

1 **Ammonia volatilization factors following the surface application of dairy cattle**
2 **slurry to grassland in Japan: Results from pot and field experiments**

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17 Type of contribution: Full-length paper

18

19 Division of the manuscript: Environment

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21 A short running title: Ammonia volatilization from cattle slurry

1 **Abstract**

2 Objective of this paper is to suggest ammonia (NH_3) volatilization factors (as a ratio of
3 volatilized $\text{NH}_3\text{-N}$ to applied ammonium nitrogen ($\text{NH}_4\text{-N}$)) following the application of
4 dairy cattle slurry to grassland surface, based on the results from a number of pot and
5 field experiments. Pot experiments examined effects of both environmental factors (soil
6 water condition and air temperature) and properties of the slurry (dry matter content,
7 $\text{NH}_4\text{-N}$ content and pH) on NH_3 volatilization loss from the slurry applied onto soil
8 surface in the pot where grass was grown, and a grassland field trial was also carried out
9 to confirm the results from the pot experiments. Our results demonstrated that slight
10 application rate, dry soil water condition, low air temperature, low $\text{NH}_4\text{-N}$ content in the
11 slurry, low dry matter content and low pH of the slurry, and acidifying by adding
12 superphosphate to the slurry could abate the volatilization. Our experiments also
13 showed that the volatilized $\text{NH}_3\text{-N}$ was basically determined by only the application rate
14 of $\text{NH}_4\text{-N}$ from the slurry, even though the slurry was applied at different rates and
15 conditions affecting the NH_3 volatilization. From these results we estimated the
16 cumulative volatilization loss of NH_3 from the surface-applied slurry during the period
17 of complete finish of the volatilization and calculated the volatilization factor. It could
18 be deduced from this calculation that recommended values of the volatilization factor
19 (unit: $\text{g NH}_3\text{-N (g NH}_4\text{-N)}^{-1}$) from the surface-applied slurry were as follows: 0.32,
20 when the application rate of the slurry was less than 6 kg m^{-2} (60 Mg ha^{-1}); 0.42, when
21 the rate was more than that; 0.37, when it was unknown.

22

23 *Key Words:* Ammonium nitrogen, Ammonia volatilization, Grassland, Slurry, Surface
24 application

1 **Introduction**

2 Cattle manures, such as barnyard manure, slurry and liquid manure, are usually applied
3 to grassland surface in grassland dairy farming. The surface application of the manures,
4 however, is a major source of complaints from the public due to offensive odor and
5 volatilization of ammonia (NH_3) to atmosphere. The volatilized NH_3 is a potent
6 atmospheric pollutant with a wide variety of environmental impacts. The NH_3 is a
7 chemically active gas and readily combines with nitrate and sulfate in acid cloud
8 droplets to form particulates (Asman *et al.* 1998). The formation of particulates
9 prolongs their existence in the atmosphere and therefore influences the geographic
10 distribution of acidic depositions (Sommer and Hutchings 2001). In addition the NH_3
11 volatilization not only results in significant reduction in the nitrogen (N) fertilizer value
12 of the manure (Matsunaka, *et al.* 2003) but also following transport and deposition it is
13 associated with the eutrophication of the aquatic systems, soil acidification and the
14 disturbance of nutrient balance in the tree and in the soil, because it can also raise
15 nitrogen fertility levels in nutrient poor soil like forest soil (Roelofs and Houdijk 1991;
16 Sommer and Hutchings 2001). Furthermore a major source of atmospheric NH_3 is
17 agricultural farming, contributing more than 50% to the global NH_3 volatilizations
18 (FAO and IFA 2001) and over 70% in intensive livestock farming areas either in Europe
19 (Buijsman *et al.* 1987) and including Japan (Hojito *et al.* 2006).

20 Consequently it is also serious problem in Japan to control the NH_3 volatilization
21 during and following applying the manures to minimize both the risk of environmental
22 pollution and the reduction in the N fertilizer value of the manures. Nevertheless there is
23 little information on the NH_3 volatilization from animal manures applied to grassland
24 surface in Japan (Matsumura, 1988; Saito *et al.*, 1989). As the results of this situation in

1 Japan, we have a little information about the volatilization factor that is defined as a
2 ratio of volatilized NH_3 to applied ammonium N ($\text{NH}_4\text{-N}$) in this paper.

3 Then we have been carrying out several experiments to study the effects of both
4 environmental factors (soil water condition and air temperature) and properties of dairy
5 cattle slurry (dry matter content, $\text{NH}_4\text{-N}$ content and pH) on the NH_3 volatilization from
6 the applied slurry. Objective of this paper is to suggest NH_3 volatilization factors
7 following the application of dairy cattle slurry to grassland surface, based on the results
8 from a number of pot and field experiments described above.

9

10 **Materials and Methods**

11 **Pot experiments**

12 The pot experiments were conducted from 1999 to 2000. For all our experiments
13 described later we used plastic pots of which surface area is 0.02 m^2 and depth is 18 cm.
14 The pots were filled with surface layer soil of the Gray Upland soil (Aeric, Typic
15 Epiaquults) in our experimental farm. To keep bulk density of the soil in field condition,
16 we filled the pot with the soil of 2.7 kg as a dry soil basis up to 13 cm depth of the soil
17 in the pot, because the bulk density of the soil was 1.02 g cm^{-3} . This careful soil filling
18 is due to avoiding the effect of difference in the bulk density of the soil in the pots on
19 NH_3 volatilization, because it is considered that the difference in the bulk density of the
20 soil may affect infiltration of $\text{NH}_4\text{-N}$ in the applied slurry into the soil. Before filling the
21 soil, P_2O_5 as superphosphate and K_2O as potassium sulfate were applied to the soil at a
22 rate of 1.0 and 0.5 g pot^{-1} , respectively and mixed well with the soil. Since pH of the
23 soil used in our experiments was less than 5.5, we applied commercial calcium
24 carbonate based on the result from buffer curve of the soil to improve soil acidity. The

1 target soil pH was 6.5. No nitrogen of chemical fertilizer was applied to the pots in all
2 our experiments. We maintained soil matric water potential in the pots at -31 kPa by
3 irrigation of deionized water twice or third times per day until just before the application
4 of the slurry and no irrigation was done during 120 h following the application of the
5 slurry which is the time for measurement of the NH_3 volatilization. Chemical properties
6 of the original soil used to the experiment were as follows; pH(H_2O), 5.1; Total N and
7 C, 2.5 and 36.3 g kg^{-1} , respectively; Available P measured by Bray No.2 method, 0.18 g
8 kg^{-1} ; Cation exchange capacity, 26.8 $\text{cmol}(+) \text{kg}^{-1}$; Exchangeable K, Ca and Mg, 0.36,
9 1.65 and 0.19 g kg^{-1} , respectively.

