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DETERMINATION OF AIR AMMONIA AND HYDROGEN SULFIDE AT A PIG FARM IN CLUJ COUNTY

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ABSTRACT. Dispersed in the environment, ammonia and hydrogen sulphide are found in various factors (water, air, soil) from where they are taken up by animal and vegetable bodies. Air pollution from these substances mainly results from the decomposition of plant and animal debris. The quality and the composition of the manure, the way they are stored and handled are the main factors that determine the levels of emissions, while the pollutants and odor are being directly emitted by the housing system. This study has observed the determination of ammonia and hydrogen sulfide in a pig farm in Cluj County, and it was carried out during May-September 2011 and 2012. In order to determine the monitored atmospheric pollutants, analytical methods derived from STAS 10812-1976 - Air purity were used. Determination of ammonia from STAS 10814-1976 - Air purity. Determination of hydrogen sulfide. There were no values above the method detection limit (0.3 mg / mc for ammonia and 0.015 mg / mc for hydrogen sulfide) in the sampled and analyzed imissions, and these values were well below the maximum admissible concentration provided by STAS 12574-87 regarding air in protected areas. However, in Europe, a new environmental protection legislation imposes reductions in ammonia and hydrogen sulfide emissions from livestock production.

Key words: *ammonia, hydrogen sulfide, pigs, dispersions*

INTRODUCTION

Recent studies suggest that human activities accelerate the production of reactive nitrogen on a global scale. In the last 50 years, emissions of ammonia (NH_3), which represent the most abundant reactive nitrogen in the atmosphere, have increased significantly as a result of intensive agricultural management and greater animal production in many developed countries. (McCrory and Hobbs, 2001; Aneja et al., 2008)

Pig farms are important sources of emissions of ammonia (NH_3). The main factors influencing the production of NH_3 are the type of floor, the disposal of manure, climatic conditions inside the building, diet composition and feed efficiency (Philippe et al., 2011).

More than half of the world's pig production is currently industrialized and their concentration in the regional areas is observed in many parts of the world (Jorgen et al., 2010).

Emissions from swine manure storage systems are putting the quality of the air at risk because of the effects that compounds such as hydrogen sulfide, ammonia, methane, and volatile organic compounds have on the environment and on human health (Zahn et al., 2001).

Pigs' odor is usually caused by a complex mixture of odorants that can occur in any of the gaseous, liquid or solid phases. For nearby workers and neighbors who inhale smelly air emissions from swine farms, the most notable acute health effects are eye, nose, throat irritations, headaches, nausea, diarrhea, sore throat, chest spasms, nasal congestions, palpitations, shortness of breath, stress and sleepiness (Joachim et al., 2010).

The quality of the air inside animal farms is also very important for the health of workers and animals (Q.Ni et al., 2000).

Although the responsible processes are considered "natural", emissions from manure can be considered anthropogenic in nature, due to the influence of human management, both in terms of introducing nitrogen feed and spatial concentration due to intensive agricultural practices. (Dragosits et al., 2008)

Hydrogen sulfide odor, associated with the "rotten egg" smell, causes dizziness, fainting, headaches and vomiting. The smell penetrates both clothes and human tissue. Out of the approximately 300 existing substances in swine manure causing the characteristic odor, hydrogen sulfide and ammonia are the most known inorganic compounds (Apostol, 2006).

In Europe, new environmental legislation requires emissions reductions of ammonia and odor (hydrogen sulfide) from animal production. (Pahl et al., 2002)

The objective of this paper is to assess the quality of the air in neighboring human communities (sensitive receptors in order to quantify the possible effects on health and quality of life) of a pig farm in Cluj County, assessed by the presence of ammonia and hydrogen sulfide.

MATERIALS AND METHODS

The study area is a pig farm with a capacity of 4000 heads located at a distance of 70 m from the inhabited area. Ammonia concentrations near the farm were evaluated by mathematical calculation (emissions and imissions) and direct measurements (imissions).

Estimate ammonia emissions

The following data was used to estimate the emissions:

- 4000 pig heads (> 30 Kg)/set, 3 sets/year;
- 2 halls, 7 m heigh ventilation stacks, 14 fans/hall, stack ventilation with a diameter of 790 mm, air flow 3500 mc/h/fan;
- emission factors for pig weighing more than 30 kg: NH_3 = 2.87 kg/place/year as "EMEP/CORINAIR Emission Inventory Guidebook 2009", latest edition, 4. Agriculture - 4.B Animal husbandry and manure management.

