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Characterization of Unpleasant Odors in Poultry Houses Using Metal Oxide Semiconductor-Based Gas Sensor Arrays and Pattern Recognition Methods †

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Abstract: In this study, the ability of an electronic nose developed to analyze and monitor odor emissions from three poultry farms located in Meknes (Morocco) and Berlin (Germany) was evaluated. Indeed, the potentiality of the electronic nose (e-nose) to differentiate the concentration fractions of hydrogen sulfide, ammonia, and ethanol was investigated. Furthermore, the impact change of relative humidity values (from 15% to 67%) on the responses of the gas sensors was reported and revealed that the effect remained less than 0.6%. Furthermore, the relevant results confirmed that the developed e-nose system was able to perfectly classify and monitor the odorous air of poultry farms.

Keywords: poultry odorous air monitoring; electronic nose; gas sensors; pattern recognition methods

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1. Introduction

Unpleasant odors are an inherent part of poultry production. They come from the wastes and emissions of animals. In addition, poultry farms in close proximity to the population generate volatile organic compounds (VOCs) in the air, resulting in a foul odor similar to that of rotten eggs and waste [1]. Moreover, odor nuisance from poultry farms has raised serious concerns about the quality of human life worldwide. Unpleasant smelling air affects the mental and physical health of the population and causes anger [2]. Similarly, the health of hens and farm workers can be threatened by the malodorous chemical compounds (such as hydrogen sulfide and ammonia) emanating from poultry farms [3]. Therefore, appropriate methods and techniques are needed to characterize and monitor odorous air samples, thereby determining the impacts of smelly air on chickens, humans, and the agricultural environment.

Although olfactometric techniques are the most widely used to analyze odorous air based on the perception of a group of human sniffers, these techniques are very expensive and do not provide information on chemical composition [4]. Analytical methods are widely used for the quantitative analysis of odorous air samples to identify unknown organic compounds and their concentration [5]. However, they require a qualified operator, and are expensive, time-consuming, and non-portable. The problems associated with the use of conventional odor air analysis methods could be replaced by the application of faster and cheaper e-nose technology. Electronic noses are devices equipped with an array of gas sensors combined with pattern recognition methods that provide a specific signature of the analyte [6,7]. The last few decades have seen a significant increase in interest in chemical sensors, which is reflected in the growing number of papers and conferences on this topic. For this purpose, these instruments are used in various applications for routine, rapid, and inexpensive assessment related to the environmental sector [8,9]. Similarly, in recent years, odor emissions from livestock farms have received increased attention due to their large number resulting in the production of high concentrations of hydrogen sulfide and ammonia [10,11]. Electronic noses are also applied in other fields, including biomedical [12,13], pharmaceutical [14], food [15], and security [16].

In this work, the ability of an electronic nose to discriminate malodorous VOCs from three poultry farm sites was investigated. In parallel, the monitoring of malodorous air emissions from a poultry farm as a function of the time and date of collection was carried out. In addition, the effect of relative humidity on the response of the gas sensors was checked. The sensitivity to hydrogen sulfide, ammonia, and ethanol was tested. Pattern recognition methods such as principal components analysis (PCA), discriminant function analysis (DFA), and support vector machines (SVMs) were used for processing the data from gas sensor responses.

2. Materials and Methods

2.1. Odorous Air Samples Collection

Odorous air samples were collected using 2L Tedlar bags in three poultry sheds located in the Faculty of Sciences of Meknes (FSM), as well as in the agglomeration of Meknes (Morocco) and in Berlin (Germany). In parallel, to verify the ability of the e-nose to monitor odorous air samples from a poultry farm, odorous air samples were collected from the poultry farm of Meknes at different times and on three different days, with an interval of two days of one week. In total, 126 odorous air samples were collected (14 samples from each time collection performed at 09:00 a.m., 12:00 p.m., and 18:00 p.m.).

2.2. Gas Sensor System

The developed electronic nose system consists of six MQ-type chemical sensors (MQ-3, MQ-4, MQ-5, MQ-8, MQ-9, and MQ-135) from Winsen Electronics Technology Co., Ltd. (Zhengzhou, China) (Figure 1). The sensor chamber also contains a relative humidity sensor (HIH 4000) and a temperature sensor (LM35) to monitor the environmental conditions during measurements. All the sensors were installed in a Teflon chamber with a volume of 270 cm^3. The collected odorous air samples were transferred to the sensor chamber using a Tedlar bag and a micro air pump. The sensor responses were acquired by NI-USB 6212 data acquisition from National Instruments (Austin, TX, USA). It allows signal conversion and preparation for further analysis by changing the analog signal produced by the sensors into its discrete digital representation.

