Characterization of Naturally-Occurring Alpha Diketone Emissions and Exposures at a Coffee Roasting Facility and Associated Retail Café

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Abstract

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Background: Alpha diketones such as diacetyl and 2,3-pentanedione have been used as artificial flavorings in a variety of industries and are produced naturally when food products such as coffee beans are roasted. Exposure to these compounds has been associated with bronchiolitis obliterans, a rare and severe respiratory disease characterized by inflammation of the small airways of the lungs. There is evidence from previous research studies and National Institute for Occupational Safety and Health (NIOSH) Health Hazard Evaluations (HHEs) that coffee production workers have been exposed to alpha diketone emissions at levels above recommended health guidelines. However, there is a need for more research on how widespread this exposure risk is and what process elements are associated with the highest levels of exposure in the coffee industry. There are a limited number of studies characterizing occupational

exposures to and emissions of alpha diketones at coffee roasting facilities. Even fewer studies have been published on occupational exposures to and emissions of alpha diketones in retail cafés. Only one other published study has quantified differences between light roasted and dark roasted coffee beans. No published studies exist that have evaluated the potential of total VOCs, CO, and CO_2 to serve as lower-cost surrogate measurements for alpha-diketone concentrations. The purpose of this thesis was to fill these gaps in knowledge by determining which steps in the coffee production process are associated with the highest alpha-diketone emissions at a small craft coffee roaster and associated café, determining the extent to which direct reading measurements of CO, CO_2, and total VOCs can serve as lower-cost surrogate indicators for diacetyl concentrations, and conduct a limited survey to quantify the effect that the process variable of roast type (i.e. light, medium, and dark roast) has on diacetyl emissions from grinding beans.

Methods: Data were collected over 4 days of sampling in October 2019 at a single coffee roaster and associated café in Olympia, WA. Integrated personal and area air samples for diacetyl and 2,3-pentanedione were collected from 7:00 AM to 3:00 PM on each sampling day, corresponding to the full-shift roasting, grinding, and packaging operations at the facility's roastery. Area samples were collected behind the shelves in the café, on the barista counter next to the espresso grinders, next to the roaster, next to the grinders in the roaster's grinding station, and next to the hopper. Personal air samples for alpha diketones were collected on workers who operated in the coffee roasting, grinding, and packaging area adjacent to the café. A MiniRAE 3000 PID (RAE Systems, Inc.) and a Photovac 2020ppb PRO Photoionization Monitor (Photovac, Inc.) were used to measure continuous total VOC concentrations at the roasting, grinding, and packaging stations. The TSI Q-Trak Indoor Air Monitor Model 7575 was used to measure continuous CO and CO_2 concentrations at the roasting, grinding, and packaging stations. Probes of direct reading instruments and sorbent tubes were co-located at each sampling location, positioned to be facing towards the work activity being performed, and placed at approximate breathing zone height. For the emissions experiments, integrated area air samples for diacetyl were collected over 30-minute intervals for each roast type and the sorbent tubes were positioned next to the grinder at approximate breathing zone height. A MiniRAE 3000 PID (Rae Systems, Inc.) was used to measure continuous total VOC concentrations during each grinding experiment. Sorbent tube samples from the field and from the emissions experiments were analyzed for alpha diketone mass using GC/MS. 8-hour TWA diacetyl and 2,3-pentanedione personal exposures were calculated for each day of sampling. Medians and 5th and 95th percentiles of diacetyl, 2,3-pentanedione, CO, CO_2, and total VOC emissions were determined from each sampling location. Correlations between diacetyl concentrations and each direct reading measurement were assessed. Finally, diacetyl mass emission rates in ng of diacetyl per gram of coffee ground were determined for each roast type.

Results: Diacetyl concentrations were elevated in five of the seven personal samples obtained as compared to the NIOSH Recommended Exposure Limit (REL) for diacetyl – 5 ppb as an eight-hour time-weighted average (TWA) and one of seven personal samples exceeded the NIOSH REL for 2,3-pentanedione – 9.3 ppb as an eight-hour TWA. On days where workers were doing more grinding and packaging of ground beans, exposures to diacetyl and 2,3-pentanedione were higher compared to days where less grinding and packaging of ground beans was done. Median diacetyl and 2,3-pentanedione emissions were highest at the hopper (172 ppb and 110 ppb,

respectively), followed by the grinder (57.3 ppb and 21.0 ppb, respectively), roaster (7.5 ppb and 3.5 ppb, respectively), barista (3.1 ppb and 1.5 ppb, respectively), and background areas (2.0 ppb and 0.89 ppb, respectively). Correlations between diacetyl and total VOCs, CO, and CO_2 showed that the model using air concentration of total VOCs as a predictor for air concentrations of diacetyl had the highest R^2-value ($R^2 = 0.95$, p-value = $4.8 * 10^{-15}$), followed by the model using CO_2 ($R^2 = 0.58$, p-value = 0.001), and the model using CO as an indicator for diacetyl air concentrations ($R^2 = 0.09$, p-value = 0.34). Based on our limited survey, French roast was associated with the highest mass emission rate of diacetyl, followed by medium espresso, espresso, and white coffee.

Conclusions: Results from the observational study indicated that coffee production workers at this facility had elevated exposures to diacetyl and 2,3-pentanedione compared to NIOSH recommended guidelines. Area sampling showed that the areas with the highest alpha diketone emissions were the grinder and the hopper, which are both areas associated with tasks involving ground roasted coffee (i.e. grinding and packaging ground beans). Using the model that predicts air concentrations of diacetyl from the air concentration of total VOCs, the average diacetyl concentration when the total VOC concentration is 400 ppb is 7.0 ppb (95% C.I.: -2.1 – 16.2 ppb). Because the 95% confidence interval includes values both above and below the NIOSH REL, this model cannot be used to reliably predict whether an exposure is elevated compared to NIOSH health guidelines at this total VOC concentration. Constraining this model to be based on observed diacetyl concentrations that were less than 100 ppb improved both the accuracy and precision of the original model's estimates. Using the constrained model, the model predicts that an exposure is elevated compared to the NIOSH REL for diacetyl at total VOC concentrations in excess of 400 ppb. Results from the emissions tests showed that diacetyl mass emissions generated from grinding French roast were significantly higher than those of espresso, medium espresso, and white coffee. White coffee had a very low diacetyl mass emission rate compared to the other roasts, and its rate was significantly lower than that of espresso and medium espresso. While a one-way ANOVA test and post hoc pairwise comparisons showed significant differences in diacetyl mass emission rates between the different roasts, the mean diacetyl emissions from the French roast is one-third higher than that of the medium espresso and espresso roasts. For smaller operations, distributing grinding and bagging tasks more evenly throughout the work week, especially for darker roasts, could reduce worker's daily TWA exposures to alpha-diketones. While this could improve compliance with health guidelines, the benefit to worker health is dependent on whether or not cumulative exposure to alpha diketones increases risk of respiratory impairment more than peak exposure. Peak exposure would be reduced using this administrative control, but cumulative exposure would remain the same. Future research could focus on designing effective engineering controls, in the form of local exhaust ventilation, with the goal of reducing alpha diketone emissions and exposures, as well as conducting similar studies to this thesis at other small-scale craft coffee roasters and cafés in order to better understand the variability in these emissions and exposures within these types of facilities.

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Introduction

Sources of Diacetyl

Diacetyl (2,3-butanedione) is a green-yellow in liquid appearance and gives off a pleasant, buttery-odor (OSHA, 2008). It is classified as an alpha diketone, which means that it contains two carbonyl functional groups that are adjacent to each other and the oxygen molecules are bonded to carbon atoms that are bonded only with other carbon atoms (McKernan et al, 2016). Diacetyl and related alpha-diketones are added to a variety of foods and beverages to impart a characteristic buttery flavor (e.g. microwave popcorn, flour mixes, cookies, candy, and food oils) (McKernan et al, 2016). Most of the diacetyl that is used as a food additive is produced synthetically. Diacetyl is also produced in foods naturally as a product of fermentation from bacteria and yeast (i.e. in yogurt, cheese, beer, and wine) and pyrolysis, such as in the roasting of green coffee beans (McKernan et al, 2016; L&I Food Flavoring; Shibamoto, 2014). When coffee is roasted at high temperatures (i.e. >200 °C or 392 °F), the Maillard reaction takes place wherein amino acids chemically react with sugars to form carbonyl compounds, including diacetyl and other alpha diketones (Shibamoto, 2014; Tamanna and Mahmood, 2014). Diacetyl and other alpha diketones are also found in cigarette smoke and some flavored e-cigarettes (Beckett et al, 2018; McKernan et al, 2016).

Table 1

Properties of Diacetyl and Related Alpha-Diketones

Compound	Molecular weight (g/mol)	Vapor pressure (at 20°C, mmHg)	Boiling point (°C)
Diacetyl (2,3-butanedione)[1]	86.09	52.2	88.0
2,3-pentanedione[2]	100.12	20.0	108
2,3-hexanedione[3]	114.14	10.0	128
2,3-heptanedione[4]	128.17	3.06	150
Acetoin (3-hydroxybutanone)[5]	88.11	2.06	148

[1] Sigma-Aldrich (n.d.). 2,3-Butanedione. Retrieved May 7 2020 from https://www.sigmaaldrich.com/catalog/product/sigma/d3634?lang=en&region=US
[2] PubChem (n.d.). 2,3-Pentanedione. Retrieved May 7, 2020 from https://pubchem.ncbi.nlm.nih.gov/compound/2_3-pentanedione
[3] Sigma-Aldrich (n.d.). 2,3-Hexanedione. Retrieved May 7, 2020 from https://www.sigmaaldrich.com/catalog/product/aldrich/144169?lang=en&region=US
[4] ChemSpider (n.d.). Acetylvaleryl. Retrieved May 7, 2020 from http://www.chemspider.com/Chemical-Structure.54944.html
[5] The Good Scents Company (n.d.). R-acetoin. Retrieved May 7, 2020 from http://www.thegoodscentscompany.com/data/rw1660331.html

Sentinel Cases of Bronchiolitis Obliterans

Health effects regarding diacetyl exposure were relatively unknown until 2000, when a pulmonologist in Missouri contacted the Missouri Department of Health and Senior Services (MoDHSS) to report eight cases of severe lung disease in former microwave popcorn plant workers (CDC, 2002; Kreiss, 2017). The workers had all been employed at the same popcorn plant at some time during 1992-2000 and the durations of their employment ranged from 8 months to 9 years (CDC, 2002). Their symptoms included dyspnea on exertion, a chronic cough, and fatigue (NIOSH, 2017b). The symptoms did not improve when the workers went home after work, over the weekends, or when they were on vacation (NIOSH, 2017b; OSHA, Safety & Health Topics). Their symptoms did not improve with corticosteroid treatment or bronchodilator medication (McKernan et al, 2016). The pulmonologist diagnosed them with bronchiolitis obliterans, a rare, severe fixed airway disease characterized by inflammation of the small airways of the lungs, called the bronchioles (American Lung Association, 2018; CDC, 2002). Though progression of the disease can be stopped through cessation of exposure, dyspnea on exertion and spirometric abnormalities persist and the disease is “often serious and life-shortening” (Kreiss, 2017; NIOSH, Health Information; McKernan et al, 2016). Among these 8 former workers, the disease was severe enough in half of them to require being placed on lung transplant waiting lists (Kreiss, 2017).

MoDHSS requested assistance from the National Institute for Occupational Safety and Health (NIOSH) to investigate respiratory hazards at the Missouri plant (CDC, 2002). Interviews with the cases and current employees indicated that the exposure was volatile in nature because of the disproportionate number of flavoring mixers and packaging workers affected with respiratory symptoms (Kreiss, 2017; CDC, 2002). Volatile organic compounds are carbon-containing compounds characterized by their ability to off gas at normal conditions of temperature and pressure (EPA Volatile). While there were other respiratory irritants present, the main volatile organic compound (VOC) found in the atmosphere of the microwave popcorn plant was diacetyl, which gave the popcorn its buttery taste (OSHA Sampling; Kreiss, 2017).

Exposure assessment at this microwave popcorn plant where the sentinel cases were employed found that mean area diacetyl air concentrations were highest in the mixing room (57.2 ppm), followed by the packaging area (2.8 ppm) (McKernan et al, 2016). Average personal exposures to diacetyl measured at five other microwave popcorn plants that NIOSH investigated were lower: 0.023 to 1.16 ppm in the mixing room and 0.35 to 1.33 ppm in the packaging rooms (McKernan et al, 2016). During this time, NIOSH also investigated worker exposure to diacetyl at ten different flavoring manufacturing facilities and found that mean personal full-shift diacetyl air concentrations ranged from 0.07 to 2.73 ppm (McKernan et al, 2016).

In 2013 the Morbidity and Mortality Weekly Report (MMWR) published two cases of occupational bronchiolitis obliterans found in workers who had been employed at a coffee roasting and packaging facility that produced both flavored and unflavored coffee (Huff et al, 2013). Both employees initially worked in the flavoring room of this facility for at least one year before being transferred to similar jobs in the unflavored coffee area and were eventually dismissed or placed on medical leave (Huff et al, 2013). The employees first sought care for respiratory symptoms at least one year after employment and initially received misdiagnoses of asthma and bronchitis (Huff et al, 2013). Their symptoms progressed in severity to the point of one employee being placed on a lung transplant waiting list (Huff et al, 2013). A NIOSH health hazard evaluation at this facility found diacetyl concentrations in the air were elevated compared to recommended health guidelines and identified three sources of elevation: 1) flavoring chemicals added to the roasted coffee beans in the flavoring rooms; 2) grinding unflavored roasted coffee beans and packaging unflavored ground and whole bean roasted coffee; and 3) storing roasted coffee in hoppers to off-gas (NIOSH, 2017a). Based on medical evaluations of employees at this facility, NIOSH investigators concluded that those workers had excess pulmonary obstruction and shortness of breath compared to the general population, and respiratory illness and symptoms associated with exposure to alpha diketones were not limited to the flavoring rooms (Bailey et al, 2015).

Health effects of exposure in human and animal studies

The main health endpoint of concern associated with exposure to diacetyl and other alpha diketones is bronchiolitis obliterans – colloquially referred to as “popcorn lung.” Bronchiolitis obliterans is a rare, severe fixed airway disease characterized by inflammation of the small airways of the lungs (bronchioles) (NIOSH, 2017a). Symptoms of the disease include cough, dyspnea on exertion or wheezing, and do not typically improve away from work (NIOSH, 2017a). A range of other obstructive lung diseases (e.g. asthma, chronic pulmonary disease, and hypersensitivity pneumonitis) have been associated with exposure to diacetyl in flavorings, but the strength of these associations is weaker than that between exposure to diacetyl and bronchiolitis obliterans (SCOEL, 2014). In addition to respiratory symptoms, workers exposed to flavoring vapors containing diacetyl reported eye, skin and nasal irritation in facilities where the air concentrations of diacetyl ranged from 1.1 to 98 ppm (SCOEL, 2014).

In the 1980s and 1990s there were case clusters of bronchiolitis obliterans in flavoring manufacturing plants, but at the time it was not possible to identify a single causal exposure due to the wide variety of ingredients used in flavoring (Kreiss, 2017). It wasn’t until late 2000, after NIOSH was alerted to the sentinel cases in Missouri, that the toxicity of diacetyl in occupational settings came to be recognized (Kreiss, 2017). In vivo testing in mice and rats showed that acute diacetyl exposure caused necrosis in the epithelial lining of their nasal and pulmonary airways (McKernan et al, 2016). In vitro studies showed that exposure to diacetyl in airway epithelium caused structural changes in proteins which altered their function and reduced epithelial integrity (McKernan et al, 2016). In reaction to growing demands for diacetyl-free flavorings, flavoring manufacturing companies began substituting diacetyl with 2,3-pentanedione and other alpha diketones (e.g. acetoin, 2,3-hexanedione, and 2,3-heptanedione) that imparted a similar taste (Kreiss, 2017). However, in vitro and in vivo research on these compounds showed that they posed a similar risk to human health as diacetyl, as exposure to these other alpha diketones also resulted in airway epithelial damage (McKernan et al, 2016).

Risk Assessment and Occupational Exposure Limits for Alpha Diketones

Based on the results of NIOSH's investigations into other microwave popcorn and flavoring production facilities and the corroboration of toxicological studies in animals, NIOSH concluded that there was "substantial evidence" of a causal relationship between worker exposure to diacetyl and subsequent development of bronchiolitis obliterans (McKernan et al, 2016).

NIOSH analyzed exposure-response relationships from several plants where health hazard evaluations were conducted, but due to limited consistency across plants, data from the Missouri plant (the site of the sentinel health event), which comprised approximately 600 exposure assessments, was selected for the risk assessment (SCOEL, 2014). At the plant, medical personnel from NIOSH measured employee lung function using spirometry (NIOSH, 2018, OELs). The test results were compared to expected normal values, the range of which encompasses 95% of a healthy, non-smoking population (NIOSH, 2018, OELs). Within the range of these models, based on FEV_1 and FEV_1/FVC, about 1-2 workers out of 1000 exposed to 5 ppb diacetyl over a working lifetime are estimated to develop spirometric evidence of exposure-related decrease in lung function (NIOSH, 2018, OELs). At an exposure of 1 ppb of diacetyl, it was predicted that the risk is reduced to 2-4 in 10,000 workers, and at 10 ppb the risk increases to about 2-4 workers in 1000 (NIOSH, 2018, OELs). These estimates were based on several assumptions and limitations in the data utilized for this risk assessment (NIOSH, 2018, OELs). The NIOSH health hazard evaluations at microwave popcorn plants were not specifically designed for quantitative risk assessment and have limitations in terms of unknown selection of study subjects and limited historical exposure information (McKernan et al, 2016). NIOSH based its recommended exposure limit on a one per thousand excess risk of respiratory impairment, a conservative approach that favors protection of workers when using inexact estimates and coincides with the Occupational Safety and Health Administration (OSHA)'s approach in regulation for chronic diseases (McKernan et al, 2016).

The quantitative risk assessment NIOSH investigators used to derive a recommended exposure limit for diacetyl was based solely on employee data (McKernan et al, 2016). Animal risk assessments served to validate the results of the analysis of human exposure data (McKernan et al, 2016). In 2011, NIOSH proposed a recommended exposure limit (REL) of 5 ppb for diacetyl as a time-weighted average during a 40-hour work week as well as a short-term exposure limit (STEL) of 25 ppb for a 15-minute time period (McKernan et al, 2016). Because 2,3-pentanedione is often used as a substitute for diacetyl in flavoring operations, NIOSH set a REL of 9.3 ppb over an 8-hour time-weighted average (TWA) and a STEL of 31 ppb during a 15-minute period (McKernan et al, 2016). While 2, 3-pentanedione has been demonstrated to cause damage similar to that caused by diacetyl in in vitro and in vivo testing, the REL and STEL of 2,3-pentanedione is higher than those for diacetyl due to analytical limitations, since 2,3-pentanedione could only be reliably measured only above 9.3 ppb using the standard analytical method recommended at that time (McKernan et al, 2016). NIOSH examined the existing analytical methods and available engineering controls and determined that these supported establishing recommended exposure limits at these levels (McKernan et al, 2016).

In 2012, the American Conference of Governmental Industrial Hygienists proposed threshold limit values (TLVs) for diacetyl of 10 ppb over an 8-hour TWA and a STEL of 20 ppb during a 15-minute period (NIOSH, 2018, OELs). This determination was based on the same human data that NIOSH used for their REL and STEL for diacetyl. ACGIH bases their TLVs solely on human health factors, without taking economic or technical feasibility into consideration (ACGIH, 2020). TLVs are guidelines representing the opinion of a committee of experts that have reviewed existing published and peer-reviewed literature to determine health-based values at which exposure to a hazard at or below the TLV "does not create an unreasonable risk of disease or injury" (ACGIH, 2020). The TLV is an estimate based on the known toxicity in humans or animals of a given chemical substance, and the reliability and accuracy of current sampling and analytical methods (ACGIH, 2012). The NIOSH RELs and ACGIH TLVs are not legally enforceable exposure limits. OSHA has not set standards for the regulation of worker exposure to diacetyl or other alpha diketones (McCoy et al, 2017).

Outside of the United States, the European Union's European Commission's Scientific Committee on Occupational Exposure Limits (SCOEL) evaluates potential health effects of occupational exposure to chemicals (European Commission, n.d.). The committee is composed of 21 independent experts that evaluate the latest available scientific data to provide recommendations used to inform regulatory agencies in member countries on occupational exposure limit values meant to protect workers from harmful exposure to specific agents (European Commission, n.d.). In 2014, the SCOEL published a recommended exposure limit for diacetyl based on an early study in 2000 conducted at the sentinel Missouri microwave popcorn plant that utilized questionnaire responses and spirometry to evaluate the relationship between exposure to diacetyl and respiratory impairment (SCOEL, 2014; Kreiss et al, 2002). This was the same plant that NIOSH used for their REL determination. From this study, the SCOEL derived a no-observed adverse effect concentration (NOAEC) for diacetyl of 0.65 ppm-years, which was extrapolated to an 8-hour TWA OEL of 0.02 ppm, factoring in correction and uncertainty factors (SCOEL, 2014). The SCOEL recommended a 15-minute STEL of 0.10 ppm for diacetyl based on the need to prevent respiratory damage that may arise due to peak exposures (SCOEL, 2014).

There has been some debate about the practicality and necessity of enforcing an 8-hour TWA OEL in the 0.005 – 0.02 ppm range in industries where alpha-diketone emissions occur naturally and are not related to artificial flavoring processes (Beckett et al, 2019). A paper published by Beckett et al (2019) derived an occupational exposure limit for diacetyl using dose-response data from a chronic, two-year National Toxicology Program (NTP) diacetyl inhalation exposure study with rodents (Beckett et al, 2019). The chronic animal study exposed mice and rats to airborne diacetyl at doses of 0, 12.5, 25, and 50 ppm and after sacrifice the animals were assessed for a variety of health endpoints, including bronchiolar epithelial hyperplasia (Beckett et al, 2019). The authors derived a model-averaged benchmark concentration associated with a 10% extra risk (BMC_{10}) and the associated 95% lower confidence bound ($BMCL_{10}$) for the mice and rat endpoint of bronchiolar epithelial hyperplasia with the argument that "an OEL based on hyperplasia would be protective of more serious adverse endpoints" (Beckett et al, 2019, pg. 692). Beckett et al did not make any comment on whether there is a significant relationship between hyperplasia and bronchiolitis obliterans. The authors argued that while hyperplasia was not in itself considered an adverse health effect it can lead to adverse health effects such as "markers of chronic inflammation and tissue repair" which are clinical signs of a variety of serious lung diseases (Beckett et al, 2019, 697). The authors incorporated uncertainty factors to account for animal to human and inter-individual human variability in susceptibility into the derivation of their OEL (Beckett et al, 2019, 692). The authors recommended an 8-hour OEL of 200 ppb based on the endpoint of bronchiolar epithelial hyperplasia under breathing patterns associated with light exercise (Beckett et al, 2019).

The Beckett et al (2019) proposed OEL is much higher than that of NIOSH, ACGIH, or the European SCOEL. In their proposal, Becket et al (2019) offered a critique of the worker cohort studies carried out by NIOSH and used by other organizations to derive their recommended OELs. Becket et al (2019) argued that there are confounding elements in this data that include (1) that there were volatile organic and respirable compounds other than diacetyl present in the atmosphere of the mixing room that were known respiratory irritants and that were significantly correlated with bronchiolitis obliterans; (2) the majority of the participants in the cohorts reported non-occupational exposures to other possible causes of lung disease, including nitrogen oxides, which are known inducers of bronchiolitis obliterans; (3) workers known to have pre-existing respiratory conditions were included in the analysis; and (4) there was no attempt to account for significant cumulative exposures experienced by smoking workers due to their tobacco use (Beckett et al, 2019). For these reasons, the authors argue that limitations in the epidemiologically derived values may have led to "artificially low OELs" (Beckett et al, 2019). In addition to stating that their OEL is "protective of all workplace-related adverse health effects of diacetyl" the authors also argue that their OEL is enforceable in a practical sense because the proposed value is higher than diacetyl concentrations which occur naturally in "exhaled breath, foods, and food processing" (Beckett et al, 2019, 699).

In their investigation, NIOSH found that while there were other respiratory irritants present in the atmosphere of the mixing room, diacetyl was found to be the predominant volatile compound in the flavoring room and in the atmosphere of the plant (Kreiss, 2017). Moreover, toxicological investigations have shown that there is evidence that there is a mixed exposure effect when diacetyl is in the presence of other volatile components in flavoring (Kreiss, 2017). Pertaining to Beckett et al (2019)'s second critique, NIOSH investigators have stated that "the diacetyl-exposed employees who developed severe fixed airways obstruction did not have histories or medical evaluation findings to suggest that they had developed bronchiolitis obliterans from another exposure or medical condition" (McKernan et al, 2016, 74). Moreover, NIOSH investigators found that among diacetyl-exposed employees microwave popcorn and flavoring manufacturing facilities, "most affected employees denied having any pre-existing lung disease or symptoms at the start of exposure" (McKernan et al, 2016, 73).

In their quantitative risk assessment, NIOSH investigators found that in the absence of smoking interaction terms, "the diacetyl effects are somewhat underestimated in non-smokers and overestimated in smokers" (McKernan et al, 2016, 117). For example, at 0.01 ppm diacetyl, ignoring smoking determinants, NIOSH investigators found that the excess lifetime risk of decline in lung function was 3.2/1000 (McKernan et al, 2016). Including smoking determinants in the model, the excess lifetime risk at 0.01 ppm diacetyl for nonsmokers was 11.2/1000 workers, while for smokers was 2.2/1000 workers (McKernan et al, 2016). NIOSH concluded in their risk assessment that "although smoking affects the excess lifetime risk estimates, a full treatment for the purpose of developing separate REL recommendations on smoking status would require including interactions between smoking and diacetyl exposure histories for which NIOSH believes there is insufficient historical information and statistical power to implement" and there is no precedent for developing smoking-specific standards (McKernan et al, 2016, 177).

While there are some limitations present in the epidemiological data used to derive NIOSH and other recommended exposure limits, threshold levels derived solely from animal studies need to be interpreted with caution when applying them to human health outcomes due to toxicokinetic differences between species and other mitigating and uncertainty factors and when possible should be evaluated in conjunction with epidemiological data (Egilman et al, 2011).

Overview of the Coffee Production Industry

Overview of the Coffee Industry

The National Coffee Association, a U.S. trade association for the coffee industry, states that "coffee is the most commonly consumed beverage in the U.S." (NCA, Economic). In 2015, coffee-related economic activity comprised approximately 1.6% of the U.S. gross domestic product and employed nearly 2 million workers (NCA, Economic). In 2018, the U.S. Census Bureau reported that there were 17,898 coffee and tea manufacturing workers (Census, 2018). The Bureau of Labor Statistics reported that in 2017, the average hourly earnings of food and tobacco roasting, baking and drying machine operators was $15.23, and the average hourly earnings of food and tobacco processing workers was $14.52 (BLS, 2018; BLS, 2020). In 2017, the Census Bureau reported that there were 64,683 snack and nonalcoholic beverage bars employing 731,023 workers in the U.S. (Census, 2017).The Bureau of Labor Statistics reported that in 2018 there were over five million food and beverage serving and related workers who earned a median income of $10.45 per hour (BLS, 2019).

There is a lot of variability in the coffee production industry, in terms of size of facilities, number of employees, production processes, and the amount of coffee that is produced from roasting, grinding, and packaging (NIOSH, 2017a). Large-scale production facilities tend to have more automated processes, whereas smaller facilities, like craft roasters, tend to have more manual operations (NIOSH, 2017a). For example, in larger facilities conveyor systems are commonly used to load unroasted coffee into roasters that can roast 11,000 pounds of coffee per batch (Green, 2014). In these facilities, workers may oversee automated operations but may not come into direct contact with individual batches very often (Green, 2014). In smaller coffee processing facilities, roasters may have capacities of less than 50 pounds, and roasting operators and production workers manually load and unload the machines and package the roasted beans by hand (Green, 2014). Some coffee roasting and packaging facilities have cafés that are physically attached to their facility or are otherwise associated with them (NIOSH, 2017a). There is also variation in the type of coffee that is roasted and the different roast types that are produced. Arabica and Robusta are the two main types of coffee beans; Arabica is grown at high altitudes (between 2,000 to 6,000 feet above sea level) and is costlier to produce than Robusta because it is more vulnerable to disease and temperamental climates (NCA, What is Coffee). Despite the cost in cultivation, according to the National Coffee Association Arabica coffee comprises about 70% of the world's coffee production (NCA, What is Coffee). Coffee is also roasted at a variety of temperatures to produce different desired roasts – lower temperatures produce light-roasted coffee while higher temperatures produce darker roasts (NCA, Coffee Roasts Guide).

Coffee Production Process Description

In general, coffee processing at coffee production facilities begins with importing green coffee beans from different source countries (e.g. Nicaragua, Honduras, or Guatemala) (NIOSH, 2017a; NCA, What is Coffee). The green beans are typically cleaned before roasting to "remove stones, wood, and other impurities" from the product (NIOSH, 2017a). To produce different coffee blends, facilities will mix coffee beans from different sources either before or after roasting (NIOSH, 2017a). Coffee is roasted in automated roasters at preset temperatures and lengths of time. Emissions products generated by the roasting process include total VOCs, organic acids, and combustion products, including CO and CO_2 (EPA, 1995). According to the EPA's list of emissions factors for coffee roasting operations, for every ton of coffee roasted in a batch roaster, 0.86 lbs. of VOC and 180 lbs. of CO_2 are produced because of pyrolysis (EPA, 1995). It’s estimated that CO_2 comprises 87% of the gases released from roasted coffee (Anderson et al, 2003). Roasters are often connected to afterburners, which work by heating the roaster’s exhaust gases up to high temperatures in order to break down the total VOCs before releasing the emissions into the atmosphere (Parker, 2019). Once the roaster has produced the desired coffee roast, the roasted beans are discharged into the machine’s cooling tray (Diedrich, 2017). The cooling tray is equipped with down-draft ventilation that draws air through the tray in order to facilitate the removal of chaff from the beans (Diedrich, 2017).

After the beans cool, they are ready to be either ground and packaged or packaged as whole beans depending on production demand. Grinding compromises the structural integrity of the roasted bean and increases its surface area, which in turns increases the rate that the emissions products of roasting (i.e. total VOCs, CO, and CO_2) off-gas (Anderson et al, 2003; Hawley et al, 2017; NIOSH, 2017a). Ground coffee is packaged either by hand in smaller operations or by hoppers that weigh the beans into predetermined weights. Whole and ground beans are packaged in permeable bags that are fitted with a one-way valve that allows the roasted coffee to off-gas for a period before it is brewed (NIOSH, 2017a). The beans are allowed to off-gas before brewing in order to improve the flavor profile of the final product (Ospina, 2019).

Alpha diketone formation from roasting coffee

As described previously, roasting of coffee at high temperatures (i.e. >200 °C) leads to formation of carbonyl compounds, including diacetyl and other alpha diketones. Health hazard evaluations conducted by NIOSH (reviewed in the subsequent section) have demonstrated that the highest personal exposures to and area emissions of diacetyl and 2,3-pentanedione are associated with grinding and packaging ground roasted coffee. Prior to roasting, green coffee beans contain “little to no” diacetyl and 2,3-pentanedione (Gaffney et al, 2015, 1172). The beans are roasted at temperatures ranging from 180 °C to 240 °C to produce varying aromas and flavors (Lokker, 2013). Grinding roasted beans increases the surface area for off gassing of these volatile organic compounds (Blackley et al 2019; Gaffney et al, 2015). Gaffney et al (2015) is the only study to date that has quantified differences between light roasted and dark roasted and soft and hard coffee beans. The authors found that average concentrations of diacetyl and 2,3-pentanedione during grinding were 380 and 210 ppb for light roasted soft beans, 140 and 69 ppb for light roasted hard beans, and 150 and 52 ppb for dark roasted hard beans (Gaffney et al, 2015). The authors concluded that alpha diketone concentrations were higher during the grinding of soft beans than during the grinding of hard beans and there was no apparent difference between the concentration of alpha diketones measured during the grinding of light and dark hard beans (Gaffney et al, 2015). The study did not attempt to quantify the emission rate of diacetyl and 2,3-pentanedione per pound of coffee ground.

Diacetyl and 2,3-Pentanedione as Occupational Health Hazards

There is evidence from previous studies conducted at large-, medium-, and small-scale coffee roasters that production workers working with unflavored coffee beans have been exposed to diacetyl and 2,3-pentanedione above NIOSH's REL of 5 ppb and 9.3 ppb, respectively. This evidence is summarized in Table 2 for diacetyl exposure, specifically. NIOSH has conducted numerous health hazard evaluations (HHEs) at coffee roasters and some of their associated retail cafés in the United States. There is a wide range of variability in exposures to diacetyl both between the different facilities and within the different production areas. This variability may be due to variations in process elements between facilities (i.e. roast temperatures, bean type, and bean origin), the degree of automation present in this facility (i.e. how proximal the worker is to the production process), and whether there are effective ventilation systems or other controls present to reduce worker exposure to diacetyl and other alpha diketones.

Table 2
Personal and area diacetyl concentrations measured during stages of coffee production at large-, medium-, and small-scale coffee roasters and cafés.

				Diacetyl concentration in ppb		
Study	**Sample Type**	**Location**	**Number of Samples**	**Arithmetic Mean**	**Minimum**	**Maximum**
Large Roasters						
Harvey et al, 2018	Personal (full-shift TWA)	Roasting	10		2.1	19.7
	Personal (full-shift TWA)	Grinding	1		10.9	10.9
	Personal (full-shift TWA)	Packaging	18		2.2	24.5
	Area	Roasting	15		7.2	19.9
	Area	Grinding	12		4.4	88.7
	Area	Packaging	48		3.7	24.7
	Area	Production Shipping Area	4		5.0	16.6
	Area	Production Storage Area	4		3.7	13.6
Stanton et al, 2018	Personal (full-shift TWA)	Roasting	11	13.1	4.4	19.2
	Personal (full-shift TWA)	Grinding	4		10.3	13.8
	Personal (full-shift TWA)	Packaging	38	13.2	1.6	25.6
	Area	Roasting	12		7.5	37.8
	Area	Grinding	8		12.0	68.9
	Area	Packaging	16		5.9	21.6
Pengelly et al, 2019	Personal (full-shift TWA)	Packaging/control /other	18	41	31	68
	Area	Roasting	5	13	10	15
	Area	Grinding	4	252	200	396
	Area	Packaging/control /other	2	55	51	59
Pengelly et al, 2019	Area	Roasting	13	4.1	<0.1	16
	Area	Grinding/packing	16	8.1	<0.1	18
	Area	Other areas	3	1.0	0.3	1.5

Table 2 (cont.)
Personal and area diacetyl concentrations measured during stages of coffee production at large-, medium-, and small-scale coffee roasters and cafés.

