Toxicology Reports 4 (2017) 113–122

Contents lists available at ScienceDirect

Toxicology Reports

journal homepage: www.elsevier.com/locate/toxrep

Diacetyl and 2,3-pentanedione in breathing zone and area air during large-scale commercial coffee roasting, blending and grinding processes

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ARTICLE INFO

Article history:
Received 5 January 2017
Received in revised form 23 January 2017
Accepted 29 January 2017
Available online 21 February 2017

Keywords:
Diacetyl
2,3-Butanedione
2,3-Pentanedione
Alpha-diketones
Coffee roasting
Coffee grinding
Exposure assessment
Fourier transform infrared spectroscopy (FTIR)

ABSTRACT

Recently described scientific literature has identified the airborne presence of 2,3-butanedione (diacetyl) and 2,3-pentanedione at concentrations approaching or potentially exceeding the current American Conference of Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs) at commercial coffee roasting and production facilities. Newly established National Institutes of Occupational Safety and Health (NIOSH) Recommended Exposure Limits for diacetyl and 2,3-pentanedione are even more conservative. Chronic exposure to these alpha-diketones at elevated airborne concentrations has been associated with lung damage, specifically bronchiolitis obliterans, most notably in industrial food processing facilities.

Workers at a large commercial coffee roaster were monitored for both eight-hour and task-based, short-term, 15-min sample durations for airborne concentrations of these alpha-diketones during specific work processes, including the coffee bean roasting, blending and grinding processes, during two separate 8-h work periods. Additionally, the authors performed real-time Fourier transform infrared spectroscopy (FTIR) analysis of the workers' breathing zone as well as the area workplace air for the presence of organic compounds to determine the sources, as well as quantitate and identify various organic compounds proximal to the roasting and grinding processes. Real-time FTIR measurements provided both the identification and quantitation of diacetyl and 2,3-pentanedione, as well as other organic compounds generated during coffee bean roasting and grinding operations.

Airborne concentrations of diacetyl in the workers' breathing zone, as eight-hour time-weighted averages were less than the ACGIH TLVs for diacetyl, while concentrations of 2,3-pentanedione were below the limit of detection in all samples. Short-term breathing zone samples revealed airborne concentrations for diacetyl that exceeded the ACGIH short-term exposure limit of 0.02 parts per million (ppm) in two samples collected on a grinder operator. FTIR analysis of air samples collected from both the workers' breathing zone and area air samples revealed low concentrations of various organics with diacetyl and 2,3-pentanedione at concentrations less than the limit of detection for the FTIR methods. Neither the breathing zone nor area air samples measured using the FTIR reflected airborne concentrations of organic compounds that, when detected, approached the ACGIH TLVs or regulatory standards, when available. FTIR analysis of headspace of ground coffee beans revealed ppm concentrations of expected alpha diketones, carbon monoxide and other volatile organic compounds (VOCs).

Coffee roasting and grinding, with adequate building ventilation and typical roasted bean handling and grinding, appears to generate very low, if any, concentrations of diacetyl and 2,3-pentanedione in the workers' breathing zones. This study also confirmed via FTIR that roasted

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http://dx.doi.org/10.1016/j.toxrep.2017.01.004

coffee beans naturally generate alpha-diketones and other organic compounds as naturally occurring compounds resultant of the roasting and then released during the grinding process.

1. Introduction

Coffee roasting and brewing have been occurring for millennia. Specialty coffee roasting has increased dramatically during the last two decades, with the growth of specialty roasters expanding throughout the United States. The authors performed a study to collect airborne samples at a commercial coffee roaster and compare the results to regulatory and consensus standards as well as to the scientific literature (Study). This Study was conducted at the request of a specialty coffee roaster and café operator located in Wisconsin. Following its employees' concerns regarding recent reports of alleged worker exposures to 2,3-butanedione (diacetyl) and 2,3-pentanedione at coffee roasting facilities, as reported by the *Milwaukee Journal Sentinel* in winter 2015 [1]. Specifically, the concerns were due to the reports that concentrations of diacetyl and 2,3-pentanedione had been measured in other industrial food processing facilities, including coffee roasting and flavoring operations, and worker exposures to these compounds have been associated with lung disease [2].

Diacetyl is naturally present in numerous foods, including butter, wine and coffee, and is added as an artificial flavor to baked goods and oils. The Centers for Disease Control and Prevention (CDC), National Institute for Occupational Safety and Health (NIOSH) recently identified limited exposure to diacetyl and 2,3-pentanedione during work with flavoring agents in the food industry [3]. Curwin et al. evaluated 105 area samples and 74 personal samples from 10 sites encompassing several food manufacturing facilities. The majority of the samples collected for acids and ketones (including diacetyl) were non-detectable with aldehydes and respirable dust primarily detected [3]. Airborne diacetyl and other ketones, including 2,3-pentanedione, were identified in personal breathing zones and area samples almost exclusively in association with flavoring use. The research of Kreiss et al., Akpinar-Elci et al., Parmet and Von Essen, and Kullman et al. have demonstrated the potential association between airborne diacetyl and other organic compound exposure from flavoring ingredients with the suspected development of bronchiolitis obliterans in microwave popcorn workers [4–7]. Kullman et al. identified diacetyl at concentrations from below the analytical detection limits to 98 parts per million (ppm), with the geometric mean concentrations of 0.71 ppm measured at microwave popcorn manufacturing plants [12]. Alternatively, Ronk et al. [8] opined that exposures to flavoring chemicals in the workplace did not produce an increased risk of abnormal lung function, while Egilman et al. [9] suggested that very low, 1 ppb as an eight-hour time weighted average (TWA), occupational exposure limits (OELs) should be adapted for diacetyl. Clark and Winter authored a document providing a comprehensive review of naturally occurring diacetyl in foods and a review of the safety and sensory characteristics of diacetyl [10]. These authors, amongst others, illustrate the conflicting evidence as to the role of diacetyl and other alpha-diketones play in chronic lung disorders, namely bronchiolitis obliterans, which have been observed in selected cohorts of food industry employees exposed to varying concentrations of diacetyl and other organic compounds [10].

