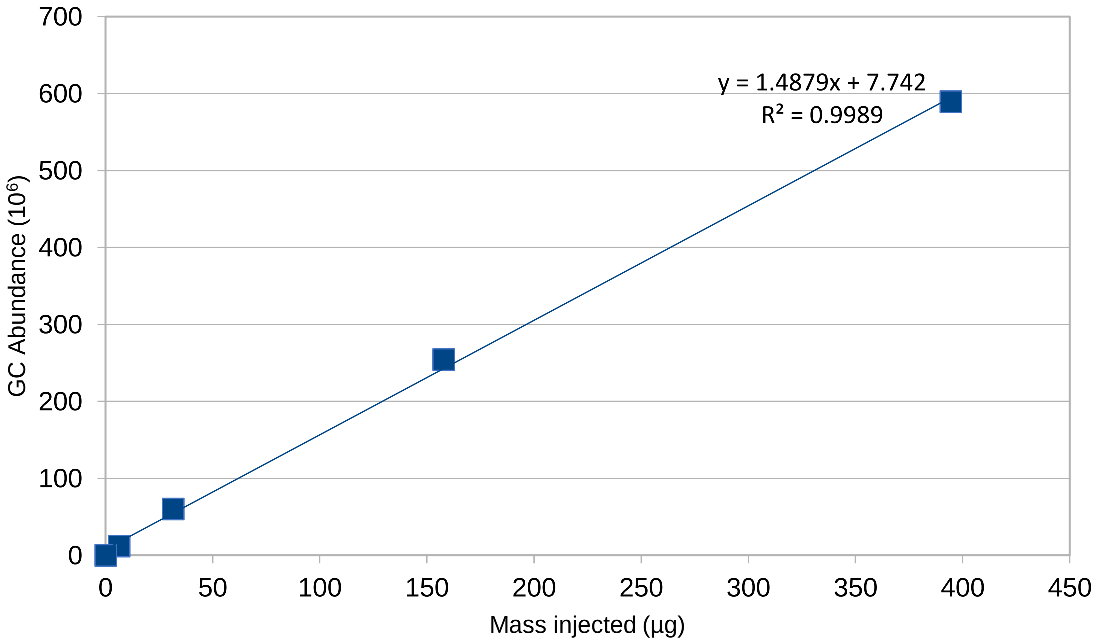


Figure 12. Lower range ethanol calibration curve

4.2.1 Absence of Calibration Curves for Ethylbenzene, Toluene, and Xylene

The original sampling plan included the quantification of ethylbenzene, toluene, and xylene. However, due to the GC-MS set-up being utilized, calibration curves were not able to be created. During trial calibration runs, ethylbenzene and xylene were unable to be identified by the GC-MS at any mass injected for analysis. Toluene was similarly difficult to quantify using the available GC-MS set-up: it was indistinguishable from the background noise during GC-MS analysis, even at the highest mass injections available. Due to these complications, only ethanol and benzene were able to be reliably quantified and analyzed. However, since fossil fuel combustion is expected to be the primary source for benzene, toluene, ethylbenzene, and xylene at the sampling locations, benzene is a reasonable indicator of exposure even without the other compounds.

4.3 Indoor Concentrations of Ethanol and Benzene Inside of Winery Workroom

Table 14. Sampling Date and Activity Type

Date	Activity Type
10/16/2018	Fermentation / Brix Content Test
11/16/2018	Fermentation
11/19/2018	Pressing Post-Fermentation
11/30/2018	Storage

Four different activites occured inside of the winery workroom during each the VOC sampling dates: fermentation, Brix content testing, post-fermentation pressing, and finished wine storage (Table 14). Samples collected from the winery workroom were analyzed with the GC-MS to produce a chromatograph (Figure 13). The chromatographs were integrated using the GC-MS software to determine the GC abundance values for ethanol and benzene. The abundance values were used in the calibration curve equations to determine the mass that was collected on each sorbent tube. The sampling volume for each tube was 4 L of air: dividing the mass collected by the sampling volume yielded the indoor air concentration for ethanol and benzene for each sample collected (Figures 14 and 15).

$$\text{Indoor Concentration}\left(\frac{\text{grams}}{\text{m}^3}\right)=\frac{\text{Mass Collected on tube (g)}}{\text{Sampling volume (L)}}*\frac{1000\text{ L}}{\text{m}^3} \qquad (4.1)$$

As stated in section 2.2.3, multiple VOC samples were collected at each pump throughout each sampling session. Samples collected at their respective pump locations were averaged to estimate the ethanol and benzene concentrations. Then, these averages were used to calculate an overall average concentration for the entire winery workroom. Sampling pump 4 was set up outside of the workroom and not representative of the indoor concentrations, thus was not included in the indoor concentration estimate. The purpose of sampling pump 4 was to determine if similar concentrations of ethanol and benzene were observed just outside of the winery workroom, testing the legitimacy of the boundary line assumed for the mass balance model. Concentrations were averaged for each of the indoor sampling locations because the AER model used assumes that the room is well mixed, i.e. the concentration of benzene or ethanol is equal throughout the room. The large peak identified between ethanol and benzene was assumed to be ethyl acetate, based on readings from the GC-MS database. However, the GC-MS database provided too many possibilities at the 3-minute peak to confidently hypothesize the corresponding chemical compound.