10 Orchardgrass (*Dactylis glomerata*, L., variety Okamidori) was sown in late April
11 and cut after growing for about 50 days. We applied the slurry onto soil surface of the
12 pots at 4 or 5 days after the cutting of the grass. The slurries used in the experiments
13 were derived from excreta by dairy cattle. Some chemical properties of the slurries in
14 each experiment were shown in Table 1. The application rate of the slurry was usually
15 following 3 levels, except for some experiments described later; no application as a
16 control, 6 kg m^{-2} (60 Mg ha^{-1}) as a recommended rate in Hokkaido, Japan to avoid
17 environmental pollution (Matsunaka *et al.* 1988) and 12 kg m^{-2} (120 Mg ha^{-1}) as a heavy
18 application.

19 We carried out the pot experiments at a glass house of our university, except for
20 experiments involved in air temperature. To prevent increasing the air temperature in the
21 glass house, all windows were opened all day long. The mean air temperature in the
22 glass house, however, ranged from 15 °C to 25 °C, since the period of the experiments
23 was usually summer season. All experiments in this paper were conducted with three
24 replications.

1 **Measurement of NH₃ volatilization**

2 We covered the pot with a hood as illustrated in Fig. 1 and trapped the volatilized NH₃
3 following the application of the slurry into 40 g L⁻¹ boric acid by using a vacuum pump
4 of which suction power was 0.3 m³ h⁻¹. The boric acid solution received indicator
5 reagents of both methyl red and bromocresol green. The solution was titrated by 0.01
6 mol L⁻¹ sulfuric acid to determine the volatilized NH₃-N. The measurement was
7 continued for 120 h following the application of the slurry. The volatilized NH₃ was
8 calculated by subtraction of the amount of volatilized NH₃ in the control pots from that
9 in each treatment receiving the slurry.

10 **The details of the pot experiments**

11 **Experiment 1.** Only this experiment was exceptionally conducted by using no grass
12 growing pots to confirm NH₃ volatilization from the surface-applied slurry and effect of
13 soil cover following the application of the slurry on the volatilization. The slurry and
14 chemical fertilizers (urea and ammonium sulfate) was applied on the soil surface.
15 Application rate of the slurry was 10 kg m⁻² and NH₄-N as the chemical fertilizers was
16 applied at a rate of 25 g m⁻². We covered the applied slurry with 2 cm depth of the soil
17 just after the application of the slurry.

18 **Experiment 2.** The effect of soil water condition on the NH₃ volatilization was
19 examined at 3 levels that were wet, medium and dry conditions. The soil water matric
20 potential in each level was -3, -31 and -310 kPa, respectively. Method of maintaining
21 the water conditions was the same described above.

22 **Experiment 3.** The effect of air temperature during the experiment of the volatilization
23 was studied. This experiment was conducted twice as follows; the first (Experiment 3-1)
24 was done under relatively low temperature levels (5, 10, 15 °C) and the second one

1 (Experiment 3-2) was at high levels (10, 15, 20 °C). We used a growth chamber to
2 control the temperature that is more than 10 °C. A large refrigerator room with enough
3 light level to plant growth was used for 5 °C treatment. As we had only one growth
4 chamber suitable for the experiment, these experiments were conducted at different
5 date, although treatment of 5 and 10 °C in Experiment 3-1 could be done at the same
6 time by using both the refrigerator room and the growth chamber. The temperature was
7 kept at each treatment level during all the experimental period.

8 **Experiment 4.** The effect of $\text{NH}_4\text{-N}$ content in the slurry on the volatilization was
9 examined. We treated the slurry with aeration to change $\text{NH}_4\text{-N}$ content in the slurry.
10 The $\text{NH}_4\text{-N}$ content decreased by the aeration treatment, but pH of the slurry increased
11 and the other properties of the slurry changed slightly (Table 1). In this experiment, the
12 application rate was only the recommended rate and measurement period of the NH_3
13 volatilization was 96 h.

14 **Experiment 5.** Three levels of dry matter content (DMC) of the slurry were treated in
15 this experiment. We prepared the slurries by diluting 2 and 3 fold with deionized water
16 prior to application. To avoid the effect of difference in the application rate of $\text{NH}_4\text{-N}$
17 derived from the slurry on the volatilization, we applied 20 g m^{-2} as $\text{NH}_4\text{-N}$ from the
18 slurries. Since original DMC in the raw slurry was 124 g kg^{-1} , DMC in the 2-fold and
19 the 3-fold diluted slurry was 62 and 41 g kg^{-1} , respectively (Table 1).

20 **Experiment 6.** We collected three kinds of slurries of which pH was 6.6, 6.9 and 7.1
21 respectively and used them for this experiment to clarify the effect of pH of the slurry
22 itself on the NH_3 volatilization.

23 **Experiment 7.** To examine the effect of lowering pH of the slurry on the NH_3
24 volatilization, we used the slurry to which superphosphate was applied to decrease pH

1 of the slurry. The application rate of the superphosphate was the amount required to
2 meet pH 6.5. The slurry used as a control received no superphosphate.

