ANNALES
UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA
LUBLIN – POLONIA
VOL. XXVI (2) SECTIO EE 2008

Katedra Higieny Zwierząt i Środowiska Uniwersytetu Przyrodniczego w Lublinie,
ul. Akademicka 13, 20-950 Lublin,
e-mail: anna.korzeniowska@up.lublin.pl

ANNA CHMIELOWIEC-KORZENIOWSKA, LESZEK TYMCZYNA,
RENATA WIĘCH

Air emission of merkaptans and other sulfur compounds from poultry farm

Emisja merkaptanów i innych związków siarki z fermy drobiu

Summary. The air chromatographic analysis conducted at the poultry farm and its surrounding area aimed at determination of organic and inorganic sulfur compound concentration. The studies revealed the presence of air sulfur compounds of a markedly odourgenic nature, such as hydrogen sulfide, sulfides, disulfides and merkaptans. The average concentration of sulfur compounds (including unidentified ones) in the air of the hen house reached 73.06 $\mu g \cdot m^{-3}$. Besides, the increased gaseous pollutant level in the air was established. The content of the determined contaminants was subject to a sampling site and time, in that atmospheric air temperature. The concentration of the identified merkaptans sum exceeded the average reference values in the air for a calendar year.

Key words: air, sulfur compounds, poultry farm

INTRODUCTION

The environment degradation process has been observed to rise so rapidly that the only chance for further economic advance is the effective environmental management program to control the actual quantity of pollutants released to the atmosphere. That refers to all the sectors of economy, both industry and municipal economy as well as agriculture.

Out of breeding farms, the poultry ones are recognized the major source of emissions [Koerkamp *et al*. 1998; Tymczyna *et al*. 2000]. The poultry industry has become increasingly consolidated, specialized and automated, consequently, it generates large amounts of by-products, including that high loads of organic and inorganic off-gases. The compounds released through the microbiological processes often show toxic and odorogenous properties that pose a threat to animal health and discomfort of neighboring residents.

The objective of the present research was to assess air hygiene in the hen houses of meat-type hens and within the poultry farm.

MATERIAL AND METHODS

The investigations were conducted in the farm of meat-type hens Cobb and Ross lines of total 60 thousand stock and annual production of over 10 million eggs, near Góra Kalwaria in 2006 and 2007.

In the present study, air hygiene evaluation included the analysis of indoor (breeding) and outdoor (atmospheric) air pollutant concentration. The air for analysis was collected at three measurements sites: 1) hen house, 2) between the hen houses (atmospheric air), 3) 100 m off the farm boundary. At each measurement site, 2 air samples were taken in 5 consecutive series. Totally, 30 air samples were obtained throughout the 7-month research period (April – October).

Volatile organic air pollutants were determined using the gaseous chromatography procedure. The air samples (2–3 l) were collected with an electrical pump into Tedlar bags. Organic compounds present in the air samples were concentrated through adsorption then desorbed using the kit for thermal desorption TDV Model 890, Dynatherm Analytical Instruments Inc. for the chromatography system HP 5890 series II, Hewlett Packard equipped with a selective flame photometric detector (FPD) combined with S-filter of 393 nm wave length.

The air samples were withdrawn to bubblers in order to determine their inorganic compound contents using a Water`s liquid chromatograph connected with analytical column IC-PAK Anion HR combined with a conductometric detector and UV.

Besides the air chromatographic analysis, there were monitored the thermal and moisture properties of atmospheric air that were maintained at a constant level 18 ± 0.5°C and 45 ± 0.5% in the hen house.

The obtained data were analyzed statistically with Student`s t test.

RESULTS AND DISCUSSION

The air chromatographic analysis conducted at the hen farm and its surroundings aimed at determination of the odorogenous inorganic and organic sulfur compound contents. The mean concentration of indoor (hen house) air sulfur compounds (including unidentified ones) was found to reach 73.06 $\mu g \cdot m^{-3}$ (Tab. 1). The established pollutant levels tended to decrease with the distance downwind from the poultry houses. The dependence was not confirmed statistically.

The analyzed air samples showed the presence of hydrogen sulfide and sulfur dioxide as well as sulfide, disulfide and merkaptans. The highest contents of nearly all gaseous pollutants were detected in the hen house. The reported differences were statistically significant only for diethyl sulfide and ethyl merkaptan, whose mean air concentrations in the poultry house averaged 1.83 $\mu g \cdot m^{-3}$ and 13.22 $\mu g \cdot m^{-3}$, respectively.