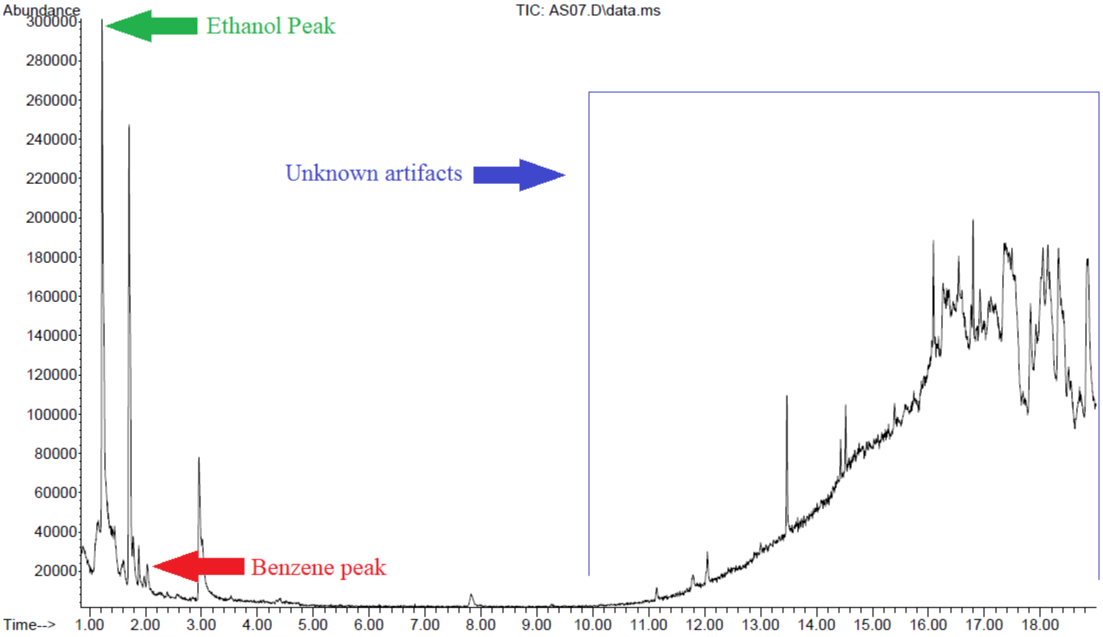


Figure 13. GC-MS chromatograph from sample AS07 collected on November 19, 2018

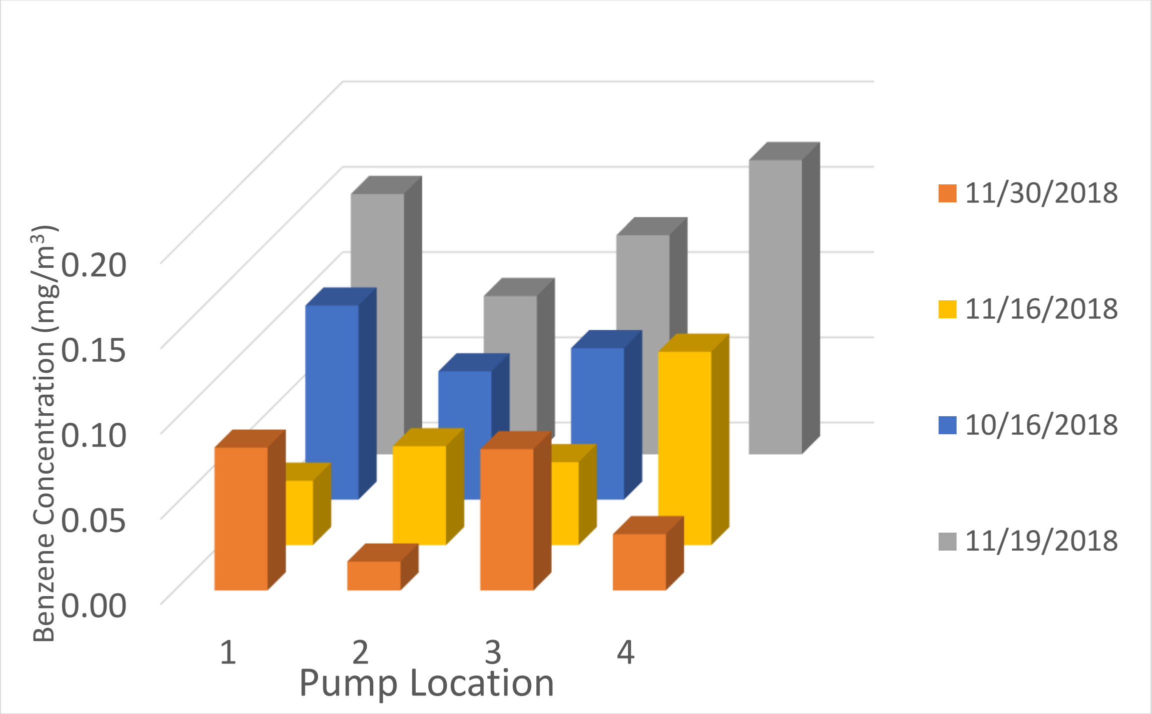


Figure 14. Benzene concentration by pump location and date

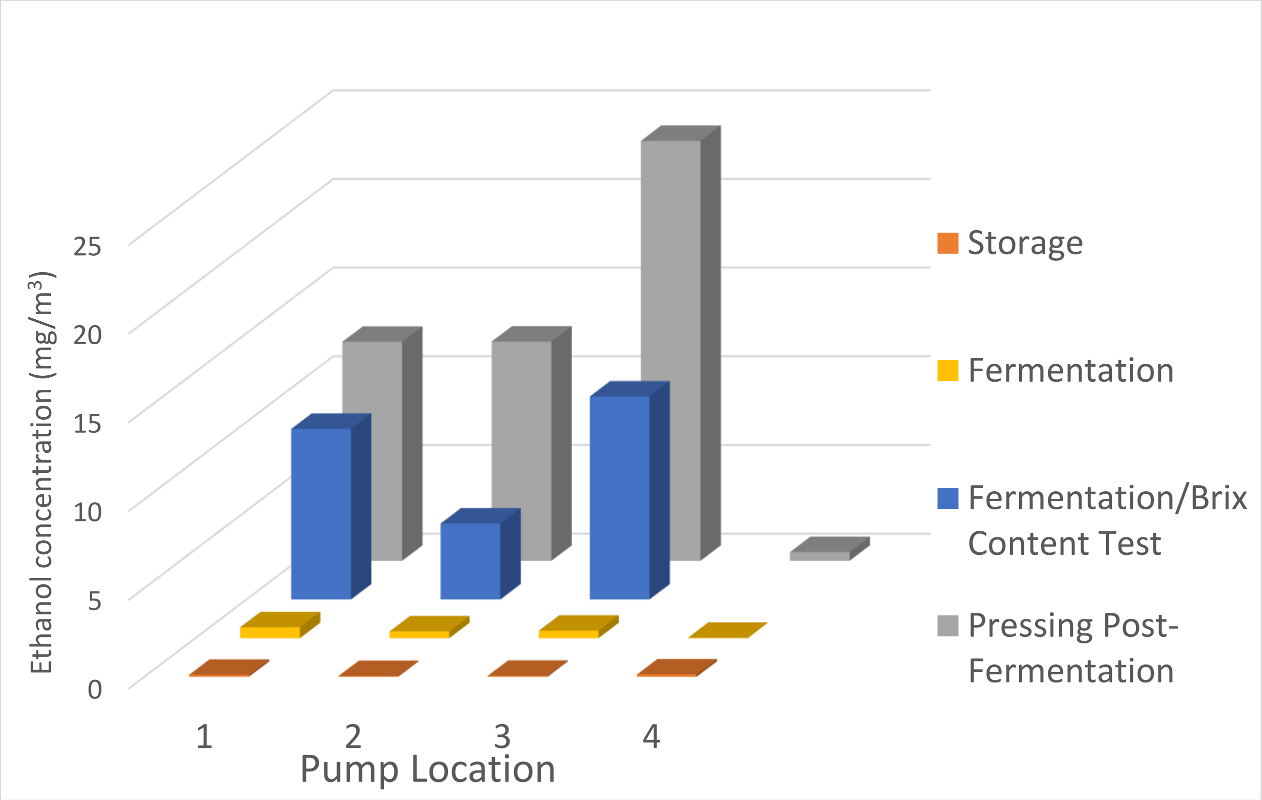


Figure 15. Ethanol concentration by pump location and activity type

Average benzene concentrations were calculated for each sampling day (Table 15). As previously stated, benzene is not a direct product of wine fermentation. Rather, it is a prevalent VOC by-product of engine combustion. All observed benzene concentrations during VOC sampling were greater than the benzene concentrations determined from the Sanjuan-Herrarez et. al study. This is likely due to the roads and agricultural fields that are so close to the pilot winery.

Table 15. Average Workroom Benzene Concentrations by Sampling Day

Date	Average Benzene Concentration (mg/m^3)
10/16/2018	0.09
11/16/2018	0.06
11/19/2018	0.12
11/30/2018	0.05

Average ethanol concentrations in the winery workroom were determined to be greatest during the pressing post-fermentation activity and the fermentation with Brix content testing activity, while the fermentation without Brix content testing and storage activities had the lowest ethanol concentrations (Table 16).

Table 16. Average Workroom Ethanol Concentrations by Activity

Activity	Average Ethanol Concentration (mg/m^3)
Fermentation	0.36
Storage	0.09
Fermentation/Brix Check	8.4
Pressing Post-Fermentation	12

The most significant field condition difference between each activity is the opening of the fermentation tanks. For Brix content testing, each fermentation vessel was opened for several minutes while Brix content was measured. In the post-fermentation pressing, each fermentation vessel is opened and emptied into the pressing equipment for full extraction of juices. During pressing, the finished wine is inadvertently sprayed into the workroom air, increasing the amount of airborne ethanol and other VOCs. As for the fermentation and storage activities, there was no opening of fermentation or storage tanks during VOC sampling. However, ethanol and CO_2 were released through the airlock system on the fermentation vessels. Airlocks and similarly functioning apparatuses are used to release the CO_2 produced during fermentation while avoiding the introduction of outside air into the vessel, keeping oxygen out of the fermentation environment to avoid spoiling (Figure 16).

Figure 16. Typical Fermentation Locks (Pressure Cooker Outlet, 2019)

4.3.1 Analysis of Sampling Quality Assurance and Quality Control

Method blanks, trip blanks, and field blanks were incorporated into the quality assurance and quality control measures to determine the efficacy of sorbent tube decontamination during desorption, as well as identify any possible issues during sample transportation and field sampling. During method and trip blank analysis, detectible levels of ethanol and benzene were detected on the sorbent tubes between sampling and conditioning sessions, averaging an equivalent ethanol and benzene sampling concentration of 0.04 and 0.02 mg/m^3, respectively (Table 17). This is likely an indicator of sorbent tube conditioning between sampling sessions not being conducted for a sufficient duration. These persistent masses of ethanol and benzene were subtracted from their respective initial concentrations calculated in Figures 14 and 15 to more accurately estimate concentrations sampled in the workroom.

Table 17. Ethanol and Benzene Concentration Equivalent Measurements on Method Blanks (mg/m^3)

	10/16/2018	11/16/2018	11/19/2018	11/30/2018
Ethanol	0.01	0.05	0.06	0.02
Benzene	0.01	0.02	0.02	0.02

4.3.2 Ethanol Concentration Variation Between Samples, Pumps, and Activity

Sample concentrations of ethanol varied between pump locations, as well as between samples at a single pump (Table 18 and Table 19). It is speculated that the observed variability is due to the imperfect circulation throughout the winery workroom, variation in activity level during sampling. For example, during fermentation and Brix content testing on October 16, 2018, calculated ethanol concentrations at Pump 2 ranged from 0.07 to 12.74 mg/m^3. Fermentation tanks near Pump 2 were intermittently opened and closed throughout sampling, possibly resulting in concentrations varying by as much as 3 orders of magnitude.

Table 18. Fermentation w/ Brix Content Test Activity Pump 3 Ethanol Concentrations by Sample Number

Sample #	Ethanol concentration (mg/m^3)	Average Concentration (mg/m^3)	Standard Deviation (mg/m^3)
AS04	52	11	23
AS10	0.49		
AS12	1.7		
AS13	2.5		
AS14	0.04		

Table 19. Fermentation w/ Brix Content Test Activity Ethanol Concentrations by Pump Number

Pump #	Average Ethanol Concentration (mg/m^3)	Average Concentration (mg/m^3)	Standard Deviation (mg/m^3)
1	9.6	8.4	3.7
2	4.2		
3	11		

This level of variability between samples and sampling pumps was also present in the post-fermentation pressing activity. However, because each activity was only sampled once, it is unknown whether the variation is consistent between different occurrences of the activity.

4.3.3 Indoor Air Concentration Compliance with OSHA Regulations

There were no OSHA or Cal/OSHA violations for either benzene or ethanol concentrations observed within the winery workroom during the sampling periods (Table 20).

