Naturally occurring diacetyl and 2,3-pentanedione concentrations associated with roasting and grinding unflavored coffee beans in a commercial setting

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A B S T R A C T

Over the last decade, concerns have been raised about potential respiratory health effects associated with occupational exposure to the flavoring additives diacetyl and 2,3-pentanedione. Both of these diketones are also natural components of many foods and beverages, including roasted coffee. To date, there are no published studies characterizing workplace exposures to these diketones during commercial roasting and grinding of unflavored coffee beans. In this study, we measured naturally occurring diacetyl, 2,3-pentanedione, and respirable dust at a facility that roasts and grinds coffee beans with no added flavoring agents. Sampling was conducted over the course of three roasting batches and three grinding batches at varying distances from a commercial roaster and grinder. The three batches consisted of lightly roasted soft beans, lightly roasted hard beans, and dark roasted hard beans. Roasting occurred for 37 to 41 min, and the grinding process took between 8 and 11 min. 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 mg/m^3, respectively. During grinding, diacetyl, 2,3-pentanedione, and respirable dust concentrations ranged from 0.018 to 0.39 ppm, 0.0089 to 0.21 ppm, and <LOD to 1.7 mg/m^3, respectively. For 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. Measured concentrations of both diketones were higher during grinding of soft beans than hard beans. The results indicate that airborne concentrations of naturally occurring diacetyl and 2,3-pentanedione associated with unflavored coffee processing: (1) are similar to the concentrations that have been measured in food flavoring facilities; (2) are likely to exceed some recommended short-term occupational exposure limits, but; (3) based on previous analyses of exposure response relationships in animal studies, are far below the concentrations that are expected to cause even minimal responses in the human respiratory tract.

1. Introduction

Diacetyl has been used for decades as a flavoring agent to impart a buttery odor and taste in coffee, flour, chocolate, cooking oils, popcorn and other snack foods, dairy products, and baked goods [45,46]. The National Toxicology Program (NTP) has suggested that "human consumption of many foods and beverages containing low levels of diacetyl constitutes a virtually universal exposure scenario for this ubiquitous diketone" [45]. Concerns have recently been raised, however, regarding apparent increased rates of respiratory disorders in certain food and flavorings manufacturing workers. Specifically, over the past ten years, the National Institute for Occupational Safety and Health (NIOSH) has investigated numerous microwave popcorn and flavoring production facilities at which diacetyl-containing flavorings were used, and have concluded that diacetyl may be contributing to or causing severe respiratory disorders, including the rare disease *bronchiolitis obliterans*, in highly exposed workers [32,42]. As a result, diacetyl has largely been phased out of the food-flavoring industries and replaced by 2,3-

pentanedione and other diketones that also possess "butter-like" qualities [5,11,53].

Occupational exposure limits (OELs) for diacetyl and 2,3-pentanedione have been recommended by various organizations. In 2011, NIOSH [44] proposed 15 min short-term exposure limits (STELs) of 0.025 parts per million (ppm) and 0.031 ppm, and 8 h time-weighted average (TWA) Recommended Exposure Limits (RELs) of 0.005 ppm and 0.0093 ppm, for diacetyl and 2,3-pentanedione, respectively. More recently, the European Commission (EC) published draft recommended diacetyl OELs of 0.1 ppm as a 15 min STEL and 0.020 ppm as an 8 h TWA [25]. The NIOSH and the EC recommended OELs have not been finalized to date. In 2012, ACGIH adopted Threshold Limit Values (TLVs) for diacetyl, including a 15 min STEL of 0.02 ppm and an 8 h TWA of 0.01 ppm, and TLVs for 2,3-pentanedione are currently under study [1,2]. The U.S. Occupational Safety and Health Administration (OSHA) has not promulgated OELs for diacetyl or 2,3-pentanedione.

Diacetyl occurs naturally in a variety of beverages (e.g., tea, coffee, beer, wine, milk and citrus juices) and food products (e.g., butter, yogurt, cheese, chicken and beef, and assorted fruits and vegetables) [4,9,12,27], and several studies have shown that diacetyl emissions from these products are easily detectable [7,30,55,59]. For some products, airborne diacetyl concentrations can exceed the aforementioned OELs by several orders of magnitude. For example, Pierce et al. reported that naturally occurring diacetyl concentrations in cigarette smoke ranged from 200 ppm to 400 ppm [51]. Diacetyl concentrations measured in the headspace of stored unflavored roasted coffee beans and ground unflavored roasted coffee have ranged from 0.4 ppm to 4.4 ppm [30,37], and a concentration of 7.0 ppm diacetyl was reportedly measured in the headspace of an open cup of brewed unflavored coffee [60].

Interestingly, green unroasted coffee beans contain little to no diacetyl or 2,3-pentanedione [14]. Coffee beans are roasted to achieve a desired aroma and flavor profile of the brewed coffee; roasting also darkens the beans, and creates the brittle texture necessary for grinding [36,54]. The roasting process results in diketone formation as a result of amino acids (e.g., glycine and alanine) and sugar molecules (e.g., glucose and mannose) reacting in the bean [14]. This reaction, sometimes referred to as a Maillard reaction, occurs at temperatures of 200 °C or higher, and diketone formation increases with increasing roasting time and temperatures; coffee roasting temperatures typically range from 220 °C to 230 °C [54].

There are hundreds of commercial coffee-processing facilities in the U.S. at which large volumes of beans are roasted and ground; many grocery store chains also have commercial size roasters and grinders at their outlets. To our knowledge, no published studies exist that describe workplace exposures to naturally occurring diketones during coffee processing in these establishments. In 2008, diacetyl concentrations were reported in an industrial hygiene survey of a coffee processing facility [17], but diacetyl-containing flavorings were in use during the survey and it is not possible to determine the relative contribution of naturally occurring versus added diacetyl in that study.