Estimate ammonia imissions

Ammonia imissions estimation is done using Gaussian mathematical models. The models are using entry data that are characteritsic to the emissions of pollutants and yearly or seasonal meteorological triplet factor frequencies: wind direction and speed, the degree of atmosphere stratification.

For the studied area, there is no data concerning the direction and speed of the wind, or on the degree of stratification. This is why it is impossible to use mathematical models to calculate the average concentrations at any point on a chosen area (usually square).

U.S. Environmental Protection Agency (EPA) recommends the use of a program for calculating immission concentrations of pollutants called SCREEN3. (http://www.weblakes.com/products/screen/index.html) This program takes into account all classes of stability featuring wind speeds for these classes to determine the maximum impact one can register from a specific source of pollution.

The modeling of the SCREEN3 results was realized using Open Source GIS Software, namely Quantum GIS 1.8. (http://qgis.osgeo.org/), and its GRASS 6.4.2. (Geographic Resources Analysis Support System) interface. (http://grass.osgeo.org/) The Stereo70 grid of the study area contains the CLC2000 dataset (Corine Land Cover 2000). (http://www.indd.tim.ro)

Sampling

Immission samples from the pig farm in Cluj County (Figure 1) were taken in 2011 and 2012 during the May - September period, for ammonia and hydrogen sulfide determination. The sampling points were established in accordance with the environmental permit limits in the South-West (SW) - sample 1, North-West (NW) - sample 2, North-East (NE) - sample 3 and South-East (SE) - sample 4.

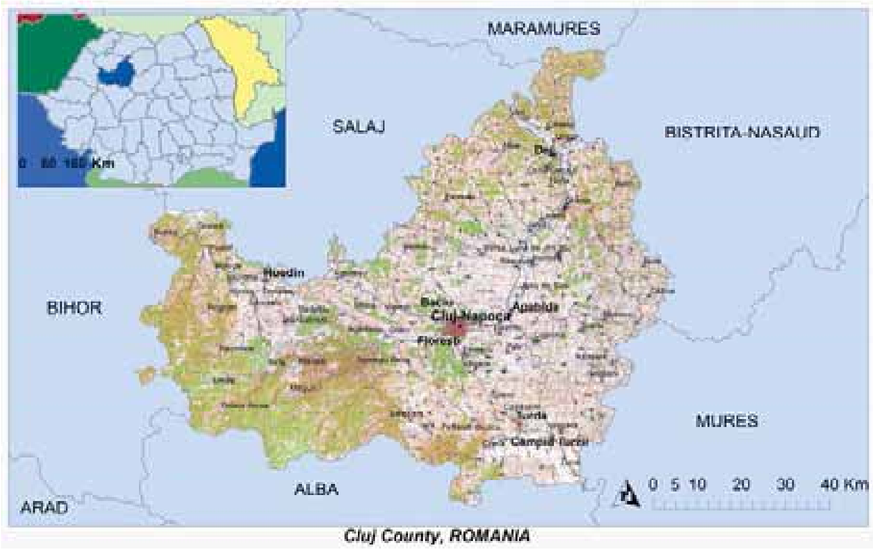

Fig. 1. *Framing in the area of Cluj County*

Air sampling is a very important step in the determination process of ammonia and hydrogen sulfide because samples must be representative and must not produce changes in the composition and air quality due to a poor technique or to improper conditions of material preparation.

Before starting the tests it is necessary to verify that the glassware is clean, with no cracks or breaches. Periodically, the glass needs to be washed with a sulfochromate mixture, rinsed thoroughly with water and then with distilled water. Next, it needs to be connected in series through silicone tubes with frit tank absorption, output capacity for ammonia of 20 ml and for hydrogen sulfide 50 ml and sampling pump. Next, one needs to adjust the flow rate to 3.2 l/min for ammonia and 0.1 l/min for hydrogen sulfide using the rotameter. 20 ml of absorbent solution is inserted in the absorption vessel through a 25 ml cylinder. After sampling, the content of the flask needs to be quantitatively transferred into 50 ml polypropylene container and kept at a temperature of 4ºC until it reaches the laboratory. Regarding the hydrogen sulfide, during the sample harvest and transportation, absorption vessels and polypropylene containers shall be protected from the light (STAS 10812-1976; STAS 10814-1976).