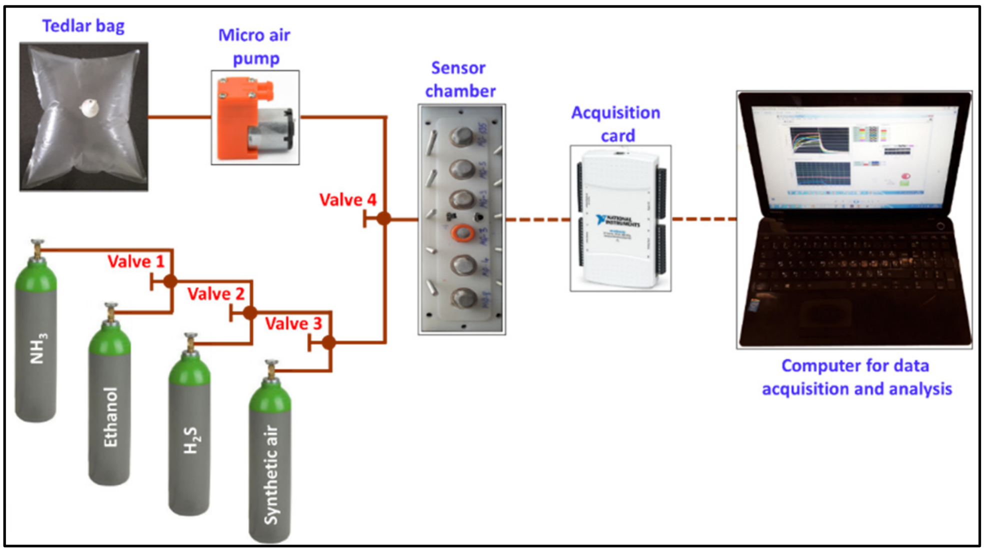

Figure 1. Electronic nose system developed for odorous air analysis and monitoring.

2.3. Sensing Measurements

During analysis, the samples were pumped for 5 min into the sensor chamber at a flow rate of 250 mL/min. The data were acquired every second. After each measurement, synthetic air was injected into the sensor chamber for 5 min to clean the surface of the sensors to return to their baselines.

The concentration fractions of hydrogen sulfide (6 ppm), ammonia (7 ppm), and ethanol (3 ppm) were adjusted with the Gas Mixing System (GMS) of BAM, Berlin, Germany.

The temperature measured inside the sensor chamber during the measurements was approximately 27.5 ± 3.1 °C.

2.4. Data Analysis

2.4.1. Features Extraction

In this study, three features were extracted from the response of each gas sensor:

- $\Delta G = (G_S - G_0)$: The difference in conductance between G_S and G_0 is the average value of the conductance in the last and first 60 s, respectively.
- A: The area under the curve of the sensor conductance between the first and the last minute of sample measurement. This area was calculated using the trapeze method.
- dG/dt: The slope of the sensor response, determined dynamically in a range of 60 to 540 s.

Eighteen variables were defined the developed system (6 sensors × 3 extracted features).

2.4.2. Pattern Recognition Methods

The extracted features were treated by using pattern recognition methods (PCA, DFA, and SVMs) to estimate the performance of the e-nose to classify and monitor odorous air samples from a poultry farm.

The aim of PCA is the multidimensionality reduction of a dataset by finding new orthogonal directions (principal components) which contain the maximum information. The main advantage of PCA is the ability to present the results on two- or three-dimensional graphs. Groups of points can be visualized on the plots, which makes it possible to assess the contribution of the sample to a particular group. The PCA algorithm generates linear combinations of principal components [17].

DFA is a linear method, but it differs from PCA in that it utilizes the cluster information that was given during the training (supervised method), while the PCA does not care about the relationship of the data points with the specified clusters. The DFA method helps to have the best discrimination by reducing distances between samples (variance within classes) and maximizing distances between clusters (variance between classes) [18].

