ABSTRACT  To clarify the emissions of volatile organic compounds (VOCs) from hen rearing in Japan, we collected air samples from inside a hen shed for the four seasons in 2019 and analyzed 34 VOCs in the air samples by gas chromatography-mass spectrometry and high performance liquid chromatography. The temperature and humidity inside and outside of the shed were monitored simultaneously during each sampling campaign. The average concentrations of VOCs in the shed ranged from 150 to 427 μg m⁻³, the concentrations being higher in summer and lower in winter. Acetone, dimethyl sulfide, 2-butanone, 2-pentanone, and acetic acid were dominant throughout all the seasons and these five compounds accounted for 70-89% of the total VOCs. The reactivity of each VOC with hydroxyl radical was also calculated and dimethyl sulfide was found to be the most reactive VOC, accounting for 84-94% of the total hydroxyl radical reactivity.

The emission rate (ER) for the total VOCs (μg h⁻¹ kg⁻¹) was 602 in winter, 7,900 in spring, 46,500 in summer and 37,600 in autumn, respectively. Acetone, dimethyl sulfide, 2-butanone, 3-pentanone and acetic acid had higher ERs throughout all the seasons, and these five components accounted for 70-90% of the ERs for the total VOCs. The ERs of the VOCs increased exponentially in accord with temperature increases inside the shed, indicating that the ERs of the VOCs depended on the ambient temperature. The annual VOC emission from one hen and from the hen shed was calculated to be 405 g y⁻¹ and 121 kg y⁻¹, respectively.

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

1. INTRODUCTION

Volatile organic compounds (VOCs) are one of the most prominent classes of chemicals in the atmosphere. Some of the ambient VOCs are known to cause odor pollution near the emission source (Shusterman, 2013; Parker et al., 2010), and have the potential to cause cancer (e.g., Jia et al., 2019) or other health impacts such as headache, respiratory disease and neurological disorders (e.g., Akdeniz et al., 2013). In addition, some VOCs react with highly reactive substances such as hydroxyl radicals (OH) under UV radiation and form secondary organic aerosols (SOAs) (e.g., Camredon et al., 2007) and/or photochemical oxidants (e.g., Dodge, 1989). In Japan, concentrations of PM₂.₅ in the atmosphere have tended to decline and in 2018, results for about 90% of the national air mon-
itoring stations were within the environmental standard for PM$_{2.5}$, whereas the achievement quotient for photochemical oxidants was less than 1% (Japanese Ministry of the Environment, 2019a). Photochemical oxidants inhibit plant growth and adversely affect human health. Short-term exposure to ozone causes airway inflammation, damage to lung cells and increased airway hyperresponsiveness (Ueda et al., 2012). In addition, continuing exposure may lead to structural changes in the lungs and reduced lung function, which is thought to progress to lung disease via chronic changes in lung function (Ueda et al., 2012). Given that VOCs are precursors of photochemical oxidants, emission control of VOCs is considered to be an important issue. Thus, the Japanese Ministry of the Environment undertakes studies on the control of emissions of VOCs with a view to achieving reductions in the exposure of photochemical oxidants (Japanese Ministry of the Environment, 2019b).

The livestock industry is thought to be one of the main emission sources of atmospheric VOCs. Rumsey et al. (2012) determined NMVOCs from a concentrated animal feeding operation (CAFO) in North Carolina in the United States and clarified that the barns had larger emissions than lagoons for all NMVOCs, contributing 68.6–100% of individual compounds estimated for the North Carolina swine CAFO emissions. Also, in the San Joaquin Valley of California in the United States, confined animal facilities were concluded to be major sources of VOCs (SJVAPCD, 2016). Chung et al. (2010) collected VOCs from six emission sources (silage, total mixed rations, lagoons, flushed lanes, open lots and bedding) at six dairy farms in central California in the United States, and found that silage and total mixed rations were the dominant sources of VOCs, with ethanol being the major VOC present. Hales et al. (2015) studied the VOC flux from manure of cattle fed diet in the United States and concluded that feeding strategies focused on decreasing the cattle’s total manure output would be beneficial in curtailing odorous emissions. Trabue et al. (2010) measured VOCs emitted from poultry production in the northwestern United States and clarified that acetic acid, 2,3-butanedione, methanol, acetone, and ethanol were the top five emitters, accounting for 70% of the total VOCs. Outside the United States, VOC emissions from livestock industries have also been reported in Europe (Sintermann et al., 2014; Hobbs et al., 2004), China (Qi et al., 2017; Qiu et al., 2014; Fu et al., 2013) and India (Varshney and Padhy, 1998). In the case of Japan, most of the previous studies related to emissions of VOCs from livestock have mainly been concerned with the odor (e.g., Yasuhara and Fuwa, 1983; Yamamoto et al., 2008) and decreasing odor (e.g., Kuroda, 2006), and there are few reports on the amount and composition of VOCs emitted from livestock. Hence, the Japanese Ministry of the Environment has been estimating VOC emissions from livestock industries in Japan based on data from other countries and where great differences exist in the scale of breeding, methods of feeding, and types of feed. This is despite the fact that breeding conditions such as the scale of breeding, breeding method, and nature of the feed are considered to affect the amount and composition of VOCs emitted from livestock. Therefore, it is highly desirable to obtain authentic data for Japan in order to evaluate accurately the emissions of VOCs from livestock in the country.

