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# Effects of Thickness of Solid Media, Ventilation Rate, and Chamber Volume on Ammonia Emission from Liquid Fertilizers Using Dynamic Chamber-Capture System (DCS)

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**Abstract:** This study was conducted with the aim of improving the dynamic chamber-capture system, which estimates ammonia emissions during the application of liquid fertilizer from livestock manure. We focused on the volume of the chamber and headspace, the height of the solid media, the flow rate of the pump, and the ventilation rate. Total ammoniacal nitrogen ( $\text{NH}_3 + \text{NH}_4^+$ ) is an important factor affecting ammonia volatilization. Even though the characteristics of liquid fertilizer were changed, the effect of total ammoniacal nitrogen on ammonia volatilization remained the largest. Increasing the thickness of solid media inside the chamber has the effect of reducing ammonia emission by reducing the contact area between liquid fertilizer and air. Although it is very difficult to measure and control the wind velocity in a chamber using a general vacuum pump, it can be indirectly evaluated through the ventilation rate in the macroscopic aspect. The higher the ventilation rate, the faster the flow of air in the chamber, which is linear with the increase in ammonia emission flux. We find that it may be necessary to improve the steady wind velocity within the chamber and of the linkages to upscale the wind tunnel system.

**Keywords:** ammonia inventory; liquid fertilizer; solid thickness; ventilation rate; wind velocity

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## 1. Introduction

Ammonia is one of the few base gases present on earth and reacts with acid gases to easily form ultrafine particulate inorganic ammonium salts [1]. In Korea, where changes in the four seasons are obvious, compost and liquid fertilizer are mainly sprayed in the spring before farming commences. A large amount of ammonia, a precursor of ultrafine particulate matter (PM 2.5), is generated. In conjunction with spring yellow dust [2,3], this is recognized as worsening the domestic PM 2.5 situation. Ammonia, a major source of odors, is released into the atmosphere through various human activities, with livestock manure being the largest. For example, livestock manure accounted for 61% of total ammonia emissions in the United States (US) and 85% in the European Union (EU-28) [4,5]. In Korea, an ammonia inventory showed that 29 million tons of ammonia are emitted annually, with more than 70% originating from livestock manure [6]. The manure generated in Korea annually is approximately 48.84 million tons, of which more than 90% is reclaimed as compost or liquor and then spread on agricultural soils. Although ammonia is emitted from all of these processes, including livestock houses, manure storage, resource recycling facilities, and agricultural land spraying, the current inventory system does not encompass the entire process.

In the US, a 10-digit source classification code (SCC) provides ammonia emission factors that consider the characteristics of manure, types of livestock houses, and manure treatment methods [4]. In Europe, the emission estimation process is divided into Tier 1, Tier 2, and Tier 3, and there is a difference in obtaining and using relevant data in each country. Among these, Tier 2, a total ammoniacal nitrogen (TAN) and mass balance-based approach, presents emission factors by subdividing housing, storage, yards, spreading, grazing/outdoor, and considers the form of manure (solid, slurry, and litter) [5]. In Korea, the amount of emissions ( $\text{kg year}^{-1}$ ) is calculated by multiplying the emission factor ( $\text{kg head}^{-1}$ ) by activity ( $\text{head year}^{-1}$ ), and most of the emission factors currently in use are based on the data published in 2007 by the European Economic Area (EEA) and in 1994 by the United States Environmental Protection Agency (USEPA). Only cattle, pigs, deer, and cats are used in domestic research data [7]. Within the same livestock species, ammonia is emitted differently depending on breeding methods, manure characteristics, manure treatment methods, and seasons. However, the manure management sector in the domestic inventory does not fully reflect this, and the assumption that ammonia is emitted equally throughout the year differs significantly from the emission factors in the US and EU-28. This is a limitation in the domestic calculation method [3].

