Zbigniew GORZKA¹, Marcin ZABOROWSKI¹, Marek KAŹMIERCZAK¹, Andrzej ŻARCZYŃSKI*¹, Tadeusz PARYJCZAK¹, Adam KĘDZIORA¹, Radosław CIESIELSKI¹ and Monika PISAREK¹

DETERMINATION OF AMMONIA AND OTHER POLLUTANTS IN AIR AND IN THE AREA OF POULTRY AND MILKER COWS KEEPING FARMS

OZNACZANIE AMONIAKU I INNYCH ZANIECZYSZCZEŃ W POWIETRZU NA TERENIE FERM HODOWLI DROBIU I KRÓW MLECZNYCH

Abstract: Polluted air in a big farm of poultry keeping (~18 thousands of chickens) and milker cows (30 animals) in Lodz province was sampled. The aim of the investigation was to determine odour pollutants, especially ammonia, in air and check the possibility of a catalytic method application in their removal. Gas samples were analyzed on the spot of sampling with an application of gases analyser Madur GA-20, as well as in a laboratory with an application of instrumental and spectrophotometric methods. The intensity of odours was estimated using five-stage scale applied by local authorities in Japan for odorous protection of air quality. Within sampling period, poultry keeping in the farm was the source of variable in time ammonia emission ranging from 0.82 to 2.65 mg/m³. Air inside the farm contained carbon dioxide (0–0.3 %) and oxygen (20.5–20.9 %). Carbon monoxide, sulphur dioxide, hydrogen sulphide (> 2.0 mg/m³) and formaldehyde (> 0.25 mg/m³) was not detected. The highest odour intensity inside the building of chicken keeping and at outlets of ventilators was at the third stage in odour scale applied in Japan (3.5), ie, clearly perceptible. However, it decreased significantly with the increase in a distance from the building. Higher ammonia concentrations were determined inside a cowhouse with milker cattle. They ranged from 3.2 to 5.6 mg/m³. Ammonia temporary concentration determined during removal of manure was higher and totalled 15.5 mg/m³. Its highest value (18.8 mg/m³) was determined in gases above slurry in the septic tank.

Keywords: chicken farms, ammonia determination, cowhouse, odours in agricultural production

Ammonia is a gas toxic not only for animals but also for people, and with negative effect on the natural environment. A global emission of ammonia is estimated at 62 mln Mg (ton) per year and 42 % of this amount originates from an animal farming [1]. In

¹ Institute of General and Ecological Chemistry, Technical University of Lodz, ul. S. Żeromskiego 116, 90–924 Łódź, Poland, phone: +48 42 631 31 18, fax: +48 42 631 31 28, email: andrzejzarcz@o2.pl

^{*} Corresponding author.

European countries, total emission is estimated at 8 mln Mg (ton) per year and 72 % of this amount comes from an animal farming [2]. In Poland, ammonia emission from agricultural sources was estimated at 314.610 Mg in 2005, according to National Emission Center. 70 % of this emission is ascribed to animal farming (Table 1) [1].

Table 1 Ammonia emission from the agriculture in Poland in 2005 [1]

Emission sources	Emission indicator	Unit	Emission [Mg (ton)]
Agriculture total			314.610
Cultivation with fertilizers application	9.8	%	87.740
Milker cows	27.8	kg per animal	76.580
Residual cattle	12.5	kg per animal	32.880
Fattening pigs	5.1	kg per animal	95.430
Sheep	1.9	kg per animal	0.600
Horses	12.5	kg per animal	3.900
Hens	0.32	kg per animal	14.460
Residual poultry	0.26	kg per animal	3.010

Poultry keeping as well as cattle keeping farms, are the biggest sources emitting pollutants of all types, *ie* chemical – gases, mechanical – dusts and biological – microorganisms. Ammonia is the most noxious gas for the environment, produced by poultry keeping farms. Ammonia is generated in poultry houses as a by-product during microbiological decomposition of organic compounds containing nitrogen in droppings and residual feed. The decomposition proceeds enzymatic or with the participation of anaerobic bacteria [1, 3, 4]. Gases removed by ventilation contain also dimethylamine, carbon monoxide and dioxide, aldehydes, ketones, organic acids and many other organic compounds belonging to odours [3–7].