				Diacetyl concentration in ppb		
Study	**Sample Type**	**Location**	**Number of Samples**	**Arithmetic Mean**	**Minimum**	**Maximum**
McCoy et al, 2017	Personal (full-shift TWA)	Roasting	3	4.2	2.8	6.4
	Personal (full-shift TWA)	Grinding	2	5.5	1.5	9.4
	Personal (15-min Short-Term)	Roasting	3	<9.7	<9.6	<9.8
	Personal (15-min Short-Term)	Grinding	3	42	17	80
Medium Roasters						
Hawley et al, 2017	Personal (full-shift TWA)	Production, Production Area	12		1.6	13.1
	Personal (full-shift TWA)	Roasting Operator, Roasting	6		4.3	10.9
	Personal (Short-term, task-based)	Roast coffee beans	38		<0.7	13.2
	Personal (Short-term, task-based)	Grind coffee beans	9		27.4	375.4
	Personal (Short-term, task-based)	Package coffee	10		≤1.1	29.7
LeBouf et al, 2017	Personal (full-shift TWA)	Roasting	6		<3.0	7.2
	Personal (full-shift TWA)	Grinding	1		5.3	5.3
	Personal (full-shift TWA)	Weigh/package	9		≤2.9	2.9
	Personal (Short-term, task-based)	Blending roasted beans by hand	3		7.5	33.4
	Personal (Short-term, task-based	Grind coffee beans	4		21.9	37.6
	Personal (Short-term, task-based)	Package coffee	19		3.0	34.3

Table 2 (cont.)

Personal and area diacetyl concentrations measured during stages of coffee production at large-, medium-, and small-scale coffee roasters and cafés.

				Diacetyl concentration in ppb		
Study	**Sample Type**	**Location**	**Number of Samples**	**Arithmetic Mean**	**Minimum**	**Maximum**
Small Roasters						
Pengelly et al, 2019	Personal (full-shift TWA)	Roasting	2	4.3	3.5	5.1
	Personal (full-shift TWA)	Grinding/packing	2	41	23	60
Hawley et al, 2018	Personal (full-shift TWA)	Roasting	2	3.1	0.7	2.4
	Personal (full-shift TWA)	Production Area	1		5.6	5.6
	Personal (Short-term, task-based)	Roasting coffee beans	11		<0.6	1.5
	Personal (Short-term, task-based)	Grinding coffee beans	3		14.8	31.7
	Personal (Short-term, task-based)	Packaging coffee	5		4.0	11.7
McClelland et al, 2019	Personal (full-shift TWA)	Roasting	1		0.8	0.8
	Personal (full-shift TWA)	Production Area	2	1.2	0.7	1.7
McClelland et al, 2019 (cont.)	Personal (full-shift TWA)	Packaging	1		2.1	2.1
Cafés of small roasters						
McClelland et al, 2019	Personal (full-shift TWA)	Uptown – Café	4		5.1	5.8
	Personal (full-shift TWA)	Downtown – Café	5		3.3	13.9
	Area	Uptown – Café	9		2.4	7.6
	Area	Downtown - Cafe	12		3.2	5.5
Pengelly et al, 2019	Personal (Full-shift TWA)	Barista/manager	2	0.2	<0.1	0.4
	Personal (Full-shift TWA)	Barista	4	0.8	0.1	1.2
	Personal (Full-shift TWA)	Barista	5	0.1	<0.1	1.4

Exposure Controls

Engineering controls can reduce workers' exposures by either removing the hazard at its source or placing a barrier between the hazard and the employee (NIOSH, 2018, Workplace Interventions). Local exhaust ventilation can be designed to capture and remove diacetyl and 2,3-pentanedione emissions at roasters, grinders, hoppers, and packaging areas (NIOSH, 2018, Workplace Interventions). Dilution ventilation can be used to reduce contaminant concentrations by increasing fresh air exchanges into the facility (NIOSH, 2018, Workplace Interventions). After the installation of local exhaust ventilation, air monitoring should be repeated to determine that the intervention is effective in reducing exposures.

Administrative controls are work practices and policies enforced by the employer that aim to reduce or prevent employee exposures to occupational hazards (NIOSH, 2018, Workplace Interventions). The effectiveness of these controls relies on employer enforcement of these policies and practices and on employee understanding and acceptance of these changes (NIOSH, 2018, Workplace Interventions). Administrative controls can include giving employees hazard communication training to ensure that employees understand the potential hazards in the workplace and how to protect themselves (NIOSH, 2018, Workplace Interventions). OSHA's Hazard Communication Standard (a.k.a. the "Right to Know Law") [29 CFR 1910.1200] requires that employees are informed of and trained on potential work hazards and associated safe practices, procedures, and protective measures (NIOSH, 2018, Workplace Interventions). Employers can also encourage their employees to report new, persistent, or worsening respiratory symptoms to their healthcare providers and to a designated individual at their workplace (NIOSH, 2018, Workplace Interventions). Reporting symptoms can prompt the employer to re-evaluate the potential for exposure to respiratory hazards (NIOSH, 2018, Workplace Interventions).

Personal protective equipment (PPE) is considered the least effective form of hazard control because it does not reduce the hazard and makes the worker responsible for their own hazard protection (NIOSH, 2018, Workplace Interventions). NIOSH-certified air-purifying respirators equipped with organic vapor cartridges in combination with particulate filters provide the minimum recommended level of protection for the exposures measured in Table 2 (OSHA). Proper use of respirators requires a comprehensive respiratory protection program that ensures that the right type of respirator is chosen for each hazard, respirators fit users and are maintained in good condition, and respirators are worn when needed (NIOSH, 2018, Workplace Interventions). Employers must implement a change-out schedule for cartridges to ensure that they do not exceed their service life (OSHA, 2010). Respirators should not be the only method used to reduce employees' exposures; they should be used as a supplement until effective engineering and administrative controls are put in place (NIOSH, 2018, Workplace Interventions).

A medical monitoring program can be implemented to help assure the health of employees who have workplace exposures known to pose risk for potentially serious conditions, such as bronchiolitis obliterans (NIOSH, 2018, Workplace Interventions). If workplace concentrations of diacetyl or 2,3-pentanedione are above recommended exposure limits, a medical surveillance program should be initiated to screen for respiratory symptoms or abnormalities in employees and should include a health questionnaire and spirometry (NIOSH, 2018, Workplace Interventions).

Need for More Information

The HHEs conducted by NIOSH and studies conducted at large- and small-scale coffee production facilities demonstrate that there is a risk of coffee workers being exposed to levels of alpha diketones that are above recommended health guidelines. Production practices within the coffee industry are widely variable, including the sources and types of beans that are roasted, the amount of beans that are roasted, what roast types are produced, and the amount of whole or ground beans that are produced. Similarly, there is wide variability in the equipment used to process coffee and the extent to which that equipment controls workers' exposure to diacetyl emissions. Production rate and presence and type of workplace ventilation are also widely variable throughout the industry. In particular, there is currently limited information on this exposure risk at smaller craft roasters and cafés as levels of diacetyl and other alpha diketones in these facilities where roasting, grinding, and brewing take place are largely unknown.

NIOSH has sampled for total volatile organic compounds (TVOCs), carbon monoxide, and carbon monoxide, all of which are produced during the roasting of coffee beans, in their HHEs conducted at various coffee processing facilities, but to date there have been no studies that have correlated these compounds with diacetyl and 2,3-pentanedione emissions and exposures. TVOCs, carbon monoxide, and carbon dioxide can all be measured with direct reading instruments, and there has not been any research on the potential of these compounds to serve as surrogate measurements for alpha-diketone concentrations, which are measured with sorbent tubes requiring laboratory analysis. Sampling for alpha-diketones can be expensive and time-consuming; sampling for these compounds requires the purchase of expensive sampling equipment and apparatuses, in some cases hiring a certified industrial hygienist to conduct sampling, paying a lab to analyze the samples, and waiting for the results. Direct reading instruments can deliver data in real-time after the initial cost of purchasing the instrument. Thus, measurement of TVOCs, carbon monoxide, and carbon dioxide which can be readily measured with direct reading instruments may provide a lower-cost alternative to estimate occupational exposure to diacetyl and related compounds in the coffee industry.

Specific Aims:

While these studies indicate that there is a risk for coffee workers to be exposed to diacetyl and other alpha diketones above exposure limits, there is a need for more research on how widespread this exposure risk is and what specific process elements are associated with the highest levels of exposure (Simpson, 2018). Specific data gaps include limited literature regarding diacetyl levels and exposures in small, craft roasters and within those roasteries which parts of the production process are associated with the highest diacetyl emissions and the highest exposures. This proposal aims to fill the gap in current research by examining exposure to and emissions of diacetyl and other alpha diketones among workers in a small craft coffee roaster and associated café and to conduct an emissions experiment with a variety of different roasts to determine if this process variable has an impact on diacetyl emission rate per mass of coffee ground.

The specific aims of this research project are to:

Aim 1. Characterize the craft roastery production employees’ exposures to alpha diketones using modified OSHA methods 1013/1016 and compare full-shift time weighted average exposures to NIOSH and ACGIH recommended exposure levels for diacetyl and 2,3-pentanedione (LeBouf et al, 2017; OSHA, 2008; OSHA, 2010).

Aim 2. Determine which parts of the coffee production process in a craft roastery are associated with the highest mean alpha diketone emissions by measuring and comparing diacetyl and 2,3-pentanedione concentrations associated with the four production stages (i.e. roasting, grinding, packaging, and brewing) using modified OSHA methods 1013/1016 (LeBouf et al, 2017; OSHA, 2008; OSHA, 2010).

Aim 3. Determine the extent to which direct reading measurements (i.e. CO, CO_2, and total VOC) can serve as lower-cost surrogate indicators for diacetyl concentrations.

Aim 3a. Measure average concentrations of CO, CO_2, and total VOC by production area sampled and day of sampling using a Q-Trak, MiniRAE PID, and ppbPRO. These samples will be co-located and paired to task-based area diacetyl concentrations taken on the same day.

Aim 3b. Compare correlations between diacetyl concentrations to CO, CO_2, and total VOC concentrations among the different production areas.

Aim 4. Conduct a limited survey to quantify the effect that the process variable of roast type (i.e. light, medium, and dark roast) has on mean alpha diketone emissions from grinding beans. To do this we will conduct emissions tests by grinding different coffee roasts and measuring diacetyl and 2,3-pentanedione emissions using modified OSHA methods 1013/1016 (LeBouf et al, 2017; OSHA, 2008; OSHA, 2010).

Successful completion of these aims will provide quantitative information on alpha diketone emissions and worker exposures from various stages of the coffee production process in a craft roastery, and will provide information on the effect of coffee roast type on these emissions. These outcomes are expected to have an important positive impact because they will increase employers’ knowledge on the extent of alpha diketone exposures and emissions and potential hazards associated with that exposure in the coffee industry.

Methods

This research project was supported by funding from the State of Washington Department of Labor and Industries' Safety and Health Investment Projects (SHIP) Program. The study involved two components:

1. Observational study of exposure conducted in a coffee roastery
2. Laboratory study of determinants of diacetyl emissions from grinding of coffee

Observational Study Design

This project was an observational study that aimed to characterize alpha diketone emissions and associated exposures experienced by coffee production workers. This project utilized area sampling using direct reading and integrated sampling methods and equipment to measure alpha diketones, CO, CO_2, and total VOC emissions in a wholesale craft coffee roastery with an associated retail café. In addition, this project utilized integrated personal sampling methods and equipment to measure coffee production workers' exposures to alpha diketones. Observations of production tasks performed by workers were recorded for the duration of each sampling day. The facility, field and experimental sampling methods, and data analysis approach are described in the following sections.

Research Study Setting

The roastery sampled in this project has been operating in Olympia, Washington for more than 20 years. In addition to operating a retail café, the facility conducts wholesale whole bean coffee roasting onsite in a Diedrich IR-12 roaster, which has a batch size of approximately 12 kg (~ 24 lbs.) and can process up to 42 kg/hr. (~93 lbs./hr.). The owner of the roastery is the primary operator of the roasting, grinding, and packaging processes and is assisted by one to two helpers when production increases during the fall season. Café operations are typically managed by two to three baristas that take orders and make food and beverages. The café also operates a drive-thru window where customers can take their orders to-go in their cars. Many of the beverages made at the café consist of espresso shots, which require the barista to grind and brew espresso beans at the counter.


[redacted] [redacted] [redacted]

Figure 1. Images showing the layout of the café area (left) and the production area (right). The production area is divided into two rooms, the roasting room and the grinding/packaging room.

Process Description

At the roastery, green coffee beans are roasted in approximately 12 kg (~24 lbs.) batches for 16-18 minutes and are subsequently dropped into the roaster's cooling tray to cool for about two minutes. The roastery produces a variety of different coffee roasts, including white coffee (coffee that is under-roasted and has a higher caffeine content than other coffee), medium espresso, espresso, and French roast (the darkest roast at this facility). The roasting temperature varies from 355 - 480 ºF. After cooling, the roasted beans are transferred to plastic totes which are manually carried into the adjacent grinding and packaging room. After three or four batches of different origins (e.g. Columbian, Honduran, Guatemalan, Nicaraguan, Sumatran, and Ethiopian) are roasted, the roasting operator mixes the different beans together by hand for one to two minutes to produce the desired coffee blend. For other coffee types (e.g. white coffee or decaf) the beans are not blended but transferred as is to be ground or packaged as whole beans.

General ventilation is provided in the roasting room through a ceiling mounted vent and rooftop blower. The roaster draws air through its after-burner and exhaust system which provides effective capture and removal of the volatile compounds generated during the roasting process. Figures 1 and 2 in Appendix II illustrate the approximate layout and room dimensions of both the roasting room and the grinding/packaging room. The roasting room was approximately 16.75 ft in length, 11,7 ft in width, and 20 ft for an approximate volume of 4000 ft^3. The grinding/packaging room was approximately 25.5 ft in length, 11.6 ft in width, and 17 ft in height for an approximate volume of 5000 ft^3

After the beans are roasted, they are either ground and packaged, or packaged as whole beans. To grind roasted beans the worker will scoop roasted beans from the totes and dump them into the two Grindmaster grinders the roastery uses. White coffee beans are ground in a smaller grinder adjacent to the Grindmaster grinders. For larger batches, the ground beans are deposited from the grinder into 5-pound capacity polyethylene bags. The ground beans in these bags are then transferred into a Logical Machines model S5 bulk scale system hopper to be weighed and packaged. This hopper weighs bags of coffee at preset weights of 0.75, 1, and 5 lbs. The ground or whole roasted coffee is loaded into the hopper and the empty bag is placed on the machine's scale. A funnel attached to the machine is adjusted so that is it inside the bag. The machine is turned on by pressing a foot pedal and the machine fills the bag by vibrating the coffee so that it flows from the hopper into the chute and down into the funnel at a preset speed. The machine automatically stops once the scale reaches the preset weight. The process is repeated by placing a new bag under the funnel and pressing the foot pedal (Logical Machines).

For smaller batches, the roasted beans are weighed in the hopper first into one- or two-pound capacity bags which are then dumped into the grinders and the ground beans are then transferred back into those same bags. The packaging and grinding processes are variable - sometimes roasted beans are weighed and packaged as whole beans, sometimes roasted beans are ground first and then weighed and packaged, and sometimes roasted beans are weighed first, ground, and then packaged.

Bagged coffee is stored in the grinding and packaging room in polyethylene bags fitted with a one-way valve that allows the roasted coffee to off-gas but does not allow outside air to enter.


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Figure 2. Images of the Diedrich IR-12 roaster (left) used in the roasting room, the Grindmaster grinders (center) used to grind roasted coffee and the shelves where packaged coffee is stored to off-gas, and a worker using the Logical Machines S5 hopper to package roasted beans.

Data Collection and Field Work

Data collection consisted of four days of sampling occurring on consecutive Tuesdays and Wednesdays in mid- to late-October 2019. Samples were collected from 7:00 AM to 3:00 PM on each sampling day, corresponding to the full-shift roasting, grinding, and packaging operations in the facility’s roastery. At the beginning of each sampling day, sampling equipment was set up in the barista area, behind the shelves in the café, next to the roaster, and next to the hopper. The area samples behind the shelves in the café were intended to capture the background concentrations of alpha diketones present in this facility. Due to equipment constraints, sampling equipment next to the hopper was moved next to the grinders halfway through the day to obtain area samples from the grinding process. To best represent worker exposures in the different production areas sampled, the fixed location sampling equipment was placed at approximately breathing zone height and as close as possible to the production tasks being performed.

Personal sampling equipment was placed on workers at the start of their shift, and sampling was paused while the workers went off-site for deliveries or took breaks.

Diacetyl and 2,3-pentanedione Sampling Devices

Integrated area and personal air samples for diacetyl and 2,3-pentanedione were collected using OSHA 1013/1016 methods with a few modifications (LeBouf et al, 2017; OSHA, 2008; OSHA, 2010). Personal air samples for diacetyl and 2,3-pentanedione were collected on workers who operated in the coffee roasting, grinding, and packaging area adjacent to the café. The sorbent tubes were positioned in the workers' breathing zones for a full-shift sampling period. Sorbent tubes were changed halfway through the day (approximately 4 hours) to prevent excessive breakthrough of the alpha-diketones.

Full shift and short-term area air samples for diacetyl and 2,3-pentanedione were collected in the different work areas in the roastery and café. Background and barista area samples were positioned at approximate breathing zone height for a full-shift, 8-hour sampling period. Again, sorbent tubes were changed halfway through the day (approximately 4 hours) to prevent excessive breakthrough of the alpha diketones. Roasting area samples were positioned at approximate breathing zone height for two 180-minute sampling periods for each day of sampling. Bagging area samples were positioned next to the hopper at approximate breathing zone height for two 120-minute sampling periods each day of sampling. Grinding area samples were positioned adjacent to the two large and one small grinders at approximate breathing zone height for two 120-minute sampling periods for each day of sampling.

Diacetyl and 2,3-pentanedione were collected on sorbent tubes composed of silica gel (SKC Inc, P/N 226-183). Per OSHA methods 1013/1016, for each sample two sorbent tubes were connected in series, with the tube closest to the pump serving as a backup to determine if breakthrough occurs (OSHA, 2008; OSHA, 2010). GilAir Plus (Sensidyne, LP) personal air sampling pumps were used for both personal and area air sampling and were used to maintain a flow rate through the sorbent tube of approximately 50 mL/min. The flow rate was calibrated for each sampling pump using a Mesa Labs Bios DryCal Defender 510 primary flow meter (Mesa Labs, Inc.), using representative calibration sorbent tubes connected in series to calibrate the sampling pumps at the specified flow rate. Immediately before sampling, the ends of the sorbent tubes were scored and broken. The sorbent tubes were either placed in a tube holder or wrapped in aluminum foil to protect them from light during the sampling periods. Sorbent tubes were labeled consecutively and demarcated A and B, where B tubes served as the backup tube closest to the sampling pump. Sampling pumps were pre- and post-calibrated for each sampling day and initial and final flow rates were averaged to obtain the average flow rate for each sample. The average flow rate was then multiplied by the total sampling time to obtain the total volume of air sampled for each personal and area air sample. After the samples were collected, the tubes were immediately wrapped in aluminum foil and refrigerated until extraction occurred. Samples were extracted and analyzed within the recommended holding time of 17 days. Two pairs of field blanks were obtained for each sampling day.

Total VOC Sampling Devices

Two photoionization detectors (PIDs) were deployed to measure continuous total VOC concentrations at the roasting, grinding, and packaging stations. These detectors were a MiniRAE 3000 PID (RAE Systems, Inc.) and a Photovac 2020ppb PRO Photoionization Monitor (Photovac, Inc.). These detectors were set up to log average total VOC concentrations every 10 seconds. The PIDs were pre- and post-calibrated in the lab with isobutylene gas prior to the start and after completion of each sampling campaign. The devices' data logging histories were cleared after the end of each sampling campaign to avoid overloading the devices' memories. Due to the limited number of PIDs available, one device was placed in the roasting area for the whole of the sampling day while the other was placed at the packaging area for approximately half of the sampling day and then moved to the grinding area to capture total VOC concentrations at that station as well. The probes of the PIDs were positioned next to the respective production machines (i.e. roaster, grinder, hopper) at approximate breathing zone height and were positioned to be facing towards the work activity being performed. Tygon tubing was used to extend the length of the probe for the PID positioned next to the hopper. The PIDs were turned on and off at the same time as the other direct reading instruments in the same location and the times of the start and stop of each production activity were noted in the work task observation forms for each sampling day.

CO and CO_2 Sampling Devices

Two TSI Q-Trak Indoor Air Monitor Model 7575 direct reading instruments were used to measure continuous CO and CO_2 concentrations at the roasting, grinding, and packaging stations. These devices were set up to log average CO and CO_2 concentrations every 10 seconds. The Q-Traks were pre- and post-calibrated in the lab prior to the start and after completion of each sampling campaign. The devices were synchronized via Q-Trak Pro software to the correct date and time and data logging histories were cleared after the end of each sampling campaign to avoid overloading the devices' memories. Due to the limited number of Q-Traks available, one Q-Trak would be placed in the roasting area for the whole of the sampling day while the other Q-Trak would be placed at the packaging area for half of the sampling day and then moved to the grinding area to capture CO and CO_2 concentrations there as well. The probes of the Q-Traks were positioned next to the respective production machines (i.e. roaster, grinder, hopper) at approximate breathing zone height and were positioned to be facing towards the work activity being performed. The Q-Traks were turned on and off at the same time as the other direct reading instruments in the same location and the times of the start and stop of each production activity were noted in the work task observation forms for each sampling day.

Work Task Observation

In addition to sampling for alpha diketones, CO, CO_2, and total VOCs, daily task observation forms were completed for the production area and the café. In the production area, one member of the sampling team would sit and observe the coffee production workers as they roasted, ground, and bagged coffee beans and would record the start and stop times of each activity for the duration of the sampling day. The observer in the production area would note when each batch of coffee began roasting and when the roasted beans dropped into the cooling tray. They would also note when grinding or bagging was taking place and which worker was performing those activities. In the café area, one member of the sampling team would sit across from the counter where the baristas worked and tally the number of espresso shots the baristas were making throughout the sampling day. They would also note when the drive-thru window was open or closed.

[redacted]

Figure 3. Images illustrating where area air samples were collected in the roastery and café. Area sampled in the café included behind the café shelves to capture the background concentrations of alpha diketones in the facility (top left) and on the barista counter adjacent to the espresso grinder (bottom right). Areas sampled in the roastery were above the cooling tray of the roaster (top middle), above one of two Grindmaster grinders (bottom left), and adjacent to the chute of the hopper (bottom left) where roasted ground or whole beans drop into the machine's funnel that fills the bags.

Emissions Study Design

The purpose of the laboratory study was to quantify the range of diacetyl concentrations that various types of coffee roasts emit during grinding. White coffee, medium espresso, espresso, and French roast purchased from the roastery were ground using a Grindmaster industrial coffee grinder. The roastery uses only Arabica coffee, and the espresso blends are Central American, South American, and Indonesian coffee. The French roast is a dark roast of Columbian coffee. White coffee is the lightest roast out of the four, and is roasted at 355 °F. The medium espresso is roasted at 458 °F and the espresso is roasted at 468 °F. The French roast is the darkest roast out of the four, and is roasted at 475 °F. Emissions tests were conducted in a Plexiglas emissions test chamber located in the University of Washington's Field Research and Consultation Group's laboratory. The dimensions of the test chamber were 50.45 cm in length, 49.5 cm in width, and 75.5 cm in height for a total volume of 188.54 liters.

Assumptions made for these experiments included that there was perfect mixing of air in the chamber and there was no emissions loss other than removal by the large volume air pump. Before conducting the series of grinding experiments, preliminary, range-finding experiments were conducted to determine the optimal flow rate through the chamber such that emissions generated from grinding would be evacuated in a "reasonable" period of time (less than one hour) and the minimum mass of diacetyl require for GC/MS analysis would be collected on the sorbent tube. The simple linear regression model created in Aim 3 that predicts mean diacetyl concentrations from measured total VOC concentrations was used to predict mass of diacetyl (in ng) from total VOC concentrations. This model can be found in figure II-3 of Appendix II. Parameters used in calculations for the model can be found in Appendix II Table II-3. Based on our model, we determined that the total VOC TWA concentration during the 30-minute sampling period should be between 1,000 and 10,000 ppb. Appendix II figure II-4 shows an example annotated time series analysis plot of continuous total VOC concentrations inside the chamber during our range-finding experiment. Based on the time-series analysis plots of continuous total VOC concentrations inside the chamber, it was determined that after 30 minutes from the start of grinding greater than 90% of emissions had been evacuated from the chamber.

To determine the emission rate of diacetyl from the various coffee roasts, a Grindmaster industrial coffee grinder was placed inside the experimental chamber. A small fan was placed in the chamber and turned on during each trial to ensure that air in the chamber was well-mixed. Perfect air mixing in the chamber was assumed, as well as no loss other than removal by the large volume air pump. The chamber had a removable top that allowed access to the inside and could be sealed during the experiment. The chamber also had a sealed glove bag attached to it that allowed the user to remove the coffee grounds during the experiment. A MiniRAE 3000 PID (RAE Systems, Inc.) was used to measure total VOC emissions during grinding and was placed inside the chamber. Diacetyl was collected on sorbent tubes composed of silica gel (SKC Inc., P/N 226-183). Air sampling was performed as previously described in the field, with the exception that the GilAir Plus (Sensidyne, LP) personal air sampling pump was used to maintain a flow rate through the sorbent tube of approximately 200 mL/min. The flow rate was calibrated for each sampling pump using a Gillian Gilibrator 3 primary flow meter (Sensidyne, LP) using representative calibration sorbent tubes connected in series to calibrate the sampling pumps at the specified flow rate. Two sets of experimental blanks were obtained for each experiment by running the entire experiment without adding coffee to the system. One experimental blank was collected before any coffee grinding was done and one blank was collected after all coffee grinding was completed. Two field blanks (tubes without air drawn through them) were obtained for each experiment. The sorbent tube samples were co-located with the MiniRAE's sampling probe in the chamber.

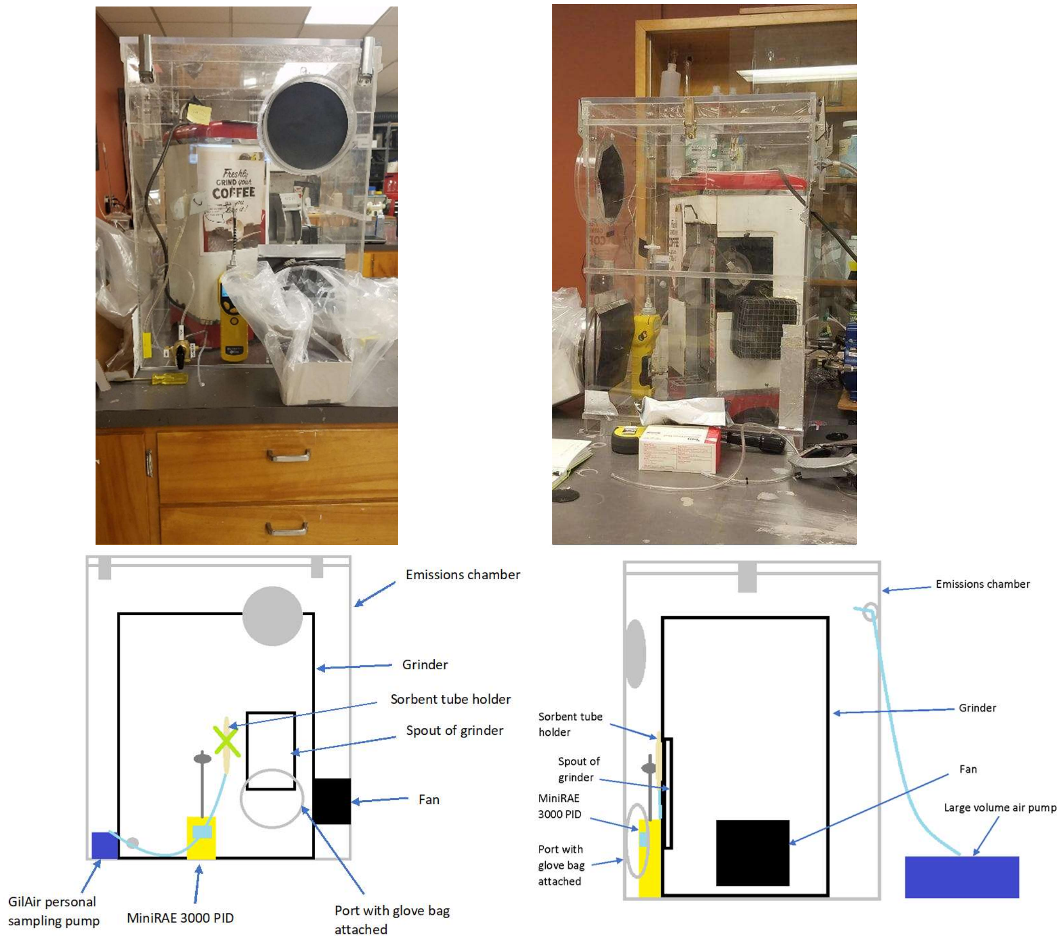


Figure 4. The top two pictures demonstrate the setup for the grinding experiments. The bottom two images are rough sketches (not to scale) of the setup of the grinding experiment illustrating where labeled components were relative to the emissions chamber. The left image is a front view of the setup and the right image is a right-side view of the setup.

The grinder was placed in the emissions chamber that was equipped with a glove bag to facilitate removing the ground beans from the chamber. The yellow MiniRAE 3000 PID was placed so the probe was adjacent to the spout where the ground beans pour out of the grinder. The sorbent tubes attached to a GilAir Plus personal sampling pump (not pictured) would have been taped in place to the right of the PID, adjacent to the grinder's spout and at approximately breathing zone height.

At the start of each experimental trial, the MiniRAE and the sorbent tubes were placed in the experimental chamber in the headspace of where the ground coffee would dispense from the machine. A large volume air pump was attached to the chamber and drew air from outside the chamber through the system at a rate of 30 L/min. This air pump was calibrated using a Gillian Gilibrator 3 (Sensidyne, LP) primary flow meter. The primary flow meter was connected in series between the large volume air pump and the emissions chamber. The pump was pre- and post-calibrated for each set of experiments and initial and final chamber flow rates were averaged to obtain the average chamber flow rate for each trial.

For each trial, 8 oz (approximately 227 g) of coffee beans were poured into the grinder, a container was placed under the grinder's spout to catch the grinds, and the top of the experimental chamber was sealed. The grinder was then turned on, the beans were ground, and the grinder continued to operate for 5 minutes after the grinding was completed, to mimic the process utilized at the coffee roastery where field work was conducted. After those 5 minutes, the grinds were removed from the chamber via the glove bag. Each trial ended after 30 minutes had passed from the start of grinding. Each experiment consisted of three trials, for a total of three samples, two experimental blank samples, and two field blanks.

Sample Analysis

Diacetyl and 2,3-pentanedione Sample Analysis

The analysis of diacetyl and 2,3-pentanedione was undertaken by the University of Washington's Environmental Health Laboratory and followed OSHA Methods 1013/1016 with some modifications (LeBouf, 2017; OSHA, 2008; OSHA, 2010). Each sorbent tube's front and back silica gel sorbent layer was transferred into a labeled 4 mL amber vial and the filter and front and back glass wool of the tube were discarded. 2 mL of 5% methanol/acetone containing 2.5 μL/mL of internal standards (ISTD) 2,3-butanedione-d^6 neat and 25 µL 2,3-pentanedione-1,1,1,4,4-d^5 neat were added to each vial for extraction. Samples were extracted on a rotator for

60 minutes and an approximate 200 - 300 μL aliquot of the solution was then transferred to a 1.8 mL amber gas chromatography vial with the remainder stored at -20 °C. The samples were analyzed with gas chromatography-mass spectrometry (GC/MS). Quality assurance samples consisting of spiked sorbent with ISTD and media blanks consisting of only sorbent material were extracted with each batch of samples. Diacetyl and 2,3-pentanedione recoveries were determined by analyzing sorbent tubes spiked with of 2, 12, and 122 ng/mL of diacetyl and 2, 11, and 115 ng/mL of 2,3-pentanedione corresponding to low, medium, and high spike values, respectively. Calibration standards in the range 0.6 – 1200 ng/mL were analyzed and calibration curves were calculated using linear regression ($R^2 > 0.99$) and applied to calculate analyte concentrations in the air samples collected.

Table II-2 in the Appendix II lists the two analytes of interest (diacetyl and 2,3-pentanedione) and their corresponding quality control data from the sampling campaign (observational) and the emissions experiments (laboratory). This includes average spike recovery percentage, recovery relative standard deviation (RSD), and limit of detection (LOD) values. Detection limits (in ppb) were determined for diacetyl and 2,3-pentanedione by dividing 0.1 ng by the lowest air volume associated with a non-detectable sample. While the average spike recovery percentage is reported, recovery was not corrected for in determining analyte concentrations in the air samples collected. There was sufficient variability in the reported recovery values that it was not clear that it was appropriate to correct each sample using a single value.

Total VOC Sample Analysis

At the end of each sampling day or grinding experiment, the total VOC data that was logged by the MiniRAE and Photovac instruments was downloaded using each device's software

- ProRae Studio II and ProComm, respectively. The data from both instruments was exported to Excel spreadsheets and each dataset was labeled with its appropriate sampling date.

CO and CO_2 Sample Analysis

Similar to the total VOC analysis, at the end of each sampling day, the CO and CO_2 data that was logged by the Q-Trak instruments was downloaded using TSI's TrakPro II software. The data was exported to an Excel spreadsheet and each dataset was labeled with its appropriate sampling date.

