



THE EFFECT OF DAIRY CATTLE HOUSING SYSTEMS ON THE CONCENTRATIONS AND EMISSIONS OF GASEOUS MIXTURES IN BARN DETERMINED BY FOURIER-TRANSFORM INFRARED SPECTROSCOPY

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Abstract

The aim of this study was to determine the concentrations and emissions of greenhouse and odorous gases in different types of dairy cattle housing systems with the use of Fourier-transform infrared (FTIR) spectroscopy. The study was performed in autumn and winter in four types of dairy cattle barns with different process and technical systems (free-stall, deep litter – FS-DL; free-stall, sub-floor manure storage – FS-SFM; free-stall, litter in stalls – FS-LS; tie-stall, litter in stalls – TS-LS) in northern Poland. Analyses of gaseous mixtures in barn air were conducted by infrared spectrometry with the multi-component Gasmeter DX4030 analyzer. A total of 200 measurement spectra were acquired and subjected to qualitative and quantitative analyses with the Calcmeter Professional program with a library of reference spectra for 200 chemical compounds. The results of the study indicate that housing systems and the technological solutions applied in barns exert a considerable influence on the production of greenhouse and odorous gases. Free-stall housing with slatted floors and sub-floor manure storage appears to be the optimal solution for reducing the animals' exposure to the presence of the analyzed chemical compounds in air, improving animal welfare and minimizing GHG emissions to the environment (considering the optimal ventilation rate). It should be noted that the concentrations of other potentially harmful compounds, for which the maximum safe levels have been specified, were also relatively low in the remaining systems, which points to the observance of high sanitary standards and the use of efficient ventilation systems in the evaluated barns.

Key words: dairy cattle, housing system, gaseous mixtures, greenhouse gases, FTIR spectroscopy

According to the Intergovernmental Panel on Climate Change (IPCC), anthropogenic greenhouse gas (GHG) emissions increased at a much faster rate in the past decade (2000–2010) than in the three preceding decades, and reached the highest level in the history of humanity. Despite numerous efforts to mitigate the consequences of GHG emissions at both the international and national levels, an even greater increase in emission levels is expected in the coming decade. The Agriculture, Forestry and Other Land Uses (AFOLU) sector is responsible for nearly one-fourth of global anthropogenic GHG emissions. The emissions from the AFOLU sector are estimated at 10–12 Gt_{CO₂eq}/year, whereas global emissions reached around 49 Gt_{CO₂eq} in 2010 (IPCC, 2014). Carbon dioxide produced in agriculture is regarded as a neutral gas (related to the annual carbon fixation and photosynthetic oxidation cycle), but the farming sector is the largest producer of GHGs such as methane (CH₄) and nitrous oxide (N₂O). In 2010, the total annual production of GHGs other than CO₂ in agriculture was estimated at 5.2–5.8 Gt_{CO₂eq}, which accounts for 10–12% of global anthropogenic GHG emissions (Smith et al., 2014).

Livestock production is responsible for 15% of GHG emissions on the global scale (Steinfeld et al., 2006), and ruminant farming accounts for 18% of GHG emissions in the EU (EFSA, 2009; Dimov et al., 2019). The air exhaled by cows as well as manure, feed, and space heating are constant sources of CO₂. Most importantly, the dairy sector is a major anthropogenic source of CH₄ (Lassen et al., 2012). Global CH₄ emissions from enteric fermentation of ruminant livestock are estimated at 4% (Wu et al., 2017), and CH₄ global warming potential is around 22 times higher in comparison with CO₂ (Lassen et al., 2012). Methane is produced during anaerobic fermentation of carbohydrates in the rumen, and it is associated with energy loss. The methanogenesis converts H₂ and CO₂ into CH₄ and H₂O, respectively. Manure is also a significant source of CH₄ because it contains cellulose that is degraded by methane-producing bacteria (Maurer et al., 2017 a; Mama and Seid, 2019). In the presence of ammonium and nitrogen, the microbial degradation of organic manure compounds also leads to the production of N₂O which is another important GHG, and ammonia (NH₃) (Garlipp et al., 2011) which is not a GHG in itself but is a precursor for GHG formation. The oxidation of NH₃ releases N₂O and nitric oxide (NO) which participate in the production of tropospheric ozone and contribute to the degradation of the ozone layer (Kamp et al., 2018). Ammonia contributes to eutrophication and soil acidification, and it exerts an adverse impact on biodiversity and ecosystems (Sheppard et al., 2011; Witkowska and Sowińska, 2017; Kamp et al., 2018).

Ammonia is the most ubiquitous gaseous compound which is released during livestock production, and its excess has a negative effect on animals and farm personnel (Witkowska et al., 2006; Witkowska et al., 2007; Kamp et al., 2018; Wi et al., 2019). Other gases that are released in smaller quantities during cattle production include sulfur dioxide (SO₂) and carbonyl sulfide (COS). These gases are toxic, and similarly to NH₃, they have a pungent smell (Herbut et al., 2010; Kwiatkowska-Stenzel et al., 2014). In addition to sulfur and nitrogen compounds, some inorganic gaseous compounds and volatile organic compounds (VOCs) also contain carbon, and they are classified as aroma compounds that are responsible for noxious odor emis-

sions from animal farms (Filipy et al., 2006; Korczyński et al., 2013; Witkowska, 2013; Cai et al., 2015). Aroma compounds are also associated with livestock production, and they are released from animal feces and liquid and solid manure stored in concrete bunkers or slurry pits (Hoff et al., 2006; Maurer et al., 2016; Maurer et al., 2017 b; Maurer et al., 2017 c; Maurer et al., 2017 d). Aroma compounds influence enzymatic and microbial mineralization of organic compounds (Herbut et al., 2010; Korczyński et al., 2013). Volatile organic compounds from livestock production contain up to several hundred compounds of various origin, and they are detected by the human sense of smell even at low concentrations (Lo et al., 2008; Herbut et al., 2010).

Mass spectrometry and gas chromatography analyses have revealed that in addition to methane (saturated carbohydrate), dairy and beef cattle farms are also a source of organic compounds such as alcohols, carboxylic acids, ketones, aldehydes, esters, ethers, aromatic and halogen hydrocarbons, terpenes, amines, other organosulfur and nitrogen compounds (Cai et al., 2006; Filipy et al., 2006; Shaw et al., 2007; Laor et al., 2008; Gentner et al., 2014; Yuan et al., 2017), and, possibly, phenols (Shaw et al., 2007). Filipy et al. (2006) have identified 113 VOCs in a barn, including 82 VOCs in the stalls of lactating cows, and 73 VOCs in slurry pits. The concentrations of these gaseous pollutants are determined by environmental conditions and process parameters that differ across animal housing systems (Herbut et al., 2010).

The concentrations of VOCs are difficult to measure accurately in a given time and place, therefore they are rarely investigated despite the fact that livestock production, including dairy cattle farming, is a major source of these compounds (Kamp et al., 2018). These compounds are usually measured with the use of sophisticated laboratory equipment for gas chromatography-mass spectrometry (GC-MS) (Koziel et al., 2006; Zhang et al., 2010; Zhang et al., 2015). Portable multi-gas detectors are not highly accurate, and they support measurements of only the most widely occurring compounds. They are prone to decalibration under aggressive operating conditions, and they are only suitable for highly generalized evaluations of air quality (Guiziou and Beline, 2005; Sobczuk et al., 2010). Therefore, the concentrations of gaseous mixtures are often estimated based on the number of animals in the herd as well as emission factors that do not account for environmental conditions or process parameters. Up to 50 such parameters have been identified, therefore, the relevant measurements can be burdened with considerable error (Herbut et al., 2010).