SVMs objective is to increase the quantity called margin to distinguish clusters with a specific hyperplane. The margin is a distance calculated between the nearest points contained in different groups. SVMs have two techniques. The first is to consider one vs. one or one vs. all and the other is to use all the data in a single formulation. This work applied a 2nd degree polynomial kernel. Indeed, a leave-one-out cross-validation technique was used to determine the prediction accuracy. The second-order of a radial basis function (polynomial) kernel was employed to project the training data to a space that maximizes the margin hyper plane [19].

3. Results and Discussion

3.1. Sensor Calibration through Relative Humidity Variation

Since humidity has a great impact on the electrical conductivity of resistive gas sensors, it is necessary to calibrate them using different relative humidity values. Figure 2 represents the normalized conductance of the sensor arrays at three different relative humidity values. We can see from this figure that when the relative humidity values increase from 15% to 67%, the variation of the conductance does not exceed 0.6% for all the sensors. In conclusion, it can be noticed that the calibration of the gas sensors at the considered relative humidity values led to a slight difference in the responses of the gas sensor arrays.

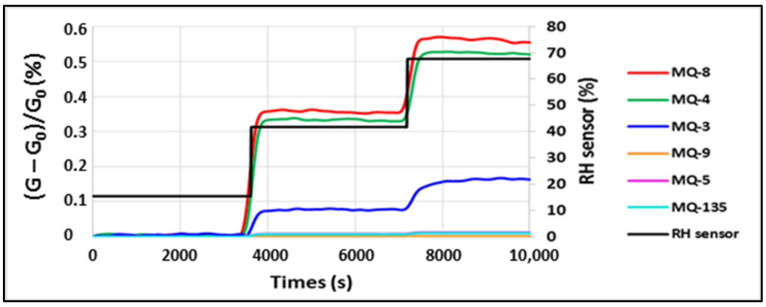

Figure 2. Conductance changes of sensor arrays and relative humidity in function of measurement time by adjusting RH values from 15% to 67%.

3.2. Sensing Behavior of Gas Sensor Arrays to Hydrogen Sulfide, Ammonia, and Ethanol at Room Temperature

Ammonia and hydrogen sulfide are harmful gases generated during the bacterial decomposition of livestock manure [20]. Therefore, it is necessary to test the sensitivity of gas sensors using ammonia and hydrogen sulfide gases. Figure 3 shows a plot of the time dependence of the difference in conductance ($G - G_0$) when the sensors are exposed to hydrogen sulfide (Figure 3a), ammonia (Figure 3b), and ethanol (Figure 3c) at fixed concentration fractions of 6, 7, and 3 ppm, respectively. It can be seen from this figure that all the gas sensors were sensitive to the three tested synthetic gases, except for the MQ-8 sensor. Furthermore, each gas sensor had a different response to the three gases studied, which means that the electronic nose was able to differentiate between these gases.

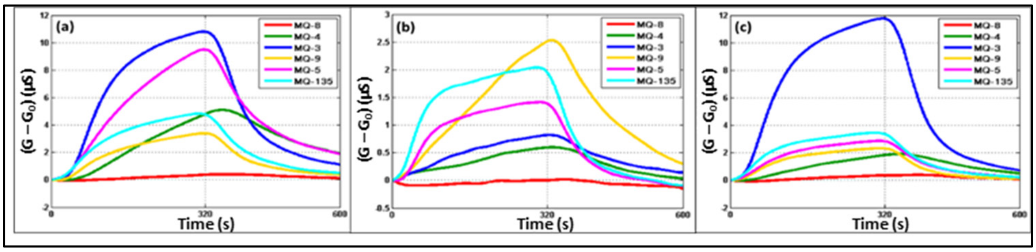

Figure 3. Conductance changes of gas sensor arrays in the presence of (**a**) hydrogen sulfide, (**b**) ammonia, and (**c**) ethanol with concentration fractions of 6, 7, and 3 ppm, respectively.

3.3. Classification Results of the Odorous Air Samples Collected from Poultry Sheds and Clean Air

3.3.1. Radar Plots

Figure 4 shows the results of the radar plot corresponding to the odorous air samples collected from three poultry sheds and synthetic air as the control. In this figure, it can be seen that the odorous air pattern (fingerprints) differed from one site to another. Indeed, the smallest one corresponds to the control.