The compost and liquid fertilizer originating from livestock manure are sprayed on agricultural soil, in accordance with agricultural activities and cropping systems and according to seasonal changes. After being sprayed on soil, nitrogen in compost and liquid fertilizer mainly follow the following four routes: (1) volatilization in the form of ammonia from the soil surface, (2) absorption through plant roots in the form of ions, (3) leaching into the subsoil, or (4) adsorption onto the surface of soil colloid particles [8]. Among these four processes, in order to improve the accuracy and fractionation of emission factors in the domestic ammonia inventory, research on the first process (1) volatilization in the form of ammonia from the soil surface, which is particularly affected by the domestic situation, should be conducted. Based on (1) route, the factors influencing ammonia emission after spraying compost and liquid fertilizer could be divided into the characteristics of compost and liquid fertilizer, climate factors, and soil characteristics. In general, the higher the pH and concentration of TAN, the more ammonia volatilization proceeds, resulting in increased ammonia emission [9,10]. It is known that ammonia emissions increase with warmer and windier conditions [11,12] and with higher soil moisture content and less macropores in soil [9,12]. The emission flux, a major factor in the emission factor, is known to be greatly influenced by the installation and operating conditions of the chamber. If the flow rate of the pump connected to the chamber is high, underpressurization will occur, leading to an overestimation of the gas flux. Decreasing the headspace of the chamber will increase the gas emission from the soil [13,14]. Furthermore, when the flow rate of the pump is the same, the emission flux increases because the chamber is smaller, and when the turnover speed is the same, the flux also increases because the volume of the chamber is larger [15]. In most cases when nitrogen fertilizers are sprayed on site, it is calculated and sprayed in the unit of kg of nitrogen per area (e.g.,  $\text{km}^2$ , acre, hectare), not per volume of soil ( $\text{m}^3$ ). However, when testing is conducted in a chamber, the amount and volume of soil determine the depth (height) of the soil in the chamber. The height of the soil in the chamber is directly related to the permeability and infiltration of liquid fertilizer, and finally affects ammonia volatilization [16]. When considering the situation in the field, it is easy to identify the trend of increasing ventilation rate and emission flux as the wind speed increases [17]. In particular, an increase in ventilation rate is known to increase the amount of gas volatilization, which has a significant effect on reducing the odor concentration in the manure [18]. Ammonia emission increased with increasing wind speed as well as temperature, and so the increase in wind speed due to climate change is expected to eventually affect the ammonia emission flux [11,19].

In order to calculate and improve the ammonia emission factor when considering the domestic situation, studies on compost and liquid fertilizer characteristics, soil characteristics, and the effects of ammonia volatilization on the combined action of climate factors should be performed, but related studies are insufficient. Using several complex factors as independent variables concurrently for actual experiments in the open field is difficult, and an alternative may be to use a chamber that can control precise experimental conditions. For this reason, we established a dynamic chamber-capture

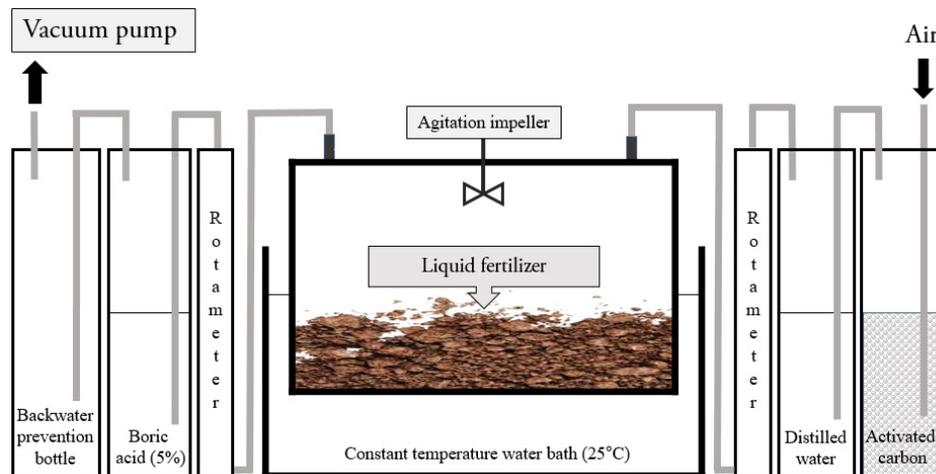
system (DCS) to evaluate the soil and liquid fertilizer characteristics affecting ammonia emission when liquid fertilizer was applied to soil. The applicability of DCS was verified using both artificial synthetic liquid fertilizer and actual livestock liquid fertilizer [20]. However, as only one type of liquid fertilizer was used under very limited experimental conditions, improving the system to reflect a realistic scenario is necessary. To be used as data for ammonia emission factor within the ammonia inventory, the process of evaluating the amount of ammonia emission during liquid fertilizer spreading at the field scale must be performed.