Samples analysis

The analytical method for determination of ammonia in the atmosphere is derived from STAS 10812-1976 - Air purity. Determination of ammonia and the hydrogen sulfide determination from STAS 10814-1976 - Air purity. Determination of hydrogen sulfide.

In order to determine the ammonia concentration, absorbent solution and Nessler reagent needs to be poured over the contents of the container hosting the sample. The new content needs to be mixed and measured after 30 minutes in order to determine the extinction of the solution to the spectrophotometer. Regarding the determination of hydrogen sulfide, N, N-dimethyl-p-phenylenediamine and ferric chloride solutions need to be poured over the absorption flask contents, and, after one hour, one needs to measure the extinction of the solution. The extinction value is read from the calibration curve and one can find out the concentration of ammonia and hydrogen sulfide in the photometric sample in µg/ml. (STAS 10812-1976; STAS 10814-1976)

RESULTS

The site inspection has showed that the eastern area is hosting the residential neighborhoods with individual households, and the nearest house is located at 70 m. The farm is compound of two identical animal stables with a capacity of approximately 2000 animals each. In addition, there is also a sanitary filter building and other buildings and facilities in accordance with the legislation. Pig farming is done in pens on slatted floors. Pigs weighting 30 kg are brought into the halls and they are fattened until they reach a weight of 100-110 kg. This involves housing pigs for 24 weeks, while they are being transferred from a youth farm. Manure and water from the washed pens is collected via the floor’s grill system, on water cushions, then they are disposed in the closed catchment area; each stall hosts one. From here, they are transferred to the decanter and then, after a decomposition cycle lasting 6 months, the sludge is removed and used as fertilizer in agriculture.

Ambient air quality in Romania is regulated by Law no. 104/15.06.2011, and aims to protect human health and the environment as a whole by regulating measures to maintain ambient air quality where it meets the objectives for ambient air quality established by this law and improving it in other cases. (Law no. 104/15.06.2011)

According to the environmental permit, the farm monitoring period lasts from May to September.

The estimated value of ammonia emissions from the pig farm is of 0.37 g/s.

The estimation of ammonia emissions was done considering two situations:

Situation I: NH_3 emission at maximum ventilation capacity 504000 m³/h
NH_3 = 2,6 mg/m³ < 30 mg/m³

Situation II: NH_3 emissions at half of the maximum ventilation capacity 252000 m³/h
NH_3 = 5,2 mg/m³ < 30 mg/ m³ (Order no. 462 of 1 July 1993)

As a result of dispersion calculation via the SCREEN3 program, the modeling results reveal the following ammonia immission values:

Situation I: dispersion of ammonia (NH_3) with ventilation operating at full capacity

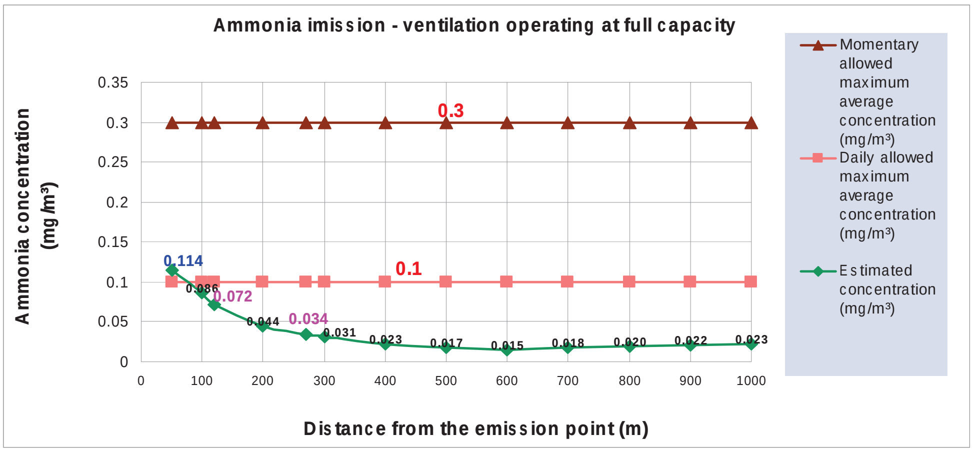

Fig. 2. *Ventilation operating at full capacity*

According to STAS 12574/87, ammonia is standardized at 0.1 mg/mc daily average and 0.3 mg/mc momentary average. The estimated maximum concentration of 0.12 mg/m³ is located at 54 m from the emission point. The estimated value of the NH_3 indicator at the distances where the first human sensitive receptors are found is 0.072 mg/m³ at 120 m and 0.034 mg/m³ at a distance of 270 m from the emission point (Figure 2).

