

Review of methods for determination of ammonia volatilization in farmland

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Abstract. Ammonia is one of the most abundant alkaline trace gases in the atmosphere, which is one of the important factors affecting atmospheric quality. Excessive application of nitrogen fertilizer is the main source of global ammonia emissions, which not only exacerbate greenhouse gas emissions, but also leads to eutrophication of water bodies. In this paper, the basic principle, the operation process, the advantages and disadvantages, and the previous research results of the method are summarized in detail, including the enclosure method, the venting method, the continuous airflow enclosure method, the wind tunnel method and the micro- meteorological method. So as to provide a theoretical basis for selecting the appropriate method for determination of ammonia volatilization.

1. Introduction

Ammonia (NH₃) is an important alkaline gas in air, which plays very important roles in neutralizing the acidic substances in the atmosphere and maintaining the ecological balance. At present, there are about 9.3×10^6 mol NH₃ entering the atmosphere every year, and showed an increasing trend[1]. Gaseous NH₃ react with sulphuric acid, nitric acid and hydrochloric acid to form ammonium salt, which increases the concentration of PM2.5 particles in atmospheric pollutants[2].

The ammonia entering the atmosphere can re-enter the farmland and natural ecosystem with dry and wet settlement, which results in the increase of nitrogen content in the soil and water, resulting in eutrophication, leading to the replacement of plant species and the extinction of some species[3]. At present, the amount of nitrogen fertilizer lost from farmland soil accounts for about 1%-47% of the total amount of nitrogen applied[4]. The results show that the nitrogen use efficiency of farmland soil in China is low, and the utilization rate of traditional nitrogen fertilizer is about 35%[5]. Therefore, it is one of the key points in the field of agriculture and environmental protection to improve the nitrogen utilization rate of farmland, reduce the pollution of ecological environment and establish of farmland ammonia volatilization system which is used to evaluate the different soil types, meteorological conditions and agricultural technology[6].

At present, there are many methods to determine ammonia volatilization from farmland soil, mainly including two types: indirect method and direct method[7]. The indirect method mainly refers



to the soil balance method. The volatilization of ammonia is estimated by the amount of fertilizer, the amount of plant absorption, the amount of soil residue and the amount of leaching loss. However, due to the large number of measurement items, it is difficult to accurately estimate the nitrogen loss caused by nitrification denitrification process. Therefore, the indirect method has more errors and bad practicability[8]. The direct method includes the enclosure method, the venting method, the continuous airflow enclosure method, the wind tunnel method and the micrometeorological method, etc. The amount of ammonia volatilization was analyzed by collecting ammonia in the field air by means of an acidic solution or a trapping device impregnated with acid. Such methods are more accurate, but have different requirements for the experimental area of the test. Common ammonia absorption solutions are boric acid[9], orthophosphoric acid[10], sulfuric acid[11-12] and oxalic acid[13]. Indoor analysis methods include titration, conductivity method, colorimetry method[14]. The factors that affect the volatilization of ammonia are more, which increases the uncertainty and complexity of ammonia volatilization measurement. Different measurement methods have a great influence on ammonia volatilization measurement results[15]. By comparing the similarities and differences between different methods, the purpose of this paper is to provide the theoretical guidance and reference for selecting suitable methods for in-situ determination of ammonia volatilization in farmland soil.

2. Enclosure method

The principle of the enclosure method is to place the soil, fertilizer and plant in the same airtight container, and absorb the ammonia from the system by acid or alkaline substance, and then make quantitative determination. It is directly through the ammonia capture device to capture ammonia from the soil surface, commonly used in cell experiments, with advantages of simple equipment, easy to operate, good mobility, multi-point simultaneous measurement and spatial distribution measurement, high sensitivity[16]. But the ammonia in the sealed state of the process is completely different from the natural state. Because the internal pressure, temperature, humidity, wind speed and so on of the capture device are quite different from the real environment, only the ammonia volatilization of the soil is usually measured, and the influence of the field crop on the ammonia volatilization is neglected, which leads to the great degree of variability in point measurement and the large amount of labor.

The airtight sampling device of enclosure method is made of polyvinyl chloride rigid plastic bucket (15 cm in diameter and 10 cm in height), add 20 mL 2% boric acid solution to the evaporating dish, then set up with a iron wire to keep the top of the evaporating and the ground at a distance of about 7 cm, and then covered with a rigid plastic bucket sealed at the top. The ammonia absorbed by boric acid is titrated directly with a standard H_2SO_4 of 0.005 mol L^{-1} . The experimental device shown in Figure 1(a)[7].