The objective of this study was to improve the DCS by identifying the factors (thickness of solid media, ventilation rate, and chamber volume) of the chamber experiments affecting the ammonia emission flux to derive the optimum operating conditions and set the conditions that simulate the field situation.

## 2. Materials and Methods

### 2.1. Dynamic Chamber-Capture System (DCS)

In this study, a dynamic chamber-capture system (DCS) is used to rapidly analyze all ammonia emitted in the chamber (Figure 1). This chamber system was used in a current study and more information is available in the literature [20]. Briefly, the chamber was placed in a water bath (20 °C), which could maintain a constant temperature. On one side, clean air was introduced into the chamber, and on other side of the chamber, a single channel vacuum pump was connected to suck out all the air in the chamber and to pass it through the prepared boric acid solution (5%) to capture the entire amount of ammonia. In addition, rotameters were installed at the front and rear of the system to check and control the flow rate. For detection accuracy, captured  $\text{NH}_3$  recovery, and a sensitivity test for this chamber-capture system, 1.5 ppm standard gas was used. The  $\text{NH}_3$  gas was absorbed into boric acid solution at a rate of 1.5 liters per minute (LPM) for 20 minutes. The mean, standard deviation, and relative standard deviation were 1.484 ppm, 0.049 ppm, and 3.304%, respectively, and the recovery was 98.2%. Sensitivity was also conducted for the method detection limit (MDL) using a t-value of 3.14 (degree of freedom:  $n_1 - 1 = 6$  at 99% confidence); the mean was 0.030 ppm, and MDL was 5.128 ppb.



**Figure 1.** Schematic of dynamic chamber-capture system (DCS) with a constant temperature water bath.

### 2.2. Preparation and Analysis of Samples

In order to confirm the ammonia gas emission and collection through the DCS, synthetic liquid fertilizer (SLF) was prepared using  $(\text{NH}_4)_2\text{SO}_4$  reagent (Junsei, Tokyo, Japan). One type of liquid fertilizer was collected from public resource facility (liquid fertilizer 1) in Hongcheon-gun, Kangwon-

do province, Korea. Another two types of livestock liquid fertilizers were collected from swine farms (liquid fertilizer 2 and 3) in Yeosu-si, Gyeonggi-do province, Korea. Collected samples were stored at  $-60\text{ }^{\circ}\text{C}$  until used in the experiment. Granite weathered soil (GWS) was used as an experimental media to find out the ammonia emission flux when solution was sprayed on farmland. In evaluating and verifying the applicability of DCS, we selected GWS (particle size between 4 and 10 mm) instead of field soil as a medium to minimize the effects of complex soil characterization factors (void ratio, macropore, micropore, aggregation, etc.). GWS was collected through the domestic local gardening market. GWS was washed three times with tap water and twice with distilled water in the laboratory, air-dried, and used in the experiment.

The pH and electrical conductivity (EC) of livestock liquid fertilizer were determined with a combination pH-EC meter (Thermo Orion 920A, Thermo Fisher Scientific, Waltham, MA, USA). Total nitrogen (TN) and total ammoniacal nitrogen (TAN) was determined using a Kjeldahl digester (KjeldDigester K-446, BÜCHI, Flawil, Switzerland), distillation (Distillation Unit B-324, BÜCHI, Flawil, Switzerland), and titration. Other characteristics of liquid fertilizer were determined by “Method for quality test of fertilizer and sampling standards Annexed list 1. Chemical test method of fertilizer” in Korea. The pH and EC of GWS were measured in a 1:5 solid:water suspension using a combination pH-EC meter (Thermo Orion 920A, Thermo Fisher Scientific, Waltham, MA, USA). The weight loss on ignition (LOI) was conducted to determine both the water at  $105\text{ }^{\circ}\text{C}$  and carbon content at  $400\text{ }^{\circ}\text{C}$  over 16 hours [21].