The purpose of this analysis was to assess diacetyl, 2,3-pentanedione, and respirable dust concentrations associated with the roasting and grinding of unflavored coffee beans in a commercial setting. We collected task-duration stationary air samples during routine operations of a small commercial coffee roastery. A variety of different bean types and roast conditions were evaluated. The airborne data were characterized via comparisons to concentrations measured in food processing facilities where diacetyl-containing flavorings were handled. The results were also compared to applicable recommended OEL concentrations, as well as diacetyl exposure levels that have, and have not, caused respiratory effects in animal inhalation studies. We also reviewed the epidemiology literature for reported health effects in coffee pro-
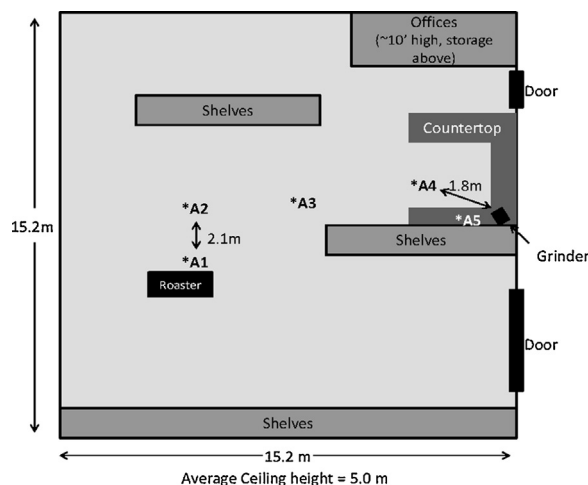

Fig. 1. Schematic of coffee roaster facility.

cessing workers, and conclude with suggestions for future areas of research.

2. Methods

2.1. Study site

The study took place in November of 2013, during a single day at a commercial coffee roasting facility. The dimensions (i.e., width, length, height) of the facility were approximately 15.2 m (50 ft), 15.2 m (50 ft), and 4.9 m (16 ft), respectively, for an estimated total volume of 1133 m^3 (40,000 ft^3) (Fig. 1). The facility had one roaster with a capacity of 13.6 kg (30 lb) per roast (Ditting, Switzerland) and an industrial grinder (Diedrich, Ponderay, ID, USA). The production volume at this facility is typically about 568 kg (1250 lbs) of roasted coffee beans per week.

The coffee processing facility was not operating any mechanical exhaust ventilation; however, the hot air from the coffee roaster was removed to the outside through a passive canopy hood and vertical stack. During the summer, a large garage door and personnel door are often kept open to allow for increased air circulation during operations. However, for the duration of the study, both the personal and roll-up garage doors were closed.

2.2. Characterization of the ventilation rate

The ventilation rate in the facility was characterized in accordance with ASTM Standard Method E741 [6]. Carbon dioxide (CO_2) was used as the tracer gas, and measurements were collected using a Q-Trak Indoor Air Quality Monitor 7565 (TSI, Inc., 500 Cardigan Road, Shoreview, MN, USA). A target concentration of approximately 800 ppm for CO_2 was chosen based on the anticipated ventilation conditions, the volume of the facility, and to minimize the influence of potential additional emission sources (e.g., workers and researchers present in the facility). A compressed gas cylinder of CO_2 (100%, food grade; AirGas, Inc., San Francisco, CA, USA) was used to disperse the gas evenly throughout the facility, and four fans located at opposite ends of the space were turned on during the release to facilitate even dispersion of the gas. Air measurements were collected at four evenly spaced locations throughout the facility using the Q-Trak analyzer, beginning 1 min after the release of the CO_2 and until the steady—state concentration (approximately 760 ppm) was reached. Once steady state was confirmed, measurements were collected and logged at the four locations, every 2 min for approximately 1 h. Assuming constant air change, the air

exchange rate was calculated by performing a linear regression on the following equation, where t corresponds to time in minutes (after the steady state was achieved), C_t represents concentration at time t, and C_0 was the initial concentration:

$$\ln C_t = -At + \ln C_0 \tag{1}$$

The air exchange rate in the facility was determined to be approximately 2.1 air changes per hour.

2.3. Sampling protocol and study participants

Stationary, breathing zone-height air samples were collected while coffee beans were roasted and subsequently ground; all tasks were performed by a skilled worker employed at the facility who was not wearing respiratory protection. The coffee beans, which included hard and soft beans cultivated in Honduras and Brazil, respectively, were purchased by the facility operator, and were representative of the products typically handled at this location. The "hard vs. soft" distinction relates to cultivation altitude, which affects growth rate (e.g., hard beans are grown at higher altitudes, where they grow slower). Soft beans are typically considered inferior in terms of flavor and aroma (and yield a lower price), and they are commonly used in commercial coffee blends [15,50]. We chose to evaluate both soft and hard beans because the physical and chemical properties of the coffee bean may influence the degree of diketone formation, and because both types are commonly used in commercially available blends of coffee. In order to evaluate differences between light and dark roasts, we also evaluated hard bean/light roast vs. hard bean/dark roast (soft beans may only be roasted lightly). In summary, we evaluated the following coffee products: hard bean/dark roast, hard bean/light roast, and soft bean/light roast.

The general production process evaluated in this study was consistent with the routine operations performed at the facility. It included:

1. *Roasting:* The operator dumped a bucket of 13.6 kg (30 lbs) of coffee beans into a pre-heated roaster and intermittently stirred the beans. Each sampling event encompassed two consecutive roasts, thus corresponding to processing 27.2 kg (60 lbs) of green coffee beans per event. The final temperature of the light roasts varied from 219 °C (427 °F) to 221 °C (429 °F), whereas the final temperature during the dark roast was 233 °C (451 °F). The operator then transferred the hot coffee beans onto a cooling tray attached to the roaster and stirred the beans to accelerate the cooling. This complete roasting step took between 37 and 41 min.
2. *Grinding:* The operator added one batch of roasted coffee beans to the hopper of the grinder, placed an empty paper bag beneath the spout, selected the appropriate grade (e.g., 'drip, cone filter'), and ground the coffee beans. Each bag held approximately 2.3 kg (5 lbs). During the roasting process, the coffee beans become dehydrated and lose approximately 20% mass; as a consequence, the resulting total mass of ground coffee beans was about 10.9 kg (24 lbs) per batch, packaged in five bags. The grinding process lasted 8 to 11 min.

Airborne diacetyl and 2,3-pentanedione concentrations were evaluated separately during a total of three roasting and three grinding events, for a total of six separate sampling events (in order of event occurrence):

- E1–Roast: Light roast, soft bean.
- E2–Roast: Light roast, hard bean.
- E3–Roast: Dark roast, hard bean.
- E4–Grind: Light roasted soft bean.
- E5–Grind: Light roasted hard bean.
- E6–Grind: Dark roasted hard bean.

In addition, airborne diacetyl and 2,3-pentanedione concentrations were evaluated during the roasting only of decaffeinated coffee beans, which took place in the morning before the main sampling events, while the roaster was heating to full temperature. These data were not considered a separate event because the roasting of the decaffeinated beans was not planned as part of the evaluation *a priori*, and, therefore, a complete characterization of the decaffeinated bean roasting and grinding process was not performed.