Previously, we reported the concentrations, compositions and seasonal variations of VOCs emitted from swine (Osaka et al., 2018) and dairy cattle (Tanaka et al., 2019) in Japan, and showed that the emission rate (ER) of VOCs from a swine shed and a dairy cattle shed was about 1–2×10$^3$ μg (h kg-swine)$^{-1}$ and 0.5–2×10$^3$ μg (h kg-dairy cattle)$^{-1}$, respectively. Based on these data, the total annual emissions of VOCs from one swine shed and one dairy cattle shed were estimated to be both on the order of 10$^3$ g year$^{-1}$. In Japan, about 9.2 million head of swine and about 1.3 million head of dairy cattle are reared annually. Hence, it is considered that the nation’s annual emissions of VOCs due to the rearing of swine and dairy cattle is not negligible.

Hens are another common livestock and 180 million hens are bred domestically in Japan annually. Nevertheless, there are few reports on the amount and composition of VOCs emitted from laying hens in Japan. In this study, the emissions of VOCs from hens in Japan were studied with the aim of clarifying the concentrations, compositions, seasonal variations and ERs of the VOCs.

2. EXPERIMENTAL

2.1 Target Compounds

Compounds targeted in this study were selected accor-
According to our previous studies (Tanaka et al., 2019; Osaka et al., 2018). The target compounds were as follows: eight volatile fatty acids (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-methylphenol, and 4-ethylphenol), two sulfur compounds (dimethyl sulfide and dimethyl disulfide), two indoles (indole and skatole), four ketones (acetone, 2-butanone, 2-pentanone, and 3-pentanone), and 11 aldehydes (formaldehyde, acetaldehyde, acrolein, propionaldehyde, crotonaldehyde, methacrolein, n-butyraldehyde, benzaldehyde, valeraldehyde, m-tolualdehyde, and hexaldehyde). All reagents and solvents for sample treatment were prepared from analytical grade chemicals.

### 2.2 Sampling Site

Air samples were collected from a hen shed at Asahi 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 presented in Fig. 1. The volume of the shed was 343.4 m³ (8.1 m width × 15.7 m depth × 2.7 m height). There were two cages for breeding hens across the central passage in the shed, both of which are divided into upper and lower tiers. The windows in the shed were opened or closed depending on the season. The windows were mainly kept open in summer whereas most of them were closed in winter. Also, the windows were closed when there was adverse weather (e.g., strong winds and/or heavy rain). The doors were always closed. A ventilation fan was installed in the shed but it did not operate during the sampling campaigns. Therefore, ventilation during the sampling campaigns was only from natural ventilation via the windows. The waste from the hen shed was removed daily at 11:00 or 14:00.

Boris Brown, one of the major breeds of hen in Japan, was raised in the cages. The number and total weight of the hens in this study are shown in Table 1. The hens were fed daily about 100 g day⁻¹ hen⁻¹ of formula feed at 8:00. They were able to drink water freely at any time from a water gutter in front of the cage.

### 2.3 Sampling Procedure

Air sampling in the hen shed was conducted in winter (January 2018), spring (April 2018), summer (July and August 2018) and fall (October 2018) for 3 or 4 days during each season (Table 1). Sample collection was performed according to previous studies (Osaka et al., 2018; Tanaka et al., 2019). The VFAs, phenols, sulfur compounds, indoles, some ketones (2-butanone, 2-pentanone, and 3-pentanone) and some alcohols (2-butanol, 1-propanol, and 1-butanol) were collected.
using stainless steel or glass sorbent tubes filled with Tenax TA® sorbent (3.5 in × 0.25 in outer diameter, 60/80 mesh, COMSCO). Prior to the 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 for 1 h. The air samples were collected at the center of the shed, as shown in Fig. 1. Based on our previous study (Osaka et al., 2018), we regard that the VOC concentration of the sample collected at the center point in the hen shed represent the average concentration of the shed. In the previous study, we measured the spatial distribution of VOCs at 11 points in a swine shed. The swine shed had a similar structure to the hen shed and adopted the same ventilation method (natural ventilation) as the hen shed. The VOC concentrations at the central point of the swine shed were about 20% lower than the average in the shed at a height of 1.2 m, and about 20% higher than the average in the shed at a height of 1.9 m. The VOC concentrations at 11 points were in the ranges of −30 to +40% of the average concentration. From these results, we concluded that the VOC concentrations at the center point of the swine shed were approximately the same as the average VOC concentrations in the shed (Osaka et al., 2018). The air in the shed was continuously collected every hour in the sorbent tubes using a tube sampler (MTS-32, Markes International) at a flow rate of 0.1 L min⁻¹ in the spring, summer and autumn sampling campaigns. For the winter sampling period, the samples were collected at 0:00, 8:00, 12:00 and 16:00 for 30 min at a flow rate of 0.1 L min⁻¹. After the sampling, the tubes were closed and placed in a cool, dark place. Field blanks were also processed along with the sorbent tube samples.

The 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 the 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 tube samples. The number of samples collected in each sampling campaign are shown in Table 1.