There is limited published information regarding occupational exposure to naturally occurring diacetyl and 2,3-pentanedione in workers employed in the coffee roasting industry. A manuscript currently in press identified that mean estimated eight-hour TWA diacetyl exposures for the barista grinding of roasted coffee beans and pouring of the coffee ranged from 0.007 to 0.013 ppm [11]. The study was conducted in a small residential kitchen. Also, Gaffney et al. recently measured naturally occurring diacetyl, 2,3-pentanedione and respirable dust at a facility that roasts and grinds coffee beans [17]. Diacetyl, 2,3-pentanedione and respirable dust concentrations measured during roasting ranged from less than the limit of detection (<LOD) to 0.0039 ppm, <LOD to 0.018 ppm and <LOD to 0.31 milligrams per cubic meter (mg/m^3), respectively [12]. During grinding, diacetyl, 2,3-pentanedione and respirable dust concentrations ranged from 0.018 to 0.39 ppm, 0.0089–0.21 ppm and <LOD to 1.7 mg/m^3, respectively [12]. These authors noted that "[f]or any given bean/roast combination and sample location, diketone concentrations during grinding were higher than those measured during roasting. During grinding, concentrations decreased with increased distance from the source."[12] Gaffney et al.'s study was performed at a commercial roasting and grinding facility with a of volume 1133 m^3 with approximately 40,000 square feet (ft^2) of the floor surface and with 2.1 air exchanges per hour [12]. The authors reported a total of 1250 pounds of coffee roasted per week at this facility [12]. In 2016, Duling et al. reported workers in the grinding/packing area of unflavored coffee had the highest mean diacetyl exposures, with mean personal breathing zone concentrations of 93 ppb and mean personal breathing zone 2,3-pentanedione concentrations of 53 ppb [13]. It is important to note that local exhaust systems operating proximal to the coffee processes may substantially reduce the airborne concentrations detected in the employee's personal breathing zone and in area sampling.

Previously, it has been well described that roasted coffee beans contain a wide variety of volatile organic compounds (VOCs) and semi-VOCs (SVOCs). Hertz-Schünemann et al. identified that roasted coffee contains 0.1% VOCs and SVOCs per dry weight, respectively, while containing 850 identified compounds [14]. Akiyama et al. identified 47 organic compounds released during the coffee bean grinding process, including: diacetyl; 2,3-pentanedione; 2,3-hexanedione; and 3,4-hexanedione [15]. It has been reported that the roasting temperature and duration in which the coffee beans are roasted can alter the concentrations of organic compounds contained within the roasted beans. Additionally, different varieties of freshly brewed coffees have differing profiles of released organic compounds in their aroma [16,17]. Therefore, the organic compounds emitted during coffee processing are dependent on the coffee bean variety, temperature and duration of the roasting, and the grinding processes. Wang and Lim utilized Fourier transform infrared spectroscopy (FTIR) and physicochemical analysis to characterize roasted coffee beans to evaluate the roasting temperature and duration effects on the profiles of organic compounds [18]. Wang and Lim identified that the low temperature, long-duration roasting process resulted in the released of organic compounds with a greater infrared absorbance for aldehyde, ketones, aliphatic acids, aromatic bands and caffeine carbonyl bands on the FTIR spectra [18].

The United States Department of Labor, Occupational Safety and Health Administration (OSHA) has established regulatory standards as an eight-hour TWA Permissible Exposure Limit (PEL) and Short-term Exposure Limit (STEL) to be protective of worker health.

However, OSHA has not established a standard for either diacetyl or 2,3-pentanedione. The American Conference of Governmental Industrial Hygienists (ACGIH) has established an eight-hour TWA Threshold Limit Value (TLV) for diacetyl of 0.01 ppm and a Short-Term Exposure Limit (STEL) of 0.02 ppm; however, the ACGIH has not established a TLV or STEL for 2,3-pentanedione. In 2011, NIOSH issued a draft recommendation for a Recommended Exposure Limit (REL) for diacetyl of 5 parts per billion (ppb) or 0.005 ppm as a TWA for up to a ten-hour work day during a 40-h workweek and a 15-min STEL for diacetyl of 25 ppb or 0.025 ppm. In 2011, NIOSH also proposed an REL of 9.3 ppb or 0.0093 ppm for 2,3-pentandione as a TWA during a 40-h workweek and a STEL of 31 ppb or 0.031 ppm for a 15 min period [19]. In October 2016, NIOSH confirmed these RELs in its Criteria for a Recommended Standard for Occupational Exposure to Diacetyl and 2,3-Pentanedione and Recommended RELs [20]. The new NIOSH RELs have been established as 8-h TWAs of 5 ppb and 9.3 ppb for diacetyl and 2,3-pentanedione, respectively. The new NIOSH 15-min STELs were established at 25 and 31, ppb for diacetyl and 2,3-pentanedione, respectively.

1.1. Aim of the work

We evaluated airborne concentrations of diacetyl, 2,3-pentanedione, and other compounds during roasting, blending and grinding operations associated with a coffee bean roasting operation, which has exhaust ventilation systems at the cooling tables of roasting stations and a large volume of make-up supply air. Additionally, the authors confirmed and identified the operations at the commercial coffee roaster that contributed to the quantifiable airborne concentrations of diacetyl, 2,3-pentanedione, and other compounds. The authors utilized real-time FTIR to evaluate and quantify concentrations of these alpha-diketones and other organic compounds in the breathing zone of the workers and the headspace proximal to the roasted beans and ground coffee. Additionally, environmental conditions were collected in the Facility for other parameters which are described latter in this manuscript. Finally, the authors compared the airborne concentrations of the compounds that were detected to regulatory and consensus standards, where applicable.