High concentration of ammonia increases birds susceptibility to diseases, causes inflammation of eyes mucous membrane, problems with respiration and decreases a body mass increment [5, 6]. The main sources of ammonia are as follows:

- direct emission from poultry houses,
- places where litter and droppings are stored,
- cultivated field during poultry manure distribution [8-12].

The most important aim in the limitation of ammonia emission is maintenance of hygiene at the high level in the poultry house as well as equipment of efficient ventilation system. Well designed ventilation system prevents concentration of gases in the building and keeps temperature and humidity at the level which guarantees good mood and health of birds [1, 4].

Stock-farming is accompanied also by emission of different gases which causes air pollution and noxiousness of odours. The sources of gaseous pollutants are animals, their droppings, feeds and technological systems. Animals emit first of all carbon dioxide, and methane and odours gases (sulphur organic compounds, aromatic hydro-

carbons, organic acids, aldehydes, etc.) in lower amounts. Animal droppings are the source of ammonia which is the most noxious gas in this farming [1, 4, 9–20].

Experimental

Polluted air in a big farm of poultry keeping (\sim 18 thousands of chickens) in Łodz province was sampled. The aim of the investigation was to determine odour pollutants, especially ammonia, in air and check the possibility of a catalytic method application in their removal [2–4]. Gases sampling was carried out in the central part of the building (Fig. 1) and near outlets of ventilators at the height of 0.5 m [17–21], in the period of poultry fattening – 5^{th} and 6^{th} week of the keeping, at various day-times and seasons.



Fig. 1. Poultry house inside

Gases containing odours from milker cows farming were sampled in one farm building with two series of places for animals, taken up by 30 milker cows and in the septic tank collecting outflows from this building. The cowhouse length, width and average height was 25, 12.5 and 2.6 m inside, respectively. Cubic capacity of this building was 840 m³. The building was equipped with roof and side natural ventilation and fulfilled domestic and EU requirements. The septic tank was located behind the cowhouse and its dimensions were as follows: length – 11 m, width – 4 m, height – 2 m. This tank was filled up to one third of its volume during sampling.

Gas samples were analyzed on the spot of sampling with an application of gases analyser Madur GA-20, as well as in a laboratory with an application of spectrophotometric methods and gas chromatography (GC-MS). Colorimetric or spectrophotometric analyses included the determination of ammonia [22–24], hydrogen sulphide [25] and formaldehyde [26]. The intensity of odours was estimated using five-stage scale applied by local authorities in Japan for odorous protection of air quality. Table 2 presents concentration values of 4 among 8 obligatory air pollutants (ammonia, methanethiol,

hydrogen sulphide, dimethyl disulfide, trimethylamine, acetaldehyde and styrene), which determine potential harmfulness on five-stage scale applied by local authorities in Japan for determination of the highest allowable concentrations of odours in the environment [3]. The intensity of odour in air in work-places, as well as in air outside production buildings should not be higher than 3.5 stage (for ammonia 3.55 mg/m³) which is the upper level (clear) of this stage.

Table 2

A dependence of odour intensity on concentration of selected odours applied by local authorities in Japan during determination of the highest allowable concentrations [3]

		Odour concentration				
Odour intensity		[ppm]				[mg/m ³]
		Methanethiol CH ₃ SH	Acetaldehyde CH ₃ CHO	Styrene C ₆ H ₅ CHCH ₂	Ammonia NH ₃	Ammonia NH ₃
1	Detection threshold	0.0001	0.002	0.03	0.1	0.07
2	Recognition threshold	0.0007	0.01	0.2	0.5	0.36
2.5		0.002	0.05	0.4	1	0.71
3.0	Clear	0.004	0.1	0.8	2	1.42
3.5		0.01	0.5	2	5	3.55
4	Strong	0.03	1	4	10	7.10
5	Extreme strong	0.2	10	20	40	28.4

Results and discussion

Selected results of the pollutants determination in air from the poultry keeping farm (poultry house) and cowhouse with milker cattle are presented in Tables 3–5 and Tables 6–7, respectively.