Data Analysis

Diacetyl and 2,3-pentanedione Data

The results from the GC/MS analysis of the air samples collected in the roastery and café provided the masses of diacetyl and 2,3-pentanedione per sample. The mass of each compound on the front and back tubes were added together to get the total sample mass in nanograms (ng). This mass was then converted from nanograms to micrograms and then divided by the total volume of air that was sampled by each sampling pump to result in an air concentration in micrograms per cubic meter for both diacetyl and 2,3-pentanedione. This mass concentration was then converted into concentration by volume in parts per million by multiplying the mass concentration by 0.0821 L atm mol^{-1} K^{-1} and the temperature in Kelvin of either the roasting room or the processing/barista area depending on the location of the sample. The product of this was then divided by the pressure of either room in atmospheres and the molecular weight of either diacetyl or 2,3-pentanedione in grams per mole. Finally, this concentration by volume in parts per million was converted into parts per billion to facilitate easy comparison to the RELs, which are also in parts per billion (ppb).

Following the analysis by GC/MS, the data for the samples were reviewed for errors. If an error was present, a flag was assigned to the sample that corresponded to the particular error. Errors included the difference in air flow at the start of the sampling period and at the end being larger than 10%, the mass of diacetyl or 2,3-pentanedione in an individual tube being less than the limit of detection (LOD; 1 ng), and the mass of the sample on the backup tube being more than 10% of the total mass of the sample, indicating oversaturation occurred. In three samples, high levels of alpha diketones on the backup tubes were detected as a result of the plastic tubing between the front and back tubes coming off and disconnecting the sampling train during the sampling period. The back tube was still connected to the air sampling pump, so air continued to flow through the back tube. None of our samples where disconnection did not occur demonstrated breakthrough, so we can be confident that breakthrough did not occur in the tubes where the sampling train disconnected. Samples where disconnecting did occur were removed from subsequent analyses.

The data analysis of diacetyl collected in the grinding experiments was similar to the analysis stated above. The mass of diacetyl on the front and back tubes were added together to get the total sample mass in nanograms (ng). To determine the mass emission rate of diacetyl per sample, the total sample mass of diacetyl in nanograms was multiplied by the ratio of the total air volume pulled through the chamber, divided by the air volume pulled through the sorbent tube. This product was then divided by the grams of coffee ground per experiment to get the mass emission rate in units of ng diacetyl per gram of ground coffee.

To determine the concentration of diacetyl emitted during each experimental trial, the total sample mass in nanograms was then converted from nanograms to micrograms and then divided by the total volume of air that was sampled by the personal sampling pump to result in an air concentration in micrograms per cubic meter for diacetyl. This mass concentration was then converted into concentration by volume in parts per million by multiplying the mass concentration by 0.0821 L atm mol^{-1} K^{-1} and the temperature in Kelvin of the Field Research and Consultation Group's laboratory. The product of this was then divided by the room pressure of the laboratory and the molecular weight of diacetyl in grams per mole. Finally, this concentration by volume in parts per million was converted into parts per billion to facilitate easy comparison to the RELs, which are also in parts per billion (ppb).

Statistical Analysis Based on Specific Aims

Aim 1 of this study was to characterize the exposures of production employees who operate in the coffee roasting, packaging, and grinding areas of the roastery and compare full-shift time-weighted average exposures to NIOSH and ACGIH recommended exposure levels for diacetyl and 2,3-pentanedione. Because the full-shift sampling periods were less than eight hours in total for each day of sampling, eight-hour time weighted average diacetyl and 2,3-pentanedione concentrations were calculated for each day of sampling based on two exposure scenarios. The first assumed zero exposure for the remainder of the eight hours, because in most cases the employee was either finished with coffee processing tasks for the day or the employee went offsite to make deliveries for the remainder of their shift. The second scenario assumed that there was steady exposure for the remainder of the eight hours and would represent a time-weighted average exposure if the worker were to continue their coffee production tasks for a full eight hours.

Aim 2 of this study was to determine which parts of the coffee production process are associated with the highest alpha-diketone emissions. Summary statistics for diacetyl and 2,3-pentanedione concentrations measured at each sampling location were calculated, including sample sizes, arithmetic means, medians, standard deviations, and ranges (5th - 95th percentiles). Finally, bar charts with error bars were created which displayed the average and standard deviations of diacetyl and 2,3-pentanedione emissions measured at each sampling location.

Aim 3 of this study was to determine the extent to which lower cost direct reading instruments can serve as surrogate measurements for diacetyl concentrations. Medians and ranges (minimum - maximum) of CO, CO_2, and total VOC emissions measured at each sampling location were calculated to fulfil the first part of this aim. The second part of this aim was focused on using linear regression to determine which direct reading measurement was the best indicator for diacetyl emissions. Microsoft Excel software was used to create simple linear regression models that correlated median CO, CO_2, or total VOC source-based area concentrations measured at each sampling location to corresponding median diacetyl concentrations measured at that same location. Additionally, simple linear regression models were created that correlated median CO, CO_2, or total VOC emissions to corresponding diacetyl emissions measured at all sampling locations as a whole. P-values and R^2 values were determined for each model and were compared across the three indicators to determine which one was the best indicator for diacetyl emissions. 95% confidence intervals for predicted average diacetyl concentrations at given total VOC concentrations were created using the “predict” function in the R software package to determine if the linear regression model had the ability to determine if diacetyl air concentrations were elevated compared to the NIOSH REL and the ACGIH TLV.

Aim 4 of this study was to quantify the effect that roast type has on diacetyl emissions during grinding. Arithmetic mean, 5th, and 95th percentiles of total VOC and diacetyl emissions were calculated for each roast type ground. Diacetyl mass emission rates were calculated for each set of grinding experiments and these values were compared across the different roast types. A one-way ANOVA test with a significance level of $\alpha = 0.05$ was utilized to determine if there was a significant overall difference in mean diacetyl mass emission rates by roast type. The hypotheses associated with this aim were H_0: $\mu_w = \mu_{me} = \mu_e = \mu_{fr}$ vs. H_a: not all μ's are equal, where μ_w = mean diacetyl mass emission rate for white coffee, μ_{me} = mean diacetyl mass emission rate for medium espresso, μ_e = mean diacetyl mass emission rate for espresso, and μ_{fr} = mean diacetyl mass emission rate for French roast. The F statistic and p-value from this test were reported and conditional on the ANOVA test showing test showing significant differences, post-hoc Tukey HSD pairwise comparisons (with a Bonferroni-adjusted significance level of α = 0.01) of the mean diacetyl concentration for each location were carried out to determine significant differences in mean diacetyl emission rates between specific roasts. Finally, the paired diacetyl and total VOC emissions measured during the grinding experiments were added to the measurements at the roastery to update the regression model predicting diacetyl emissions from total VOC emissions.

Results

The table below summarizes the number of samples collected during the course of the sampling campaign at the coffee roastery and associated café. The top row indicates the sampling location while the leftmost column indicates the number of samples taken at that location for each analyte of interest. Half-day direct reading measurements were taken at the hopper and the grinder due to limitations on the amount of equipment available. In the morning, a TVOC, CO, and CO_2 samples were taken at the hopper for about four hours, and then the equipment was moved to the grinding location in the afternoon. While four days of sampling took place during the campaign, there were some issues with downloading data from the direct reading instruments that resulted in data loss during the beginning of the campaign. These issues were identified and resolved by the end of the sampling campaign. The number of sorbent tube samples taken at the grinder were approximately half of the other locations due to the amount of time spent packaging beans as compared to grinding on a typical sampling day. We were able to obtain two two-hour area samples at the hopper on each day of sampling, but by the time the sampling equipment was moved to the grinders in the afternoon, the workers would only have about two hours left of grinding to do. For each day of sampling, we were only able to obtain one two-hour area sample at the grinder.

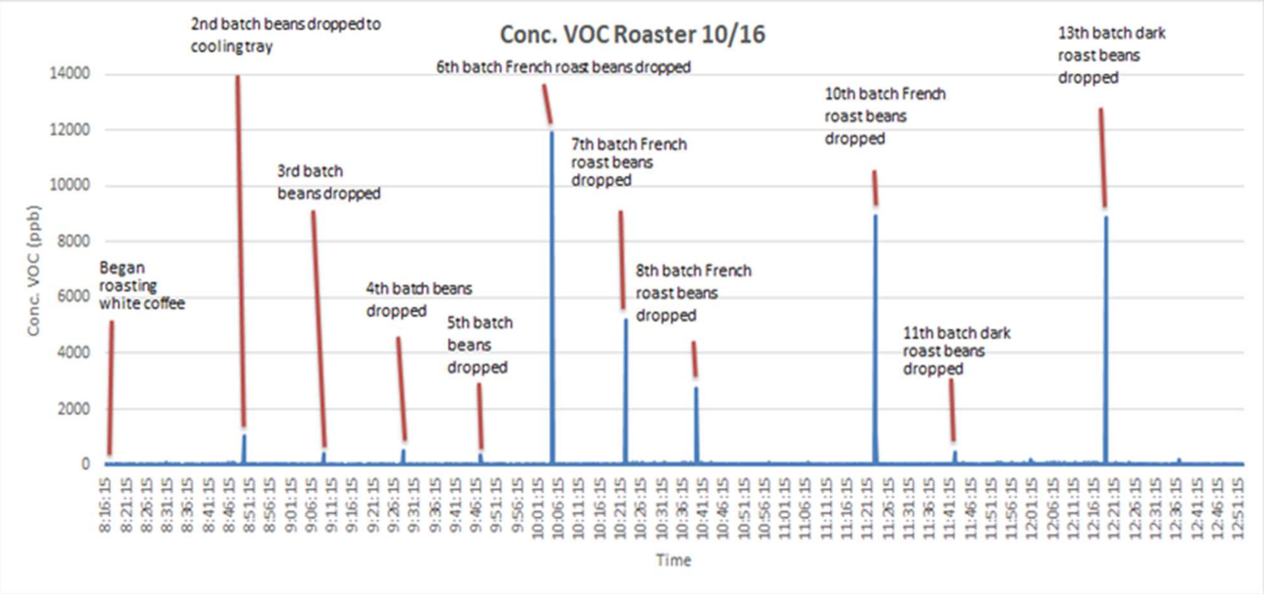
Table 3

Summary of Sampling Campaign

	Roaster	**Grinder**	**Hopper**	**Barista**	**Background**
No. of sorbent tube samples	8	4	8	7	8
No. of TVOC samples	4 full-day	3 half-day	3 half-day	1 half-day	2 full-day
No. of CO & CO_2 samples	3 full-day	3 half-day	3 half-day	None	None

Time-Series Analysis

Time-series analysis graphs of CO, CO_2, and total VOC emissions measured at each sampling location were created for each day of sampling in order to better understand where in the coffee production process peaks in emissions were occurring. All time-series analysis graphs can be found in Appendix III. Figure 5a is one example of such a graph and shows the continuous concentration of total VOCs at the roasting station during one day of sampling. In this graph, peaks occurred when the roaster dumped the beans into the cooling tray as illustrated in Figure 5b. Overall, this graph demonstrates the effectiveness of the roaster's afterburner in controlling emissions, as these are relatively low concentrations. Moreover, this is a self-limiting emission, as the process of cooling the beans is relatively quick and the emissions dissipate quickly.



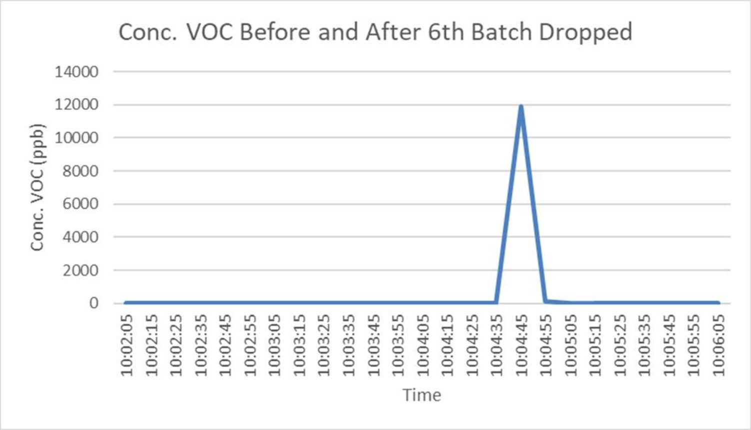


Figure 5a. Time-series analysis graph of total VOC emissions measured at the roaster on October 16, 2019. Peaks in the graph occurred when the roasted beans were expelled from the roasting chamber into the machine's cooling tray. The bottom chart shows the continuous concentration of total VOCs before and after the sixth batch of French roast beans dropped into the machine's cooling tray. The concentration quickly returns to background after the batch drops. Each of these peaks represent one ten-second average total VOC concentration measured by the PID.

Figure 5b. After the roasting is completed, the beans are automatically dropped from the roasting chamber into the machine's cooling chamber to cool before further processing.

Figure 6 shows the continuous concentration of total VOCs at the grinding station measured on October 29, 2019. Compared to the graph in Figure 5a, there is more variability in total VOC emissions at the grinding station than at the roaster. During the first part of this day (prior to ~ 2:30pm), white coffee was ground in a smaller grinder of the type that is commercially available at grocery stores. Grinding white coffee released much less total VOC emissions compared to grinding darker roasts. This may be because white coffee is roasted at low temperatures (around 353 °F) which may not be high enough to drive the Maillard reaction and subsequent formation of volatile organic compounds from the reaction of amino acids and sugars. The smaller grinder also processes a smaller coffee mass than the other grinders, which may be another factor in why total VOC emissions for white coffee were lower than those of the darker roasts. The emissions experiments will be able to quantify this difference in mass emissions.

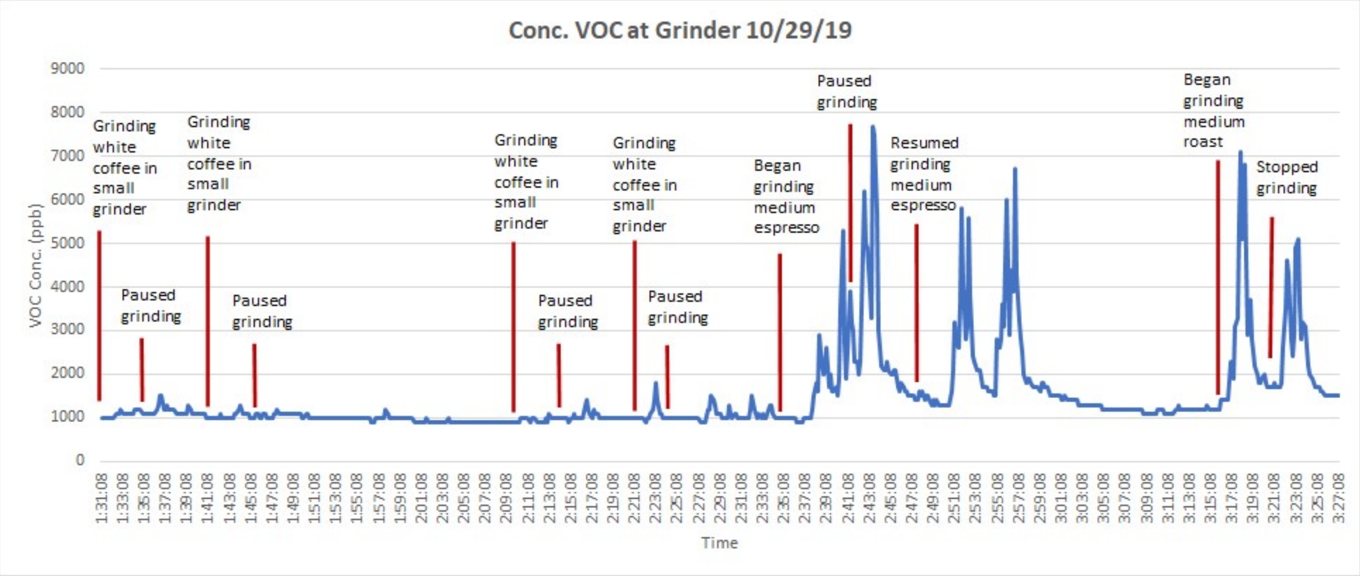


Figure 6. Time-series analysis graph of total VOC emissions measured at the grinding station on October 29, 2019. VOC emissions were lower when white coffee was ground compared to when darker roasts were ground.

Figure 7 shows the continuous concentration of total VOCs at the packaging station measured on October 30, 2019. Similar to the grinding station, compared to the graph in Figure 5a, there is more variability in total VOC emissions at the packaging station than at the roaster. There are also higher emissions of total VOCs at the packaging station than at the roaster or grinder and higher emissions of total VOCs when ground beans are being packaged compared to whole beans. This is consistent with findings from previous studies which have shown that VOCs created during roasting are not released in significant amounts until the structural integrity of the bean is compromised by grinding (Gaffney et al, 2015).

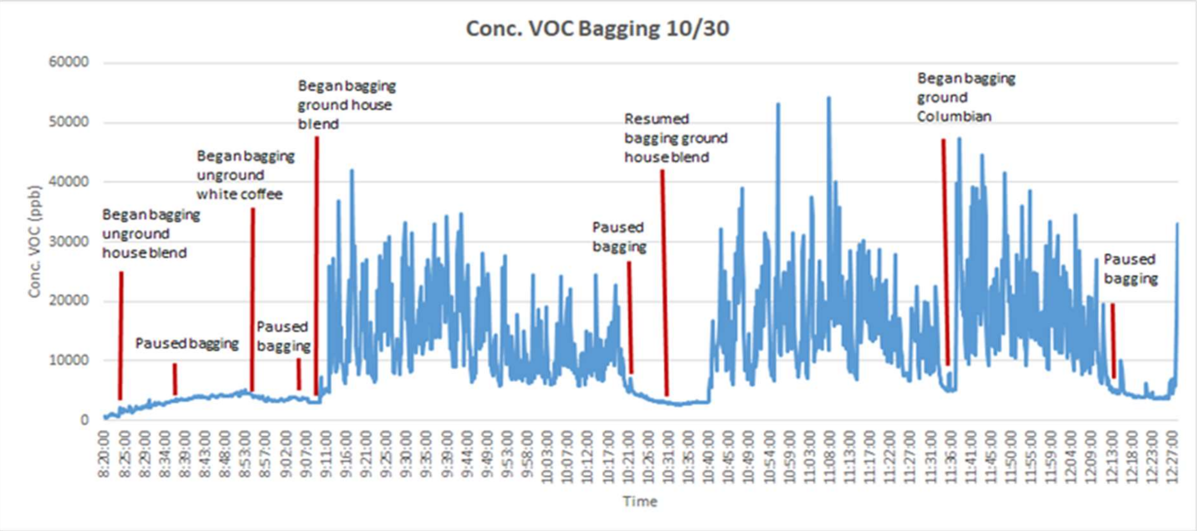


Figure 7. Time-series analysis graph of total VOC emissions measured at the packaging station on October 30, 2019. Total VOC emissions were higher when ground beans were packaged compared to when whole beans were packaged.

Aim 1

Employee Exposure Monitoring Results

This study evaluated two coffee roaster employees' exposures to diacetyl and 2,3-pentanedione on October 15, 16, 29, and 30, 2019. These employees worked in the roastery's coffee roasting and processing areas. Table 4 summarizes the 8-hour time-weighted average (TWA) personal exposures of these workers on each day of sampling and compares these values to the NIOSH and ACGIH recommended exposure limits and threshold limit values for these chemicals.

Assuming no exposure for the remainder of the eight hours, during coffee production diacetyl exposures were elevated compared to NIOSH and ACGIH 8-hour recommended exposure levels (Table 4). Five of seven samples exceeded the NIOSH 8-hour recommended exposure level for diacetyl. Three of seven samples exceeded the ACGIH 8-hour recommended exposure level for diacetyl. One four-hour sample also exceeded the ACGIH short-term exposure level for diacetyl (20 ppb) with an exposure of 21.0 ppb. One 2,3-pentanedione exposure that exceeded the NIOSH 8-hour exposure level, but none exceeded the NIOSH or ACGIH short-term exposure levels.

Assuming steady exposure to diacetyl and 2,3-pentanedione for the remainder of an eight-hour shift, six of seven samples would have exceeded the NIOSH 8-hour recommended exposure level for diacetyl. Five of seven samples would have exceeded the ACGIH 8-hour recommended exposure level for diacetyl. One four-hour sample also would have exceeded the ACGIH and NIOSH short-term exposure level for diacetyl (20 and 25 ppb, respectively) with an exposure of 39.0 ppb. Three of seven samples would have exceeded the NIOSH 8-hour exposure level for 2,3-pentanedione, but none would have exceeded the NIOSH short-term exposure level. These exposures also represent the actual exposure to diacetyl and 2,3-pentanedione over the task monitoring period.

Overall, 2,3-pentanedione exposures were less than diacetyl exposures by approximately 50-70%. Furthermore, on days where workers were doing more grinding and packaging ground beans, their exposures to diacetyl and 2,3-pentanedione were higher compared to days where they were doing less grinding and packaging. For example, workers ground coffee for only about an hour total on October 29th and packaged only whole beans for about three hours total, whereas on October 15th workers ground coffee for about two hours total and packaged only ground beans for almost five hours. These differences in amount of time spent on production activities and the type of product being processed (i.e. whole versus ground beans) may explain why diacetyl and 2,3-pentanedione exposures were much higher on October 15th than they were on October 29th.

Table 4

Diacetyl and 2,3 – Pentanedione Personal Exposure Results

October 15, 16, 29, and 30, 2019

Sample Date	**Sample Duration (min)**	**Diacetyl No Exposure 8-hr TWA[1] (ppb)**	**Diacetyl Steady Exposure* 8-hr TWA[1] (ppb)**	**2,3-Pentanedione No Exposure 8-hr TWA[1] (ppb)**	**2,3-Pentanedione Steady Exposure* 8-hr TWA[1] (ppb)**
10/15	238	9.1	18.3	4.8	9.6
10/15	316	21.0	31.9	11.4	17.3
10/16	408	13.4	15.8	5.8	6.9
10/16	352	8.2	11.2	3.5	4.8
10/29	148	1.9	6.3	0.9	3.0
10/29	329	1.0	1.5	0.5	0.68
10/30	359	13.7	18.3	7.6	10.2
Average (SD)	307 (87)	9.8 (7.0)	14.8 (9.8)	4.9 (3.8)	7.5 (5.5)
Reference Values					
NIOSH[2] REL		**5**		**9.3**	
ACGIH[3] TLV		**10**		**N/A**	

*Actual exposure determined over the sample duration
[1]TWA: Time-weighted average exposure
[2]NIOSH REL: National Institute for Occupational Safety and Health Recommended Exposure Limit (REL)
[3]ACGIH TLV: American Conference of Governmental Industrial Hygienists Threshold Limit Value (TLV)

Aim 2

The purpose of this aim was to determine which parts of the coffee production process are associated with the highest alpha-diketone emissions. Table 5 presents summary statistics for diacetyl and 2,3-pentanedione emissions measured at each sampling location. Figures 8 and 9 present histograms showing arithmetic mean and standard deviations of diacetyl and 2,3-pentanedione emissions for each area sampled.

Area concentration measurements can be useful in determining what work processes are contributing to heightened exposure levels. As shown in Figures 8 and 9 and in the table below, diacetyl and 2,3-pentanedione source-based area concentrations were highest at the hopper, followed by the grinder, roaster, barista, and background areas. Overall, diacetyl emissions were approximately 50% higher than 2,3-pentanedione emissions. Area measurements of diacetyl and 2,3-pentanedione collected in the barista and café were consistently below NIOSH and ACGIH recommended exposure guidelines, indicating that exposure of café workers and customers were below levels of concern. In contrast, median levels of diacetyl and 2,3-pentanedione at the hopper and the grinder exceeded the NIOSH and ACGIH recommended exposure guidelines, and median levels of diacetyl at the roaster exceeded the NIOSH REL. These data suggest that workers near the hopper and the grinder in particular are at risk to be exposed to hazardous levels of diacetyl and 2,3-pentanedione, consistent with our measurements of exposure on the two roastery workers which were described above.

Table 5

Summary of Diacetyl and 2,3-Pentanedione Area Concentrations

Analyte Concentration (median; 5th - 95th percentile) N = # of sorbent tubes	**Roaster**	**Grinder**	**Hopper**	**Barista**	**Background**
Diacetyl (ppb)	**7.5** (1.2 - 39.1) N = 8	**57.3** (7.0 - 105) N = 4	**172** (10.6 - 315) N = 8	**3.1** (0.28 - 9.1) N = 7	**2.0** (0.56 - 2.9) N = 8
2,3-Pentanedione (ppb)	**3.5** (0.52 - 21.2) N = 8	**21.0** (3.4 - 56.6) N = 4	**110** (5.3 - 187) N = 8	**1.5** (0.11 - 4.4) N = 7	**0.89** (0.25 - 1.5) N = 8

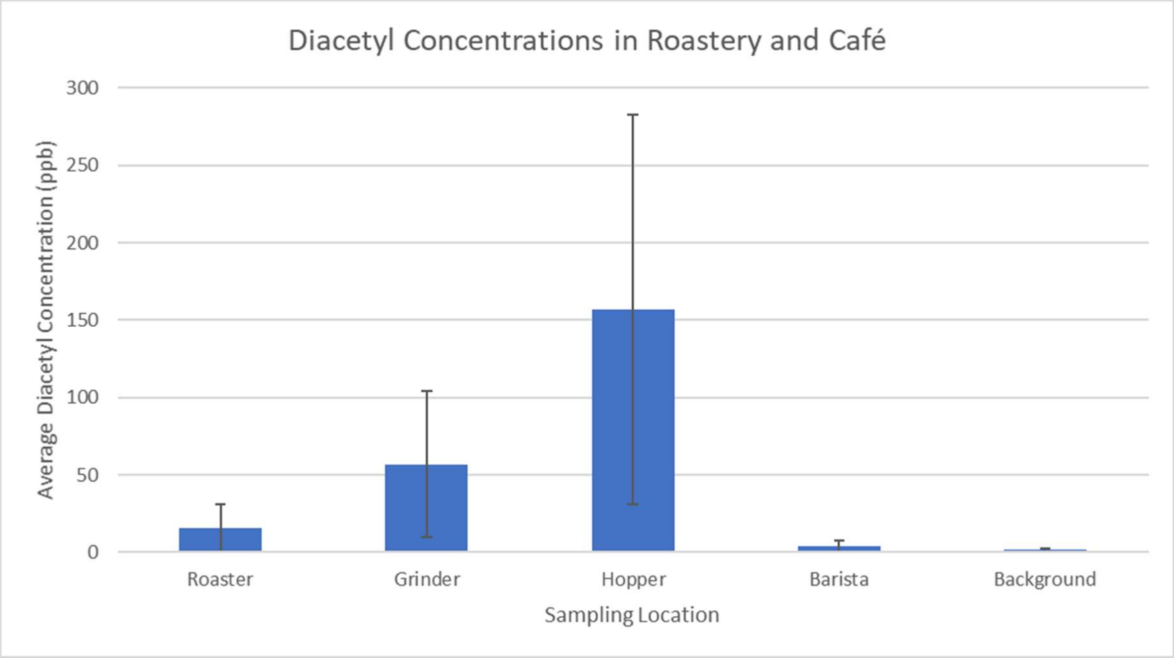


Figure 8. Bar chart of arithmetic mean and standard deviations of diacetyl concentrations by sampling location.

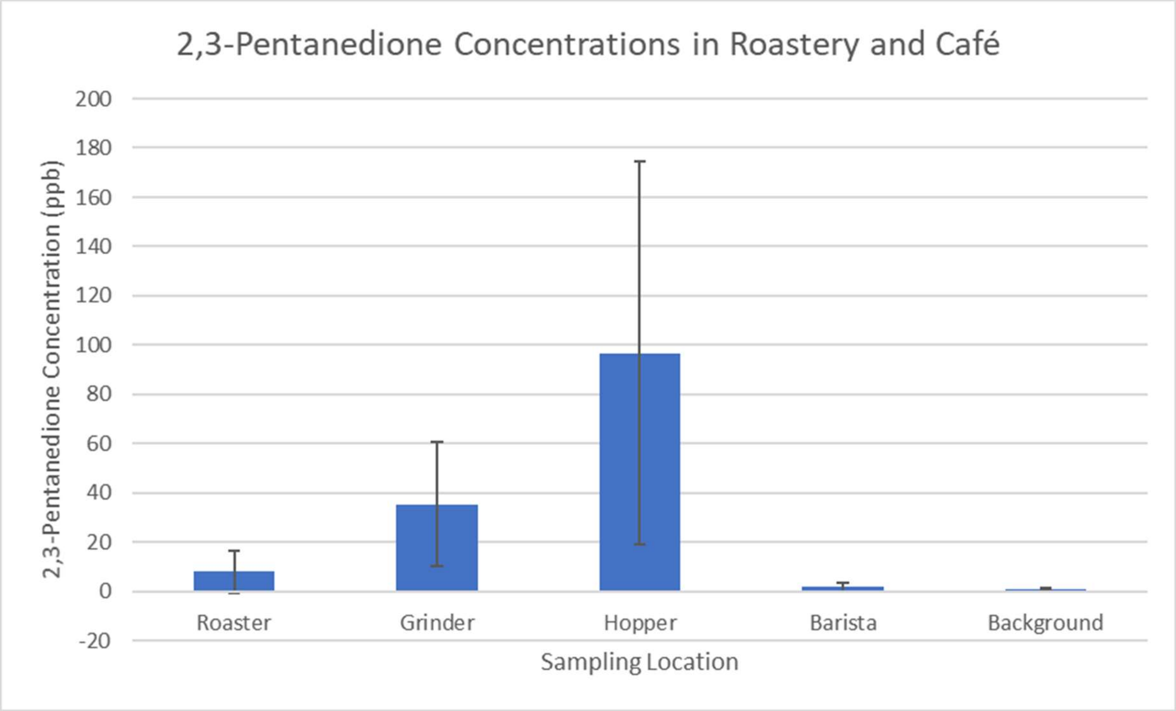


Figure 9. Bar chart showing arithmetic mean and standard deviations of 2,3-pentanedione concentrations by sampling location.

Aim 3

The purpose of aim 3 of this thesis was to determine the extent to which direct reading measurements of CO, CO_2, or total volatile organic compounds could serve as a lower cost surrogate indicator for diacetyl air concentrations at a given coffee production area. Table 6 below summarizes area emissions of CO, CO_2, and total volatile organic compounds at each sampling location.

Table 6

Summary of CO, CO_2, and Total VOC Area Concentrations

Analyte Concentration (median; minimum-maximum) N = # of half-days of sampling	**Roaster**	**Grinder**	**Hopper**	**Barista**	**Background**
CO (ppm)	**13.1** (1.6 – 14.3) N = 6	**16.4** (<LOD – 27.9) N = 3	**17.6** (1.8 – 21.5) N = 3	NM*	NM
CO_2 (ppm)	**801** (470 - 840) N = 6	**711** (580- 970) N = 3	**1100** (910 - 1100) N = 3	NM	NM
Total VOC (ppb)	**65** (20 - 420) N = 6	**3400** (1100 - 3600) N = 3	**7000** (1300 - 9300) N = 2.5	**<LOD** N = 0.5	**<LOD** N = 3

* NM: not measured

Similar to diacetyl and 2,3-pentanedione emissions, CO, CO_2, and total volatile organic compound emissions were highest at the hopper, followed by the grinder and roaster areas. Median CO and CO_2 concentrations measured at each sampling location were well below OSHA PELs of 50 and 5,000 ppm, respectively (OSHA, Annotated PELs). The American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE), a professional association, recommends that steady-state CO_2 concentrations indoors should be maintained at no more than about 700 ppm greater than the concentration found outdoors (ASHRAE). This recommendation is based on ensuring comfort, rather than preventing negative health effects. The typical outdoor concentration ranges from about 300 to 500 ppm, so acceptable concentrations of CO_2 indoors would range from 1000 to 1200 ppm (ASHRAE). None of the CO_2 concentrations measured were above this range. The median total volatile organic compound emissions were 3200 (5th - 95th percentile = 1100 - 24000), 2800 (5th - 95th percentile = 1000 - 14000), and 70 (5th - 95th percentile = <LOD - 700) ppm for the hopper, grinder, and roaster, respectively. Median and 95th percentile concentrations of total volatile organic compounds in air were less than the instrument's limit of detection at both the barista and background areas.

Simple linear regression models that correlated direct reading measurements to diacetyl air concentrations were created for each indicator (i.e. for CO, CO_2, and total volatile organic compounds) using data pooled from each location sampled. The R^2-value generated for each model was used as a measure of how successful the regression was in explaining the response (Baldi et al, 2013).

Plots of the relationships between the indicator variables and diacetyl air concentrations for all the sampling locations combined are shown in figures 10 - 12 below. Out of the three linear regression models created, the model using the air concentration of TVOCs as a predictor for air concentrations of diacetyl had the highest R^2-value ($R^2 = 0.95$, p-value = $4.8 * 10^{-15}$), followed by the model using CO_2 ($R^2 = 0.58$, p-value = 0.001), and the model using CO as an indicator for diacetyl air concentrations ($R^2 = 0.09$, p-value = 0.34). Moreover, when the relationship between air concentrations of diacetyl and TVOCs is broken down by sampling location, the relationship was the same for the two areas with the highest emissions - the packaging area and the grinding area (as shown in Figures 13 and 14). The slopes and R^2-values for the models predicting diacetyl air concentrations from TVOC air concentrations at the grinding and packaging area are very similar (for the grinding area: slope = 0.017, $R^2 = 0.98$, p-value = 0.1; for the packaging area: slope = 0.019, $R^2 = 0.98$, p-value = 0.001).