2.4. Sampling and analytical methods

A set of three stationary air samples (two duplicate samples to measure both diacetyl and 2,3-pentanedione, and one sample to measure respirable dust) were collected at several locations throughout the facility, as can be seen in Fig. 1 (denoted A1 through A5). Two short-term (9–25 min) samples were collected at locations A1 and A4 immediately prior to commencing the study to evaluate the background concentrations of diacetyl and 2,3-pentanedione in the facility. During roasting, stationary samples were collected at two heights that were chosen to be representative of the breathing zones of an operator standing on a platform adding coffee beans to the roaster and stirring the coffee beans in the roaster, and an operator monitoring the cooling process from the ground (these locations are denoted area A1). Sampling was conducted for the entire duration of the roasting task, and the event times varied from 37 min to 41 min. Task-duration (8–11 min) samples were also collected at a location representative of the breathing zone of an operator during coffee bean grinding (A5). During all sampling events, two diketone and two respirable dust side-by-side area samples were also collected at breathing zone-height at locations 2.1 m or 7 ft (A2), and 4.6 m or 15 ft (A3) from the roaster, and 1.8 m or 6 ft (A4) from the grinding operations; concentrations measured at these locations were intended to be indicative of exposures to potential bystanders.

Sample collection equipment, materials, and analytical procedures for diketones were in accordance with OSHA Method 1012 [49]; the analytical method was modified only (by the laboratory) for simultaneous quantification of diacetyl and 2,3-pentanedione, since this method is not specified for 2,3-pentanedione. The limit of detection (LOD) was 0.02 μg/sample for both compounds, corresponding to LODs for the air samples varying from 0.0018 ppm to 0.003 ppm and from 0.0011 ppm to 0.0032 ppm for diacetyl and 2,3-pentanedione, respectively. Respirable dust was collected and analyzed by the laboratory in accordance with NIOSH Method 0600 [40], with the limit of quantitation (LOQ) ranging from 0.19 mg/m^3 to 1 mg/m^3. All sampling media were analyzed by an American Industrial Hygiene Association (AIHA) accredited laboratory (ALS Global, Salt Lake City, UT, USA).

Blank samples for all agents were provided to the laboratory for quality control purposes; diacetyl and 2,3-pentanedione spiked tubes were not provided to the laboratory for analysis. The sampling pumps were calibrated using primary flow calibrators (Bios DryCal, MesaLabs, Butler, NJ, USA) before and after sample collection.

2.5. Estimation of short-term (15 min) and full-shift (8 h) time-weighted average diketone concentrations

As described below, many of the samples collected during roasting did not contain detectable levels of diketones, and, therefore, TWAs were not estimated for roasting tasks; however, diketones were readily detected during grinding, and short-term TWAs were

calculated for the grinding tasks. Because the duration of the grinding task (and the associated sampling event) was less than 15 min (i.e., 8–11 min), the 15 min short-term TWA concentrations (TWA$_{15min}$) for each grinding event were estimated according to Eq. (2) below. For each event i, we assumed the mean grinding concentration in area A5 ($C_{grinding, i}$) for the duration of grinding for the particular event ($t_{grinding, i}$); for the remaining duration $[(15 - t_{grinding, i}) \text{ min}]$, we assumed that the concentration corresponded to the overall (i.e., based on all events) mean concentration measured during roasting ($C_{roasting, overall mean}$):

$$\text{TWA}_{15 \, min, \; i} (ppm)$$
$$= \frac{C_{grinding, \; i} \times t_{grinding, \; i} + C_{roasting, overall mean} \times (15 \, min - t_{grinding, \; i})}{15 \, min} \quad (2)$$

Full-shift TWA diketone concentrations were estimated as a function of the total time spent grinding per day. The full-shift TWA concentrations were estimated based on the assumption that in addition to the time spent grinding ($t_{grinding}$), a worker would spend the remainder of the day roasting coffee or performing other tasks in the vicinity of the coffee roasting process. It was also assumed that a worker was not exposed during one 30 min lunch break and two shorter (15 min) breaks; thus, the duration of the remainder of the workday was calculated to be (480–60–$t_{grinding}$) min. The overall mean diketone concentrations for grinding ($C_{grinding, overall mean}$, in the immediate work area, as reported in Table 2) were used to estimate exposure during grinding, and the mean diketone concentrations measured during roasting at all locations ($C_{roasting, overall mean}$; Table 2) were used to estimate the exposure for the remainder of the eight-hour workday. The duration of grinding required for the TWA$_{8 h}$ to exceed a given OEL ($t_{grinding, OEL}$) was calculated by solving Eq. (3) for $t_{grinding}$ (Eq. (4)), where C_{OEL} is equivalent to the OELs for diacetyl and 2,3-pentanedione.

$$\text{TWA}_{8 h} (ppm)$$
$$= \frac{C_{grinding, overall mean} \times t_{grinding} + C_{roasting, overall mean} \times (420 \, min - t_{grinding})}{480 \, min} \quad (3)$$

$$t_{grinding, OEL} (min) = \frac{480 \, min \times C_{OEL} - 420 \, min \times C_{roasting, overall mean}}{C_{grinding, overall mean} - C_{roasting, overall mean}} \quad (4)$$

2.6. Estimation of representative short-term diacetyl concentrations in food processing facilities

Several industrial hygiene surveys have reported airborne diacetyl concentrations at food processing facilities where diacetyl-containing flavorings were used. For the purposes of this analysis, we summarized the personal short-term diacetyl samples reported in these surveys and compared them to the calculated short-term TWA concentrations from the present study. We only considered those samples (1) collected for 15 min or less, (2) for which a task description indicated that diacetyl-containing flavorings were handled during the sample collection, and (3) a validated sampling/analytical method was employed (e.g., we excluded samples collected in accordance with NIOSH Method 2557, which have been found to have specific limitations, or by methods that are still under development).

The identified studies, all of which were conducted by the Eastern Research Group (ERG) at the request of OSHA, included data collected at facilities producing flavored crackers, popcorn, ice cream, and other food items [16,18–24].

All data were based on samples collected in accordance with OSHA Methods 1012 or 1013.

3. Results

3.1. Airborne diacetyl and 2,3-pentanedione concentrations

A total of 40 samples were collected and analyzed for both diacetyl and 2,3-pentanedione, including two short-term background samples and 36 event-duration samples collected during the roasting (24 samples) and grinding (12 samples) of regular coffee beans. As described above, two additional samples were collected during the roasting of decaffeinated coffee beans before the sampling events of interest began while the roaster was warming to the optimum temperatures.

