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Research Article

Emissions of Volatile Organic Compounds from a Hen Shed in Japan

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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 $PM_{2.5}$ 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 $1–2 \times 10^3$ μg (h kg-swine)$^{-1}$ and $0.5–2 \times 10^3$ 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-

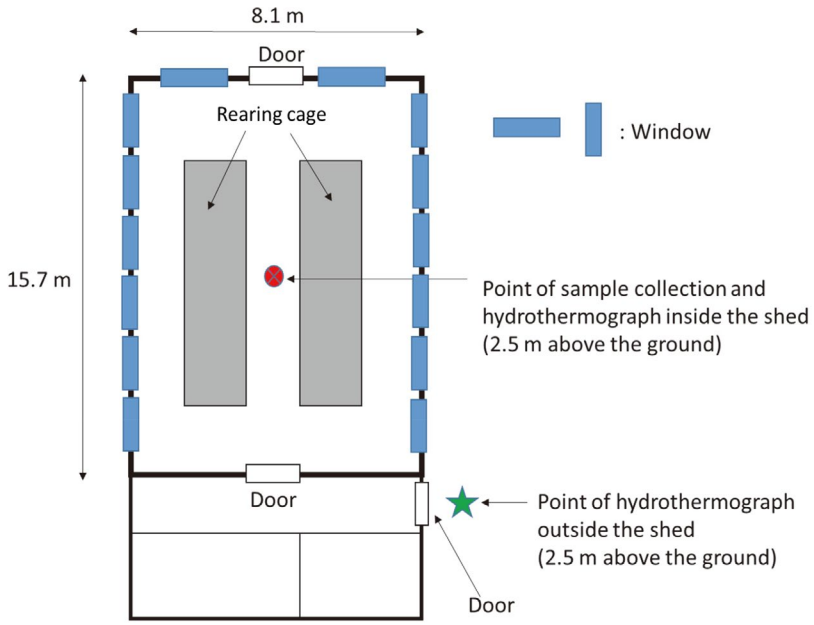

Fig. 1. Basic outline of the hen shed.

ding 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 m^3 (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

Table 1. Outline of sample collection.

Sampling campaign	Number of hens[1)]	Total weight of hens [kg][2)]	Number of samples		
			Tenax	DNPH cartridge	Florisil
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.

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 stored in a cool, dark place. In addition, blank and field blank samples were collected for each sampling campaign.

For measurement of aldehydes and acetone, samples were collected using two 2,4-dinitrophenylhydrazine (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.

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

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 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°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.

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 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 mode.

The blanks in triplicate for all the target compounds were below or near the detection limits. The field blanks were detected at or below the 10 ng level, and, in general, the blank values were very low compared with the values of the samples. The measured values of the samples were corrected by subtracting the blank values.

2.6 Estimation of ER of VOCs from the Shed

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 evaluated using Eq. (1),

$$E = \frac{C \times V_{out}}{W} \quad (1)$$

where E (μg [h kg-hen]$^{-1}$) is the ER, C (μg m^{-3}) is the VOC concentration in the hen shed, V_{out} (m^3 h^{-1}) is the ventilation rate of the shed, and W (kg) is the total weight of the hens 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 estimat-

