ABSTRACT To clarify the nature and characteristics of volatile organic compounds (VOCs) emitted from dairy cattle within a cattle shed located in Chiba, Japan, air samples were collected and analyzed for the four seasons in 2017–2018. Thirty-four VOCs were determined by gas chromatography-mass spectrometry and high performance liquid chromatography. In addition, air temperature and relative humidity inside and outside of the shed were monitored during each sampling campaign to estimate the ventilation rate of the shed. The average concentrations of total VOCs (μg m⁻³) in the shed in each season were 50.5 (spring), 128.4 (summer), 168.8 (autumn), and 199.5 (winter). Ketones were always the most dominant components followed by alcohols and volatile fatty acids (VFAs). The sum of ketones, alcohols, and VFAs accounted for more than 80% of the total VOCs in all seasons. Acetone, 3-pentanone, 1-butanol, and acetic acid were the major components regardless of the season, accounting for more than 60% of the total VOCs. The average emission rates of total VOCs from the shed (μg h⁻¹ kg⁻¹) were calculated to be 623 (spring), 1520 (summer), 585 (autumn) and 469 (winter). The emission rates of almost all the VOCs except alcohols increased exponentially with increase of air temperature in the shed. The ranges of the emission rates for each class of chemical (μg h⁻¹ kg⁻¹) were 39–170 (VFAs), 247–913 (ketones), 65–134 (alcohols), 40–122 (phenols), 10–122 (aldehydes), 4.17–22.3 (sulfur compounds), and 0.0067–0.74 (indoles). Furthermore, the annual emissions of VOCs for a single dairy cattle and for the cattle shed were estimated to be 5.5 kg and 44 kg, respectively.

KEY WORDS Volatile organic compounds, Dairy cattle, Chemical composition, Seasonal variation, Emission rate

1. INTRODUCTION

Volatile organic compounds (VOCs) are one of the most prominent class of chemicals in the atmosphere. VOCs in the atmosphere impact on climate, the atmospheric environment, and human health. Some of the ambient VOCs are known to cause odor pollution near the emission source (Shusterman, 2013; Parker et al., 2012), and have the potential to cause cancer or other health impacts such as headache, respiratory disease, and neurological disorders (e.g., Akdeniz et al., 2013). In addition, gas-phase oxidation of VOCs leads to the formation of secondary organic aerosols (SOAs) (e.g., Camredon et al., 2007). Such SOAs may influence
cloud formation and, especially for polar organic compounds such as those with carboxyl groups, have the potential to act as cloud condensation nuclei, which can form cloud droplets (Nga et al., 2005). In addition, the presence of atmospheric VOCs causes a rise in the concentration of atmospheric ozone (World Health Organization, 2000). Ozone in the troposphere is a prevalent photochemical oxidant, is known to be highly phytotoxic (Krupa and Manning, 1988), and has impacts on human health (e.g., Finlayson-Pitts and Pitts Jr., 1997). In addition, tropospheric ozone contributes to the formation of airborne toxic chemicals (e.g., Finlayson-Pitts and Pitts Jr., 1997). Therefore, VOCs are of great concern from the perspective of human health and environmental management.

Recently, the livestock industry has been reported to be one of the major sources of atmospheric VOCs in the USA (Hafer et al., 2010; Howard et al., 2008; Shaw et al., 2007), Europe (Sintermann et al., 2014), China (Qi et al., 2017; Qiu et al., 2014; Fu et al., 2013), and India (Varshney and Padhy, 1998). Livestock feed-yard operations are major stationary source of odorous VOCs emissions from agriculture and cause public odor contamination in the USA (Lu et al., 2008). Borhan et al. (2012) studied seasonal emissions of phenol and p-cresol, the primary odorous VOCs, in a dairy operation in central Texas, and reported that emission rates (ERs) for phenol and p-cresol amounted to several hundred to several thousand mg head$^{-1}$ day$^{-1}$, respectively. Chung et al. (2010) evaluated non-methane VOC (NMVOC) emissions from dairy operations in California, and indicated that silage and total mixed rations were the dominant sources of VOCs.

Odorous compounds are also emitted from livestock waste including manure, feces, and urine (Parker et al., 2013; Mackie et al., 1998). Some of the VOCs from livestock waste are produced from the incomplete anaerobic fermentation of waste by bacteria (Mackie et al., 1998). Major classes of chemicals emitted from livestock waste include volatile fatty acids (VFAs), ammonia, aldehydes, ketones, alcohols, indoles, and sulfur compounds (Rabaud et al., 2003; Sunesson et al., 2001; Mackie et al., 1998). Furthermore, VOCs are also emitted from exhalation by livestock (Sintermann et al., 2014; Ngwabie et al., 2008; Shaw et al., 2007). Thus, VOCs are emitted from various sources related to livestock operations.

The ER, flux, and emission inventory of VOCs from livestock have been estimated in various studies (Qi et al., 2017; Qiu et al., 2014; Fu et al., 2013; Borhan et al., 2012; Hu et al., 2012; Hales et al., 2012; Parker et al., 2010; CDPR, 2006; Varshney and Padhy, 1998). For example, in California, VOCs emitted from the stock-breeding industry have been estimated to account for 9.6% of the total VOC emissions (CDPR, 2006). Hence, VOCs from livestock have the potential to adversely impact the environment. In fact, Hu et al. (2012) estimated that the O$_3$ formation potential of VOCs due to animal feed emissions was almost at the same level as that of mobile-source VOC emissions.

In contrast to the situation in the USA, VOCs emitted from livestock in Japan have rarely been reported. In 2018 for example, approximately 1.3 million head of dairy cattle, 2.5 million head of beef cattle, 9.2 million head of swine, 139 million head of hens, and 139 million head of broiler chicken were reared in Japan (Japanese Ministry of Agriculture, Forestry and Fisheries, 2018). Therefore, the VOC emissions from these livestock may adversely impact on human health and the environment in Japan. Previously, we reported the concentrations, compositions, and seasonal variations of VOCs emitted from swine in Japan and showed that the ER of VOCs from a swine shed was about $1\text{–}2 \times 10^3$ μg (kg-swine)$^{-1}$ (Osaka et al., 2018). On this basis, the total annual emissions of VOCs from one swine shed was estimated to be on the order $10^3$ g year$^{-1}$. As indicated above, about 9.2 million head of swine are reared on an annual basis. Hence it is considered that the nation’s annual emissions of VOCs due to swine rearing is not negligible.