3.1.1. Background sampling
As shown in Table 1, diacetyl and 2,3-pentanedione were not detected in the facility prior to the first roasting event.

3.1.2. Roasting
Neither diacetyl nor 2,3-pentanedione were detected in the immediate work area during roasting of decaffeinated beans (Table 1). Since these data were collected while the roaster was warming, and were not part of the study objectives, these results were not evaluated further in this analysis.

As shown in Table 1, diacetyl was detected in the majority of samples (75%), and the mean diacetyl concentrations in locations A1–A3 during roasting were 0.0019 ppm, 0.0024 ppm, and 0.0024 ppm, respectively (Table 2). The mean 2,3-pentanedione concentrations in locations A1–A3 during roasting were 0.00096 ppm, 0.00094 ppm, and 0.0037 ppm, respectively; however, greater than 80% of the samples in each of the locations had non-detectable airborne concentrations of 2,3-pentanedione (Table 2).

At all locations, airborne diacetyl concentrations during the hard bean/dark roast were consistently higher than for the other bean/roast combinations (Table 1). As shown in Table 2, mean diacetyl and 2,3-pentanedione concentrations during roasting did not vary as a function of distance from the source; for instance, the overall mean concentrations for all bean and roast types combined at locations A1–A3 fell within a narrow range of 0.0005 ppm (range: 0.0019–0.0024 ppm) for diacetyl and 0.0028 ppm (range: 0.00094–0.0037 ppm) for 2,3-pentanedione.

3.1.3. Grinding
The airborne concentrations of diacetyl and 2,3-pentanedione measured during the grinding task differed from those measured during roasting in several ways. First, during grinding, diacetyl and 2,3-pentanedione were detected in all sample locations with all bean/roast combinations. As shown in Tables 1 and 2, for any given bean/roast combination and sample location, diacetyl and 2,3-pentanedione concentrations during grinding were higher than those measured during roasting. Second, for all bean/roast combinations, the diacetyl and 2,3-pentanedione concentrations decreased with increased distance from the source (Fig. 2), which was also true for the aggregated bean/roast data (Table 2). Third, diketone concentrations were higher at the location nearest the emission source (A5) during grinding of the soft beans than during grinding of the hard beans, regardless of roast type (Fig. 2). There were no apparent differences between the concentrations of diketones measured during the grinding of light versus dark roast hard beans (Table 1).

Table 1
Task-based airborne diacetyl and 2,3-pentanedione concentrations (ppm) associated with roasting and grinding, indexed by event.

Task	Event	Area	Location Description	Duration (min)	Diacetyl			2,3-Pentanedione		
					Number of Samples (% < LOD)	Mean Concentration (ppm)	Range (ppm)	Number of Samples (% < LOD)	Mean Concentration (ppm)	Range (ppm)
Background	NA	A2	~2.1 m from roaster	9	2 (100)	ND§	< 0.0029 - < 0.0030^	2 (100)	ND	< 0.0025 - < 0.0026
Roasting	0. Decaffeinated Roast	A1	Immediate work area	27	2 (100)	ND	< 0.0020 - < 0.0026	2 (100)	ND	< 0.0017 - < 0.0022
	1: Light Roasted Soft Beans	A1	Immediate work area	38	4 (100)	ND	< 0.0018 - < 0.0019	4 (100)	ND	< 0.0015 - < 0.0016
		A2	~2.1 m from roaster	38	2 (0)	0.0020	0.0019 - 0.0021	2 (100)	ND	< 0.0015 - < 0.0016
		A3	~4.6 m from roaster	38	2 (50)	0.0012^Y	< 0.0019 - 0.0014	2 (100)	ND	< 0.0011 - < 0.0017
		All	**~0-4.6 m from roaster**	**38**	**8 (63)**	**0.0013^Y**	**< 0.0018 - 0.0021**	**8 (100)**	**ND**	**< 0.0011 - < 0.0017**
	2: Light Roasted Hard Beans	A1	Immediate work area	41	4 (25)	0.0017	< 0.0020‡ - 0.0020	4 (100)	ND	< 0.0015 - < 0.0016
		A2	~2.1 m from roaster	41	2 (0)	0.0025	0.0024 - 0.0026	2 (100)	ND	< 0.0014 - < 0.0015
		A3	~4.6 m from roaster	41	2 (0)	0.0024	0.0020 - 0.0028	2 (100)	ND	< 0.0014 - < 0.0015
		All	**~0-4.6 m from roaster**	**41**	**8 (13)**	**0.0021**	**< 0.0020‡ - 0.0028**	**8 (100)**	**ND**	**< 0.0014 - < 0.0017**
	3: Dark Roasted Hard Beans	A1	Immediate work area	37	4 (0)	0.0031	0.0026 - 0.0036	4 (50)	0.0013^Y	< 0.0015 - 0.0020
		A2	~2.1 m from roaster	37	2 (0)	0.0028	0.0023 - 0.0033	2 (50)	0.0013^Y	< 0.0017 - 0.0018
		A3	~4.6 m from roaster	19-37†	2 (0)	0.0037	0.0034 - 0.0039	2 (50)	0.0098^Y	< 0.0032 - 0.018
		All	**~0-4.6 m from roaster**	**19-37†**	**8 (0)**	**0.0031**	**0.0023 - 0.0039**	**8 (50)**	**0.0034^Y**	**< 0.0015 - 0.018**
Grinding	4: Light Roasted Soft Beans, Grind	A5	Immediate work area	11	2 (0)	0.38	0.36 - 0.39	2 (0)	0.21	0.21
		A4	~1.8 m from grinder	11	2 (0)	0.020	0.018 - 0.021	2 (0)	0.010	0.0089 - 0.011
		All	**~0-1.8 m from grinder**	**11**	**4 (0)**	**0.20**	**0.018 - 0.39**	**4 (0)**	**0.11**	**0.0089 - 0.21**
	5: Light Roasted Hard Beans, Grind	A5	Immediate work area	8	2 (0)	0.14	0.13 - 0.14	2 (0)	0.069	0.064 - 0.073
		A4	~1.8 m from grinder	8	2 (0)	0.027	0.018 - 0.035	2 (0)	0.013	0.010 - 0.016
		All	**~0-1.8 m from grinder**	**8**	**4 (0)**	**0.081**	**0.018 - 0.14**	**4 (0)**	**0.041**	**0.010 - 0.073**
	6: Dark Roasted Hard Beans, Grind	A5	Immediate work area	9	2 (0)	0.15	0.11 - 0.19	2 (0)	0.052	0.041 - 0.062
		A4	~1.8 m from grinder	9	2 (0)	0.030	0.023-0.036	2 (0)	0.014	0.011 - 0.017
		All	**~0-1.8 m from grinder**	**9**	**4 (0)**	**0.090**	**0.023 - 0.19**	**4 (0)**	**0.033**	**0.011 - 0.062**