Table 20. Comparison of OSHA and CAL/OSHA Exposure Limits to Calculated Concentrations

Substance	OSHA 8-hour TWA (ppm)	Cal/OSHA 8-hour TWA (ppm)	10/16/18 (ppm)	11/16/18 (ppm)	11/19/18 (ppm)	11/30/18 (ppm)
Benzene	10	1	0.03	0.02	0.04	0.02
Ethanol	1000	1000	4.48	0.19	6.48	0.05

Compliance with the benzene limits was expected: the winery workroom was located approximately 60 ft. north and 130 ft. west of the two adjacent roads. Being upwind from the roads also reduced the amount of benzene (i.e. engine emissions) introduced into the workroom. As for ethanol, the batches of wine that were stored and worked with inside of the workroom were relatively small, not exceeding one ton of grape crush. If grape crush were to be increased, indoor ethanol concentrations would be expected to increase as well. In addition, opening the large roll-up door creates a large air exchange rate which reduces the concentration within the workroom. Although the OSHA and Cal/OSHA requirements were met, field observations and personal accounts of the students who have worked in the workroom determined that the aroma in the winery workroom is quite pungent, especially in previous years when the crush tonnage was larger. Graduate students assisting this study with their time and data confirmed that in years with larger crush tonnage, the build-up of fermentation emissions when the workroom was closed overnight was overpowering to the point of needing to air the space out before coming inside. For a hypothetical situation of ethanol levels exceeding the OSHA 8-hour time weighted average, the air exchange rate of the winery workroom would be 0.00011 hr^{-1} during the day with the highest VOC concentrations calculated.

4.4 Calculated Emissions for Each Workroom Activity

Emission rates were calculated using the estimated AER model from Section 4.1 and the indoor concentration values that were calculated in Section 4.3.

$$\text{Emission Rate} = C_{\text{indoor}} * V_{\text{room}} * \lambda \qquad (4.2)$$

C_{indoor} = average indoor concentration (g/m^3)

V_{room} = volume of room (m^3)

λ = AER of room ($hour^{-1}$)

To assess the emission levels, regulatory agencies in California have relied on emission units of pounds ethanol per 1000 gallons of wine produced. The following assumptions were used to determine the source generation per units of wine production:

1. Emissions were assumed constant over the 3-hour VOC sampling to calculate a per-hour ethanol emission rate.
2. Three-fourths ton grapes were crushed to produce the batches of wine being fermented and stored in the winery workroom during VOC sampling.
3. 1 ton of grapes produces 150 gallons of wine (Gerling, 2011).
4. Total hours of activity durations were assumed to determine emission rates over the duration of a 14-day wine-making process (Table 21). These activities do not encompass all activities in vinification, but rather the ones sampled for in this study.

Table 21. Ethanol Generation Values by Activity

Activity	Assumed Duration (hours)	Emission Rate (lb/hour)	Total Estimated Emissions (lb)	Emission Rate (lb/1000 gallons)
Fermentation	168	4.80E-04	0.08	0.72
Storage	96	1.18E-04	0.01	0.10
Fermentation/Brix Check	14	1.13E-02	0.16	1.40
Pressing Post-Fermentation	6	1.63E-02	0.10	0.87

Total ethanol emissions (lb/1000 gallons)	3.1

The calculated value of 3.09 lbs. ethanol emissions per 1000 gallons wine produced is less than the emission factor of 6.20 lbs. ethanol per 1000 gallons wine produced that is currently used by CARB for their red wine emission calculations. This emission rate is also lower than the red wine ethanol emission rates determined in studies reviewed by the *USEPA Emission Factor Documentation for AP-42 Section 9.12.2 Wine and Brandy Final Report*, which range from 3.6 to 5.9 lbs. ethanol per 1000 gallons of wine produced.

4.5 Issues Encountered During Study

Desorption duration proved to be insufficient for lower ethanol-emission activities. While this is a minor issue that was encountered, future research using thermal desorption should perform a preliminary study on sufficient desorption times for contaminant removal.

Each activity type in this study was sampled for only once for one day, rather than multiple times throughout the wine season. As a result, possible variations between multiple instances of one activity were not captured in this study. These variations could affect the indoor concentrations of ethanol within the winery workroom, and ultimately result in a different ethanol emission rate. Thus, the calculated 3.1 lbs. ethanol per 1000 gallons wine produced is specifically for the four activities that were sampled for in this study.

5. Conclusion

This thesis project focused on two objectives:

1. Evaluate the indoor concentrations of ethanol and benzene in the Cal Poly pilot winery using active sampling.
2. Calculate ethanol emission rates within the winery workroom during the selected wine making activities.

Active sampling allowed for the controlled intake of workroom air, which was used for the calculation of the indoor air concentrations of benzene and ethanol. Additionally, the use of thermal desorption (TD) and GC-MS technology to asses VOCs collected on the sorbent tube was simple to perform when equipment was operational. Replicated TD GC-MS operating parameters from previous studies allowed for quality control during GC-MS result analysis.

Ethanol concentrations within the winery varied between the four activities: average indoor concentrations of ethanol ranged from 0.09 to 12 mg/m^3, and average indoor concentrations of benzene ranged from 0.05 to 0.12 mg/m^3. Assuming the duration of each activity over a 14-day wine-making process, ethanol emissions were calculated to be 3.1 lbs. of ethanol per 1000 gallons of wine produced. This ethanol emission rate is specifically for the activities sampled for during this study for this winery and is not directly applicable to any other winery. However, studies on other wineries and their process emissions should be evaluated

5.1 Future Areas of Research

This study focused on two primary VOCs: ethanol and benzene. Outdoor emissions of both VOCs contribute to the formation of photochemical smog and degrade into more photoreactive compounds (Slominska, Konieczka, & Maniesnik, 2014) (Alvim, et al., 2018). Ethanol is produced by the winery and benzene is introduced from outdoor sources. Future winery emissions studies should focus on identifying and quantifying indoor and outdoor concentrations of emitted VOCs and their photodegradation products. Other VOCs contained in the wine aroma should also be identified and evaluated for their potential to contribute to photochemical smog formation.

The indoor air model used to calculate the winery workroom concentrations of ethanol and benzene was a simplification that assumed a single AER for the entire winery workspace. The reality is that there are likely different AERs throughout the room: the space near the large, open, roll-up door may have had a different AER than a corner of the room far away from open windows and doors. Air currents within the room due to the open windows and doors may also influence the AER around the room. A future study that measures indoor concentrations of VOCs within an indoor space should evaluate the AER using a multiple-space model, rather than a single-space model. This would allow for a more accurate representation of the air flowing in and out of the room and estimation of the movement of VOCs in and out of the indoor space. However, it would also require a significant increase in the number of sampling locations.

The use of an averaged indoor air concentration to estimate the average ethanol emission rate of all activity in the winery workroom during sampling may not be the most accurate method of evaluating emissions. Previous studies identified by the EPA sampled for ethanol emissions at the direct outlet of the CO_2 stream from an individual fermentation tank. However, this method does not capture fugitive emissions from other sources. Future ethanol emission studies should compare the efficacy of individual-stream analysis versus the evaluation methods used in this study for both large and small-scale wineries.

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A. CARB 2016 ROG Emissions Inventory

YEAR	AREA	SRC_TYPE	CATEGORY	SUBCATEGORY	ROG (tons per day)
2012	CALIFORNIA	STATIONARY	FUEL COMBUSTION	ELECTRIC UTILITIES	2.8
2012	CALIFORNIA	STATIONARY	FUEL COMBUSTION	COGENERATION	2.38
2012	CALIFORNIA	STATIONARY	FUEL COMBUSTION	OIL AND GAS PRODUCTION (COMBUSTION)	1.98
2012	CALIFORNIA	STATIONARY	FUEL COMBUSTION	PETROLEUM REFINING (COMBUSTION)	2.9
2012	CALIFORNIA	STATIONARY	FUEL COMBUSTION	MANUFACTURING AND INDUSTRIAL	6.07
2012	CALIFORNIA	STATIONARY	FUEL COMBUSTION	FOOD AND AGRICULTURAL PROCESSING	3.06
2012	CALIFORNIA	STATIONARY	FUEL COMBUSTION	SERVICE AND COMMERCIAL	8.17
2012	CALIFORNIA	STATIONARY	FUEL COMBUSTION	OTHER (FUEL COMBUSTION)	0.79
2012	CALIFORNIA	STATIONARY	WASTE DISPOSAL	SEWAGE TREATMENT	0.9
2012	CALIFORNIA	STATIONARY	WASTE DISPOSAL	LANDFILLS	16.17
2012	CALIFORNIA	STATIONARY	WASTE DISPOSAL	INCINERATORS	1.43
2012	CALIFORNIA	STATIONARY	WASTE DISPOSAL	SOIL REMEDIATION	0.16
2012	CALIFORNIA	STATIONARY	WASTE DISPOSAL	OTHER (WASTE DISPOSAL)	34.03
2012	CALIFORNIA	STATIONARY	CLEANING AND SURFACE COATINGS	LAUNDERING	1.23
2012	CALIFORNIA	STATIONARY	CLEANING AND SURFACE COATINGS	DEGREASING	32.15
2012	CALIFORNIA	STATIONARY	CLEANING AND SURFACE COATINGS	COATINGS AND RELATED PROCESS SOLVENTS	56.14
2012	CALIFORNIA	STATIONARY	CLEANING AND SURFACE COATINGS	PRINTING	17.36
2012	CALIFORNIA	STATIONARY	CLEANING AND SURFACE COATINGS	ADHESIVES AND SEALANTS	19.68
2012	CALIFORNIA	STATIONARY	CLEANING AND SURFACE COATINGS	OTHER (CLEANING AND SURFACE COATINGS)	8.95
2012	CALIFORNIA	STATIONARY	PETROLEUM PRODUCTION AND MARKETING	OIL AND GAS PRODUCTION	30.64
2012	CALIFORNIA	STATIONARY	PETROLEUM PRODUCTION AND MARKETING	PETROLEUM REFINING	11.9
2012	CALIFORNIA	STATIONARY	PETROLEUM PRODUCTION AND MARKETING	PETROLEUM MARKETING	64.9
2012	CALIFORNIA	STATIONARY	PETROLEUM PRODUCTION AND MARKETING	OTHER (PETROLEUM PRODUCTION AND MARKETING)	0.28
2012	CALIFORNIA	STATIONARY	INDUSTRIAL PROCESSES	CHEMICAL	16.8
2012	CALIFORNIA	STATIONARY	INDUSTRIAL PROCESSES	FOOD AND AGRICULTURE	17.42
2012	CALIFORNIA	STATIONARY	INDUSTRIAL PROCESSES	MINERAL PROCESSES	3.44
2012	CALIFORNIA	STATIONARY	INDUSTRIAL PROCESSES	METAL PROCESSES	0.42
2012	CALIFORNIA	STATIONARY	INDUSTRIAL PROCESSES	WOOD AND PAPER	2.47
2012	CALIFORNIA	STATIONARY	INDUSTRIAL PROCESSES	GLASS AND RELATED PRODUCTS	0.02
2012	CALIFORNIA	STATIONARY	INDUSTRIAL PROCESSES	ELECTRONICS	0.28