2. Methods

2.1. Background

The Study was conducted at an approximately 24,000 ft^2 facility located in Wisconsin ("Facility"). The space was converted in 2007, from a manufacturing space to the current Facility, which uses the space for coffee roasting and grinding, as a warehouse, for shipping and receiving, for administrative and training offices, and as a café. During each day of the Study, the Facility roasted approximately 6500 pounds of raw coffee beans of various varieties and geographic origins. The green or unroasted beans were stored in burlap bags and unloaded into hoppers for automatic feeding into the roasting equipment. The Facility operates two coffee bean roasters, including a Probat G90 roaster that can roast 90 kg per roasting cycle and a Probat UG45 roaster that can roast 45 kg per roasting cycle. The beans are typically emptied from the roaster after reaching a maximum temperature of 435–440 degrees Fahrenheit (°F), 224–227 degrees Celsius (°C), depending on the desired roast of the coffee beans. The roasted beans are emptied onto a cooling table that is equipped with an automated rotating mixer and a downdraft ventilation system, the roasting operation is described in further detail below. After cooling, the freshly roasted beans are loaded into plastic-lined totes for short-term storage and subsequent bagging or grinding and then bagging. Small-batch grinding of 1-pound bags occurs at the Facility when an individual café customer purchases ground beans. Small-batch grinding was not evaluated in this Study, as it was conducted intermittently, was very short in duration and was located near other large-scale grinding equipment. Large-scale grinding of more than one pound of roasted coffee beans was generally conducted for the Facility's commercial customers, including food service companies and other regional independent cafés. Continuous coffee roasting and frequent large-scale grinding occurred at the Facility during the sampling periods.

Production areas at the Facility total approximately 10,000 ft^2 and are contiguous with the café space, although the production areas have separate and distinct heating, ventilation and air-conditioning (HVAC) systems. The entire Facility is supplied by one continuously operating 1200 cubic feet per minute (CFM) make-up supply air system, and a variable supply-air system with a maximal output or discharge of 5000 CFM. The Facility has exterior and interior atmospheric pressure sensors that automatically adjusts the variable 5000 CFM unit to maintain a net positive pressure in the Facility.

2.2. Facility environmental conditions

Temperature, relative humidity, carbon monoxide and carbon dioxide concentrations were measured and data logged during the duration of the sampling period utilizing a calibrated TSI Q-TRAK™ Indoor Air Quality Monitor 7575. Due to the Facility layout, specifically the adjoining café, offices, shipping docks and warehouse areas, a formal evaluation of the air exchange rate or proficiency was infeasible. Real-time area samples were collected to evaluate the total dust concentration and respirable dust including the particulate matter that was less than or equal to 4 micrometers (μm) in aerodynamic diameter (PM_4). Also, PM_{10} and $PM_{2.5}$ measurements of particulate matter less than or equal to 10 μm and 2.5 μm, respectively, in aerodynamic diameter were collected utilizing a calibrated and zeroed TSI DustTrak™ DRX Aerosol Monitor 8533. The aerosol monitor was placed in the center of the production portion of the Facility to evaluate the general airborne dust concentrations.

2.3. Employee Breathing zone and area sampling

The sampling was performed during work days representative of high-volume roasting and grinding production to evaluate the conditions expected to generate maximal concentrations of diacetyl and 2,3-pentanedione. Employees were fitted with calibrated GilAir® Plus sampling pumps that were pre- and post-sampling calibrated with a primary calibrator (Bios Defender 510). Sampling pumps were connected with Tygon® tubing to a sampling train consisting of two glass sample tubes containing washed silica gel (SKC Inc.) connected in series and positioned in the employees' personal breathing zones (PBZ). Air samples were collected at a flow rate of 0.05 Liters per minute (LPM) for long-term samples (approximately four hours in duration). The short-term samples (approximately 15 min in duration) were collected at a flow rate of 0.2 LPM. It should be noted that two four-hour samples were collected to determine the workers' eight-hour TWA concentrations and short-term sampling was collected for 15 min to provide for comparison with applicable consensus standards, as identified previously. Area samples were attached to tripods and positioned in the approximate breathing zone of an employee. One area sample was positioned between the roasters and the other was proximal to the bulk grinding operations. Two area samples were collected at each location during a 4 h sample duration, or 8 h in total. The sample tubes were contained in a light-resistant tube holder during sampling and samples were protected from light using light-resistant storage bags and shipped on ice via overnight courier

to an American Industrial Hygiene Association (AIHA)-accredited laboratory via chain-of-custody protocol. Samples were analyzed via OSHA Method 1012 for the quantification of diacetyl and 2,3-pentanedione by gas chromatography (GC) with electrochemical detection (ECD).

2.4. Fourier transform infrared spectroscopy (FTIR)

The Gasmet™ DX4040 real-time FTIR (Helsinki, Finland) instrument collected air through Tygon® tubing at a rate of 1.50 LPM into a 0.4 L sampling cell for FTIR analysis. The Gasmet™ FTIR was zeroed with 99.999% nitrogen (N_2) gas (Raeco) prior to sampling and was operated per manufacturer's instructions. The Gasmet™ FTIR performs 600 scans during a 60-s analysis period and provides the results of the measured gas concentrations in ppm. The FTIR was utilized to perform breathing zone, area and headspace measurements for the identification and quantification of various organic compounds, including diacetyl, 2,3-pentanedione and acetaldehyde. Measurements were collected during selected tasks in the employees' PBZs and headspace measurements were collected within the air space above recently ground and bagged coffee beans at a distance of approximately 20 centimeters from the surface of the ground beans contained in a storage tote lined with a plastic bag.

The FTIR (Fourier Transform Infrared) gas analyzer is capable of detecting gas compounds based on their absorbance of infrared radiation. Each compound produces a unique infrared spectrum which enables qualitative and quantitative analyses of organic and inorganic gases. Advanced and easy-to-use Calcmet software uses sophisticated and patented CLS (Classical Least Square) analysis algorithm for final calculations of gas concentrations. In addition, the Calcmet software, provides for cross-interferences to be automatically compensated for and the high performance and accuracy of the analyzer is achieved even in complex gas mixtures. The DX4040 portable real-time multi-component FTIR gas analyzer is capable of measuring 50 compounds simultaneously while providing reliable and accurate results in few minutes. DX4040 is a ready-to-use analyzer and it does not require any preparation prior to its use other than ultra-pure nitrogen gas (99.999%) zero. FTIR technology provides versatile and flexible gas analyses for various applications under varying conditions. FTIR spectra were analyzed with Gasmet's software, Calcmet™ version 12.140. The limit of detection (LOD) in Calcmet for individual compounds is calculated using modified classical least square (CLS) method for analysis. The calculated LOD values for the FTIR using the Calcmet software were 0.06 ppm for diacetyl and 0.22 ppm for 2,3-pentadione.

