Ammonia Contents and Desorption from Dusts Collected in Livestock Buildings

H. Takai[1], K. Nekomoto[2], P.J. Dahl[1], E. Okamoto[3], S. Morita[3] & S. Hoshiba[3]

1. Danish Institute of Agricultural Sciences, Dept. of Agricultural Engineering, Research Centre Bygholm, P.O. Box 536, DK-8700 Horsens, Denmark <Hisamitsu.Takai@agrisci.dk>
2. Zukohsha Co., Ltd. Nishi 18 Jo Kita 1 chome 17, Obihiro-shi, Hokkaido, 080, Japan
3. Rakuno Gakuen University, Bunkyoudai Midorimachi 582, Ebetsu-shi, Hokkaido, 069-8501, Japan

Abstract

The objective of this study was to determine rates of ammonia desorption from sediment dust and ammonia levels in airborne dust in animal houses in order to explore the nature of ammonia in the dust particles. This is assumed to be important for obtaining better understanding of the role of dust in the perception of odor and the development of respiratory diseases in farmers' lungs.

Sediment dust samples were collected in swine and poultry houses. About 3 g of dust was packed between two glass fiber filters in a 37 mm dust sampler cassette and exposed to clean air at an airflow rate of 0.001m^3 min^{-1}. The ammonia emitted to the air was determined by using the 0.5% boric acid trap and indo-phenol method. On the basis of the obtained data, desorption models for ammonia desorption from the swine and the poultry dusts were developed. The results indicate that the ammonia molecules are strongly bound inside dust particles.

The ammonia contents of airborne dust samples were determined by using distillation in alkaline water solution, the 0.5% boric acid trap and indo-phenol method. The ammonia contents in inhalable dust collected in dairy, poultry and farrowing houses ranged from 1 to 6 μg per mg of dust, i.e. 1,000 and 6,000 ppm on a weight basis, while about 7 μg NH_3 per mg of dust, i.e. 7,000 ppm, was found in respirable dust.

These results indicate that the dust particles are capable of carrying ammonia molecules. This may cause much higher local ammonia concentration at the points where the particles deposit, e.g. in the olfactory organ and the respiratory system, than it can cause by aerial ammonia concentration.

Takai, H., K. Nekomoto, P. Dahl, E. Okamoto, S. Morita, and S. Hoshiba. "Ammonia Contents and Desorption from Dusts Collected in Livestock Buildings". Agricultural Engineering International: the CIGR Journal of Scientific Research and Development. Manuscript BC 01 005. Vol. IV. June, 2002.

Keywords: Ammonia in dust, ammonia desorption, dust, livestock building

Introduction

It is generally assumed that dust particles are capable of transporting different chemical compounds and microorganisms from one livestock building to the other, or from a livestock building to the farmhouse and to the neighboring houses. This may cause increased risks of airborne infections of animals and malodor problems. Farmers in animal houses are exposed to gases and a complex aerosol of bacteria, fungi, endotoxin and organic dust, which are linked to development of respiratory diseases in farmers' lungs (Donham et al., 1984, Dosman et al., 1987, Rylander et al. 1989, Iversen and Pedersen, 1990). Interactive and or synergistic effects of gases and aerosoles may exist (Reynolds et al., 1998). Furthermore, the dust particles are expected to play an important role in the perception of odor.

Ammonia and volatile fatty acids (VFA) are the main components of malodors emitted from livestock farms. In general, cattle and poultry houses mainly emit ammonia, and swine houses mainly emit VFA (Tanaka, 1988). Hartung (1985) showed that dust from swine confinement buildings contains VFA, phenols, indoles and scatole. Manure contains the same compounds, and dried manure may turn into airborne dust. Dust particles from other sources, e.g. feed, may adsorb and absorb odorous compounds. Hammond et al. (1981) estimated that the concentration of butyric acid and p-cresol will be about 4×10^7 greater in a dust particle than in an equal volume of air. Reynolds et al. (1998), estimated that a significant proportion (15 to 23%) of airborne ammonia in enclosed livestock facilities is associated with particles. However, no report on direct measurement of ammonia contents in dust particles is found in the literature. This may be related to the sampling methods used. When dust particles are exposed to air currents during the sampling process, ammonia on the dust particles may evaporate instantaneously, and it will not appear in the analysis. However, adsorption of ammonia onto dust particles will undoubtedly occur in livestock buildings, and adsorption-desorption equilibrium will take place. It is also likely that dust particles originating from manure will contain ammonia.