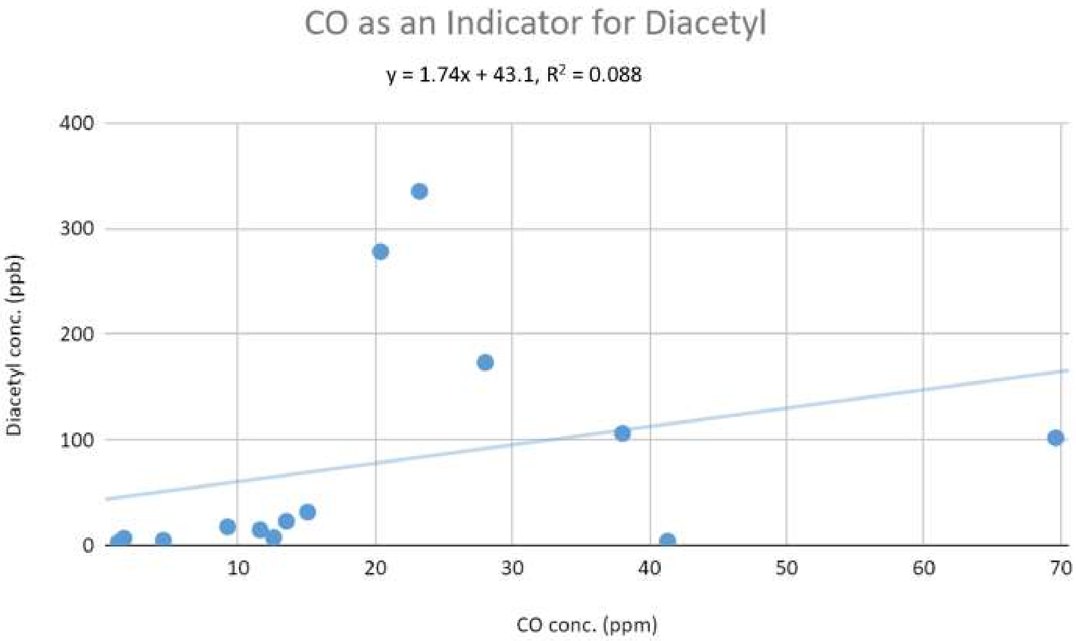


Figure 10. Scatterplot showing correlation between CO and diacetyl air concentrations measured at all sampling locations.

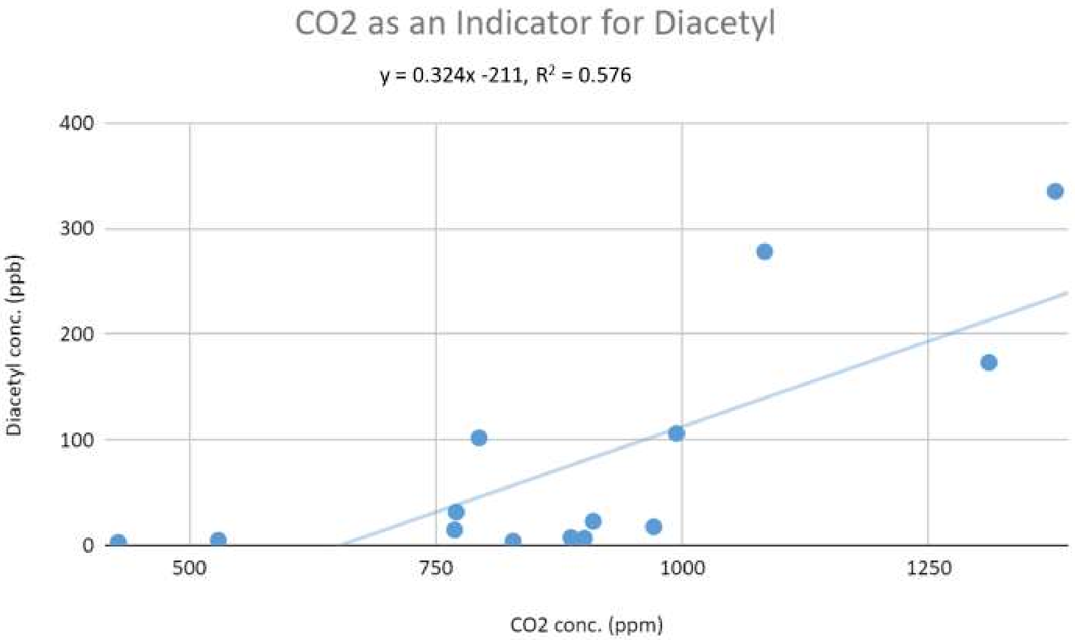


Figure 11. Scatterplot showing correlation between CO_2 and diacetyl air concentrations measured at all sampling locations.

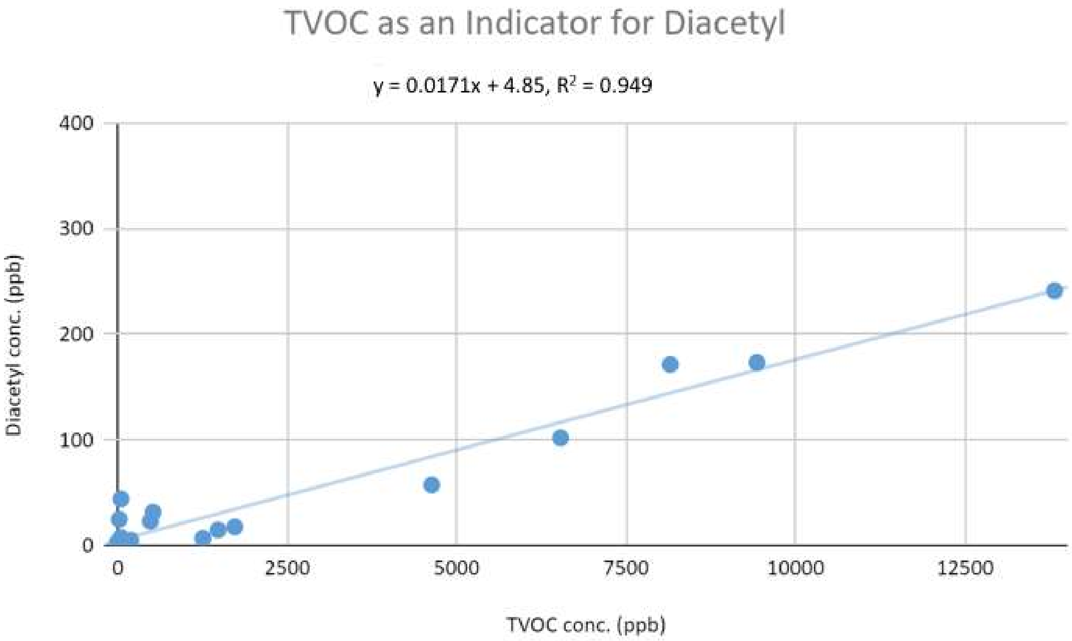


Figure 12. Scatterplot showing correlation between total volatile organic compounds and diacetyl air concentrations measured at all sampling locations.

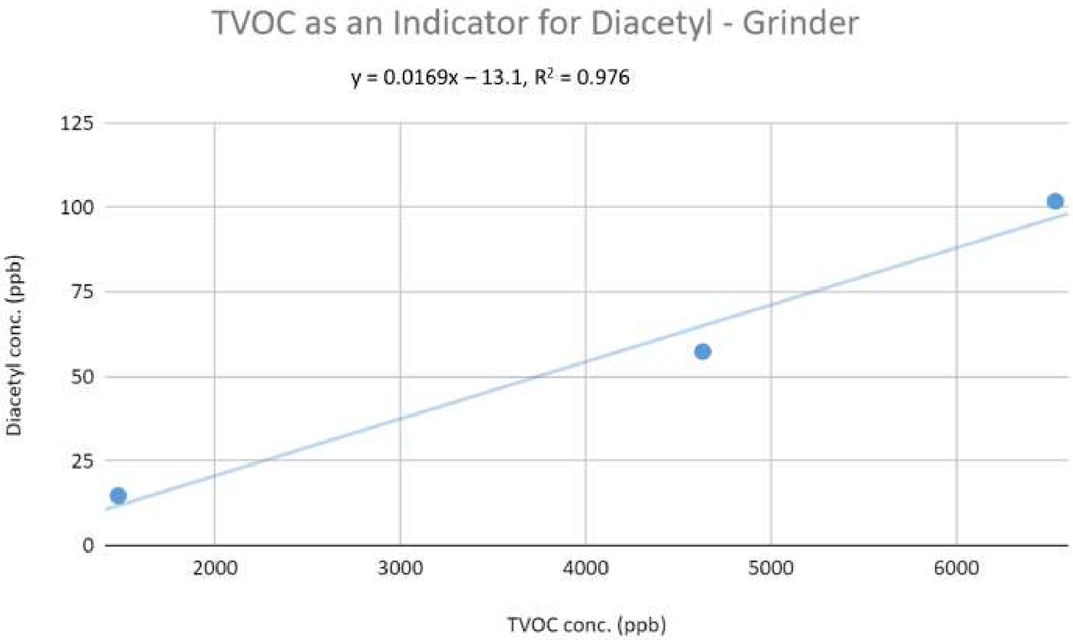


Figure 13. Scatterplot showing correlation between total volatile organic compounds and diacetyl air concentrations measured at the coffee grinding area.

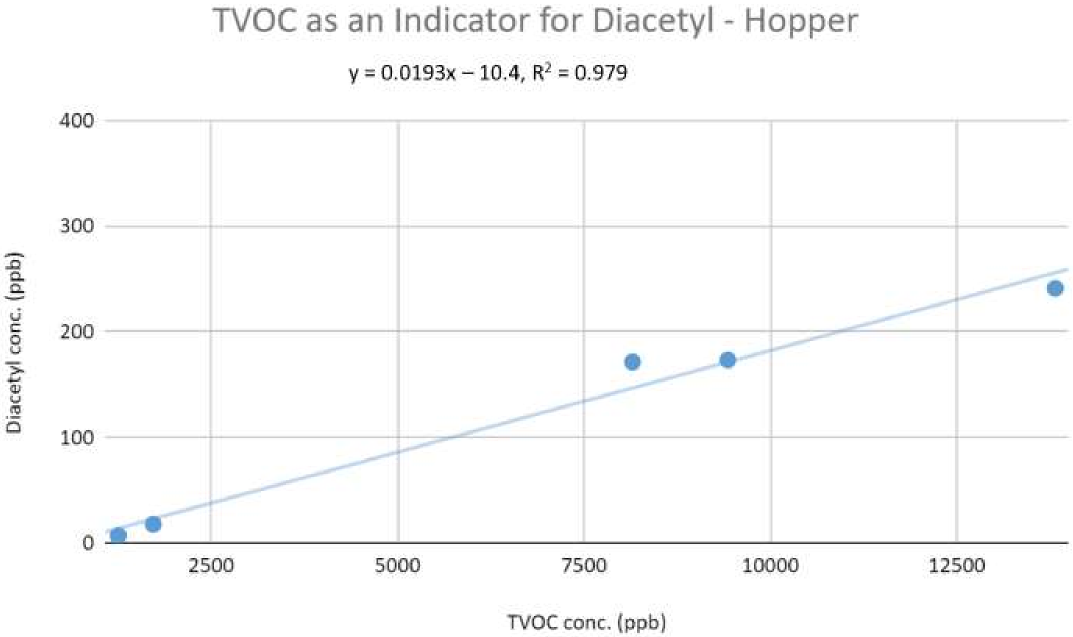


Figure 14. Scatterplot showing correlation between total volatile organic compounds and diacetyl air concentrations measured at the coffee packaging area.

In addition to quantifying the diacetyl mass emission rates for the various types of coffee roasts, total VOC emissions were also measured and co-located with the sorbent tube samples during the course of the grinding experiments in order to be able to add these additional data points to the regression model correlating total VOC emissions with diacetyl emissions that was created in Aim 3. A plot of the relationship between total VOC air concentrations and diacetyl air concentrations for all the sampling locations at the roastery and from the grinding experiments is shown in Figure 15.

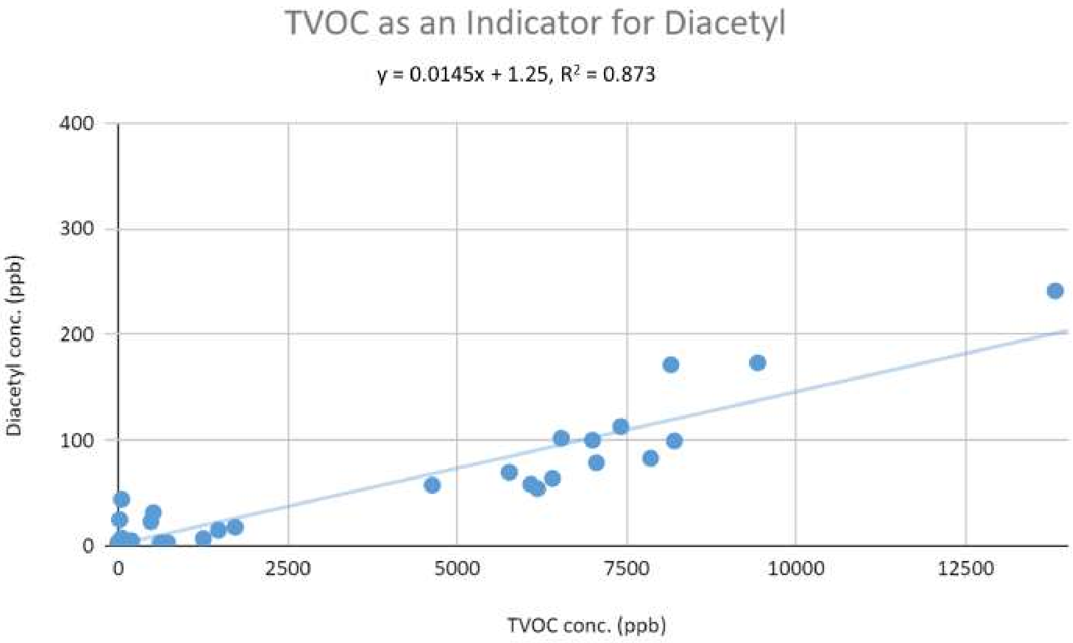


Figure 15. Scatterplot showing correlation between total volatile organic compounds and diacetyl air concentrations measured at all sampling locations at the roastery and from the grinding experiments.

While the R^2-value decreased slightly with the addition of the data points from the grinding experiments (from $R^2 = 0.95$ to $R^2 = 0.88$, p-value = $2.32 * 10^{-16}$), this value is still higher than the R^2-values from the linear regression models that use CO or CO_2 as indicators for diacetyl air concentrations. Moreover, as shown in Figure 18, when the relationship between air concentrations of diacetyl and total VOCs is again broken down by sampling location, the relationship was still similar between grinding process and the pooled data with the addition of the data points from the grinding experiments (for the grinding process: slope = 0.013, $R^2 = 0.89$, p-value = $1.545 * 10^{-7}$).

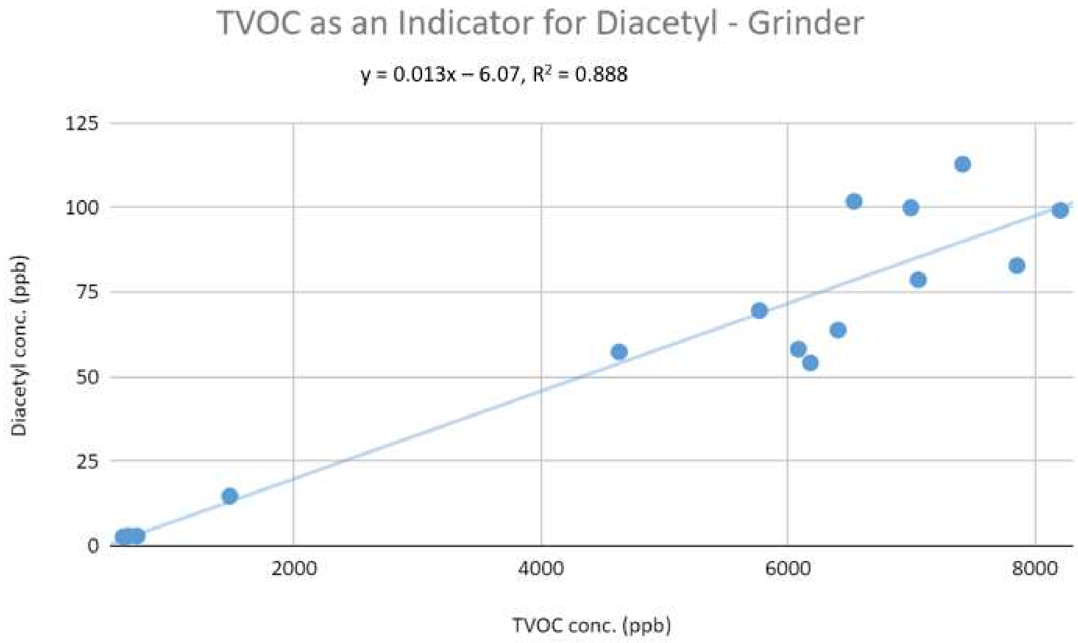


Figure 16. Scatterplot showing correlation between total volatile organic compounds and diacetyl air concentrations measured at the coffee grinding area of the roastery and during the grinding experiments.

The model in figure 15 can be used to estimate the mean diacetyl concentration in ppb for a given total VOC concentration. A 95% confidence interval around this estimate can give a margin of error that tells us how precise this estimate is. Table 7 uses the model in figure 15 to estimate mean diacetyl concentrations for given total VOC concentrations and provides 95% confidence intervals for these estimates.

Table 7

Estimated Mean Diacetyl Concentrations for Given Total VOC Concentrations

TVOC Concentration (ppb)	**Estimated Mean Diacetyl Concentration (ppb)**	**95% Confidence Interval for Estimate**
100	2.7	(-6.8, 12.2)
200	4.1	(-5.2, 13.5)
400	7.0	(-2.1, 16.2)
800	12.8	(4.1, 21.5)
1600	24.4	(16.4, 32.3)
3200	47.5	(40.2, 54.8)
6400	93.7	(84.2, 103.3)
12800	186.2	(166.2, 206.3)

From the table above, when the total VOC concentration is measured to be 400 ppb, the estimated mean diacetyl concentration using the model in figure 15 is 7.0 ppb. Using this estimate alone, we would conclude that the mean diacetyl concentration at this total VOC concentration is elevated compared to the NIOSH REL for diacetyl. However, the 95% confidence interval for the true mean diacetyl concentration at the total VOC concentration of 400 ppb is (-2.1, 16.2 ppb). This tells us we can be 95% confident that the true mean diacetyl concentration at a total VOC concentration of 400 ppb lies between -2.1 and 16.2 ppb. The lower part of this range is less than the NIOSH REL for diacetyl while the upper part of this range exceeds it, so we would not be able to reliably predict whether an exposure was elevated compared to the NIOSH REL at this total VOC concentration. Moreover, we would not be able to use this model to reliably predict whether an exposure was elevated compared to the NIOSH REL for diacetyl at total VOC concentrations below 1600 ppb. When the total VOC concentration is 1600 ppb, the model predicts that the mean diacetyl concentration is 24.4 ppb, with a 95% confidence interval for the true mean diacetyl concentration of (16.4, 32.3) ppb. Because both the lower and upper confidence interval limits are above the NIOSH REL for diacetyl, we can say that the mean diacetyl concentration at this total VOC concentration is elevated compared to the NIOSH REL.

Because this model would not reliably predict whether an exposure was elevated compared to the NIOSH REL for diacetyl at total VOC concentrations below 1600 ppb, we can either constrain the model or weight the model to attempt to obtain more accurate and precise predictions of mean diacetyl concentrations close to the NIOSH REL. Figures 17, 18, and 19 below show models created using total VOC concentrations as a predictor for diacetyl concentrations using a weighted least squares linear regression model, constraining the model to only use diacetyl concentration data of <100 ppb, and constraining the model to only use diacetyl concentration data of <75 ppb. The weighted model weighted each observation by the reciprocal of its total VOC concentration, giving more weight to smaller total VOC concentrations than larger ones.

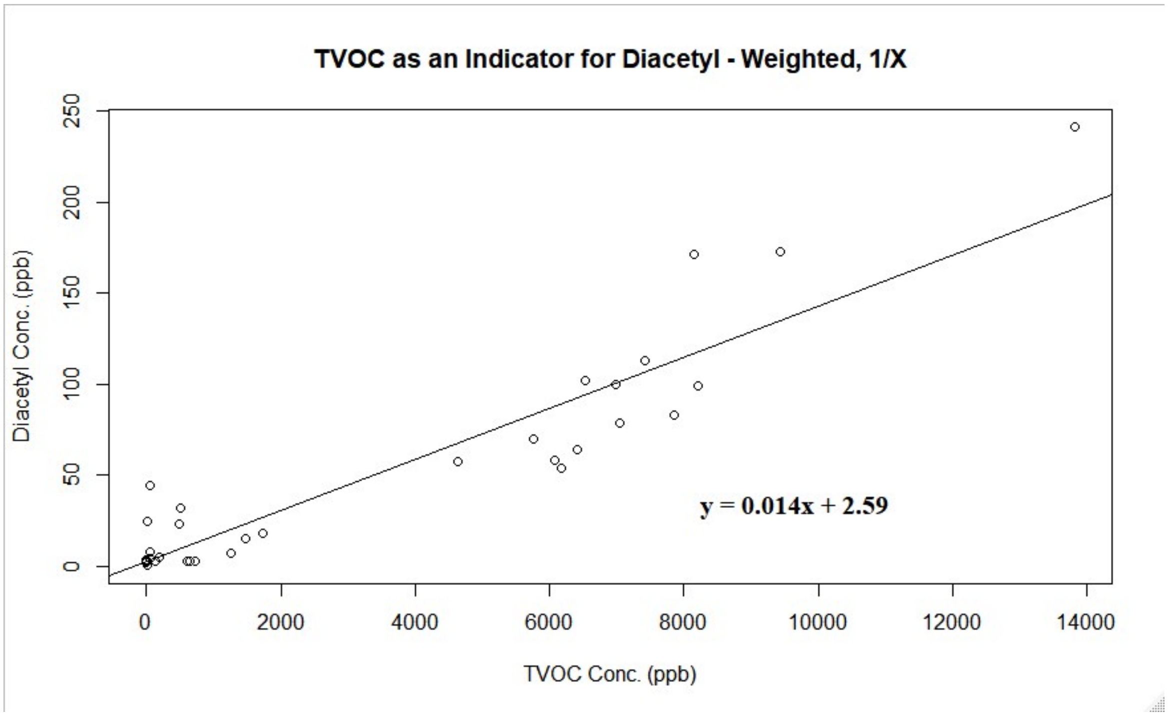


Figure 17. Scatterplot showing correlation between total volatile organic compounds and diacetyl concentrations using a weighted least-squares linear regression model

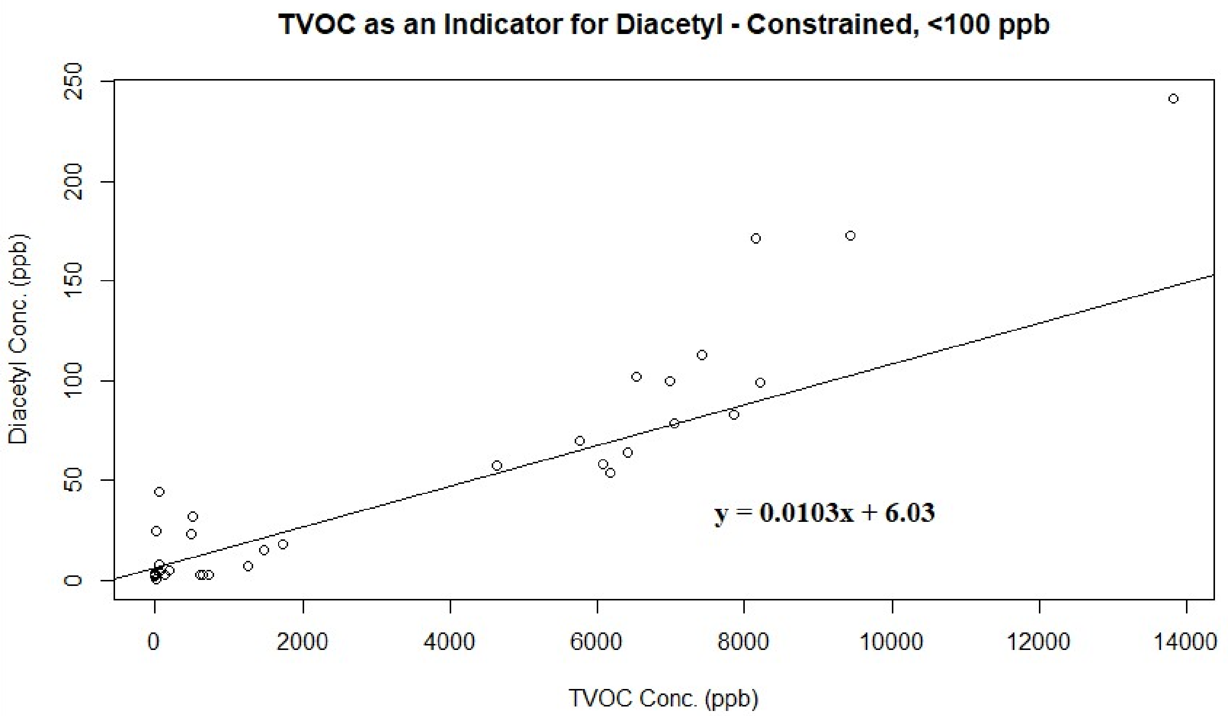


Figure 18. Scatterplot showing correlation between total volatile organic compounds and diacetyl concentrations using a linear regression model constrained to diacetyl concentrations of less than 100 ppb.

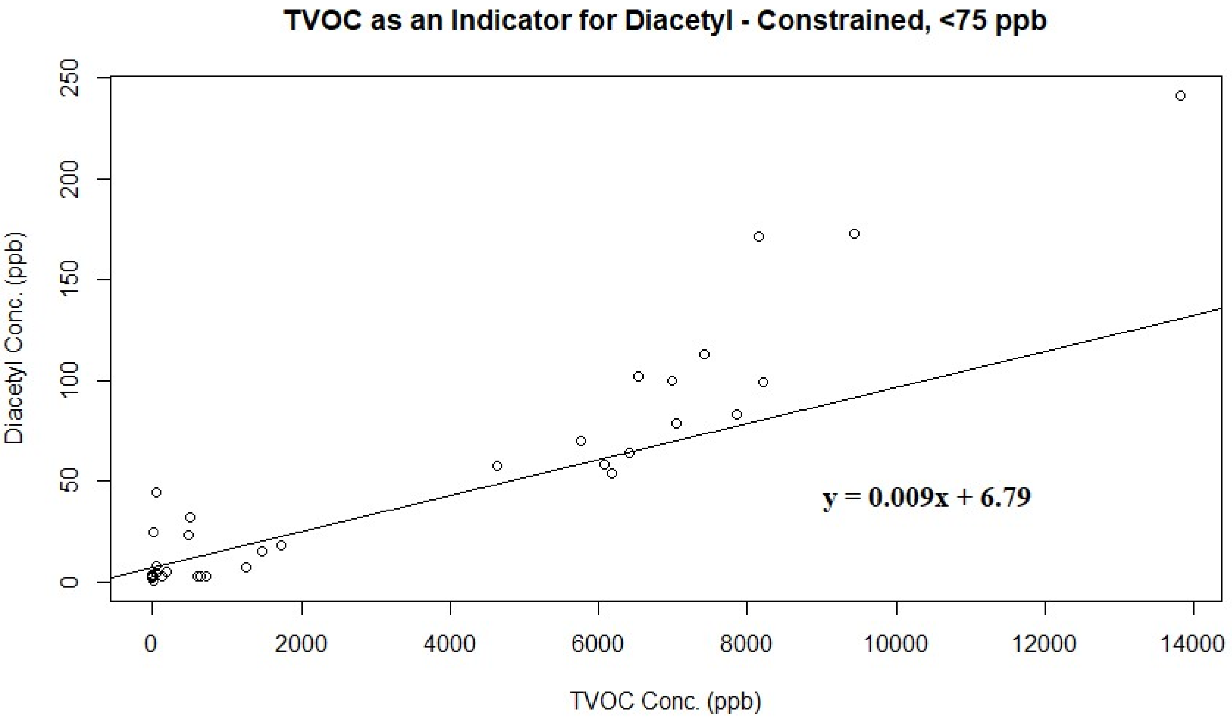


Figure 19. Scatterplot showing correlation between total volatile organic compounds and diacetyl concentrations using a linear regression model constrained to diacetyl concentrations of less than 75 ppb.

Table 8 compares the R^2-values and root mean square errors associated with each model that uses total VOC concentrations to predict diacetyl concentrations. Root mean square error (RMSE) is a measure of the standard deviation of the residuals in the regression model. Residuals are a measure of how far the regression line is from the observed values, so the RMSE measures "how concentrated the data is around the line of best fit" (Statistics, RMSE). In general, RMSE is used as a measure of comparison between different models, with smaller values indicating a closer line of best fit (Statistics, 2013). Of the linear regression models below, the model that was constrained to observations where the diacetyl concentration was less than 100 ppb has both the lowest RMSE and highest R^2-value (RMSE = 11.6, $R^2 = 0.87$). Table 9 uses this model to estimate mean diacetyl concentrations for given total VOC concentrations and provides 95% confidence intervals for these estimates.

Table 8

R^2-Values and Root Mean Squared Errors for Each Total VOC and Diacetyl Regression Model

Model	**RMSE (ppb Diacetyl)**	**R^2-value**	**P-value of Slope Coefficient ($\widehat{\beta_1}$)**
All data points	20.6	0.87	$2.32 * 10^{-16}$
Weighted Linear Regression	20.7	0.21	0.0051
Constrained, <100 ppb	11.6	0.87	$5.70 * 10^{-14}$
Constrained, <75 ppb	25.8	0.76	$5.84 * 10^{-9}$

Table 9

Estimated Mean Diacetyl Concentrations for Given Total VOC Concentrations

TVOC Concentration (ppb)	Estimated Mean Diacetyl Concentration (ppb)	95% Confidence Interval for Estimate
100	7.1	(1.5, 12.6)
200	8.1	(2.6, 13.5)
400	10.1	(4.9, 15.4)
800	14.2	(9.3, 19.2)
1600	22.4	(17.9, 27.0)
3200	38.8	(34.1, 43.5)
6400	71.6	(63.9, 79.4)
12800	137.3	(120.5, 154.0)

From the table above, when the total VOC concentration is measured to be 100 ppb, the estimated mean diacetyl concentration is 7.1 ppb. Using this estimate alone, we would conclude that the mean diacetyl concentration at this total VOC concentration is elevated compared to the NIOSH REL for diacetyl. However, the 95% confidence interval for the true mean diacetyl concentration at the total VOC concentration of 100 ppb is (1.5, 12.6) ppb. This tells us we can be 95% confident that the true mean diacetyl concentration at a total VOC concentration of 100 ppb lies between 1.5 and 12.6 ppb. The lower part of this range is less than the NIOSH REL for diacetyl while the upper part of this range exceeds it, so we would not be able to reliably predict whether an exposure was elevated compared to the NIOSH REL at this total VOC concentration. Moreover, we would not be able to use this model to reliably predict whether an exposure was elevated compared to the NIOSH REL for diacetyl at total VOC concentrations below 400 ppb. When the total VOC concentration is 400 ppb, the model predicts that the mean diacetyl concentration is 10.1 ppb, with a 95% confidence interval for the true mean diacetyl concentration of (4.9, 15.4) ppb. Because both the lower and upper confidence interval limits are above the NIOSH REL for diacetyl, we can say that the mean diacetyl concentration at this total VOC concentration is elevated compared to the NIOSH REL.

Compared to the original model shown in figure 15, this model provides a wider range of total VOC concentrations that can be used to reliably predict whether an exposure is elevated compared to the NIOSH REL for diacetyl. The original model predicts that for total VOC concentrations in excess of 1600 ppb the estimated diacetyl concentration exceeds the NIOSH REL, while the constrained model predicts the estimated diacetyl concentration exceeds the REL for total VOC concentrations in excess of 400 ppb. Additionally, the 95% confidence intervals for the constrained model's mean diacetyl estimates are narrower than the original model's, indicating that the constrained model offers more precise estimates of mean diacetyl concentrations than the original model.

Aim 4

The purpose of this aim was to conduct a limited survey to quantify the effect that the process variable of roast type has on mean alpha diketone emissions generated from grinding coffee beans. Figure 20 represents a typical annotated time series plot for the controlled grinding experiments. In this example, this was the second trial of three for the grinding of French roast. The chart begins three minutes before the actual start of the grinding experiment to give a sense of the background levels of total VOCs present in the chamber prior to grinding the coffee. After the grinding began, the total VOC concentration rose sharply. It took approximately 30 seconds for the grinder to grind a pound of coffee, after which the total VOC levels began to decay steadily, and declined more rapidly once the ground beans were removed from the chamber via the glove bag.

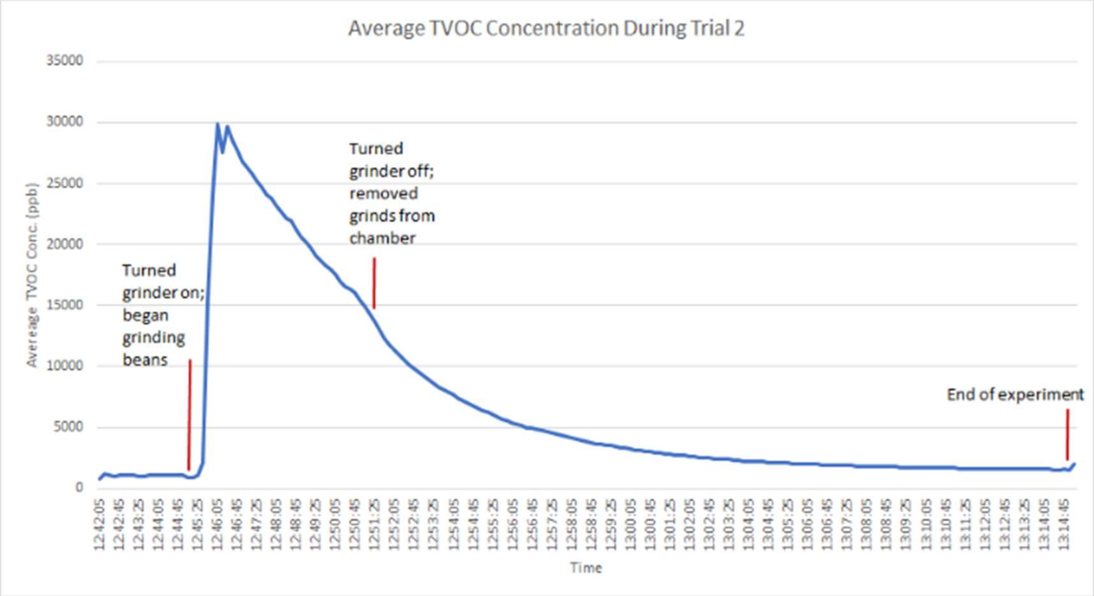


Figure 20. Example of an annotated time series plot for the controlled grinding experiments. This plot represents the continuous concentration of total VOCs in the emissions chamber during the second trial of grinding French roast.