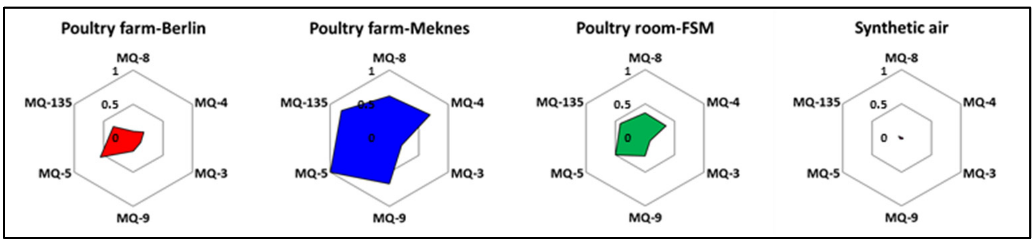

Figure 4. Radar plots of poultry odorous air samples and synthetic air (control) expressed as the difference in conductance ($\Delta G = (G - G_0)$) extracted from gas sensor responses.

3.3.2. PCA Classification

The PCA method was applied to the database gathered from gas sensor responses upon exposure to odorous air samples collected from the three poultry farms and synthetic air as a control. Figure 5 represents the projections of the experimental results onto a two-dimensional (2D) graph. In this figure, it can be seen that all the groups of odorous air samples are clearly separated, with no overlap with synthetic air (control). In fact, the first two principal components account for 94% of the data variance.

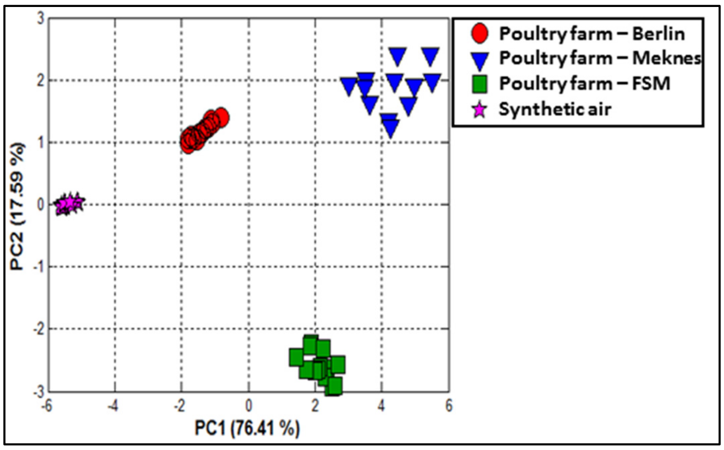

Figure 5. PCA plot performed on poultry odorous air samples and synthetic air by using the features (ΔG, area, and slope) extracted from gas sensor responses.

3.4. Classification Results Depending on the Time and Date of Samples Collection

3.4.1. DFA Classification

DFA was applied to the database gathered from the sensors' responses to verify the ability of the developed e-nose to monitor odorous air samples collected at different dates and times in a poultry farm in Meknes. Figure 6 shows the DFA plot with 89% of the data variance explained by the first two discriminant functions (DFs). It can be seen from this figure that all the clusters are separated from each other. Furthermore, DF1 discriminates odorous air samples based on the date of collection from the poultry shed, while DF2 separates them based on the time of collection. The DFA results prove that the e-nose system was capable of clearly discriminating odorous air samples from a poultry farm according to the date and time of collection.

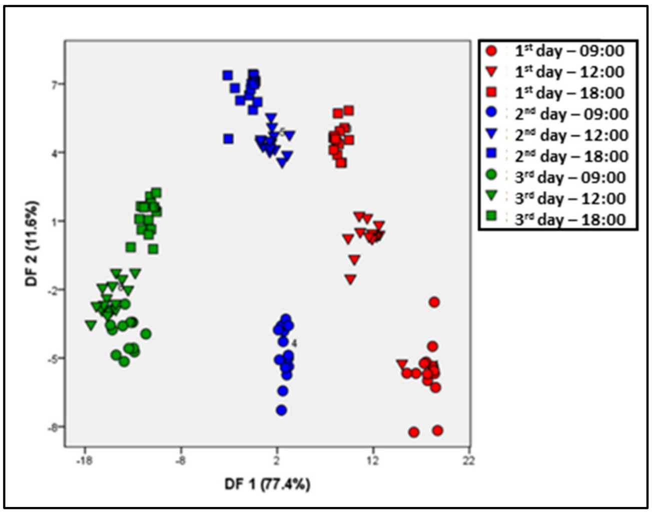

Figure 6. DFA plot performed on odorous air samples collected at different times and dates on a poultry farm (Meknes) using the features (ΔG, area, and slope) extracted from gas sensor array responses.