Ammonia in the respirable fraction of inhaled dust particles may reach the lower parts of the respiratory tract, i.e. the bronchi and the alveoli, and irritate the organs. If this hypothesis is true, ammonia in dust particles will play an important role in the development of respiratory diseases in farmers' lungs. A deposition of dust particles in the nose may result in high local concentrations of ammonia in the olfactory organ, which will affect the perception of odor.

Improved knowledge on contents of chemical compounds, e.g. ammonia, in dust and gas desorption from dust may lead to better understanding on the synergistic effects of gases and aerosols on farmers' health and malodor problems.

The objective of this study was to determine rates of ammonia desorption from sediment dust and ammonia levels in airborne dust in animal houses.

Materials and Methods

The study has involved an experimental study and a field survey, i.e. 1) ammonia desorption from sediment dust and 2) ammonia contents in airborne dust, respectively.

Ammonia desorption from sediment dust

Sediment dust samples were collected in a house for sows and fattening pigs with solid floor, and in a house for caged layers. Both buildings were located in Hokkaido in Northern Japan. Until the laboratory experiments have taken place, i.e. a period of about 2 weeks, the samples were kept in airtight glass bottles (vials) in room temperature, i.e. from 19 to 24 ^{o}C. The dust samples from the poultry house were cleaned of feathers and other large particles by use of a 0.5 mm (mesh 30) sieve before it was used for the experiments.

The ammonia contents in the sediment dust samples were determined by means of distillation in water solution, the 0.5% boric acid trap and indo-phenol method.

About 3 g of dust sample was packed between two glass fiber filters in a dust sampler cassette and exposed to clean air by sucking the room air through the layer of dust, Figure 1. Then, ammonia concentrations in the air before, i.e. inlet air to the filter cassette, and after it was drawn through the layer of dust, i.e. outlet air from the filter cassette, were measured at different times of exposure in order to determine the ammonia desorption curves. Modified method of Japanese standard (JIS 42.1 and 42.2), i.e. the 0.5% boric acid trap and indo-phenol method, was used to measure the ammonia concentrations in the air.

Temperature and relative humidity in the room were measured by using psychrometer with dry and wet bulbs.

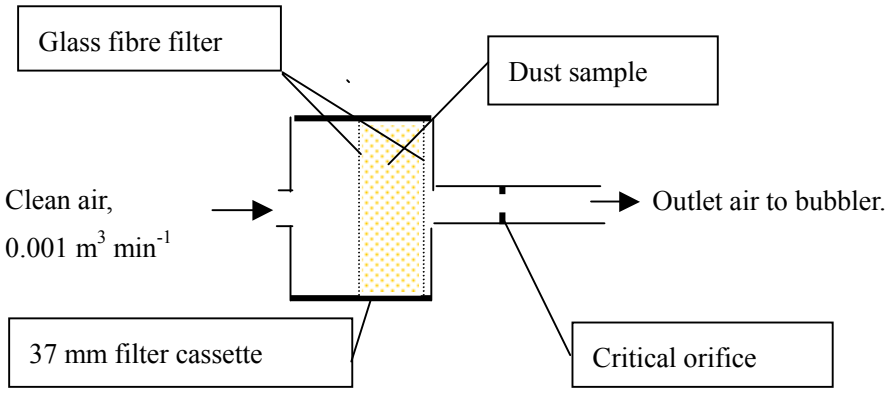

Figure 1. Experimental set-up for measurement of ammonia desorption from dust.