Xu Wanli et al.[17] have shown that compared with the venting method and the continuous airflow enclosure method, the enclosure method has lower measurement results, mainly due to the temperature and stagnation of air flow between confined room and natural state. Shangguan Yuxian et al.[18] studied the dynamic process of ammonia volatilization from soil winter wheat mulching cultivation conditions under furrow with enclosure method and achieved good results.

3. Venting method

The venting method is improved on the basis of enclosure method, and it overcomes the shortcomings of airtight in the traditional venting method. Compared with other methods, this method is simple, convenient combination, low cost, and easy to control the conditions, the determination results is accuracy, the recovery rate is 99.51%, the coefficient of variation is only 0.77%, When equipped with a rainproof device, it is still possible to keep up with the rainy weather[19]. However, the effect of field wind velocity on ammonia volatilization could not be considered.

The sampling device was also made of polyvinyl chloride rigid plastic bucket (15 cm in diameter, 10 cm in height). Two sponges with a thickness of 2 cm and a diameter of 16 cm were uniformly impregnated with 15 mL of glycerol solution (50 mL of phosphoric acid + 40 mL of glycerol, constant volume to 1000 mL) and placed in a hard plastic bucket. The lower sponge is 5 cm from the bottom of the

bucket and the upper sponge is flat with the top of the bucket. Upper sponges absorb ammonia in the air and prevent it from entering the lower sponge is absorbed within the device. The experimental device shown in Figure 1(b)[20]. The lower sponge was used to absorb the volatile ammonia of the soil. After the absorption time was reached, it was extracted with 1 mol L⁻¹ KCl solution and then analyzed by a continuous flow analyzer.

Zhang YunHai et al.[21]study the relationship between ammonia volatilization and grazing intensity of grassland in Inner Mongolia from 2009 to 2010 with venting method. The results show that the recovery rate of ammonia volatiles is more than 87% by this method. Yang Yang et al.[22]study the response of winter wheat field on Loess Plateau NH₃ volatilization southern ridge made. The recovery rate of NH₃ was 99% in the field of winter wheat during the winter of 2011-2013. Xu Wanli et al.[17]showed that the amount of ammonia absorbed by the venting method ranged from 0.54 to 36.09 kg hm⁻², indicating that the method can not only absorb low ammonia gas, but also absorb high ammonia gas.

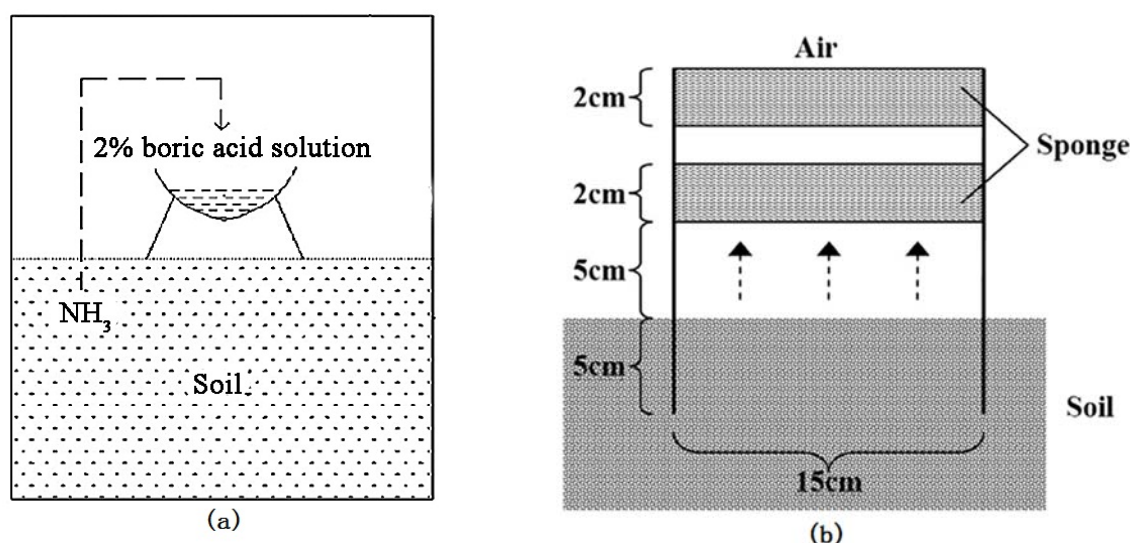


Figure 1. Enclosure(a) and Venting(b) methods for determination of ammonia volatilization.

4. Continuous airflow enclosure method

The principle of the continuous airflow enclosure method is to pump the gas from the sampling tank at a steady flow rate. The experimental device shown in Figure 2[23]. The ammonia volatilization rate is calculated by measuring the ammonia content of the inlet and outlet of the sampling box[24]. Ammonia in the air can be installed in the sampling box before the intake of acid absorption solution to remove.