The modeling shown in Figure 3 reveal the distribution of ammonia concentrations, starting with the highest values placed between 50-100 m from the farm and finishing with the lowest values recorded at the distance of 3000 m from the pig farm.

Fig. 3. *Modeling of the SCREEN3 results*

<u>**Situation II**</u>: dispersion of ammonia (NH_3) with ventilation running at half of the maximum capacity

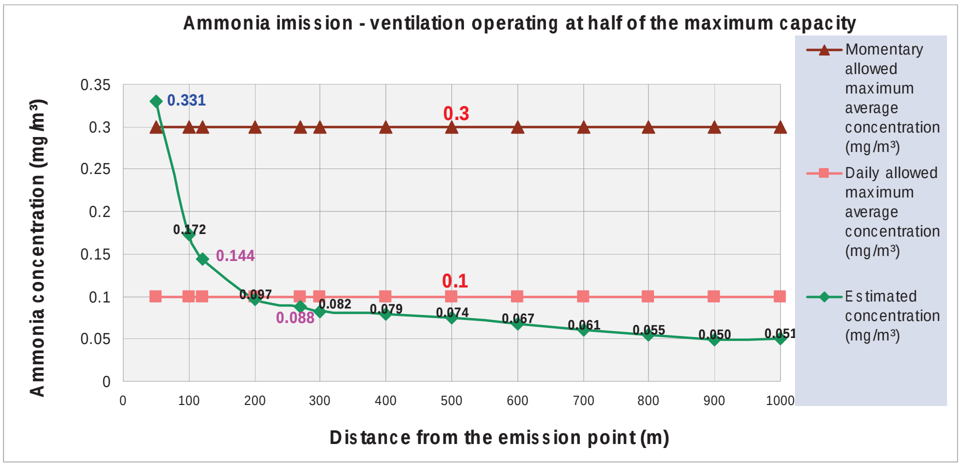

Fig. 4. *Ventilation running at half of the maximum capacity*

According to STAS 12574/87, ammonia is standardized at 0.1 mg/mc daily average and 0.3 mg/mc momentary average. The estimated maximum concentration of 0.331 mg/m³ is located at 50 m from the emission point. The estimated value of the NH_3 indicator at the distances where the first human sensitive receptors are found is 0.144 mg/m³ at 120 m and 0.088 mg/m³ at a distance of 270 m from the emission point (Figure 4).

If the shelters' floors are cleaned frequently – at a rate of at least 3 washes/24 hours - and if appropriate nutritional management is applied, the concentration of ammonia emissions can be reduced. In a specialized literature review, Ajinomoto Animal Nutrition reported data from tests on the effects of low-protein diet (supplemented with industrial amino acids) on nitrogen and manure mixture from pigs, being selected from a big variety of sources inside and outside of Europe. The findings of the experiments have shown that, in combination with 3-phase feeding, nitrogen excretion decreased by 10% per 1% reduction in dietary protein for pigs between 25 and 110 kg. Tests have also shown that it is possible to reduce the protein in food by up to 20% for all categories of pigs, resulting in a decrease in nitrogen excretion by 20% without any specific technical skill.

Ammonia emissions vary on a daily and seasonal basis, higher emissions being recorded during warmer periods. High livestock production can be a significant source of NH_3 emissions in the atmosphere in a relatively small geographical area (Harper et al., 2004).