In this study, emissions of VOCs from dairy cattle in Japan have been studied with the aim of clarifying the concentrations, compositions, seasonal variations, and ERs for the VOCs.

2. EXPERIMENTAL

2.1 Target Compounds

Compounds targeted in this study were eight VFAs (acetic acid, propanoic acid, isobutyric acid, butyric acid, isovaleric acid, valeric acid, hexanoic acid, and heptanoic acid), five alcohols (methanol, ethanol, 2-butanol, 1-propanol, and 1-butanol), three phenols (phenol, 4-methoxyphenol, and 4-ethylphenol), two sulfur compounds (dimethyl sulfide and dimethyl disulfide), two indoles (indole and skatole), four ketones (acetone, 2-but酮, 2-pentanone, and 3-pentanone), and eleven aldehydes...
VOCs from a Dairy Cattle Shed

(formaldehyde, acetaldehyde, acrolein, propionaldehyde, crotonaldehyde, methacrolein, n-butyraldehyde, benzaldehyde, valeraldehyde, m-tolualdehyde, and hexaldehyde). These compounds were previously reported to be emitted from livestock industries (e.g., Parker et al., 2013; Filipy et al., 2006). All standard reagents and solvents for sample treatment were prepared from analytical grade reagents.

2.2 Sampling Site

Air samples from a cattle shed were collected at Asahia Agricultural High School (latitude 35°43’00”N, longitude 140°39’36”E) located in the northeast of Chiba Prefecture, Japan. A schematic of the shed is given in Fig. 1. The volume of the shed was 522.7 m$^3$ (11.0 m width × 14.4 m depth × 3.3 m height). Most of the doors and windows of the shed were kept open throughout the day regardless of season, except when there were strong winds due to typhoons, so the air within the shed was regarded as being naturally ventilated. The floor was made of concrete and some of that was covered with straw. Waste from the cattle was removed daily at 7:00, 11:00, and 16:00.

Holstein and Japanese Black cattle, both major species for dairy cattle in Japan, were raised in the shed. All the cattle stayed in the shed in stalls throughout the day. The number and total weight of the cattle are shown in Table 1. The cattle were fed about 2 kg day$^{-1}$ head$^{-1}$ of hay (Sudan grass and Bermuda grass), 1 kg day$^{-1}$ head$^{-1}$ of hay (Phleum pretense and alfalfa), and 6–12 kg day$^{-1}$ head$^{-1}$ of formula feed (Miracle U 70, Marubeni Niisshin Feed) every day, the feedstuffs being split into three portions and provided at 7:00, 11:00, and 16:00. The cattle were able to drink water freely at any time from the watering stations within the facility and they could also take mineral salt.

![Fig. 1. Basic outline of the cattle shed.](image)
2.3 Sampling Procedure

Air sampling in the cattle shed was conducted in spring (April 2017), summer (July and August 2017), fall (October 2017), and winter (January 2018) for three or four days in each season (Table 1). Sample collection was performed according to a previous study (Osaka et al., 2018). The VFAs, phenols, sulfur compounds, indoles, and some ketones (2-butanone, 2-pentanone, and 3-pentanone), and some alcohols (2-butanol, 1-propanol, and 1-butanol) were collected with stainless steel or glass sorbent tubes filled with Tenax TA® sorbent (3.5 in. × 0.25 in. OD, 60/80 mesh, COMSCO). Prior to sample collection, all tubes were conditioned by a stream of pure nitrogen gas at a flow rate of 50 mL min⁻¹ at 300°C. Air samples were collected at the center of the shed, as shown in Fig. 1. Air in the shed was continuously collected every hour in the sorbent tubes using a tube sampler (MTS-32, MARKES) at a flow rate of 0.1 L min⁻¹ throughout every sampling period. After sampling, the tubes were closed and stored in a cool, dark place. In addition, trip blank and field blank samples were also collected for each sampling campaign.

For measurement of aldehydes and acetone, samples were collected with two 2,4-dinitrophenylhydrazine (DNPH) cartridges containing DNPH derivatizing agents (InertSep mini AERO DNP-LG, GL Sciences) that connected to an ozone scrubber cartridge (InertSep mini AERO Ozone Scrubber, GL Sciences) upstream. Sample air was collected at the center of the shed at a flow rate of 0.1 L min⁻¹ from 8:00 to 16:00 and from 16:00 to 8:00. After sampling, the DNPH cartridges were closed at both ends and placed in a cool, dark place. Field blanks were also processed along with the sorbent tube samples.

Air samples for methanol and ethanol were collected from the center of the shed using a Florisil® cartridge (Presep-C® Florisil, Wako Pure Chemical Industries) at a flow rate of 0.1 L min⁻¹ for 30 min at 0:00, 8:00, 12:00, and 16:00 in each season. After sampling, the Florisil cartridges were closed at both ends and placed in a cool, dark place. Field blanks were also processed along with the sorbent tubes.

Number of samples collected in each sampling campaign were shown in Table 1.

2.4 Monitoring of Air Temperature and Relative Humidity

The air temperature and relative humidity (RH) inside and outside of the shed were monitored using hydrothermographs (RTR-503, T&D, ±0.3°C, ±5% RH). Monitoring points inside the shed were the same as for the air sampling. The hydrothermograph for outside measurement was located at 10 m distance from the shed (Fig. 1). The external hydrothermograph was covered with tin foil to give protection from the effects of direct sunlight and rain. The air temperature and RH were monitored every 10 min throughout the sampling campaigns. The differences in temperature and RH between the two hydrothermographs were 0.07 ± 0.08°C and 0.36 ± 0.55% RH, respectively. Based on these data, the air temperature and RH were judged to be calibrated.