The presence of ammonia was found inside the poultry house at varying concentrations in the range from 0.82 to 2.65 mg/m³ (Tables 3–5). Results of the analyses show that the ammonia concentration inside the building was a little bit higher at noon and in the evening. The ammonia concentration was only 0.26 mg/m³ (Table 5) in the air removed from the poultry house by the outlet of the side ventilator. Chromatographic analyses in the GC-MS system did not show ammonia content higher than 0.1 % or organic compounds concentrations higher than 1 mg/m³ possible for the detection in this system. Carbon monoxide, sulphur dioxide, hydrogen sulphide (> 2.0 mg/m³) and formaldehyde (> 0.25 mg/m³) was not detected. Traces of dust (not detected) arising from the building and covering ventilators casing or plants below their outlets, were observed.

Significant concentrations of ammonia (3.2–5.6 mg/m³) were determined in the cowhouse also in the height of 0.5 m above the sewer with temporary stored manure (Table 6). An increase in this odour concentration to 15.5 mg/m³ (Table 6) occurred during mechanical removal of manure (twice a day). The ammonia content in air was the highest inside the septic tank and totalled 18.8 mg/m³ (Table 7).

 $\label{eq:Table 3}$ Analysis results of air sampled in a large building of the poultry keeping farm [16]

Analogad	Air temperature insid	Measurements – 24.09.2009 (midday). r temperature inside the building 24 °C and outside the building 19 °C		Measurements – 01.10.2010 (evening). Air temperature inside the building 22 °C and outside the building 9 °C		
Analysed component	Air in the central part of the building at the height of 0.5 m	Air at the outle of a ventilator	Air in the central part of the building at the height of 0.5 m	Air at the outlet of a ventilator		
O ₂ [%]	20.5	20.9	20.9	20.9		
CO ₂ [%]	0.3	0	0	0		
CO [ppm]	0	0	0	0		
NH ₃ , mg/m ³	1.45-2.59	N.d.*	0.82-1.37	N.d.		
Formaldehyde [mg/m ³]	< 0.25	< 0.25	< 0.25	< 0.25		
Odour intensity: stage; description	3.0; clear	3.5; clear	2.5; clear	3.0; clear		

^{*} N.d. - not determined.

Table 4 Analysis results of air sampled inside the poultry house on November 30, 2009 (midday). Air temperature in the poultry house 22 $^{\circ}$ C and outside 6 $^{\circ}$ C

Analysed component	Analysis of gases supplied to a laboratory	Analysis of sorptive solutions collected in gas washers [16]	Air at the outlet of a ventilator [16]	Air in a distance of 10 m from the outlet of a ventilator [16]
O ₂ [%]	20.5	_	20.5	20.9
CO ₂ [%]	0.3	_	0.3	0
CO [ppm]	0	_	0	0
SO ₂ [ppm]	0	_	0	0
TOC in a solution in a gas washer [mgC/dm ³]	_	2.493	_	_
NH ₃ [mg/m ³]	1.29-2.39	1.97-2.65	N.d.	N.d.
Formaldehyde [mg/m ³]	< 0.25	N.d.	< 0.25	N.d.
Hydrogen sulphide [mg/m ³]	< 2.0	N.d.	< 2.0	N.d.
Odour intensity: stage; description	< 3.0; clear	_	3.5; clear	2.0–2.5; recognition threshold – clear

Air sampled in the poultry house, cowhouse and septic tank contained carbon dioxide in the concentration range 0–0.3 % and oxygen in the concentration range 20.5–20.9 %, determined using automatic gas analyser Madur GA-20. Carbon monoxide and sulphur dioxide were not detected. These pollutants are often present in gases emitted from municipal wastes dumps and fermented wastewater sludge, in which microbiological processes occurs under anaerobic conditions or under oxygen deficiency.