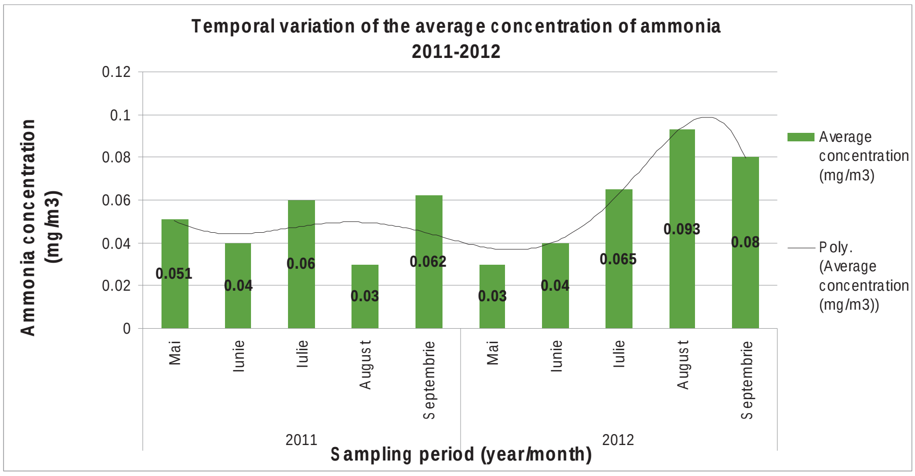

Fig. 5. *Temporal variation of the average concentration of ammonia*

According to the samplings results from the pig farm, we can see an increasing trend of the average ammonia concentrations in the summer (Figure 5), especially in 2012.

Since measurements are performed in Romania, it was found that the summer of 2012 was the hottest, through the number and especially persistence of hot days, with temperatures above 35 º C, and tropical nights, with over 20º C.

According to the National Administration of Meteorology, in Romania, the summer of 2012 surpassed the 2007 summer, known as the hottest summer of the past 62 years. The 2012 average summer temperature was 0.3 degrees Celsius higher than the summer of 2007, throughout the Romanian territory and 3.34 degrees Celsius higher than the average temperature of the 1961-1990 reference interval. (http://www.meteoromania.ro/)

Table 1 shows that the temperatures recorded at the moment of sampling in 2012 were extremely high for that particular period, the maximum average concentration been 0.093 mg / m³ in August.

Table 1. *Average temperatures at the time of sampling*

Date and time of sampling	The average temperature recorded
31.05.2012/ 11:20-13:45	24.5º C
29.06.2012/ 10:30-12:55	27.6 º C
30.07.2012/ 10:35-13:10	27 .5º C
02.08.2012/ 11:33-14:00	29 º C
11.09.2012/ 11:30-13:57	28.2 º C

The hydrogen sulfide concentration during sampling periods was placed below the detection limit (<0.005 mg / m³). The STAS 12574-87 maximum permissible concentration of hydrogen sulfide is of 0.015 mg/m³ for air in protected areas.

The highest average concentrations of ammonia were determined in the South-East (SE) limit enclosure, the sampling point being closest to sensitive receptors in 2011 (0.0742 mg/m³) and 2012 (0.082 mg/m³) (Figure 6, Figure 7).

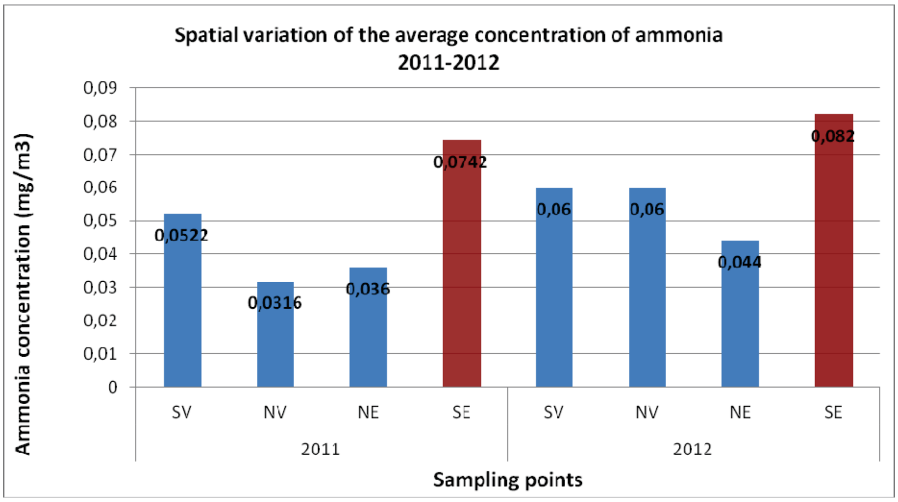

Fig. 6. *Spatial variation of the average concentration of ammonia*

Fig. 7. *Maximum average concentrations of ammonia*

Comparing the estimated distance of 50 m (0.114 mg/m³) following ammonia dispersion and the measured values at the distance of 50 m from the enclosure boundaries in 2011, it is clear that there are no breaches of maximum allowed concentration (0.3 mg / m³). In September (2011), a slight excess of measured ammonia concentration was recorded, 0.042 mg/m³ higher than the estimated ammonia concentration from the dispersion modeling obtained with the "SCREEN3" program (Figure 8).