### 2.3. Experimental Set-Up

#### 2.3.1. Effect of the Characteristic of Liquid Fertilizer on Ammonia Emission Flux

SLF and three types of livestock liquid fertilizer were utilized to confirm the effect of the characteristic of liquid fertilizer on ammonia emission flux. However, in order to compare the effects of various characteristics of liquid fertilizer on ammonia emission flux, it was necessary to minimize the effects of pH and TAN, which have a significant effect on ammonia emission flux. Therefore, the TAN was prepared in various concentrations (190, 500, 1000, 1500, and 2000  $\text{mg L}^{-1}$ ) using  $(\text{NH}_4)_2\text{SO}_4$ . Immediately before entering the chamber, the pH of all liquid fertilizer was adjusted to 8 using 1M NaOH and HCl solutions. After closing the chamber, the vacuum pump was operated and the ammonia gas emitted from the liquid fertilizer was captured in boric acid (5%) and quantified by 0.01N  $\text{H}_2\text{SO}_4$  titration. On the basis of the result of a previous study (Kim et al., 2020), the capture time was set to 1 h after the start of the experiment. Ammonia emission flux ( $\text{mg m}^{-2} \text{h}^{-1}$ ) was calculated considering the footprint ( $\text{m}^2$ ) of the chamber and the operation time ( $\text{h}^{-1}$ ). The slope of the graph through this experiment could confirm the difference in the trend of ammonia emission flux according to the characteristics of liquid fertilizer. In addition, from the next experiment, the experiment was conducted only using liquid fertilizer 1, which has the largest amount of ammonia emission flux and is advantageous for comparing the amount of change.

#### 2.3.2. Effect of Thickness of Solid Media on Ammonia Emission Flux

In field agricultural soil, effective soil depth affects ammonia emission flux, which needs to be considered in chamber experiments. The input of liquid fertilizer was calculated according to the input ration of  $200\text{ kg-N ha}^{-1}$ , which is widely used in liquid fertilizer research in Korea [20,22,23]. Thus, to vary the thickness of solid media, the GWS was input to vary the height of the solid in the chamber (0.5, 1, 2, 3, 4, 5, 6, 7, and 8 cm) while the volume of liquid fertilizer into the chamber was fixed. In this section, liquid fertilizer was not further modified and used as it was. After sealing the chamber, the subsequent process proceeded as before the experiment.

#### 2.3.3. Effect of Ventilation Rate on Ammonia Emission Flux

In the case of a chamber system, the ventilation rate means the exchange of air in the chamber, which is partly in agreement with the flow rate of air in the chamber. Since only the vacuum pump

connected to the outside could not determine the wind velocity inside the chamber, the experiment was performed by variously setting the ventilation rates (0.3, 0.5, 0.6, 0.9, 1, 1.25, 2, 3, 3.5, 4, and 5  $\text{min}^{-1}$ ) by adjusting the chamber volume and the pump flow rate. In this section, liquid fertilizer was not further modified and used as it was. After sealing the chamber, the subsequent process proceeded as before the experiment. The flow velocity in the chamber was measured using thermo anemometer after calibration (Testo 405i, Testo SE & Co. KGaA, Titisee-Neustadt, Germany). The general measurement range and relative error were 0–30  $\text{m s}^{-1}$  and 5%, respectively. The measurement uncertainty at 2, 5, 10, 15, and 20  $\text{m s}^{-1}$  was 2.3%, 1.4%, 1.1%, 1.1%, and 1.1%, respectively.

#### 2.3.4. Confirmation Experiment

When the ventilation rate was constant (in contrast to Section 2.3.4.), the experiment was conducted to confirm the degree of interference or obstruction by the chamber volume and/or headspace. Therefore, various volumes of the chamber were prepared (2, 3, 5, 8, 10, and 15 L) and used for the experiment, while the ventilation rate was constant at 1  $\text{min}^{-1}$ . After the same volume of liquid fertilizer was placed in the chamber without any treatment, the chamber was immediately sealed. Then the subsequent process proceeded as before the experiment.

#### 2.4. Statistical Analysis

All measurements were performed in triplicate. One-way analysis of variance (one-way ANOVA) tests were used to compare the means of different treatments. When significant  $p$ -values ( $p < 0.05$ ) were obtained, the differences between the means were evaluating using Tukey's test. The data were analyzed using a statistical analysis system program (SAS 9.4, SAS Institute Inc., Cary, CA, USA).