Table 10 summarizes diacetyl mass emission rates (ng diacetyl per gram of coffee ground) for each roast type. Figure 21 presents arithmetic mean and standard deviations of diacetyl mass emission rates for each roast type that was ground.

Table 10

Mass Emission Rates of Diacetyl (ng) per Gram of Coffee Ground for Each Roast Type

	White Coffee	**Medium Espresso**	**Espresso**	**French Roast**
Arithmetic mean **(Standard Deviation)** **N = # of sorbent tubes**	43.1 (1.77) N = 3	1060 (183) N = 3	906 (78.5) N = 3	1610 (149) N = 3

* ng diacetyl/g of coffee ground

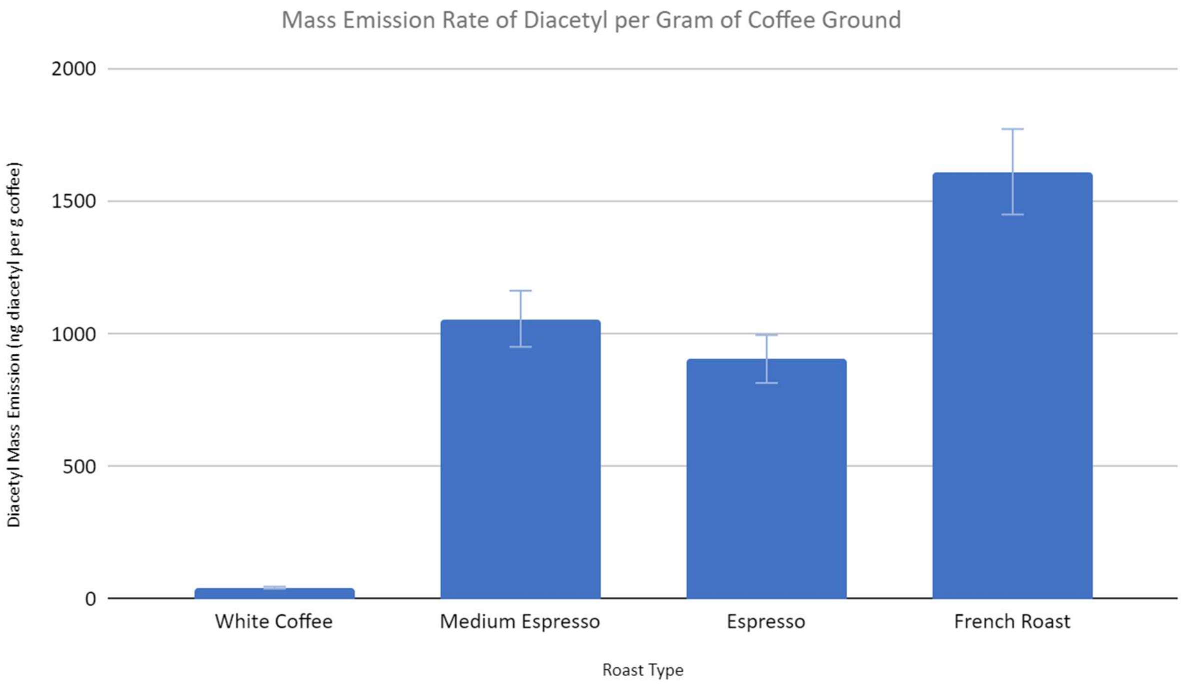


Figure 21. Bar chart showing arithmetic mean and standard deviations of diacetyl mass emission rates for each roast type ground.

Based on our limited survey, French roast was associated with the highest mass emission rate of diacetyl, followed by medium espresso, espresso, and white coffee. A one-way ANOVA test was performed to determine if there was a significant overall difference in mean diacetyl mass emission rates by roast type. Assumptions associated with the one-way ANOVA test are that the observations in and between each group are independent of one another and the residuals are normally distributed and of equal variance. In this survey, diacetyl mass emission rates for each trial and between each roast type were independent of each other. Appendix III Fig. 26 shows a QQ-Plot of residuals from the ANOVA test. The QQ-plot showed that most of the points fell on the reference line and the results of the Shapiro-Wilk's test showed that the residuals were normally distributed (p-value = 0.3616). Appendix III Fig. 27 shows a plot of the residuals in order to assess the equal variance assumption. While the residual plot shows some evidence of heteroscedasticity, the results of the Levene's Test indicated that the assumption of equal variance was valid (p-value = 0.506). The results of the one-way ANOVA test showed that there is a significant overall difference in mean diacetyl mass emission rates by roast type ($F_{3,8}$ = 81.5, p-value = $2.45 * 10^{-6}$). Post-hoc Tukey HSD pairwise comparisons of the mean diacetyl mass emission rate for each roast type showed that the mean diacetyl mass emission rate for French Roast was significantly higher than those for espresso [95% C.I. for difference in means: (381, 1032 ng diacetyl per gram of coffee ground), p-value = 0.001)], medium espresso [95% C.I. for difference in means: (229, 881 ng diacetyl per gram of coffee ground), p-value = 0.003)], and white coffee [95% C.I. for difference in means: (1243, 1895 ng diacetyl per gram of coffee ground), p-value << 0.001)]. The mean diacetyl mass emission rate for white coffee was also significantly lower than espresso [95% C.I. for difference in means: (537, 1188 ng diacetyl per gram of coffee ground), p-value < 0.001)] and medium espresso [95% C.I. for difference in means: (688, 1340 ng diacetyl per gram of coffee ground), p-value << 0.001)]. There was no significant difference between mean diacetyl mass emission rates for espresso and medium espresso. There was a large difference between the diacetyl mass emission rates for white coffee and the darker roasts, and the diacetyl mass emission rate for the French roast was approximately one-third greater than the espresso, which had the lowest rate of the darker roasts.

Discussion

Findings from Aim 1

Results from this observational study showed that coffee production workers at this facility had elevated exposures to diacetyl and 2,3-pentanedione compared to NIOSH and ACGIH recommended guidelines. Assuming no exposure for the remainder of the eight hours, workers' mean 8-hr TWA diacetyl exposure was 9.8 ppb (minimum: 1.0 ppb, maximum: 21.0 ppb) and their mean 8-hr-TWA 2,3-pentanedione exposure was 4.9 ppb (minimum: 0.5 ppb, maximum: 11.4). If the workers had continued their coffee processing tasks for a full eight hours their mean 8-hr TWA diacetyl exposure would have increased to 14.8 ppb (minimum: 1.5 ppb, maximum: 31.9 ppb) and their mean 8-hr TWA 2,3-pentanedione exposure would have increased to 7.5 ppb (minimum: 0.68 ppb, maximum: 17.3 ppb). Overall, 2,3-pentanedione exposures were less than diacetyl exposures by approximately 50-70%. Furthermore, exposure appeared to increase on days where workers were spending more time on tasks involving ground roasted coffee (i.e. grinding and packaging ground beans) compared to days where workers were handling mainly whole roasted beans. These results along with the emissions data suggest that efforts to reduce coffee production workers' exposures to these compounds should focus on the process elements where workers are handling ground beans.

Findings from Aim 2

Diacetyl and 2,3-pentanedione emissions were highest in coffee production areas where activities involving grinding roasted beans or packaging ground roasted beans were completed. The area with the highest diacetyl and 2,3-pentanedione emissions was the packaging area followed by the grinding area. The median diacetyl emission at the packaging area measured at the hopper was 172 ppb, and the median diacetyl emission at the grinding area measured at the grinder was 57 ppb. The median 2,3-pentanedione emissions at the packaging area measured at the hopper was 110 ppb, and the median 2,3-pentanedione emission at the grinding area measured at the grinder was 21 ppb. Similar to previous studies, these data suggest that processing tasks associated with ground coffee are the biggest contributors to workers' exposure to diacetyl and 2,3-pentanedione. A NIOSH HHE at a small-scale coffee roasting and packaging facility found that air concentrations of diacetyl during short-term sampling were highest for tasks involving grinding roasted coffee (maximum: 31.7 ppb) (Hawley et al, 2018). Another NIOSH HHE conducted at two associated cafés of a small-sale coffee roasting and packaging facility found that diacetyl concentrations in the air measured during short-term task-based sampling were higher for tasks involving grinding of roasted beans (maximum: 125 ppb). At the facility studied in this thesis, alpha diketone emissions were highest at the hopper which is likely due to this machine providing a greater surface area for the ground beans to spread out compared to the grinding machines. Moreover, the design of the grinding machines makes the process of grinding coffee much more enclosed than the process of packaging the ground coffee. Finally, the hopper works by vibration to move the ground coffee down a chute from the hopper to the bag and scale. This vibration agitates the ground beans, which may further encourage release of volatile organic compounds.

Findings from Aim 3

Out of the three linear regression models created, the model using the air concentration of total volatile organic compounds as a predictor for air concentrations of diacetyl had the highest R^2-value ($R^2 = 0.95$, p-value = $4.8 * 10^{-15}$) using data collected over the course of the field work at the roastery. The slope from this equation showed that for every 1 ppb increase in total VOC concentration, the concentration of diacetyl increases by 0.0171 ppb. Moreover, when the relationship between air concentrations of diacetyl and total volatile organic compounds was broken down by sampling location, the relationship was similar for the two areas with the highest emissions - the packaging area and the grinding area. Total VOC emissions were also measured and co-located with sorbent tube samples during the course of the grinding experiments and these additional data points were added in order to refine the linear regression model. The addition of these data points slightly decreased the R^2-value ($R^2 = 0.88$, p-value = $2.32 * 10^{-16}$), but this R^2-value is still higher than those from the linear regression models that use CO or CO_2 as indicators for diacetyl air concentrations. The slope with the addition of the grinder data also decreased slightly – for every 1 ppb increase in total VOC concentration, the concentration of diacetyl increases by 0.0145 ppb.

Using the model with the data from the field survey and emissions experiments, the width 95% confidence intervals for the true mean diacetyl concentrations at given total VOC concentrations showed that this model provided imprecise predictions and could not reliably predict whether an exposure was elevated compared to the NIOSH REL at total VOC concentrations that were less than 1600 ppb. A modification to the model that consisted of constraining the observations it was based on to concentrations of diacetyl that were less than 100 ppb provided more accurate and precise estimates of mean diacetyl concentrations at given total VOC concentrations. The modification reduced the root mean square error of the residuals, indicating that the residuals were concentrated more closely to the regression line. Additionally, the width of the 95% confidence intervals for the true mean diacetyl concentrations at given total VOC concentrations were narrower than those for the original model, indicating that the precision of these estimates increased with this modification. Finally, the modified model would predict that the mean diacetyl concentration is elevated compared to the NIOSH REL for total VOC concentrations in excess of 400 ppb.

Despite the original model having a fairly high R^2-value, it provides very inaccurate and imprecise predictions of mean diacetyl concentrations compared to the constrained model. This may be due to violations in assumptions associated with linear regression models, which can have an impact on the width of the confidence intervals associated with their estimates (Baldi et al, 2013). These assumptions include that the response varies normally about the population regression line (Baldi et al, 2013). Figure 28 in Appendix III shows a QQ-plot of the residuals of the original model. The plot indicates that there is substantial deviation from normality. Figure 29 in Appendix III shows a QQ-plot of the residuals in the constrained model. While there is still some skewness, this departure from normality does not appear as extreme as it does in the residuals in the original model. The other important assumption that needs to be valid in order to meet the conditions for inference is that the standard deviation of the responses is the same for all values of the explanatory variable (Baldi et al, 2013). Figure 30 in Appendix III shows a scatterplot of the residuals versus fitted values of the original model. The plot indicates heteroscedasticity in the residuals, as the residuals are scattered unevenly above and below the "residual=0" line (Baldi et al, 582, 2013). Figure 31 in Appendix III shows a scatterplot of the residuals versus fitted values for the constrained model. While there is still some heterogeneity of variance, this is less pronounced than in the previous residual plot.

Most of the observed diacetyl concentrations from the field survey and emissions experiments were in the range of 50 to 250 ppb, so the constrained model is not able to reliably predict whether the diacetyl concentration is elevated compared to the REL at levels close to this value. Moreover, there is a lot of variability in these observations, reasons for which could include poor temporal and spatial collocating of samples. The applicability of the constrained model is limited because this data comes from one specific facility, so the relationship between diacetyl and total VOC concentrations is limited by the equipment used at this facility, the range of temperatures the beans were roasted at, and the types of beans that were roasted. Where processes differ, the relationship between total VOC concentrations and diacetyl concentrations may vary based on these process parameters. Future research could focus on collecting more data at different coffee processing facilities in order to better capture the variability in production practices throughout the industry. Finally, this model is limited to the coffee industry, as the relationship between diacetyl concentrations and total VOC concentrations may vary with the different emissions products generated from products in different industries (e.g. fermenting beer or flavoring popcorn).

Findings from Aim 4

Based on the limited survey conducted, French roast was associated with the highest mass emission rate of diacetyl, followed by the medium espresso, the espresso, and the white coffee. White coffee is the lightest roast out of the four, and is roasted at 355 °F. The medium espresso is roasted at 458 °F and the espresso is roasted at 468 °F. The French roast is the darkest roast out of the four, and is roasted at 475 °F. The average diacetyl mass emission rate was 1610 ng diacetyl per gram of coffee ground (SD = 149) for the French roast, 1060 ng diacetyl per gram of coffee ground (SD = 183) for the medium espresso, 906 ng diacetyl per gram of coffee ground (SD = 78.5) for the espresso, and 43.1 ng of diacetyl per gram of coffee ground (SD = 1.77) for the white coffee. Results of a one-way ANOVA test and post-hoc Tukey pairwise comparisons revealed that the mean diacetyl emissions from white coffee were significantly lower than the darker roasts, and of the darker roasts, the mean diacetyl emissions from French roast were the highest. For smaller operations that do not engage in 40-hours per week of processing activities distributing the roasting, grinding, and bagging activities more evenly throughout the week, especially for darker roasts could greatly reduce daily TWA alpha diketone exposures. Distributing the activities throughout the work week rather than devoting two days per week entirely to grinding and bagging could improve compliance with NIOSH and ACGIH recommended health guidelines, but what determines if this control has an impact on worker health is if peak exposures matter more than cumulative exposures. NIOSH recommended STELs for diacetyl and 2,3-pentanedione based on the concern that peak exposures may have greater toxicity than the same dose spread out over a longer period of time (McKernan et al, 2016). This recommendation was based off of limited evidence found in animal studies (McKernan et al, 2016). For diacetyl, without a STEL a worker could theoretically be exposed to 480 ppb for 5 minutes in an eight-hour workday with no additional exposure for the remainder of their eight-hour shift (McKernan et al, 2016). With the NIOSH STEL in place, the exposure is limited to 75 ppb for 5 minutes in an eight-hour workday with no additional exposure for the remainder of their eight-hour shift (McKernan et al, 2016). Engineering controls such as local exhaust ventilation could also be an effective approach to reducing employee exposures during coffee processing tasks involving ground beans.

Limitations

There are a number of limitations associated with this research that could have been mitigated given a more robust timeline and budget. Time constraints during field work at the roastery resulted in only four days of sampling at a single facility over a period of one month. The primary reason for the short duration of field work was to minimize inconvenience to the business while we were conducting our sampling. This short study period resulted in small sample sizes for each production area and for personal samples and thus was a limiting factor in our ability to conduct robust statistical analyses of the data. An important additional limiting factor is that the samples taken at this facility were purposely scheduled to be taken during the facility's busy season of production and on days that the owner and staff had set aside specifically for roasting coffee beans. It is important to note that this facility is not doing this level of production every day of the week or even every week of the year, and so the results of our study represent a worst-case emissions and exposures scenario. Conducting the field work at a variety of different times of the year may have given a more representative characterization of these workers' exposures to alpha diketones. Our survey was focused on one facility, and while this limits our ability to generalize our results, we were also limited in that this facility was the only one we reached out to that was willing to work with us. Production processes vary throughout the coffee industry, so it is possible that the facility studied in this thesis is not representative of other small-scale coffee-processing facilities.

On a more technical note, the equipment used in the field resulted in some limitations as far as unexpected malfunctions during the beginning of the sampling campaign that resulted in some data loss. In an ideal world, all sampling equipment used in industrial hygiene surveys would operate smoothly, but this is often not the case. While the loss of data was unfortunate, it did provide a positive learning experience as far as learning how to adapt to unexpected scenarios in the field and being able to make the most out of what did go as planned.

Future Research Areas

This thesis focused on the characterization of exposures to and emissions of alpha diketones at a coffee roaster and associated retail café and quantified the difference in diacetyl mass emission rates from grinding different coffee roasts. This thesis did not address other important aspects of exposure assessment, namely implementation and evaluation of exposure controls. The aims of industrial hygiene are not just to identify and evaluate hazards, but also to mitigate these hazards to the greatest extent possible through the hierarchy of controls. Because alpha diketones are a natural by-product of the coffee roasting process, it is impossible to eliminate or substitute these compounds. Engineering controls could be effective in reducing diacetyl emissions because the difference in mass emission rates between the different roasts was relatively small. Future research could focus on designing effective engineering controls, in the form of local exhaust ventilation, with the goal of reducing alpha diketone emissions and exposures. As an epilogue to this thesis, the UW Field Research and Consultation Group will be designing local exhaust ventilation for the hopper and grinders used at this coffee roastery, evaluating the effectiveness of this ventilation in reducing alpha diketone emissions and exposures. The goal in the design of the final product will be to ensure that it is easy for other roasters to replicate these controls and install them on their own machines.

In addition to evaluating the effectiveness of local exhaust ventilation in reducing alpha diketone emissions and exposures, future research could also include conducting similar studies to this thesis at other small-scale craft coffee roasters and cafés in order to better understand the variability in these emissions and exposures across these types of facilities. As stated in the Introduction chapter, there have been very few studies at small-scale craft coffee roasters, and even fewer at retail cafés.

Despite evidence that coffee workers are being exposed to alpha diketones at levels above recommended guidelines there have not been reports of an increased incidence of occupational lung disease among workers in this industry. Coffee processing workers and baristas are a population with poor surveillance data so it's possible that we don't know how prevalent occupational lung disease is among these workers. Future research could focus on improving medical surveillance among this population of workers, including assessments of general health and lung function.

Conclusion

Alpha diketones such as diacetyl and 2,3-pentanedione have been used as artificial flavorings in a variety of industries and are produced naturally when food products such as coffee beans are roasted. Exposure to these compounds has been associated with bronchiolitis obliterans, a rare and severe respiratory disease characterized by inflammation of the small airways of the lungs. There is evidence from previous research studies and NIOSH HHEs that coffee production workers have been exposed to alpha diketone emissions at levels above recommended health guidelines. However, there is a need for more research on how widespread this exposure risk is and what process elements are associated with the highest levels of exposure in the coffee industry. There are a limited number of studies characterizing occupational exposures to and emissions of alpha diketones at coffee roasting facilities. Even fewer studies have been published on occupational exposures to and emissions of alpha diketones in retail cafés. Only one other published study has quantified differences between light roasted and dark roasted coffee beans. No published studies exist that have evaluated the potential of total VOCs, CO, and CO_2 to serve as lower-cost surrogate measurements for alpha diketone concentrations. The purpose of this thesis was to fill these gaps in knowledge by determining which steps in the coffee production process are associated with the highest alpha diketone emissions at a small craft coffee roaster and associated café, determining the extent to which direct reading measurements of CO, CO_2, and total VOCs can serve as lower-cost surrogate indicators for diacetyl concentrations, and conduct a limited survey to quantify the effect that the process variable of roast type (i.e. light, medium, and dark roast) has on mean diacetyl emissions from grinding beans.

Data were collected over 4 days of sampling in October 2019 at a single coffee roaster and associated café in Olympia, WA. Integrated personal and area air samples for diacetyl and

2,3-pentanedione were collected from 7:00 AM to 3:00 PM on each sampling day, corresponding to the full-shift roasting, grinding, and packaging operations at the facility's roastery. Area samples were collected at the barista area, behind the shelves in the café, next to the roaster, next to the grinders, and next to the hopper. Personal air samples for alpha diketones were collected on workers who operated in the coffee roasting, grinding, and packaging area adjacent to the café. A MiniRae 3000 PID (RAE Systems, Inc.) and a Photovac 2020ppb PRO Photoionization Monitor (Photovac, Inc.) were used to measure continuous total VOC concentrations at the roasting, grinding, and packaging stations. The TSI Q-Trak Indoor Air Monitor Model 7575 was used to measure continuous CO and CO_2 concentrations at the roasting, grinding, and packaging stations.

Results from this observational study showed that coffee production workers at this facility had elevated exposures to diacetyl and 2,3-pentanedione compared to NIOSH and ACGIH recommended guidelines. Furthermore, exposure appeared to increase on days where workers were spending more time on tasks involving ground roasted coffee (i.e. grinding and packaging ground beans) compared to days where workers were handling mainly whole roasted beans. Area emission measurements can be useful in determining what work processes are contributing to heightened exposure levels, and the results of our study showed diacetyl and 2,3-pentanedione emissions were highest at the packaging and grinding stations. Similar to previous studies, these data suggest that processing tasks associated with ground coffee are the biggest contributors to workers' exposure to diacetyl and 2,3-pentanedione.

Correlations between diacetyl and total VOCs, CO, and CO_2 showed that the model using air concentration of total VOCs as a predictor for air concentrations of diacetyl had the highest R^2-value ($R^2 = 0.95$, p-value = $4.8 * 10^{-15}$), followed by the model using CO_2 ($R^2 = 0.58$, p-value

= 0.001), and the model using CO as an indicator for diacetyl air concentrations ($R^2 = 0.09$, p-value = 0.34). Using the model that predicts air concentrations of diacetyl from the air concentration of total VOCs, the average diacetyl concentration when the total VOC concentration is 400 ppb is 7.0 ppb (95% C.I.: -2.1 – 16.2 ppb). We are 95% confident that the true average diacetyl concentration when the total VOC concentration is 400 ppb is between -2.1 and 16.2 ppb. Because the 95% confidence interval includes values both above and below the NIOSH REL, we would not be able to use this model to reliably predict whether an exposure was elevated compared to NIOSH health guidelines at this total VOC concentration. Constraining this model to be based on observed diacetyl concentrations that were less than 100 ppb improved both the accuracy and precision of estimated mean diacetyl concentrations. The constrained model predicts that mean diacetyl concentrations will be elevated compared to the NIOSH REL for total VOC concentrations in excess of 400 ppb. This model is not able to reliably predict whether the diacetyl concentration is elevated compared to the REL at levels close to this value. The applicability of this model is limited due to this data coming from only one facility with specific production process parameters (e.g. equipment used, roast temperature, and bean type). Where processes differ, the relationship between total VOC concentrations and diacetyl concentrations may vary based on these parameters. Future research could focus on collecting more collocated data at different coffee processing facilities in order to better capture the variability in production practices throughout the industry.

The purpose of the laboratory study was to quantify the range of diacetyl concentrations that various types of coffee roasts emit during grinding. White coffee, medium espresso, espresso, and French roast purchased from the roastery were ground using a Grindmaster industrial coffee grinder. Results from the emissions tests showed that diacetyl mass emissions generated from grinding French roast were significantly higher than those of espresso, medium espresso, and white coffee. White coffee had a very low diacetyl mass emission rate compared to the other roasts, and its rate was significantly lower than that of espresso and medium espresso. There is potential for smaller operations to reduce workers' daily TWA exposures to alpha diketones by more evenly distributing grinding and packaging activities, especially for darker roasts, more evenly throughout the work week. This would improve compliance with recommended health guidelines, but the effect on worker health would be contingent on if peak exposures are associated with higher toxicity than cumulative exposures, where the same dose is spread out over a longer period of time. Future research could focus on designing effective engineering controls, in the form of local exhaust ventilation, with the goal of reducing alpha diketone emissions and exposures, as well as conducting similar studies to this thesis at other small-scale craft coffee roasters and cafés in order to better understand the variability in these emissions and exposures within these types of facilities.

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Appendices

Appendix I. Observational and Laboratory Sampling Plans

Coffee Study Sampling Plan and Related Information

Nancy Beaudet

Revised on May 4, 2020 by Hannah Echt

Overview

This document presents the air monitoring protocol for assessing airborne levels of and worker exposures to diacetyl and 2,3-pentanedione. The primary objective of initial sampling efforts is to characterize exposures and airborne levels of the analytes of interest associated with roasting, blending, grinding, packaging and café operations. Direct reading instruments will also be used to determine area levels of CO, CO_2 and total organic vapor for the purpose of determining if these analytes are associated with diacetyl and 2,3 pentanedione levels, a secondary project objective.

Air Monitoring Protocol

Basic elements of the air monitoring protocol are summarized in Table 1. Air monitoring for diacetyl and 2,3-pentanedione will entail the collection of a personal samples for the roasting operator and the grinder during routine activities. To assess the baristas exposures, which entails coffee grinding, brewing, and espresso machine operations, the sampling will be staged after hours in the café.

In addition, area samples for these analytes will be collected during roasting, blending and grinding operations, as well as café operations. Direct reading instruments will be placed adjacent to area sampling pumps to measure CO, CO_2 and total organic vapor levels. In addition, relative humidity and temperature will also be recorded by the Q-Trak monitoring device (Table I-1).

Table I-1: Sampling Protocol Summary

Personal samples	- Production workers (all operations, full shift sample – 2 samples, ≈240 mins each)
Area samples	- Roasting (two samples for 120 minutes each during roasting **concurrent** with DRIs) - Grinding (two samples for 120 minutes each during grinding **concurrent** with DRIs) - Hopper –blending/packaging (two samples for 120 minutes each **concurrent** DRIs) - Café operations, near grinder (full shift – 2 samples) - Café background sample – behind storage shelves distant from brewing (full shift – 2 samples)
Analytes	Diacetyl, 2,3-Pentanedione
Lab MDL	2 ng
Sampling rate	**0.05 lpm per LeBouf and OSHA 1013**
Max Volume	**12 L (240 minutes max) (Per Chris' professional judgement)**
Time for 1 ppb DL	3 minutes
Sampling pumps	SKC AirCheck (9 total, 3 personal, 5 area, 1 spare)
Sample media	Washed silica gel, 600 mg, two tubes in tandem (SKC 226-183)
Holding/storage	Samples placed in cooler with ice after sampling, then refrigerated
Holding time	17 days (from sample collection to analysis)
Direct reading devices	- TSI Q Trak 9306, CO_2, CO, RH & Temp; 2 devices, FG & CS labs - MiniRAE 3000 PID, Mini-PID, total organic vapors devices FG & CS - Teaching Lab PID/FID, total organic vapors - 1 ppm detection level (all devices) - 10 second logging period (all devices)

Sampling equipment set-up at the site is briefly described as follows. Shortly after arrival at the site at around 6:45 AM, an area sampling pump, with two silica gel sorbent tubes in tandem, will be placed between the coffee grinder and the espresso machine for full shift sampling. A second area sample will be collected distant from the brewing area and out of view behind the coffee product shelves in the cafe. The sorbent tubes will be changed per the protocol. The equipment will be monitored throughout the day.

The area sampling equipment will be positioned in the roasting and grinding areas. For task sampling of the roasting operations, the area sampling pumps and direct reading instruments will be held on a tripod that is placed in an area that is acceptable to the roasting operator; the probe or inlets for these devices will be extended and positioned directly over the actual process. Photographs taken during the initial site visit will be used in subsequent site visits to allow for the direct reading instruments to be positioned in the same locations.

For task sampling in the Grindmaster grinders area, the sampling pump and direct reading instruments will be positioned in a location suitable to management. The shelf over the grinders or the tripod will be used as needed. The probe or inlets for these devices will be extended and positioned directly over the actual process. Photographs taken during the initial site visit will be used in subsequent site visits to allow for the direct reading instruments to be positioned in the same locations.

After the human subject consenting process, the personal sampling pumps, outfitted per the protocol, will be deployed on the production workers. After each sample is collected, the silica gel sorbent tubes will be capped, wrapped in aluminum foil, and then placed in a cooler. After transit, the samples will be stored in the field group's refrigerator.

Area task samples will be collected using the pumps and DRIs in the roasting, grinding and hopper/packaging areas. Two samples will be collected during each process, for approximately 2-3 hours each following the protocol. Sampling will be initiated when the roasting, grinding or packaging tasks are active at each location. The researchers will record all required data as outlined in the Monitoring Activity Sequence section and the field data collection forms. The DRIs and the pump near the roaster will remain in that location all day. After sample collection near the grinder, the sampling pump media will be changed and the DRIs and sampling pump will be moved to a location near the hopper suitable to management. After each sample is collected, the silica gel sorbent tubes will be capped, wrapped in aluminum foil, and then placed in a cooler.

All direct reading equipment will be started simultaneously to allow for these devices to be temporally synchronized. This equipment will run continuously through the entire monitoring period until the roasting/grinding/packaging processes are finished. The recording of start and stop times of the various roasting operations on the task observation form will allow for the mean CO, CO_2 and total organic vapor levels for each task to be determined at a later time. The task observation form will also be used to record the mass and type of coffee for each batch of coffee roasted and the number of espresso shots made by the barista being monitored.

The standard Field Group form will be used to record air sampling pump flow rates, start and stop times, sample IDs, and sample location. Direct reading equipment will be downloaded at the end of each day in the field or in the Field Group lab. A master data base will be generated to which all data will be transferred; the original data download files will still be maintained. Field site observations will also be transcribed to the master database to align with the direct reading monitoring data.

Analysis

Analysis of alpha diketone samples followed OSHA Methods 1013/1016 with some modifications. Sorbent tubes were analyzed using GC/MS to enhance the sensitivity of the OSHA methods. Diacetyl and 2,3-pentanedione concentrations by volume (ppb) were determined for each sample. Sample data were reviewed for errors. Time series analyses of CO, CO_2, CO, and total VOC emissions were created for each sampling location.

Equipment Logistics

The equipment will be pre/post-calibrated by the IHs on this project (See Appendix A for details). Since the FRCG equipment will be used, all equipment and supplies will be requested through the Field Group calendar. In the very unlikely event of a conflict with another Field Group project, the roaster site visit would need to be rescheduled.

Production Rate Measures

In the roasting/packaging areas, the total pounds of coffee produced (roasting, grinding and packaging) per day will be recorded, as well as the time spent on specific tasks (roasting, grinding and packaging). All data will be captured and recorded on the field observation form.

Human Subjects

The study will follow established protocols as required by the UW Human Subjects office. Refer to IRB approval re participant recruitment and consent procedures.

Pre-Sampling Activities in FRCG Lab

- Prepare Direct Read Instruments
    - Verify max durations of sampling with fresh batteries
    - SPAN gas ck for PIDs
    - SPAN gas ck for Q-Traks if possible (is there a sleeve or use a plastic bag?)
    - New batteries
    - Set/harmonize date/time stamps

  - Set 10 second logging period for all devices
  - Clear memories
  - Silence CO, CO2 alarms
  - Add recalibration/zeroing procedures when finalized as needed
- Label all silica gel tubes using FRCG convention
  - Around 200 tubes total
- Calibrate sampling pumps
  - Use either the FRCG or Chris' primary standard
  - Position the **two** silica gel sorbent tubes in tandem between the pump and the primary calibration standard (instead of the filter cassette in this photo)
  - Adjust pump flow rate as needed until three or more consecutive readings are within 2% of each other. Record the average of those readings of pump calibration form
- Assemble all Field Data collection forms
  - Use FRCG air sampling forms for sampling pumps
  - Use field observation forms
- Prepare the Human Subjects Packet
  - Study statement
  - Consent form

Monitoring Activity Sequence

The sequence of monitoring activities to be performed is summarized as follows:

Initial Visit

- Check in with owner and staff to review monitoring protocol

- Identify locations for area monitoring equipment
- Discuss and identify procedure for logging number of espresso shots brewed by barista or pounds of coffee consumed, or other measure of production
- Take pictures of area sampling locations
- Discuss employee and customer study education and customer care information.