Lassen et al. (2012) relied on infrared spectroscopy to determine the concentrations of CH₄ exhaled by cows. Their results were largely consistent with expectations, and they concluded that infrared spectroscopy is a reliable tool in large-scale studies. Portable Fourier-transform spectrophotometers support accurate *in situ* measurements of many volatile compounds, and they can be used to evaluate the influence of cattle housing conditions on VOC emissions.

The aim of this study was to determine the concentrations and emissions of greenhouse and odorous gases in different types of dairy cattle housing systems with the use of Fourier-transform infrared spectroscopy.

Material and methods

The study was performed in autumn and winter (October – January) in four types of dairy cattle barns with different process and technical systems (free-stall, deep litter – FS-DL; free-stall, sub-floor manure storage – FS-SFM; free-stall, litter in stalls – FS-LS; tie-stall, litter in stalls – TS-LS) in northern Poland (Table 1). The barns differed in herd size, housing system, and manure management (Table 1).

Table 1. Description of dairy barns

Parameter	FS-DL ¹	FS-SFM	FS-LS	TS-LS
Number of cows	80	80	90	60
Maintenance system	free-stall	free-stall	free-stall	tie-stall
Floor	deep litter in the resting area; slatted floor in feed passage	rubber mats in stalls; slatted floor with sub-floor manure storage	solid concrete; litter in stalls	solid concrete; litter in stalls
Management system	straw is added every 2 days; used litter is removed using a front loader every 3 months	feces are removed through floor gaps due to cow movement; additionally, ground-floor scrapers run 3 times a day to remove manure	straw is added every two days and is changed once a week	straw is changed twice a day
Ventilation system	natural – inflow through curtains, outflow through a roof ridge vent with a skylight	natural – inflow through curtains, outflow through a roof ridge vent with a skylight	natural – inflow through curtains, outflow through a roof ridge vent	natural – inflow through windows, outflow through a roof ridge vent

¹FS-DL = free-stall, deep litter; FS-SFM = free stall, sub-floor manure storage; FS-LS = free stall, litter in stalls; TS-LS = tie-stall, litter on stalls.

Barns

In all barns the cows were housed indoors around the year. They were fed a total mixed ration (TMR) supplied by a feed wagon and an automatic feeder. During the study, basal diets were composed of maize silage, grass haylage, straw, protein concentrates, mineral and vitamin supplements in all treatments. All forages came from a known source and were of good quality. The barns had a natural ventilation system where air was vented through a roof ridge opening with a skylight. Fresh air was supplied through sidewall curtains (FS-DL, FS-SFM, FS-LS) or windows (TS-LS).

The FS-DL barn was a free-stall barn with deep litter, separate resting areas, and a separate feeding passage. The barn was fully stocked with 80 Polish Holstein-Friesian Black-and-White and Red-and-White cows. The barn had a slatted floor in the feed passage and a solid concrete floor with deep litter in the resting area. Fresh rye and wheat straw was added every two days. Manure was removed with a front loader every three months.

The FS-SFM barn was a free-stall barn with a slatted concrete floor. The barn was fully stocked with 80 Polish Holstein-Friesian Black-and-White and Red-and-White cows. Stalls measuring 1.2 m in width and 2.5 m in length had rubber mats to improve the animals' well-being during resting. The floor was composed of slats with a width of 12 cm and 4 cm spaces in-between. Manure was collected in slurry pits under the floor. Manure was pushed down through the slats by moving cows. Floor scrapers were additionally used three times a day. Every three months, slurry was pumped out from the pit by a slurry tank.

The free-stall FS-LS barn housed 90 Holstein-Friesian dairy cows. The barn had separate resting areas (1.25 × 2.60 m) with straw litter, two feed and stall passages with a solid concrete floor and grates for draining liquid manure. Manure was removed before each milking (twice daily) with a front loader into a concrete bunker.

The tie-stall TS-LS barn was fully stocked with 60 Holstein-Friesian cows. The barn had resting areas (1.25 × 1.85 m) bedded with barley and wheat straw, which was replaced twice daily with a front loader.

Sampling and analyses

The environmental parameters in barns were monitored during the study. Temperature (°C) and relative humidity (%) were measured with the LB 520 thermo-hygrometer (Label, Poland), and airspeed was calculated based on the rate of heat loss measured with a dry-bulb thermometer (Togo, Poland) with a standard formula (Janowski, 1979).

The ventilation rate (VR) was calculated based on the CO₂ emission model (Equation 1) for dairy cattle (CIGR, 2002):

$$VR = \frac{0.185}{(CO_2 \text{ indoors} - CO_2 \text{ outdoors}) 10^{-6}} \quad (1)$$

where *VR* is the ventilation rate in m³ h⁻¹ HPU⁻¹, 1 HPU (heat producing unit) is 1000 W of the total heat produced by the animals at 20°C, 0.185 is CO₂ production in m³ h⁻¹ HPU⁻¹ at a medium feeding level, *CO₂ indoors* is CO₂ indoor concentration in ppm, and *CO₂ outdoors* is CO₂ outdoor concentration in ppm.

The heat produced by a cow (HPC) was calculated according to Equation 2 (CIGR, 2002):

$$HPC_{tot} = 5.6m^{0.75} + 22Y \quad (2)$$

where *m* is the standard body weight of a cow (700 kg) and *Y* is average milk production (24 L d⁻¹).

Qualitative and quantitative analyses of gaseous mixtures in barn air were conducted by infrared spectrometry with the multi-component Gasmeter DX4030 analyzer for on-site measurements of chemical compounds at low concentrations in ambient air (Gasmeter Technologies, Finland). The analyzer was calibrated with pure nitrogen as zero gas before each measurement series. Four series of measurements were con-

ducted during the experiment, one series per month. In all farms, the measurements were performed on successive days at 5.00 a.m., before milking. In each series, 10 measurement spectra were acquired successively at five points in each barn (one point in the center, and two points on each diagonal line) at head level. Before each series of measurements, the analyzer was warmed up for 10 minutes for better stability. The measurement time for every spectrum was 20 seconds, according to the producer's recommendations. A total of 200 measurement spectra, 4 series \times 50N (10 samples \times 5 points), were acquired (with the portable Gasmeter DX4030 analyzer), recorded (using the PDA interface in Calcmet Lite software communicating with the analyzer by Bluetooth) and subjected to qualitative (detection of chemical compounds) and quantitative (determination of compound concentrations) analyses with the Calcmet Professional program for Windows. A library of reference spectra for 200 chemical compounds that could be present in the sample was used to perform a multi-component analysis of sample spectra. A reference spectrum is a spectrum of a single gas component at a specific concentration. The spectral analysis routine in Calcmet Pro software performs all calculations automatically. It combines the reference spectra with appropriate multipliers to obtain a spectrum that is as close as possible to the sample spectrum. If the concentrations of the reference gases are known, the concentration of each gas component in the sample can be determined using the multipliers of individual reference spectra. Gas concentrations were expressed in parts per million (ppm).