### Table 1. Outline of sample collection.

| Sampling campaign          | Number of hens¹ | Total weight of hens [kg]² | Number of samples |
|----------------------------|-----------------|---------------------------|-------------------|
| Winter (Jan. 9–12, 2018)   | 300             | 600                       | 12, 6, 12         |
| Spring (Apr. 3–6, 2018)    | 300             | 600                       | 72, 6, 12         |
| Summer (Jul. 31–Aug. 3, 2018) | 300          | 600                       | 72, 6, 12         |
| Autumn (Oct. 16–19, 2018)  | 300             | 600                       | 72, 6, 12         |

¹)Rearing numbers fluctuated slightly.  
²)Calculated as 2 kg weight per hen.

(DNPH) cartridges containing DNPH derivatizing agent (InertSep mini AERO DNPH-LG, GL Sciences). The cartridges were connected to an ozone scrubber cartridge (InertSep mini AERO Ozone Scrubber, GL Sciences) upstream. The 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 the 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.

2.4 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 those for the air sampling, i.e., at the center point of the shed. Regarding the temperature and humidity inside the shed, we performed preliminary measurements at multiple points inside the shed and confirmed that the temperature and humidity at the center of the shed were generally average. Thus we can assume that the air in the shed is sufficiently mixed. However, the air in the shed could not have been mixed completely, as evidenced by the results of Osaka et al. In that sense, the VOC concentration, the temperature and humidity
at the sampling point in this study may contain an error, but on the other hand, it does not deviate significantly from the average. The hydrothermograph for outside measurement was installed at the entrance of the shed (Fig. 1). The external hydrothermograph was covered with tin foil as 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 0.69 ± 0.51% RH, respectively. Based on these data, the air temperature and RH were judged to have been calibrated and reliable.

2.5 Analytical Procedures

Analytical procedures were conducted according to a previous study (Tanaka et al., 2019). The VFAs, phenols and indoles were determined by gas chromatography-mass spectrometry (GC/MS; GCMS-QP2020, Shimadzu Corporation) equipped with an InertCap WAX capillary column (30 m × 0.25 mm × 0.25 μm, GL Sciences) and the ion source were 200°C and 210°C, respectively. 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°C and 210°C, respectively. The samples were analyzed using the selected ion monitoring (SIM) mode. For signal quantitation, 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 to 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 8°C min⁻¹) → 230°C (hold 5 min). The temperatures of the injection port and the ion source were 200°C 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 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 strong cation 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 was 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 [Deltabond 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 water (10% by volume) were used as 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.

The ERs of VOCs from the shed were estimated according to previous studies (Tanaka et al., 2019; Osaka et al., 2018). The ERs of VOCs from the shed were estimated according to previous studies (Tanaka et al., 2019; Osaka et al., 2018). The ERs of VOCs from the shed were estimated according to previous studies (Tanaka et al., 2019; Osaka et al., 2018). The ERs of VOCs from the shed were estimated according to previous studies (Tanaka et al., 2019; Osaka et al., 2018).
ed 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:

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

(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. Assuming 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):

\[
V_c \frac{d(x_i/v_i)}{dt} = V_{in} (x_i/v_0) - V_{out} (x_i/v_i) + W_g 
\]  

(3-a)

\[
V_c \frac{d(1/v_i)}{dt} = V_{in}/v_0 - V_{out}/v_i 
\]  

(3-b)

where \( V_c \) (m\(^3\)) is the volume of the shed, \( V_{in} \) (m\(^3\) s\(^{-1}\)) is the volume of intake air of the shed, \( V_{out} \) (m\(^3\) 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, \( v_i \) (m\(^3\) kg\(^{-1}\)) is the specific volume in the shed, \( v_0 \) (m\(^3\) 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 psychromet-
ric chart. The absolute humidity inside the shed was always larger than that outside the shed throughout the sampling campaigns in this study. Moisture emission, that is, the amount of moisture removed from the room, was referred to the regression equation reported by Longhouse et al. (1968). Longhouse et al. created the estimation method for the amount of moisture generation from feces and respiration of broiler in the shed based on the monitoring data. In this study the data regarding broiler reported by Longhouse et al. were used because there were no suitable data for estimating the moisture generation from hens. The moisture generation from the hen shed was estimated using this method. \( V_{out} \) may be determined from Eqs. (3-a) and (3-b) as follows:

\[
V_{out} = \frac{V_e v_i}{(x_i - x_o) \Delta t} \left( x_0 - x_i^* \right) + \frac{W g v_i}{x_i - x_0}
\]

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

\[
V_{out} = \frac{W g v_i}{x_i - x_0}
\]

The ventilation rate of the shed was estimated according to Eq. (5) on the assumption that the air exhaust was equal to the air intake. As described in a previous study (Tanaka et al., 2019), in cases where the differences in 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 were estimated according to Eq. (6):

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

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

### 3. RESULTS AND DISCUSSION

#### 3.1 Breakthrough of Target VOCs on Sample Collection

To confirm that the target compounds were collected in the adsorbent without breakthrough, two adsorption tubes/cartridges were connected in series for each sampling method, and the air in the shed was collected for 30 min (8 h for the DNPH cartridges). The results of the analyses are shown in Fig. 2. More than 80% of the total amount of VOC was collected in the first tube/cartridge for all compounds. The retention volume of acetic acid for Tenax TA was 0.1 L (200 mg-adsorbent at 20°C; Markes, 2017), which is remarkably low compared with that of most of the other VOCs; however, most of acetic acid was detected in the first tube. Therefore, based on the above results, it was considered that the sampling method used in this study provided mostly efficient collection of the target VOCs.