Some pollutants had the highest levels recorded between the poultry buildings due to poultry manure stored in this place that constituted the source of air pollution with odorogenous compounds. Hence, the highest contents of hydrogen sulfide, SO_2 and methyl ethyl sulfide were detected there. However, higher concentrations of the identified compounds recorded off-farm were likely to emerge through these compounds release to the atmosphere from the ventilation system.

Table 1. Air sulfur compound concentration in each site (μg·m^{-3})
Tabela 1. Koncentracja związków siarki w powietrzu w poszczególnych miejscach (μg·m^{-3})

Compound Związek	Place, Miejsce					
	poultry house kurnik		between poultry houses między kurnikami		100 m from the farm boundary 100 m od granicy fermy	
	M	SD	M	SD	M	SD
Hydrogen sulfide Siarkowodór	3.804	2.761	4.417	1.420	2.745	1.474
SO_2	15.999	10.083	19.492	13.095	14.317	13.845
CS_2	10.262	5.005	8.072	2.246	nd	
Diethyl sulfide Siarczek dwuetylowy	1.839 A, B	0.001	0.688 B	0.437	1.174 A	0.000
Methyl sulfide Siarczek metylowy	9.731	0.010	nd		6.970	10.587
Dipropyl sulfide Siarczek dwupropylowy	2.738	4.587	0.886	0.173	0.977	0.324
Methyl ethyl sulfide Siarczek metyloetylowy	1.680	0.710	2.121	0.715	1.393	1.305
Methyl propyl sulfide Siarczek metylopropylowy	0.271	0.010	nd		nd	
Dimethyl disulfide Dwusiarczek dwumetylowy	0.776	0.010	nd		0.045	0.008
Ethyl merkaptan Merkaptan etylowy	13.222 a	7.505	7.018	2.925	3.640 a	4.027
Methyl merkaptan Merkaptan metylowy	0.128	0.010	nd		0.830	0.000
Isopropyl merkaptan Merkaptan izopropylowy	6.881	0.010	1.123	1.380	2.722	1.875
Butylic merkaptan Merkaptan butylowy	1.092	0.010	0.762	0.010	0.081	0.001
Total, including unidentified Razem (w tym niezidentyfikowane)	73.063	49.653	58.948	15.596	51.12	109.39

a, b… – values denoted with the same letters differ significantly at $p \leq 0.05$ (a, b…) and $p \leq 0.01$ (A, B…), wartości zaznaczone tymi samymi literami różnią się statystycznie dla $p \leq 0{,}05$ (a, b…) i $p \leq 0{,}01$ (A, B…)
nd – not detected, nie występuje

The concentration of air gaseous pollutants showed marked fluctuations. The microbial change rate of sulfur compounds, and consequently the air pollutant level, was significantly affected by the outdoor air temperature.

The content of merkaptans and sulfides was observed to increase over the research period with the peak in IV study series when the atmospheric air temperature recorded was over 15°C (Tab. 3). Only for methyl ethyl sulfide, this difference proved to be statistically significant ($p \leq 0.01$). In IV study series, its highest concentration – 2.556 μg·m^{-3} was determined, which was three times the lowest value – 0.79 μg·m^{-3} established in III series.

Table 2. Air sulfur compound level in each series (μg·m^{-3})
Tabela 2. Koncentracja związków siarki w powietrzu atmosferycznym w poszczególnych seriach (μg·m^{-3})