3 **Field Experiment**

4 We carried out a field experiment from September 1999 to July 2000 to assess NH₃
5 volatilization factor found in the pot experiments. Grassland used in the experiment was
6 timothy (*Phleum pratense* L., variety Nosappu) sward established in 1997. The
7 grassland was usually cut two times per year to produce hay or silage. Some chemical
8 properties of soil in this experimental field were as follows; pH(H₂O), 6.4; Total N and
9 C, 3.0 and 40.3 g kg⁻¹, respectively; Available P measured by Bray No.2 method, 0.25 g
10 kg⁻¹; Cation exchange capacity, 24.9 cmol(+) kg⁻¹; Exchangeable K, Ca and Mg, 0.28,
11 1.71 and 0.26 g kg⁻¹, respectively.

12 Vinyl chloride pipes with a cross-section area of 0.023 m² were set onto the
13 grassland soil. The slurry was applied within the pipes at different 3 times that were at
14 late autumn after 2nd cut (Oct. 30, 1999), the following spring (May 5, 2000), and
15 summer after 1st cutting (June 30, 2000). The treatments of application rate at each time
16 were 3 levels that were 0, the recommended rate (6 kg m⁻²) and the heavy rate (12 kg
17 m⁻²). We used the same equipment as illustrated in Fig.1 to measure the volatilized NH₃
18 from the slurry applied to grassland surface in the pipe. The experiment was conducted
19 with three replications.

20

21 **Results**

22 **NH₃ volatilization from the slurry applied on soil surface**

23 We clearly recognized NH₃ volatilization from the surface-applied slurry and there was
24 no volatilization from the slurry covered with only 2 cm depth of the soil (Fig. 2). These

1 results confirmed that NH_3 volatilization occurred only in the surface application of the
2 slurry. Among the treatments of the topdressing of chemical fertilizers, only urea
3 showed continuous NH_3 volatilization and its volatilization factor, which is a ratio of
4 volatilized $\text{NH}_3\text{-N}$ to N applied as urea, was 0.06 over 96 h period (Fig. 2).

5 **Change in NH_3 volatilization rate with time**

6 NH_3 volatilization rate with time in Experiment 2 was illustrated in Fig. 3 as typical
7 pattern of the rate. In all our experiments, as shown in Fig. 3, NH_3 volatilization rate
8 increased usually to maximum level within 2 h following the application of the slurry in
9 every treatment and then decreased rapidly. Since the peak rate in each experiment was
10 basically dependent on the $\text{NH}_4\text{-N}$ applied from the slurry, the volatilization rate shown
11 in the heavy application was usually higher than in the recommended application. Each
12 treatment in the same application rate affected the volatilization, although the effect was
13 relatively slighter than that of application rate. In every experiment, there was no
14 significant difference in the volatilization rate among the treatments in the same
15 application rate after 24 h or more since the application.

16 **Cumulative amount of volatilized NH_3 and its estimation**

17 In every experiment, it was very clear that the cumulative amount of the volatilized NH_3
18 in the heavy application rate was usually higher than that in the recommended
19 application rate (Fig. 4). Fig. 4 also showed clearly that the following conditions abated
20 the NH_3 volatilization; dry soil water condition, low temperature, and low $\text{NH}_4\text{-N}$
21 content in the slurry, low DMC of the slurry, low pH of the slurry, and acidifying by
22 adding superphosphate to the slurry. Consequently the cumulative amount of the
23 volatilized NH_3 decreased under those conditions.

24 In order to estimate the amount of the volatilized NH_3 from the surface-applied

1 slurry we tried to analyze all our data by fitting a model to the measured NH₃
 2 volatilization loss. At first, we used a model based on the Michaelis-Menten-type
 3 equation presented by Sommer and Ersbøll (1994) who fitted this type of model directly
 4 to cumulative NH₃ loss data. The fitting, however, was not well in our data (data not
 5 shown). It may be one of the causes that the NH₃ volatilization process in many of our
 6 experiments does not completely reach steady state during the measurement period for
 7 120 h, as illustrated in Fig. 4.

8 Then we examined to use another type of model as illustrated in Fig. 5 and equation
 9 (1).

$$10 \quad N(t) = N_{\max}(1 - \exp(-s t)) \quad (1)$$

11 This model describes the cumulative NH₃ volatilization, N(t), over time, t, since the
 12 application. The model parameter N_{max} is the total loss of NH₃-N as time approached
 13 infinity, and the parameter s is the positive constant derived from the fitting to the
 14 observation using the least square method and it is involved in the slope of the curve
 15 illustrated in Fig. 5. The curve fitting based on the equation (1) was considerably
 16 significant in each experiment (Table 2) and the observed cumulative amount of the
 17 volatilized NH₃-N (V_n) showed well approximated 1:1 relationship with the N_{max}
 18 (Fig.6). In addition the N_{max} could be significantly estimated by only NH₄-N applied
 19 from the slurry (Fig. 7), even though the data in Fig. 7 included results in all our
 20 experiments in which treatments were widely different from each other. From the
 21 results, the volatilized NH₃-N from the surface-applied slurry could be more precisely
 22 estimated by the following equation (2) than that was estimated by a linear regression in
 23 which R² was 0.834.

$$24 \quad N_{\max} = 0.110 N_s^{1.43} \quad (R^2=0.904) \quad (2)$$

1 where N_s is the amount of $\text{NH}_4\text{-N}$ applied from the slurry.

2 **NH_3 volatilization factor**

3 The observed NH_3 volatilization ratio (VR) was calculated by the equation (3),

$$4 \quad \text{VR} = V_n/N_s \quad (3)$$

5 where V_n is the cumulative amount of the volatilized $\text{NH}_3\text{-N}$ for measurement period in
6 each experiment and N_s is the same in equation (2). The VR ranged from 0.23 to 0.50 in
7 the recommended application and from 0.26 to 0.55 in the heavy application (Table 2).
8 The mean VR in the recommended application and the heavy application was 0.33 and
9 0.39, respectively, and overall mean of VR was 0.36.