2.5 Analytical Procedure

Analytical procedures, except for the determinations of methanol and ethanol, were conducted according to a previous study (Osaka et al., 2018). The VFAs, phenols, and indoles were determined by gas chromatography-mass spectrometry (GC/MS; GCMS-QP2020, Shimadzu Corporation) equipped with a thermal desorption injector (TD-GC/MS; TDTS-2020, Shimadzu Corporation). An InertCap WAX capillary column (30 m × 0.25 mm × 0.25 μm, GL Sciences) was used for separation. Chemical compounds collected on the adsorbent were desorbed for 3 min at 230°C with a purge flow of 50 mL min⁻¹ with trapping at ~20°C. The cold trap was rapidly heated to 230°C and the trapped chemical substances were injected into the GC/MS. The GC oven temperature program was as follows: 40°C (hold 3 min) → (ramp 8°C min⁻¹) → 230°C (hold 5 min). The temperatures of the injection port and the ion source were 200 and 210°C, respectively. The samples were analyzed using the selected ion monitoring (SIM) mode. For signal quantitation, standard solutions of the analytes at 1, 10, and 100 ng μL⁻¹ were measured by TD-GC/MS.

Aldehyde and ketone samples were processed before analysis. A strong cation (SC) exchange resin (InertSep mini AERO SC, GL Sciences) was conditioned with 5 mL acetonitrile, 5 mL purified (ion-exchange) water, 20 mL 0.1 M hydrochloric acid solution, and 5 mL acetonitrile. After conditioning, the SC cartridge was connected downstream of the DNPH cartridge and the DNPH derivatives were eluted with 5 mL acetonitrile at a flow rate of 1 mL min⁻¹. The eluate was concentrated and the volume adjusted to 1 or 10 mL with acetonitrile prior to analysis by high-performance liquid chromatography (HPLC) with UV detection (HP 1100, Hewlett Packard, equipped with an InertCap WAX capillary column [Del-
VOCs from a Dairy Cattle Shed

tabond Resolution AK: 200 mm × 4.6 mm × 5 μm; Thermo Fisher Scientific). The oven temperature was maintained at 40°C throughout the separation. Acetonitrile (A) and acetonitrile solution (B) containing 10% water were used for the eluents. The gradient was performed as follows: A/B = 35%/65% to 65%/35% (0.0 → 35.0 min), 65%/35% to 80%/20% (35.0 → 35.2 min), 80%/20% (35.2 → 40.0 min), 80%/20% to 35%/65% (40.0 → 40.2 min), and 35%/65% (40.2 → 45.0 min). The detection wavelength for UV measurement was 365.8 nm. For quality control purposes, standard solutions of aldehydes and ketones at concentrations of 0.375–15 μg mL⁻¹ were analyzed by HPLC using the same conditions as described above.

Methanol and ethanol samples were processed before analysis. Three mL of purified water were added onto a Florisil cartridge for extraction of methanol and ethanol. The eluate was analyzed by GC/MS (GCMS-QP2020, Shimadzu Corporation) equipped with an InertCap WAX capillary column (30 m × 0.25 mm × 0.25 μm, GL Sciences). The GC oven temperature program was as follows: 40°C (hold 1 min) → (ramp 5°C min⁻¹) → 75°C → (ramp 15°C min⁻¹) → 120°C (hold 1 min). The temperatures of the injection port and the ion source were 200 and 210°C, respectively. The samples were analyzed using the SIM mode.

The trip blanks for all of the target compounds were below or near the detection limit. The field blanks were detected at most 10 ng, but they were sufficiently low compared with the measured values of the samples. The measured values of the samples were corrected by subtracting the blanks.

2.6 Estimation of ERs of VOCs from the Shed

The ERs of VOCs from the shed were estimated according to a previous study (Osaka et al., 2018). ERs of VOCs from the shed were evaluated using Eq. (1),

\[
E = \frac{C \times V_{out}}{W} \tag{1}
\]

where \(E\) (μg [h kg-cattle]⁻¹) is the ER, \(C\) (μg m⁻³) is the VOC concentration in the cattle shed, \(V_{out}\) (m³ s⁻¹) is the ventilation rate of the shed, and \(W\) (kg) is the total weight of cattle in the shed. The concentrations of the VOCs in the air in the shed were measured by the air sampling method. The ventilation rate was estimated using the water balance method (Urano and Katayama, 1985), which established the vapor equilibrium based on the water balance of the shed. In the shed, where air was exchanged by ventilation, the mass balance formula (Eq. (2)) can be written as follows:

\[
\frac{dG^*}{dt} = G_{in} - G_{out} + G_g \tag{2}
\]

where \(G^*\) (kg) is the weight of air in the shed, \(t\) (s) is the time, \(G_{in}\) (kg s⁻¹) and \(G_{out}\) (kg s⁻¹) are the weights of intake air and exhaust air, respectively, and \(G_g\) (kg s⁻¹) is the weight of waste material, such as feces and urine, generated in the shed. On the assumption that humid air in the shed consists of vapor and dry air that are well mixed by ventilation, the two mass balance formulae (Eqs. (3-a) and (3-b)) for vapor and dry air, respectively, may be derived from Eq. (2):

\[
V_i \frac{d(x_i/v_i)}{dt} = V_{in}(x_i/v_i) - V_{out}(x_i/v_i) + W_g \tag{3-a}
\]

\[
V_i \frac{d(1/v_i)}{dt} = V_{in}/v_i - V_{out}/v_i \tag{3-b}
\]