3.4.2. SVM Classification

An SVM is a supervised learning method. It was applied to the same dataset as DFA to verify the ability of the developed e-nose to monitor odorous air samples in a poultry farm from Meknes city. Table 1 shows the SVM confusion matrix for odorous air samples recognition. In this study, only two misclassified samples were observed in the data matrix. Therefore, a 98.41% accuracy in the recognition of the odorous air samples was achieved. This outcome was in good agreement with the obtained DFA results. This finding confirms that the e-nose system was able to monitor odorous air samples from a poultry farm.

Table 1. SVM classification results of odorous air samples collected at different times and dates on a poultry farm from Meknes using the features (ΔG, area, and slope) extracted from gas sensor responses (total score: 98.41%).

	1st Day–09:00	**1st Day–12:00**	**1st Day–18:00**	**2nd Day–09:00**	**2nd Day–12:00**	**2nd Day–18:00**	**3rd Day–09:00**	**3rd Day–12:00**	**3rd Day–18:00**
1st day–09:00	13	1							
1st day–12:00	1	13							
1st day–18:00			14						
2nd day–09:00				14					
2nd day–12:00					14				
2nd day–18:00						14			
3rd day–09:00							14		
3rd day–12:00								14	
3rd day–18:00									14

4. Conclusions

The present study demonstrated that the low-cost, portable, and easy-to-use e-nose system was able to distinguish odorous air samples from poultry sheds based on the sampling site, and also depending on the date and time of collection. The effect of relative humidity on gas sensor responses was also investigated and showed that when relative humidity increased from 15% to 67%, there was a slight difference in sensor responses that did not exceed 0.6%. Similarly, the sensitivity of the sensor array to hydrogen sulfide, ammonia, and ethanol was tested and showed that all gas sensors are sensitive to these three synthetic gases, with the exception of the MQ-8 sensor. Radar plots revealed a significant change in odorous air sample patterns based on the sampling sites. In addition, PCA showed that the e-nose system was able to clearly distinguish odorous air samples from three sites of poultry farms without any overlap with the unpolluted air samples (synthetic air) with 94% of the data variance. In order to monitor odorous air samples from a poultry farm according to their date and time of collection, the database was also processed by DFA and SVM. These two pattern recognition methods show a clear discrimination between the studied samples with a success rate of 89% and 98.41%, respectively. We can conclude that the developed e-nose system can be effectively used as a fast, easy-to-use, and inexpensive tool for the analysis and monitoring of odorous air samples from poultry farms.