### 3. Results and Discussion

#### 3.1. Characteristics of Liquid Fertilizer and GWS and Their Ammonia Emission Flux

Initially, the pH, EC, and LOI of GWS (4–10 mm) were 6.9, 0.01  $\text{ms cm}^{-1}$ , and 0.8%, respectively. As a result of several washing cycles, the EC was very low. Compared to the media used in a recent study [20], there were no significant differences in the chemical properties and only a difference in size distribution.

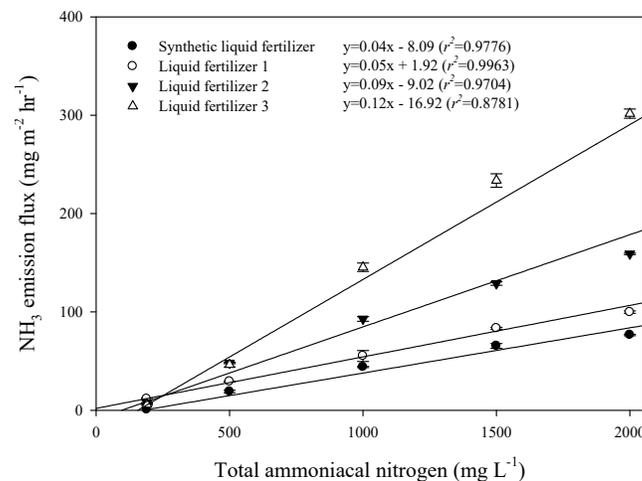
The physicochemical properties of the three types of liquid fertilizer were also determined (Table 1). The pH, EC, and total phosphorous (TP) were the highest in liquid fertilizer 1 (LF1), which was manufactured in a public resource facility that treats domestic sewage and livestock manure together. TN and TAN, which directly affect ammonia emissions, were also highest in LF1. Conversely, liquid fertilizer 2 (LF2) and liquid fertilizer 3 (LF3), manufactured by aeration directly from swine farms, showed lower pH and nitrogen contents than LF1. Kang et al. [24] analyzed the characteristics of completely decomposed liquid fertilizer collected from 46 sites nationwide in Korea. The results showed that the mean values of pH, EC, TN, TAN, TP, and suspended solids were 8.0, 11.6  $\text{ms cm}^{-1}$ , 847  $\text{mg L}^{-1}$ , 317  $\text{mg L}^{-1}$ , 193, and 5,188  $\text{mg L}^{-1}$ , respectively. Due to the lower decomposition, the nitrogen content of the LF1, LF2, and LF3 samples was slightly higher than that of the 46 nationwide samples. Nonetheless, considering the overall characteristics of the liquid fertilizer and the fact that liquid fertilizer is distributed in the neighborhood, they were considered to be suitable for the experiment. The high pH and TAN of liquid fertilizer readily act on the volatilization of ammonium ions in the solution [25], and therefore, all liquid fertilizers are also expected to release ammonia gas during soil application.

**Table 1.** Basic properties of liquid fertilizers.

	Liquid Fertilizer 1	Liquid Fertilizer 2	Liquid Fertilizer 3
pH	9.07	8.19	7.57
Electrical conductivity (ms cm <sup>-1</sup> )	18.02	10.72	8.73
Total nitrogen (%)	0.20	0.11	0.03
Total ammoniacal nitrogen (mg L <sup>-1</sup> )	1899	1021	189
Total organic carbon (%)	0.15	0.16	0.35
Total phosphorous (mg L <sup>-1</sup> )	190	48	183
Suspended solid (mg L <sup>-1</sup> )	4827	3373	6027

\*Different letters within the same column indicate significant differences at the 5% level by Tukey's test.

To assess the influence of the characteristics of liquid fertilizer except pH and TAN, which have the greatest effect on ammonia emission, the pH of the liquid fertilizer was adjusted to 8.0, and TAN was adjusted to various concentrations to estimate the ammonia emission flux using DCS (Figure 2). In the case of SLF, made using only reagent, the ammonia emission flux was 0.59, 19.04, 43.99, 65.37, and 76.57 mg m<sup>-2</sup> hr<sup>-1</sup> at 190, 500, 1000, 1500, and 2000 mg L<sup>-1</sup>, respectively. The slope and r-square of the regression line were 0.04 and 0.9776, respectively, indicating a good linear relationship between TAN and ammonia emission flux. In a previous study, the same experiments were performed at 25 °C, resulting in a slope three times higher [20]. Fundamentally, changes in solution temperature affect most physical characteristics of the solution, for example, viscosity, density, and mass diffusivity [26]. According to He et al. [27], while the temperature increases, the ammonia volatilization process is attributed to an enhanced production of ammonia gas. In addition, if the temperature rises above 40 °C, the nitrification process is suppressed, and ammonia volatilization occurs more actively. The increase in ammonia emission is known to increase not only when the temperature of the solution rises, but also when the soil temperature increases [28].