Subsequent visits

- Bring flow calibration data for all pump to Oly Days 1 and 3.
- Check in with owner and/or staff
- Deploy area sampling pumps in the café (in espresso area and background location); 2 samples each location per day, ≈240 mins each)
    - Take photos showing the location of the equipment
- Set up the area task monitoring equipment in roasting area
    - Take photos showing the location of the equipment
- Set up the area task monitoring equipment in grinding area
    - Take photos showing the location of the equipment
- Measure dimensions of the roaster room, grinder room, and café (first day only)
- Record time stamps on DRIs and time on timepiece used for recording sampling pump times
- Human Subject consent process for production workers (first sampling day only unless there are staff change). Explain the study to participants, walk them through the consent form and answers any questions that they have (15 minutes)
- Initiate personal sampling for production employees; (around 240 minutes each sample)
    - Record start/stop times, media changes per standard procedures

- Start the TASK area monitoring equipment in the roasting area taking care to minimize disruption of production activities. Sample collection 120 minutes-for each sample
    - Collect two roasting task samples (2 tubes in tandem. **Change tubes every 120 minutes**.
    - Record start/stop times, media changes per standard procedures
    - Record the types of coffee beans roasted and blended, and mass of coffee roasted during sampling, capture the number of batches of beans roasted during the sampling events
    - Record observations on the reporting form (time roaster starts/stops, when beans dropped to cooling tray, when beans dropped into bin, roasting temp for various beans roasted)
    - Take photograph/video of roaster operations and area sampling equipment
    - Remove roasting area sample media, put on ice; install new sampling media
- Start TASK area equipment in the grinding location taking care to minimize disruption of production activities. Sample collection 120 minutes for each sample
    - Collect two grinding task samples. **Change tubes every 120 minutes.**
    - Record start/stop times, media changes per standard procedures
        - Record coffee blend(s) names
        - Note if the operation is continuous or intermittent. Record start and stop times of grinding process if intermittent or describe pattern
        - Record if/when the grinding and hopper blending occur simultaneously
        - Record the number of staff members doing the work

    - Record any relevant distances (like between sampler inlets and top of Grindmaster hopper and/or Grindmaster product outlet)
    - Take photograph of grinding operations and task area sampling equipment
    - Remove grinding area sample media, put on ice; install new sampling media
- For sorbent tubes, collect two hopper task samples. **Change tubes every 120 minutes**.
- Move TASK area equipment from grinding area to hopper/packaging location taking care to minimize disruption of production activities.
- Start the TASK area equipment by the hopper
  - Record blends of coffee packaged
  - Record start and stop times of hopper/packaging process
    - Note if the operation is continuous or intermittent. Record start and stop times of grinding process if intermittent or describe pattern
    - Measure relevant distances such as DRI inlets to top of hopper and dispensing chute?
    - Record if/when the grinding and hopper blending occur simultaneously
  - Take photograph/videos of hopper/packaging operations and area sampling equipment
  - Remove hopper/packaging task area sample media, put on ice
- Stop and collect all personal sampling equipment (roaster operator, grinder and helper); remove samples and place on ice
  - Record start/stop times, media changes per standard procedures
- Store all samples on ice and hotel refrigerator

Equipment and Supplies Checklist

DRIs

- Laptop loaded with software for the Q-Traks AND the PIDs
- Q Traks (2), 10 second logging time
- PIDs (2), 10 second logging time
- Charging stations for both PIDs
- Ensure directions available for all instruments, including how to download the logged data and need to clear the memory at end of each day
- Zero and span gases for Q-Trak & PID (use of FRCG gases per Mark is OK)
- Prep equipment (Nancy and Hannah)

Sampling pumps

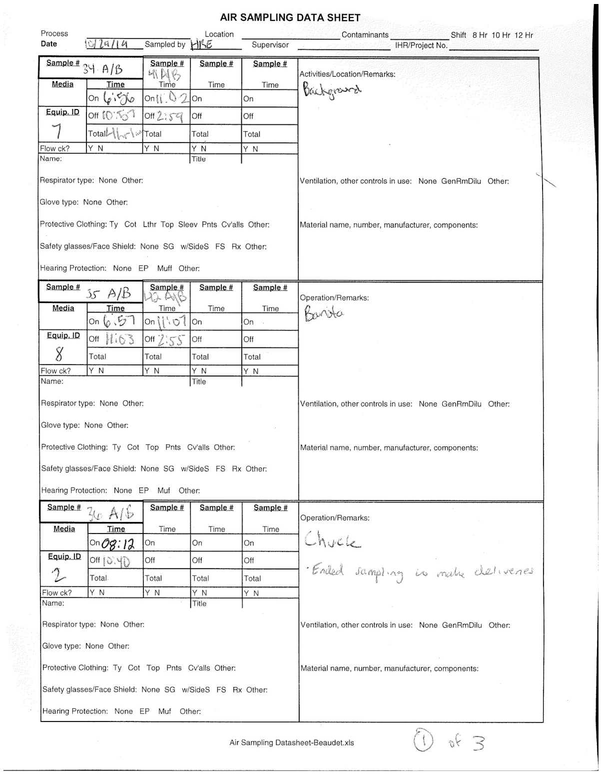
- 9 sampling pumps (including one spare) calibrated 0.05 lpm using two tubes in tandem
- 9 sampling trains include tandem tubes covers
- Chris' primary pump calibration device for calibration in Oly
- Pump charging stations (2)
- 120+ tubes same lot: SKC 226-183
    - Washed silica gel sorbent tubes (≈57 tubes per day; ≈42 samples; 5 FB + 4 QC + 6 spares) and end caps
- Label 60 silica gel tubes for each day
    - Convention: Sample # (Day 1 samples 1-59; Day 2 60 – 119; etc.; Label with "A" and "B" designations for front and back tubes
    - Sampling dates (Oct 14,15, Oct 28, 29)
    - Package in baggies of 30 tubes in numbered sequence

Misc.

- 2 Sorbent tube breakers
- Short pieces of tubing for tandem sampling
- Tubing to extend PIDs inlet (bring box)
- Highlighters
- Tripod with equipment basket (3)
- Scissors or utility knife to cut tubing
- Clipboard & paper
- Camera, video equipment
- Hot wire anemometer
- Laser and conventional tape measures
- Blue tape – 2 inch wide
- Batteries for Q-Trak (AA), FRCG PID (rechargeable); Chris' PID???
- Aluminum foil
- 2 Coolers with Ice packs

Forms

- Task observation monitoring form (Jerry will finalize)
- Air sample collection form
- Pump calibration form
- Consent forms
- Sampling pumps (9) calibrated at 0.05 lpm



AIR SAMPLING DATA SHEET

Process ______ Location ______ Contaminants ______ Shift 8 Hr 10 Hr 12 Hr
Date 10/29/19 Sampled by HRE Supervisor ______ IHR/Project No. ______

Sample # 34 A/B		Sample # 41 A/B	Sample #	Sample #
Media	Time	Time	Time	Time
	On 6:56	On 11:02	On	On
Equip. ID	Off 10:57	Off 2:59	Off	Off
7	Total 4hr1m	Total	Total	Total
Flow ck?	Y N	Y N	Y N	Y N
Name:			Title	

Activities/Location/Remarks: Background

Respirator type: None Other:
Glove type: None Other:
Protective Clothing: Ty Cot Lthr Top Sleev Pnts Cv'alls Other:
Safety glasses/Face Shield: None SG w/SideS FS Rx Other:
Hearing Protection: None EP Muff Other:
Ventilation, other controls in use: None GenRmDilu Other:
Material name, number, manufacturer, components:

Sample # 35 A/B		Sample # 42 A/B	Sample #	Sample #
Media	Time	Time	Time	Time
	On 6:57	On 11:07	On	On
Equip. ID	Off 11:03	Off 2:55	Off	Off
8	Total	Total	Total	Total
Flow ck?	Y N	Y N	Y N	Y N
Name:			Title	

Operation/Remarks: Barista

Respirator type: None Other:
Glove type: None Other:
Protective Clothing: Ty Cot Top Pnts Cv'alls Other:
Safety glasses/Face Shield: None SG w/SideS FS Rx Other:
Hearing Protection: None EP Muf Other:
Ventilation, other controls in use: None GenRmDilu Other:
Material name, number, manufacturer, components:

Sample # 36 A/B		Sample #	Sample #	Sample #
Media	Time	Time	Time	Time
	On 08:12	On	On	On
Equip. ID	Off 10:40	Off	Off	Off
2	Total	Total	Total	Total
Flow ck?	Y N	Y N	Y N	Y N
Name:			Title	

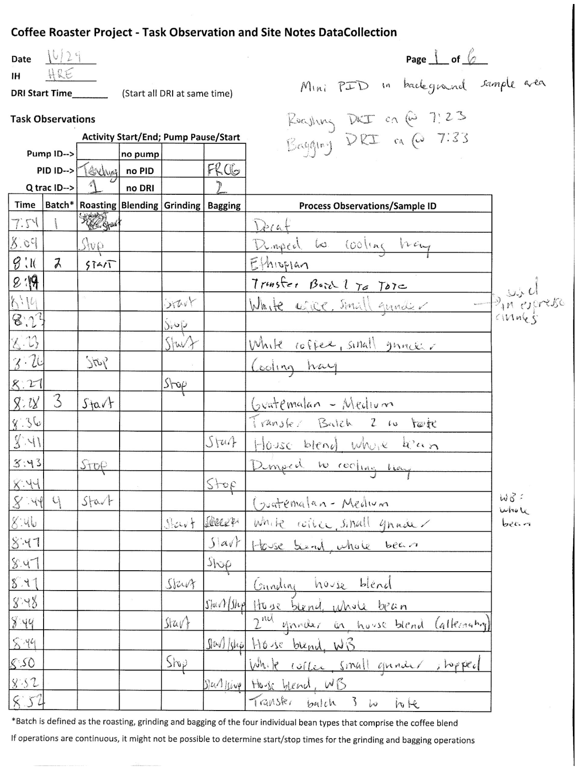
Operation/Remarks: Chuck

- Ended sampling to make deliveries

Respirator type: None Other:
Glove type: None Other:
Protective Clothing: Ty Cot Top Pnts Cv'alls Other:
Safety glasses/Face Shield: None SG w/SideS FS Rx Other:
Hearing Protection: None EP Muf Other:
Ventilation, other controls in use: None GenRmDilu Other:
Material name, number, manufacturer, components:

Air Sampling Datasheet-Beaudet.xls ① of 3

Figure I-1. Example air sampling collection form.



Coffee Roaster Project - Task Observation and Site Notes DataCollection

Date 10/29
IH HRE
DRI Start Time______ (Start all DRI at same time)

Page 1 of 6

Mini PID in background sample area

Roasting DRI on @ 7:23
Bagging DRI on @ 7:33

Task Observations

	Activity Start/End; Pump Pause/Start			
Pump ID-->		no pump		
PID ID-->	Teaching	no PID		FROG
Q trac ID-->	1	no DRI		2

Time	Batch*	Roasting	Blending	Grinding	Bagging	Process Observations/Sample ID
7:54	1	Start				Decaf
8:09		Stop				Dumped to cooling tray
8:11	2	START				Ethiopian
8:19						Transfer Batch 1 To Tote
8:14				Start		White coffee, small grinder ✓
8:23				Stop		
8:23				Start		White coffee, small grinder ✓
8:26		Stop				Cooling tray
8:27				Stop		
8:28	3	Start				Guatemalan - Medium
8:36						Transfer Batch 2 to tote
8:41					Start	House blend whole bean
8:43		Stop				Dumped to cooling tray
8:44					Stop	
8:44	4	Start				Guatemalan - Medium
8:46				Start	[illegible]	White coffee, small grinder ✓
8:47					Start	House blend, whole bean
8:47					Stop	
8:47				Start		Grinding house blend
8:48					Start/Stop	House blend, whole bean
8:49				Start		2nd grinder on house blend (alternating)
8:49					Start/Stop	House blend, WB
8:50				Stop		White coffee, small grinder, stopped
8:52					Start/Stop	House blend, WB
8:52						Transfer batch 3 to tote

→ used in espresso drinks

WB = whole bean

*Batch is defined as the roasting, grinding and bagging of the four individual bean types that comprise the coffee blend
If operations are continuous, it might not be possible to determine start/stop times for the grinding and bagging operations

Figure I-2. Example task observation form.

Grinding Experiment Protocol

Hannah Echt

Revised on May 4, 2020

Introduction

The purpose of these grinding experiments is to quantify the range of diacetyl concentrations that various types of coffee roasts emit during grinding. We will be grinding light, medium, and dark-roasted beans and measuring subsequent diacetyl emissions. This first experiment is a range-finding experiment to determine if our experimental design will yield enough diacetyl mass to be measured in the lab or if we need to redesign or experiment. Results from our regression analysis of our field work data determined that there is potentially a useful relationship between TVOC concentrations and diacetyl concentrations, and this relationship may be used to predict the mass of diacetyl emitted from coffee grinding given the average TVOC emissions.

Equipment

- MiniRAE 3000
- GilAir Plus personal air sampling pump
- Gillian Gilibrator 3 primary flow meter
- Sorbent tubes
- Whole coffee beans (white coffee, medium espresso, espresso, and French roast)
- Scale
- Container for ground beans
- Grindmaster grinder
- Polycarbonate emissions test chamber
- Small fan

Procedure

- Turn the MiniRAE on and place inside the chamber, near the grinder's spout. Make note of the time. Turn on GilAir Plus personal air sampling pump set to an air flow of 200 mL/min (verified using primary flow meter) and attached sorbent tubes (connected in series). Make note of the time. Take photographs of the system.
- Turn on fan and place in chamber to ensure air in chamber is well mixed.
- Dump 8 oz of whole coffee beans into the grinder. Place container inside chamber beneath grinder's spout in order to collect coffee grinds. Place lid on chamber and seal with clasps.
- Turn on large volume pump set to an air flow of 30 L/min (verified using primary flow meter).
- Turn on the grinder and note both the time the grinder is turned on and when the grinding is finished.
- Leave the container of ground beans in the chamber for 5 minutes and continue grinding during this time to mimic the process that is done at the coffee shop.
- Turn off the grinder. Using the glove bag, remove the container from the chamber and note the time.
- After 30 minutes have passed from the start of the experiment, turn off the chamber flow, take the lid of the chamber, and remove and turn off the air sampling pump. Note the time.
- Cap the sorbent tubes and wrap them in foil. Place inside field group's refrigerator to be stored until turned into the lab for analysis.

- Post-calibrate the air sampling pump and large volume air pump.
- Download data from the MiniRAE and export into Excel. Plot TVOC vs time and annotate plot.
- Submit samples to lab for GC/MS analysis.
- Determine the mass of diacetyl per sample. Determine the mass emission in units of ng of diacetyl per gram of ground coffee by:

mass emission (units: ng diacetyl/g coffee) = (ng diacetyl per tube * (average chamber flow in liters)/ (average pump flow in liters))/ (grams of coffee ground).

Appendix II. Methods - Supplementary Information

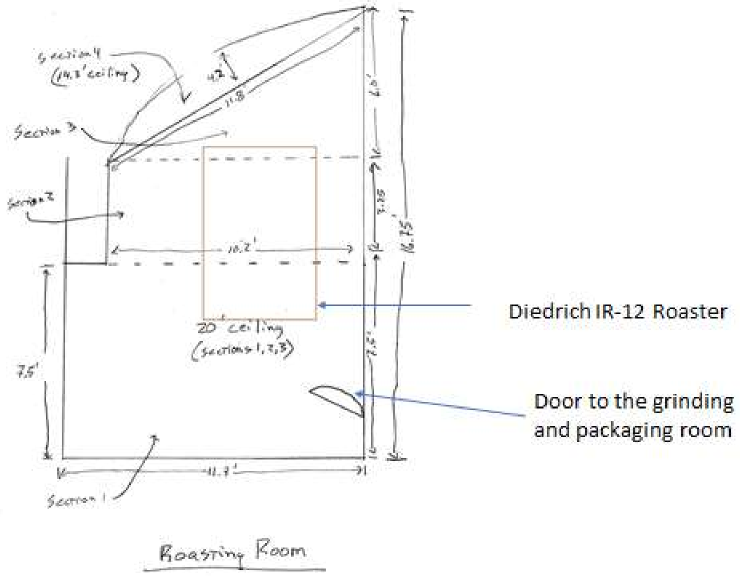


Figure II-1. Approximate layout and room dimensions of the facility's roasting room.

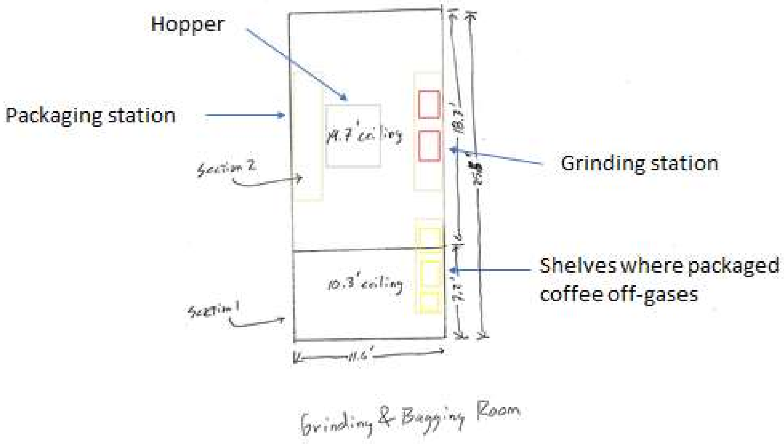


Figure II-2. Approximate layout and room dimensions of the facility's grinding and packaging room.

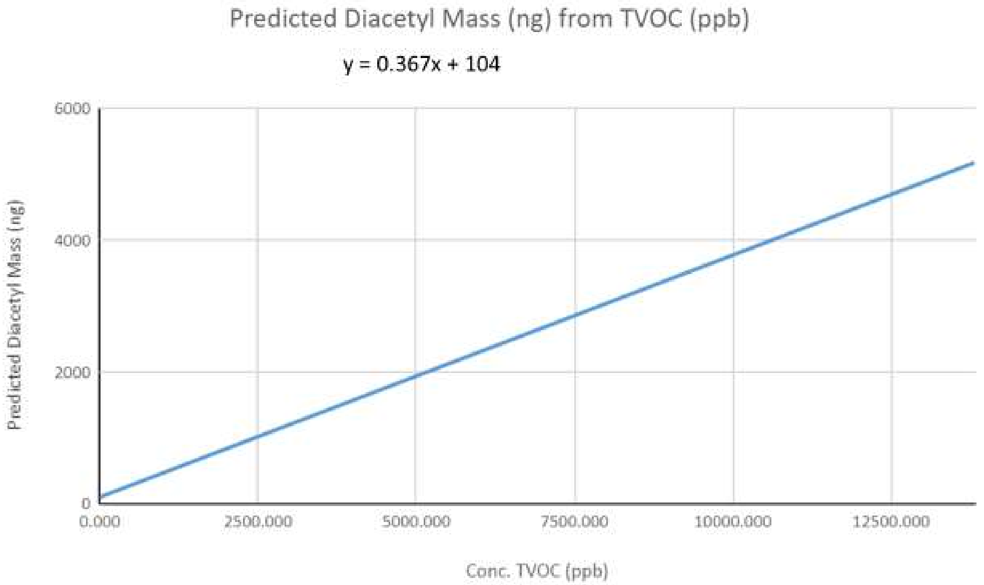


Figure II-3. Model used to predict the mass of diacetyl (in ng) from measured total VOC concentrations

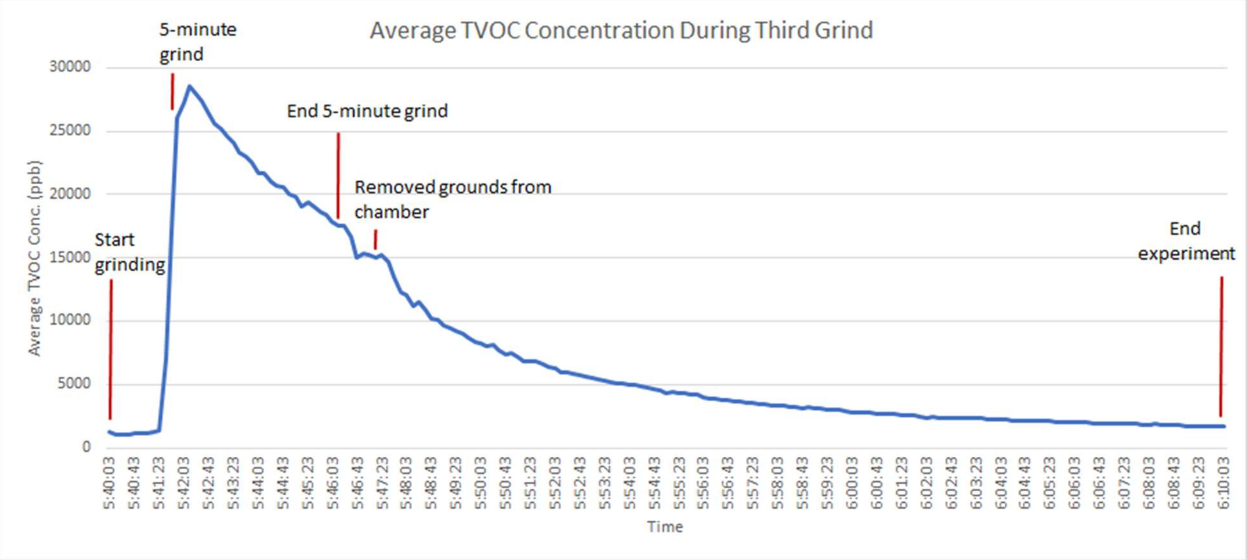


Figure II-4. Example time-series analysis plot of the continuous concentration of total VOCs inside the chamber during one trial of the range-finding experiment. After 30 minutes passed from the start of grinding, over 90% of the emissions generated from grinding had evacuated the chamber.

Custom-Built mini PID

In addition to the two PIDs sampling in the production areas, a custom-built direct reading photoionization monitor was used to measure continuous total VOC concentrations in two areas in the café. This device was placed behind the counter where the baristas take and make orders, next to their espresso grinder. It was also placed in a control area behind shelves holding café products. The device was placed there to measure background concentrations of total VOCs in the café area. This custom-built device is comprised of a PID sensor installed on an Arduino microcontroller attached to a battery pack (Silvey, 2019). It has an SD card which enables the device to log and store data (Silvey, 2019). The device begins detecting total VOCs immediately after the device is plugged into an outlet and logs data points onto the SD card or directly to a computer at five second intervals (Silvey, 2019). The device does not measure total VOC concentrations in parts per million (ppm) but rather in an arbitrary voltage number in analog-to-digital (ADC) units (Silvey, 2019). Post-calibration of this device involves producing a standard curve experimentally in an exposure chamber, allowing the user to convert the total VOC concentrations into ppm (isobutylene equivalents) (Silvey, 2019).

In order to analyze the data from the custom-built PID, a standard calibration curve was derived from data created in a laboratory setting (Silvey, 2019). In this calibration experiment, the PID was calibrated by filling an exposure chamber with a known concentration of span gas, specifically isobutylene (Silvey, 2019). The PID was placed inside the chamber, which was located in the Seto Lab at the University of Washington’s Health Sciences Building (Silvey, 2019). The chamber, approximately 1 cubic foot in volume, was filled with 5 ppm of isobutylene. The chamber was also supplied with dry air at a flow rate of 7 L/minute. The chamber contained a circulation fan to ensure that the air within the chamber was well mixed (Silvey, 2019). The concentration of isobutylene in the chamber decays as a first order process (Silvey, 2019). The equation that approximates this decay, assuming a well-mixed chamber, is as follows:

$C = C_0 e^{-kt}$, where

$k =$

C_0 = initial span gas concentration (isobutylene)\

C = span gas concentration at any time, t

e = base of natural logarithm

This decay equation was used to calculate the value of C at any point in time in the decay process (Silvey, 2019). The slope of this decay was used to determine the value of the decay constant, k (Silvey, 2019). The decay constant was then inserted into the first order equation above to determine the value of C at any point in time (Silvey, 2019). A calibration curve was then created by plotting the PID's response by the calculated concentration (Silvey, 2019). Simple linear regression was used to calculate the slope of this relationship, and this value was then used to convert the voltage response ADC units produced by real-time sampling into units of concentration of isobutylene (ppm) (Silvey, 2019). The upper calibration limit was the level to which the PID was calibrated, 5 ppm isobutylene, which corresponded to roughly 700 ADC units. The lower limit of detection (LLOD) for this device was calculated to be 0.05 ppm isobutylene, which corresponded to roughly 11 ADC units. This LLOD was determined based on the lowest PID sensor value that was clearly distinguishable from background VOC concentration levels (Silvey, 2019). A concentration of zero ppm isobutylene corresponded to a PID sensor value of roughly 4 ADC units. In the field, all measurements from this device were at or close to its LLOD.

Table II-1

Summary of Sorbent Tube Data Errors

Flag	**Description**	**Action**
*	Difference between initial and final flow rate was greater than 10%	Added flag to value, no change in value
ND	Mass of sample is below the limit of detection (LOD)	Added flag to value, no change in value
Tubing between A and B came off	Plastic tubing between the front and back tubes came off and disconnected the sampling train during the sampling period	Added flag to value, did not use value in statistical analysis
Mass greater than >10% of total	Mass of the sample on a back tube that was not disconnected from a front tube was more than 10% of the total mass of the sample	No samples met this criterion

Table II-2

Diacetyl and 2,3-Pentanedione QA/QC Data from Extraction

Study	**Analyte**	**Average Recovery (%)**	**Recovery RSD (%)**	**Limit of Detection (ng)**
Observational	Diacetyl	98	7.3	1
Observational	2,3-Pentanedione	86	4.9	1
Laboratory	Diacetyl	89	18	1

Table II-3

Parameters Used to Estimate Mass of Diacetyl (ng) From Measured Total VOC Concentration for Emissions Range-Finding Experiments

Parameter (units)	
Temperature (C°)	19.72[1]
Pressure (atm)	1[2]
Sorbent tube flow rate (liters per minute)	0.2
Sorbent tube sampling time (minutes)	30
*minimum sorbent tube mass (ng)	100
*maximum sorbent tube mass (ng)	2400

* Minimum mass required for GC/MS analysis of diacetyl; maximum mass allowed without overloading sorbent tube of GC/MS

[1] Based on Q-Trak reading of temperature in room where experiment took place

[2] Based on Q-Trak reading of pressure in room where experiment took place

Appendix III. Results - Supplementary Information

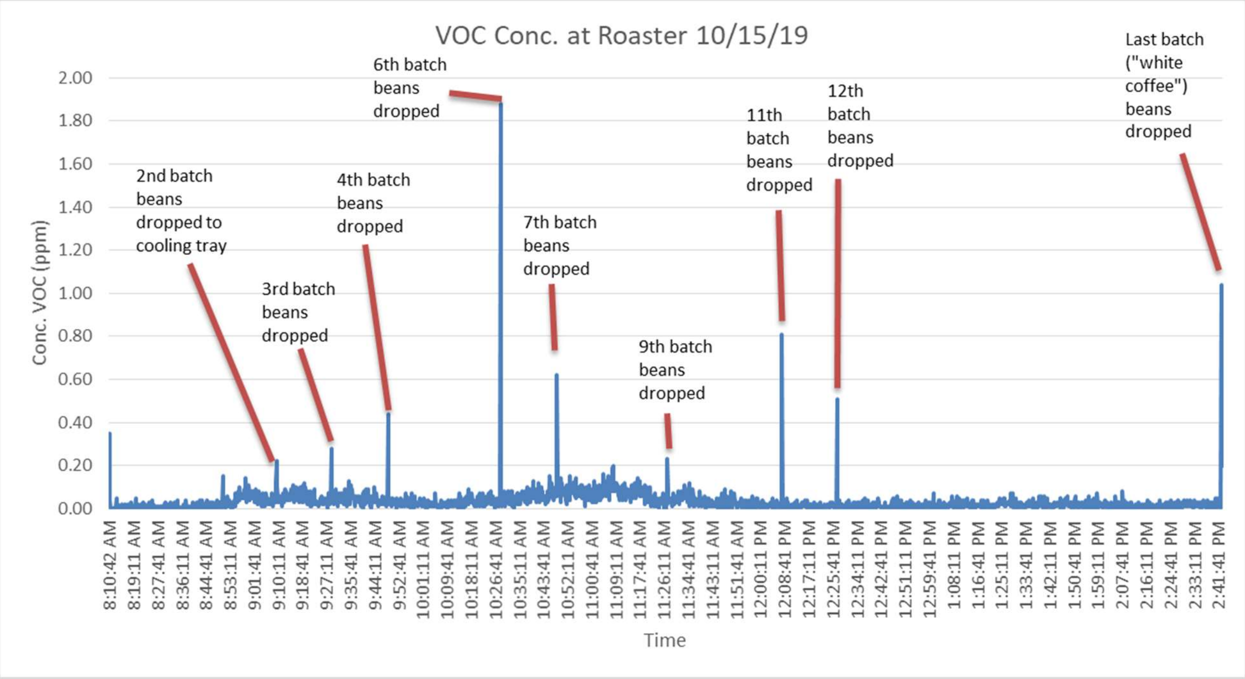


Figure III-1. Time-series analysis graph of total VOC emissions measured at the roaster on October 15, 2019.

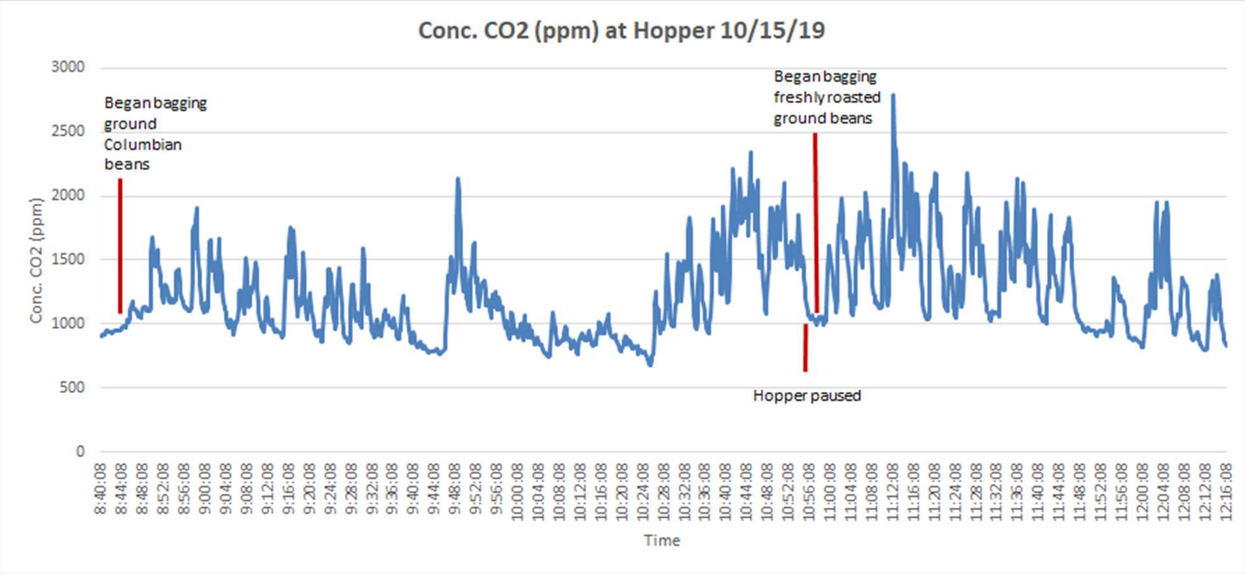


Figure III-2. Time-series analysis graph of CO_2 emissions measured at the hopper on October 15, 2019.

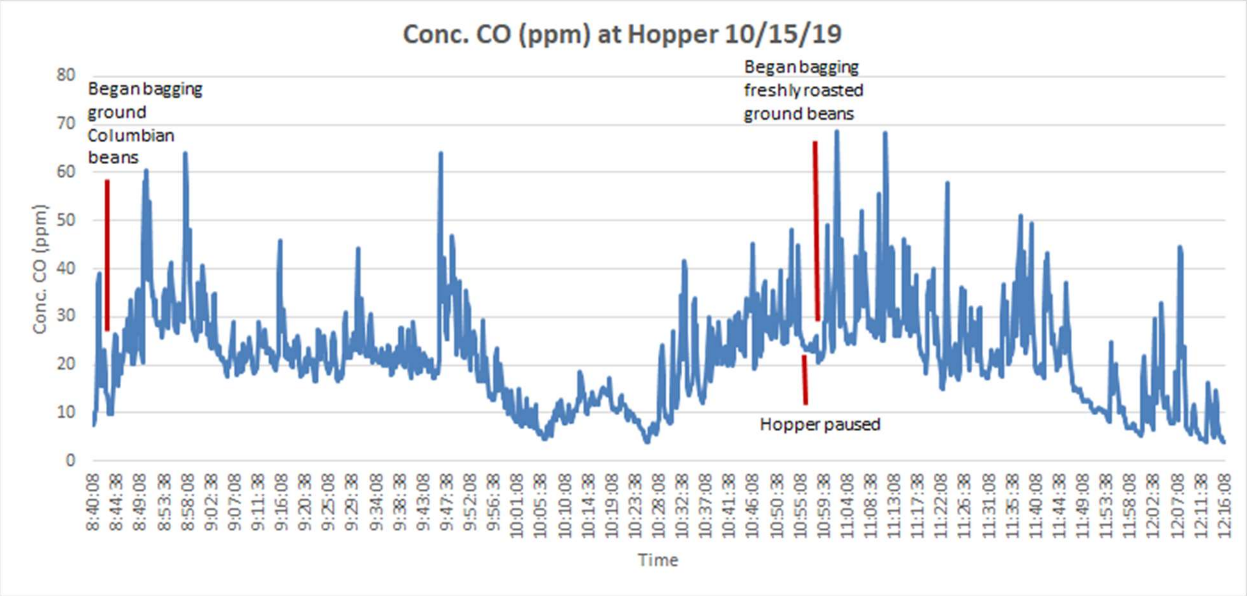


Figure III-3. Time-series analysis graph of CO emissions measured at the hopper on October 15, 2019.

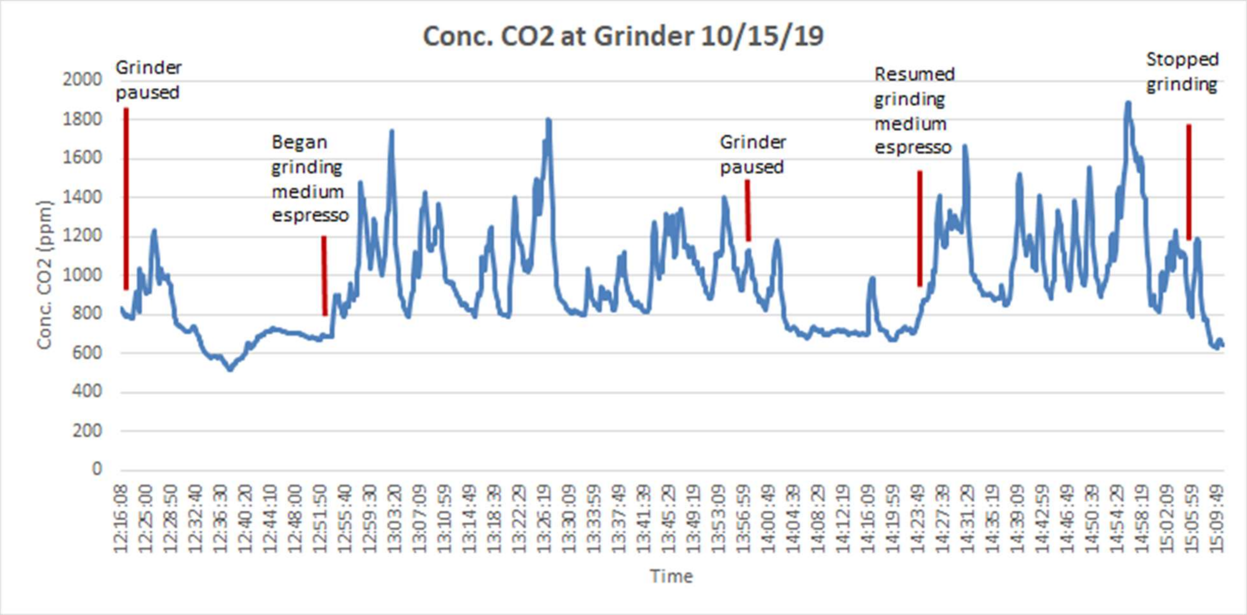


Figure III-4. Time-series analysis graph of CO_2 emissions measured at the grinding station on October 15, 2019.