2012	CALIFORNIA	STATIONARY	INDUSTRIAL PROCESSES	OTHER (INDUSTRIAL PROCESSES)	11.18
2012	CALIFORNIA	AREAWIDE	SOLVENT EVAPORATION	CONSUMER PRODUCTS	208.71
2012	CALIFORNIA	AREAWIDE	SOLVENT EVAPORATION	ARCHITECTURAL COATINGS AND RELATED PROCESS SOLVENTS	71.74
2012	CALIFORNIA	AREAWIDE	SOLVENT EVAPORATION	PESTICIDES/FERTILIZERS	44.65
2012	CALIFORNIA	AREAWIDE	SOLVENT EVAPORATION	ASPHALT PAVING / ROOFING	24.48
2012	CALIFORNIA	AREAWIDE	MISCELLANEOUS PROCESSES	RESIDENTIAL FUEL COMBUSTION	54.38
2012	CALIFORNIA	AREAWIDE	MISCELLANEOUS PROCESSES	FARMING OPERATIONS	127.84
2012	CALIFORNIA	AREAWIDE	MISCELLANEOUS PROCESSES	CONSTRUCTION AND DEMOLITION	0
2012	CALIFORNIA	AREAWIDE	MISCELLANEOUS PROCESSES	PAVED ROAD DUST	0
2012	CALIFORNIA	AREAWIDE	MISCELLANEOUS PROCESSES	UNPAVED ROAD DUST	0
2012	CALIFORNIA	AREAWIDE	MISCELLANEOUS PROCESSES	FUGITIVE WINDBLOWN DUST	0
2012	CALIFORNIA	AREAWIDE	MISCELLANEOUS PROCESSES	FIRES	0.67
2012	CALIFORNIA	AREAWIDE	MISCELLANEOUS PROCESSES	MANAGED BURNING AND DISPOSAL	23.62
2012	CALIFORNIA	AREAWIDE	MISCELLANEOUS PROCESSES	COOKING	5.77
2012	CALIFORNIA	AREAWIDE	MISCELLANEOUS PROCESSES	OTHER (MISCELLANEOUS PROCESSES)	1.88
2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	LIGHT DUTY PASSENGER (LDA)	157.77
2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	LIGHT DUTY TRUCKS - 1 (LDT1)	47.21
2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	LIGHT DUTY TRUCKS - 2 (LDT2)	68.61
2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	MEDIUM DUTY TRUCKS (MDV)	57.75
2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	LIGHT HEAVY DUTY GAS TRUCKS - 1 (LHDGT1)	19.59
2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	LIGHT HEAVY DUTY GAS TRUCKS - 2 (LHDGT2)	2.22
2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	MEDIUM HEAVY DUTY GAS TRUCKS (MHDGT)	5.64
2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	HEAVY HEAVY DUTY GAS TRUCKS (HHDGT)	1.3
2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	LIGHT HEAVY DUTY DIESEL TRUCKS - 1 (LHDDT1)	2.82
2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	LIGHT HEAVY DUTY DIESEL TRUCKS - 2 (LHDDT2)	0.74
2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	MEDIUM HEAVY DUTY DIESEL TRUCKS (MHDDT)	7.83
2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	HEAVY HEAVY DUTY DIESEL TRUCKS (HHDDT)	27.33
2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	MOTORCYCLES (MCY)	30.34
2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	HEAVY DUTY DIESEL URBAN BUSES (UBD)	2.82
2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	HEAVY DUTY GAS URBAN BUSES (UBG)	0.99
2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	SCHOOL BUSES - GAS (SBG)	0.51

2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	SCHOOL BUSES - DIESEL (SBD)	0.48
2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	OTHER BUSES - GAS (OBG)	0.6
2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	OTHER BUSES - MOTOR COACH - DIESEL (OBC)	0.26
2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	ALL OTHER BUSES - DIESEL (OBD)	0.35
2012	CALIFORNIA	MOBILE	ON-ROAD MOTOR VEHICLES	MOTOR HOMES (MH)	0.8
2012	CALIFORNIA	MOBILE	OTHER MOBILE SOURCES	AIRCRAFT	25.95
2012	CALIFORNIA	MOBILE	OTHER MOBILE SOURCES	TRAINS	5.94
2012	CALIFORNIA	MOBILE	OTHER MOBILE SOURCES	SHIPS AND COMMERCIAL BOATS	0.04
2012	CALIFORNIA	MOBILE	OTHER MOBILE SOURCES	OCEAN GOING VESSELS	9.34
2012	CALIFORNIA	MOBILE	OTHER MOBILE SOURCES	COMMERCIAL HARBOR CRAFT	4.7
2012	CALIFORNIA	MOBILE	OTHER MOBILE SOURCES	RECREATIONAL BOATS	94.62
2012	CALIFORNIA	MOBILE	OTHER MOBILE SOURCES	OFF-ROAD RECREATIONAL VEHICLES	16.16
2012	CALIFORNIA	MOBILE	OTHER MOBILE SOURCES	OFF-ROAD EQUIPMENT	119.55
2012	CALIFORNIA	MOBILE	OTHER MOBILE SOURCES	FARM EQUIPMENT	18.63
2012	CALIFORNIA	MOBILE	OTHER MOBILE SOURCES	FUEL STORAGE AND HANDLING	17.76

B. USDA Grape Crush by Type and Activity for 2017 Wine Crush Season

TABLE 1: STATE TOTALS OF GRAPES FOR CRUSHING BY TYPE AND VARIETY, WEIGHTED AVERAGE DEGREES BRIX, AND WEIGHTED AVERAGE DOLLARS PER TON, 2016-17

Type and Variety	Total Tons Crushed		Avg. Brix Crushed		Total Purchased Tons		Avg. Brix Purchased		Wtd. Avg. Dollars Per Ton	
	2017	2016	2017	2016	2017	2016	2017	2016	2017	2016
WINE GRAPES (WHITE):										
Albarino	2,143.7	2,111.5	22.3	22.8	1,756.5	1,651.2	22.2	22.6	1108.91	1157.96
Arneis	111.8	175.0	23.1	23.0	81.4	111.9	23.6	23.1	2,126.91	1,939.00
Burger *	25,004.3	26,067.7	17.4	17.4	24,802.3	25,901.2	17.4	17.4	267.84	266.79
Chardonnay *	614,565.4	675,966.1	23.5	23.7	459,110.8	516,970.3	23.5	23.5	923.67	886.65
Chenin Blanc	35,565.7	42,555.7	20.4	20.6	32,660.4	39,667.8	20.4	20.6	405.86	383.29
Cortese	75.6	71.7	21.6	21.8	63.0	69.5	21.2	21.9	713.62	712.40
Fiano	66.0	52.8	22.6	22.5	35.0	27.4	22.0	22.2	1,802.30	1,582.46
Flora	27.7	33.6	22.1	22.4	24.0	28.8	21.9	22.1	2,113.71	2,031.13
Folle Blanche	0.0	18.7	0.0	23.6	0.0	0.0	0.0	0.0	0.00	0.00
French Colombard	335,762.3	303,480.0	19.9	20.6	327,265.3	294,717.4	19.9	20.5	267.39	260.92
Gewurztraminer	16,874.6	18,097.3	22.3	22.4	15,287.6	15,947.6	22.1	22.3	713.07	716.53
Gray Riesling *	96.0	87.4	21.9	23.1	89.2	87.4	21.4	22.2	1,764.66	1,534.01
Grenache Blanc	1,921.6	1,427.5	22.4	22.7	1,344.1	888.2	22.2	22.9	1,471.74	1,778.65
Gruner Veltliner	697.0	637.4	22.6	23.6	530.7	431.7	22.4	23.3	1,227.38	1,281.13
Malvasia Bianca	6,068.7	6,215.7	21.5	22.0	3,470.8	3,596.4	22.1	22.9	614.40	637.21
Marsanne	478.8	394.6	23.4	23.7	233.8	247.0	23.8	24.0	1,774.73	1,878.72
Melon	32.5	20.6	21.3	23.0	32.3	13.9	21.3	24.2	2,239.45	2,052.14
Moscato Gaillo *	16.7	12.4	21.7	22.9	5.4	2.7	22.9	22.4	1,477.78	1,355.56