#### 3.2 Concentrations and Compositions of VOCs

The average concentrations and chemical compositions of the VOCs in the hen shed are shown in Fig. 3, and the concentrations of each VOC are shown in Table 2. The average concentrations of VOC (\( \mu g \text{ m}^{-3} \)) were 150 in winter, 324 in spring, 427 in summer and 248 in autumn, indicating that the VOC concentrations in the shed increased from winter to summer. The concentrations of ketones, sulfur compounds and VFAs were relatively high in every season, the sum of these three chemical groups accounting for 81-95% of the total VOCs in the shed. Sulfur compounds were the dominant components in every season except winter. Acetone, dimethyl sulfide, 2-butanone, 2-pentanone and acetic acid were detected in all seasons, and these five compounds accounted for 70-89% of the total VOCs. Previous studies have reported that acetone and acetic acid are also predominant VOCs emitted from swine sheds (Osaka et al., 2018) and dairy cattle sheds (Tanaka et al., 2019), thus confirming that these compounds are the main components emitted from livestock. In contrast, dimethyl sulfide was mainly detected only in the hen shed, suggesting that it was a characteristic VOC emitted from hens. Hobbs et al. (2004) measured VOCs emitted from livestock in the United Kingdom and reported that sulfur compounds were the main components emitted from the manure of laying hens. Their findings support the results obtained in the present study. Sulfur compounds such as dimethyl sulfide are formed by bacterial degradation of the sulfur-containing amino acids such as methionine (Saksrithai and King, 2018) and are required for growth of poultry (Almquist, 1952). The formula feed used in this study contained...
## Table 2. Concentrations of VOCs in the hen shed for each season (in μg m$^{-3}$).

|               | Winter          | Spring         | Summer         | Autumn         |
|---------------|-----------------|----------------|----------------|----------------|
|               | Average | Max  | Min  | SD  | Average | Max  | Min  | SD  | Average | Max  | Min  | SD  |
| VFAs          |          |      |      |     |          |      |      |     |          |      |      |     |
| Acetic Acid   | 13.3     | 69.6 | 2.1  | 19.1 | 14.0     | 37.1 | 0.4  | 7.8 | 16.1     | 43.3 | 0.2  | 10.3 |
| Propanoic Acid| 0.01     | 0.07 | ND   | 0.02 | 4.19     | 10.0 | 0.83 | 2.02 | 5.16     | 11.9 | 1.00 | 2.70 |
| Isobutyric Acid| 0.16    | 0.29 | 0.05 | 0.07 | 1.22     | 5.96 | 0.47 | 0.72 | 1.26     | 2.78 | ND   | 0.43 |
| Butyric Acid  | 0.22     | 2.53 | ND   | 0.73 | 1.89     | 4.42 | 0.63 | 0.74 | 2.21     | 5.78 | 0.57 | 1.10 |
| Isovaleric Acid| 0.50    | 2.14 | ND   | 0.63 | 0.80     | 1.47 | 0.50 | 0.19 | 0.89     | 1.47 | 0.48 | 0.20 |
| Valeric Acid  | 0.32     | 2.62 | ND   | 0.73 | 1.20     | 1.97 | 0.67 | 0.32 | 1.40     | 4.45 | ND   | 0.69 |
| Hexanoic Acid | 1.23     | 3.85 | 0.08 | 1.02 | 2.86     | 5.12 | 0.83 | 1.21 | 2.84     | 15.9 | 0.72 | 2.16 |
| Heptanoic Acid| 0.65     | 5.27 | ND   | 1.47 | 1.41     | 2.28 | 0.76 | 0.45 | 1.83     | 4.74 | ND   | 0.89 |
| Alcohols      |          |      |      |     |          |      |      |     |          |      |      |     |
| Methanol      | 0.93     | 1.27 | 0.58 | 0.23 | 0.26     | 0.41 | 0.11 | 0.11 | 1.28     | 3.61 | 0.42 | 1.00 |
| Ethanol       | 0.04     | 0.10 | ND   | 0.03 | 0.06     | 0.18 | 0.01 | 0.05 | 0.06     | 0.15 | 0.03 | 0.03 |
| 2-Butanol     | 6.03     | 21.9 | 0.95 | 5.90 | 7.90     | 18.7 | 0.37 | 5.36 | 6.30     | 25.2 | ND   | 6.22 |
| 1-Butanol     | 7.02     | 20.3 | 1.98 | 5.05 | 9.09     | 35.3 | 0.35 | 6.78 | 1.70     | 9.88 | ND   | 1.44 |
| Aldehydes     |          |      |      |     |          |      |      |     |          |      |      |     |
| Formaldehyde  | 2.28     | 3.08 | 1.25 | 0.69 | 3.27     | 6.03 | 1.94 | 1.64 | 4.05     | 8.10 | 0.75 | 2.34 |
| Acetaldehyde  | 5.42     | 7.48 | 3.45 | 1.46 | 6.82     | 12.5 | 4.55 | 2.88 | 2.19     | 4.95 | 1.09 | 1.20 |
| Acrolein      | 0.11     | 0.64 | ND   | 0.25 | 0.25     | 1.50 | ND   | 0.61 | ND       | ND   | ND   | ND   |
| Propionaldehyde| 0.11   | 0.63 | ND   | 0.25 | 2.40     | 6.67 | ND   | 2.27 | ND       | ND   | ND   | ND   |
| Crotonaldehyde| 0.38     | 1.32 | ND   | 0.57 | ND       | ND   | ND   | ND   | ND       | ND   | ND   | ND   |
| Methylaldehyde| ND       | ND   | ND   | ND   | ND       | ND   | ND   | ND   | ND       | ND   | ND   | ND   |
| Benzaldehyde  | ND       | ND   | ND   | ND   | ND       | ND   | ND   | ND   | ND       | ND   | ND   | ND   |
| Salicylaldehyde| ND     | ND   | ND   | ND   | ND       | ND   | ND   | ND   | ND       | ND   | ND   | ND   |
| M-Tolualdehyde| ND       | ND   | ND   | ND   | ND       | ND   | ND   | ND   | ND       | ND   | ND   | ND   |
| Hexaldehyde   | 2.20     | 1.20 | ND   | 0.47 | 1.67     | 2.22 | 1.35 | 0.30 | ND       | ND   | ND   | ND   |