The emission rates of CO₂, CH₄ and NH₃ were calculated according to Equation 3 (Ngwabie et al., 2011):

$$ER = VR (C_{in} - C_{out}) \quad (3)$$

where *ER* is the emission rate in g h⁻¹ cow⁻¹, *VR* is the ventilation rate in m³ h⁻¹ cow⁻¹, *C_{in}* and *C_{out}* are gas concentrations inside and outside the building.

Statistical analysis

Data on climatic parameters, gas concentrations and emissions in four barns with different housing systems were processed statistically using the general linear model (GLM). Since all variables had a normal distribution, one-way ANOVA was performed. The significance of differences between the mean values of gas concentrations in barns was determined by Tukey's test. All calculations were made using Statistica 13 for Windows (StatSoft Inc., Tulsa, OK, USA).

Results

The evaluated barns were characterized by similar dry-bulb temperature, relative humidity, and airspeed throughout the experiment (Table 2). No significant differences in the above parameters were noted between barns FS-DL and TS-LS. Relative humidity was significantly ($P \leq 0.01$) lower in barn FS-LS than in the remaining barns (FS-DL, FS-SFM, and TS-LS). In barns FS-SFM and FS-LS, dry-bulb temperature was lower by 2°C, and the ventilation rate in FS-SFM group was higher ($P \leq 0.05$)

than in barn TS-LS. Similar trends were observed in successive months of the study (Table 2). The major GHGs, including carbon dioxide and methane, were detected in all barns and in all measurement series at the highest concentrations (Table 3, Figures 1 and 3). However, the mean GHG concentrations differed significantly ($P<0.01$) between barns. Barn FS-SFM (with a slatted floor and sub-floor manure storage) was characterized by the lowest ($P<0.01$) mean concentrations of CO_2 and CH_4 in all measurements. The mean concentration of CO_2 was highest ($P<0.01$) in barn FS-DL (with deep litter), where it exceeded the values noted in barn FS-SFM by 20%, in barn FS-LS by 12%, and in barn TS-LS by 4% throughout the study, with significant differences between barns ($P<0.01$). However, in October and January, the highest CO_2 levels ($P<0.01$) were observed in barn TS-LS (with the smallest number of cows). Barn TS-LS was also characterized by the highest maximum CO_2 concentration and the greatest fluctuations in this parameter (Figure 1). The smallest difference between the minimum and maximum CO_2 levels was noted in barn FS-SFM. Mean CO_2 emission was highest in this building ($P<0.05$) and the lowest ($P<0.05$) CO_2 emission was noted in barn TS-LS (Figure 2).

Table 2. Average dry-bulb temperature, relative humidity, airspeed, and ventilation rate¹ in dairy barns (mean \pm SD, N = 5)

Month	Parameter	Barn				P-value
		FS-DL ²	SF-SFM	FS-LS	TS-LS	
October	Dry-bulb temperature ($^{\circ}\text{C}$)	13.5 \pm 1.1	11.3 \pm 1.3	11.0 b \pm 0.9	13.8 a \pm 1.2	$P\leq 0.05$
	Relative humidity (%)	69 a \pm 3.5	66 a \pm 2.8	60 b \pm 2.2	69 a \pm 3.0	$P\leq 0.01$
	Airspeed (m s^{-1})	0.2 b \pm 0.0	0.3 \pm 0.0	0.4 a \pm 0.0	0.2 b \pm 0.0	$P\leq 0.05$
	Ventilation rate ($\text{m}^3 \text{h}^{-1} \text{cow}^{-1}$)	1372 c \pm 84	2022 a \pm 69	1693 b \pm 42	840 d \pm 76	$P\leq 0.01$
November	Dry-bulb temperature ($^{\circ}\text{C}$)	13.7 \pm 1.0	13.2 \pm 0.9	11.8 \pm 0.8	13.7 \pm 1.1	NS
	Relative humidity (%)	67 a \pm 3.2	70 a \pm 3.7	61 b \pm 2.5	74 a \pm 3.6	$P\leq 0.01$
	Airspeed (m s^{-1})	0.2 b \pm 0.0	0.4 a \pm 0.0	0.3 \pm 0.0	0.2 b \pm 0.0	$P\leq 0.05$
	Ventilation rate ($\text{m}^3 \text{h}^{-1} \text{cow}^{-1}$)	780 d \pm 62	1464 a \pm 46	1033 b \pm 67	951 c \pm 48	$P\leq 0.01$
December	Dry-bulb temperature ($^{\circ}\text{C}$)	11.2 a \pm 0.5	8.6 b \pm 0.6	8.2 b \pm 0.4	11.0 a \pm 0.8	$P\leq 0.05$
	Relative humidity (%)	77 a \pm 3.9	73 b \pm 2.5	63 c \pm 2.8	70 b \pm 3.5	$P\leq 0.01$
	Airspeed (m s^{-1})	0.2 \pm 0.0	0.2 \pm 0.0	0.3 \pm 0.0	0.2 \pm 0.0	NS
	Ventilation rate ($\text{m}^3 \text{h}^{-1} \text{cow}^{-1}$)	782 c \pm 46	1388 a \pm 39	990 b \pm 43	768 c \pm 48	$P\leq 0.01$
January	Dry-bulb temperature ($^{\circ}\text{C}$)	10.5 a \pm 0.8	8.4 \pm 1.3	8.0 b \pm 0.7	9.9 \pm 1.1	$P\leq 0.05$
	Relative humidity (%)	71 a \pm 2.8	69 a \pm 3.2	64 b \pm 2.5	72 a \pm 3.4	$P\leq 0.05$
	Airspeed (m s^{-1})	0.1 \pm 0.0	0.2 \pm 0.0	0.2 \pm 0.0	0.2 \pm 0.0	NS
	Ventilation rate ($\text{m}^3 \text{h}^{-1} \text{cow}^{-1}$)	772 c \pm 54	890 a \pm 42	806 b \pm 61	668 c \pm 51	$P\leq 0.05$
Average	Dry-bulb temperature ($^{\circ}\text{C}$)	12.3 \pm 1.5	10.2 \pm 2.3	9.8 \pm 1.7	12.0 \pm 1.9	NS
	Relative humidity (%)	71 a \pm 4.3	70 a \pm 2.9	62 b \pm 1.8	71 a \pm 2.2	$P\leq 0.01$
	Airspeed (m s^{-1})	0.2 \pm 0.0	0.3 \pm 0.0	0.3 \pm 0.0	0.2 \pm 0.0	NS
	Ventilation rate ($\text{m}^3 \text{h}^{-1} \text{cow}^{-1}$)	927 \pm 297	1441 a \pm 464	1131 \pm 387	808 b \pm 120	$P\leq 0.05$

¹ CO_2 mass balance (CIGR, 2002).

²FS-DL = free-stall, deep litter; FS-SFM = free-stall, sub-floor manure storage; FS-LS = free-stall, litter in stalls; TS-LS = tie-stall, litter in stalls.

a, b, c, d – mean values in rows with the same letter do not differ significantly at $P\leq 0.05$.

³NS = non-significant.