10 As illustrated in Fig. 4, however, it appeared that NH_3 volatilization did not
11 completely finish during the measurement period in some of the experiments where the
12 slurry was applied at heavy rate. This means that V_n may be underestimated compared
13 with N_{max} defined above. The NH_3 volatilization factor (V_f) should be therefore
14 calculated by the revised equation (4),

$$15 \quad V_f = N_{\text{max}}/N_s \quad (4)$$

16 because N_{max} can be considered as the total volatilization loss of $\text{NH}_3\text{-N}$. The V_f was
17 from 0.22 to 0.48 in the recommended application and from 0.31 to 0.61 in the heavy
18 application (Table 2). The mean V_f in the recommended application and the heavy
19 application was 0.32 and 0.42, respectively. Overall mean of V_f was 0.37. Consequently
20 the difference between V_f and VR in the heavy application rate was relatively wider
21 than that in the recommended application rate. This confirmed the suggestion that V_n
22 was underestimated compared with N_{max} , particularly in the treatments of the heavy
23 application of the slurry.

24 **Field experiment**

1 The V_n in each application time increased significantly with the application rate of the
2 slurry (Table 3). In the same application rate the effect of application time on the V_n was
3 very clear, thus the V_n in autumn application was usually the lowest, followed by the
4 spring application and the highest was in summer application (Table 3). Therefore the
5 VR in the autumn application was the lowest and it in the summer application was the
6 highest regardless of the application rates (Table 3). The VR in the autumn application
7 with the recommended application rate of the slurry (6 kg m^{-2}) was slightly out of range
8 of the V_f found in the pot experiments. The VR in spring and summer application,
9 however, was within the range of the V_f regardless of the application rate of the slurry. It
10 is therefore likely that the V_f found in our pot experiments can be generally adaptable to
11 the field condition.

12 Difference in VR among the application time was not corresponding to the difference
13 in both pH and DMC of the slurries applied at each time (Table 3 and 1). Among the
14 same application rate of the slurry the N_s was very similar in each application time,
15 because $\text{NH}_4\text{-N}$ content in the applied slurries did not show wide difference among the
16 application times (Table 3 and 1). In addition, mean water condition in the surface layer
17 soil (0-20 cm) during the experiment was also similar among the application time of
18 autumn, spring and summer; those were -42, -31, -49 kPa as soil water matric potential,
19 respectively. However mean air temperature during the experiment in autumn, spring
20 and summer was 7, 11 and 20 °C, respectively. This wide difference in the mean
21 temperature was corresponding to the difference in VR among the application time.
22 These results in field condition also supported the findings in our Experiment 3.

23

24 **Discussion**

1 NH_3 volatilization is controlled by two equilibriums, i.e., the association-dissociation
2 equilibrium between NH_4^+ and NH_3 in the liquid phase and the partition equilibrium of
3 NH_3 between the liquid and gas phase in immediate contact to the slurry applied on the
4 soil surface. Therefore many factors directly or indirectly affect to the volatilization
5 (Sommer and Hutchings 2001). Our experimental results were also consistent with
6 many scientific findings as follows; dry soil water condition (Donovan and Logan 1983;
7 Sommer *et al.* 1991), low air temperature (Sommer *et al.* 1991; Moal, *et al.* 1995;
8 Braschkat *et al.* 1997; Sommer *et al.* 1997), low $\text{NH}_4\text{-N}$ content in the slurry (Sommer
9 and Hutchings 2001), low DMC of the slurry (Sommer and Olsen, 1991; Stevens *et al.*
10 1992; Frost JP 1994), low pH of the slurry (Saito *et al.* 1989), and acidifying by adding
11 acidic substances to the slurry (Saito *et al.* 1989; Stevens *et al.* 1989, 1992; Frost *et al.*
12 1990; Bussink *et al.* 1994) could abate the volatilization. NH_3 volatilization from the
13 surface-applied slurry is therefore affected by a multitude of the factors, and hence the
14 proportion of $\text{NH}_4\text{-N}$ lost as NH_3 is highly variable. Because of this high variation of the
15 NH_3 volatilization, we need a prediction model of the volatilization including the factors
16 discussed above to estimate N fertilizer value of the surface-applied slurry.

17 A theoretical model (ALFAM model) including not only the factors discussed above
18 but also some others such as the application method has been already offered to estimate
19 the loss (Søgaard *et al.* 2002). We could not establish a model like ALFAM, although
20 we found that the NH_3 volatilization losses under many different experimental
21 conditions could be estimated by only the application rate of the $\text{NH}_4\text{-N}$. It might be due
22 to that the applied $\text{NH}_4\text{-N}$ from the slurry was only source of the volatilization and
23 controlled principally the amount of cumulative NH_3 volatilization loss. We should
24 remind, however, that the effect of the applied $\text{NH}_4\text{-N}$ on the cumulative amount of NH_3

1 loss like N_{\max} was exponential function rather than linear function, as shown in Fig.7.
2 This suggests therefore that the NH_3 volatilization factor in the heavy application of the
3 slurry should be distinguished from that in the recommended rate, when we offer the
4 NH_3 volatilization factor.

5 As for the NH_3 volatilization factor, Stevens and Laughlin (1997) summarized from
6 many experimental results that the volatilization factor ranged from 0.31 to 0.93. Our
7 volatilization factors, which ranged from 0.22 to 0.61 as results of V_f defined by
8 equation (4), were located relatively lower position in the data summarized by them.
9 This lower position of the volatilization factor was also found by Saito et al. (1989) who
10 reported the factor ranged from 0.2 to 0.4.

11 In our experiments we examined major factors affecting the NH_3 volatilization, but
12 the examined factors did not cover some another important factors such as rainfall, wind
13 speed, solar radiation, nature of the vegetative cover on the field and soil properties such
14 as cation exchange capacity, soil texture and hydraulic conductivity (Sommer and
15 Hutchings 2001). In addition we carried out only one field experiment to confirm the
16 volatilization factors. From these conditions it is likely that our volatilization factors are
17 not always regarded as recommended values in Japan. Even so, they are useful and
18 valuable, because there is no recommended value of the NH_3 volatilization factor based
19 on the scientific results found in Japan at present. Further field scale experiments and
20 the model describing NH_3 volatilization process from the animal manures applied to
21 grassland surface will be needed to obtain the recommendation value of the
22 volatilization factor that can be adoptable to grassland in all over Japan.