where \(V_i\) (m³) is the volume of the shed, \(V_{in}\) (m³ s⁻¹) is the volume of intake air of the shed, \(V_{out}\) (m³ s⁻¹) is the volume of exhaust air of the shed, \(x_i\) (kg kg⁻¹) is the indoor absolute humidity, \(x_0\) (kg kg⁻¹) is the outdoor absolute humidity, \(v_i\) (m³ kg⁻¹) is the specific volume in the shed, \(v_0\) (m³ kg⁻¹) is the specific volume exiting out of the shed, and \(W_g\) (kg s⁻¹) is the amount of moisture emission. The absolute humidity and the specific volume were determined from the air temperature and the RH inside and outside of the shed using a psychrometric chart. Moisture emission, that is, the amount of moisture to be removed from the room, was referred to the regression equation reported by Yeck et al. (1959). Yeck et al. (1959) described the relationship between the air temperature and the moisture ER for dairy cattle (water emission (lb.) per body weight of dairy cattle (lb.)) in the shed. Moisture emission may be converted to the latent heat of the room by multiplying the moisture released from the cattle by the latent heat of vaporization of the body temperature of the cattle, and by multiplying the moisture picked up from sources such as urine and feces by the latent heat of vaporization for the air temperature of the room (Yeck et al., 1959). Thus, moisture emission was estimated from the regression curves for the weight of one dairy cattle and the temperature in the shed. \(V_{out}\) may be determined from Eqs. (3-a) and (3-b) as follows:
\[
V_{out} = \frac{V_i v_i}{(x_i-x_0)\Delta t} \left( x_0-x_i^{*} \right) + \frac{W_g v_i}{x_i-x_0} \quad (4)
\]

where \(\Delta t\) is the time interval, \(x_i^{*}\) is the indoor absolute humidity after \(t\) min, and \(v^{*}\) is the specific volume in the shed after \(t\) min. On the assumption that the air in the shed was at a steady state, Eq. (4) may be re-written as Eq. (5).

\[
V_{out} = \frac{W_g v_{in}}{x_i-x_0} \quad (5)
\]

The ventilation rate of the shed was estimated according to Eq. (5) on the assumption that the air exhaust is equal to the air intake. As described in the next section, in cases where the differences of temperature and RH between the inside and outside of the shed were below the measurement errors of the hydrothermographs, such data were removed from the calculation of the ventilation rate of the shed. The total annual emissions of VOCs from the shed was estimated according to Eq. (6):

\[
N = E \times W \times 24 \text{ hours/day} \times 365 \text{ days/year} \times 10^6 \quad (6)
\]

where \(N\) (g/year) is the amount of total annual emissions of VOCs from the shed.

3. RESULTS AND DISCUSSION

3.1 Temperature and RH Inside and Outside of the Shed

The time variation of the temperature and RH differences between the inside and outside of the cattle shed during the spring sampling campaign is shown in Fig. 2. It was found that the differences in temperature and RH between the two locations were often smaller than the measurement errors (±0.3°C, ±5% RH) of the hydrothermographs used for measurement. Similar trends were also observed in summer, autumn, and winter. During the sampling campaigns, the windows and the doors of the cattle shed were kept open throughout the year except when typhoons occurred, so the shed was considered to be well-ventilated. Hence, relatively small differences in temperature and RH between the inside and outside of the shed occurred regardless of the season. The data whereby the temperature and RH differences were below the measurement errors were not considered reliable for calculating the absolute humidity and the specific volume (see former section). Therefore, these data were not used for estimating the ER of VOCs from the cattle.

3.2 Concentration and Composition of VOCs in the Cattle Shed

The average concentrations for each VOC in the air in the shed for the four seasons are shown in Table 2. The average concentrations of total VOCs (μg m\(^{-3}\)) were 50.5 (spring), 128.4 (summer), 168.8 (autumn), and 199.5 (winter). In general, emissions of VOCs from the shed tended to increase with increase in the air temperature. Nevertheless, the concentrations of VOCs in the air in the shed were not particularly high in summer relative to the other seasons. This indicated that the shed was well-ventilated by the outside air. Especially in summer, a large fan was always operated in addition to having the doors and windows of the shed open to control the phys-
### Table 2. Concentrations of VOCs in the cattle shed for each season (in μg m\(^{-3}\)).

|                   | Spring       | Summer       | Autumn       | Winter       |
|-------------------|--------------|--------------|--------------|--------------|
| **VFAs**          |              |              |              |              |
| Acetic acid       | 13.2         | 25.9         | 0.38         | 7.6          |
| Propanoic acid    | 1.8          | 3.6          | 0.19         | 0.11         |
| Isovaleric acid   | 0.31         | 0.95         | 0.004        | 0.19         |
| Butyric acid      | 0.54         | 1.0          | 0.004        | 0.32         |
| Isovaleric acid   | 0.40         | 0.55         | 0.003        | 0.14         |
| Valeric acid      | 0.52         | 1.9          | 0.006        | 0.37         |
| Heptanoic acid    | 0.29         | 0.63         | 0.005        | 0.18         |
| VFAs              | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |
| **Alcohols**      |              |              |              |              |
| Methanol          | 2.9          | 7.5          | 0.8          | 2.4          |
| Ethanol           | 0.21         | 2.0          | BDL          | 0.56         |
| 1-Propanol        | 0.40         | 1.1          | 0.010        | 0.25         |
| 1-Butanol         | 1.7          | 30.1         | 0.019        | 5.7          |
| 2-Butanol         | 0.14         | 0.33         | 0.005        | 0.062        |
| Alcohols          | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |
| **Phenols**       |              |              |              |              |
| Phenol            | 2.4          | 5.1          | 0.10         | 1.0          |
| 4-Methyl phenol   | 2.3          | 7.9          | 0.082        | 1.5          |
| 4-Ethyl phenol    | 0.11         | 0.41         | 0.002        | 0.08         |
| Phenols           | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |
| **Sulfur compounds** |           |              |              |              |
| Dimethyl sulfide  | 0.67         | 2.6          | 0.052        | 0.58         |
| Dimethyl disulfide| 0.08         | 0.80         | 0.003        | 0.17         |
| Sulfur compounds  | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |
| **Indoles**       |              |              |              |              |
| Indole            | 0.003        | 0.036        | 0.001        | 0.005        |
| Indole            | 0.003        | 0.018        | BDL          | 0.003        |
| Indoles           | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |
| **Ketones**       |              |              |              |              |
| Acetone           | 24.6         | 41.3         | 8.8          | 12.3         |
| 2-Butanone        | 1.1          | 12.3         | BDL          | 2.1          |
| 2-Pentanone       | 0.15         | 0.58         | BDL          | 0.14         |
| 3-Pentanone       | 0.26         | 6.94         | BDL          | 1.0          |
| Ketones           | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |
| **Aldehydes**     |              |              |              |              |
| Formaldehyde      | 2.9          | 3.4          | 2.4          | 0.43         |
| Acetaldehyde      | 0.69         | 1.7          | BDL          | 0.60         |
| Acrolein          | BDL          | BDL          | BDL          | BDL          |
| Acrolein          | BDL          | BDL          | BDL          | BDL          |
| Propionamide      | BDL          | BDL          | BDL          | BDL          |
| Crotonaldehyde    | BDL          | BDL          | BDL          | BDL          |
| Methacrolein      | BDL          | BDL          | BDL          | BDL          |
| n-Butylaldehyde   | BDL          | BDL          | BDL          | BDL          |
| Benzaldehyde      | BDL          | BDL          | BDL          | BDL          |
| Valeraldehyde     | BDL          | BDL          | BDL          | BDL          |
| Hexaldehyde       | BDL          | BDL          | BDL          | BDL          |
| Aldehydes         | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |
|                   | Average      | Max          | Min          | SD           |