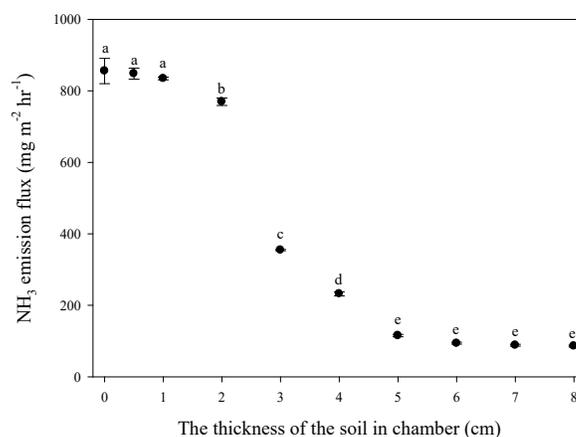
**Figure 2.** Changes in ammonia emission flux by liquid fertilizer type using a dynamic chamber-capture system at 20°C and pH 8 condition. Error bar means standard deviation (SD,  $n = 3$ ).

Despite the same TAN concentration and fixed pH condition, LF3, LF2, and LF1 emitted approximately 1.16, 1.92, and 3.90 times more ammonia, respectively, than SLF based on emission flux. The next argument of note is suspended solid (SS). Hichri et al. [29] reported that solids in liquid fertilizer could affect both the solubility and mass transfer coefficient of ammonia. However, Arago et al. [26] demonstrated that the presence of a solid under 1% had no significant influence on ammonia volatilization. As the SS concentration of all liquid fertilizers was under 1%, and the trends were not seen, it is difficult to conclude that the differences in slope were influenced by SS. By

comparing pure solution and livestock manure liquid, Lee et al. [30] suggested that the original TAN concentration in manure liquid might have influenced ammonia emission. In this study, TAN of initial liquid fertilizer seems to play an important role in the volatilization of ammonia. The difference in the aerobic microbial community in the liquid fertilizer may affect ammonia volatilization [31,32], but it is difficult to have a significant effect during the one-hour capture time. Therefore, it will be necessary to collect and analyze a much larger variety of liquid fertilizer samples in order to identify differences caused by components other than those mentioned here.

### 3.2. Effect of Thickness of Solid Media on Ammonia Emission Flux

After the nitrogen source is introduced into the soil, various properties of the soil such as soil pH, water content, groundwater level, and pores affect ammonia volatilization [33]. Among the various factors, the changes in ammonia emission flux were confirmed for effective soil depth where LF1 would be infiltrated (Figure 3). First, after filling the GWS with various thicknesses in the chamber, the volume of LF1 was set to the same amount calculated for 200 kg N ha<sup>-1</sup>. The zero *x*-axis indicated no GWS with the highest ammonia emission flux, 855.52 mg m<sup>-2</sup> hr<sup>-1</sup>. Ammonia emission flux significantly decreased until the thickness of the solid media increased to 5 cm ( $p < 0.05$ ), and there was no change in emission flux until 8 cm. Deep solid thickness in the chamber means that the liquid fertilizer can infiltrate into the lower layer and far away from the surface layer in a short time. A similar situation frequently occurs when spraying liquid fertilizer on agricultural field soil. If the soil has a high water content, or a high groundwater level after intensive rainfall, the liquid fertilizer sprayed onto the soil surface cannot easily infiltrate underground [16,34]. Alternatively, when spraying too much liquid fertilizer, it cannot infiltrate smoothly and forms a puddle on the surface [35]. This phenomenon causes the effect of increasing the surface area of liquid fertilizer and air, thereby increasing the ammonia emission flux [36]. With this in mind, liquid fertilizer applications that can reduce ammonia emissions have been studied through the use of crop height, adjustment of viscosity, timing of application, injection, and more [36–38]. In this section, washed and dried GWS was used, and the initial water content was not considered, and so there is a limit to continuously using 5 cm. Nevertheless, it will be meaningful to investigate the effect of the thickness of solid media in the chamber and to gain a significantly meaningful result.