Table 3. Concentrations (ppm) of greenhouse gases and ammonia in dairy barns (mean \pm SD, N = 50)

Month	Parameter	Barn				P-value
		FS-DL ¹	SF-SFM	FS-LS	TS-LS	
October	CO ₂	934 b \pm 54	674 d \pm 33	843 c \pm 24	1066 a \pm 46	P \leq 0.01
	CH ₄	68.9 a \pm 9.4	54.8 d \pm 5.8	63.6 b \pm 6.3	60.6 c \pm 4.4	P \leq 0.01
	N ₂ O	0.46 a \pm 0.01	0.44 b \pm 0.00	0.41 c \pm 0.02	0.44 b \pm 0.02	P \leq 0.01
	NO	0.27 a \pm 0.01	0.00 b \pm 0.00	0.00 b \pm 0.00	0.00 b \pm 0.00	P \leq 0.01
	NO ₂	0.34 c \pm 0.03	0.16 d \pm 0.02	0.49 a \pm 0.03	0.43 b \pm 0.04	P \leq 0.01
	SO ₂	1.34 a \pm 0.06	0.98 b \pm 0.09	0.35 c \pm 0.12	0.99 b \pm 0.17	P \leq 0.01
	NH ₃	5.12 a \pm 0.34	1.56 d \pm 0.19	1.69 c \pm 0.11	2.68 b \pm 0.39	P \leq 0.05
November	CO ₂	1112 a \pm 43	907 c \pm 28	951 b \pm 47	947 b \pm 32	P \leq 0.01
	CH ₄	69.8 a \pm 6.8	56.5 c \pm 4.5	64.3 b \pm 6.4	58.9 c \pm 5.9	P \leq 0.01
	N ₂ O	0.47 a \pm 0.01	0.45 \pm 0.01	0.39 b \pm 0.03	0.41 \pm 0.03	P \leq 0.05
	NO	0.10 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00	NS ²
	NO ₂	0.50 a \pm 0.06	0.24 b \pm 0.05	0.43 a \pm 0.09	0.02 c \pm 0.01	P \leq 0.05
	SO ₂	1.09 a \pm 0.04	1.17 a \pm 0.03	0.82 b \pm 0.04	0.75 b \pm 0.02	P \leq 0.05
	NH ₃	4.67 a \pm 0.12	2.39 c \pm 0.13	2.58 c \pm 0.15	3.26 b \pm 0.19	P \leq 0.01
December	CO ₂	1283 a \pm 41	892 d \pm 32	991 c \pm 38	1079 b \pm 43	P \leq 0.01
	CH ₄	74.4 b \pm 4.1	53.9 d \pm 3.2	84.5 a \pm 2.6	64.1 c \pm 4.4	P \leq 0.01
	N ₂ O	0.48 a \pm 0.00	0.48 a \pm 0.00	0.22 b \pm 0.02	0.42 a \pm 0.03	P \leq 0.01
	NO	0.00 b \pm 0.00	0.00 b \pm 0.00	0.31 a \pm 0.03	0.00 b \pm 0.00	P \leq 0.05
	NO ₂	0.50 a \pm 0.09	0.44 a \pm 0.08	0.05 b \pm 0.01	0.03 b \pm 0.01	P \leq 0.05
	SO ₂	0.60 b \pm 0.02	1.43 a \pm 0.01	0.36 c \pm 0.03	0.72 b \pm 0.13	P \leq 0.05
	NH ₃	6.06 a \pm 0.12	3.23 d \pm 0.15	3.89 c \pm 0.21	4.65 b \pm 0.19	P \leq 0.01
January	CO ₂	1129 b \pm 33	1088 d \pm 18	1115.6 c \pm 33	1177 a \pm 29	P \leq 0.01
	CH ₄	120.3 a \pm 2.3	78.5 d \pm 3.4	121 a \pm 11.0	99.5 c \pm 6.2	P \leq 0.01
	N ₂ O	0.46 a \pm 0.03	0.45 a \pm 0.01	0.09 b \pm 0.01	0.45 a \pm 0.03	P \leq 0.01
	NO	0.06 b \pm 0.00	0.00 b \pm 0.00	0.24 \pm 0.04	0.57 a \pm 0.07	P \leq 0.05
	NO ₂	0.65 \pm 0.02	0.42 \pm 0.02	0.87 a \pm 0.07	0.03 b \pm 0.01	P \leq 0.05
	SO ₂	1.42 b \pm 0.03	1.46 a \pm 0.05	1.15 c \pm 0.18	0.93 d \pm 0.10	P \leq 0.01
	NH ₃	4.96 a \pm 0.04	1.75 d \pm 0.16	1.94 c \pm 0.33	2.19 b \pm 0.50	P \leq 0.01
Average	CO ₂	1116 a \pm 43	889 d \pm 28	977 c \pm 28	1067 b \pm 43	P \leq 0.01
	CH ₄	83.7 a \pm 6.8	59.4 c \pm 4.5	83.0 a \pm 5.3	71.3 b \pm 5.1	P \leq 0.01
	N ₂ O	0.47 a \pm 0.01	0.46 a \pm 0.01	0.28 b \pm 0.02	0.45 a \pm 0.01	P \leq 0.01
	NO	0.11 b \pm 0.00	0.00 c \pm 0.00	0.14 a \pm 0.01	0.14 a \pm 0.00	P \leq 0.01
	NO ₂	0.50 a \pm 0.06	0.34 c \pm 0.05	0.46 b \pm 0.05	0.13 d \pm 0.01	P \leq 0.01
	SO ₂	1.12 b \pm 0.03	1.37 a \pm 0.09	0.08 d \pm 0.01	0.43 c \pm 0.02	P \leq 0.01
	NH ₃	5.26 a \pm 0.12	2.25 d \pm 0.13	2.43 c \pm 0.13	3.05 b \pm 0.11	P \leq 0.01

¹FS-DL = free-stall, deep litter; FS-SFM = free stall, sub-floor manure storage; FS-LS = free-stall, litter in stalls; TS-LS = tie-stall, litter in stalls.

a, b, c, d – mean values in rows with the same letter do not differ significantly at P \leq 0.05.

²NS = non-significant.

The mean concentration of methane was significantly (P<0.01) higher in barns FS-DL and FS-LS throughout the study, but no significant differences in total CH₄ concentration were noted between the above barns throughout the experiment or in January. Methane levels were highest in barn FS-DL (with deep litter) in October and November, and in barn FS-LS (with the highest number of cows) in December. Barn FS-LS was characterized by the highest maximum CH₄ concentration and the great-

est fluctuations in CH_4 levels. In the above barn, the difference between the minimum and maximum concentrations of CH_4 reached 120 ppm (Figure 3). Mean methane levels in barns FS-DL and FS-LS were 30% higher than in barn FS-SFM and 15% higher than in barn TS-LS. CH_4 emission was highest in FS-LS and SF-SFM barns ($P < 0.05$) and lowest in TS-LS (Figure 4).