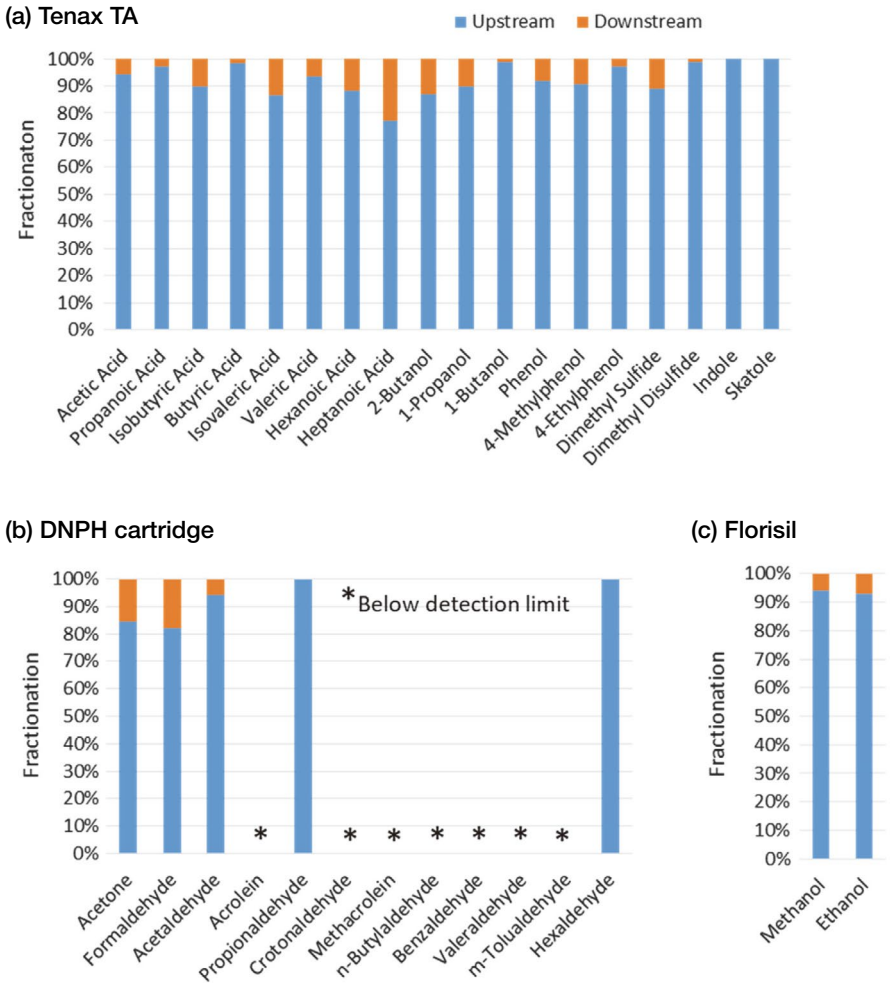

Fig. 2. Distribution of each VOC upstream and downstream of adsorbent. (a) Tenax TA adsorbent, (b) DNPH cartridge, (c) Florisil adsorbent

ed using the water balance method (Urano and Kataya-ma, 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:

$$\frac{dG^*}{dt} = G_{in} - G_{out} + G_g \quad (2)$$

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):

$$V_c \frac{d(x_i/v_i)}{dt} = V_{in}(x_0/v_0) - V_{out}(x_i/v_i) + W_g \quad (3\text{-a})$$

$$V_c \frac{d(1/v_i)}{dt} = V_{in}/v_0 - V_{out}/v_i \quad (3\text{-b})$$

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:

$$V_{out} = \frac{V_c v_i}{(x_i - x_0)\Delta t}\left\{\frac{x_0 - x_i^*}{v_i^*} - \frac{x_0 - x_i}{v_i}\right\} + \frac{W_g v_i}{x_i - x_0} \quad (4)$$

where Δt 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,

$$V_{out} = \frac{W_g v_i}{x_i - x_0} \quad (5)$$

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):

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

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 (μg 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 $\mu g\,m^{-3}$).