Desorption rate based on the dust weight (Dm) was estimated as follows:

$$Dmi = W_i / (Q \times s) \qquad [\text{mol kg}^{-1} \text{ sec}^{-1}] \qquad (1)$$

where i is the sampling number, W is gram-molecular weight of the trapped ammonia in the bubbler with boric acid solution (mol), Q is weight of the dust sample (kg) and s is sampling interval (= 600 sec). The exposure time (X) for i-th sampling is defined as follow:

$$Xi = xi + 300 \qquad [\text{sec}]$$

where x is the total exposure time from the start of the experiment to the start time of i-th sampling. On the basis of the data-set for Dm and X, regression models were developed:

$$Dm = f(X) \qquad (2)$$

The ammonia concentration in the dust sample (Ci) at an exposure time of Xi was estimated as follow:

$$Ci = C_0 - \int_0^{Xi} f(X)dX \qquad [\text{mol kg}^{-1}] \qquad (3)$$

where C_0 is the ammonia concentration before exposure, i.e. $X = 0$. The ammonia desorption curve, i.e. ammonia desorption rates at different ammonia concentrations in dust, was developed by using formulas 2 and 3.

The desorption rate can be expressed in the general form (Nix, 2002):

$$Ds = kN^z \qquad [\text{mol m}^{-2} \text{ sec}^{-1}] \qquad (4)$$

where *Ds* is surface-based desorption rate, *N* is the surface concentration of adsorbate (mol m^{-2}), *k* is the rate constant for the desorption process (sec^{-1}) and *z* is the kinetic order of desorption. It is reasonable to assume that *N* is proportional to the concentration of the adsorbate in the substrate, i.e. $N \propto f(C)$. Thus, the desorption rate can be expressed as:

$$Dm = k'C^{z'} \qquad [\text{mol kg}^{-1}\ \text{sec}^{-1}] \qquad (5)$$

where *C* is ammonia concentration in the dust sample (mol kg^{-1}). This desorption model is applied to describe the ammonia desorption from the swine and the poultry sediment dusts.

Ammonia contents in airborne dust

For the determinations of airborne dust concentrations and ammonia contents in the airborne dust, inhalable and respirable dust samples were collected by means of stationary sampling. They were collected in a free stall barn for dairy cows, in a free-range system for layers and in a farrowing house with slatted floor. All three buildings are located in Denmark. Inhalable dust samples were taken by means of IOM (the Institute of Occupational Medicine, Edinburgh, U.K) dust samplers, described by Mark and Vincent (1986), and cyclone dust samplers from SKC INC. (50% cut-off effectiveness value of 5μm) were used to collect the respirable dust samples. The sampling rates were adjusted to 0.002 m^3 min^{-1} ±2% for inhalable dust and 0.0019 m^3 min^{-1} ±2% for respirable dust by use of critical orifices constructed according to Vaughan (1989)

The ammonia contents in the airborne dust were determined by means of distillation in alkaline water solution, the 0.5% boric acid trap and indo-phenol method. As low ammonia contents in airborne dust were expected, alkaline water has been used to obtain high extraction efficiency.

Aerial ammonia concentrations were determined by means of gas detector tubes (Kitagawa-type) at the start and the end of the periods for airborne dust sampling.

Structures of airborne dust particles were studied by means of an electron microscope.

Results and Discussions

Ammonia desorption from sediment dusts:

Three series of experiments have been carried out. For these experiments, 7 repetitive samples of swine sediment dust and 5 samples of poultry sediment dust were used. Measurement of ammonia concentrations in air, i.e. desorption rate measurements, have been made more

intensively during the first period of exposure than the later period; i.e. intervals between *i*-th and (*i*+1)-th measurements increased and measuring repetition decreased with increasing exposure time. The total numbers of desorption rate measurements for the swine and the poultry dust samples were 65 and 40, respectively.

The average air temperature was 21.2 ^{o}C (s.d. 1.1 ^{o}C) and the average relative humidity was 33% (s.d. 6%).