Table 5 Analysis results of air from the poultry keeping farm on May 25, 2010 (morning). Air temperature inside the building 22 $^{\circ}$ C and outside 20 $^{\circ}$ C [16]

Analysed component	Air sampled inside the poultry house at the height of 0.5 m from the ground	Air removed from the inside of the poultry house and sampled at the side ventilator outlet
O ₂ [%]	20.9	20.9
CO ₂ [%]	0	0
CO [ppm]	0	0
SO ₂ [ppm]	0	0
CH ₄ [ppm]	1.0	0
NH ₃ [mg/m ³]	0.84-1.19	0.26
Formaldehyde, mg/m ³	< 0.25	< 0.25
Hydrogen sulphide [mg/m³]	< 2.0	< 2.0
Odour intensity: degree; description	3.0–3.5; clear	2.5–3.0; clear

 $\label{eq:Table 6}$ Analysis results of air sampled inside the cowhouse before and during removal of manure from the storing sewer in March 17, 2010. Air temperature inside the cowhouse was 18 $^{\circ}\text{C}$

Analysed component	Air inside the cowhouse sampled at the height of 0.5 m, before manure removal	Air inside the cowhouse sampled at the height of 0.5 m, during manure removal
O ₂ [%]	20.9	20.9
CO ₂ [%]	0	0
CO [ppm]	0	0
SO ₂ [ppm]	0	0
NH ₃ [mg/m ³]	3.2–5,6	15.5
TOC of a solution in a scrubber [mgC/dm ³]	5.961	6.342
Formaldehyde [mg/m ³]	< 0.25	< 0.25
Hydrogen sulphide [mg/m³]	< 2.0	< 2.0
Odour intensity: stage; description	3.0–3.5; clear	3.5–4.0; clear – strong

Odour intensity was estimated using five-stage scale developed in Japan with the third stage splitted for three levels labelled as: 2.5, 3.0 and 3.5 (clear). The measurements proved that odour intensity in the air inside the poultry house and removed by the ventilators was the highest in the third stage, *ie*, clear, and reached the value of 3.5. The odour intensity decreased quickly with an increase in the distance from the ventilator in spite of air flow in the same direction (2–3 m/s), because in the

Table 7 Analysis results of air sampled inside the septic tank in March 17, 2010. Air temperature outside and inside the septic tank was 4 and 8 $^{\circ}$ C, respectively

Analysed component	Air sampled inside the septic tank
O ₂ [%]	20.9
CO ₂ [%]	0
CO [ppm]	0
SO ₂ [ppm]	0
NH ₃ , mg/m ³	18.8
TOC of a solution in a scrubber [mgC/dm ³]	5.362
Formaldehyde [mg/m³]	< 0.25
Hydrogen sulphide [mg/m³]	< 2.0
Odour intensity: stage; description	4.0; strong

distance of about 10 m, this intensity was only at the level of the stage limit – recognition threshold and clear, *ie*, 2.0–2.5. Odour intensity in the cowhouse was at the level of 3.0–3.5 (clear) but it increased to the level of 4 (strong) during removal of manure.

Summary

Within sampling period, poultry keeping in the farm was the source of variable in time ammonia emission ranging from 0.82 to 2.65 mg/m³. Higher concentrations of ammonia (3.2–5.6 mg/m³) were determined in air sampled in the cowhouse. Temporary increase in ammonia concentration to 15.5 mg/m³ occurred during removal of manure. However, the highest concentration (18.8 mg/m³) was determined in the underground septic tank. Air inside in farm contained carbon dioxide (0–0.3 %) and oxygen (20.5–20.9 %). Concentrations of ammonia determined in the poultry house in the evening were lower than in the morning and at noon.

Carbon monoxide, sulphur dioxide, hydrogen sulphide (> 2.0 mg/m³) and formaldehyde (> 0.25 mg/m³) was not detected. The highest odour intensity inside the building of chicken keeping and at outlets of ventilators was at the third stage in odour scale applied in Japan (3.5), *ie*, clearly perceptible. However, it decreased significantly with the increase in a distance from the building. Odour intensity in the cowhouse was at the level of 3.0–3.5 (clear) and increased to the level of 4 (strong) during removal of manure.

References

- [1] Wójcik A. Emisja amoniaku w budynkach dla trzody chlewnej. Hodowca Trzody Chlewnej. 2008;4:28-33.
- [2] Sapek A. Emisja amoniaku z produkcji rolnej. Post Nauk Rol. 1995;2(95):3-23.
- [3] Kośmider J, Mazur-Chrzanowska B, Wyszyński B. Odory. Warszawa: Wyd Nauk PWN; 2002.
- [4] Szynkowska MI, Zwoździak J, editors. Współczesna problematyka odorów. Warszawa: Wyd Nauk Techn; 2010.