	Winter				Spring				Summer				Autumn			
	Average	Max	Min	SD[1)]	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	6.9	16.5	0.0	4.1
Propanoic Acid	0.01	0.07	ND[2)]	0.02	4.19	10.0	0.83	2.02	5.16	11.9	1.00	2.70	1.96	3.56	0.79	0.74
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	0.69	1.00	ND	0.20
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	1.10	2.10	0.56	0.42
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	0.59	0.91	0.48	0.09
Valeric Acid	0.32	2.62	ND	0.73	1.20	1.97	0.67	0.32	1.40	4.45	ND	0.69	0.90	1.77	0.63	0.30
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	1.27	2.35	0.68	0.48
Heptanoic Acid	0.65	5.27	ND	1.47	1.41	2.28	0.76	0.45	1.83	4.74	ND	0.89	0.90	1.65	ND	0.26
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	0.55	1.01	0.27	0.19
Ethanol	0.04	0.10	ND	0.03	0.06	0.18	0.01	0.05	0.06	0.15	0.03	0.03	0.06	0.17	0.02	0.05
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	5.61	13.9	0.82	3.03
1-Propanol	7.02	20.3	1.98	5.05	9.09	35.3	0.35	6.78	1.70	9.88	ND	1.44	2.66	4.57	0.57	1.14
1-Butanol	3.77	11.4	0.90	3.08	19.9	364	0.59	50.3	2.51	25.1	0.49	4.08	1.61	9.80	0.35	1.83
Phenols																
Phenol	1.64	3.17	0.65	0.88	2.73	4.09	0.81	0.60	3.21	5.00	0.21	1.03	1.87	3.49	0.17	0.78
4-Methyl Phenol	0.43	0.89	0.17	0.20	0.43	1.23	0.28	0.36	0.23	0.93	ND	0.26	0.05	0.39	ND	0.09
4-Ethyl Phenol	0.12	0.24	0.05	0.06	0.54	0.86	0.29	0.14	0.66	1.40	ND	0.34	0.45	0.69	0.28	0.10
Sulfur compounds																
Dimethyl Sulfide	4.12	10.9	0.34	3.08	89.1	1100	0.22	208	170	1910	0.28	461	131	772	0.38	156.4
Dimethyl Disulfide	0.51	1.11	0.10	0.35	1.75	11.5	ND	2.05	4.47	57.4	0.45	10.0	1.86	10.2	0.40	1.97
Indoles																
Indole	0.01	0.06	ND	0.02	0.24	0.38	ND	0.08	0.30	0.51	0.25	0.05	0.26	0.30	0.24	0.02
Skatole	0.00	0.01	ND	0.00	0.07	0.26	ND	0.12	0.13	0.35	ND	0.14	0.14	0.26	ND	0.13
Ketones																
Acetone	57.6	136	26.9	38.7	98.2	208	19.2	64.8	122	285	46.5	93.6	65.6	129	23.92	35.23
2-Butanone	21.7	53.1	8.28	14.2	34.6	98.4	ND	21.5	31.1	139	2.72	31.7	2.03	3.78	ND	1.09
3-Pentanone	13.3	70.2	0.99	21.5	3.96	24.4	0.43	4.49	0.84	28.6	ND	3.89	2.30	31.1	ND	6.18
2-Pentanone	7.65	26.3	2.45	6.95	33.2	166	1.29	32.8	17.0	226	ND	31.6	20.9	195	0.10	36.08
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	1.40	3.39	0.13	1.16
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	1.26	2.87	0.85	0.59
Acrolein	0.11	0.64	ND	0.25	0.25	1.50	ND	0.61	ND	ND	ND	–	ND	ND	ND	–
Propionaidehyde	0.11	0.63	ND	0.25	2.40	6.67	ND	2.27	ND	ND	ND	–	ND	ND	ND	–
Crotonaldehyde	0.38	1.32	ND	0.57	ND	ND	ND	–	ND	ND	ND	–	ND	ND	ND	–
Methacrolein	ND	ND	ND	–	ND	ND	ND	–	ND	ND	ND	–	ND	ND	ND	–
n-Butylaldehyde	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	–
Valeraldehyde	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	0.20	1.20	ND	0.47	1.67	2.22	1.35	0.30	ND	ND	ND	–	ND	ND	ND	–

[1)] Standard diviation. [2)] Not detected.

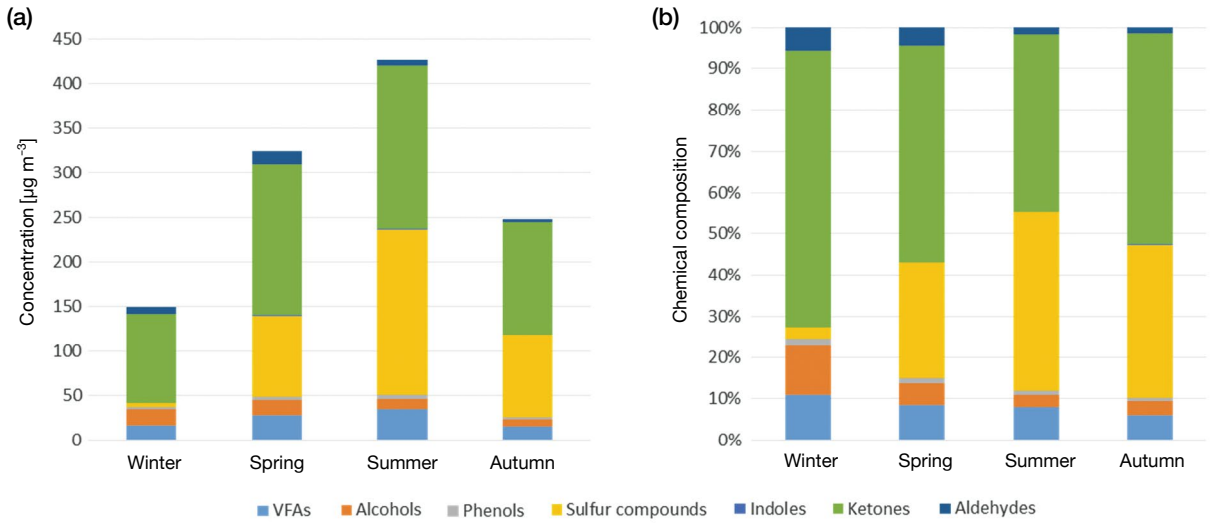

Fig. 3. (a) Average concentrations and (b) composition of VOC in the hen shed in each season.