23 As a conclusion of this paper we suggest provisionally three NH_3 volatilization
24 factors (unit: $\text{g NH}_3\text{-N (g NH}_4\text{-N)}^{-1}$), because the volatilization factor should be

1 distinguished by the application rate of the slurry, as described above. The first one is
2 0.32, when the application rate of the slurry is less than 6 kg m^{-2} , and the next is 0.42,
3 when the application rate is more than that. Finally it is 0.37, when the application rate
4 of the slurry was unknown. These values are mean values found in our experiments
5 including 6 factors affecting the volatilization at each application rate of the slurry.

6

7 **Acknowledgements**

8 We would like to express our thanks to Dr Takuji Sawamoto for his great help and
9 important suggestion to our experiments and also to the following undergraduate
10 students of Laboratory of Soil Fertility and Plant Nutrition in Rakuno Gakuen
11 University for their assistances during the experiments; Mr Yoshiyuki Hara, Mr Koichi
12 Takakura, Miss Kaori Noda and Miss Eri Ozawa.

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1 **Figures legends**

2

3 **Figure 1** Outline of trapping equipment for volatilized $\text{NH}_3\text{-N}$ from surface-applied
4 cattle slurry.

5

6 **Figure 2** Change in cumulative amount of volatilized $\text{NH}_3\text{-N}$ from surface-applied
7 cattle slurry (SA-Slurry), chemical fertilizers (urea and ammonium sulfate, AS) and
8 surface-applied slurry with soil cover (Soil cover) following the application over 96 h
9 period. Vertical bars indicate the standard deviation (n=3).

10

11 **Figure 3** The profile of NH_3 volatilization rate over 48 h of the measurement period of
12 120 h for different soil water conditions and application rates of cattle slurry. Wet soil
13 water condition (-3 kPa) and recommended application rate (6 kg m^{-2}), WR; wet soil
14 water condition and heavy application rate (12 kg m^{-2}), WH; medium soil water
15 condition (-31 kPa) and recommended application rate, MR; medium soil water
16 condition and heavy application rate, MH; dry soil water condition (-310 kPa) and
17 recommended application rate, DR; dry soil water condition and heavy application rate,
18 DH. Vertical bars indicate the standard deviation (n=3).

19

20 **Figure 4** Change in cumulative amount of the volatilized $\text{NH}_3\text{-N}$ with time following
21 the application of cattle slurry. Open and solid mark in Experiment 2, 3, 4, 6 and 7
22 indicates the recommended application rate (6 kg m^{-2}) and the heavy application rate
23 (12 kg m^{-2}), respectively; circle, triangle, and square shows treatment level, respectively.
24 The application rate of the slurry in Experiment 5 was referred to Table 2. Each

1 treatment level was shown in each figure. In the figure of Experiment 7, SP means
2 superphosphate. Vertical bars indicate the standard deviation (n=3).

3

4 **Figure 5** A model of the cumulative amount of volatilized $\text{NH}_3\text{-N}$ expressed by a
5 equation of $N(t) = N_{\text{max}}(1 - \exp(-s t))$. N_{max} , the total loss of $\text{NH}_3\text{-N}$ as time approached
6 infinity; parameter s , positive constant derived from the fitting to the observation using
7 the least square method.

8

9 **Figure 6** Relationship between the observed cumulative amount of the volatilized
10 $\text{NH}_3\text{-N}$ (V_n) and the predicted amount (N_{max}). Real line in the figure indicates the line of
11 $y=x$. r in the figure is correlation coefficient.

12

13 **Figure 7** Relationship between the applied $\text{NH}_4\text{-N}$ from the slurry (N_s) and the
14 predicted amount of the volatilized $\text{NH}_3\text{-N}$ (N_{max}).

15

Table 1 Some chemical properties of cattle slurries used in the experiments

Number	Experiment		pH	EC (S m ⁻¹)	DMC (g kg ⁻¹)	Total C (g kg ⁻¹)	N (g kg ⁻¹)			P (g kg ⁻¹)	K (g kg ⁻¹)
	Factor	Remarks					NH ₄ -N	Org. N [†]	Total N		
1	Soil cover		6.9	1.95	73	27.3	2.0	1.9	3.9	1.3	3.0
2	Soil water condition		7.1	1.79	129	46.5	1.8	3.1	4.9	1.9	4.1
3-1	Temperature	5 and 10 °C	7.8	2.24	131	45.6	2.3	3.3	5.6	1.5	6.3
		15 °C	7.7	1.81	88	41.4	2.3	3.7	6.0	1.5	5.4
3-2	Temperature	10 °C	7.4	1.94	116	40.5	2.0	3.1	5.1	1.3	5.3
		15 °C	7.2	2.12	122	41.9	1.8	3.3	5.1	1.3	5.5
		20 °C	7.2	2.11	117	40.5	1.9	3.1	5.0	1.3	5.5
4	NH ₄ -N content	aeration	8.9	2.02	55	16.4	0.9	2.7	3.6	1.0	2.4
		no aeration	7.6	1.36	57	19.7	1.9	2.7	4.6	0.9	2.0
5	DMC (dilution)	raw slurry	7.3	2.43	124	37.6	2.0	2.5	4.5	1.2	4.9
		2-fold dilution	7.5	1.43	62	18.4	1.0	1.2	2.2	0.6	2.5
		3-fold dilution	7.5	1.04	41	10.9	0.7	0.8	1.5	0.4	1.8
6	pH	low	6.6	1.85	89	35.3	1.7	2.4	4.1	0.6	4.0
		middle	6.9	2.22	83	31.1	2.0	2.9	4.9	1.0	4.5
		high	7.1	1.89	81	30.6	1.9	2.7	4.6	1.2	3.7
7	Acidifying	raw slurry	7.5	2.33	122	36.7	2.1	3.7	5.8	1.5	5.8
Field Experiment		autumn	7.7	1.97	70	24.4	2.0	2.6	4.6	1.4	4.3
		spring	7.4	1.93	103	35.7	2.1	2.9	5.0	1.3	5.2
		summer	7.0	2.12	83	27.2	2.1	2.3	4.4	1.1	4.9

EC, Electric Conductivity; DMC, dry matter content of the slurry.