2.5. Similar exposure groups and sampling plan

The sampling plan included the following evaluations for airborne diacetyl and 2,3-pentanedione in the various worker Similar Exposure Groups (SEGs) for short-term (15 min), long-term (four h) and spot evaluations (60 s) via real-time FTIR. The FTIR also reported concentrations of additional compounds. Long-term samples were utilized to calculate eight-hour TWA concentrations.

(Table 1) A description of each SEG and sampling plan is as follows:

Table 1
Sampling Plan for Airborne Diacetyl and 2,3-Pentanedione in SEGs.

	Short-Term (15 min)	Long-Term (4 h)	Real-Time FTIR
Roaster 1 Operator	√ n = 3	√ n = 2	√
Roaster 2 Operator	√ n = 3	√ n = 2	√
Roaster 1 and 2- Area[a]		√ n = 2 (area)	√
Coffee Blending	√ n = 1		
Bulk Coffee Grinding-Area[a]		√ n = 2 (area)	√
Bulk Grinding and Bagging	√ n = 3	√ n = 2	√
Sample Roasting	√ n = 1		√

√ Sample collected in worker breathing zone, unless otherwise specified as area samples.
[a] Area samples were attached to a tripod and positioned in the approximate breathing zone.

2.5.1. Coffee roaster operators

The operators of Roasters 1 and 2 had similar work practices, with the primary difference being the size (total coffee bean volume) of the roasting equipment being operated by each operator. Roaster 1 is a Probat brand roaster with a capacity of 90 kg of coffee beans per roasting cycle. Roaster 2 is a Probat brand roaster with a capacity of 45 kg of coffee beans per roasting cycle. A complete roasting cycle required approximately 15 min and, upon completion of roasting, the front roasting oven door was manually opened and the roasted beans were directed onto the circular cooling tray located below. Coffees of different roasts and varieties may have shorter or longer roasting cycles; however, the roast cycles generally do not exceed 20 min. After roasting, the beans are mixed and cooled on the cooling tray by stainless-steel rotating arms with paddles affixed to a circular cooling tray. The cooling trays operate as down-draft tables, which were connected to the local exhaust ventilation (LEV) system, both cooling the beans and eliminating odors and gases. Once the beans were appropriately cooled to room temperature, the beans were transported through a vacuum conveyance system, that included an air separator to remove foreign objects (stones, debris), and stored in temporary, plastic-lined transport totes. Both operators of Roasters 1 and 2 monitored the roasting coffee beans by visual, auditory and olfactory inspections. Specifically, the roaster operators evaluated auditory "crackles" during the roasting and by removing the "bean sampler" located on the front of the Probat roasters during the cycle to perform one or two olfactory evaluations of the roasted beans for approximately 5 s in duration. The "bean sampler" is a cylindrical tool that pulled roasted beans out of the roast cycle for the operator to observe and smell the beans.

The job duties of the roaster operators also included loading raw coffee beans into the roaster, cleanup and emptying the chaff collection system. Both operators of Roasters 1 and 2 were fitted with a sampling pump and sampling train for the collection of long-term samples during their performance of their full work shift activities. For short-term sampling, each roaster was fitted with a sampling pump and sampling train, as previously described, which was operated for approximately 15 min during the active roasting process, olfactory and visual observation of the beans, discharge of the roasted beans, cooling of the beans on the cooling tray, and vacuum transport of the roasted beans into transport totes.

The roasters, chaff collection system and conveyance system were each connected to the Facility's LEV system. The authors understand that the Facility operated at a net positive pressure to the exterior. A review of the Facility's ventilation system plans generally reflected these observations and a net positive pressure was indicated by air movement from indoors to outdoors through the Facility's exterior doors.

2.5.2. Coffee blending

Coffees of three to four different roasts and varieties are often mixed together to prepare specialty blends. Transport totes of roasted beans were lifted by an automated system, which discharged the roasted beans onto a circular, rotary blending table that is equipped with a LEV downdraft table. Approximately three to four totes of different roasts were loaded onto the blending table and allowed to thoroughly mix for approximately 15 min. The employee operating the blending table loaded the roasted beans

onto the automated system and mixed the beans with a stainless-steel scoop while the beans rotated on the blending table. Once a consistent mix of roasted beans had been established, the beans are discharged into temporary, plastic bag-lined, storage totes for later packaging and occasionally grinding. The employee performing the coffee blending job duties was fitted with a sample train, as described above, and sampled for approximately 15 min during a cycle of blending and mixing of the roasted coffee beans.

2.5.3. Bulk coffee grinding

Bulk coffee bean grinding occurs approximately once per week at the Facility. Approximately 40 pounds of roasted coffee beans are loaded into the bulk grinder and an approximately 35-gallon, plastic bag-lined, temporary storage tote is placed below the grinder to capture the freshly ground beans. The grinder does not require continuous manual operation or surveillance; thus the operator loads the beans, activates the grinder and then performs other tasks around the Facility. The grinding cycle requires approximately 20–25 min and approximately three to five cycles of grinding are conducted during one work day. The coffee grinding process occurs intermittently throughout the day and is often conducted by various employees. The employee who operated the bulk grinding equipment during the day of sampling was fitted with a sampling train, as described above, and was sampled for approximately eight hours (two 4 h samples) during the bulk grinding and other warehouse and housekeeping job duties. An area sample was also collected proximal to the grinding operations.

2.5.4. Bulk grinding and bagging

When bulk orders of the coffee beans are bagged for sale and/or distribution immediately after grinding, the work process differs as compared to when only bulk grinding is performed. When the beans that were bulk ground are immediately bagged, a smaller total volume of beans is ground per cycle. The bulk grinding and bagging occurs on a daily basis. The beans are ground in a lower volume grinder, which expels the ground coffee directly into 5-pound bags that are held by an employee. Additionally, the lower volume ground coffee may be collected in temporary storage totes and manually dumped into a separate bagging machine, which weighs the coffee and fills a single 1-pound bag. The worker then heat-seals the bag and proceeds to fill another bag until the supply of ground coffee is exhausted from the hopper. The employee then grinds another batch of beans and repeats the process. The employee who operated the bulk grinding and bagging equipment was fitted with a sampling train, as described above, and was sampled for approximately eight hours (two 4 hour samples) during the bulk grinding and other housekeeping duties. This employee was also sampled for several short-term sample periods.