1) SD: standard deviation  
2) BDL: below detection limit
ical conditions inside the shed. Thus, the concentrations of VOCs in the shed were not high in the summer.

The chemical composition of the VOCs for each season are indicated in Fig. 3. It was found that the ketones were always the most dominant component followed by alcohols and VFAs. The sum of ketones, alcohols, and VFAs accounted for more than 80% of the total VOCs in all seasons. Acetone, 3-pentanone, 1-butanol, and acetic acid were the major chemicals regardless of the season, accounting for more than 60% of the total VOCs. Filipy et al. (2006) and Chung et al. (2010) showed that acetone was one of the dominant VOCs emitted from dairy cattle. Alanis et al. (2010) estimated the VFA flux emitted from dairies and clarified that more 90% of the VFAs emitted was in the form of acetic acid. The present data are generally consistent with previous reports concerning this latter point.

### 3.3 ERs of VOCs

The ERs of VOCs from the cattle shed in each season are shown in Fig. 4. The average ERs for the total VOCs from the shed (μg h⁻¹ kg⁻¹) were calculated to be 623 (spring), 1520 (summer), 585 (autumn), and 469 (winter), indicating that more VOCs were emitted in the summer. The ER ranges for each chemical class (μg h⁻¹ kg⁻¹) were 39–170 (VFAs), 247–913 (ketones), 65–134 (alcohols), 40–122 (phenols), 10–122 (aldehydes), 4.17–22.3 (sulfur compounds), and 0.0067–0.74 (indoles). Thus, of the VOC classes, ketones exhibited the highest ER in all seasons, accounting for 40–69% (average: 59%) of total VOC emissions. Furthermore, acetone, acetic acid, 1-butanol, and 3-pentanone gave higher ERs among the VOCs targeted in this study. High ERs for acetone and acetic acid from dairy cattle feeding operations were also found in previous studies (e.g., Yuan et al., 2017; Chung et al., 2010; Alanis et al., 2010, 2008). However, in another study on dairy cattle, 1-butanol and 3-pentanone were not found to be major emitters (Filipy et al., 2006). The reason for this is unclear. Borham et al. (2012) reported that the ERs of phenol and p-cresol (4-methylphenol) from a dairy cattle facility in Texas were a few thousand mg head⁻¹ day⁻¹, respectively. The ERs of phenol and 4-methylphenol for the present study

---

![Fig. 3. Seasonal compositions of VOCs in the shed.](image1)

![Fig. 4. Seasonal ERs of VOCs for the cattle shed.](image2)

![Fig. 5. Relationship between the temperature in the shed and ER of total VOCs. The error bars show the standard deviation.](image3)
VOCs from a Dairy Cattle Shed

were calculated to be 337 and 687 mg head\(^{-1}\) day\(^{-1}\), respectively, levels similar to that reported by Borham et al. (2012).

The relationships between the temperature inside the shed and the ER of total VOCs, each VOC class and each individual VOC (except for the compounds which were not detected in all four seasons) are shown in Figs. 5–7. The ERs of total VOCs and each VOC class except alcohols increased exponentially with increase of temperature inside the shed (Figs. 5 and 6). In addition, similar trends were also observed regarding the ER of each VOC (Fig. 7a–7g). The Claperyon equation, which describes the relationship of vapor pressure and temperature, is as follows:

\[
\ln P = - \frac{\Delta v_{a m} H_m}{RT} + \text{const.} \quad (7)
\]

where \(P\) is the vapor pressure, \(\Delta v_{a m} H_m\) is the molar enthalpy of vaporization, \(R\) is the molar gas constant, and \(T\) is the temperature. According to the equation, vapor pressure increases rapidly with rise in temperature. Hence VOCs contained in feces, urine, feed, and bedding in the shed would undergo increased emission with rise of
temperature. Also, the amount of transpiration from the body surface of the livestock would generally increase as air temperature rises. Moreover, Shibata and Mukai (1981) reported that the respiratory quotient of dairy cattle increased with rise of temperature, suggesting that the amounts of VOCs in expired air increase with increase in temperature. Thus, in general, the ER of VOCs is considered to increase with rise of air temperature within the shed.

Previous studies also support the trends observed in this work. For instance, Hafner et al. (2012, 2010) reported that the ER of ethanol from loose corn silage increased exponentially with rise of temperature. In addition, Rumsey et al. (2012) showed that ethanol emissions weakly correlated with the air temperature of the swine barn. Osaka et al. (2018) estimated that the mean ERs of VOCs from a swine shed in each season were $1-2 \times 10^3$ μg (h kg-swine)$^{-1}$. In addition, VFAs were found to be the dominant emission component from the swine, accounting for 47–75% of the total VOCs (Osaka et al., 2018). Compared with those from swine, the ERs of VOCs from dairy cattle were almost at the same level as those of swine, although the compositions of VOCs emitted from the swine and cattle were different.