Muscat Blanc *	27,186.0	26,369.3	22.9	23.3	22,887.7	22,087.1	23.0	23.6	481.32	439.78
Muscat Orange	3,263.4	3,789.6	23.8	23.6	2,622.2	3,039.1	23.6	23.8	564.54	542.64
Muscat of Alexandria	203,941.7	170,431.3	20.9	21.7	176,816.6	150,135.8	20.9	21.8	281.63	281.80
Palomino *	662.1	699.9	19.7	20.2	648.1	682.4	19.6	20.2	353.89	301.05
Pecorino	24.0	21.2	23.5	24.0	24.0	21.2	23.5	24.0	2,300.00	2,200.00
Picpoul Blanc	155.6	117.4	22.2	22.1	84.5	64.1	22.2	21.7	2,140.03	2,014.13
Pinot Blanc	1,299.6	1,417.0	23.6	23.5	867.2	929.8	23.8	24.2	1,571.94	1,469.36
Pinot Gris *	252,440.2	243,742.0	21.7	21.6	234,307.9	223,357.3	21.8	21.6	518.97	521.12
Ribolla Gialla *	41.0	41.3	20.6	20.9	35.3	37.4	20.4	20.9	3,299.70	3,092.92
Roussanne	1,237.2	1,143.6	23.2	23.8	589.3	595.3	23.5	24.2	2,063.66	1,999.13
Sauvignon Blanc	106,637.6	107,734.4	22.4	22.3	77,411.0	80,801.4	22.1	22.0	1,067.69	1,032.18
Sauvignon Gris	24.0	0.0	23.5	0.0	0.0	0.0	0.0	0.0	0.00	0.00
Sauvignon Musque	1,070.3	1,025.2	24.0	23.6	654.1	592.7	24.3	23.6	1,616.28	1,581.83
Sauvignon Vert *	23.6	18.8	22.3	23.4	23.6	18.8	23.1	23.4	2,580.27	2,549.88
Semillon	4,293.5	4,100.4	19.1	19.4	3,135.5	2,942.6	18.2	18.3	836.45	845.76
St. Emilion *	23.3	47.2	21.4	21.0	10.0	9.4	20.4	19.0	2,121.00	2,229.79
Sylvaner	18.6	36.9	20.5	20.5	0.0	0.0	0.0	0.0	0.00	0.00
Symphony	35,993.9	24,737.1	19.8	21.3	15,086.4	10,995.2	21.2	21.9	300.60	320.29
Tocai Friulano	60.9	75.4	22.2	22.2	42.5	47.8	21.3	21.8	1,929.71	1,952.83
Torrontes	32.3	40.1	21.9	22.1	29.9	32.3	22.4	22.1	1,420.07	1,346.13
Triplett Blanc	14,117.5	13,833.0	21.7	21.5	14,031.8	13,754.4	21.7	21.5	211.81	201.58
Verdejo	139.0	71.8	23.0	22.2	26.3	57.3	23.4	22.1	1,506.27	1,234.73
Verdelho	3,175.9	3,240.0	23.0	23.1	2,956.5	2,978.9	22.9	23.0	589.29	583.36
Vermentino *	1,047.9	1,307.3	21.7	20.1	833.2	1,069.8	21.7	19.8	1,015.65	824.48
Vernaccia	9.9	26.1	23.8	24.4	9.9	26.1	23.8	24.4	2,266.67	2,089.56
Viognier	19,812.8	22,698.0	25.0	25.5	16,309.7	18,702.0	25.0	25.6	695.71	659.67
White Riesling *	37,257.0	41,274.8	20.9	21.4	17,165.0	24,108.2	22.0	21.8	738.63	667.60

Other White 1/	11,926.8	5,951.0	21.0	22.2	11,741.7	4,751.2	20.9	22.1	278.31	268.05
Total White	1,765,424.0	1,751,415.8	21.8	22.3	1,465,142.5	1,462,198.0	21.7	22.1	587.73	598.44
WINE GRAPES (RED):										
Aglianico	188.8	142.9	24.4	24.1	106.8	81.7	24.5	23.4	1,639.03	1,567.09
Aleatico	23.5	26.9	25.5	24.6	21.9	23.2	25.9	24.7	2,738.29	2,653.53
Alicante Bouschet *	5,388.8	6,327.7	23.4	23.1	3,243.9	3,876.9	23.0	22.9	451.45	504.46
Alvarinho	0.5	0.0	23.0	0.0	0.0	0.0	0.0	0.0	0.00	0.00
Arinarnoa	3,297.9	3,496.0	23.9	24.3	3,297.7	3,495.5	23.9	24.3	385.13	350.00
Barbera	43,405.4	45,750.1	23.8	23.3	41,808.8	44,514.8	23.8	23.2	378.94	368.49
Blaufraenkisch *	16.3	20.1	24.9	23.3	10.8	10.2	24.2	22.4	1,473.91	1,810.78
Cabernet Franc	11,238.3	10,472.2	25.6	25.8	7,478.3	6,441.1	25.8	25.7	2,794.28	2,705.44
Cabernet Sauvignon	601,472.9	566,486.7	25.1	25.1	468,760.9	441,540.7	25.1	25.1	1,552.83	1,470.48
Carignane	12,112.7	14,397.1	22.7	22.4	11,741.9	14,018.4	22.7	22.3	506.62	473.06
Carmenere	50.4	48.5	24.9	24.8	23.4	27.2	25.2	25.1	2,572.82	1,684.99
Carnelian	889.9	2,474.9	27.0	24.8	865.2	2,461.9	27.1	24.8	250.00	249.29
Centurian	1,460.6	986.2	22.9	24.3	1,457.2	982.8	22.9	24.3	358.96	386.13
Charbono	292.0	313.8	23.4	23.7	180.6	213.0	23.6	24.0	2,685.69	2,613.21
Ciliegiolo	5.7	10.7	24.6	24.5	5.7	9.5	24.6	24.1	1,340.35	1,297.37
Cinsaut *	441.1	501.7	22.7	23.3	323.0	362.7	22.5	23.0	1,677.02	1,615.18
Counoise	213.7	193.2	23.2	22.9	137.0	119.8	23.5	22.9	1,879.29	1,813.24
Dolcetto	243.4	380.2	23.5	23.9	193.4	297.1	23.5	23.7	1,456.64	1,513.38
Dornfelder	1,791.8	1,531.5	22.2	23.1	914.9	887.6	22.5	22.8	440.51	422.20
Durif	31.4	33.9	25.5	24.8	1.1	1.2	24.3	23.9	1,450.00	1,450.00
Freisa	17.0	15.6	25.3	26.8	4.9	5.8	25.4	25.4	1,734.69	963.36
Gamay (Napa) *	1,836.3	1,704.3	21.7	21.8	1,568.7	1,359.7	21.4	21.6	980.43	858.55

Gamay Noir Au Jus Blanc	43.3	35.9	21.9	21.2	43.3	31.7	22.0	21.3	2,393.76	2,057.10
Graciano	324.2	296.8	25.4	25.2	213.3	209.7	25.5	25.3	993.74	916.60
Grenache *	37,999.8	38,684.4	22.7	22.4	34,113.0	35,133.8	22.4	22.1	735.39	617.82
Grignolino	41.9	51.9	22.7	23.2	0.0	0.6	0.0	23.5	0.00	1,500.00
Lagrein	462.5	451.1	25.4	25.0	137.1	155.9	26.1	25.8	2,412.80	2,008.21
Lambrusco	260.9	257.6	25.6	25.0	0.0	0.0	0.0	0.0	0.00	0.00
Malbec	33,804.6	37,058.5	24.1	24.2	26,578.4	28,113.9	24.1	24.1	988.53	1,007.96
Merlot	255,195.8	268,761.6	25.0	25.2	201,472.5	214,647.7	24.9	25.1	770.26	774.91
Meunier *	878.3	785.2	20.0	20.4	452.1	357.8	20.2	20.3	2,200.11	2,099.82
Mission	994.8	2,422.0	23.7	21.7	976.2	2,383.7	23.7	21.7	289.37	219.84
Monastrell	25.5	19.3	26.7	26.1	12.9	6.0	26.1	27.3	2,261.58	2,003.33
Montepulciano	517.3	573.5	23.9	23.3	195.9	274.9	24.8	25.2	1,867.20	1,484.44
Mourvedre *	4,069.6	4,614.5	24.3	24.4	2,926.5	3,619.2	24.3	24.3	1,700.06	1,619.61
Muscat Hamburg *	1,181.7	612.5	24.8	25.3	1,155.8	563.0	24.8	25.3	689.58	630.86
Nebbiolo	466.8	511.7	24.3	24.4	305.4	401.1	24.6	24.7	1,432.37	1,184.74
Negrette *	14.5	29.1	25.6	25.6	0.5	19.2	25.0	25.8	2,250.00	1,928.91
Negroamaro	108.6	73.0	25.5	25.9	96.7	67.2	25.7	25.9	1,247.63	1,183.84
Nero D'Avola *	102.0	73.7	23.8	24.3	82.3	54.9	24.0	24.2	1,261.54	1,134.15
Petit Verdot	35,317.4	32,087.4	25.5	25.3	26,983.7	23,743.9	25.5	25.4	1,142.87	1,242.09
Petite Sirah	97,608.0	105,041.8	25.7	25.5	81,261.3	85,359.3	25.7	25.6	1,000.03	1,024.24
Pinot Noir	263,464.3	254,192.0	24.7	24.9	193,278.4	186,316.0	24.8	24.9	1,688.14	1,638.11
Pinotage	86.4	76.6	25.3	25.4	33.6	29.6	26.0	25.7	1,399.38	1,458.17
Primitivo	2,131.4	1,783.2	25.3	25.9	814.6	975.6	25.8	26.1	1,694.73	1,580.09
Refosco *	470.8	533.0	22.6	23.5	449.5	518.2	22.6	23.5	456.95	356.52
Royalty	33.0	31.3	25.3	24.7	33.0	31.3	25.3	23.0	475.00	475.00
Rubired *	239,625.0	247,539.2	24.1	24.3	228,760.9	238,827.2	24.1	24.4	276.95	279.28
Ruby Cabernet	59,505.2	54,733.6	24.5	24.7	58,907.2	54,326.1	24.6	24.7	301.10	304.18