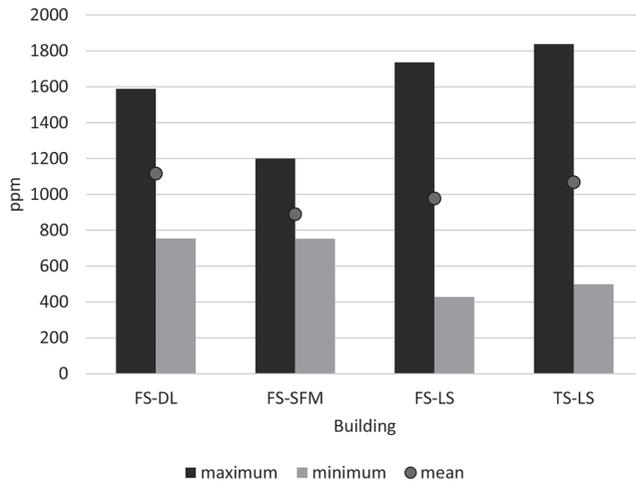
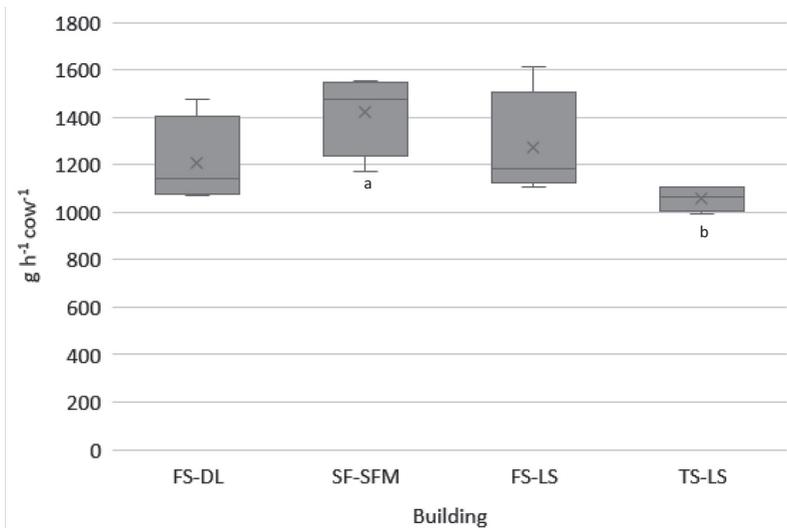


Figure 1. Mean CO_2 concentrations and their minimum~maximum range in dairy barns



a, b – mean values with the same letter do not differ significantly at $P \leq 0.05$

Figure 2. CO_2 emissions from dairy barns

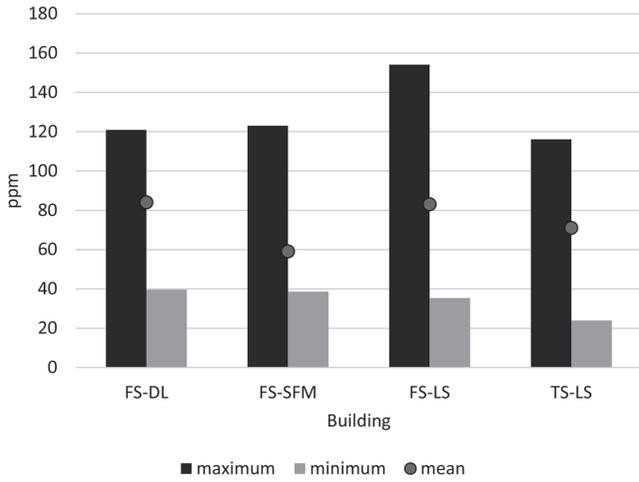
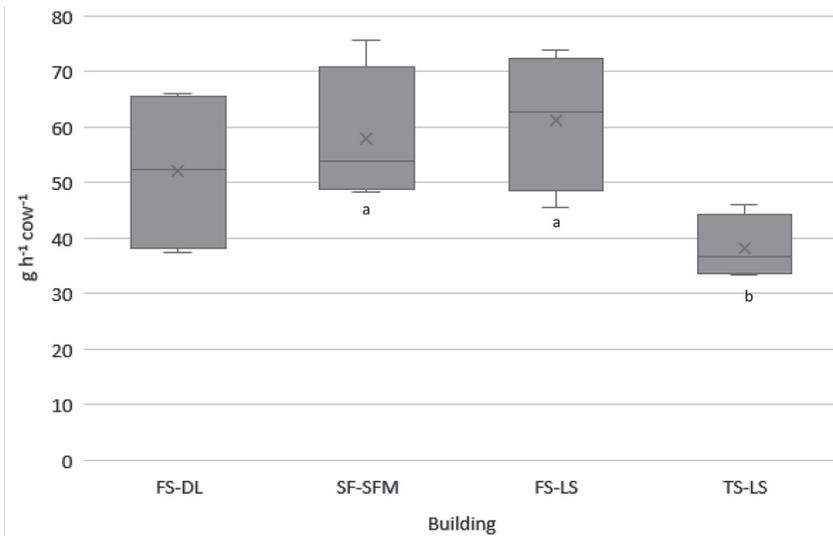


Figure 3. Mean CH₄ concentrations and their minimum-maximum range in dairy barns



a, b – mean values with the same letter do not differ significantly at $P \leq 0.05$

Figure 4. CH₄ emissions from dairy barns

Ammonia, a common gas in livestock farms, was also identified in all barns throughout the entire study. Ammonia concentrations differed significantly ($P < 0.01$) between barns in all measurements, except for November when significant differences in this parameter were not observed between barn FS-LS (with the highest number of cows) and barn FS-SFM. In each measurement series, the highest

($P < 0.01$) concentration of NH_3 was determined in barn FS-DL (with deep litter), and the lowest ($P < 0.01$) concentration was noted in barn FS-SFM (with a slatted floor). The mean ammonia concentration was more than 40% higher in barn FS-DL than in the remaining barns. Barn FS-DL was also characterized by the highest maximum concentration of NH_3 (up to 8 ppm) and the greatest difference between the minimum and maximum values of this parameter (Figure 5). The emission of NH_3 was also significantly highest ($P < 0.05$) in barn FS-DL (Figure 6).

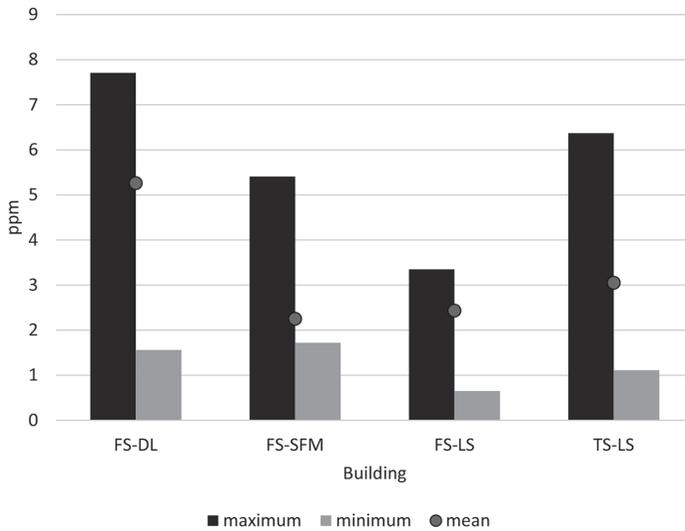
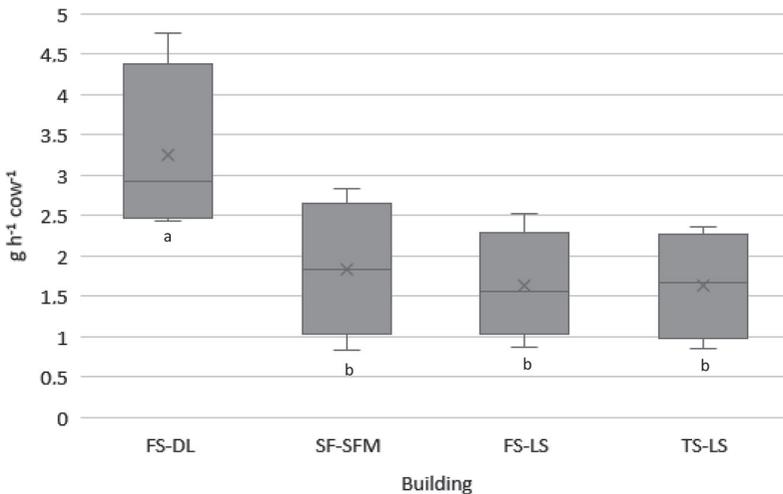