1) Standard deviation. 2) Not detected.
methionine and cysteine, which are both sulfur-containing amino acids. In contrast, Trabue et al. (2010) reported that dimethyl sulfide was not present in the top five VOCs detected in the poultry production facilities in the northwestern United States. This may be due to differences in the feed.

The tendency that the concentrations of VOCs in the shed were higher in summer and lower in winter was thought to be due to how VOCs were more readily volatilized owing to the higher temperatures in the shed in the summer months. In addition, it was considered that higher temperatures in the shed prompted an increase in the hens’ respiration and transpiration and VOCs contained in such emissions would also be elevated.

In addition, hydroxyl radical reactivity (OHR) is determined as the product of the VOC concentration (C) and the respective reaction rate constants of the VOC with the oxidant (kO/H; Yuan et al., 2017; Atkinson et al., 2006) (OHR = Ci × kOH,i). The results for the OHR are shown in Fig. 4. Indoles were excluded from the calculation because reaction rate constant data were not available for these compounds.

Sulfur compounds were the largest contributors after the spring season whereas ketones and alcohols were dominant in winter. Dimethyl sulfide was a huge contributor to the OHR in the spring, summer and autumn seasons, accounting for 84–94% of the total OHR. Yuan et al. (2017) measured the atmospheric VOC concentrations downwind of the CAFOs located near Greeley in northwestern Colorado in the United States, and demonstrated that alcohols were the largest contributors (40–75%) to OHR at the sites, although the fractions from carbonyls, phenolic and sulfur-containing species were also significant. The target sites selected by Yuan et al. were dairy cattle, beef cattle, sheep and chicken CAFO facilities, so VOCs from various livestock were emitted. The differences in contributions to the OHR between the study of Yuan et al. and the present study may be due to the above reason. In Fig. 4, OHR of each component were calculated from the VOC concentrations in the hen shed. OHR should be calculated from the VOC concentration in the atmosphere originally, but in this study it was calculated from the VOC concentrations in the hen shed in order
to clarify the contribution ratio of each VOC component from the hen shed to OHR.

3.3 ERs of VOCs from the Shed

The average ERs of VOCs from the hen shed in every season are shown in Fig. 5. The average ERs of VOCs (in μg h⁻¹ kg⁻¹) from the shed were calculated as 602 in the winter, 7,900 in the spring, 46,500 in the summer and 37,600 in the autumn. Similar to the concentrations of VOCs in the shed (Fig. 3), the ERs of VOCs tended to be low in winter and high in summer. In particular, the ERs in winter were significantly lower than in other seasons. The reason for this is considered to be the exceedingly small ventilation rate in winter because of the very small number of window openings in the shed in winter compared with the other seasons.

The relationship between the average temperature in the shed and the average ERs of total VOCs is shown in Fig. 6. The average ERs of VOCs tended to increase exponentially according to the increase in average temperature in the shed. A similar tendency was also observed for the dairy cattle shed (Tanaka et al., 2019).

Also, the relationship between the average temperature in the shed and the average ERs for each chemical class is shown in Fig. 7. In addition to the ERs of total VOCs, the ERs for each chemical class rose drastically in accordance with the increased average temperature in the shed. This indicates that volatilization of the VOCs was accelerated as the temperature in the shed rose. Furthermore, it was considered that the temperature increase in the shed stimulated the hen’s activity, resulting in an increase in the hens’ respiration and transpiration, which included emissions of VOCs. From the above results, it was concluded that the ERs of VOCs from the hen shed may be estimated from the shed temperature as was the case for the dairy cattle shed (Tanaka et al., 2019).

In terms of chemical composition (Fig. 5), the ERs of ketones, alcohols and VFAs were high in winter whereas the ERs of sulfur compounds increased after the spring. As described above, sulfur compounds were generated by anaerobic decomposition of sulfur-containing amino acids (Saksrithai and King, 2018). Given that anaerobic decomposition is considered to accelerate with increase in temperature, it is reasonable that the ERs of sulfur compounds were higher in summer than in winter. Moreover, significant positive correlations between litter moisture and sulfur compounds, phenols and indoles were observed (Sharma et al., 2016). The average RH in the shed was 62% in winter, 75% in spring, 80% in summer and 75% in autumn. These humidity differences may have also contributed to the slow emis-
sion rate of sulfur compounds in winter.