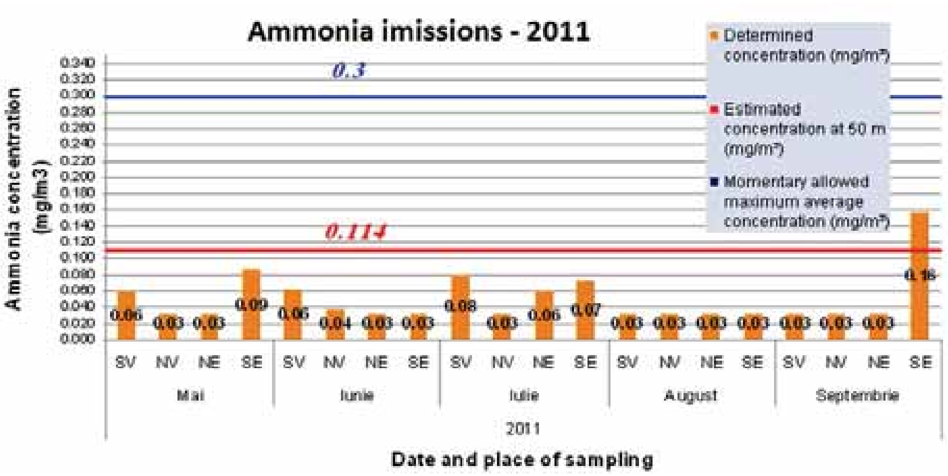

Fig. 8. *Ammonia imission of 2011*

Unlike the previous year, in 2012 there were two minor overflows of the measured ammonia concentrations, both having values of 0.13 mg/m³, 0.016 higher than the estimated concentration at 50 m. Again, no overflows of momentary maximum allowable average concentration of 0.3 mg/m³ were determined (Figure 9).

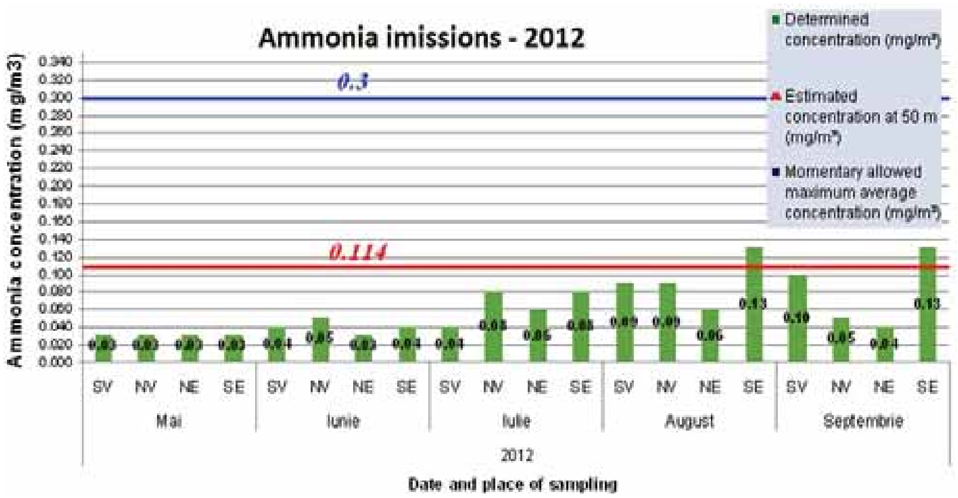

Fig. 9. *Ammonia imission of 2011*

CONCLUSIONS

Following direct measurements and mathematical calculations to determine the concentrations of ammonia and hydrogen sulfide in the air from the studied area, it was found that there are no overflows of the maximum permitted levels, turning the pig farm in Cluj Country into one of the happy cases that do not involve any major contaminations.

However, there were minor overflows of ammonia concentrations in the warm periods when high temperatures were recorded (2012), but that shows no health risk to the people in neighboring areas.