Figure 5. Mean NH_3 concentrations and their minimum~maximum range in dairy barns



a, b – mean values with the same letter do not differ significantly at $P \leq 0.05$

Figure 6. NH_3 emissions from dairy barns

The concentrations of the remaining inorganic GHGs, including nitrogen oxides (NO_x) and sulfur dioxide (SO₂), were considerably lower (1 ppm and less) in all barns and measurement series (Table 3). Sulfur dioxide was the predominant GHG (up to 1.5 ppm). Its mean concentration was highest in barn FS-SFM (with a slatted floor) and lowest (trace amounts) in barn FS-LS, but considerable variations were observed between barns and measurement series. In October, SO₂ levels were highest in barn FS-DL. The concentrations of nitrogen oxides also varied across barns and months. Barn FS-LS was characterized by the lowest ($P < 0.01$) mean concentration of N₂O and the highest mean concentration of nitric oxide (NO) (similarly to barn TS-LS). The concentration of N₂O was highest in barn FS-DL and lowest in barn TS-LS. Nitric oxide was the least abundant NO (trace amounts), and it was not detected in barn FS-SFM (Figure 7).

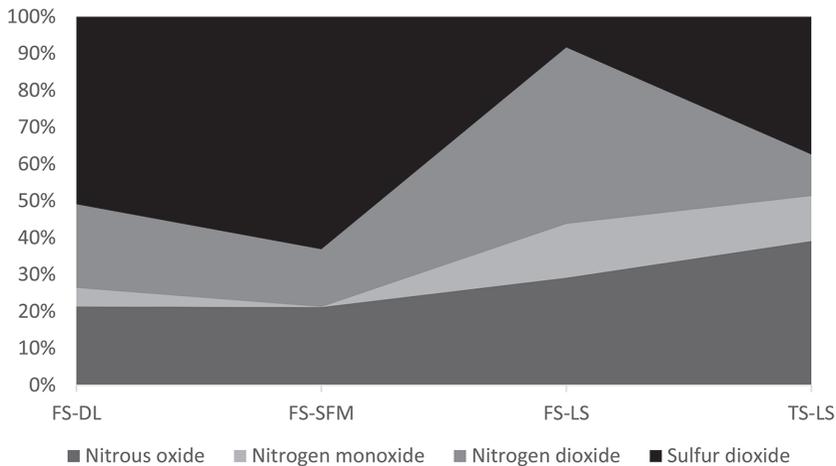


Figure 7. Percentage differences in the concentrations of N₂O, NO, NO₂, and SO₂ between dairy barns

A total of 32 VOCs from various chemical groups were identified in the evaluated barns (Figure 8). The concentrations of VOCs were lowest in barn FS-SFM and highest in barn FS-LS. A total of 30 gaseous admixtures were detected in barns FS-LS and TS-LS each. The presence of 25 VOCs was identified in barns FS-DL and FS-SFM each. Twenty organic compounds were detected in all barns. The following VOCs occurred in the highest maximum concentrations (Figure 9): methanethiol (22 ppm in barn FS-LS; 15 ppm in barn TS-LS), 1-butene (9 ppm in barns FS-LS and TS-LS), vinyl chloride (6 ppm in barn FS-LS), chloromethane (5 ppm in barn FS-DL), 1,3-butadiene (3 ppm in barns FS-DL and FS-LS), aniline (3 ppm in barn FS-LS) and 2-methoxyethanol (3 ppm in barn FS-LS). The maximum concentrations of the remaining VOCs were estimated at 1-2 ppm.

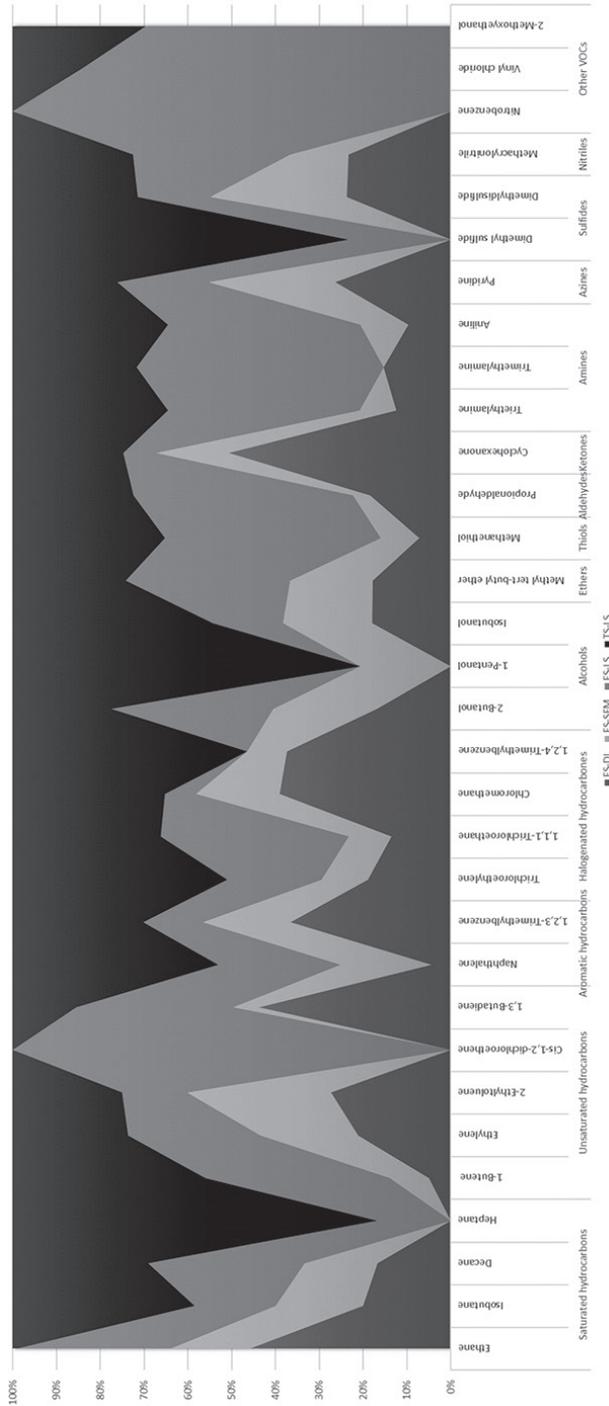


Figure 8. Percentage differences in the concentrations of volatile organic compounds (VOCs) between dairy barns