Sagrantino	59.8	53.4	25.4	25.4	37.4	28.8	25.6	24.9	1,170.88	884.98
Salvador	327.9	448.1	25.4	23.0	327.9	448.1	25.4	23.0	291.47	301.29
Sangiovese *	6,360.6	6,399.4	23.4	24.3	3,954.4	3,976.6	23.5	24.0	1,308.08	1,187.20
Segalin	1,290.2	1,107.5	23.5	24.3	1,289.4	1,106.4	23.5	24.3	350.00	300.00
Souzao	637.6	554.2	25.0	25.1	553.3	445.4	24.9	25.1	605.03	727.66
St Laurent	26.2	34.5	19.7	20.9	18.0	18.4	19.5	19.7	2,296.67	2,256.52
Syrah *	100,714.4	108,406.6	24.9	25.5	78,897.5	84,172.1	24.8	25.4	810.98	785.61
Tannat	6,434.0	6,239.2	26.2	26.3	4,614.8	4,221.0	26.6	26.2	656.73	666.61
Tempranillo *	12,369.6	12,409.7	23.9	23.3	10,581.1	10,782.7	23.9	23.0	621.99	600.68
Teroldego	11,541.0	7,964.3	24.9	25.7	8,113.6	5,211.3	24.9	25.6	636.07	795.07
Tinta Cao	449.4	485.1	24.0	24.0	418.0	450.0	23.9	24.0	516.03	572.61
Tinta Madeira	58.2	91.8	24.9	26.7	0.8	32.7	25.0	27.1	1,284.54	712.69
Touriga Nacional *	4,226.1	2,485.9	24.1	24.4	4,051.8	2,309.0	24.1	24.3	554.88	706.37
Trousseau *	53.3	75.3	22.2	22.7	33.8	54.8	22.1	23.0	2,587.13	1,080.29
Zinfandel	364,833.9	416,648.0	22.2	22.1	337,916.6	395,278.1	22.1	21.9	591.05	604.62
Other Red 1/	19,725.3	10,107.7	23.0	22.3	18,561.6	9,092.8	23.0	22.2	259.83	355.38
Total Red	2,248,259.5	2,280,155.3	24.3	24.3	1,870,800.2	1,914,526.5	24.2	24.2	965.54	919.04
TOTAL WINE	4,013,683.5	4,031,571.1	23.2	23.4	3,335,942.7	3,376,724.5	23.1	23.3	799.60	780.21

C. Measured GC Abundance and Calculated Indoor Concentrations of Ethanol and Benzene

October 16, 2018

		GC Abundance		Corresponding Air Concentration (g/m3)		Average Ethanol Conc (g/m3)	Std Dev	Std. Error	Average Benzene Conc (g/m3)	Std Dev	Error
		Ethanol	Benzene	Ethanol	Benzene						
Method Blanks	M01	1.75E+05	3.94E+04	2.30E-05	5.74E-06	1.42E-05			1.13E-05		
	M02	4.92E+04	8.64E+04	5.50E-06	1.69E-05						
Trip Blanks	T01	1.58E+05	2.65E+05	2.06E-05	5.90E-05	6.58E-05			3.61E-05		
	T02	8.06E+05	7.08E+04	1.11E-04	1.32E-05						
Pump 1	F01	7.20E+05	1.89E+05	9.89E-05	4.10E-05						
	AS01	1.46E+08	4.36E+05	2.32E-02	9.96E-05	9.61E-03	1.10E-02	2.76E-03	1.14E-04	1.36E-04	3.40E-05
	AS05	1.37E+07	6.38E+05	1.00E-03	1.47E-04						
	AS06	2.01E+06	2.73E+05	2.78E-04	6.10E-05						
	AS07	9.12E+07	8.30E+05	1.40E-02	1.93E-04						
Pump 2	F02	5.39E+05	1.17E+05	7.38E-05	2.40E-05						
	AS02	8.36E+07	1.91E+05	1.27E-02	4.16E-05	4.28E-03	5.33E-03	1.07E-03	7.52E-05	7.68E-05	1.54E-05
	AS03	2.56E+07	7.65E+04	3.01E-03	1.45E-05						
	AS08	1.52E+07	8.24E+05	1.26E-03	1.91E-04						
	AS09	1.30E+06	4.33E+05	1.80E-04	9.87E-05						
	AS11	5.13E+05	3.89E+04	7.01E-05	5.60E-06						
Pump 3	AS04	3.20E+08	1.19E+06	5.25E-02	2.77E-04	1.14E-02	2.30E-02	4.59E-03	8.89E-05	1.02E-04	2.04E-05
	AS10	3.54E+06	1.19E+05	4.92E-04	2.45E-05						
	AS12	1.79E+07	4.24E+05	1.70E-03	9.67E-05						
	AS13	2.29E+07	2.44E+05	2.55E-03	5.41E-05						
	AS14	2.89E+05	2.20E+05	3.89E-05	4.86E-05						

November 16, 2018

		GC Abundance		Corresponding Air Concentration (g/m3)							
		Ethanol	Benzene	Ethanol	Benzene	Average Ethanol Conc (g/m3)	Std Dev	Std. Error	Average Benzene Conc (g/m3)	Std Dev	Error
Method Blanks	M01	3.83E+05	1.58E+05	5.20E-05	3.39E-05	4.61E-05			2.50E-05		
	M02	2.98E+05	8.29E+04	4.02E-05	1.60E-05						
Trip Blanks	T01	3.47E+05	7.62E+04	4.70E-05	1.44E-05	4.10E-05			3.34E-05		
	T02	2.62E+05	2.37E+05	3.51E-05	5.24E-05						
Pump 4	F02	9.53E+04	8.94E+04	1.19E-05	1.76E-05						
	AS02	7.52E+05	2.66E+05	1.03E-04	5.94E-05	1.94E-05	3.49E-05	1.16E-05	3.30E-05	1.29E-05	4.31E-06
	AS06	2.58E+05	2.03E+05	3.45E-05	4.44E-05						
	AS11	4.30E+05	3.12E+05	5.85E-05	7.02E-05						
Pump 3	AS08	4.59E+06	8.14E+05	6.37E-04	1.89E-04	4.20E-04	3.18E-04	7.95E-05	8.29E-05	5.59E-05	1.40E-05
	AS09	5.60E+06	4.02E+05	7.79E-04	9.16E-05						
	AS10	2.85E+06	3.97E+05	3.95E-04	9.02E-05						
	AS13	3.88E+05	2.71E+05	5.27E-05	6.06E-05						
Pump 1	F01	2.38E+05	9.39E+04	3.18E-05	1.86E-05						
	AS03	9.65E+06	5.13E+05	3.20E-04	1.18E-04	6.15E-04	2.97E-04	9.89E-05	8.38E-05	3.83E-05	1.28E-05
	AS12	5.84E+06	2.97E+05	8.12E-04	6.67E-05						
	AS14	6.13E+06	6.15E+05	8.53E-04	1.42E-04						
Pump 2	AS01	3.35E+06	6.56E+04	4.66E-04	1.19E-05	3.81E-04	2.46E-04	6.16E-05	1.69E-05	3.77E-05	9.43E-06
	AS04	2.56E+06	1.21E+05	3.56E-04	2.50E-05						
	AS05	1.21E+07	4.25E+05	7.39E-04	9.69E-05						
	AS07	8.62E+06	1.58E+05	1.47E-04	3.38E-05						