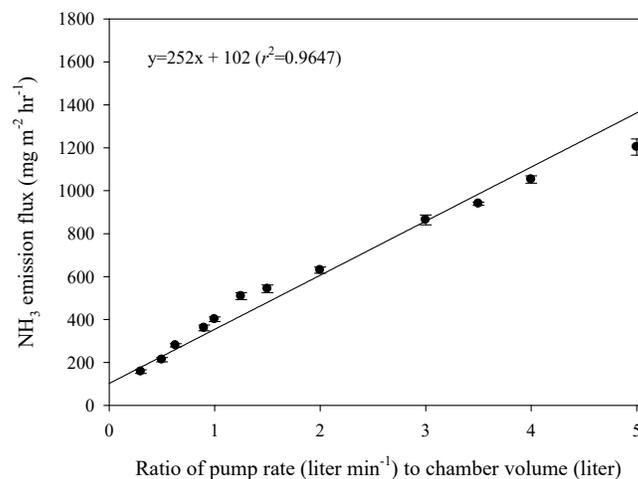


**Figure 3.** Changes in ammonia emission flux with different soil media thickness using dynamic chamber-capture system at 20 °C and pH 8 condition. Means with different letters are significantly different (Tukey's test,  $p < 0.05$ ). Error bar means standard deviation (SD,  $n = 3$ ).

### 3.3. Effect of Ventilation Rate on Ammonia Emission Flux

The relationship between wind velocity and ammonia volatilization has long been studied, and as the wind velocity increases, the volatilization rate also proceeds rapidly, resulting in an increase in total emission [39–41]. It is difficult to maintain or regulate the wind velocity at various points

inside the chamber and thus, relatively few studies have been conducted compared to field-scale studies. Nevertheless, because wind velocity is a negligible part of the experimental design process, we controlled the ventilation rate ( $\text{min}^{-1}$ ) of the chamber by adjusting the pump rate ( $\text{L min}^{-1}$ ) and the volume of the chamber (liter) and confirmed the change in ammonia emission flux accordingly (Figure 4). The higher the flow rate of the pump relative to the chamber volume, the greater the amount of air passing through the chamber, and the greater the ventilation rate. The increase in the  $x$ -axis shown in Figure 4 indicates that the flow rate of the pump increases with respect to the chamber volume, which means that a large amount of air passes through the chamber, which in turn means an increase in the ventilation rate. When the ventilation rate is high and the ammonia discharged to the chamber headspace is quickly removed from the chamber, a greater amount of ammonia will be volatilized from the liquid fertilizer. Therefore, the total amount of ammonia emissions per unit time increased with increasing ventilation rate, and the regression equation was calculated as  $y = 252x + 102$  with high  $r^2$  (0.9647). Considering the cross-sectional area of the chamber and the flow rate of the pump, the theoretical flow velocity at the center of the chamber increased from  $0.08 \text{ m s}^{-1}$  to  $0.83 \text{ m s}^{-1}$ , while the ventilation rate increased from  $2 \text{ min}^{-1}$  to  $5 \text{ min}^{-1}$ . In the actual measurement using a thermo anemometer, the flow velocity at the center of the chamber was approximately  $0.05 \text{ m s}^{-1}$ , and there was no significant change. Compared to the 30 year average wind velocity of  $2.21 \text{ m s}^{-1}$  reported by the Korea Meteorological Administration [42], the flow velocity in the chamber is relatively slow. Therefore, although it is difficult to directly conclude the effect of wind velocity on ammonia emission flux, it could be used as a value in the calm state ( $< 0.4 \text{ m s}^{-1}$ ) based on wind rose graphics. To analyze the change in ammonia emission due to wind velocity, future studies need to use a wind tunnel system, an experimental tool on a scale larger than the chamber. Recently, large wind tunnel systems on scales larger than chambers have been utilized for concise scientific results [43–45]. Sommer et al. [46] presented new emission factors from European livestock manure management systems at housing, manure storage, field-applied manure, and grazing states using a wind tunnel.