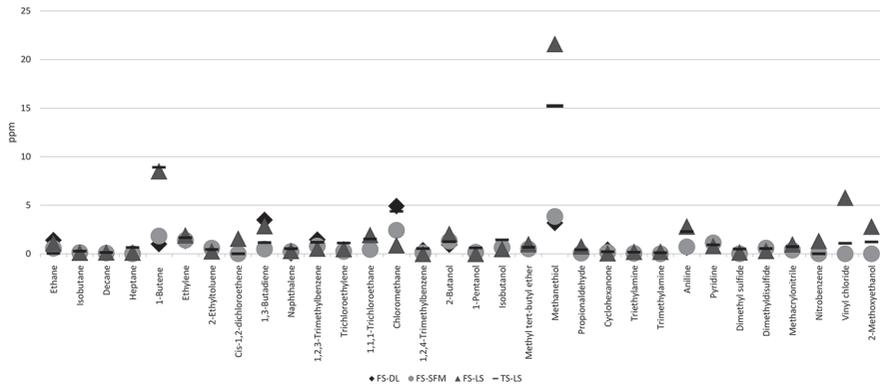


Figure 9. Maximum concentrations of volatile organic compounds (VOCs) in dairy barns

Discussion

The study was conducted in barns located in northern Poland which has a temperate climate with considerable variations in weather conditions. Northern Poland abounds in lakes, and it is characterized by high humidity in fall and winter as well as cold and long winters. During the study, the outdoor temperature ranged from 8°C in November to -8°C in January, and relative humidity ranged from 63% in November to 75% in December. Despite severe weather conditions, the microclimate parameters in the studied barns were similar (Table 2) and consistent with the welfare requirements for dairy cattle. Relative humidity was 5–10% lower in barn FS-LS than in the remaining barns, but it was within the recommended range of values for dairy cattle (60–85%). Dry-bulb temperature was around 2°C lower in barns FS-SFM and FS-LS than in barns FS-DL and TS-LS, but it also approximated the optimal level for dairy cattle (8–16°C) (Kończak and Dobrzański, 2019). The minor differences in temperature and relative humidity between barns could be attributed to the ventilation rate which was highest in barn FS-LS, followed by barn FS-SFM.

The barn microclimate exerts both direct and indirect effects on cow health because it considerably influences the emissions and ambient concentrations of gaseous compounds such as GHGs, ammonia, and VOCs. The release of NH_3 and CO_2 from manure is determined, among other factors, by the temperature and moisture content of straw. High values of these parameters increase the activity of microorganisms that decompose urea to NH_3 and CO_2 (Nahm, 2003; Witkowska, 2013). Methane and other VOCs are also released during enzymatic and microbial mineralization of fresh and stored manure and slurry (Korczyński et al., 2013). The rate at which these processes occur is influenced by environmental and technical factors in a given housing system. Gas emissions are also affected by floor type, straw type, quantity and hygiene, manure collection and storage system, and ventilation (Herbut et al., 2010; Garlipp et al., 2011).

The evaluated barns were characterized by different housing systems and technological solutions. Also, caution should be exercised when interpreting the identity of compounds and concentrations. This is because the FTIR technology and spectral analyses are burdened with inherent biases and confounding factors. Nevertheless, the presented measurements provide valuable insights to the quality of air in the evaluated dairy housing systems.

Carbon dioxide and CH₄, the most ubiquitous GHGs, were detected in all barns and in all measurement series, which is consistent with the literature (Table 3). The observed differences in GHG concentrations can be attributed to various technological systems in the analyzed barns. In this study, GHG emissions were lowest in barn FS-SFM with a slatted floor, where manure was removed through openings in the floor and with the use of mechanical scrapers. Carbon dioxide and methane levels were lowest in barn FS-SFM during all measurements. In other studies (Romaniuk and Mazur, 2014; Dimov et al., 2019), the lowest CO₂ concentration and the lowest variations in CO₂ levels were noted in barns with automated and robotized cleaning systems, which is consistent with our findings. In the current study, the mean CO₂ concentration in barn FS-DL (with an identical number of cows kept on deep litter) was 20% higher than in barn FS-SFM (with a slatted floor). Accumulated manure is a steady source of CO₂ in barns, and manure shuffling induces an even greater increase in CO₂ levels (Dimov et al., 2019). In some periods, the concentration of CO₂ was highest in barn TS-LS which had the smallest number of cows in tie-stalls and where straw was changed twice daily. Barn TS-LS was characterized by the highest CO₂ concentration which exceeded 1800 ppm (Figure 1). Despite the above, even the maximum value of this parameter was significantly below the safety threshold for cattle (3000 ppm) (Kołacz and Dobrzański, 2019), which indicates that all of the evaluated barns were effectively ventilated. In other studies, maximum CO₂ levels were determined at 2130 ppm in semi-open barns (Dimov et al., 2019), 2450 ppm in a tie-stall barn (Kavolelis, 2006), or even at 2680 ppm (Karandušovská et al., 2015). According to Dimov et al. (2019), temperature and relative humidity are correlated with CO₂ levels.

Our results confirm that CO₂ concentration in livestock buildings is a key measure of ventilation efficiency (Witkowska, 2013) because CO₂ levels peaked in a period characterized by the lowest ventilation rate and the highest temperature and relative humidity.

Kavolelis (2006) also reported the highest concentration of CO₂ in a tie-stall barn (relative to a free-stall barn) with good thermal insulation. In the present study, barn SF-SFM with the highest ventilation rate was characterized by the lowest mean and maximum concentrations of CO₂ as well as the smallest fluctuations in CO₂ levels. In comparison with barns FS-DL and TS-LS, the minimum concentration of CO₂ was lowest in barn FS-LS which was characterized by the smallest number of cows kept in free stalls, frequent straw replacement, a higher ventilation rate, and the lowest temperature and relative humidity.

A reverse trend was noted in mean methane levels which were highest in barn FS-LS (similarly to deep litter housing). In barns FS-DL and FS-LS, the mean CH₄ concentration was even 30% higher than in barn SF-SFM where manure was stored

under the floor. Barn FS-LS was also characterized by the highest maximum CH₄ levels (154 ppm) and the highest variation in CH₄ concentration (Figure 3), which could be attributed to considerable differences in airspeed and ventilation rate (Table 2). Similar variations were noted in the barn with a slatted floor, where CO₂ and CH₄ concentrations were lowest in all measurements, and where the difference between the minimum and maximum values was smallest. These observations suggest that housing conditions influence the emissions of the major GHGs in dairy cattle production. The mean levels of CO₂ and CH₄ point to a very important role of ventilation rate in GHG emissions from dairy barns. Despite the lowest concentration of CO₂ in barns SF-SFM and FS-LS, CO₂ emissions and the ventilation rate were highest in these buildings (Table 2, Figures 1 and 2). The average CO₂ emission from the evaluated barns was 1238 g h⁻¹ cow⁻¹ which is consistent with the literature. In a study by Mazur (2012), the average CO₂ emission from dairy cattle barns in the winter season reached 1300 g h⁻¹ cow⁻¹.

The mean CH₄ emission was also highest ($P < 0.05$) in SF-SFM and FS-LS groups (Figure 4). In the literature, CH₄ concentrations in barns were rarely investigated at different points. Karandušovská *et al.* (2015) used a photoacoustic gas detector with a multi-channel sampling system to measure methane levels at different points in two barns. The mean CH₄ concentration was determined at 14–51 ppm, which approximates the minimum values noted in the present experiment. In the cited study, the maximum CH₄ concentration was determined at 205 ppm in stalls and at 870 mm above the slurry pit. Methane poses a threat for cattle when its concentration exceeds 1000 ppm (Karandušovská *et al.*, 2015), which indicates that the technological systems deployed in the evaluated barns were effective in maintaining methane concentrations within safe limits for the animals and the staff. It should be noted that in our study, the mean CH₄ emission (52 g h⁻¹ cow⁻¹) was relatively high. Ngwabie *et al.* (2011) and Snell *et al.* (2003) found that average CH₄ emissions from naturally ventilated buildings for dairy cows were 15 and 26 g h⁻¹ cow⁻¹, respectively. Lower levels of CH₄ emissions in the cited studies probably resulted from a two- to three-fold lower ventilation rate, although the differences between the measurement methods could also play an important role.