§ ND: Means were not computed for subsets that contained 100% of samples < LOD

^ Range represents the two sample values when the number of samples was two

† The sampling duration for one sample was 19 min due to pump malfunction; the sampling duration was 37 min for the remaining samples for diacetyl and 2,3-pentanedione

¥ 50% or more of samples were < LOD

‡ Minimum detected sample was 0.0018 ppm

3.2. Airborne respirable dust concentrations

A total of 19 samples were collected and analyzed for respirable dust. The mean concentration of respirable dust measured at all locations during light roasting of soft beans was 0.22 mg/m^3. For all other roasting events, respirable dust was not detected in the air (range: <0.19 to <0.22 mg/m^3). Similarly, during grinding only, one sample resulted in a detectable concentration of respirable dust (1.7 mg/m^3 was measured in location A5 during grinding of light roasted soft beans); all other samples ($n = 5$) were below the LOQ (range: < 0.73 to 1.0 mg/m^3). All measured concentrations of respirable dust were well below both the current OSHA 8 h TWA permissible exposure limit of 5 mg/m^3 and ACGIH's 8 h TLV-TWA of 3 mg/m^3 [44]. Because of the limited number of samples result-

ing in detectable concentrations of respirable dust, these data are not included in Tables 1 and 2.

3.3. Estimated short-term (15 min) time-weighted diketone concentrations

3.3.1. Current study

As shown in Table 2, the mean estimated 15 min TWA concentrations of diacetyl and 2,3-pentanedione in area A5 (closest to the grinder) were 0.15 ppm (range: 0.080–0.28 ppm) and 0.10 ppm (range: 0.040–0.20 ppm) during grinding, respectively. In area A4, approximately 1.8 m from the grinder, the corresponding diacetyl and 2,3-pentanedione 15 min TWA estimates
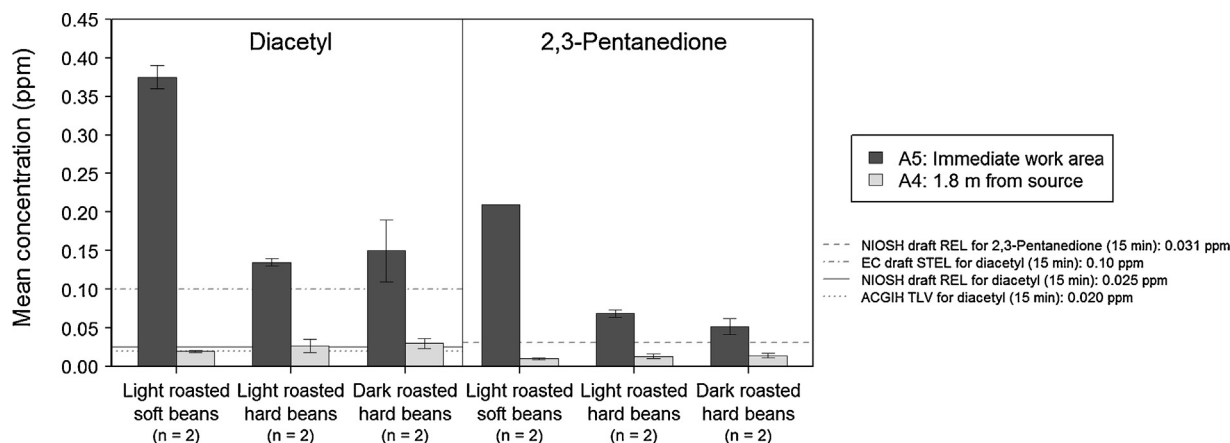

Fig. 2. Comparison of diacetyl and 2,3-pentanedione concentrations during grinding activities to recommended or proposed occupational exposure limits (OELs). Error bars represent minimum and maximum detected concentrations. There were two samples ($n = 2$) collected at each location for each bean/roast combination.

were 0.017 ppm (range: 0.015–0.019 ppm) and 0.011 ppm (range: 0.0090–0.012 ppm), respectively.

3.3.2. Other facilities

Fig. 3 summarizes all personal samples of 15 min duration (or less) collected while food processing workers handled diacetyl-containing flavorings, as reported by the ERG (all data included in the analysis are listed in Supplementary Table 1). All samples that met this duration criterion were, in fact, collected for 15 min. Task descriptions from the surveys included "weighing flavoring", "pumping flavoring", "adding flavor to tanks," and others. A total of 22 samples were identified; in 2 samples (9.1%), diacetyl was not detected (LOD range: 0.0039–0.006 ppm). Thus, overall, the diacetyl concentrations ranged from < 0.0039 ppm to 4.82 ppm, with a mean and median of 0.54 ppm and 0.12 ppm, respectively.

3.4. Estimated full-shift (8 h) time-weighted average diacetyl concentrations

Estimated 8 h TWA diacetyl and 2,3-pentanedione concentrations, as a function of the total time spent grinding per day, are shown in Fig. 4. For grinding durations of 2 h per day, the estimated full-shift concentrations of diacetyl and 2,3-pentanedione were 0.056 ppm and 0.029 ppm, respectively. Furthermore, these estimates indicate that, based on the measurements obtained and task duration assumptions used in this analysis, the proposed and adopted 8 h TWA diacetyl OELs of NIOSH (0.005 ppm), ACGIH (0.01 ppm), and EC (0.02 ppm) would be exceeded after approximately 7 min, 18 min, and 40 min of grinding, respectively. Similarly, NIOSH's proposed 8 h TWA OEL for 2,3-pentanedione (0.0093 ppm) would be exceeded by a worker performing at least 35 min of grinding per day.