2.5.5. Sample roasting

The supervisory coffee roaster also performs sample roasting daily for approximately 15–30 min. The sample roasting is performed on small quantities (1/4-pound or less) of raw coffee beans on a Jabez Burns & Sons three-barrel, small batch coffee roaster. The small batch roaster has three separate tumbling barrels that roasts the coffee with an approximate 6-inch opening for inserting and removing the coffee beans. The sample roasting emanates visible smoke and was not connected to the LEV system. Test roasting allows the supervisory coffee roaster to sample raw beans prior to a large-scale procurement. The supervisory coffee roaster was equipped with sampling media and a 15-min short-term sample was collected while performing the small batch sample roasting job duties.

Table 2
Personal and Area Sampling for Airborne Diacetyl on September 8, 2015.

Sample Location	Eight-Hour TWA[a] (ppm)[b]
Roaster #1	0.0028
Roaster #2	0.0064
Roaster #3	0.0033
Grinder #1	0.0094
Grinder #2	0.0015
Area – Roasters	0.0025
Area – Grinders	0.0012

[a] TWA = Time-Weighted Average.
[b] ppm = parts per million.

Table 3
Short-Term (15-min) Sampling Results for Personal Samples For Airborne Diacetyl Performed on September 8 and 22, 2015.

Work Process	Date Sampled	Concentration (ppm)[a]
Roasting #1	9/8/15	<0.0097
Roasting #2	9/22/15	<0.0098
Roasting #3	9/22/15	<0.0096
Grinding #1	9/8/15	0.08
Grinding #2	9/22/15	0.030
Grinding #3	9/22/15	0.017
Blending #1	9/22/15	<0.0099
Blending #2	9/22/15	0.015
Test Roasting	9/22/15	<0.0083

[a] ppm = parts per million.

3. Results

3.1. Long-term sampling (Eight-hour TWA) for diacetyl

Table 2 provides the sample results for eight-hour TWA personal and area sampling conducted on September 8, 2015.

3.2. Short-term sampling results for diacetyl

Table 3 provides the sample results for the 15-min, short-term sampling events that occurred on September 8 and 22, 2015. Two short-term samples exceeded the ACGIH STEL of 0.02 ppm for a 15-min sample duration. These samples were collected from Grinder #1 on September 8, 2015, and Grinder #2 on September 22, 2015.

3.3. Sampling for 2,3-pentandione

The samples that were analyzed for the presence of 2,3-pentanedione were below the laboratory's LOD of 1 microgram (μg) of 2,3-pentanedione for the long-term sampling conducted on September 8, 2015 and the short-term sampling performed at the Facility on September 8 and 22, 2015 for a total of 20 samples, including two field blanks.

3.4. Environmental conditions

The area sampling for total dust, temperature, relative humidity, carbon monoxide and carbon dioxide concentrations were all within acceptable ranges and did not exceed regulatory or consensus standards. Table 4 provides the results of carbon dioxide, carbon monoxide, temperature, and relative humidity levels during roasting, blending and grinding operations at the Facility on September 8 and 16, 2015.

3.5. Real-time FTIR

On September 16, 2015 air samples were measured in worker breathing zones during the previously described work activities and analyzed using real-time FTIR for each of the SEGs.

Table 4
Arithmetic Mean and Range of Indoor Air Quality Parameters.

Date	Carbon Dioxide (ppm)[a]	Carbon Monoxide (ppm)	Temperature (°F)[b]	Temperature (°C)[c]	Relative Humidity (%)[d]
9/8/15	472 (429–623)	1.8 (0.8–6.6)	79 (77–84)	26 (25–29)	78 (63–86)
9/16/15	464 (399–1135)	3.4 (1.1–52.6)	80 (76–83)	27 (24–28)	51 (47–58)

[a] ppm = parts per million.
[b] °F = degrees Fahrenheit.
[c] °C = degrees Celsius.
[d] % = percent.

Non-detectable concentrations of diacetyl and 2,3-pentanedione were measured in the SEGs for breathing zone and area samples. However, samples collected from the enclosed headspace directly proximal to freshly ground coffee beans revealed varying concentrations of alpha-diketones, aldehydes, carbon monoxide and various organic compounds. Fig. 1 illustrates the three major gas constituents identified in the headspace above the freshly ground beans and displays airborne concentrations of diacetyl, 2,3-pentanedione and acetaldehyde as a function of time. The FTIR measured the concentrations of the gases as the ground coffee beans exited the grinder into a plastic lined storage tote, Fig. 1 section Number 1. At approximately 12:05 P.M., the grinding was completed and the plastic bag filled with the freshly ground coffee was twisted closed with the FTIR probe inserted into the headspace, Fig. 1 Number 2. As can be seen on Fig. 1, section Number 3, concentrations increased until approximately 12:12 PM when the plastic bag was opened. Airborne concentrations of diacetyl peaked at 10.88 ppm, 2,3-pentanedione at 7.46 ppm and acetaldehyde at 16.37 ppm. As also can be seen on Fig. 1, the concentration of the gases quickly dissipated after the plastic bag was opened. While air concentrations measured by the FTIR are quantitative, the direct relationship between the mass of ground coffee and the air concentrations detected can only be inferred, thus, requiring further investigation.

Fig. 2 illustrates the airborne carbon monoxide concentrations during the same grinding operations as described in Fig. 1. As illustrated, the concentrations in the enclosed headspace peaked at approximately 12:15, coinciding with the peak gas concentrations depicted in Fig. 2.

As illustrated in Fig. 2, carbon monoxide concentrations peaked at over 450 ppm in the enclosed headspace of the roasted coffee beans. Again, as noted previously, airborne carbon monoxide concentrations in the breathing zone at the Facility ranged from non-detectable to a maximum of 6.6 ppm, with an arithmetic mean of 1.79. Carbon monoxide concentrations decreased rapidly after the plastic bag was opened.

Various aldehydes were also measured from the headspace of the freshly ground coffee beans. Fig. 3 displays airborne aldehyde concentrations (excluding acetylaldehyde) as a function of time, in the same headspace location. Similarly, Fig. 4 displays airborne VOC (excluding alpha-diketones) concentrations as a function of time, in the same location. Interestingly, these peaks in concentrations did not occur when the plastic bag was enclosed and may therefore may be a result of other factors in the coffee production facility.