Different and statistically significant levels of NH₃, one of the major gaseous pollutants which can be toxic for humans and animals, were also detected in all barns. In comparison with the values reported by other authors, NH₃ concentration was low (2–5 ppm). In the work of Karandušovská *et al.* (2015), the mean NH₃ concentration in stalls with litter ranged from 2 to 9 ppm. In the cited study, the maximum NH₃ levels were determined at 20 ppm in stalls and at 63 ppm above the slurry channel. In our study, NH₃ levels were more than 40% higher in the barn where cows were kept on deep litter than in the remaining barns (Table 3, Figure 5). The mean NH₃ emission was also highest in this building (Figure 6). In the current study, the average NH₃ emissions from the evaluated barns (2.1 g h⁻¹ cow⁻¹) were comparable with the emissions calculated by other authors, which ranged from 1.2 g h⁻¹ cow⁻¹ (Ngwabie *et al.*, 2011; Schrade *et al.*, 2012) to 2.6 g h⁻¹ cow⁻¹ (Pereira *et al.*, 2010). In the work of Snell *et al.* (2003), the average NH₃ emission from four naturally ventilated dairy houses was around 35% higher than in our study. Barn FS-SFM with a slatted

floor was characterized by the lowest mean concentration of NH_3 . The minimum and maximum values of the above parameter were lowest in barn FS-LS (with the smallest number of cows) despite higher mean NH_3 concentration than in barn FS-SFM. In barn FS-SFM, low mean NH_3 levels could be responsible for trace amounts of N_2O (Table 3) which is produced during ammonia oxidation (Garlipp et al., 2011). Despite the fact that N_2O is also a major GHG in dairy cattle farms (Smith et al., 2014), its concentration in the remaining three barns (nearly two-fold higher than in barn FS-LS) was also very low and did not exceed 0.5 ppm. In a study by Karandušová et al. (2015), the mean concentration of N_2O in barns was determined at 0.5–0.8 ppm, and the maximum concentration exceeded 5 ppm. The above study was conducted in Slovakia where the maximum allowable concentration of N_2O for farmworkers is 98 ppm; therefore, the noted emissions were low. In the present study, other nitrogen oxides were detected in trace amounts, and they were not identified in several measuring series (Figure 7).

Sulfur dioxide levels were higher (up to 1.5 ppm) in the barn where manure was stored under the floor and lower in barns with deep litter. This compound is produced during protein transformation processes, and it is characterized by an irritating odor with a low odor threshold (Yuan et al., 2017). Sulfur dioxide concentration was higher in barns where manure was less frequently removed.

Volatile organic compounds in dairy production also have a strong chemical odor. Odor emissions from livestock farms (Filipy et al., 2006) often lead to local protests against producers who are planning to start or expand their business operations (Korczyński et al., 2013). The quantification and qualitative analysis of aroma compounds are required to develop rational regulations for controlling odor emissions from livestock farms. In the studied barns, VOC concentrations were generally below the odor detection threshold, but a combination of various aroma compounds in the air can be perceived by the human sense of smell. The relevant knowledge is limited because odor quantification and characterization is a difficult process (Filipy et al., 2006; Shaw et al., 2007; Herbut et al., 2010; Bell et al., 2014). The conducted measurements suggest that VOC emissions in dairy farms can be even ten times lower than the estimated values (Shaw et al., 2007). A limited number of studies indicate that in addition to CH_4 (saturated carbohydrate), dairy cattle farms are also a source of organic compounds such as alcohols, carboxylic acids, ketones, aldehydes, esters, ethers, aromatic and halogen hydrocarbons, terpenes, amines, other organosulfur and nitrogen compounds, and phenols (Filipy et al., 2006; Shaw et al., 2007; Gentner et al., 2014; Yuan et al., 2017). A total of 32 VOCs were identified in our study (20 VOCs were present in each barn), and most of them belonged to the chemical groups identified in the cited research, including saturated, unsaturated, aromatic and halogenated hydrocarbons, alcohols, ethers, thiols, aldehydes, ketones, amines, azines, sulfides and nitriles (Figure 8). The lowest concentrations of VOCs were noted in barn FS-SFM with sub-floor manure storage, and the identified compounds differed considerably between barns. The highest number of 30 compounds was detected in barn FS-LS with the highest number of animals and in barn TS-LS with the smallest number of cows. Interestingly, cows were kept on shallow litter, and manure was removed regularly in these barns. Barns FS-LS and TS-LS were

characterized by particularly high concentrations of methanethiol, the sulfur analog of methanol, and 1-butene (Figure 9). In a mass spectrometry analysis, Shaw et al. (2007) also detected relatively high levels of methanethiol in cattle barns. In the current study, elevated concentrations of vinyl chloride, aniline, 2-methoxyethanol and 1,3-butadiene were observed in barn FS-LS with the highest number of cows. High levels of 1,3-butadiene were also associated with deep litter. Barn FS-LS was also characterized by a high concentration of chloromethane. In the literature, high levels of alcohol (ethanol and methanol) and acetic acid were also identified in barns in addition to methane (Gentner et al., 2014; Yuan et al., 2017). In the present study, the above compounds were not detected in air, but the presence of related compounds was confirmed. The compounds that were frequently identified in other studies (Filipy et al., 2006; Shaw et al., 2007; Yuan et al., 2017) include dimethyl sulfide (DMS), dimethyl disulfide (DMDS) and trimethylamine (Filipy et al., 2006). The above compounds were detected in our experiment, but DMS was not identified in barns FS-DL and FS-SFM, and trimethylamine was not found in barn FS-SFM. In barns, fermentation processes in the rumen and the fermentation of feed and manure are the main sources of organic gaseous admixtures in air, which is why the composition of exhaled air is largely influenced by feed ingredients, including silage (Bell et al., 2014). In general, secondary products from the chemical oxidation of other compounds are responsible for the formation of many oxygenated species (Gentner et al., 2014).

Agricultural production is one of the largest sources of GHG, but since 2000, it has been the only sector of the economy where GHG emissions decreased due to improvements in the management of farmland and livestock production (IPCC, 2014). According to published research, GHG emissions from livestock facilities can be decreased by modifying animal diets. In recent years, selective breeding has also emerged as an option for lowering GHG emissions in agriculture. The results of the present study indicate that housing systems, ventilation systems and the technological solutions applied in barns exert a considerable influence on the production of greenhouse and odorous gases. Free-stall housing with slatted floors and sub-floor manure storage appears to be the optimal solution for reducing the animals' exposure to the presence of the analyzed chemical compounds in air, improving animal welfare and minimizing GHG emissions to the environment (considering the optimal ventilation rate). It should be noted that the concentrations of other potentially harmful compounds, for which the maximum safe levels have been specified, were also relatively low in the remaining systems, which points to the observance of high sanitary standards and the use of efficient ventilation systems in the evaluated barns.

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