November 19, 2018

		GC Abundance		Corresponding Air Concentration (g/m3)							
		Ethanol	Benzene	Ethanol	Benzene	Average Ethanol Conc (g/m3)	Std Dev	Std. Error	Average Benzene Conc (g/m3)	Std Dev	Error
Method Blanks	M01	8.84E+05	1.50E+05	1.22E-04	3.20E-05	6.44E-05			2.32E-05		
	M02	5.98E+04	7.64E+04	6.98E-06	1.45E-05						
Trip Blanks	T01	7.07E+04	7.11E+04	8.50E-06	1.32E-05	9.01E-06			1.60E-05		
	T02	7.80E+04	9.45E+04	9.52E-06	1.88E-05						
Pump 4	AS01	GC Fault				4.88E-04	6.14E-05	3.07E-05	1.73E-04	1.35E-05	6.77E-06
	AS12	3.83E+06	8.02E+05	5.32E-04	1.86E-04						
	AS04	3.20E+06	8.83E+05	4.45E-04	2.05E-04						
Pump 3	AS06	1.44E+08	5.84E+05	2.29E-02	1.34E-04	2.37E-02	1.78E-02	4.46E-03	1.28E-04	7.94E-05	1.98E-05
	AS09	1.75E+08	9.48E+05	2.81E-02	2.21E-04						
	AS11	2.44E+06	2.13E+05	3.39E-04	4.67E-05						
	AS13	2.66E+08	8.82E+05	4.34E-02	2.05E-04						
Pump 1	AS05	5.09E+06	8.56E+05	7.07E-04	1.99E-04	1.23E-02	1.90E-02	4.75E-03	1.53E-04	5.34E-05	1.34E-05
	AS10	2.12E+08	9.20E+05	3.43E-02	2.14E-04						
	AS14	1.99E+07	5.01E+05	2.05E-03	1.15E-04						
Pump 2	F01	1.70E+05	6.33E+04	2.23E-05	1.14E-05						
	F02	1.34E+06	1.47E+05	1.85E-04	3.12E-05						
	AS02	8.38E+06	6.83E+05	1.07E-04	1.58E-04	1.24E-02	1.48E-02	3.69E-03	9.28E-05	3.25E-05	8.12E-06
	AS03	1.85E+08	4.56E+05	2.98E-02	1.04E-04						
	AS07	8.46E+06	3.57E+05	1.21E-04	8.08E-05						
	AS08	1.23E+08	5.27E+05	1.94E-02	1.21E-04						

November 30, 2018

		GC Abundance		Corresponding Air Concentration (g/m3)							
		Ethanol	Benzene	Ethanol	Benzene	Average Ethanol Conc (g/m3)	Std Dev	Std. Error	Average Benzene Conc (g/m3)	Std Dev	Error
Method Blanks	M01	8.17E+04	1.21E+05	1.00E-05	2.51E-05	1.72E-05			2.27E-05		
	M02	1.84E+05	1.01E+05	2.43E-05	2.02E-05						
Trip Blanks	T01	nd	nd			3.74E-05			1.10E-05		
	T02	2.78E+05	6.17E+04	3.74E-05	1.10E-05						
Pump 4	F01	4.92E+05	4.57E+05	6.72E-05	1.05E-04						
	AS01	9.45E+05	3.22E+05	1.30E-04	7.25E-05	1.34E-04	9.09E-05	2.27E-05	1.13E-04	5.83E-05	1.46E-05
	AS07	4.00E+05	8.67E+05	5.43E-05	2.01E-04						
	AS10	1.97E+06	7.15E+05	2.73E-04	1.66E-04						
	AS12	1.05E+06	7.88E+04	1.45E-04	1.51E-05						
Pump 3	F02	3.43E+05	1.39E+05	4.65E-05	2.94E-05						
	AS04	4.39E+05	4.32E+05	5.97E-05	9.87E-05	5.88E-05	2.30E-05	5.75E-06	4.86E-05	3.88E-05	9.69E-06
	AS09	6.72E+05	2.01E+05	9.23E-05	4.39E-05						
	AS14	GC Faults here									
Pump 1	AS02	7.08E+05	3.12E+05	9.73E-05	7.02E-05	1.14E-04	4.80E-05	1.20E-05	3.77E-05	1.39E-05	3.47E-06
	AS03	GC Faults here									
	AS05	GC Faults here									
	AS13	1.20E+06	2.29E+05	1.65E-04	5.06E-05						
Pump 2	AS06	4.58E+05	3.56E+05	6.25E-05	8.06E-05	4.53E-05			5.80E-05		
	AS08	GC Faults here									
	AS11	GC Faults here									

D. Ethanol and Benzene GCMS Calibration Points

Mass Ethanol Injected (µg)	GC Abundance
394.50	589598572
157.80	254357370
31.56	60561135
6.31	12312027
1.26	2278306
0.25	441286
0.05	132658
0.01	23636
0.00	0

Mass Benzene Injected (µg)	GC Abundance
1.00E+00	1067683
1.00E-01	164321
2.00E-02	38538
4.00E-03	7707
8.00E-04	1541
0.00E+00	0

E. AER Calculation Data

9/7/2018

CO2 1 (ppm)	CO2 2 (ppm)	Avg	ln Avg CO2	time (min)	Expected CO2 conc
	627	627	6.440947	0.5	
	591	591	6.381816	1	
	583	583	6.368187	1.5	
	579	579	6.361302	2	
	567	567	6.340359	2.5	
	567	567	6.340359	3	
	559	559	6.326149	3.5	
	568	568	6.342121	4	
	598	598	6.393591	4.5	
	963	963	6.870053	5	
	1670	1670	7.420579	5.5	
	2755	2755	7.921173	6	
	3819	3819	8.247744	6.5	
	3967	3967	8.285765	7	
	3535	3535	8.170469	7.5	
1964	3167	2565.5	7.849909	8	
1904	2858	2381	7.775276	8.5	
1870	2704	2287	7.734996	9	
1896	2695	2295.5	7.738706	9.5	
1755	2577	2166	7.680637	10	
1428	2017	1722.5	7.451532	10.5	
1149	1470	1309.5	7.177401	11	

956	1154	1055	6.961296	11.5	
822	1017	919.5	6.82383	12	920
816	953	884.5	6.785023	12.5	886
790	912	851	6.746412	13	855
752	906	829	6.72022	13.5	826
725	875	800	6.684612	14	800
724	867	795.5	6.678971	14.5	776
684	838	761	6.634633	15	754
682	794	738	6.603944	15.5	734
667	770	718.5	6.577166	16	715
636	765	700.5	6.551794	16.5	698
629	735	682	6.52503	17	682
633	714	673.5	6.512488	17.5	668
638	705	671.5	6.509514	18	654
605	680	642.5	6.465367	18.5	642
622	676	649	6.475433	19	631
614	656	635	6.453625	19.5	621
601	636	618.5	6.427297	20	611
581	647	614	6.419995	20.5	603
573	628	600.5	6.397763	21	595
573	615	594	6.386879	21.5	587
560	607	583.5	6.369044	22	581
568	596	582	6.36647	22.5	575
545	583	564	6.335054	23	569
547	582	564.5	6.33594	23.5	564
539	569	554	6.317165	24	559
541	563	552	6.313548	24.5	555

525	567	546	6.302619	25	550
504	556	530	6.272877	25.5	547
509	572	540.5	6.292495	26	543
532	566	549	6.308098	26.5	540
519	560	539.5	6.290643	27	537
507	552	529.5	6.271933	27.5	535
516	542	529	6.270988	28	532
509	540	524.5	6.262445	28.5	530
488	532	510	6.234411	29	528
	519	519	6.251904	29.5	526

9/9/2019

CO2 1	CO2 2	Avg CO2	ln Avg Co2	time (min)	Expected CO2 conc
774	651	712.5	6.47851	0.5	
874	625	749.5	6.437752	1	
820	613	716.5	6.418365	1.5	
727	587	657	6.375025	2	
647	590	618.5	6.380123	2.5	
619	575	597	6.35437	3	
614	565	589.5	6.336826	3.5	
591	562	576.5	6.331502	4	
591	548	569.5	6.306275	4.5	
604	549	576.5	6.308098	5	
602	549	575.5	6.308098	5.5	
603	563	583	6.33328	6	
592	565	578.5	6.336826	6.5	
582	547	564.5	6.304449	7	
582	553	567.5	6.315358	7.5	
589	542	565.5	6.295266	8	
561	538	549.5	6.287859	8.5	
553	534	543.5	6.280396	9	
569	543	556	6.297109	9.5	
570	542	556	6.295266	10	
554	538	546	6.287859	10.5	
536	535	535.5	6.282267	11	
535	512	523.5	6.238325	11.5	
538	518	528	6.249975	12	

550	516	533	6.246107	12.5	
532	507	519.5	6.228511	13	
520	515	517.5	6.244167	13.5	
515	519	517	6.251904	14	
517	506	511.5	6.226537	14.5	
523	500	511.5	6.214608	15	
531	509	520	6.232448	15.5	
537	510	523.5	6.234411	16	
539	503	521	6.22059	16.5	
515	488	501.5	6.190315	17	
511	491	501	6.196444	17.5	
500	505	502.5	6.224558	18	
504	504	504	6.222576	18.5	
498	502	500	6.2186	19	
505	499	502	6.212606	19.5	
495	520	507.5	6.253829	20	
502	520	511	6.253829	20.5	
518	514	516	6.242223	21	
607	541	574	6.293419	21.5	
921	792	856.5	6.674561	22	
1013	1038	1025.5	6.945051	22.5	
1120	1428	1274	7.26403	23	
1228	2290	1759	7.736307	23.5	
1314	2652	1983	7.883069	24	
1369	2745	2057	7.917536	24.5	
1472	2788	2130	7.93308	25	
1571	2999	2285	8.006034	25.5	

1637	3178	2407.5	8.064007	26	
1665	3208	2436.5	8.073403	26.5	
1671	3158	2414.5	8.057694	27	
1741	3070	2405.5	8.029433	27.5	
1777	3085	2431	8.034307	28	
1617	2998	2307.5	8.005701	28.5	
1458	2852	2155	7.955776	29	
1217	2771	1994	7.926964	29.5	
1032	2627	1829.5	7.873598	30	
893	2424	1658.5	7.793174	30.5	
831	2091	1461	7.645398	31	
766	1806	1286	7.49887	31.5	
727	1533	1130	7.334982	32	
737	1341	1039	7.201171	32.5	
719	1208	963.5	7.096721	33	964
682	1118	900	7.019297	33.5	936
686	1066	876	6.971669	34	910
688	1041	864.5	6.947937	34.5	885
674	1028	851	6.93537	35	862
704	985	844.5	6.892642	35.5	840
675	983	829	6.890609	36	820
666	976	821	6.883463	36.5	801
650	956	803	6.862758	37	783
616	926	771	6.830874	37.5	766
622	905	763.5	6.807935	38	750
601	887	744	6.787845	38.5	736
589	866	727.5	6.763885	39	722