The ERs of each VOC for each season are presented in Table 3. Acetone, dimethyl sulfide, 2-butanone, 3-pentanone and acetic acid had relatively high ER values throughout the four seasons, and these five components accounted for 70–90% of total VOCs.

Based on the above results, the annual average ER of VOCs from the hen shed was calculated to be $23,100 \mu g \cdot h^{-1} \cdot kg^{-1}$. According to our previous studies (Tanaka et al., 2019; Osaka et al., 2018), the ERs of VOCs from the swine and dairy cattle sheds were estimated as $1–2 \times 10^3 \mu g \cdot h^{-1} \cdot kg^{-1}$. Thus, it is suggested that the ERs of VOCs from hens are much higher than that of swine and dairy cattle. One of the reasons for the large ERs of VOCs from hen in this study was the large amount of moisture emission ($W_g$: see Eqs. 3-5) in the hen shed. In our previous study (Osaka et al., 2018), the amount of moisture emission in the swine was estimated to be $0.08–0.13 \ kg \cdot h^{-1}$, whereas the amount of moisture emission in the hen shed was $2.5 \ kg \cdot h^{-1}$, which was an order of magnitude larger than that of the swine. Since the ERs of VOCs are proportional to the amount of moisture emis-

![Fig. 7. (a–g) Relationship between the temperature in the shed and the ERs of each class of VOC. The error bars show the standard deviation.](image-url)
Table 3. Emission rates of VOCs from the hen shed (in μg h$^{-1}$ kg$^{-1}$).

|               | Winter                  | Spring                  | Summer                  | Autumn                  |
|---------------|-------------------------|-------------------------|-------------------------|-------------------------|
|               | Average Max Min SD 1)  | Average Max Min SD    | Average Max Min SD    | Average Max Min SD    |
| VFAs          |                         |                         |                         |                         |
| Acetic Acid   | 54 445 5 35            | 398 2480 35 178        | 1920 11800 13 885      | 1020 2520 2 269        |
| Propanoic Acid| 0 1 2) 0              | 123 804 17 57          | 652 4090 58 306        | 298 822 98 70          |
| Isobutyric Acid| 1 5 0 0              | 35 239 7 16           | 156 806 * 62           | 108 385 * 27           |
| Butyric Acid  | 2 62 * 3            | 56 331 8 24           | 265 1020 25 100        | 169 489 53 42          |
| Isovaleric Acid| 3 52 * 2            | 23 110 4 9            | 106 395 16 36          | 91 315 32 21          |
| Valeric Acid  | 2 64 * 3            | 35 186 6 14           | 166 716 * 64           | 139 440 48 35          |
| Hexanoic Acid | 6 94 0 4           | 83 543 8 39           | 331 1580 33 135        | 191 524 67 43          |
| Heptanoic Acid| 4 129 * 6           | 42 244 7 19           | 225 1240 * 98          | 141 475 * 34          |
| Alcohols      |                         |                         |                         |                         |
| Methanol      | 4 21 1 1             | 8 33 1 3             | 143 1170 14 81        | 88 389 25 27          |
| Ethanol       | 0 1 * 0             | 2 10 0 1            | 7 70 1 4             | 11 101 2 8           |
| 2-Butanol     | 28 196 4 12         | 229 780 9 76         | 731 4930 * 390        | 903 3340 123 291      |
| 1-Propanol    | 32 182 6 11         | 267 1520 7 116       | 210 1620 * 111        | 232 1130 44 99        |
| 1-Butanol     | 15 58 4 4           | 333 2920 13 220      | 272 2170 * 173        | 418 1230 74 113       |
| Phenols       |                         |                         |                         |                         |
| Phenol        | 7 28 2 2             | 82 388 10 32         | 369 1560 43 137       | 289 877 21 75         |
| 4-Methyl Phenol| 2 13 1 1            | 14 72 * 6            | 26 141 * 15           | 5 44 * 4             |
| 4-Ethyl Phenol| 1 6 0 0             | 16 66 2 5             | 75 277 * 29           | 72 260 26 18          |
| Sulfurcompounds|                     |                         |                         |                         |
| Dimethyl Sulfide| 20 161 1 8         | 1780 24500 1 1830     | 18800 288000 12 17700 | 18100 88700 50 8370   |
| Dimethyl Disulfide| 2 24 0 1         | 40 234 3 17            | 470 5570 18 426       | 277 1170 41 114       |
| Indoles       |                         |                         |                         |                         |
| Indole        | 0 1 * 0             | 7 32 * 3            | 37 177 6 15           | 40 150 13 10          |
| Skatole       | 0 0 * 0             | 1 11 * 1            | 17 119 * 12           | 25 154 * 13           |
| Ketones       |                         |                         |                         |                         |
| Acetone       | 261 3340 76 147     | 2110 15700 258 1080   | 14800 100000 907 7630 | 11300 78100 1133 5610 |
| 2-Butanone    | 27 96 4 5            | 967 3150 49 302       | 3590 22800 110 1950   | 327 1290 * 2140       |
| 3-Pentanone   | 33 229 6 13         | 90 509 8 42           | 115 4690 * 257        | 278 2790 * 249        |
| 2-Pentanone   | 59 611 2 35         | 747 3690 27 324       | 2230 37000 * 2140     | 2700 17400 14 1430    |
| Aldehydes     |                         |                         |                         |                         |
| Formaldehyde  | 10 73 4 3            | 77 546 14 36         | 478 3050 31 225       | 215 1090 6 91         |
| Acetaldehyde  | 25 107 7 5           | 224 954 23 93         | 271 1870 29 7630      | 190 655 40 47         |
| Acrolein      | 1 6 * 0             | 17 157 * 14           | * * * * * * * * * * * |
| Propionic acid| 1 3 * 0             | 50 812 * 52          | * * * * * * * * * * * |
| Crotonaldehyde| 2 7 * 1             | * * * * * * * * * * * |
| Methacrolein  | * * * * * * * * * * * |
| n-Butyraldehyde| * * * * * * * * * * * |
| Benzaldehyde  | * * * * * * * * * * * |
| Valeraldehyde  | * * * * * * * * * * * |
| m-Tolualdehyde| * * * * * * * * * * * |
| Hexaldehyde   | 1 6 * 1             | 45 270 8 19           | * * * * * * * * * * * |