### 3.4 Annual Emissions of VOCs from Dairy Cattle

The annual VOC emissions from one dairy cow and

---

**Fig. 7a.** Relationship between the temperature in the shed and ER of VFAs. The error bars show the standard deviation.
**Fig. 7b.** Relationship between the temperature in the shed and ER of alcohols. The error bars show the standard deviation.

**Fig. 7c.** Relationship between the temperature in the shed and ER of phenols. The error bars show the standard deviation.

**Fig. 7d.** Relationship between the temperature in the shed and ER of sulfur compounds. The error bars show the standard deviation.
Fig. 7e. Relationship between the temperature in the shed and ER of indoles. The error bars show the standard deviation.

Fig. 7f. Relationship between the temperature in the shed and ER of ketones. The error bars show the standard deviation.

Fig. 7g. Relationship between the temperature in the shed and ER of aldehydes. The error bars show the standard deviation.
Table 3. Annual emissions of VOCs from one cow and from the cattle shed.

| Emissions per one head | Total | VFAs | Alcohols | Phenols | Sulfur compounds | Indoles | Ketones | Aldehydes |
|------------------------|-------|------|----------|---------|------------------|---------|---------|-----------|
| Spring [kg head\(^{-1}\)] | 1.0   | 0.25 | 0.22     | 0.07    | 0.013            | 0.0001  | 0.41    | 0.061     |
| Summer [kg head\(^{-1}\)] | 2.5   | 0.28 | 0.15     | 0.20    | 0.037            | 0.0012  | 1.5     | 0.33      |
| Autumn [kg head\(^{-1}\)] | 1.2   | 0.08 | 0.21     | 0.08    | 0.009            | 0.00005 | 0.81    | 0.020     |
| Winter [kg head\(^{-1}\)] | 0.77  | 0.07 | 0.11     | 0.020   | 0.013            | 0.00001 | 0.53    | 0.032     |
| Annual [kg head\(^{-1}\)] | 5.5   | 0.68 | 0.69     | 0.37    | 0.07             | 0.0013  | 3.2     | 0.45      |

| Emissions per the shed | Total | VFAs | Alcohols | Phenols | Sulfur compounds | Indoles | Ketones | Aldehydes |
|------------------------|-------|------|----------|---------|------------------|---------|---------|-----------|
| Spring [kg shed\(^{-1}\)] | 7.9   | 2.0  | 1.7      | 0.55    | 0.10             | 0.0005  | 3.1     | 0.47      |
| Summer [kg shed\(^{-1}\)] | 19    | 2.1  | 1.2      | 1.5     | 0.28             | 0.0093  | 12      | 2.5       |
| Autumn [kg shed\(^{-1}\)] | 11    | 0.71 | 1.9      | 0.73    | 0.077            | 0.0004  | 7.2     | 0.18      |
| Winter [kg shed\(^{-1}\)] | 6.2   | 0.57 | 0.87     | 0.16    | 0.11             | 0.0001  | 4.3     | 0.26      |
| Annual [kg shed\(^{-1}\)] | 44    | 5.4  | 5.6      | 3.0     | 0.6              | 0.010   | 26      | 3.5       |

| Percentage | 9.1 | 13.9 | 2.6 | 1.7 | 0.0014 | 68.5 | 4.1 |

from the cattle shed were estimated using the ERs of VOCs shown above. The results are given in Table 3. The annual emissions of VOCs per single dairy cattle and the dairy cattle shed were estimated to be 5.5 kg and 44 kg, respectively. The number of dairy cattle raised in Japan in 2018 was reported to be approximately 1.3 million heads (Japanese Ministry of Agriculture, Forestry and Fisheries, 2018). As mentioned above, emissions of VOC from dairy cattle are considered to depend on the temperature. Average temperature in Japan in 2018 was 16.0°C (Japan Meteorological Agency, 2019), whereas the average temperature at the Yokoshiba-hikari weather station, located 16 km WSW from the sampling point, was 16.3°C in 2018 (Japan Meteorological Agency, 2019), being almost equal to that in Japan. Hence the annual emissions of VOC per one head of dairy cattle estimated in this study were considered to be roughly average in Japan from the point of view of temperature. Assuming that the annual emissions of VOCs from dairy cattle for the present study is taken as the average for Japan, the annual VOC emissions from dairy cattle in Japan are estimated to be 7.3 Gg. Kannari et al. (2007) reported NMVOCs emitted from several sources in Japan and estimated that the annual emissions from industrial combustion and navigation were 45 Gg and 14 Gg, respectively. The annual emissions of VOCs from dairy cattle estimated in this study is of a similar level as that of industrial combustion and navigation. This finding confirms that emissions associated with the livestock industry represent a substantial fraction of the VOC emissions inventory in Japan. Clearly, there will be differences in husbandry practices and environmental conditions for dairy cattle operations in Japan; hence, emissions and compositions of VOCs from each cattle shed are expected to cover wide ranges. Accordingly, the value of annual emissions of VOCs from dairy cattle in Japan estimated by using only the data obtained in this study will be subject to a degree of uncertainty and potential error. Given that there is currently no other data available for VOC emissions from dairy cattle in Japan, the annual emissions of VOCs from dairy cattle estimated in the present study is considered to have great significance despite being subject to considerable uncertainty.