Compound Związek	Serie, Seria									
	I		II		III		IV		V	
	M	SD	M	SD	M	SD	M	SD	M	SD
Hydrogen sulfide Siarkowodór	5.05 A	0.64	5.36 B	1.09	3.57	1.83	2.38	1.30	1.42 A,B	1.05
SO_2	26.91 A	6.49	15.58	5.83	18.50	14.36	19.50	14.32	2.51 A	0.46
CS_2	11.32	2.59	11.67	2.07	7.35	0.01	4.85	0.53	nd	
Diethyl sulfide Siarczek dwuetylowy	1.36	0.41	1.35	0.41	0.27	0.01	nd		0.35	0.01
Methyl sulfide Siarczek metylowy	2.40	0.01	2.33	0.01	5.04	6.63	22.78	0.01	nd	
Dipropyl sulfide Siarczek dwupropylowy	0.72	0.17	0.78	0.11	0.83	0.28	1.04	0.30	10.94	0.01
Methyl ethyl sulfide Siarczek metyloetylowy	1.98 A	0.31	1.98 B	0.31	0.79ABC	0.35	2.55 C	0.30	nd	
Methyl propyl sulfide Siarczek metylopropylowy	0.27	0.01	nd		nd		nd		nd	
Dimethyl disulfide Dwusiarczek dwumetylowy	nd		nd		nd		0.03	0.01	0.41	0.51
Ethyl merkaptan Merkaptan etylowy	7.06	5.16	6.85	4.84	5.59	0.01	13.13	0.01	12.54	11.62
Methyl merkaptan Merkaptan metylowy	0.83	0.01	0.83	0.01	0.12	0.01	nd			
Isopropyl merkaptan Merkaptan izopropylowy	nd		nd		1.74	0.49	3.69	3.38	nd	
Butylic merkaptan Merkaptan butylowy	nd		nd		0.76	0.01	0.58	0.71	nd	
Total, including Unidentified ones Razem (w tym niezidentyfikowane)	51.92	18.24	51.80	18.14	41.30	27.66	85.92	139.33	67.81	80.42

nd – not detected, nie występuje

Table 3. Results of air measurements over the study period
Tabela 3. Wyniki pomiarów powietrza atmosferycznego w okresie badawczym

Serie Seria	Temperature, °C Temperatura, °C	Relative humidity, % Wilgotność względna, %
I	7.4	72
II	7.9	72
III	8.6	76
IV	15.2	76
V	8.8	85

The present research revealed a significant decline in the rate of air pollution with hydrogen sulfide and sulfur dioxide ($p \leq 0.01$). The highest level of these substances was noted in I study series, while the lowest in the last, i.e. V series.

The gaseous pollutants being the source of noxious odors, mostly appear as mixtures of a large number of contributing compounds, whose qualitative composition still re-

mains unknown. They include sulforganic compounds, widely occurring in the environment where rapid decomposition of organic matter comprising sulfur proceeds [Rosenfeld *et al*. 2001]. An offensive rotten odor is detectable at low concentrations, e.g. ethyl merkaptan odor strength detectability is only 0,04 $\mu g \cdot m^{-3}$ [Chyba 1975].

Exposure to malodor involves a subjective response of organism and thus is a factor producing development or enhancement of psychic discomfort that may lead to some disorders of the somatic system. The long-term exposure, however, has serious effects like immunity impairment, reduced performance and a higher rate of disease prevalence [Wood 1978].

The chemical characteristics of sulforganic substances frequently resemble those of hydrogen sulfide which is recognized to possess highly toxic properties. The compounds paralyze the respiratory and the central nervous system, while at high levels may damage pulmonary alveolus walls and cause necrosis [Roh *et al*. 1998; Sills *et al*. 2005]. Carbon dioxide is the main contributor to the atherosclerosis-based cardiovascular changes producing myocardial ischemia and hypertension. As a lyophillic compound, it penetrates the central and peripheral nervous system. Workers occupationally exposed to carbon dioxide were commonly reported to have gastrointestinal disorders, i.e. gastritis and bile ducts dysfunction [Seńczuk 2005].

According to the regulations laid out in the Act on Environmental Protection dated 2001 [Ustawa... 2001], no emission standards or acceptable levels of substances in the air impose establishment of acceptable quantities of gaseous air components so that they do not exceed the reference values which are specified by the Regulation of the Ministry of Environment of 2002 [Rozporządzenie... 2002]. Comparison of the data obtained for gaseous pollutants in the analyzed air revealed that only the concentration of merkaptan sum surpassed the average reference values for a calendar year 2.0 $\mu g \cdot m^{-3}$ and 20.0 $\mu g \cdot m^{-3}$ for an hour. On the other hand, the levels of sulfur dioxide, carbon disulfide and dimethyl disulfide under the same air emission regulation did not exceed the established reference values.