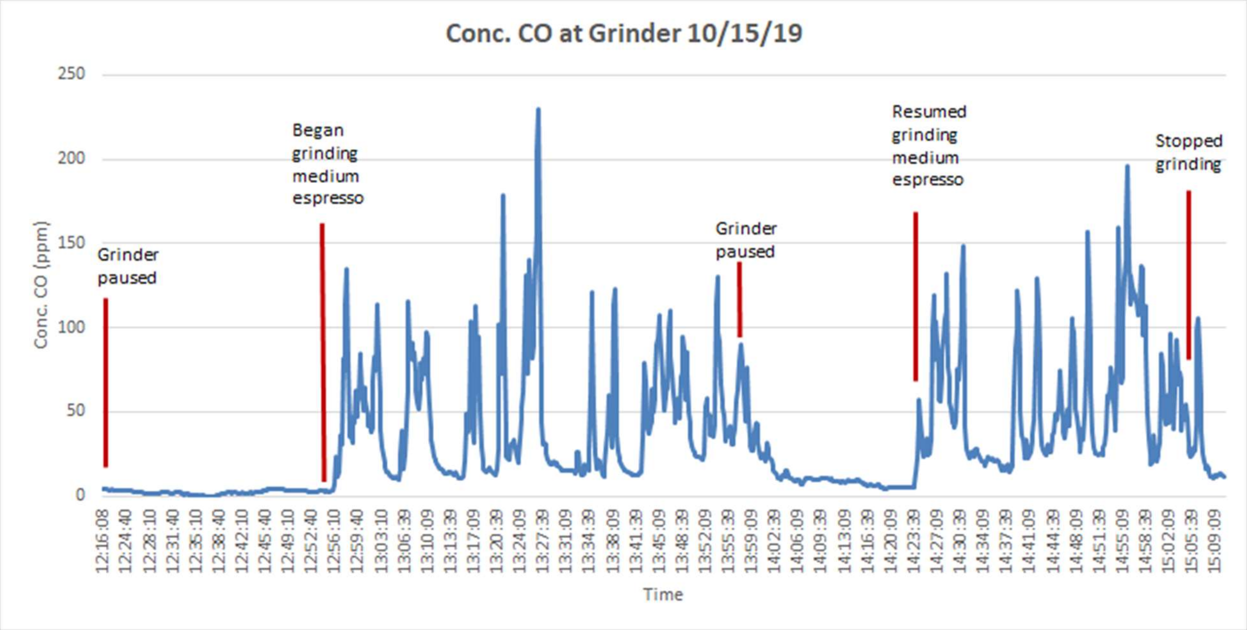


Figure III-5. Time-series analysis graph of CO emissions measured at the grinding station on October 15, 2019.

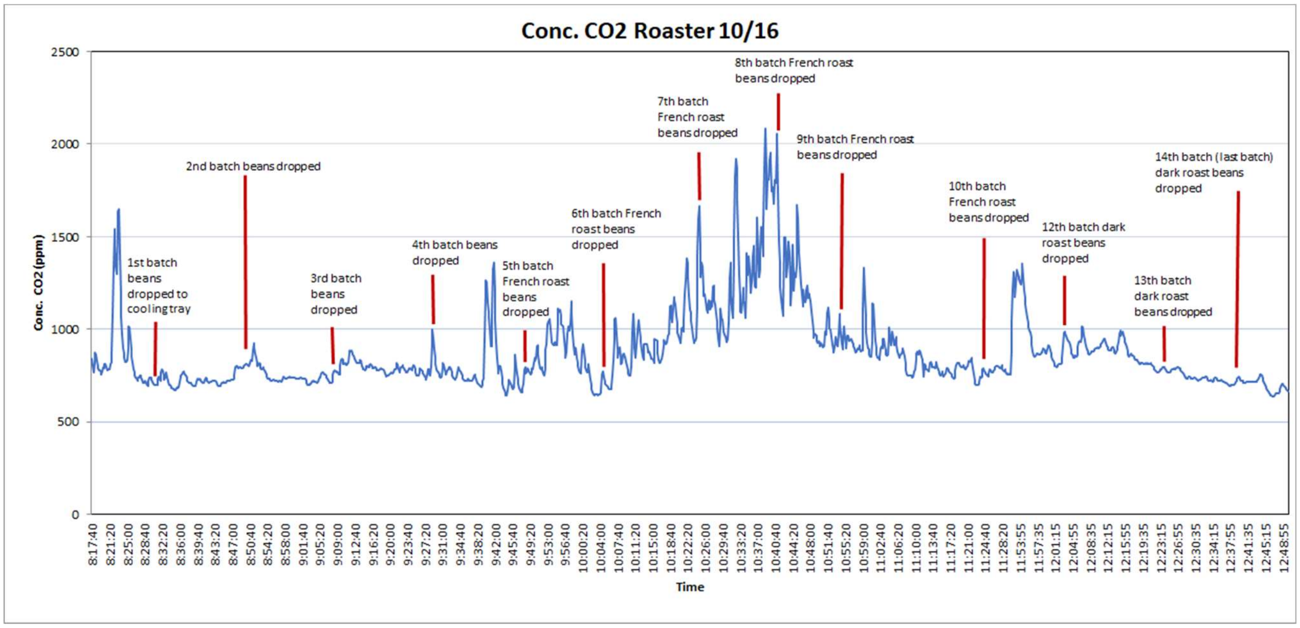


Figure III-6. Time-series analysis graph of CO_2 emissions measured at the roaster on October 16, 2019

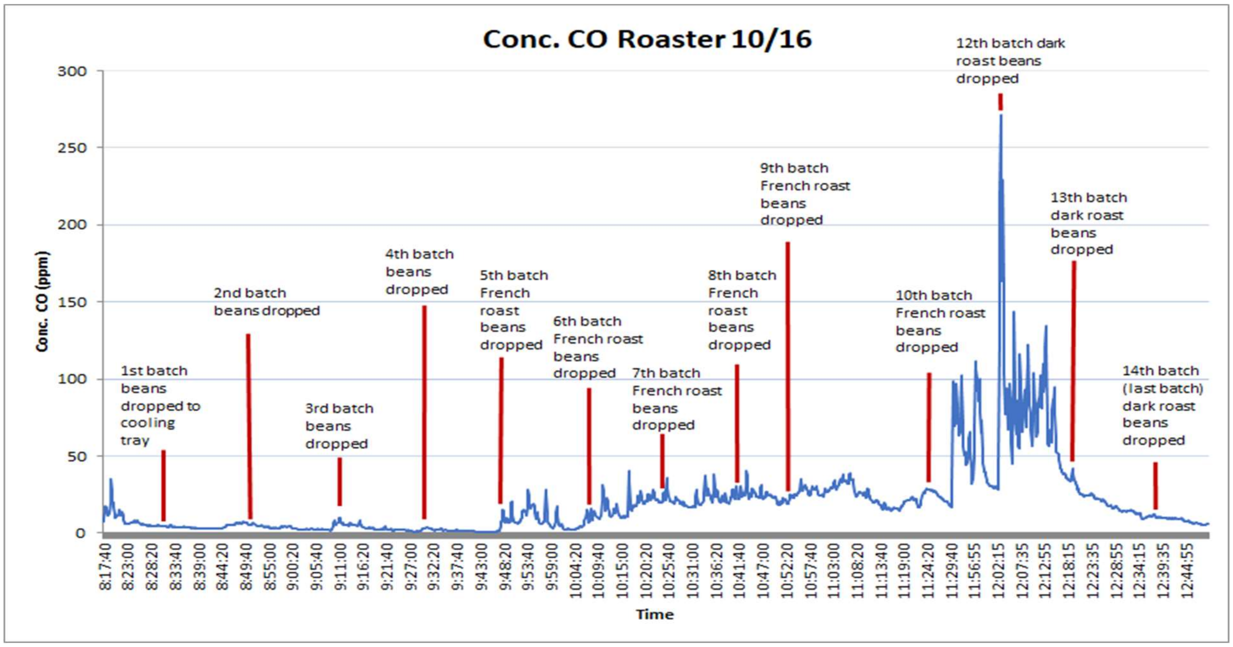


Figure III-7. Time-series analysis graph of CO emissions measured at the roaster on October 16, 2019.

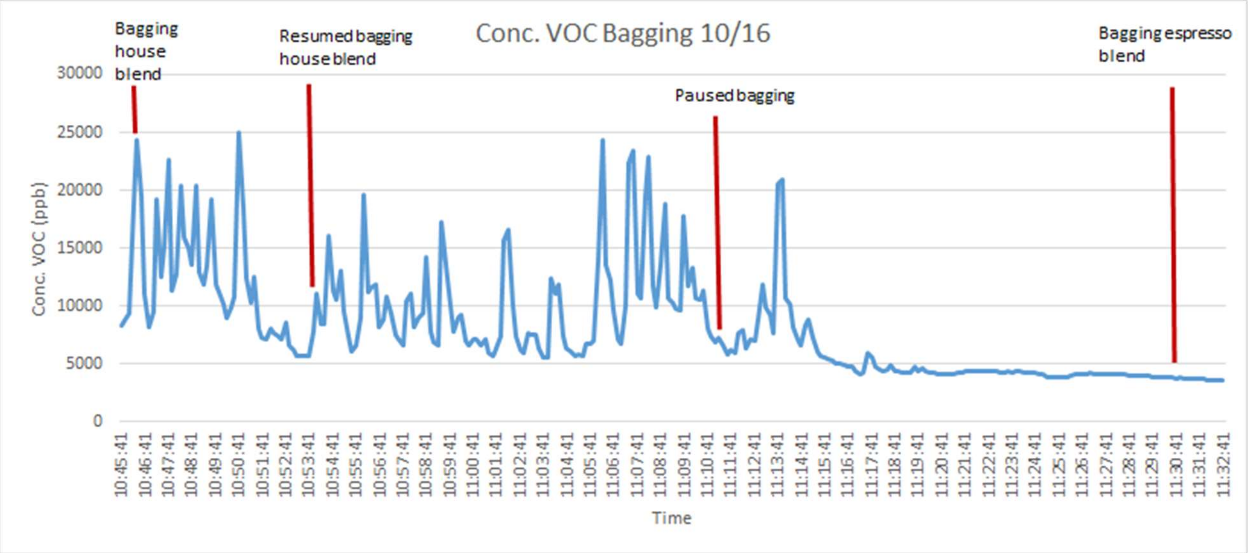


Figure III-8. Time-series analysis graph of total VOC emissions measured at the hopper on October 16, 2019.

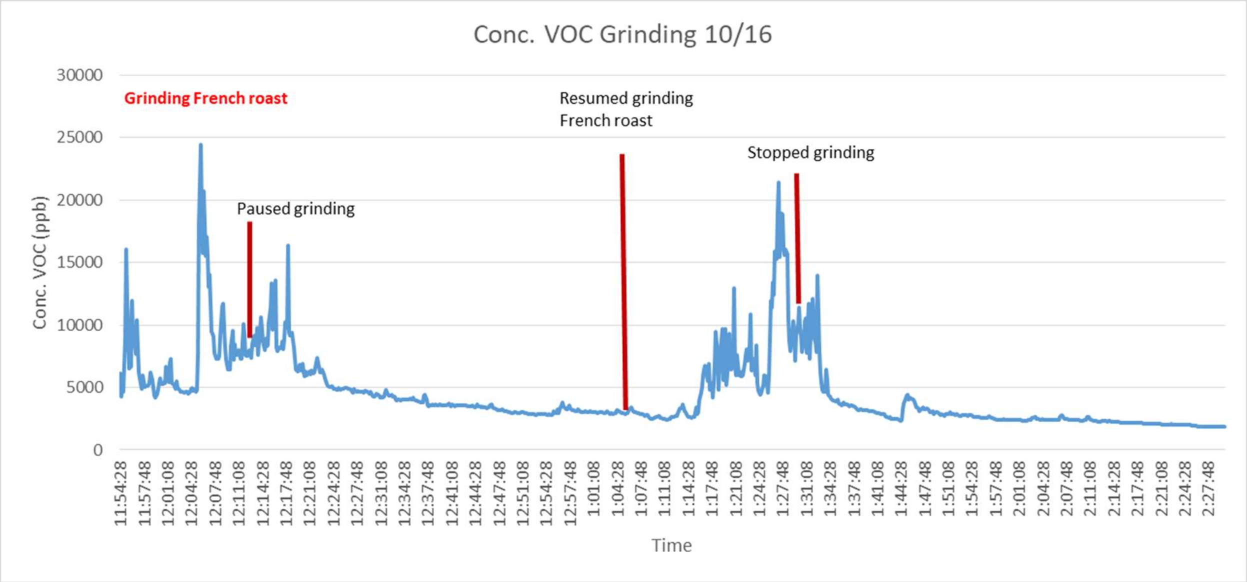


Figure III-9. Time-series analysis graph of total VOC emissions measured at the grinding station on October 16, 2019.

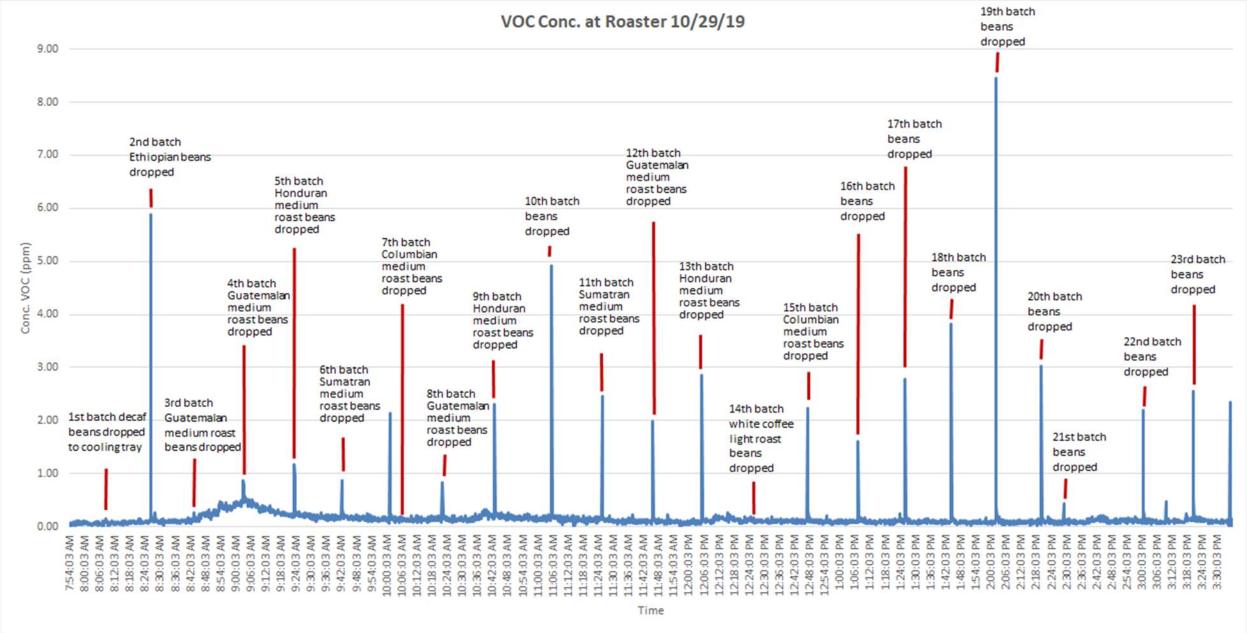


Figure III-10. Time-series analysis graph of total VOC emissions measured at the roaster on October 29, 2019.

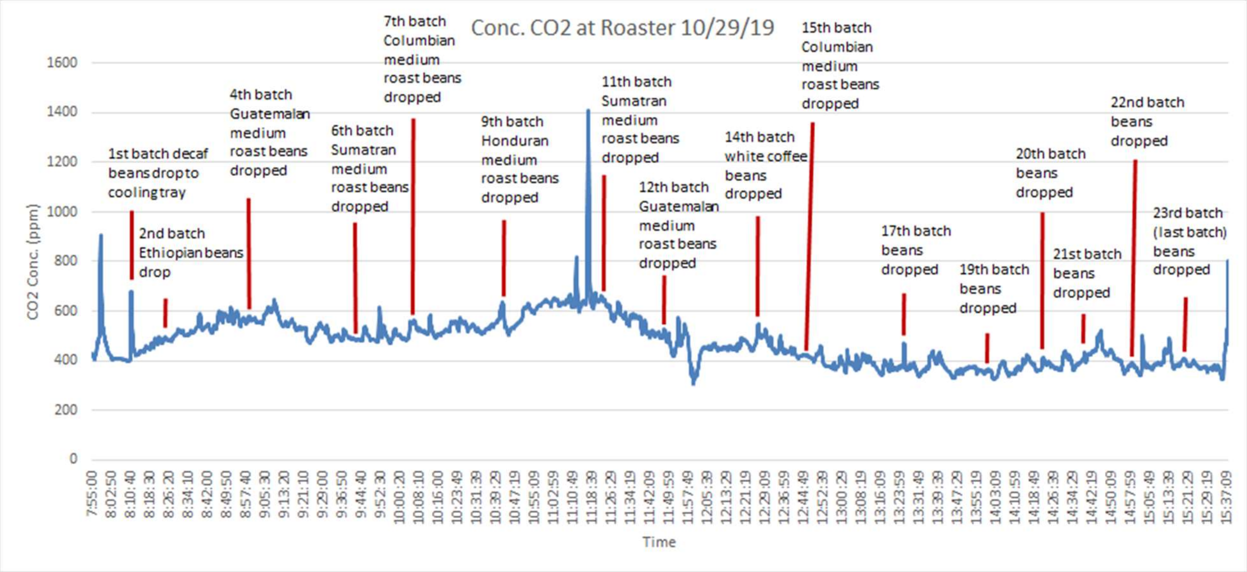


Figure III-11. Time-series analysis graph of CO_2 emissions measured at the roaster on October 29, 2019.

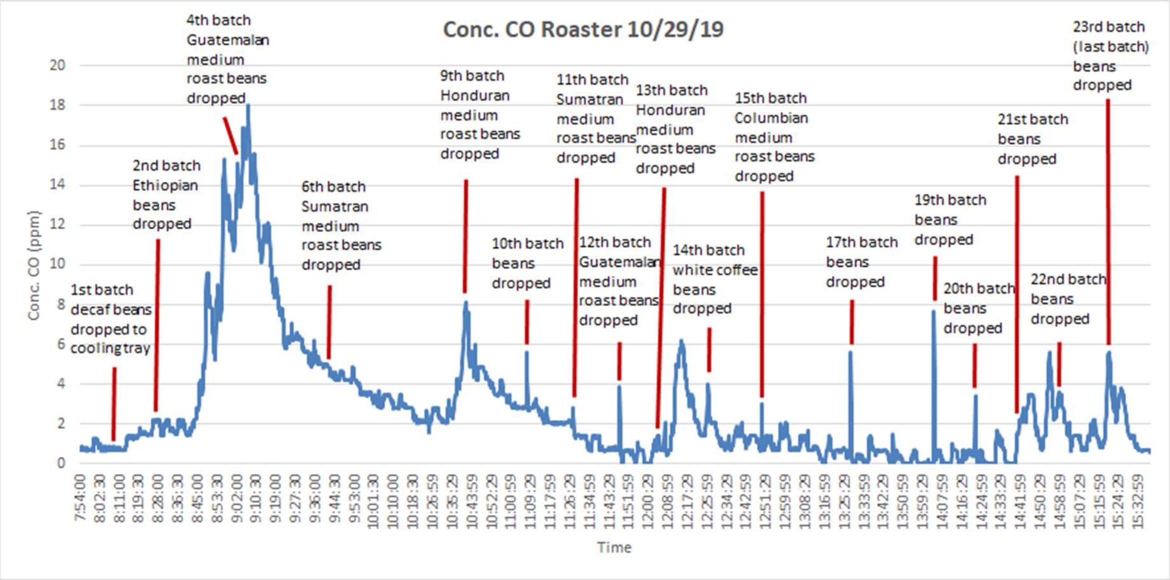


Figure III-12. Time-series analysis graph of CO emissions measured at the roaster on October 29, 2019.

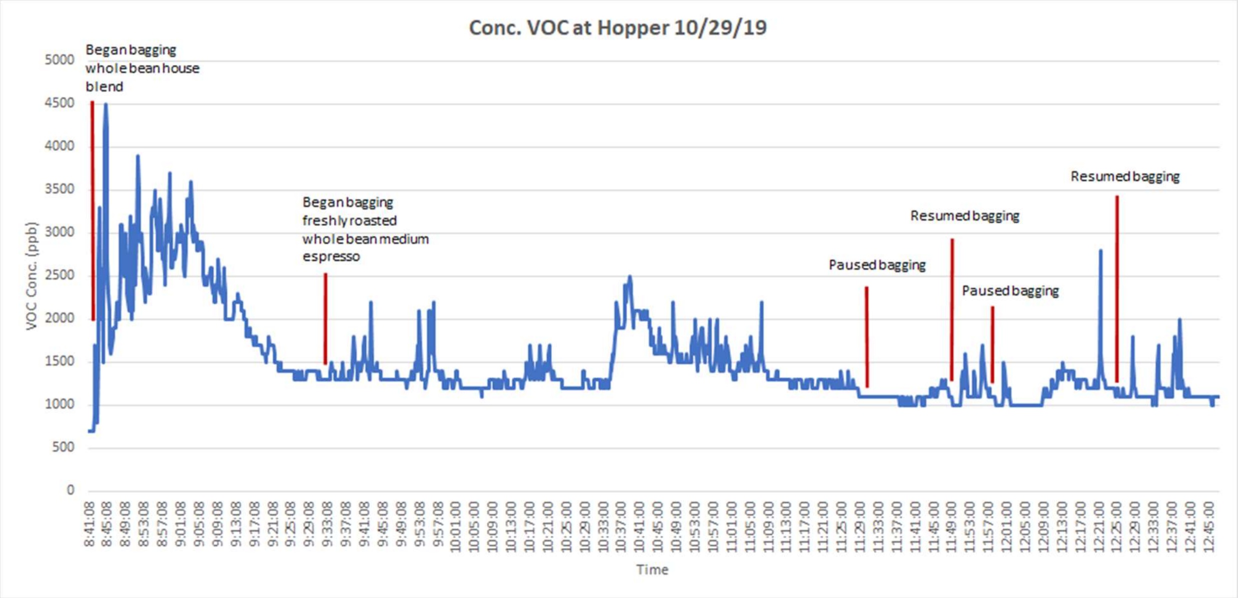


Figure III-13. Time-series analysis graph of total VOC emissions measured at the hopper on October 29, 2019.

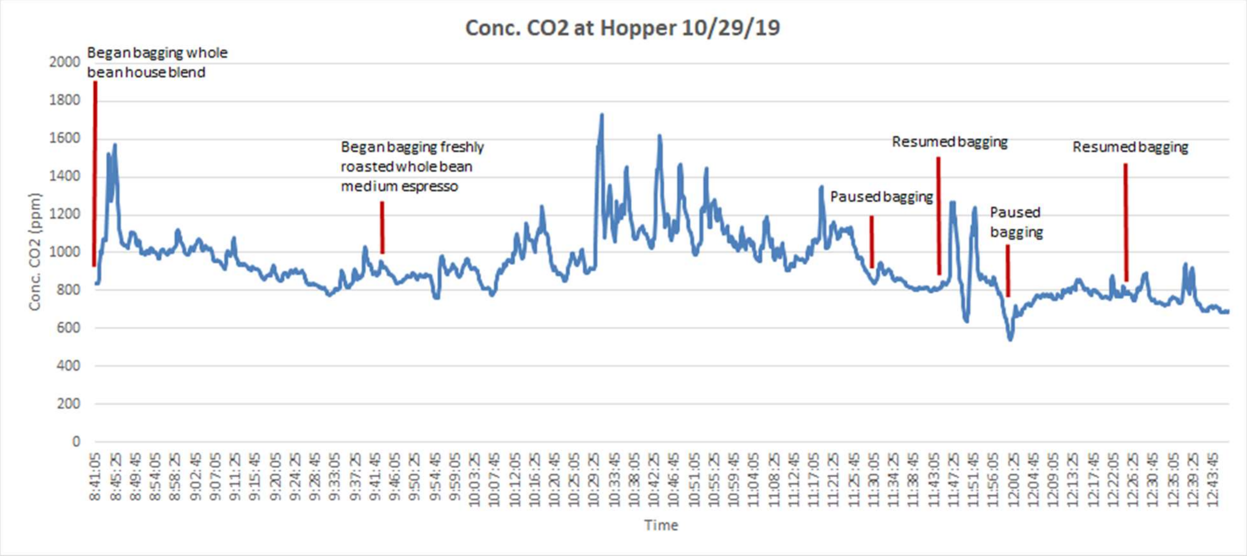


Figure III-14. Time-series analysis graph of CO_2 emissions measured at the hopper on October 29, 2019.

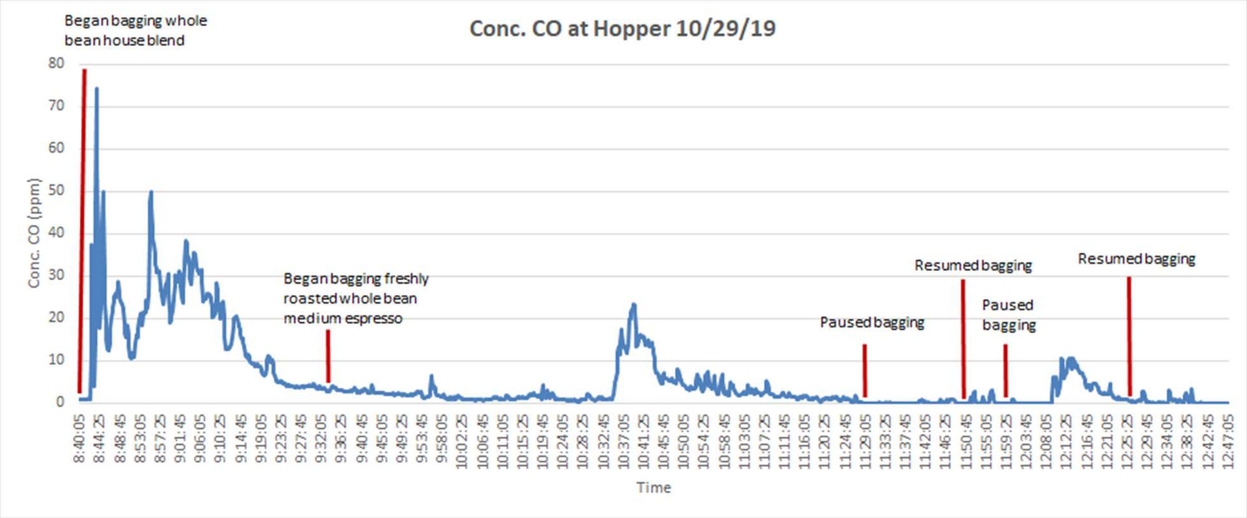


Figure III-15. Time-series analysis graph of CO emissions measured at the hopper on October 29, 2019.

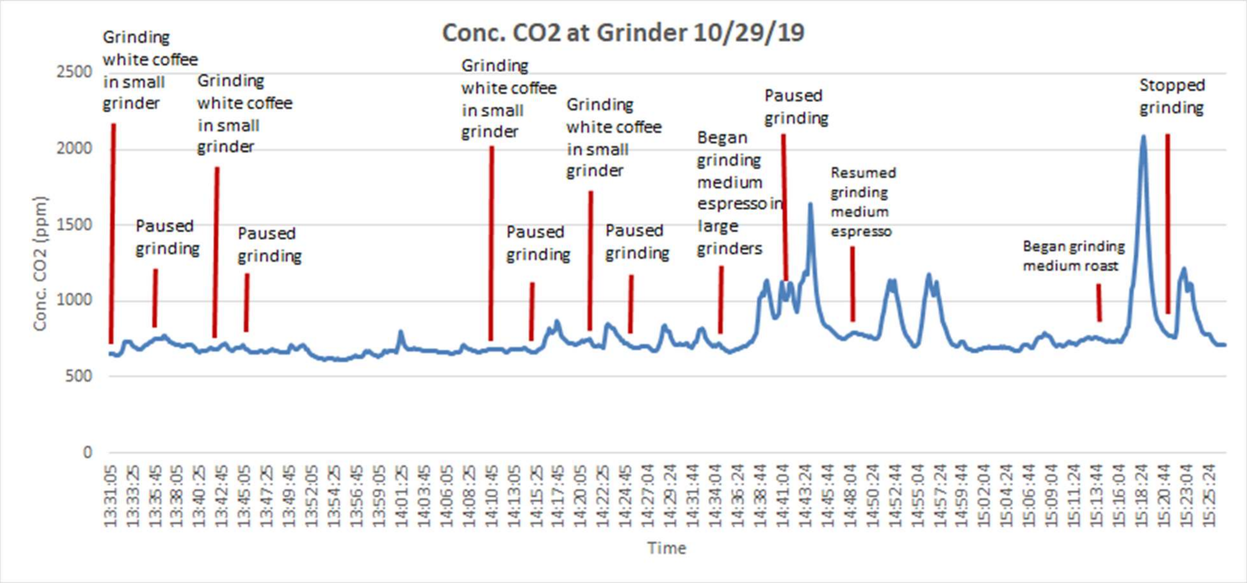


Figure III-16. Time-series analysis graph of CO_2 emissions measured at the grinding station on October 29, 2019.

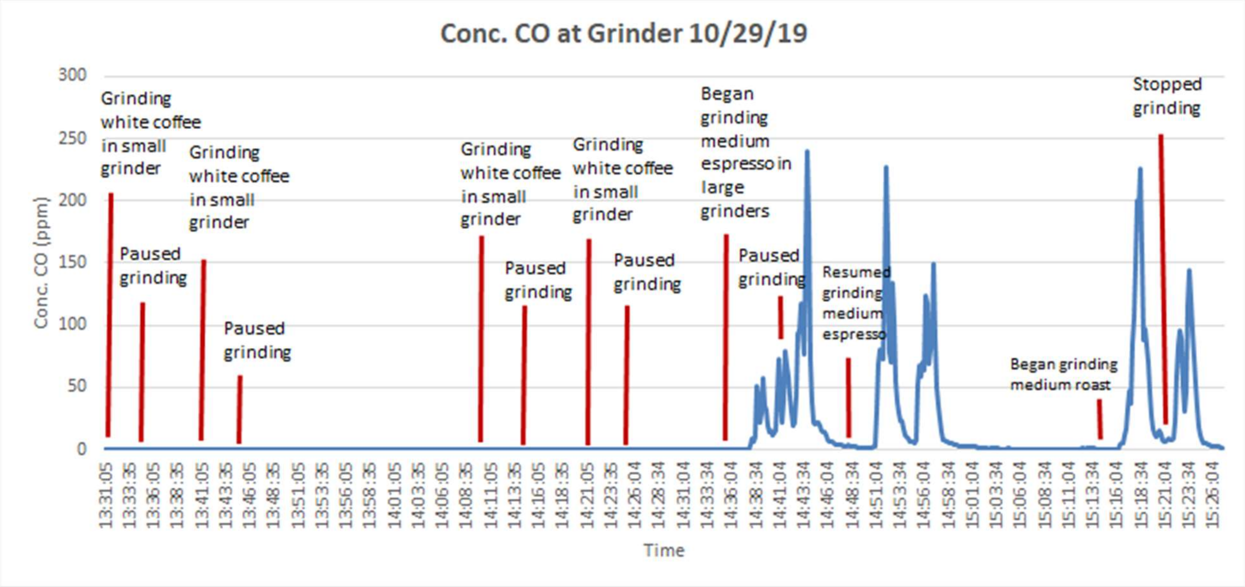


Figure III-17. Time-series analysis graph of CO emissions measured at the grinding station on October 29, 2019.

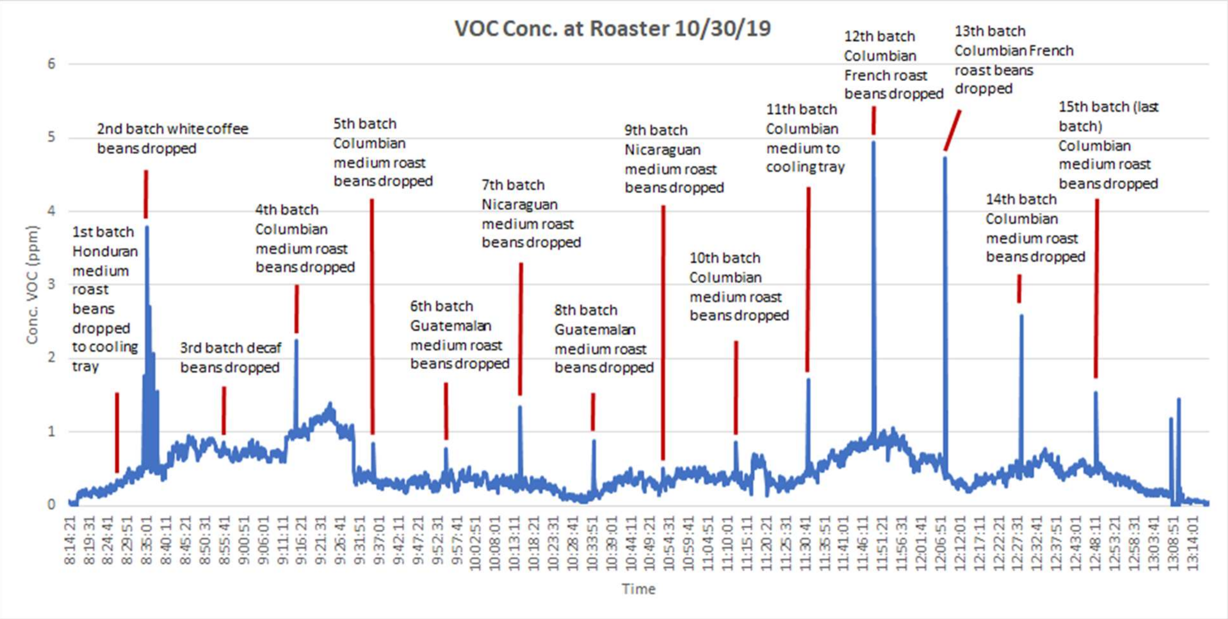


Figure III-18. Time-series analysis graph of total VOC emissions measured at the roaster on October 30, 2019.