4. Discussion

4.1. Environmental conditions

The authors measured relatively low carbon dioxide concentrations in the Facility which generally reflects rapid and sufficient air exchanges at the Facility. The American Society of Heating,

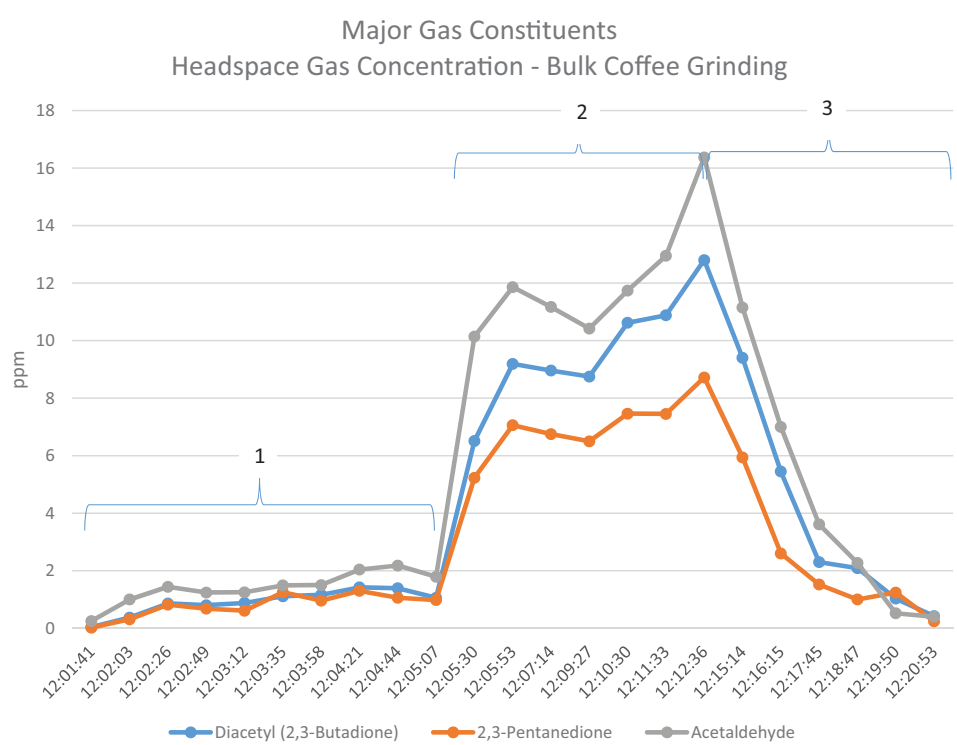

Fig. 1. Major Gas Constituents during Bulk Grinding.

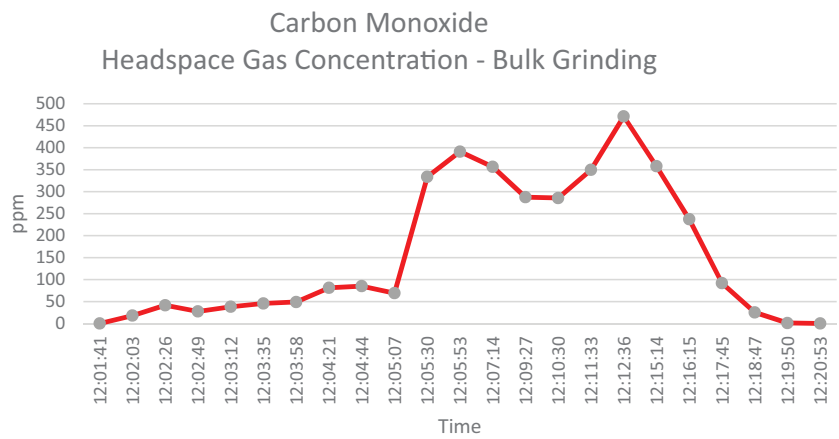

Fig. 2. Carbon Monoxide Concentration During Bulk Grinding.

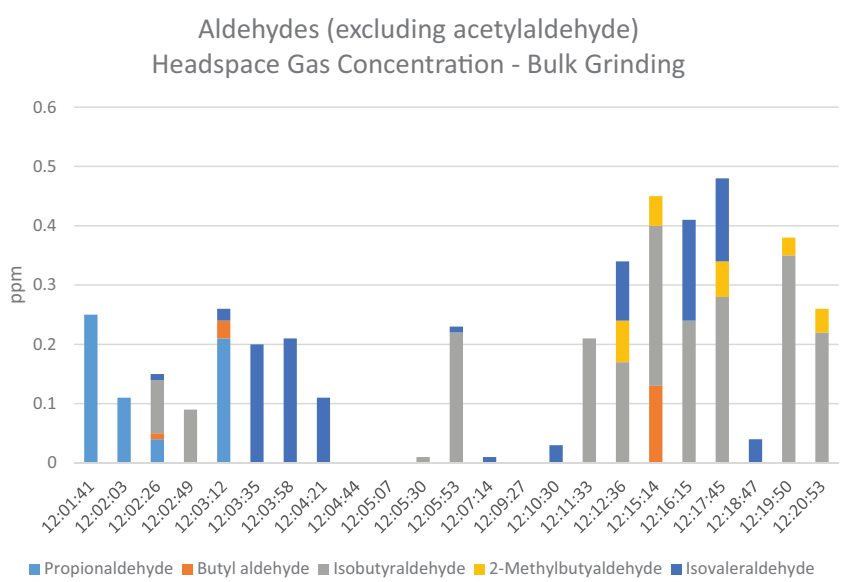

Fig. 3. Aldehyde Concentrations (excluding acetaldehyde) During Bulk Grinding.