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 volatized 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 (kOH; Yuan *et al.*, 2017; Atkinson *et al.*, 2006) ($OHRi = Ci \times kOH,i$). 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,

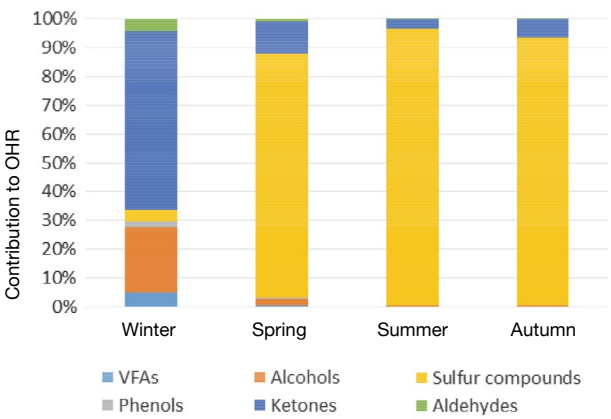

Fig. 4. Contribution of each chemical group to hydroxyl radical reactivity.

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

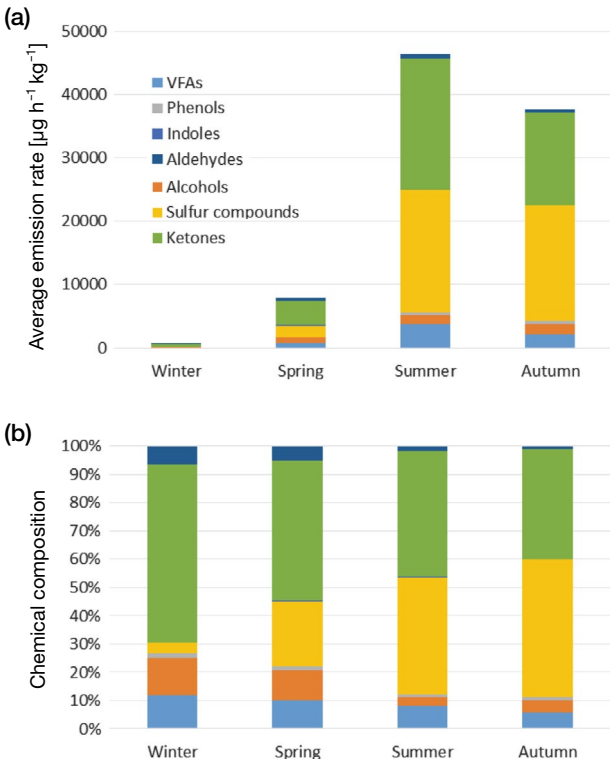

Fig. 5. (a) Average emission rates and (b) composition of VOCs from the hen shed.

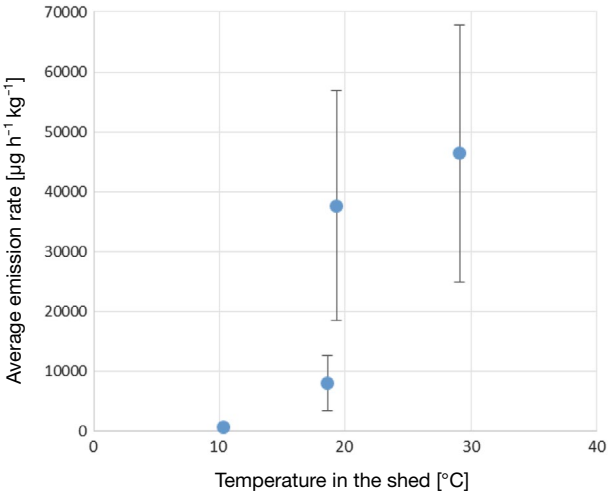

Fig. 6. Relationship between the temperature in the shed and emission rates of VOCs. The error bars show the standard deviation.

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 $\mu g\,h^{-1}\,kg^{-1}$) 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-