The continuous airflow enclosure method has its unique advantages. Compared with the micrometeorological method, it can obviously eliminate the interference between two adjacent lands, and the micrometeorological conditions in the measured area are improved. Therefore, the measurement result is more similar. However, the disadvantage is that the method is to extract ammonia from the sampling chamber by pumping gas, resulting in a large difference in pressure between the inner and outer of the sampling chamber, resulting in greater errors in the determination results[25-26]. In addition, the system is controlled by the pumping rate and can only partly consider the influence of field wind velocity on ammonia volatilization when other conditions are relatively stable in the field. The pumping rate determines the rate of soil ammonia volatilization.

Qingyin Shang et al.[27]measured between 2007 and 2009 ammonia volatilization flux of paddy closed with continuous airflow enclosure method. Xia Wenjian et al.[28]studied using a closed chamber under continuous aeration process optimization of nitrogen Hubei rice-wheat cropping farmland ammonia volatilization loss system, and achieved good results.

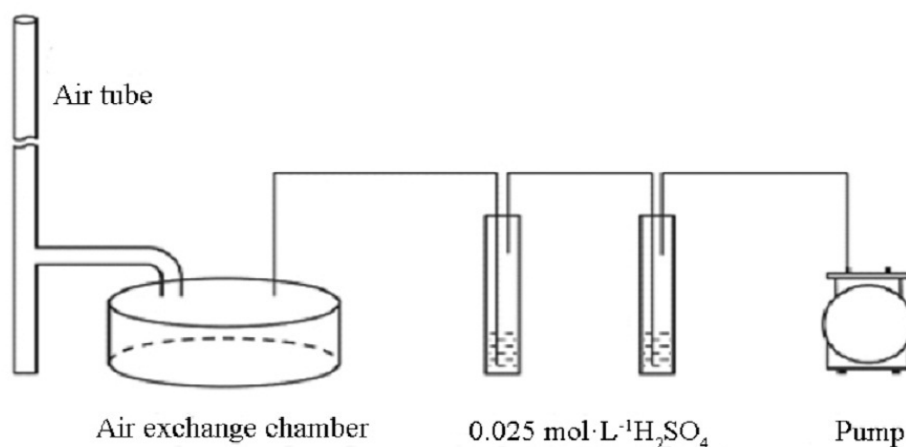


Figure 2. Continuous airflow enclosure method for determination of ammonia volatilization.

5. Wind tunnel method

The principle of the wind tunnel method is that under the action of the sampling pump, the gas sample is absorbed by a specific gas collecting bottle through the Teflon pipe. The remaining gas is expelled by the air pump and the solution in the bottle is determined by colorimetric method[29]. Finally, the ammonia volatilization per unit soil area at a given period of time was calculated by the difference between the outlet and the air inlet. The experimental device shown in Figure 3[23].

The wind tunnel method achieves continuous automatic sampling. By adjusting the wind speed, so that the wind tunnel inside and outside the temperature, humidity, light and other factors remain consistent, which greatly improved the experimental area of micrometeorological conditions[30]. In this method, the soil condition and biological condition are close to the external conditions, and the measurement results are representative. It is suitable for multi-processing and multi-repeat measurement in small scale range. It is especially suitable for multi-factor contrast experiment and has been widely used in Europe. But the wind tunnel method also has its shortcomings. For example, the wind tunnel method can not simulate the static wind conditions and precipitation conditions, when the wind speed is less than 0.3 m s^{-1} , the error is large; In the evening the wind tunnel prone to condensate moisture which absorb ammonia and lead to errors[31]. In addition, the wind tunnel boundary, wind speed and concentration distribution will also affect the determination results[32-34]. At present, due to the wind tunnel method equipment is expensive, so the research on this method is very few in China.

Braschkat et al.[34]found that the maximum temperature difference between inside and outside is about 1°C , the relative humidity was basically same, and the wind speed uniformity was better. The recovery rate of wind tunnel was 97% ~ 103%. The recovery rate of wind tunnel designed by Lockyer is 77% ~ 87%[35]. The recovery rate of the wind tunnel designed by Moal is 70% ~ 80%[36-37].