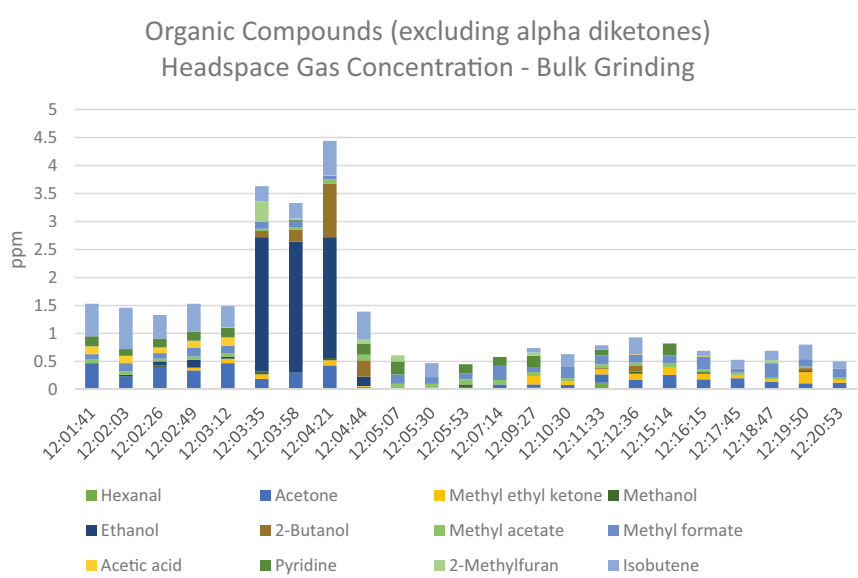

Fig. 4. Organic Compound Concentrations (excluding alpha diketones) During Bulk Grinding.

Refrigerating, and Air-Conditioning Engineers (ASHRAE) standard 62.2-2010 Ventilation and Acceptable Indoor Air Quality in Low-Rise Residential Buildings (Consensus Standard), recommends maintaining a steady-state airborne carbon dioxide concentration which does not exceed 700 ppm above the outdoor air concentrations, which typically ranges from 300 to 500 ppm [21]. The concentration of carbon dioxide measured in the Facility did not approach these concentrations.

Additionally, airborne carbon dioxide concentrations did not approach the OSHA PEL of 5000 ppm. A quantitative study of air exchange utilizing a tracer gas, such as carbon dioxide or sulfur hexafluoride, was not feasible as the Facility is an active business and production facility. Customers entered and exited the café, the Facility received frequent material deliveries and the employees entered and exited the Facility for breaks and other job tasks. Additionally, the owners of the Facility had designed its HVAC system with a variable make-up air system based on exterior and interior atmospheric pressures. As selected roasting processes operate, make-up air fluctuates, precluding the ability to perform an accurate air-exchange study.

While elevated carbon monoxide concentrations were measured in the enclosed headspace of the roasted and ground coffee beans, area carbon monoxide concentrations at the Facility were less than the ACGIH TLV of 25 ppm and the OSHA PEL of 35 ppm throughout the sampling. Other authors have identified the release of carbon monoxide during grinding of roasted coffee beans. Newton described a near fatality from worker exposure when a worker entered a coffee roasting holding tank, without following the appropriate OSHA confined space regulations [22]. Keil et al. similarly reported on inhalational exposures to particulates and carbon monoxide during Ethiopian Coffee Ceremonies in homes in Addis Ababa, Ethiopia [23]. Clearly, the ventilation and make-up air system installed in the Facility is effective in mitigating potential increases in carbon monoxide generated during the roasting and grinding processes. Additionally, beans are stored in small totes and roasted beans or ground coffee are not stored in areas that would be designated as "confined spaces." There were no identifiable locations at the Facility that could present similar hazards as noted by Newton [22]. Airborne dusts were negligible likely due to minimal dust generation of the production processes, adequate make-up air and good Facility housekeeping practices.

4.2. Diacetyl

Airborne diacetyl concentrations measured at the Facility on both days were below the TLV of 0.010 ppm, expressed as eight-hour TWA concentrations. Generally, airborne concentrations below the TLVs are expected to be protective of adverse health effects for most workers over their working lifetime. Two short-term (15-min) worker breathing zone samples, with measured airborne diacetyl concentrations of 0.08 and 0.030 ppm on different days, respectively, exceeded the ACGIH STEL for diacetyl of 0.02 ppm. These concentrations were measured on workers operating the bulk grinding and bagging operations which included working in close proximity to freshly ground beans when operating both grinding and bag filling work stations. After receiving the sample results the Facility immediately implemented a LEV system for this work station to capture these fugitive organic compounds. Additional sampling conducted following the implementation and optimization of the LEV for the grinding area confirmed airborne concentrations of diacetyl decreased to 0.016 ppm, below the ACGIH STEL and new NIOSH STEL. As previously discussed, OSHA has not promulgated a PEL for occupational exposure to diacetyl or other alpha-diketones. Alpha-diketone concentrations, as identified by Bailey et al. at other roasting facilities exceeded 160 ppb of 2,3-pentanedione and diacetyl, in the flavoring room and grinding areas [2]. Significantly different from the Facility in this Study is that the location evaluated by Bailey et al. included flavoring operations and, according to the authors, these areas were not completely isolated from the grinding and other areas of this operation [2]. Thus, Bailey et al. could not independently evaluate the diacetyl contribution from coffee roasting and grinding. It should be noted that, 2,3-pentanedione was not detected in this Study in the breathing zone or area samples, but was identified as generated by roasted coffee beans by FTIR. The generally low to non-detectable concentrations of diacetyl and the non-detectable concentrations of 2,3-pentanedione, were likely due to the Facility's robust, well-designed ventilation system providing a significant volume of return air. Duling, et al. identified average and short-term concentrations of diacetyl and 2,3-pentanedione for unflavored coffee grinding and packing as significantly exceeding the ACGIH TLVs and NIOSH RELs, primarily associated with ventilation deficiencies at the studied facility [13]. While Duling et al. evaluated the ventilation system and pressure relationships of this roasting facility, it appeared as if the system at this facility was significantly less robust than what has been described in the Facility evaluated in this manuscript. It appeared as if the coffee roasting operations evaluated by Duling et al. [13] may not have been balanced and ventilated under similar conditions to the Facility which the authors evaluated in this study, therefore confirming our observations of lower airborne concentrations of diacetyl and non-detectable concentrations of 2,3-pentanedione at this Facility.