1) Standard division. 2) Not calculated.
sion, the fact that the ERs of VOCs from hen was an order of magnitude higher than that of swine was considered to be due to the difference in the amount of moisture emission. One possible cause of high moisture emission in the hen shed is that broiler have higher physiological activity than other livestock, and their oxygen consumption per unit weight/time is about 3.5 times that of swine and cattle (Matsuzaka Cobb Farm, 2009). It is thought that this contributes to the amount of moisture emission because some of the oxygen taken up by the body eventually becomes water. This may be one reason why the amount of moisture emission in the hen shed was high. However, the broiler and the hen targeted in this study differ in species. Therefore the details are not clear. On the other hand, Hobbs et al. (2004) estimated the ERs of NMVOC (g m⁻³ day⁻¹) from slurry/manure of swine, cattle and hen, and found that the ERs of NMVOC from manure of hen were 1–2 orders of magnitude larger than that of swine and cattle, and it was revealed that most of them were occupied by sulfur compounds. As described above, the sulfur compound is considered to be produced by the anaerobic decomposition of sulfur-containing amino acids such as methionine contained in the feed. Therefore, it is considered that one of the reasons why the ERs of VOCs in the hen shed is an order of magnitude higher than that in the swine and the dairy cattle shed is due to feed. On the other hand, the high ER of acetone was also observed. Acetone is produced by fat metabolism (European Environmental Agency, 2019). The temperature inside the shed was high in summer, which may accelerate fat metabolism and produce a large amount of acetone. However, details are unknown.

### 3.4 Annual Emissions of VOCs from the Shed

The annual VOC emissions from one hen and from the hen shed were calculated using the ERs of VOCs shown in Fig. 5 and Table 3. The results are given in Table 4. The annual emission of total VOCs from one hen was estimated to be 405 g y⁻¹ and around half this amount was emitted in summer. Moreover, the annual total amount of VOCs emitted from the hen shed, a primary objective of this study, was calculated as 121 kg y⁻¹. Ketones and sulfur compounds were the two major chemical groups, accounting for 85% of the total VOC emissions. Our previous studies (Tanaka et al., 2019; Osaka et al., 2018) estimated that the total VOC emission from one swine and from one dairy cow was 1.4–4.7 kg and 5.5 kg, respectively. The amount of VOC emission from one hen was clearly lower than the values for one swine or dairy cow, given that the body weight of the hen was much less than that of the swine or dairy cow.

Using the above results, the annual emission inventory of VOCs originating from the rearing of hens in Japan was roughly estimated. The number of reared hens in Japan in 2018 was 175,711,000 hens (Japanese Ministry of Agriculture, Forestry and Fisheries, 2019). The ERs of VOCs from the hen shed obtained in this study were assumed to be representative of the rough average value for Japan. Also, on the assumption that the average body weight of one hen in Japan is 2 kg, the annual emissions

### Table 4. Annual emissions of VOCs from one hen and from the hen shed.

| Emission per one hen (g hen⁻¹) | Total | VFAs | Alcohols | Phenols | Sulfur compounds | Indoles | Ketones | Aldehydes |
|-------------------------------|-------|------|----------|---------|------------------|---------|---------|-----------|
| Winter                        | 2.64  | 0.310| 0.350    | 0.042   | 0.099            | 0.00034 | 1.67    | 0.170     |
| Spring                        | 34.6  | 3.49 | 3.67     | 0.488   | 7.98             | 0.038   | 17.2    | 1.81      |
| Summer                        | 203   | 16.7 | 5.97     | 2.06    | 84.2             | 0.235   | 90.5    | 3.28      |
| Autumn                        | 165   | 9.46 | 7.24     | 1.60    | 80.4             | 0.284   | 63.9    | 1.77      |
| Annual                        | 405   | 30.0 | 17.2     | 4.19    | 173              | 0.558   | 173     | 7.03      |