4. CONCLUSION

In this study, VOCs in a cattle shed located in Asahi Agricultural High School, Chiba Prefecture, Japan, were collected over four seasons in an attempt to clarify the emission characteristics and composition of VOCs from the livestock industry in Japan. As part of the study, the temperature and humidity inside and outside of the cattle shed were also monitored. The average VOC concentrations in the cattle shed for the four seasons were in the range 50.5–199.5 μg m\(^{-3}\). Ketones were always the most dominant VOC class followed by alcohols and VFAs irrespective of season. Acetone, 3-pentanone, 1-butanol, and acetic acid were the major chemicals regardless of the season, accounting for more than 60% of the total VOC. The average ERs of total VOCs from the cattle shed (μg h\(^{-1}\) kg\(^{-1}\)) were calculated to be 469 (winter), 623 (spring), 1520 (summer), and 585 (autumn). The ERs for almost all the VOCs increased exponentially
with increase in the air temperature of the shed. Furthermore, the annual emissions of VOCs for a single dairy cattle and for the cattle shed were estimated to be 5.5 kg and 44 kg, respectively.

ACKNOWLEDGEMENT

The authors would like to heartily thank Mr. Y. Ando (Chiba Prefectural Asahi Agricultural High School, Japan) for his support in sampling. We also thank Mr. S. Fukumori (Electric Power Engineering Systems Co., Ltd., Japan) for assistance in sample collection and sample preparation, and Mr. J. Saito and Mrs. S. Sekiguchi (Waseda University Environmental Safety Center, Japan) for their technical support in HPLC analysis.

CONFLICT OF INTEREST

The authors declare no conflicts of interest.

REFERENCES

Akdeniz, N., Jacobson, L.D., Hetchler, B.P. (2013) Health risk assessment of occupational exposure to hazardous volatile organic compounds in swine gestation, farrowing and nursery barns. Environmental Sciences: Processes and Impacts 15(3), 563–572, DOI: 10.1039/C2EM30722G.

Alanis, P., Sorenson, M., Beene, M., Krauter, C., Shamp, B., Hason, A.S. (2008) Measurement of non-enteric emission fluxes of volatile fatty acids from a California dairy by solid phase micro-extraction with gas chromatography/mass spectrometry. Atmospheric Environment 42, 6417–6424, DOI: 10.1016/j.atmosenv.2008.05.015.

Alanis, P., Ashkan, S., Krauter, C., Campbell, S., Hasson, A.S. (2010) Emissions of volatile fatty acids from feed at dairy facilities. Atmospheric Environment 44, 5084–5092, DOI: 10.1016/j.atmosenv.2010.09.017.

Borhan, M.S., Capareda, S., Mukhtar, S., Faulkner, W.B., McGee, R., Parnell Jr., C.B. (2012) Comparison of seasonal phenol and p-cresol emissions from ground-level area sources in a dairy operation in central Texas. Journal of the Air & Waste Management Association 62, 381–392, DOI: 10.1080/10473289.2011.646050.

Camredon, M., Aumont, B., Lee-Taylor, L., Madronich, S. (2007) The SOA/VOC/NOx system: an explicit model of secondary organic aerosol formation. Atmospheric Chemistry Physics 7, 5599–5610, DOI: 10.5194/acp-7-5599-2007.

CDPR (2006) Pesticide air initiative: Strategy to reduce toxic and volatile organic compound emissions from agricultural and commercial structural pesticides.

Chung, M.Y., Beene, M., Ashkan, S., Krauter, C., Hasson, A.S. (2010) Evaluation of non-methane volatile organic compound (NMVOC) emissions from dairies. Atmospheric Environment 44, 786–794, DOI: 10.1016/j.atmosenv.2009.11.033.

Filipp, J., Rumburg, B., Munt, G., Westberg, H., Lamb, B. (2006) Identification and quantification of volatile organic compounds from a dairy. Atmospheric Environment 40, 1480–1494, DOI: 10.1016/j.atmosenv.2005.10.048.

Flayason-Pitts, B.J., Pitts Jr., J.N. (1997) Tropospheric air pollution: Ozone, airborne toxics, polycyclic aromatic hydrocarbons, and particles. Science 276, 1045–1051, DOI: 10.1126/science.276.5315.1045.

Fu, X., Wang, S., Zhao, B., Xing, J., Cheng, Z., Liu, H., Hao, J. (2013) Emission inventory of primary pollutants and chemical speciation in 2010 for the Yangtze River Delta region, China. Atmospheric Environment 70, 39–50, DOI: 10.1016/j.atmosenv.2012.12.034.

Hafner, S.D., Montes, F., Rotz, C.A., Mitloehner, F. (2010) Ethanol emission from loose corn silage and exposed silage particles. Atmospheric Environment 44, 4172–4180, DOI: 10.1016/j.atmosenv.2010.07.029.

Hafner, S.D., Montes, F., Rotz, C.A. (2012) A mass transfer model for VOC emission from silage. Atmospheric Environment 54, 134–140, DOI: 10.1016/j.atmosenv.2012.03.005.

Hales, K.E., Parker, D.B., Cole, N.A. (2012) Potential odorous volatile organic compound emissions from feces and urine from cattle fed corn-based diets with wet distillers’ grains and solubles. Atmospheric Environment 60, 292–297, DOI: 10.1016/j.atmosenv.2012.06.080.

Howard, C., Yang, W., Green, P., Mitloehner, F., Malkina, I., Flocchini, R., Kleeman, M. (2008) Direct measurements of the ozone formation potential from dairy cattle emissions using a transportable smog chamber. Atmospheric Environment 42, 5267–5277, DOI: 10.1016/j.atmosenv.2008.02.064.

Hu, J., Howard, C.J., Mitloehner, F., Green, P.G., Kleeman, M.J. (2012) Mobile source and livestock feed contributions to regional ozone formation in central California. Environmental Science and Technology 46(5), 2781–2789, DOI: 10.1021/es203369p.

Japan Meteorological Agency (2019) http://www.data.jma.go.jp/obd/stats/etrn/index.php (in Japanese).

Japanese Ministry of Agriculture, Forestry and Fisheries. (2018) The statistical year book of MAFF. https://www.e-stat.go.jp/stat-search/files/data?sinfid=000031761476&ext=pdf. (in Japanese)

Kannari, A., Tonooka, Y., Baba, T., Murano, K. (2007) Development of multiple-species 1 km × 1 km resolution hourly basis emissions inventory for Japan. Atmospheric Environment 41, 3428–3439, DOI: 10.1016/j.atmosenv.2006.12.015.