The ammonia desorption rate of the sediment swine dust decreased quickly during the first exposure period of about 10,000 sec (2.8 hours) from about $1 \cdot 10^{-5}$ to $1.5 \cdot 10^{-6}$ mol kg^{-1} sec^{-1}. After this period, the ammonia desorption rate showed moderate changes. In the subsequent period of 180,000sec (50 hours), the ammonia desorption rate reduced to $3.7 \cdot 10^{-7}$ mol kg^{-1} sec^{-1}. The poultry dust showed moderate changes in ammonia desorption rate throughout the experiment period. The initial desorption rate of about $8.3 \cdot 10^{-7}$ mol kg^{-1} sec^{-1} was reduced to about $2.4 \cdot 10^{-7}$ mol kg^{-1} sec^{-1} during an exposure period of 172,500 sec (48 hours). The lack of a high desorption rate for poultry dust may be due to the treatment, during which the dust sample was cleaned of feathers and other large particles by use of a sieve. The regression models developed for these two desorption process are:

Swine dust:	$Dm = 4.99 \cdot 10^{-4} T^{-0.628}$	($r = 0.977$, $n=65$)
Poultry dust:	$Dm = 1.81 \cdot 10^{-6} T^{-0.158}$	($r = 0.748$, $n=40$)

On the basis of these models and the initial ammonia concentrations of 0.265 mol kg^{-1} for swine dust and 0.163 mol kg^{-1} for poultry dust, ammonia desorption curves were developed as shown in Figures 2 and 3, respectively. The ammonia desorption rates changed quickly when the ammonia concentrations in dust were above some levels, i.e. C-values of about 0.24 mol kg^{-1} for swine dust and 0.16 mol kg^{-1} for poultry dust. Below these concentration levels, the changes in ammonia desorption rates were shown to be slow. This suggests that the energy requirement for the ammonia desorption undergo a considerable change when the ammonia concentrations in dusts are around these levels. Therefore, the desorption curves are divided at these concentration levels, and called part I for the desorption curves for C-vales lower than 0.24 mol kg^{-1} for swine dust and 0.16 mol kg^{-1} for poultry dust, and part II for the higher C-values. Four different desorption models are therefore applied to describe each part of the desorption curves shown in Figures 2 and 3. Parameters for the models (formula 5) are shown in Table 1. The difference between the initial ammonia concentrations and the levels, where the slow desorption rates begin were 0.029 mol kg^{-1} for swine dust and 0.004 mol kg^{-1} for poultry dust. It is likely that these amounts of ammonia were on or near the surface of the dust particles,

and it was a stage achieved by diffusion process occurred during the storage period between sampling and the start of experiments. Moisture diffusion may also have occurred in the same period. As ammonia reacts strongly with water, desorption models for part II are probably affected by desorption of water molecules from the dust particles. Therefore, it is assumed that the part I describe more real picture of the desorption phenomenon between ammonia and dust particles than part II.

The rate constant may be expressed in an Arrhenius form (Nix, 2002):

$$k' = A \times e^{(-Ea/RT)} \qquad [\text{sec}^{-1}] \qquad (6)$$

where A is the frequency factor (sec^{-1}), Ea is the activation energy (kJ mol^{-1}), R is the universal gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}) and T is the temperature (degrees Kelvin). Under a constant temperature, which is considered in this study, larger A and smaller Ea will result in larger k', and vice versa. Frequency factor A is process dependent, and its value must be determined from experiments. However, the order of magnitude value of A is 10^{13} s^{-1} (Nix, 2002) if the ammonia desorption from dust is a first-order gas phase reaction. Applying this value and k'-values into Arrhenius form, the activation energies of the ammonia desorption from dust with C-values less than 0.236 mol kg^{-1} for swine sediment dust and 0.159 mol kg^{-1} for poultry sediment dust, i.e. for the part I desorption curves, are about 90 and 100 kJ mol^{-1},

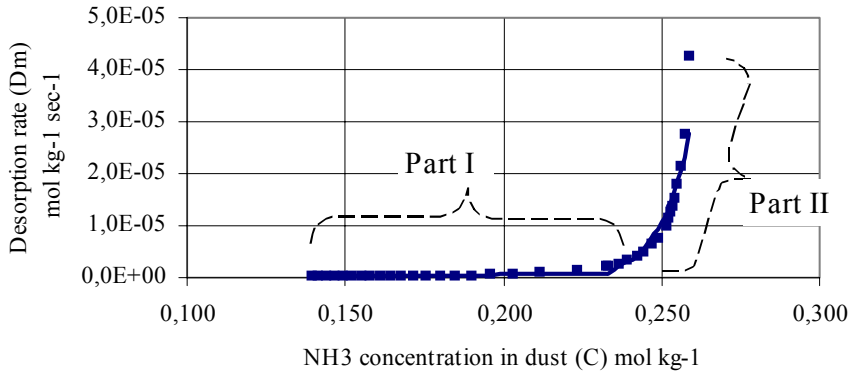

Figure 2. Ammonia desorption rate from swine dust at different ammonia concentrations in the dust.