- [5] Guz M, Guz L. Emisja amoniaku do powietrza z fermy indyków. Annal Universit Mariae Curie--Skłodowska, Lublin Polonia, Sectio DD. 2005;LX(21):158-165.
- [6] Pescatore AJ, Casey KD, Gates RS. Ammonia Emissions from Broiler Houses. J Appl Polut Res. 2005;14(3):635-637.
- [7] Lahav O, Mor T, Heber AJ, Molchanov S, Ramirez JC, Li C, Broday DM. A New Approach for Minimizing Ammonia Emissions from Poultry Houses. Water Air Soil Pollut. 2008;191:183-197. DOI: 10.1007/s11270-008-9616-0.
- [8] Domagalski Z, Podleski J. Co z tym amoniakiem?. Indyk Polski. 2007;3:26-31.
- [9] Delaune PB, Moore PA, Daniel TC, Lemunyon JL. Effect of chemical and microbial amendments on ammonia volatization from composting polutry litter. J Environ Qual. 2004;33(2):728-734. DOI: 10.2134/jeq2004.7280.
- [10] Ferm M, Marcinkowski T, Kieronczyk M, Pietrzak S. Measurements of ammonia emissions from manure storing and spreading stages in Polish commercial farms. Atmos Environ. 2005;39(37):7106-7113. DOI.org/10.1016/j.atmosenv.2005.08.014.
- [11] Oenema O. Oudendag DA, Witzke HP, Monteny GJ, Velthof GL, Pietrzak S, Pinto M, Britz W, Schwaiger E, Erisman JW, de Vries W, van Grinsven JJM, Sutton M. Integrated measures in agriculture to reduce ammonia emissions. Final summary report. Contract number 070501/2005/422822/MAR/C1. Tenderer Consortium Alterra, Wageningen UR, The Netherlands; EuroCare, University of Bonn, Germany; ASG, Weningen UR, The Netherlands. Weningen: Alterra; 2007, pp 186.
- [12] HJ, Xin H, Mendes LB, Li H, Bailey TB. Ammonia emission and performance of laying hens as affected by different dosages of Yuccaschidigera in the diet. J Appl Polut Res. 2012;21:522-530. DOI: 10.3382/japr.2011-00420.
- [13] Makles Z, Domański W. Odory w środowisku pracy rolnika-hodowcy. Źródła, zagrożenia, usuwanie. Bezpieczeństwo Pracy. 2008;437(2):10-13.
- [14] Burgos SA, Embertson NM, Zhao Y, Mitloehner FM, DePeters EJ, Fadel JG. Prediction of ammonia emission from dairy cattle manure based on milk urea nitrogen: relation of milk urea nitrogen to ammonia emissions. J Dairy Sci. 2010;93(6):2377-2386. DOI: 10.3168/jds.2009-2415.
- [15] Bieńkowski J. Regionalne zróżnicowanie emisji amoniaku w polskim rolnictwie w latach 2005–2007. Fragm Agron. 2010;27(1):21-31.
- [16] Gorzka Z, Zaborowski M, Kaźmierczak M, Żarczyński A, Paryjczak T, Kędziora A, Ciesielski R, Pisarek M. Determination of ammonia and other pollutants in air and in the area of polutry keeping farms. Proc ECOpole. 2011;5(1):41-45.
- [17] Pisarek M. Oczyszczanie powietrza z substancji odorowych metodą termokatalitycznego utleniania. Praca dyplomowa magisterska. Łódź: IChOiE, Politechnika Łódzka; 2010.
- [18] Szynkowska M, Wojciechowska E, Węglińska A, Paryjczak T. Katalizatory stosowane w reakcji utlenienia związków złowonnych. Przem Chem. 2008;87(8):834-843.
- [19] Sówka I, Szklarczyk M, Zwoździak J, Zwoździak P, Nych A. Charakterystyka metod poboru gazów odorotwórczych w świetle przepisów europejskich. Przem Chem. 2009;88(5):571-573.
- [20] Sówka I, Skrętowicz M, Zwoździak J, Kunecka J. Application of a GIS technique to odour emission inventory. Ecol Chem Eng S. 2011;18(4):445-453.
- [21] PN-Z-004008-7. Ochrona czystości powietrza. Pobieranie próbek. Zasady pobierania próbek powietrza w środowisku pracy i interpretacji wyników. Warszawa: Polski Komitet Normalizacyjny; 2002.
- [22] Wiktorowski S, Anielak P. Instrukcja do ćwiczenia pt.: Oznaczanie różnych form azotu. Oznaczanie azotu amonowego według PN-76/C-04576, Łódź: IChOiE PŁ; 1999.
- [23] PN-76/C-04576. Badania zawartości azotu i jego związków. Oznaczanie amoniaku na stanowiskach pracy metodą spektrofotometryczną w świetle widzialnym. Warszawa: PKNMiJ; 1990.
- [24] PN-90/Z-04009/03. Ochrona czystości powietrza. Badania zawartości związków azotu. Oznaczanie amoniaku na stanowiskach pracy metodą spektrofotometryczną w świetle widzialnym. Warszawa: PKNMiJ; 1990.
- [25] PN-Z-04015-13. Ochrona czystości powietrza. Badania zawartości związków siarki i jej związków. Oznaczanie siarkowodoru na stanowiskach pracy metodą spektrofotometryczną. Warszawa: PKNMiJ; 1996
- [26] PN-76/Z-04045/02. Oznaczenie formaldehydu na stanowiskach pracy metodą kolorymetryczną z chlorowodorkiem fenylohydrazyny. Warszawa: PKNMiJ; 1990.