Author Contributions: Investigation, Formal analysis, Methodology, software, Experimentation, Original Draft Preparation: M.M.; design of experiment for gas mixing system to investigate the sensor system in the laboratory, scientific exchange of the time-series data and coordination of the tasks in BAM: C.T.; Review & Editing: N.E.B. and M.B.; Conceptualization, Visualization, Supervision, Validation, Resources, Funding acquisition, Review & Editing: B.B. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Abdullah, A.H.; Shakaff, A.Y.; Adom, A.H.; Zakaria, A.; Saad, F.S.; Kamarudin, L.M. Poultry farm malodor monitoring using portable electronic nose system. *Chem. Eng.* **2012**, *30*, 55–60.
2. Horton, R.A.; Wing, S.; Marshall, S.W.; Brownley, K.A. Malodor as a trigger of stress and negative mood in neighbors of industrial hog operations. *Am. J. Public. Health* **2009**, *99*, 610–615. [CrossRef] [PubMed]
3. McCubbin, D.R.; Apelberg, B.J.; Roe, S.; Divita, F. Livestock Ammonia Management and Particulate-Related Health Benefits. *Environ. Sci. Technol.* **2002**, *36*, 1141–1146. [CrossRef] [PubMed]
4. Pan, L.; Yang, S.X. A new intelligent electronic nose system for measuring and analysing livestock and poultry farm odors. *Environ. Monit. Assess.* **2007**, *135*, 399–408. [CrossRef] [PubMed]
5. Murphy, K.R.; Wenig, P.; Parcsi, G.; Skov, T.; Stuetz, R.M. Characterizing odorous emissions using new software for identifying peaks in chemometric models of gas chromatography-mass spectrometry datasets. *Chemom. Intell. Lab. Syst.* **2012**, *118*, 41–50. [CrossRef]
6. Deisingh, A.K. *Sensors for Chemical and Biological Applications*; Taylor and Francis: Boca Raton, FL, USA, 2010.
7. Gardner, J.W.; Bartlett, P.N. A brief history of electronic noses. *Sens. Actuators B Chem.* **1994**, *18*, 210–211. [CrossRef]
8. Gębicki, J.; Dymerski, T.; Namieśnik, J. Monitoring of odour nuisance from landfill using electronic nose. *Chem. Eng. Trans.* **2014**, *40*, 85–90.
9. Li, H.; Luo, D.; Sun, Y.; GholamHosseini, H. Classification and Identification of Industrial Gases Based on Electronic Nose Technology. *Sensors* **2019**, *19*, 5033. [CrossRef] [PubMed]
10. Akter, S.; Cortus, E.L. Comparison of Hydrogen Sulfide Concentrations and Odor Annoyance Frequency Predictions Downwind from Livestock Facilities. *Atmosphere* **2020**, *11*, 249. [CrossRef]
11. Wang, Y.-C.; Han, M.-F.; Jia, T.-P.; Hu, X.-R.; Zhu, H.-Q.; Tong, Z.; Lin, Y.-T.; Wang, C.; Liu, D.-Z.; Peng, Y.-Z.; et al. Emissions, measurement, and control of odor in livestock farms: A review. *Sci. Total Environ.* **2021**, *776*, 145735. [CrossRef] [PubMed]
12. Saidi, T.; Moufid, M.; Zaim, O.; El Bari, N.; Bouchikhi, B. Voltammetric electronic tongue combined with chemometric techniques for direct identification of creatinine level in human urine. *Measurement* **2018**, *115*, 178–184. [CrossRef]
13. Diouf, A.; Bouchikhi, B.; El Bari, N. A nonenzymatic electrochemical glucose sensor based on molecularly imprinted polymer and its application in measuring saliva glucose. *Mater. Sci. Eng. C* **2019**, *98*, 1196–1209. [CrossRef] [PubMed]
14. Wasilewski, T.; Migoń, D.; Gębicki, J.; Kamysz, W. Critical review of electronic nose and tongue instruments prospects in pharmaceutical analysis. *Anal. Chim. Acta* **2019**, *1077*, 14–29. [CrossRef] [PubMed]
15. Tahri, K.; Duarte, A.A.; Carvalho, G.; Ribeiro, P.A.; Da Silva, M.G.; Mendes, D.; El Bari, N.; Raposo, M.; Bouchikhi, B. Distinguishment, identification and aroma compound quantification of Portuguese olive oils based on physicochemical attributes, HS-GC/MS analysis and voltammetric electronic tongue. *J. Sci. Food Agric.* **2018**, *98*, 681–690. [CrossRef] [PubMed]
16. Bonfanti, M.E. From sniffer dogs to emerging sniffer devices for airport security: An opportunity to rethink privacy implications? *Sci. Eng. Ethics* **2014**, *20*, 791–807. [CrossRef] [PubMed]
17. Wold, S.; Esbensen, K.; Geladi, P. Principal component analysis. *Chemom. Intell. Lab. Syst.* **1987**, *2*, 37–52. [CrossRef]
18. Brown, M.T.; Tinsley, H.E. Discriminant analysis. *J. Leis. Res.* **1983**, *15*, 290–310. [CrossRef]
19. Ivanciuc, O. Applications of Support Vector Machines in Chemistry. *Rev. Comput. Chem.* **2007**, *23*, 291–400. [CrossRef]
20. Park, J.; Kang, T.; Heo, Y.; Lee, K.; Kim, K.; Lee, K.; Yoon, C. Evaluation of short-term exposure levels on ammonia and hydrogen sulfide during manure-handling processes at livestock farms. *Saf. Health Work* **2020**, *11*, 109–117. [CrossRef] [PubMed]