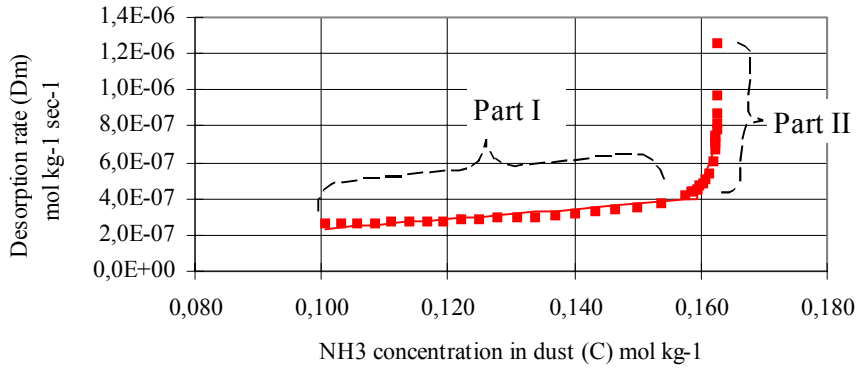

Figure 3. Ammonia desorption rate from poultry dust at different ammonia concentrations in the dust.

Table 1. Parameters for the desorption model: $Dm = k'C^{z'}$

		Rate constant k' sec^{-1}	*Kinetic order of desorption* z'
Swine dust	Part I: C ≤0.236 mol kg^{-1}	1.11×10^{-3}	4.38
	Part II : C ≥0.236 mol kg^{-1}	1.11×10^{14}	31.5
Poultry dust	Part I: C ≤0.159 mol kg^{-1}	2.95×10^{-6}	1.09
	Part II: C ≥0.159 mol kg^{-1}	5.81×10^{22}	36.6

respectively. Further studies on desorption of ammonia and other gases under different conditions, e.g. different temperatures and humidity, are needed to determine the values of A, and Ea, and to obtain better understanding on the nature of gases in dust particles.

Ammonia content in airborne dust:

Table 2 shows the aerial ammonia concentrations, the airborne dust concentrations and the ammonia contents in the airborne dusts collected in the different livestock buildings. There was no correlation between aerial ammonia concentrations and ammonia contents in the airborne dust. This indicates that the equilibrium condition of adsorption-desorption between aerial ammonia and ammonia in dust particles had been disturbed during sampling, transport and storage of the samples. The ammonia molecules that had been adsorbed onto the particle surfaces had desorbed during these operations.

However, the measurements showed that there are considerable amounts of ammonia left in the dust. This, and the laboratory experiments on ammonia desorption from sediment dusts,

indicates that the ammonia in dust is relatively stable, and it can be carried by dust particles for a long time. The porous structure of dust particles, which might affect the ammonia molecule diffusion inside the particles, may explain this phenomenon.

The high ammonia content in the cattle dust shown in Table 2 may indicate that a great part of the cattle dust is originated from manure. Extremely high concentrations of aerial ammonia in the poultry house reveal a high ammonia emission rate in the building. The source must be the pile of manure under the elevated floor of steel net. As feeders and drinking troughs were installed above the elevated floor, there were always many birds on it. This caused a high level of animal activity on the elevated floor and an upward going airflow due to the heat from the

Table 2. Aerial ammonia concentrations, dust concentrations, ammonia contents in airborne dust in dairy, poultry and farrowing houses.