[†]Org. N, Organic N = Total N - NH₄-N, because NO₃-N was not detected in all cases.

Table 2 $\text{NH}_4\text{-N}$ applied from the slurry (N_s), cumulative amount of volatilized $\text{NH}_3\text{-N}$ for measurement period (V_n), the estimation of cumulative volatilized $\text{NH}_3\text{-N}$ using the equation of $N(t)=N_{\max}(1-\exp(-s t))$, volatilization ratio (VR) and the volatilization factor (V_f) calculated from the estimated total volatilized $\text{NH}_3\text{-N}$ (N_{\max}) and N_s in each experiment

Number	Experiment		N_s (g m^{-2})	V_n (g m^{-2})	$N(t)=N_{\max}(1-\exp(-s t))^\dagger$				$VR=V_n/N_s$ ($\text{g NH}_3\text{-N (g NH}_4\text{-N)}^{-1}$)		$V_f=N_{\max}/N_s$ ($\text{g NH}_3\text{-N (g NH}_4\text{-N)}^{-1}$)	
	Factor	Application rate of the slurry (kg m^{-2})			Level of the factor	N_{\max} (g m^{-2})	s	Curve fitting R^2	application rate of the slurry		application rate of the slurry	
									< 6 kg m^{-2}	> 6 kg m^{-2}	< 6 kg m^{-2}	> 6 kg m^{-2}
2	soil water condition	6	-3 kPa	10.8	3.0	2.8	0.063	0.988	0.27		0.26	
		6	-31 kPa	10.8	3.1	2.9	0.070	0.992	0.28		0.27	
		6	-310 kPa	10.8	2.5	3.0	0.068	0.990	0.23		0.28	
		12	-3 kPa	21.6	9.0	9.1	0.030	0.999		0.42		0.42
		12	-31 kPa	21.6	8.4	7.6	0.030	0.999		0.39		0.35
		12	-310 kPa	21.6	7.1	7.0	0.036	0.999		0.33		0.33
3-1	Air temperature, relatively low condition	6	5 °C	13.8	5.5	5.1	0.047	0.959	0.40		0.37	
		6	10 °C	13.8	6.0	5.6	0.043	0.976	0.43		0.41	
		6	15 °C	13.8	6.9	6.7	0.040	0.984	0.50		0.48	
		12	5 °C	27.6	10.9	11.1	0.023	0.984		0.40		0.40
		12	10 °C	27.6	12.4	13.3	0.019	0.994		0.45		0.48
		12	15 °C	27.6	14.5	15.8	0.019	0.996		0.52		0.57
3-2	Air temperature, relatively high condition	6	10 °C	12.0	3.7	3.4	0.054	0.944	0.31		0.29	
		6	15 °C	10.8	4.8	4.5	0.046	0.966	0.44		0.41	
		6	20 °C	11.4	5.1	4.9	0.044	0.988	0.45		0.43	
		12	10 °C	24.0	7.8	8.3	0.022	0.982		0.33		0.34
		12	15 °C	21.6	10.7	11.7	0.019	0.996		0.50		0.54
		12	20 °C	22.8	12.4	13.9	0.018	0.999		0.55		0.61
4	$\text{NH}_4\text{-N}$ content	6	aeration	5.4	1.2	1.2	0.095	0.975	0.23		0.22	
		6	no aeration	11.4	3.0	2.8	0.093	0.987	0.26		0.25	
5	DMC	10	raw slurry	20.0	8.1	7.8	0.079	0.993		0.40		0.39
		20	2-fold dilution	20.0	7.9	8.0	0.038	0.999		0.40		0.40
		30	3-fold dilution	20.0	6.2	6.2	0.037	0.998		0.31		0.31
6	pH	6	pH6.6	10.2	2.8	2.7	0.043	0.999	0.27		0.27	
		6	pH6.9	12.0	3.8	3.7	0.033	0.994	0.32		0.31	
		6	pH7.1	11.4	3.6	3.4	0.075	0.986	0.32		0.30	
		12	pH6.6	20.4	6.1	6.3	0.026	0.998		0.30		0.31
		12	pH6.9	24.0	8.4	8.6	0.026	0.998		0.35		0.36
		12	pH7.1	22.8	9.4	9.1	0.034	0.985		0.41		0.40
7	Acidifying	6	raw slurry	12.6	3.9	4.0	0.029	0.999	0.31		0.31	
		6	superphospahte	12.0	2.9	3.5	0.015	0.995	0.24		0.29	
		12	raw slurry	25.2	10.3	12.3	0.015	0.999		0.41		0.49
		12	superphospahte	24.0	6.2	9.3	0.009	0.996		0.26		0.39
minimum									0.23	0.26	0.22	0.31
maximum									0.50	0.55	0.48	0.61
mean									0.33 ^a	0.39 ^b	0.32 ^c	0.42 ^d
Overall mean									0.36 ^e		0.37 ^f	