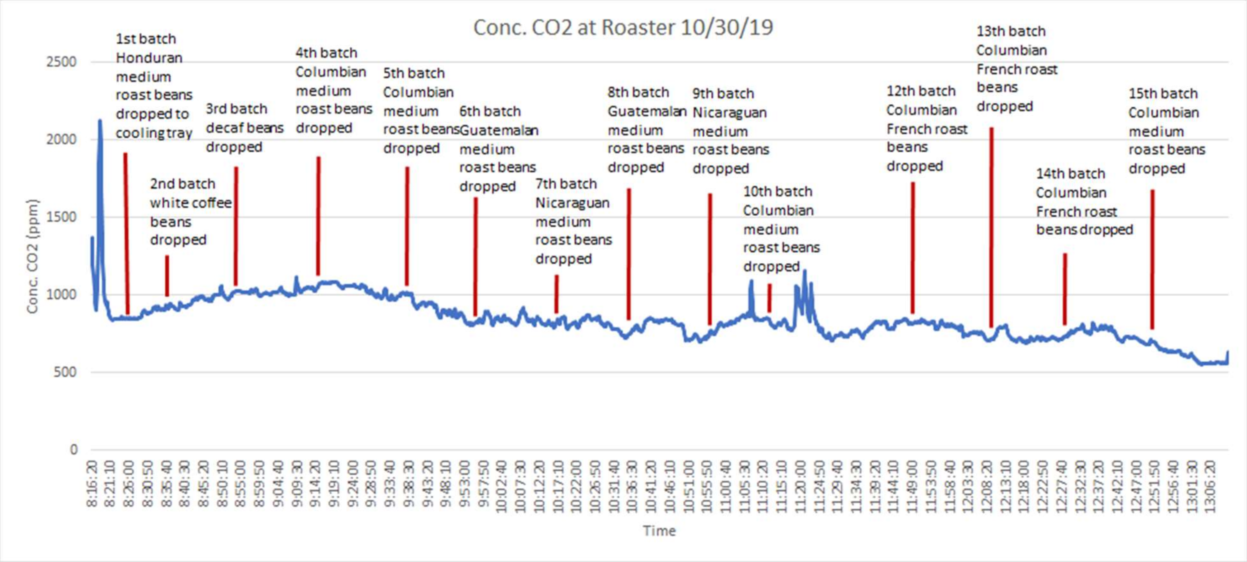


Figure III-19. Time-series analysis graph of CO_2 emissions measured at the roaster on October 30, 2019.

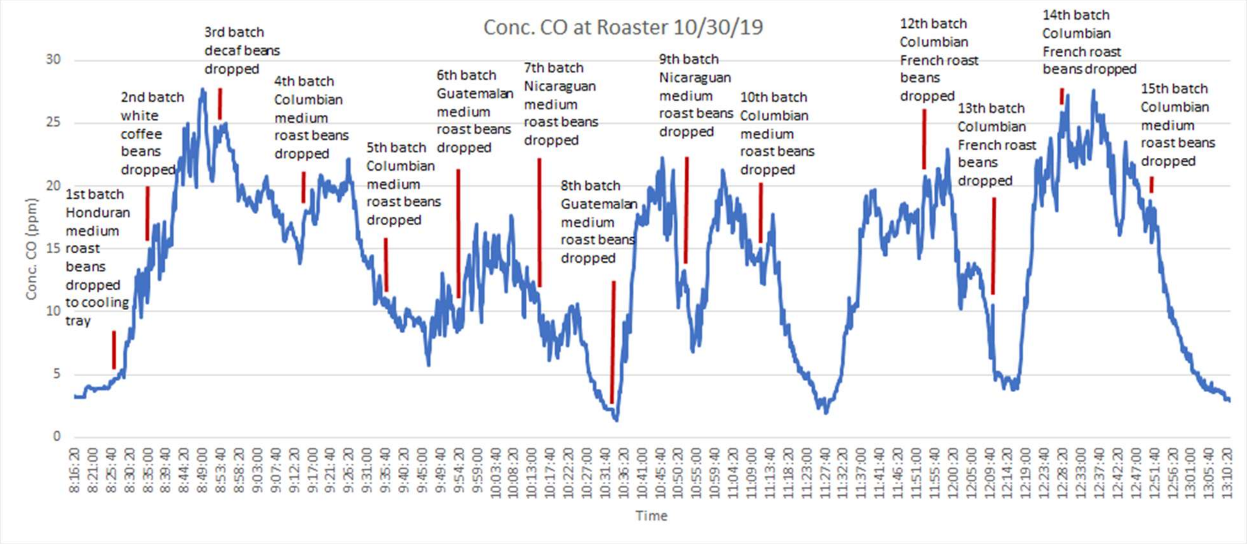


Figure III-20. Time series analysis graph of CO emissions measured at the roaster on October 30, 2019.

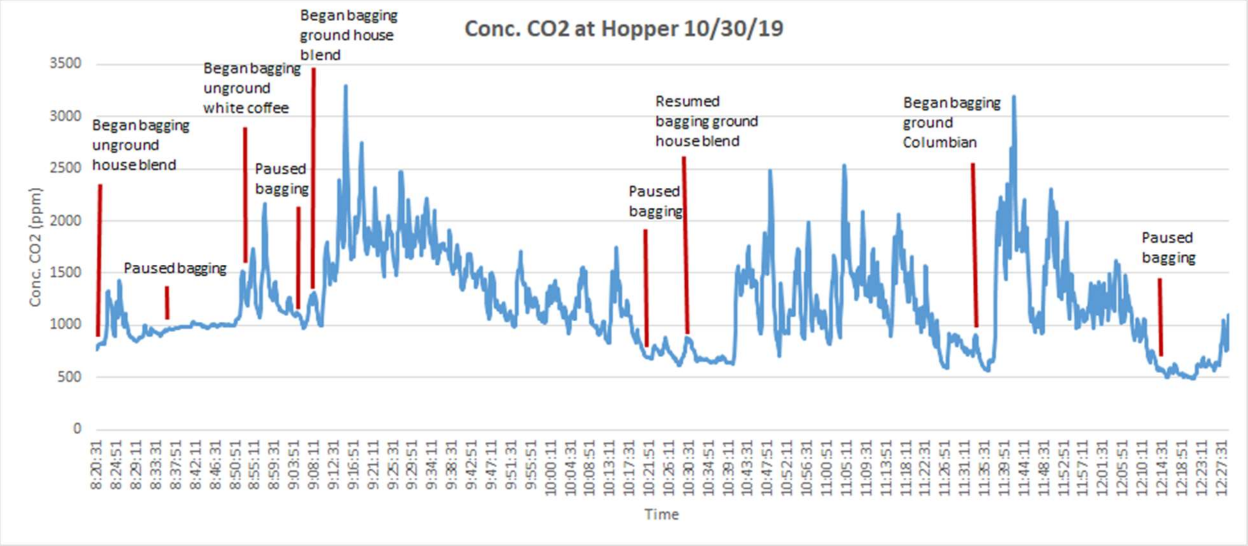


Figure III-21. Time-series analysis graph of CO_2 emissions measured at the hopper on October 30, 2019.

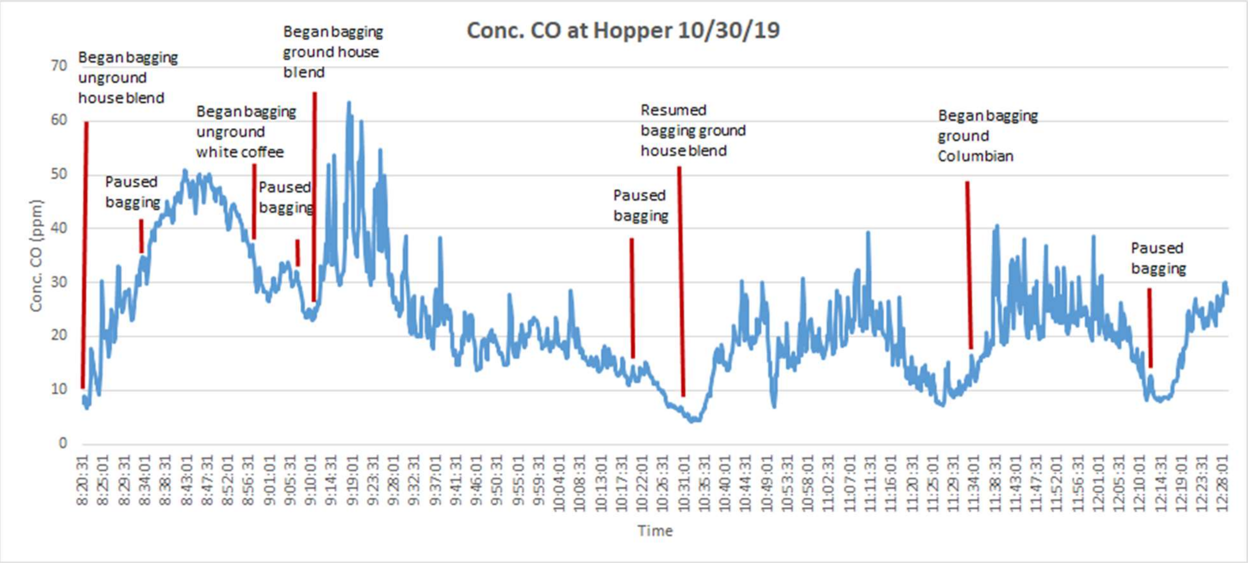


Figure III-22. Time-series analysis graph of CO emissions measured at the hopper on October 30, 2019.

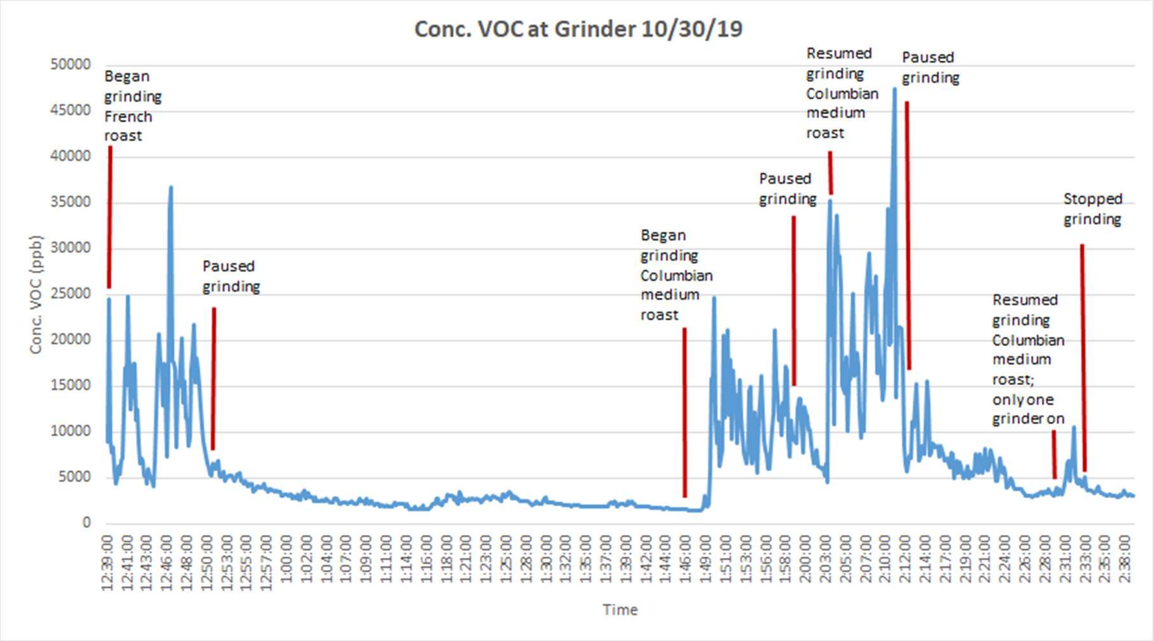


Figure III-23. Time-series analysis graph of total VOC emissions measured at the grinding station on October 30, 2019.

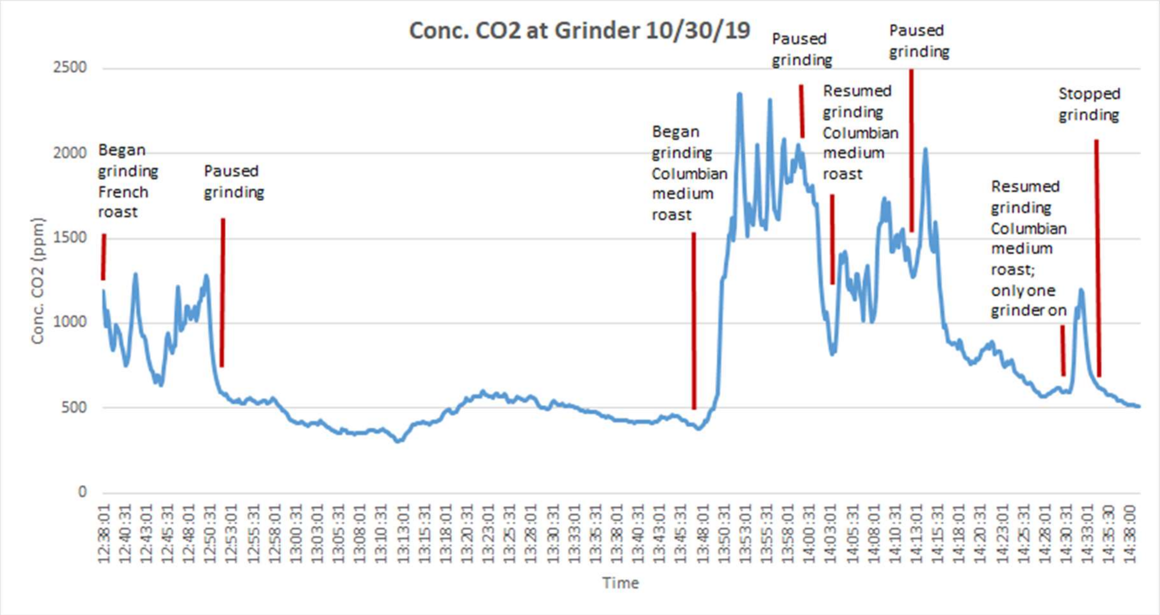


Figure III-24. Time-series analysis graph of CO_2 emissions measured at the grinding station on October 30, 2019.

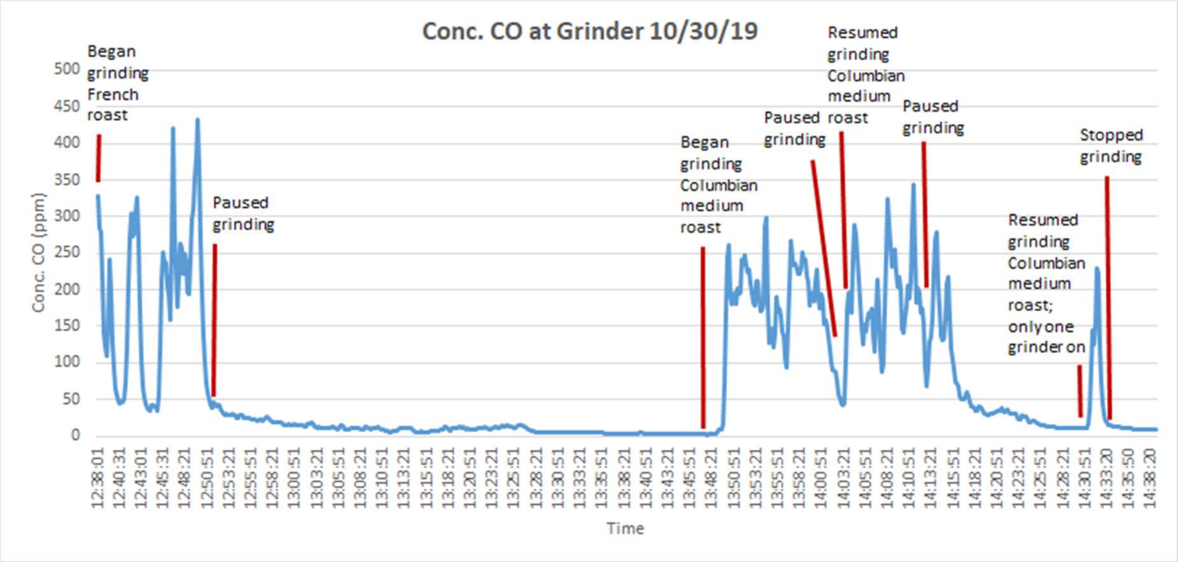


Figure III-25. Time-series analysis graph of CO emissions measured at the grinding station on October 30, 2019.

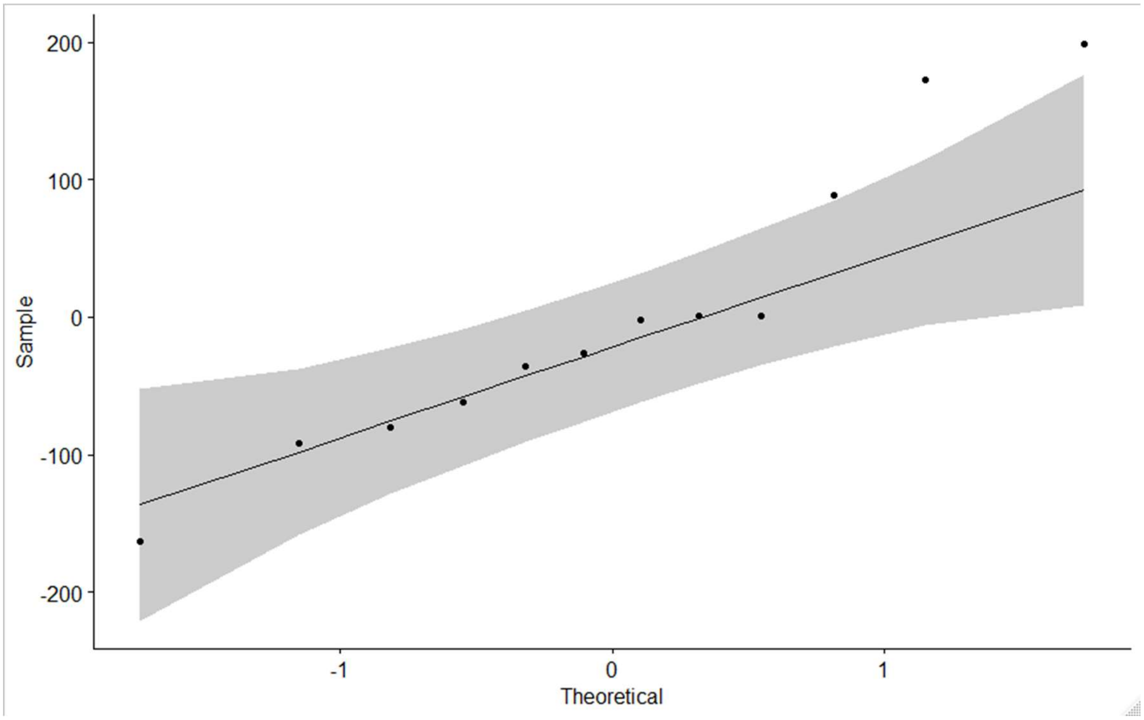


Figure III-26. QQ-plot of residuals from one-way ANOVA model to determine if there is a significant difference in mean diacetyl mass emissions from grinding of different coffee roasts (i.e. white coffee, medium espresso, espresso, and French roast).

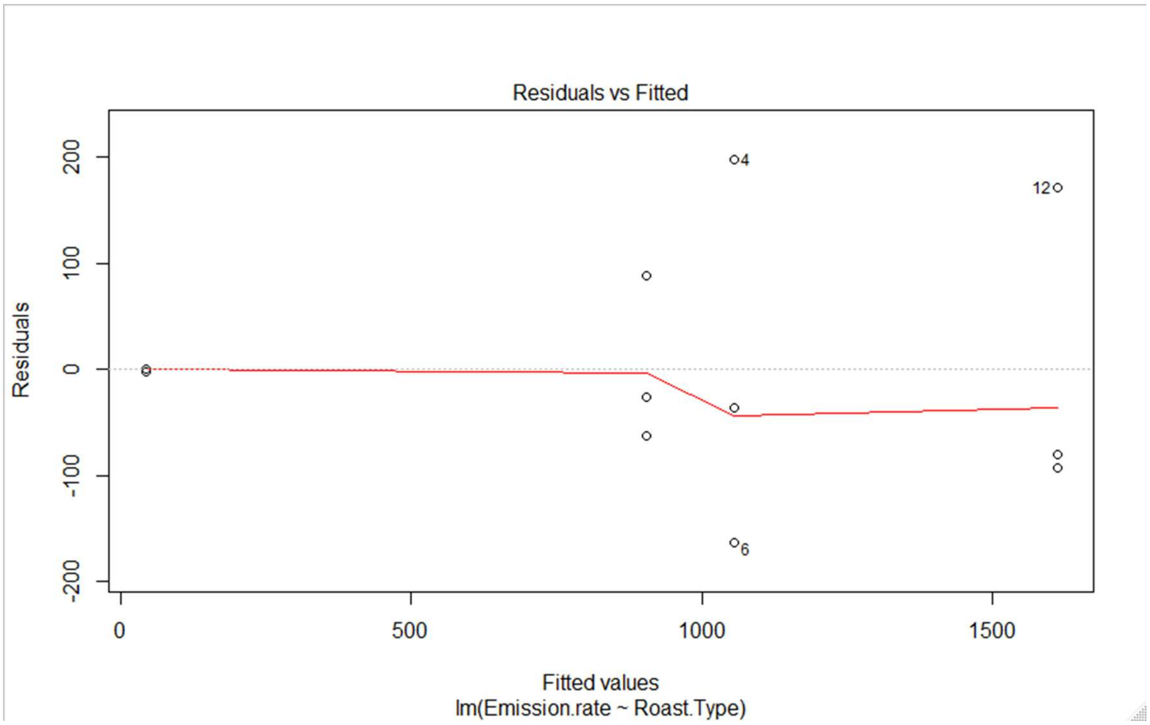


Figure III-27. Plot of residuals vs. fitted values from one-way ANOVA model to determine if there is a significant difference in mean diacetyl mass emissions from grinding of different coffee roasts (i.e. white coffee, medium espresso, espresso, and French roast).

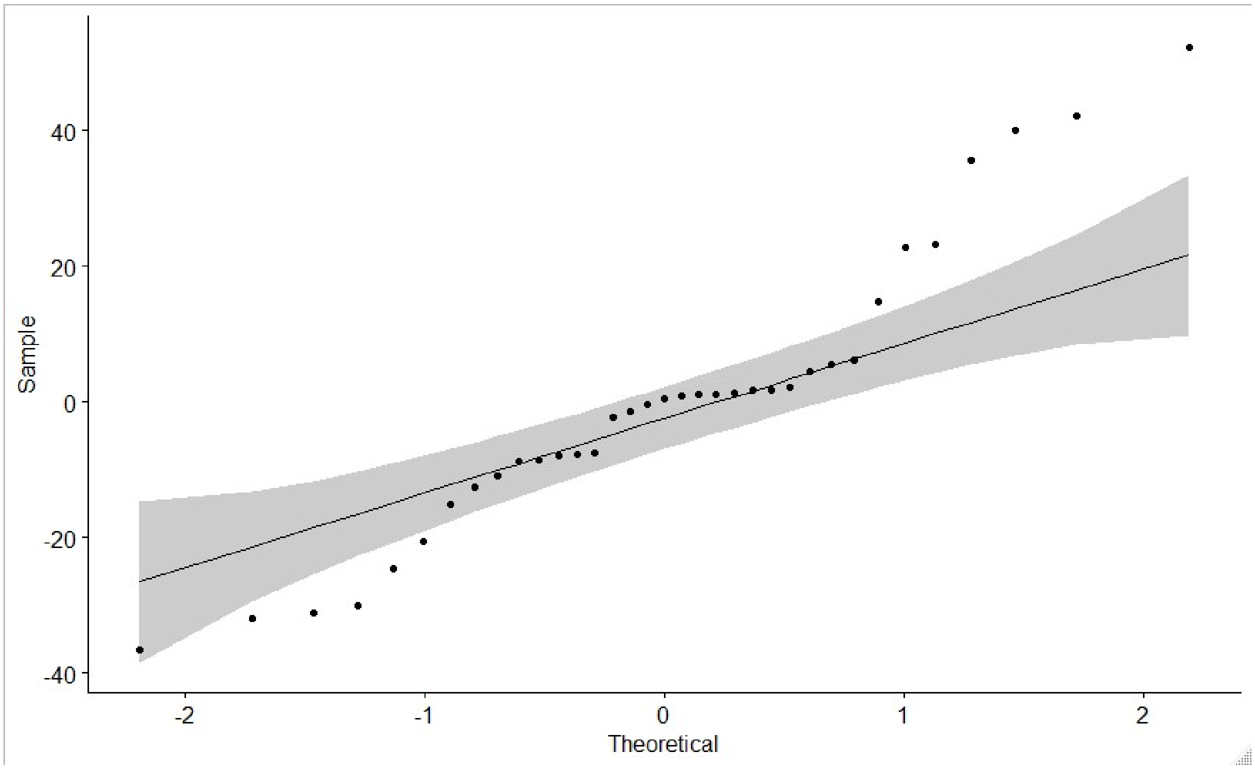


Figure III-28. QQ-plot of residuals from simple linear regression model predicting mean diacetyl concentrations from total VOC concentrations.

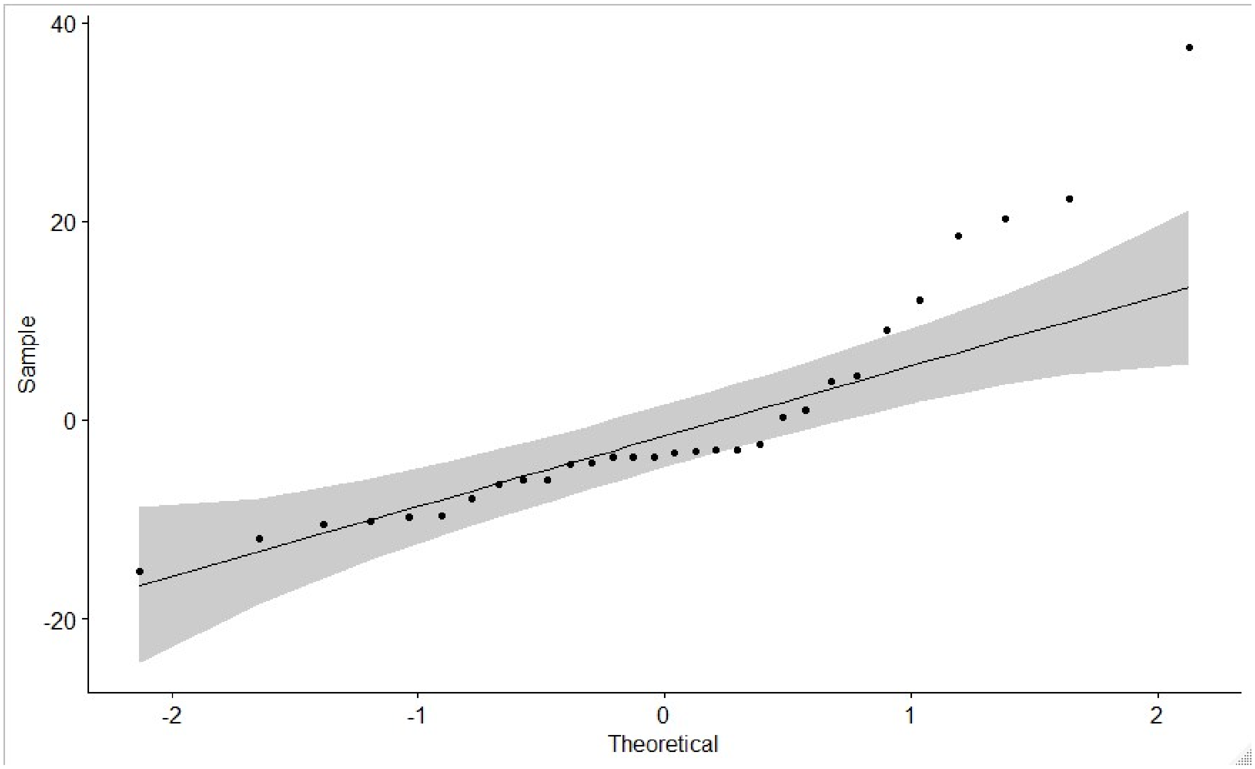


Figure III-29. QQ-plot of residuals from the constrained model, based on observed diacetyl concentrations that were less than 100 ppb, predicting mean diacetyl concentrations from total VOC concentrations.

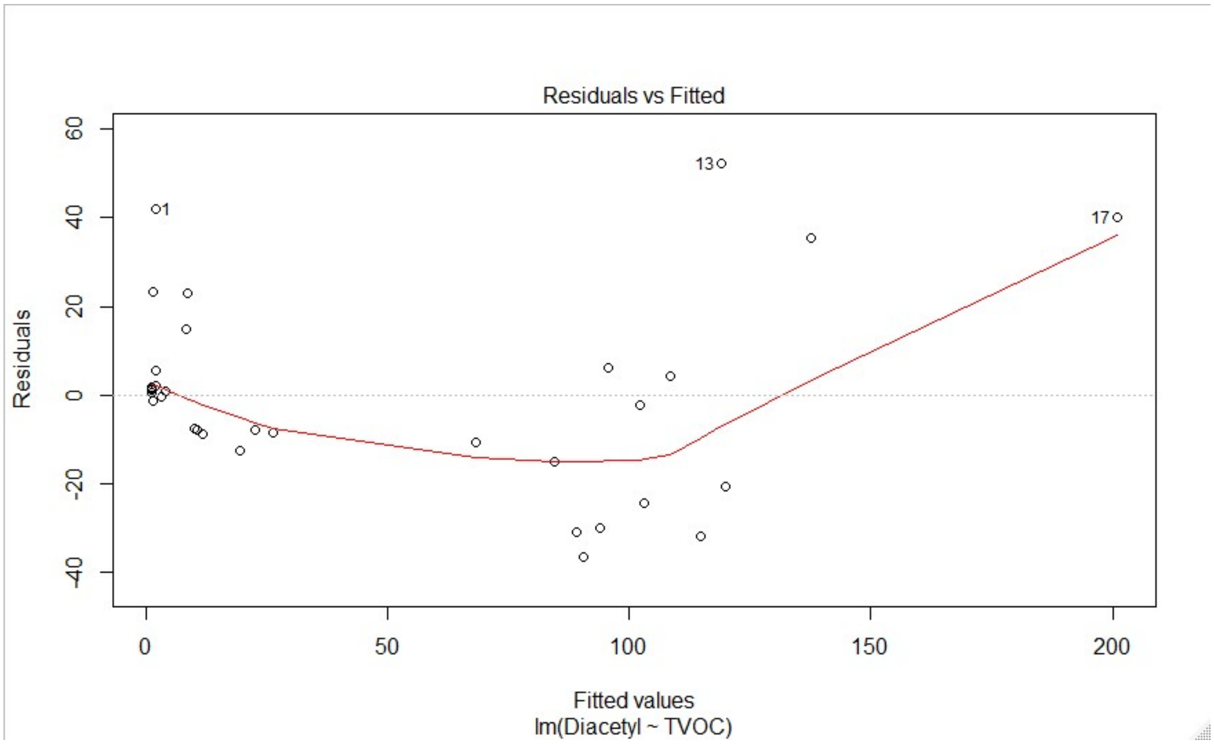


Figure III-30. Plot of residuals vs. fitted values from simple linear regression model predicting mean diacetyl concentrations from total VOC concentrations.

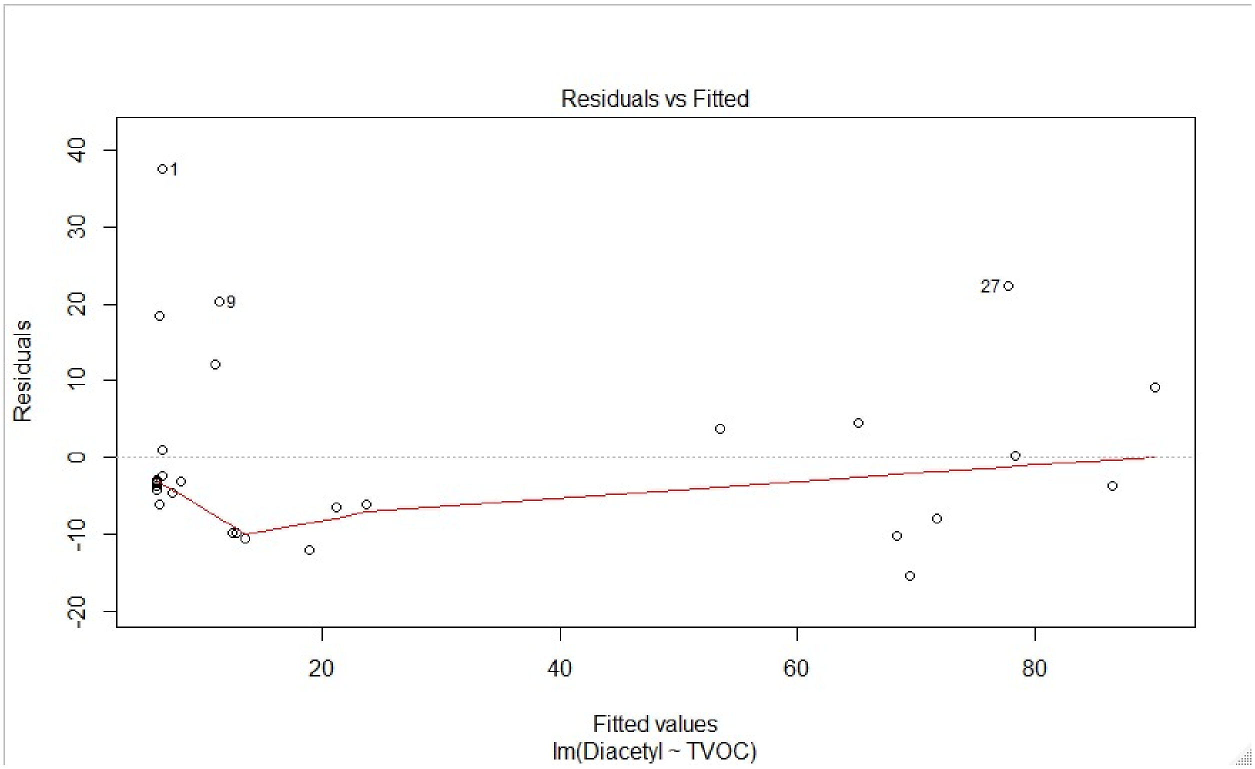


Figure III-31. Plot of residuals vs. fitted values from the constrained model, based on observed diacetyl concentrations that were less than 100 ppb, predicting mean diacetyl concentrations from total VOC concentrations.