	Aerial NH_3 concent-ration at start/end ppm	Dust fraction	Dust concentration			Ammonia content in dust		
			n	Ave. mg/m^3	S.D. mg/m^3	n	Ave. µg/mg (mol/kg)	S.D. µg/mg
Dairy house	3 / 3	Inhalable	7	0.18	0.01	6	5.43 (0.318)	1.79
		Respirable	7	0.02	0.01	*	*	*
Poultry house	55 / 35	Inhalable	7	2.50	0.12	6	3.48 (0.114)	0.31 2.56
		Respirable	7	0.54	0.47	7	7.05 (0.413)	
Farrowing house	15 / 15	Inhalable	7	2.18	0.10	6	0.90 (0.052)	0.30
		Respirable	7	0.16	0.02	7	7.18 (0.421)	4.67

*: Because deficient amounts of respirable dust were collected in the dairy house, the ammonia contents in the dust were not analyzed.

animals. It is therefore probable that a great part of the airborne dust originated from the manure pile. This may explain the high ammonia content in the inhalable dust from the poultry house.

The ammonia contents in inhalable dust varied from about 1 to 6 µg NH_3 per mg of dust (1,000 to 6,000 ppm), while a content of about 7 µg NH_3 per mg of dust (7,000 ppm) was found in respirable dust. These concentrations were from 100 to 1000 times higher than the typical aerial ammonia concentrations in livestock buildings. Filtration of dust from the air before gas analysis or odor measurement is commonly practiced. However, the high ammonia contents

seen in this study suggest that this process of dust filtration will cause not-negligible measuring error.

Conclusions

The results from the study lead to the following conclusions:

1. Ammonia molecules are strongly bound inside dust particles.
2. Airborne dusts in animal houses contain relatively large amount of ammonia.
3. Dust particles are capable of carrying ammonia molecules.

Acknowledgment.

Appreciation is extended to the Danish Ministry of Food, Agriculture and Fisheries, the Danish Research Councils, the Japan Society for the Promotion of Science and Rakuno Gakuen University for sponsoring this project.

References

Donham, K. J., Zavala, D. C., Merchant, J. A. Acute effects of the work environment on pulmonary functions of swine confinement workers. Am. Jr. Ind. Med. 1984, 5: 367-375.

Dosman, J. A., Gragam, B. L., Hall, D., Van Loon, P., Bhasin, P., Froh, F. Respiratory symptoms and pulmonary function in farmers. J. Occup. Med. 1987, 29: 39-43.

Hammond, E.G., Fedler, C. & Smith, R.J., 1981. Analysis of particle-borne swine house odors. Agriculture and environment, 6 (1981): 395-401.

Hartung, J., 1985. Gas chromatographic analysis of volatile fatty acid and phenolic/indolic compounds in pig house dust after ethanolic extraction. Environmental Technology Letters, Vol. 6, 1985: 21-30.

Iversen, M., Pedersen, B. The relationship between respiratory symptoms, type of farming and lung function disorders in farmers. Thorax 1990, 45: 919-923.

Mark, D. and Vincent, J.H., 1986. A new personal sampler for airborne total dust in workplaces. An. Occup. Hyg. No. 1, 1986: 89-102.

Nix R., 2002. An Introduction to surface chemistry. Queen Mary University of London. http://www.chem.qmw.ac.uk/surfaces/scc/sccinfo.htm

Reynolds, S.J., D.Y. Chao, P.S. Thorne, P. Subramanian, P.F. Waldron, M. Selim, P.S. Whitten, and W.J. Popendorf. 1998. Field comparison of methods for evaluation of vapor/particle phase distribution of ammonia in livestock buildings. J. Agr. Safety and Health 4(2):81-93.

Rylander, R., Donham, K. J., Hjort, C., Brouwer, R., Heederick, D. 1989. Effects of exposure to dust in swine confinement buildings - a working group report. Scand. Jr. Work Environ Health 1989, 15: 309-312.

Tanaka, H., 1988. Characteristics of odors from animal Industry (in Japanese). Journal of Agricultural Machinery Association 51-4: 99-104.

Vaughan, N.P., 1989. Construction of critical orifices for sampling applications. Proceedings of 3rd Annual Conference of the Aerosol Society, 1989: 77-82.