4. Discussion

This study is the first to describe airborne diacetyl and 2,3-pentanedione concentrations associated with commercial roasting and grinding of unflavored coffee. The bean/roast combinations evaluated in this study (soft bean/light roast, hard bean/light roast, and hard bean/dark roast) represent the main varieties sold and consumed in the U.S. The airborne diacetyl and 2,3-pentanedione concentrations during grinding of all bean/roast combinations far exceeded those measured during roasting (Table 2), suggesting that the diketone vapors created during roasting are not released in significant amounts until the structural integrity of the bean is compromised (e.g., through grinding). This finding is consistent with the fact that these compounds are highly volatile, and grinding allows for increased mass balance chemical transfer to the air. The volatility of these compounds also has implications for controlling exposure, since they are unlikely to be particle-bound either under roasting temperatures or in cooled coffee beans; thus attempting to control exposure through dust filtration is unlikely to be effective.

Diketone concentrations were detectable at the most distant sampling locations (4.6 m from the roaster, 1.8 m from the grinder). We found that grinding soft beans resulted in higher diacetyl concentrations (at the source) than hard beans. The reasons for this finding are unclear, although it may be a result of the difference in microstructural properties between soft and hard beans, which have been reported to affect grinding and brewing performances [52].

In most samples, the concentration of diacetyl was higher than that of 2,3-pentanedione; however, the levels of the two compounds were not well correlated. Research on this topic is limited, but it appears that the formation of 2,3-pentanedione is
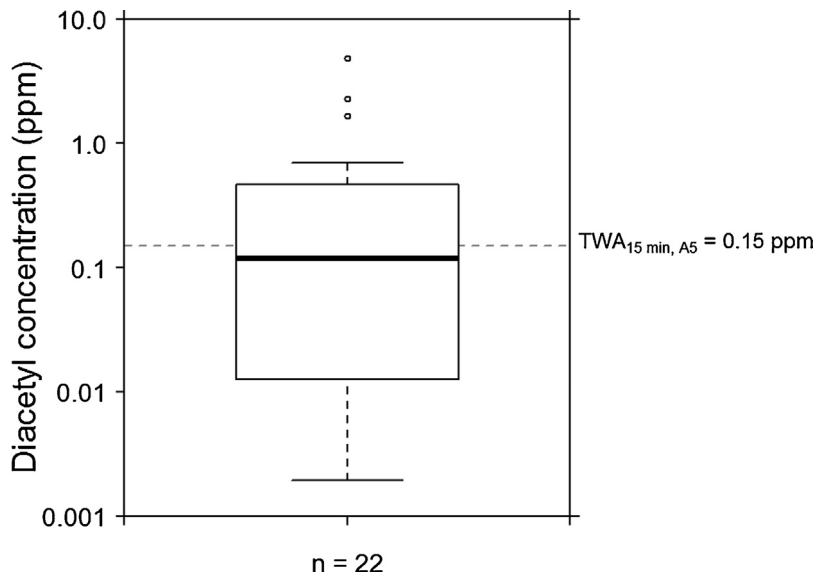
Table 2
Task-based airborne diacetyl and 2,3-pentanedione concentrations (ppm) associated with roasting and grinding, indexed by task.[a]

Task	Area	Location description	Duration (min)	Diacetyl				2,3-Pentanedione			
				Number of samples (% < LOD)	Mean concentration (ppm)	Range (ppm)	Estimated mean 15 min TWA concentration (ppm)	Number of samples (% < LOD)	Mean concentration (ppm)	Range (ppm)	Estimated mean 15 min TWA concentration (ppm)
All roasting	A1	Immediate work area	37–41	12 (42)	0.0019	<0.0018–0.0036	–	12 (83)	0.00096[c]	<0.0015–0.0020	–
	A2	~2.1 m from roaster	37–41	6 (0)	0.0024	0.0019–0.0033	–	6 (83)	0.00094[c]	<0.0014–0.0018	–
	A3	~4.6 m from roaster	19–41[b]	6 (17)	0.0024	<0.0019[d]–0.0039	–	6 (83)	0.0037[c]	<0.0011–0.018	–
	All	~0–4.6 m from roaster	19–41[b]	24 (25)	0.0022	<0.0018[d]–0.0039	–	24 (83)	0.0017[c]	<0.0011–0.018	–
All grinding	A5	Immediate work area	8–11	6 (0)	0.22	0.11–0.39	0.15	6 (0)	0.11	0.041–0.21	0.1
	A4	~1.8 m from grinder	8–11	6 (0)	0.025	0.018–0.036	0.017	6 (0)	0.012	0.0089–0.017	0.011
	All	~0–1.8 m from grinder	8–11	12 (0)	0.12	0.018–0.39	0.084	12 (0)	0.061	0.0089–0.21	0.056

a Respirable dust was excluded from this table due to the high percentage of samples below the LOD.
b The sampling time for one sample was 19 min due to pump malfunction; the remaining sampling times were 37–41 min.
c 50% or more of samples were <LOD.
d Minimum detected sample was 0.0014 ppm.

Fig. 3. Task-based (≤15 min) airborne concentrations of diacetyl associated with handling flavorings.

substrate, or reactant-limited, and less dependent on roasting time and temperature than diacetyl, and although both diketone compounds are structurally similar, the formation and degradation pathways of diacetyl and 2,3-pentanedione may be different [8].

Low concentrations of respirable dust were found in the facility. Conversely, in the literature, concentrations of respirable dust during coffee handling and processing have been reported to range from 0.15 mg/m^3 to 11.65 mg/m^3 [48,56,57]. These discrepancies are likely due to differences in the production volumes and/or processes and to general housekeeping and dust control measures.

In this analysis, we evaluated diketone emissions from one relatively small commercial coffee bean grinder. Depending on facility-specific conditions, it is possible that large-scale industrial operations, with several grinders simultaneously processing greater coffee volumes, could be associated with higher airborne concentrations of diketones. While ventilation conditions are likely to vary greatly between different facilities, we evaluated our study site under normal operating and ventilation conditions, which may be typical for such an operation. It is also possible that smaller grinding volumes, such as those found in a coffee shop or perhaps even in the home, could be associated with detectable diketone levels near the grinding source.