While two of the 8-h TWA samples (one Roaster and one Grinder employee) slightly exceeded the newly recommended NIOSH RELs for diacetyl, the Facility's owner and the consulting Certified Industrial Hygienist (CIH) focused on controlling employee exposures to the short-term, higher intensity airborne concentrations of diacetyl present during grinding and packing operations. After the Facility installed a LEV hood over grinding and packing operations, workers' exposures to more-intense short term exposures to diacetyl were lowered to below both the ACGIH STEL and new NIOSH STEL. The Facility owner has not yet resampled other workers at the Facility since the installation of the LEV over the grinding and packing processes, but it is feasible yet unconfirmed that Facility-wide diacetyl levels will decrease due to this additional focused ventilation capturing fugitive diacetyl. It is well accepted in the industrial hygiene profession that OELs do not delineate "safe" from "harmful" atmospheres, but rather provide guidance for professional industrial hygiene decision-making to provide for a healthful and safe work environment.

4.3. Real-time FTIR

Air samples were collected from worker breathing zones during the previously described work activities and SEGs. Non-detectable concentrations of diacetyl, 2,3-pentanedione and other organic compounds were measured with the FTIR during both roasting and grinding in both breathing zone and area sampling. Air samples collected from the enclosed headspace of freshly ground coffee revealed ppm concentrations of diacetyl, 2,3-pentanedione and acetylaldehyde. As can be seen in Fig. 1, concentrations of alpha-diketones increased for a period of approximately 10 min and dissipated rapidly after the bag of freshly ground beans was opened. This finding confirms that these diketones are released by coffee beans but that under normal operating conditions, the concentrations quickly volatize into the atmosphere at concentrations below analytical detection limits. The authors found that while real-time FTIR will likely not measure ppb concentration measurements, FTIR is well-suited for multi-gas characterization of organic compound emissions during food processing or other chemical processes to evaluate breathing zone and area concentrations, particularly in the 500 ppb- to 100 ppm-concentration range. For compounds

with applicable OELs in the ppb-concentration range, traditional industrial hygiene sampling and analytical laboratory methods will likely need to accompany FTIR analysis. In this Study, airborne concentrations of VOCs in the workers' breathing zones, work areas and also in the headspace, were well below applicable OELs. The identified organic compounds, as well as various aldehydes in this Study confirmed some of the findings of others including Akiyama et al., Hertz-Schünemann et al. and Clark and Winter, and these results were generally unremarkable [10,14,15]. Since flavoring activities were conducted in a separate, enclosed room apart from the production room with designated LEVS operated, the flavoring activities were likely not contributing to the sampling being conducted at the Facility. The coffee flavoring products were not contributing to measured concentrations of organic compounds, aldehydes, or alpha-diketones.

4.4. Limitations and future research

The primary limitations of the Study related to the limited FTIR evaluation of various processes on one day, when a single coffee variety was being roasted and ground at the Facility. It is important to note that personal and area sampling using traditional sample pumps and media for diketones was performed while employees were working with and around several varieties and roasts over several work days. Future work could include FTIR measurements of various organic compounds and alpha-diketones at varying distances from ground coffee, as well as with varying coffee roasts and coffee bean varieties. Further research could involve a comprehensive evaluation of air exchanges in a roasting facility to evaluate the airborne concentrations of alpha-diketones which could provide clarity as to the impact of airflow and overall ventilation. While the measurement of the number of air exchanges would have been preferable for this Study, the variable make-up air system at the Facility precluded the authors from conducting this type of evaluation. A study of a large-scale coffee roaster with limited ventilation could provide valuable information on workplace exposures to alpha-diketones in a different size roasting facility operating under different ventilation conditions.

Future research is also needed to clarify the basis of the OELs and the potential toxicity of alpha-diketones in relationship to the development of bronchiolitis obliterans. While Bailey et al. [2] identified elevated standard mortality rates (SMRs) in current workers for dyspnea and pulmonary obstruction in coffee processing workers, the contribution, if any, of alpha-diketones from flavoring processes should be evaluated in any morbidity evaluation. Are alpha-diketones or the composition and concentration of various VOCs liberated from unflavored coffee similar in mechanistic toxicity to alpha-diketones and other VOCs associated with artificial food flavorings? Additionally, consideration of current OELs and its protectiveness should be carefully evaluated. While NIOSH provides a very robust and well-intentioned Criteria for a Recommended Standard for Occupational Exposure to Diacetyl and 2,3-Pentanedione and recommended RELs, this 394-page document is applicable to the overall industrial use of diacetyl and 2,3-pentanedione in food flavoring, food manufacturing, in addition to coffee roasting. Many small- and medium-sized coffee roasters cannot and likely will not implement cost-prohibitive Facility-wide ventilation systems or burdensome respiratory protection systems for airborne concentrations of diacetyl which are several parts-per-billion above the new, and very low NIOSH RELs without an understanding of the true health risk to their employees.

While the Facility evaluated in this Study implemented local exhaust ventilation over its grinding and bagging operations, which was based on the ACGIH STEL and NIOSH RELs for diacetyl, the question remains if these STELs are applicable for this coffee worker cohort or if they are overly conservative and therefore, unnecessarily burdensome on coffee roasters and other food manufacturers whose processes generate low ppb concentrations of these alpha-diketones. Again, the costs of installing local exhaust ventilation, or in worst-cases, implementing an appropriate respiratory protection programs, for small to medium sized commercial roasters, may be economically and practically infeasible. As identified by Gaffney et al. [12], the basis for current OELs for alpha-diketones is subject to debate of whether concentrations above these OELs are associated with obstructive lung diseases. Future epidemiologic and exposure studies will clarify the current understanding of the dose-response relationship between alpha-diketones and lung disease specifically in coffee workers.

Conflict of interest

Mr. McCoy and Dr. Anderson have served as expert witnesses for defendants in diacetyl-associated litigation. Colectivo Coffee Roasters, Inc. financed the industrial hygiene consulting services, some of which were reported by this study. Collectivo Coffee Roasters, Inc. did not have direct involvement in the study design, data analysis, data interpretation, or the manuscript preparation. GZA GeoEnvironmental, Inc. financed some of the laboratory analytical costs and funded the labor costs of its staff in the preparation of this manuscript. Mr. Cornish and Mr. Haapala are employed by Gasmet Technologies whose FTIR instrument and software was utilized in this study, and Mr. Greivell is a distributor for Gasmet FTIR instrumentation.

Acknowledgements

The authors wish to thank Colectivo Coffee Roasters, Inc. for its willingness to report these findings and for its commitment to worker health and safety. Gasmet provided its DX-4040 FTIR instrument and performed data analysis of FTIR spectral data during this study, which was greatly appreciated.

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