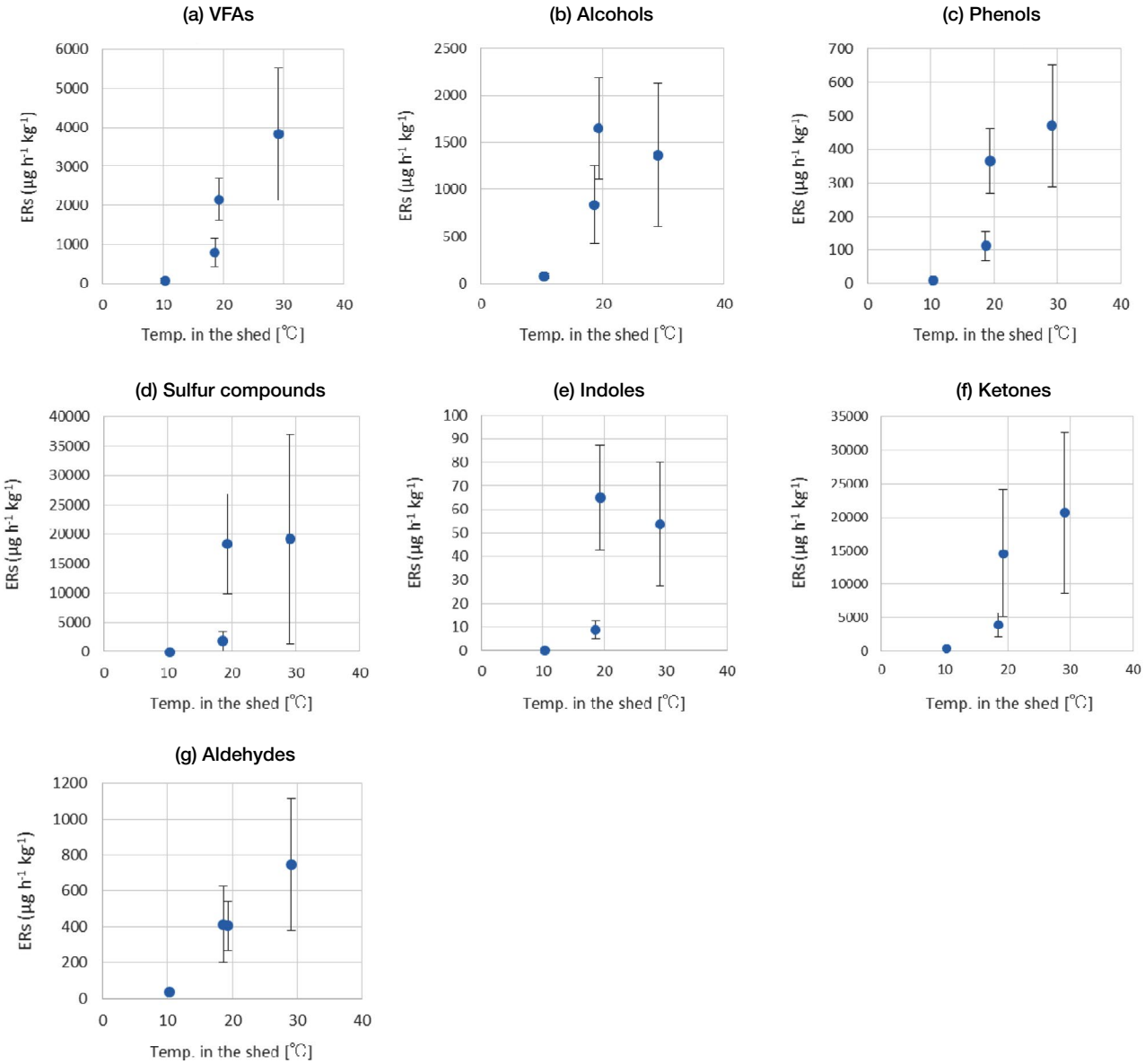

Fig. 7. (a–g) Relationship between the temperature in the shed and the ERs of each class of VOC. The error bars show the standard deviation.

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 μg h^{-1} 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 × 10^3 μg h^{-1} 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 (Wg: 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 h^{-1}, whereas the amount of moisture emission in the hen shed was 2.5 kg 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-

Table 3. Emission rates of VOCs from the hen shed (in $\mu g\,h^{-1}\,kg^{-1}$).

	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	*	*	*	*	*	*	*	*
Propionaidehyde	1	3	*	0	50	812	*	52	*	*	*	*	*	*	*	*
Crotonaldehyde	2	7	*	1	*	*	*	*	*	*	*	*	*	*	*	*
Methacrolein	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
n-Butylaldehyde	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Benzaldehyde	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Valeraldehyde	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
m-Tolualdehyde	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Hexaldehyde	1	6	*	1	45	270	8	19	*	*	*	*	*	*	*	*

[1)] Standard division. [2)] Not calculated.

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

	Total	VFAs	Alcohols	Phenols	Sulfur compounds	Indoles	Ketones	Aldehydes
Emission per one hen (g hen^{-1})								
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})								
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

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

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-butanone, 2-pentanone 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-butanone, 3-pentanone 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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SUPPLEMENTARY MATERIALS

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.

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

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

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

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^3h^{-1})
Winter	2.5	1,100
Spring	2.5	7,900
Summer	2.5	31,000
Autumn	2.5	38,000