As future directions if the shelters' floors are cleaned frequently – at a rate of at least 3 washes/24 hours - and if appropriate nutritional management is applied, the concentration of ammonia emissions can be reduced. Also, increasing the cart exhaust diameter and the air flow fans can help reduce ammonia emissions.

REFERENCES

Aneja V. P., Blunden J., James K., Schlesinger W. H., Knighton R., Gilliam W., Jennings G., Niyogi D., and Cole S., 2008, Ammonia Assessment from Agriculture: U.S. Status and Needs, *Journal of Environmental Quality*, **37**:515–520.

Apostol I., 2006, Smithfield case Study in Romania, *Industrial pig farms and their environmental impact*, TERRA Third Millennium Foundation, Bucharest, p. 16.

Dragosits U., Dore A.J., Sheppard L.J., Vieno M., Tang Y.S., Theobald M.R., Sutton M.A., 2008, Chapter11 – Sources, Dispersion and Fate of Atmospheric Ammonia, Eds. J.L. Hatfield and R.F. Follett, *Nitrogen in the Environment — Sources, Problems, and Management,* Second Edition, Elsevier, **39**:333–393.

Harper L. A., Sharpe R. R. and Simmons J. D., 2004, Atmospheric Pollutants and Trace Gases-Ammonia Emissions from Swine Houses in the Southeastern United States, *Journal of Environmental Quality*, **33**: 449–457.

Joachim H. S., Goïtaa K. and Desmaraisb C., 2010, Analysis of Air Pollution from Swine Production by Using Air Dispersion Model and GIS in Quebec, *Journal of Environmental Quality,* **39**:1975–1983.

Jorgen E., Adamsen A. P. S., Nørgaard J. V., Poulsen H. D., Jensen B. B. and Petersen S. O., 2010, Emissions of Sulfur-Containing Odorants, Ammonia, and Methane from Pig Slurry: Eff ects of Dietary Methionine and Benzoic Acid, *Journal of Environmental Quality*, **39**:1097–1107.

McCrory D. F. and Hobbs P. J., 2001, Additives to Reduce Ammonia and Odor Emissions from Livestock Wastes: A Review, *Journal of Environmental Quality,* **30**: 345–355.

Pahl O., Williams A. G., Sneath R. W., 2002, Reduction of ammonia and odour emissions from pig slurry under slats using oil and foam layers, *Environmental technology,* **39**:395-403.

Philippe F. X., Cabaraux J. F., Nicks B., 2011, Ammonia emissions from pig houses: Influencing factors and mitigation techniques, *Agriculture, Ecosystems and Environment*, **141**:245–260.

Q.Ni J., Hendriks J., Vinckier C., Coenegrachts J., 2000, A new concept of carbondioxide accelerated ammonia release from liquid manure in pig house, *Environment International*, **26**:97–104.

Zahn J. A., Hatfield J. L., Laird D. A., Hart T. T., Do Y. S. and DiSpirito A. A., 2001, Functional Classification of Swine Manure Management Systems Based on Effluent and Gas Emission Characteristics, *Journal of Environmental Quality,* **30**:635–647.

***http://www.weblakes.com/products/screen/index.html

***http://www.meteoromania.ro/

*** EEA, 2007, *Corine Land Cover 2000,* Copenhagen (http://eea.europa.eu), acknowledgements to the Romanian Ministry of Environment and Sustainable Development (http://www.mmediu.ro) and the “Danube Delta” National Institute of Research and Development (http://www.indd.tim.ro);

*** GRASS Development Team, *"Geographic Resources Analysis Support System (GRASS) Software"*, Open Source Geospatial Foundation Project (http://grass.osgeo.org/)
***Law no. 104/15.06.2011 on Ambient air quality (Romanian)
***Order no. 462 of July 1, 1993 for approval of technical conditions for the protection of air and Methodological Norms regarding the determination of emissions of air pollutants produced by stationary sources (Romanian)
*** Quantum GIS Development Team, *"Quantum GIS geographic information system"*, Open Source Geospatial Foundation Project (http://qgis.osgeo.org/)
***STAS 10812-1976: Air purity. Determination of ammonia (Romanian)
***STAS 10814-1976: Air purity. Determination of hydrogen sulfide (Romanian)
***STAS 12574-87: The air in protected areas (Romanian)