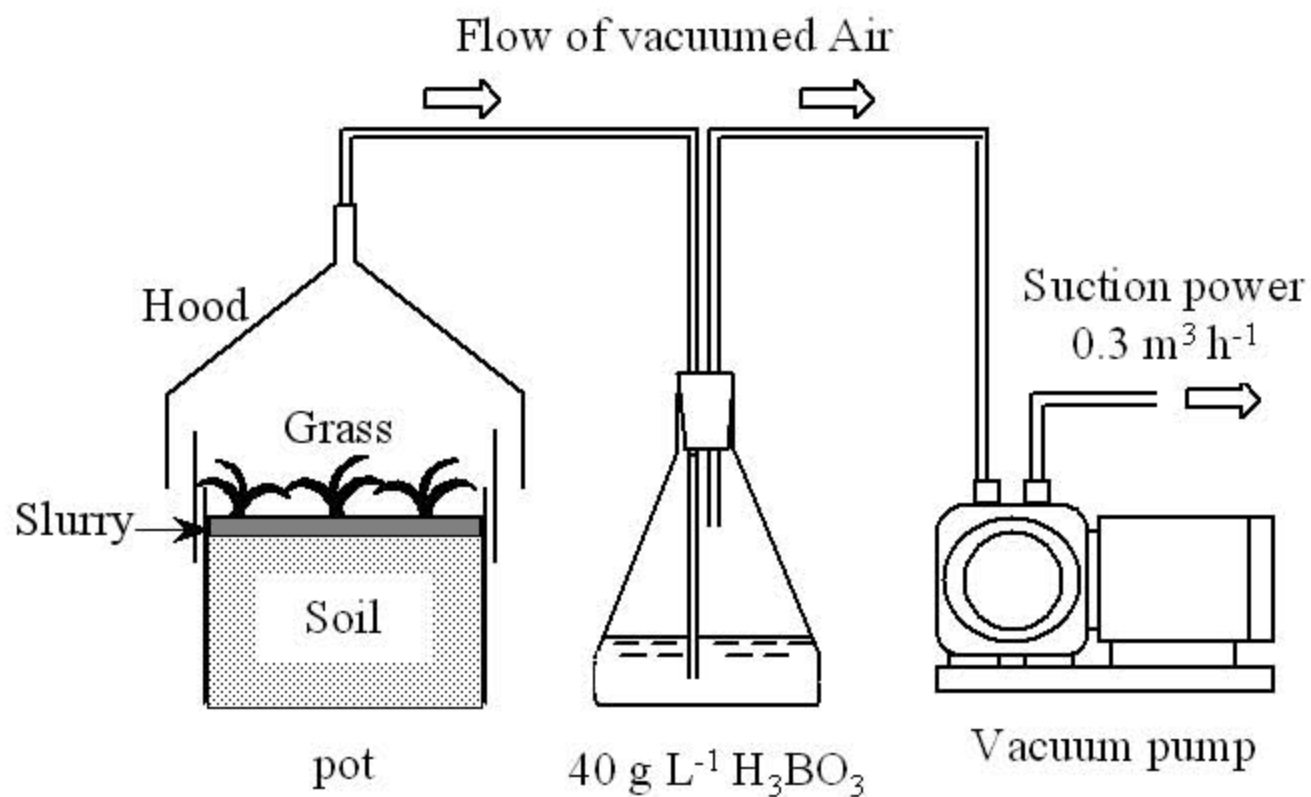
[†] $N(t)$ is the estimated cumulative volatilized $\text{NH}_3\text{-N}$ over time, t. N_{\max} and parameter s; see Fig. 5.

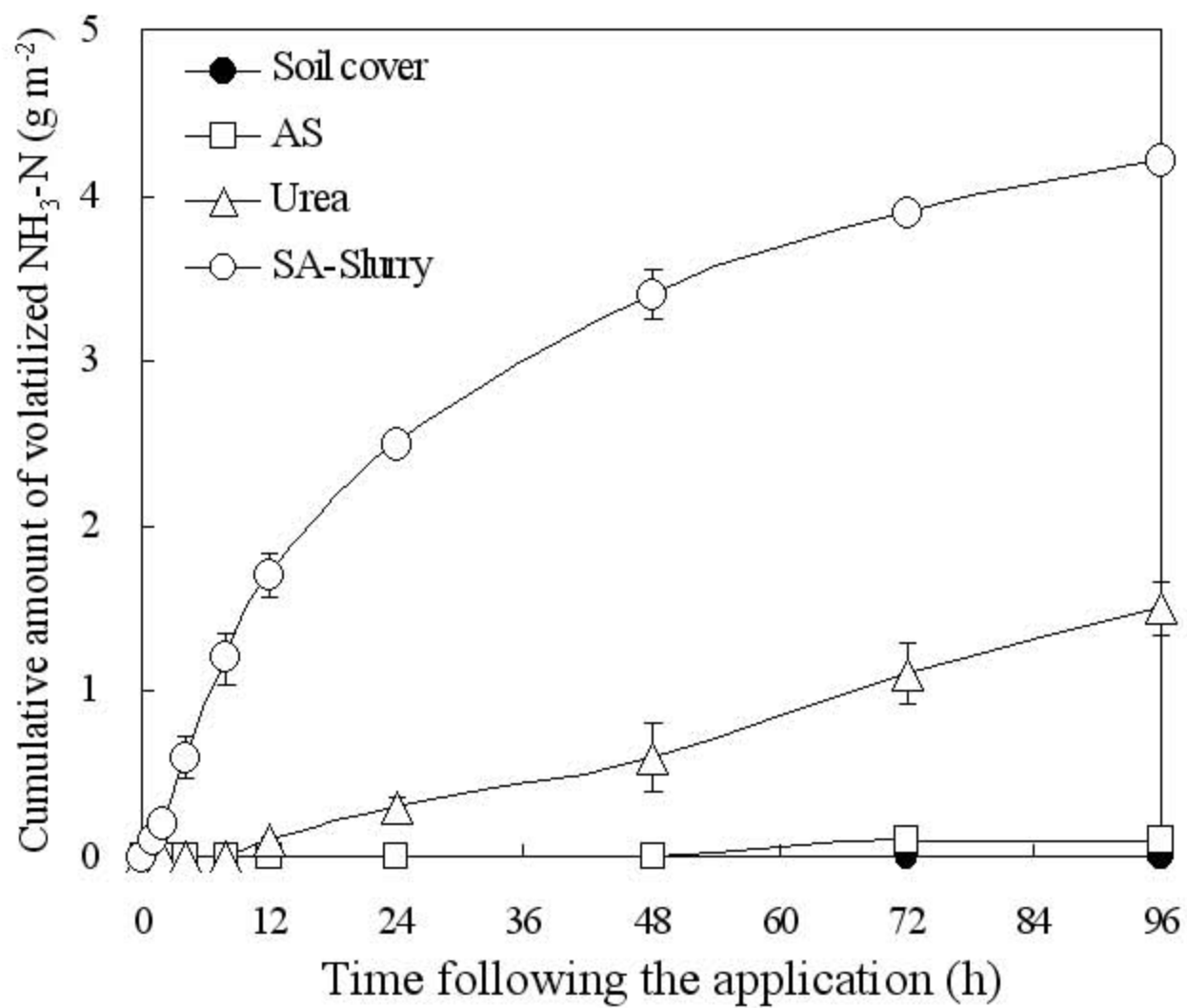
^a and ^b, statistically significant between them by t-test of the difference in the population mean ($P<0.05$); ^c and ^d, statistically significant between them ($P<0.01$); ^e and ^f, there was no significant difference between them.