4.1. Comparison to diketone measurements in other studies

The workplace airborne diketone concentrations measured in our study are generally lower than those measured in the headspaces of open or closed containers of roasted whole beans or ground coffee (e.g., 0.4 ppm to 4.4 ppm, as reported by Grosch and
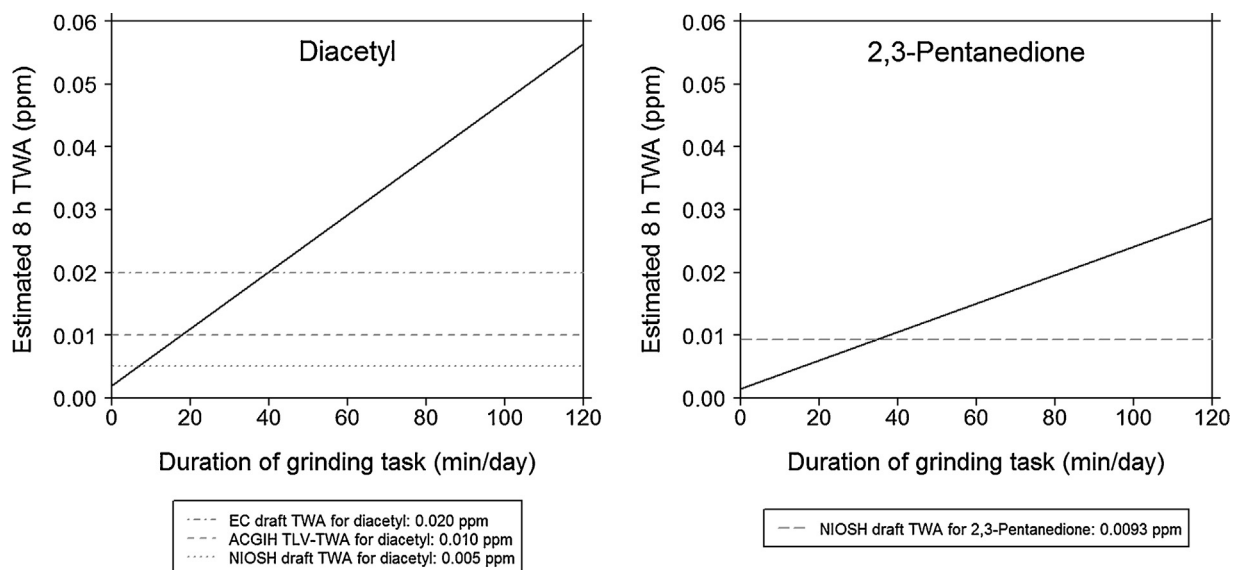

Fig. 4. Estimated mean 8-h TWA diacetyl and 2,3-pentanedione concentrations, as a function of the total time spent grinding per day.

Mayer [29] and Mayer and Grosch [37]). This finding is likely due to dilution between the headspace and the worker breathing zone, in which air movement rapidly decreases the concentration with distance from the emission source. The published headspace measurements of the diketones indicate higher concentrations were generated by roasted ground coffee relative to whole beans, which is consistent with our findings [29].

Interestingly, the diacetyl concentrations measured in this study are comparable to those that have been reported in workplaces at which diacetyl was used as a food additive. As can be seen in Fig. 3, the mean estimated short-term concentration measured near coffee grinding in this study (0.15 ppm) is at the 63rd percentile of the distribution of short-term samples collected by ERG while workers were handling diacetyl-containing flavorings [mean = 0.54 ppm]. Hence, short-term measurements of diacetyl associated with small, commercial-scale grinding of roasted unflavored coffee beans are not dissimilar from those measured in food manufacturing facilities at which diacetyl-containing flavorings are handled, often in significant volumes.

4.2. Comparison to diketone proposed and recommended OELs

Fig. 2 compares the 15 min TWA diketone concentrations from grinding, estimated in this analysis, to the proposed and recommended 15 min STELs. All of the estimated 15 min TWA concentrations exceeded all 15 min recommended and proposed STELs in the immediate work area, while estimated 15 min TWA concentrations exceeded ACGIH and NIOSH proposed STELs several meters from the grinder for both light and dark roasted hard coffee beans. The results indicate that, in coffee processing facilities where commercial grinding occurs, potential worker exposure could exceed the proposed and/or adopted diacetyl and 2,3-pentanedione STELs because of release of naturally occurring diketones from the roasted coffee beans.

Potential exceedances would most likely be experienced by workers stationed near the emission source (the grinder), and may also occur for workers performing activities several meters from the source, depending upon the duration of grinding activities and the facility or process ventilation.

STEL values are often established to minimize peak exposure and potential exceedances of the full-shift OELs. For example, the diacetyl 15 min STEL of 0.025 ppm proposed by NIOSH was to protect against exceedances of the 8 h proposed diacetyl REL of 0.005 ppm. As NIOSH noted in the supporting documentation, "On the basis of general industrial hygiene principles, the STEL, which is five times the [REL], would serve to reduce peak exposures and tend to reduce overall worker exposures to diacetyl. The selection of a STEL that is five times the [REL] is based upon past precautionary practice" [42]. Because the estimated 15 min TWAs indicate that the diketone STEL values were exceeded during grinding operations evaluated in this study (Fig. 2), it is reasonable to suggest that the 8 h diketone TWA OELs could have also been exceeded. Collection and analysis of full-shift personal TWA data were not part of the objectives in this study (only task-based area samples were collected), but plausible daily TWA airborne concentrations were approximated using the task-based data and various assumptions regarding task duration (Fig. 4).

4.3. Other potential worker and consumer exposures to diketones in processed coffee

Downstream workers, or those that work with processed coffee, could also plausibly experience natural diketone exposures, and the magnitude of any such exposure would likely depend heavily on time elapsed between roasting and grinding, as well as on storage and packaging conditions, including room ventilation. In this study,

approximately 1.3 h to 3.2 h elapsed between roasting and grinding. Our results would, therefore, seem applicable to the numerous local roasteries, at which beans are roasted and subsequently ground on the premises. In our study, one batch of about 11 kg of coffee beans were ground during each event, corresponding to about 180 L (i.e., 300 to 400 medium-sized cups) of brewed coffee [39]. This amount of coffee appears to be a plausible volume handled daily in busy coffee shops; our results are therefore conceivably within the range of potential exposures experienced by some roaster/coffee shop workers during a normal work shift.

Even household consumers could possibly experience diketone exposures due to the residual chemical levels that volatilize during brewing. As previously noted, Yeretzian et al. [60] reportedly measured 7.0 ppm diacetyl in the headspace of a cup of freshly ground and brewed coffee. The authors indicated that the goal of their experiment was to "mimic . . . the situation of an open coffee cup that was served from a thermos" [60]. Coffee processing plants often pack and ship freshly roasted whole beans in airtight bags to preserve freshness. In such instances, the manufacturer usually allows the beans to off-gas at the source facility for a short period (e.g., 24 h) before packaging to prevent package rupture from vapor emissions. Alternatively, some freshly roasted beans are packaged without an off-gas period in containers with a one-way valve to allow for gases to escape continuously from packaging to consumption. Whether packaged whole beans (airtight or vented) emit measurable diketones upon grinding is an area for further study.