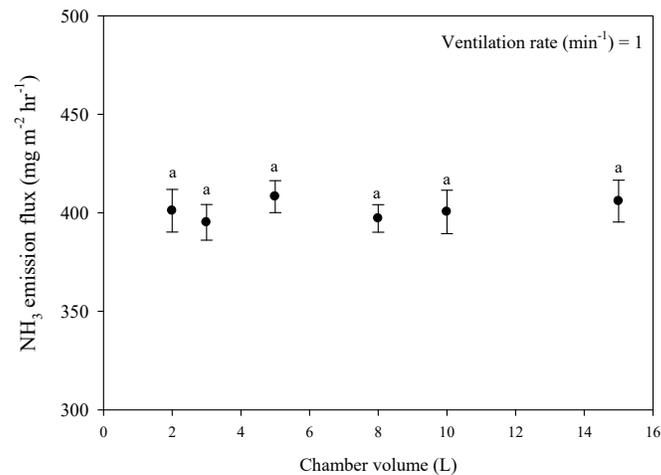


**Figure 4.** Changes in ammonia emission flux with different ventilation rate ( $\text{min}^{-1}$ ) using dynamic chamber-capture system at  $20 \text{ }^\circ\text{C}$  condition. Error bar means standard deviation (SD,  $n = 3$ ).

### 3.4. Effect of Volume of Headspace in Chamber on Ammonia Emission Flux

The experimental conditions of similar previous studies for ammonia emission were identified to select only one ventilation rate. Dattamudi et al. [47] conducted an experiment with a ventilation rate of  $0.04 \text{ min}^{-1}$  using a chamber (41.4 L) and pump (1.5 LPM). Kim et al. [20] used a  $1 \text{ min}^{-1}$  ventilation rate condition using a chamber (15 L) and pump (15 LPM). Sarwar et al. [48] and Aneja et al. [49] used ventilation rate conditions of  $1.48 \text{ min}^{-1}$  and  $4.8 \text{ min}^{-1}$  using a chamber (7.4 L and 24 L) and a pump (both 5 LPM). Among them,  $1 \text{ min}^{-1}$  was selected in consideration of the results of previous experiments and the condition to minimize turbulence in ammonia emission [30]. To

confirm the effect of volume of headspace in the chamber, various volumes of chambers were utilized, but there was no significant difference ( $p > 0.05$ ) (Figure 5). This result demonstrates that if the ventilation rate is kept constant, there is no significant effect on gas volatilization in the chamber system, even if the volume of the chamber changes. Based on this evidence, further studies will be able to utilize chambers of varying volumes. It was concluded that the ventilation rate is a very important factor for small-scale chamber experiments.



**Figure 5.** Changes in ammonia emission flux according to volume of chamber using dynamic chamber-capture system at 20 °C condition with ventilation rate fixed at 1 min<sup>-1</sup>. Means with different letters are significantly different (Tukey's test,  $p < 0.05$ ). Error bar means standard deviation (SD,  $n = 3$ ).

#### 4. Conclusions

It is important and necessary for research to be conducted on improving the ammonia inventory in Korea, and this study deals with the spread of liquid fertilizers. The objective of this study was to improve the DCS and focus on the volume of the chamber and headspace, the height of the solid media, the flow rate of the pump, and the ventilation rate. Experiments with various types of liquid fertilizers showed that TAN is an important factor affecting ammonia volatilization. In addition, even though the characteristics of liquid fertilizer were changed, the effect of TAN on ammonia volatilization remained the greatest. The effect of the thickness of solid media on ammonia volatilization in the chamber condition, such as the effect of water content, groundwater level, and gas phase of soil under field conditions affected the volatilization of ammonia. Although it is very difficult to measure and control the wind velocity in a chamber through a general vacuum pump, it can be indirectly utilized in terms of the ventilation rate. A higher ventilation rate in the chamber means a faster flow rate of air in the chamber and positively affects the ammonia emission flux. These results indicate that the ventilation rate is partly in agreement with the flow rate of air in the chamber. Nevertheless, if only the ventilation rate could be maintained, the effect of the volume of the chamber could be negligible. In order to develop emission factors suitable for the domestic situation, a study on wind velocity considering timing of the agricultural crop system in Korea and the improvement of the steady wind velocity within a chamber are needed.

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