Krupa, S.V., Manning, W.J. (1988) Atmospheric ozone: Formation and effects on vegetation. Environmental Pollution 50, 101–137, DOI: 10.1016/0269-7491(88)90187-X.

Lu, M., Lamichhane, O., Liang, F., Chai, M. (2008) Identification of odor causing compounds in a commercial dairy farm. Water Soil Pollution: Focus 8, 359–367, DOI: 10.1007/s11267-007-9150-x.

Mackie, R.I., Stroet, PG., Varel, V.H. (1998) Biochemical identi-
VOCs from a Dairy Cattle Shed

- Nga, L., Richard, C., Flagan, C., Seinfeld, J.H. (2005) Cloud condensation nucleus activation properties of biogenic secondary organic aerosol. Journal of Geophysical Research-Atmosphere 110, D07206, DOI: 10.1029/2004JD005465.
- Ngwabie, N.M., Schade, G.W., Custer, T.G., Linke, S., Hinz, T. (2008) Abundances and flux estimates of volatile organic compounds from a dairy cowshed in Germany. Journal of Environmental Quality 37, 565–573, DOI: 10.2134/jeq2006.0417.
- Osaka, N., Miyazaki, A., Tanaka, N. (2018) Emissions of volatile organic compounds from a swine shed. Asian Journal of Atmospheric Environment 12(2), 178–192, DOI: 10.5572/ajae.2018.12.2.178.
- Parker, D.B., Caraway, E.A., Rhoades, M.B., Cole, N.A., Todd, R.W., Casey, K.D. (2010) Effect of wind tunnel air velocity on VOC flux from standard solutions and CAFO manure/wastewater. Transactions of the ASABE 53(3), 831–845, DOI: 10.13031/2013.30066.
- Parker, D.B., Gilley, J., Woodbury, B., Kim, K., Galvin, G., Bartelt-Hunt, S.L., Li, X., Snow, D.D. (2013) Odorous VOC emission following land application of swine manure slurry. Atmospheric Environment 66, 91–100, DOI: 10.1016/j.atmosenv.2012.01.001.
- Qi, J., Zheng, B., Li, M., Yu, F., Chen, C., Liu, F., Zhou, X., Yuan, J., Zhang, Q., He, K. (2017) A high-resolution air pollutants emission inventory in 2013 for the Beijing-Tianjin-Hebei region, China. Atmospheric Environment 170, 156–168, DOI: 10.1016/j.atmosenv.2017.09.039.
- Qiu, P., Tian, H., Zhu, C., Liu, K., Gao, J., Zhou, J. (2014) An elaborate high resolution emission inventory of primary air pollutants for the Central Plain Urban Agglomeration of China. Atmospheric Environment 86, 93–101, DOI: 10.1016/j.atmosenv.2013.11.062.
- Rabaud, N.E., Ebeler, S.E., Ashbaugh, L.L., Flocchini, R.G. (2003) Characterization and quantification of odorous and non-odorous volatile organic compounds near a commercial dairy in California. Atmospheric Environment 37, 933–940, DOI: 0.1016/S1352-2310(02)00970-6.
- Rumsey, I.C., Aneja, V.P., Lonneman, W.A. (2012) Characterizing of non-methane volatile organic compounds emissions from a swine concentrated animal feeding operation. Atmospheric Environment 47, 348–357, DOI: 10.1016/j.atmosenv.2011.10.055.
- Shatt, S., Mitloehner, F., Jackson, W., Depeters, F., Fadel, J., Robinson, P., Holzinger, R., Goldstein, A. (2007) Volatile organic compound emissions from dairy cows and their waste as measured by proton-transfer-reaction mass spectrometry. Environmental Science and Technology 41, 1310–1316, DOI: 10.1021/es061475e.
- Shibata, M., Mukai, A. (1981) Seasonal changes on heat production, on some physiological responses and lactation in cows. Animal Behaviour and Management 17, 43–50. (in Japanese)
- Shusterman, D. (2013) Critical review- the health significance of environmental odor pollution. Archives of Environmental Health 47, 76–87, DOI: 10.1080/00039896.1992.9935948.
- Sintermann, J., Schallhart, S., Kajos, M., Jocher, M., Bracher, A., Münger, A., Johnson, N., Neftel, A., Ruuskanen, T. (2014) Trimethylamine emissions in animal husbandry, Biogeosciences 11, 5073–5085, DOI: 10.5194/bg-11-5073-2014.
- Sunesson, A.L., Gullberg, J., Blomquist, G. (2001) Airborne chemical compounds in dairy farms. Journal of Environmental Monitoring 3, 210–216, DOI: 10.1039/B008873K.
- Urano, S., Katayama, S. (1985) A method to measure the ventilation rate by using the water vapor balance in a livestock house. Journal of the Society of Agricultural Structures, 15, 16–23 (in Japanese).
- Varshney, C.K., Padhy, P.K. (1998) Emissions of total volatile organic compounds from anthropogenic sources in India. Journal of Industrial Ecology 2(4), 93–105, DOI: 10.1162/jiec.1998.2.4.93.
- World Health Organization (2000) Air quality guidelines, 2nd edition, Chap. 7.2, pp. 1.
- Yeck, R.G., Stewart, R.E. (1959) A ten-year summary of the psychroenergetic laboratory dairy cattle research at the University of Missouri. Transitions of the ASAE 2, 71–77.
- Yuan, B., Coggon, M.M., Koss, A.R., Warneke, C., Eilerman, S., Peischl, J., Aikin, K.C., Ryerson, T.B., De Gouw, J.A. (2017) Emissions of volatile organic compounds (VOCs) from concentrated animal feeding operations (CAFOs): Chemical compositions and separation of sources. Atmospheric Chemistry and Physics 17(8), 4945–4956, DOI: 10.5194/acp-17-4945-2017.