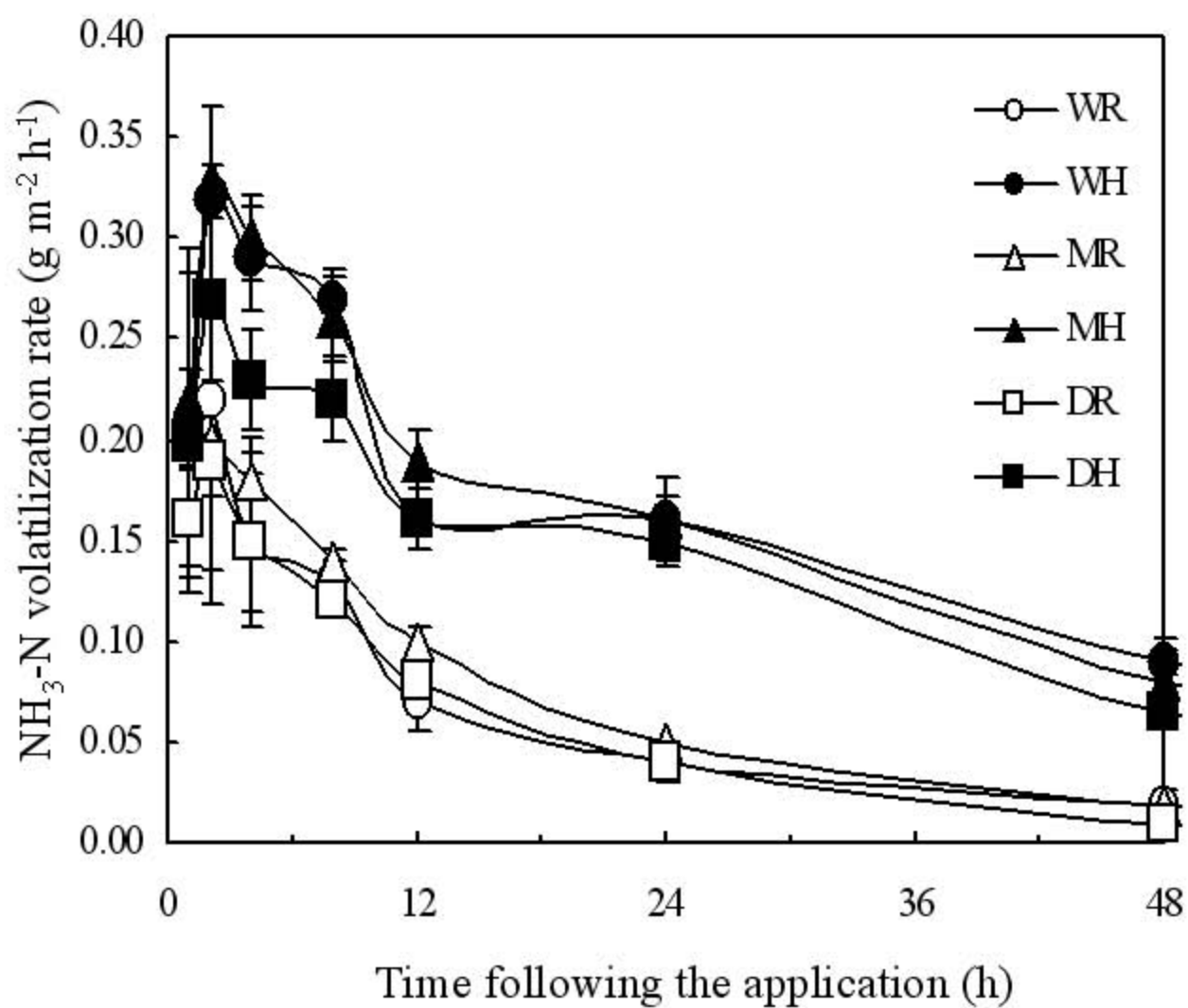
Table 3 $\text{NH}_4\text{-N}$ applied from the slurry (N_s), cumulative amount of volatilized $\text{NH}_3\text{-N}$ for measurement period (V_n), and volatilization ratio (VR) in the field experiment

Application of the slurry		N_s (g m^{-2})	V_n (g m^{-2})	VR= V_n/N_s ($\text{g NH}_3\text{-N (g NH}_4\text{-N)}^{-1}$)
rate (kg m^{-2})	time			
6	autumn	12.0	2.1 ^a	0.18 ^a
6	spring	12.6	3.9 ^b	0.31 ^b
6	summer	12.6	4.4 ^c	0.35 ^b
12	autumn	24.0	5.8 ^d	0.24 ^c
12	spring	25.2	7.8 ^e	0.31 ^b
12	summer	25.2	8.8 ^f	0.35 ^b

Different letters in the same column indicates significant difference at $P < 0.05$ using least significant difference.







Cumulative amount of the volatilized $\text{NH}_3\text{-N}$ (g m^{-2})