Toxicity, a clear odorogenous character and emission rate of these compounds released from the poultry farm as well as their persistent high concentration in the air, even 100m downwind from the farm boundary, may be a useful indicator considered when setting up the protective zone (shelterbelt) around the animal farm. The type of odor constituents and their strength is dependent on birds` health, nutrition, kind of rotting and fermentative processes occurring in the litter bed. Efficient control strategies concerning the above mentioned factors, stringent compliance with the zoohygienic procedures as well as a good management plan for manure application effectively reduce odor production and emission over the area neighboring with a poultry farm.

CONCLUSIONS

1. Air chromatographic evaluation conducted at the poultry farm revealed the presence of sulfur compounds of a strong odorogenous nature, including hydrogen sulfide, sulfides, disulfides and merkaptans. In the hen house air, the concentration of air pollution with sulfur compounds (in that unidentified) reached 73.06 $\mu g \cdot m^{-3}$. Besides, an increased level of air gaseous pollutants was also detected outside the poultry buildings.

2. The levels of the determined pollutants were affected by a sampling site and time, including ambient temperature.

3. Concentration of all the identified merkaptans exceeded the reference values in the average atmospheric air for a calendar year.

REFERENCES

Chyba A., 1975. Progi zapachu substancji zanieczyszczających powietrze atmosferyczne. Gaz, Woda Tech. Sanit., 9, 280–285.

Koerkamp P.W.G.G., Metz J.H.M., Uenk G.H., Philips V.R., Holden M.R., Sneath R.W., Short J.L., White R.P. Hartung J., Seedorf J., Schroeder M., Linkert K.h., Pedersn S., Takai H., Johnsen J.O., Wathes C.M., 1998. Concentrations and emissions of ammonias in livestock buildings in Northern Europe. J. Agric. Eng. Res., 70, 1, 79–95.

Roh J., Cho M., Kim Ch., Lee K., Won J., 1998. Acid–labile bound carbon disulfide in whole blond of rats as a biological indicator for carbon disulfide Exposure. Appl. Occup. Environ. Hyg. 13(4), 252–256.

Rosenfeld P E., Henry Ch L., Russell L. Dills, Harrison R. B., 2001. Comparison of odor from three different biosolids applied to forest soil. Water, Air, and Soil Pollution 127, 173–191.

Rozporządzenie Ministra Środowiska z dnia 5 grudnia 2002 r. w sprawie odniesienia dla niektórych substancji w powietrzu (Dz.U. z 2003 r., nr 1, poz. 12).

Seńczuk W., 2005. Toksykologia kliniczna. PZWL Warszawa.

Sills R C., Jean Harry G., W M Valentine., Morgan D L., 2005. Interdisciplinary neurotoxicity inhalation studies: Carbon disulfide and carbonyl sulfide research in F344 rats. Toxic. Appl. Pharmac., 207, 245–250.

Tymczyna L., Malec H., Odój J., 2000. Badania emisji chemicznych zanieczyszczeń powietrza w fermie niosek reprodukcyjnych. Rocz. Nauk. Zoot. 29 (1), 241–247.

Ustawa z dnia 27 kwietnia 2001 r. Prawo ochrony środowiska. (Dz.U. z 2001 r., nr 62, poz. 527).

Wood R.W., 1978. Stimulus properties of inhaled substances. Environ. Health Perspect., 26, 69–76.

Streszczenie. Analiza chromatograficzna powietrza zarówno na fermie kur, jak i w jej otoczeniu, przeprowadzona została w celu określenia wartości stężeń związków siarki pochodzenia organicznego i nieorganicznego. Badania wykazały obecność w powietrzu związków siarki o wyraźnie odorotwórczym charakterze, wśród nich: siarkowodoru, siarczków, dwusiarczków i merkaptanów. W powietrzu kurnika średnia koncentracja zanieczyszczeń związkami siarki (w tym niezidentyfikowanymi) wyniosła 73,06 $\mu g \cdot m^{-3}$. Stwierdzono również zwiększoną koncentrację gazowych zanieczyszczeń w powietrzu atmosferycznym poza budynkami inwentarskimi. Na kształtowanie się poziomów oznaczonych zanieczyszczeń wpływ miały miejsce i czas pobierania prób oraz temperatura powietrza atmosferycznego. Koncentracja sumy zidentyfikowanych merkaptanów przekraczała wartości odniesienia w powietrzu atmosferycznym uśrednione dla roku kalendarzowego.

Słowa kluczowe: powietrze, związki siarki, fermy kur