| Emission per hen shed (kg shed⁻¹) | Total | VFAs | Alcohols | Phenols | Sulfur compounds | Indoles | Ketones | Aldehydes |
|-----------------------------------|-------|------|----------|---------|------------------|---------|---------|-----------|
| Winter                            | 0.791 | 0.093| 0.105    | 0.012   | 0.030            | 0.00010 | 0.500   | 0.051     |
| Spring                            | 10.4  | 1.05 | 1.10     | 0.147   | 2.40             | 0.011   | 5.15    | 0.542     |
| Summer                            | 60.9  | 5.02 | 1.79     | 0.618   | 25.3             | 0.070   | 27.2    | 0.983     |
| Autumn                            | 49.4  | 2.84 | 2.17     | 0.481   | 24.1             | 0.085   | 19.2    | 0.532     |
| Annual                            | 121   | 9.00 | 5.17     | 1.26    | 51.8             | 0.167   | 52.0    | 2.11      |
of VOCs from hens reared in Japan is estimated to be 71 Gg y⁻¹. Tanaka et al. (2019) previously estimated the annual emissions of VOCs derived from domestic dairy cattle to be 7.3 Gg y⁻¹, based on the same assumptions mentioned above. Thus, the emission of VOCs from rearing hens was considered to be comparable to that of dairy cattle. According to the annual emissions inventory of Japan, the anthropogenic VOC emissions (all sources) were estimated to 654 Gg in 2017 (Japanese Ministry of the Environment, 2019c), so the VOC emissions from hen rearing was calculated to 10.9% of the total VOC emissions in Japan. Therefore, it is suggested that the amount of VOC emitted from the livestock industries in Japan is quite considerable.

Given that the annual emission inventory for hens was estimated based on only one set of data obtained in this study, the result may be subject to significant error. However, as mentioned above, the ERs of VOCs from the hen shed did correlate with the temperature of the shed inside. As noted in the previous study (Tanaka et al., 2019) on the annual emission inventory of VOCs from dairy cattle in Japan, the annual average temperature in 2018 at Yokoshiba-hikari national weather station, located 16 km WSW from the sampling point, was 16.3°C (Japan Meteorological Agency, 2019), which was nearly equal to the annual average temperature of Japan as a whole (16.0°C). Furthermore, the rearing of hens is evenly spread throughout the whole of Japan, so the hen shed used in this study can be considered as reasonably representative of the average hen shed in Japan from the viewpoint of temperature, and it may be assumed that the amount of VOCs emitted from the hen shed would be roughly the average amount for Japan. Of course, the types of hen and breeding methods vary widely, and these differences may also affect the VOC emissions and chemical composition from the hen. Therefore, to more accurately estimate the emission of VOCs from the rearing of hens in Japan, it would be sensible to conduct further studies on the emissions of VOCs from various breeds of hen including the associated breeding methods.

4. CONCLUSION

In this study, we measured 34 VOCs in a hen shed at Asahi Agricultural High School, Chiba Prefecture (Japan) throughout the four seasons. The average concentrations of VOCs in the shed ranged from 150 μg m⁻³ (winter) to 427 μg m⁻³ (summer). Ketones, sulfur compounds and VFAs were the dominant components in every season, and the sum of these three chemical groups accounted for 81–95% of the total VOCs in the shed. Acetone, dimethyl sulfide, 2-butane, 2-pentane and acetic acid were detected as dominant species in all the seasons, and these five compound types accounted for 70–89% of the total VOCs. In addition, the OHR was calculated and dimethyl sulfide was the predominant component, accounting for 84–94% of the total OHR in the shed. The average ERs of VOCs (in μg h⁻¹ kg⁻¹) from the shed were estimated to range from 602 to 46,500, and the values showed positive correlation with the temperature inside the shed. Acetone, dimethyl sulfide, 2-butane, 3-pentane and acetic acid had relatively high ERs throughout the four seasons, and these five components accounted for 70–90% of the total VOCs. Finally, the total annual emissions of VOCs from one hen was estimated to be 405 g y⁻¹ and that from the hen shed was 121 kg y⁻¹.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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Estimation of water production in the shed based on Longhouse et al. (1968).

The production of water in the shed is roughly divided into fecal (A) and respiration (C). In this study, we used the values presented by Longhouse et al. to estimate the rate of water production from fecal and respiration per hen shed. First, the emission rate from fecal was calculated by the following formula.

$$17.59 \text{ (lb hr}^{-1})/4587 \text{ (hen)/0.115 (lb) \times 300 (hen)}$$
$$\times 0.38 \text{ (lb)/2.205 (lb kg}^{-1}) = 1.72 \text{ (kg hr}^{-1})$$

In addition, the emission rate from respiration was calculated by the following formula.

$$1.5 \text{ (Btu lb}^{-1}) \times 300 \text{ (hen)} \times 4.4 \text{ (lb hen}^{-1})/1100$$
$$/2.205 \text{ (lb kg}^{-1}) = 0.82 \text{ (kg hr}^{-1})$$

Therefore, the total amount of water production from fecal and respiration is 2.1 kg hr\(^{-1}\).

$$1.72 \text{ (kg hr}^{-1}) + 0.82 \text{ (kg hr}^{-1}) = 2.54 \text{ (kg hr}^{-1})$$
$$= 2.5 \text{ kg hr}^{-1}$$

Note that litter water (B) and water from combustion (D) were not considered in this study because it was considered small (B) or zero (D).

Table. S1. Average moisture emission and ventilation rate at the hen shed in each season

|          | Moisture emission (kg h\(^{-1}\)) | Ventilation rate (m\(^3\)h\(^{-1}\)) |
|----------|-----------------------------------|--------------------------------------|
| Winter   | 2.5                               | 1,100                                |
| Spring   | 2.5                               | 7,900                                |
| Summer   | 2.5                               | 31,000                               |
| Autumn   | 2.5                               | 38,000                               |