580	832	706	6.723832	39.5	708
588	795	691.5	6.678342	40	696
566	777	671.5	6.65544	40.5	685
554	775	664.5	6.652863	41	674
558	771	664.5	6.647688	41.5	663
569	737	653	6.602588	42	654
544	722	633	6.582025	42.5	645
539	700	619.5	6.55108	43	636
544	704	624	6.556778	43.5	628
532	685	608.5	6.529419	44	621
554	675	614.5	6.514713	44.5	614
	669	669	6.505784	45	607

9/12/2018

CO2 1	CO2 2	Avg CO2	Ln Avg CO2	time (min)	Expected CO2 conc
545	499	522	6.257668	0.5	
528	535	531.5	6.275703	1	
510	535	522.5	6.258625	1.5	
486	519	502.5	6.219596	2	
497	517	507	6.228511	2.5	
506	500	503	6.22059	3	
500	502	501	6.216606	3.5	
481	495	488	6.190315	4	
489	492	490.5	6.195425	4.5	
476	497	486.5	6.187237	5	
475	500	487.5	6.18929	5.5	
470	476	473	6.159095	6	
483	484	483.5	6.181051	6.5	
476	477	476.5	6.166468	7	
464	485	474.5	6.162262	7.5	
467	472	469.5	6.151668	8	
482	464	473	6.159095	8.5	
475	464	469.5	6.151668	9	
466	464	465	6.142037	9.5	
461	476	468.5	6.149536	10	
456	475	465.5	6.143112	10.5	
449	463	456	6.122493	11	
442	468	455	6.120297	11.5	
457	468	462.5	6.136647	12	

474	542	508	6.230481	12.5	
662	748	705	6.558198	13	
838	784	811	6.698268	13.5	
917	859	888	6.788972	14	
967	962	964.5	6.87161	14.5	
1082	1043	1062.5	6.96838	15	
1251	1234	1242.5	7.124881	15.5	
1460	1419	1439.5	7.272051	16	
1640	1683	1661.5	7.415476	16.5	
1766	1845	1805.5	7.498593	17	
1850	1905	1877.5	7.537696	17.5	
1887	1787	1837	7.515889	18	
1840	1741	1790.5	7.49025	18.5	
1798	1685	1741.5	7.462502	19	
1744	1669	1706.5	7.4422	19.5	
1690	1621	1655.5	7.411858	20	
1641	1596	1618.5	7.389255	20.5	
1566	1561	1563.5	7.354682	21	
1315	1400	1357.5	7.2134	21.5	
1076	1170	1123	7.023759	22	
926	992	959	6.865891	22.5	
819	909	864	6.761573	23	
768	831	799.5	6.683987	23.5	800
735	771	753	6.624065	24	772
702	752	727	6.588926	24.5	748
686	725	705.5	6.558907	25	725
672	687	679.5	6.521357	25.5	704

664	696	680	6.522093	26	685
642	688	665	6.499787	26.5	668
647	657	652	6.480045	27	652
649	655	652	6.480045	27.5	638
647	654	650.5	6.477741	28	625
628	647	637.5	6.457554	28.5	613
613	641	627	6.440947	29	602
608	626	617	6.424869	29.5	592
598	618	608	6.410175	30	582
582	603	592.5	6.384351	30.5	574
565	590	577.5	6.358708	31	566
562	596	579	6.361302	31.5	559
558	558	558	6.324359	32	553
553	561	557	6.322565	32.5	547
548	572	560	6.327937	33	542
533	573	553	6.315358	33.5	537
530	551	540.5	6.292495	34	532
533	522	527.5	6.268149	34.5	528
519	538	528.5	6.270043	35	524
523	531	527	6.267201	35.5	521
	519				
	521				

9/13/2019

CO2 1	CO2 2	Average CO2	ln Avg CO2	time (min)	Expected CO2 conc
448	460	454	6.118097	0.5	
460	454	457	6.124683	1	
449	442	445.5	6.099197	1.5	
431	465	448	6.104793	2	
461	430	445.5	6.099197	2.5	
462	435	448.5	6.105909	3	
454	448	451	6.111467	3.5	
431	442	436.5	6.078788	4	
443	444	443.5	6.094698	4.5	
446	443	444.5	6.09695	5	
455	434	444.5	6.09695	5.5	
465	455	460	6.131226	6	
452	460	456	6.122493	6.5	
451	478	464.5	6.140962	7	
458	461	459.5	6.130139	7.5	
451	443	447	6.102559	8	
446	455	450.5	6.110358	8.5	
453	456	454.5	6.119198	9	
454	450	452	6.113682	9.5	
456	458	457	6.124683	10	
458	452	455	6.120297	10.5	
463	448	455.5	6.121396	11	
457	454	455.5	6.121396	11.5	
475	464	469.5	6.151668	12	
483	469	476	6.165418	12.5	

481	455	468	6.148468	13	
480	466	473	6.159095	13.5	
475	491	483	6.180017	14	
468	457	462.5	6.136647	14.5	
470	460	465	6.142037	15	
480	467	473.5	6.160152	15.5	
463	449	456	6.122493	16	
464	446	455	6.120297	16.5	
450	438	444	6.095825	17	
467	450	458.5	6.12796	17.5	
457	454	455.5	6.121396	18	
452	459	455.5	6.121396	18.5	
456	443	449.5	6.108136	19	
474	459	466.5	6.145258	19.5	
490	461	475.5	6.164367	20	
546	461	503.5	6.221584	20.5	
605	487	546	6.302619	21	
620	481	550.5	6.310827	21.5	
602	474	538	6.287859	22	
577	464	520.5	6.25479	22.5	
590	489	539.5	6.290643	23	
551	474	512.5	6.239301	23.5	
517	541	529	6.270988	24	
544	774	659	6.490724	24.5	
671	1084	877.5	6.777077	25	
862	1422	1142	7.040536	25.5	
1055	1655	1355	7.211557	26	

1322	1805	1563.5	7.354682	26.5	
1735	2051	1893	7.545918	27	
2095	2292	2193.5	7.693254	27.5	
2213	2426	2319.5	7.749107	28	
2244	2392	2318	7.74846	28.5	
2300	2391	2345.5	7.760254	29	
2243	2309	2276	7.730175	29.5	
2231	2204	2217.5	7.704136	30	
2208	2201	2204.5	7.698256	30.5	
2163	2187	2175	7.684784	31	
2119	2126	2122.5	7.66035	31.5	
2078	2082	2080	7.640123	32	
2030	2063	2046.5	7.623886	32.5	
2017	1970	1993.5	7.597647	33	
2010	1982	1996	7.5989	33.5	
1955	1882	1918.5	7.559299	34	
1736	1752	1744	7.463937	34.5	
1433	1629	1531	7.333676	35	
1251	1508	1379.5	7.229476	35.5	
1149	1415	1282	7.156177	36	
1073	1281	1177	7.070724	36.5	
985	1191	1088	6.992096	37	
940	1061	1000.5	6.908255	37.5	
879	1013	946	6.852243	38	
854	985	919.5	6.82383	38.5	920
817	941	879	6.778785	39	894
804	925	864.5	6.762151	39.5	869

803	878	840.5	6.733997	40	846
782	867	824.5	6.714777	40.5	824
768	849	808.5	6.695181	41	804
753	826	789.5	6.6714	41.5	784
728	808	768	6.64379	42	766
725	771	748	6.617403	42.5	749
699	762	730.5	6.593729	43	732
694	747	720.5	6.579945	43.5	717
674	719	696.5	6.546068	44	702
656	719	687.5	6.533062	44.5	689
634	731	682.5	6.525763	45	676
628	703	665.5	6.500539	45.5	663
633	682	657.5	6.488445	46	652
607	684	645.5	6.470025	46.5	641
598	651	624.5	6.436951	47	631
591	649	620	6.429719	47.5	621
578	649	613.5	6.41918	48	612
570	648	609	6.411818	48.5	603
563	607	585	6.371612	49	595
567	637	602	6.400257	49.5	587
561	623	592	6.383507	50	580
536	607	571.5	6.348264	50.5	573
527	611	569	6.34388	51	566
518	587	552.5	6.314453	51.5	560
519	563	541	6.293419	52	554
524	587	555.5	6.319869	52.5	549
514	589	551.5	6.312642	53	544

505	551	528	6.269096	53.5	539
507	544	525.5	6.26435	54	
486	542	514	6.242223	54.5	
488	545	516.5	6.247075	55	
491	532	511.5	6.237348	55.5	
490	525	507.5	6.229497	56	
489	523	506	6.226537	56.5	
487	510	498.5	6.211604	57	
477	523	500	6.214608	57.5	
476	523	499.5	6.213608	58	
466	511	488.5	6.191339	58.5	
462	505	483.5	6.181051	59	
466	521	493.5	6.201523	59.5	
456	491	473.5	6.160152	60	