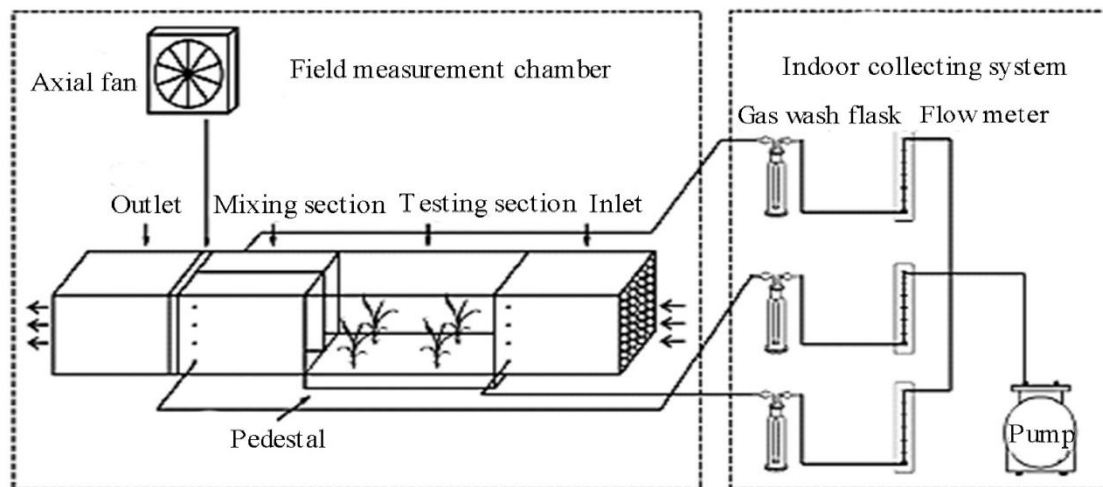


Figure 3. Wind tunnel method for determination of ammonia volatilization

6. Micrometeorological method

The micrometeorological method directly samples the air above the farmland, and does not change the natural environment, so it does not interfere with the ammonia volatilization process[38]. Because it has a larger measurement area, so more space representative. The results of micrometeorological method showed that ammonia volatilization accounted for 67% of the total loss of nitrogen fertilizer[39]. The method overcomes the shortcomings of the above methods which can not accurately quantify ammonia volatilization, especially in the monitoring of ammonia volatilization in large areas. But it requires a large and flat test area, complex, expensive measuring instruments, which also limits its application and development[40]. At present, there are mass balance method, gradient diffusion method and vorticity correlation method for the determination of ammonia volatilization in farmland.

6.1 Mass balance method

The mass balance method is the most mature and most commonly used method in the micro-meteorology method. The required area of the test area is relatively small, and the measurement of weather and gas concentration is low[41]. Its principle is to determination the volatile source downwind and upwind gas flux at the same time, and estimate the ammonia volatilization rate with the difference. The mass balance method can quantitatively measure ammonia volatilization without the need for too much test area and complex meteorological instruments, which are better in the round test area[42-43]. But the mass balance method needs to measure at least 5 levels of height, and will greatly increase the amount of labor and the determination of the time in the process of sampling, determination of different height of gas concentration, wind speed will greatly increase the cost of measurement[44].

6.2 Gradient diffusion method:

The gradient diffusion method is based on the gradient diffusion principle of gas movement. It is assumed that there is a gradient of ammonia concentration in the vertical direction over the farmland. The ammonia volatilization rate is calculated by measuring the two different concentrations of air gas concentration and a series of meteorological parameters[45]. The method is suitable for the determination of ammonia volatilization in large area farmland, and has the advantages of no stability correction and simultaneous determination of evapotranspiration. However, the method has the advantages of low concentration gradient, high requirement for instrument sensitivity, large space uniformity and little space disturbance, high demand for meteorological conditions and expensive instruments[46]. Therefore, the gradient diffusion method is far less than the mass balance method used.

6.3 Vorticity correlation method

Vorticity correlation method is used to directly measure the vertical motion of the gas to estimate the gas volatilization[47]. Unlike the gradient diffusion method, the vorticity correlation method is not affected by atmospheric stability, and there is no theoretical assumption. But the vorticity correlation method requires the rapid determination of meteorological, gas concentration monitoring instruments, and affected by heat flux, water vapor and other factors[48]. Due to NH_3 and other chemical properties of active gas easily adsorbed on the measuring instrument of the inner wall, thus affecting the accuracy of the determination results. The current vorticity correlation method is mainly used in CO_2 monitoring, and some reports are used for CH_4 , N_2O monitoring, and it is used less frequently in farmland NH_3 volatilization monitoring.

7. Conclusion

The choice of determination method is the core part to study the soil ammonia volatilization in farmland soil. In this paper, several kinds of determination methods are summarized, including the enclosure method, the venting method, the continuous airflow enclosure method, the wind tunnel method and the micrometeorological method. Each of these methods has its own characteristics, and its application is relatively mature. It plays an important role in the study of ammonia volatilization and the venting method is simple, low cost and widely used. It is very important to select the corresponding measurement method for different research purposes and research conditions. The development direction of the future ammonia volatilization method should be aimed at the development method which can easily control the conditions, reduce the error, and fast and accurate, and reasonable cost measurement method.

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