4.4. Comparison to estimated human equivalent concentrations for respiratory effects

Two subchronic animal inhalation studies of diacetyl have been conducted to ascertain whether and to what degree respiratory effects occurred following diacetyl exposure [38,47]. In both studies, mice and/or rats were exposed to a wide range of diacetyl concentrations for 6 h/day, 5 days/week, for approximately 90 days. Minimal to moderate bronchial and bronchiolar effects attributable to diacetyl exposure were observed in some of the animals at the higher exposure concentrations. None of the animals developed *bronchiolitis obliterans*, and indeed, diacetyl-related alveolar effects were not observed in either study, even at the highest concentrations (which ranged up to 100 ppm).

Several investigations have evaluated these animal studies, in conjunction with benchmark concentration (BMC) analyses, to derive "human equivalent concentrations" (HECs) associated with a 10% risk of respiratory effects relative to background. To derive the HECs, interspecies differences in the respiratory tract between mice and humans were accounted for by including dosimetric adjustments (some of which incorporated differences in breathing habits, since rats and mice are obligate nose breathers), adjustments for differences in lung region-specific surface areas, and others. Using a variety of methods, all HECs were found to be greater than 1.3 ppm for minimal effects in the bronchial and bronchiolar regions (including peribronchial lymphocytic inflammation, eosinophilic inflammation, bronchiolar epithelium hyperplasia, and peribronchiolar lymphocytic inflammation) [3,10,28,35,43].

These HEC values were derived based on minimal respiratory effects in the lung or deep lung of humans, which are expected to occur prior to adverse deep lung effects, such as *bronchiolitis obliterans*. Additionally, the derived HECs were well above the diacetyl concentrations measured in our study. Hence, it seems unlikely that coffee processing workers at facilities similar to the one evaluated in this study are at risk of developing *bronchiolitis obliterans* (or any other disease that involves scarring and destruction of the bronchiolar and alveolar region) as a result of exposure to naturally occurring diacetyl.

4.5. Health effects in coffee processing workers

The respiratory health status of coffee processing workers has been evaluated in many studies, and the most consistent finding is one of allergic respiratory responses to certain allergens in respirable green coffee dusts [26,30,31,33,34,58,61,62]. We are unaware of any published studies to date suggesting an increased risk of obstructive disorders in coffee processing workers due to naturally occurring diketones. Two cases of *bronchiolitis obliterans* were reported in workers handling diacetyl- containing flavorings at a small coffee-processing facility in Texas [13]; however, as noted by the study authors, "The relative contribution of diacetyl from flavorings and roasting or grinding to these two cases is unknown" (p. 306) and it is also apparent that because this facility likely utilized a wide range of flavorings, the potential effect from exposure to other agents was not evaluated in detail. In addition, we are not aware of any published epidemiology studies of other potentially exposed individuals, such as workers in coffee shops or other premises where coffee is ground. It is of note that though an evaluation of health status was beyond the scope of the current study, the workers in study facility did not report a history of relevant adverse health effects.

4.6. Study strengths and limitations

The main strength of this analysis is the controlled study conditions that permitted distinction of diketone emissions from roasting versus grinding tasks, and the use of unflavored beans to ensure that only naturally occurring diketones were measured. A representative set of common coffee roast/bean types (light roast/soft bean, etc.) was evaluated, and multiple source samples and samples at points distant from the operations were collected. Because a single industrial roaster/grinder was evaluated, the results are likely at least partially applicable to many of the smaller coffee processing operations (e.g., grocery stores, coffees shops), although they may underestimate exposures at facilities with much larger operations depending on facility design.

The primary limitation to our study is that only stationary samples were collected and that only one location was evaluated. Although every attempt was made to locate the samplers as close as possible to the breathing zone of the worker, they do not reflect potential movements of the workers either closer to or further from the emission source. Due to the volatility of the diketone chemicals, however, it is not expected that the personal exposures would have varied significantly from the air concentrations at breathing zone height, as measured through stationary sampling. It is also worth noting that the roaster was not in operation during the ventilation rate characterization study performed prior to the sampling events. It is expected that when the roaster was in operation, air exchange rates and air flow patterns would have only changed slightly (if at all) because of the temperature differential around the roaster, and make-up air required during the roasting process. The extent to which the overall air exchange rates and exposures would be impacted would be dependent upon a number of variables, including the degree to which the roaster was insulated and ventilated.

4.7. Conclusions and areas for future research

Our findings indicate that naturally formed diacetyl and 2,3-pentanedione are released during the roasting and grinding of coffee beans, and some airborne concentrations in coffee processing facilities may exceed the recommended short-term OELs, especially during grinding activities.

Our results, in conjunction with other studies, also suggest that exposure to diketones associated with preparation and consumption of coffee in coffee shops and in the home are possible. Future research efforts could involve: (1) analysis of naturally occurring diketone levels in personal samples collected during coffee grinding and/or brewing in industrial processing, coffee shop, and home settings, and (2) thorough epidemiology studies of workers exposed to diacetyl and/or 2,3-pentanedione alone (if such cohorts can be located) to determine if either of these diketones are capable of causing obstructive lung disease in humans exposed to plausible concentrations.

Until this relationship is known, we recommend that alternative methods for setting diketone OELs, such as the animal-based approach proposed by the recent work of Maier et al. [35] be applied to these compounds.

5. Conflict of interest

All the authors are employed by Cardno ChemRisk, a consulting firm that provides scientific advice to the government, corporations, law firms, and various scientific/professional organizations. Cardno ChemRisk has been engaged by several manufacturers and suppliers of diacetyl and diacetyl-containing flavorings in various litigation matters. Partial funding for this study and manuscript preparation was provided by Harleysville Group, Inc., an insurance carrier, and Flavor and Fragrance Specialties, Inc., a flavoring manufacturer, both involved in diacetyl litigation. The authors designed and executed the study and have sole responsibility for the writing and content of the manuscript. Neither the Harleysville Group, Inc., Flavor and Fragrance Specialties, Inc., nor their attorneys participated in any phase of this study, or reviewed the manuscript prior to publication. Three of the authors (JLH, BLF, JSP) have served as experts in diacetyl litigation, and they, along with others, may be called upon in the future to serve as experts in diacetyl litigation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.toxrep.2015.08.003.

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