OZNACZANIE AMONIAKU I INNYCH ZANIECZYSZCZEŃ W POWIETRZU NA TERENIE FERM HODOWLI DROBIU I KRÓW MLECZNYCH

Instytut Chemii Ogólnej i Ekologicznej Politechnika Łódzka

Abstrakt: Wykonano pobory próbek zanieczyszczonego powietrza z dużej fermy drobiu rzeźnego (~18 tys. kurcząt) oraz budynku hodowli bydła mlecznego (30 zwierząt) w województwie łódzkim. Celem badań było wykonanie analiz powietrza na zawartość zanieczyszczeń odorowych, zwłaszcza amoniaku, a w perspektywie zbadanie możliwości zastosowania metody katalitycznego utleniania do ich usuwania. Próbki gazów były analizowane na miejscu pobierania za pomocą automatycznego analizatora gazów Madur GA-20, a także w laboratorium metodami instrumentalnymi i spektrofotometrycznymi. Do oceny intensywności zapachu zastosowano pięciostopniową skalę wykorzystywaną przez władze lokalne w Japonii do ochrony zapachowej jakości powietrza. Hodowla drobiu w badanej fermie była w okresie pobierania źródłem zmiennej w czasie emisji amoniaku w granicach 0,82-2,65 mg/m³. W powietrzu obiektu stwierdzono 0-0,3 % ditlenku wegla i 20,5-20,9 % tlenu, natomiast nie wykryto tlenku węgla, ditlenku siarki, siarkowodoru (> 2,0 mg/m³) ani formaldehydu (> 0,25 mg/m³). Największa intensywność zapachu wewnątrz budynku hodowli kurcząt, a także na wylotach wentylatorów była w trzecim stopniu skali zapachu stosowanej w Japonii (3,5), tj. wyraźna, jednak znacznie obniżała się wraz z oddalaniem się od obiektu. Znaczniejsze były stężenia amoniaku w powietrzu budynku hodowli bydła mlecznego, które mieściły się w zakresie 3,2-5,6 mg/m³. Wyższe było stężenie chwilowe amoniaku podczas usuwania obornika 15,5 mg/m³, a najwyższe w gazach nad gnojowicą w zbiorniku szamba 18,8 mg/m³.

Słowa kluczowe: fermy drobiu, oznaczanie amoniaku, obora bydła mlecznego, odory w produkcji rolnej