Ammonia emissions from paddy fields are underestimated in China ☆

[redacted]

A R T I [redacted]

Article history:
Received 7 September 2017
Received in revised form
11 December 2017
Accepted 25 December 2017

Keywords:
Nitrogen rate
Ammonia loss proportion
Non-linear response
Air pollution
Climate factor

[redacted] N can be lost as [redacted] $^{-1}$ in 2013 in [redacted] eaching or runoff. This suggests that mitigation measures for [redacted] d should take into account not only the N lost to water, but also to [redacted]

1. Introduction

China produced 208.2 million tons of rice in 2014, accounting for 28.1% of global production (FAO, 2017). However, excessive amounts of nitrogen (N) fertilizers are being used in paddy fields, with an average N fertilizer rate of over 300 kg N ha^{-1} yr^{-1} (Deng et al., 2011), and over 50% of this input N is lost to the environment through multiple pathways. Ammonia volatilization is one of the dominant pathways of N loss in paddy fields (Yan et al., 2011; Soares et al., 2012; Xu et al., 2012). NH_3 volatilization increases farmers' production costs and causes environmental degradation (Xu et al., 2015). NH_3 is a major atmospheric pollutant that plays an important role in the formation of secondary inorganic aerosols, leading to poor air quality and adverse impacts on human health (Behera et al., 2013; Gu et al., 2014). The emitted NH_3 can also return to land and surface water through deposition, resulting in soil and water acidification, eutrophication and biodiversity loss (Hellsten et al., 2008; Guo et al., 2010).

NH_3 emission is affected by a number of factors, such as fertilizer application rate (Dattamudi et al., 2016; Huang et al., 2016; Jiang et al., 2017), climate conditions (e.g. temperature, wind speed) (Fan et al., 2011; Louro et al., 2013), and soil properties (e.g. pH, soil type) (Fan et al., 2011; Zhang et al., 2013; Webb et al., 2014). Inventories of NH_3 emissions from paddy soils in China have been conducted (Zhang et al., 2011; Chen et al., 2014). However, large uncertainties exist in these inventories due to the variations in emission factors derived from different measuring methods (Hayashi et al., 2011; Zhao et al., 2012). For example, Chen et al. (2014) calculated that NH_3 lost from paddy fields accounted for

☆ This paper has been recommended for acceptance by Dr. Hageman Kimberly Jill.

* Corresponding author. Department of Land Management, Zhejiang University, Zijingang Campus, 866 Yuhangtang Road, Hangzhou 310058, China.
** Corresponding author. Key Laboratory of Nonpoint Source Pollution Control, Ministry of Agriculture, Institute of Agricultural Resources and Regional Planning, Chinese Academy of Agricultural Sciences, No. 12 Zhongguancun South Street, Haidian district, Beijing 100081, China.
E-mail addresses: bjgu@zju.edu.cn (B. Gu), liuhongbin@caas.cn (H. Liu).
[1] These authors contributed equally to this work.

approximately 16% of N input by compiling over 265 measurements across China, while the results derived from Zhou et al. (2016), with an even bigger dataset, showed that the average NH_3 loss accounted for only 12% of N input for paddy soils. However, the methods of measuring these NH_3 emissions were quite different, and whether the results of these measurements could be comparable for a meaningful inventory is unclear. Therefore, refining the understanding of these variations is crucial for reducing the uncertainty in NH_3 emissions from paddy fields.

We established a Nationwide NH_3 Emission Monitoring Network (NNEMN) for paddy fields in 2012–2013, and measured NH_3 emissions for 2 years continuously, by using a standardized measuring method. The network included 12 field sites, which covered three types of rice cultivation (single, double and rotation with wheat or potato or a vegetable crop) located in the main rice planting regions across China (Northeast China, Southeast China and Yangtze River Basin). The objectives of this study were to (i) quantify NH_3 loss and its uncertainties from paddy fields in different types of rice cultivation, (ii) explore the influence factors affecting NH_3 emission rate, including N application rate, soil airflow enclosure (CAE), was utilized to measure NH_3 volatilization from the paddy fields in all the treatment plots at the 12 sites. The NH_3 volatilization collection device (Fig. S1) consisted of a chamber, a vent pipe, a chemical trap bottle and a vacuum pump linked by plastic pipes to form a confined space (Cao et al., 2013). A chemical trap bottle filled with 60 mL of 20 g L^{-1} boric acid (H_3BO_3) connected with another hole was used to collect NH_3 gas from paddy field. The air exchange rate was set to 15–20 headspace volumes min^{-1}. The NH_3 volatilization rate was measured twice daily: morning (9:00–11:00) and afternoon (16:00–18:00) (Hou et al., 2007; Zhao et al., 2015). The average hourly NH_3 flux observed during the 4 h was directly converted into the average hourly flux per day (Zhao et al., 2015). The NH_3 trap solutions were brought to the laboratory and the ammonium (NH_4^+) nitrogen content of the traps was titrated with 0.005 M sulfuric acid (H_2SO_4). The NH_3 volatilization was continually monitored for 10–15 days following each fertilization event until volatilization became negligible (Chen et al., 2015a). The daily NH_3 volatilization rate was calculated from the average of the rates measured each day. The NH_3 volatilization flux was calculated as following equation:

$$F = \frac{2 \times C \times V \times 14 \times 10^{-2} \times 24}{t \times S} \quad (1)$$

where F is the flux of NH_3 volatilization (kg N ha^{-1} d^{-1}), C is the concentration of H_2SO_4 (M), V is the consumption volume of H_2SO_4 (mL), t is the duration of collection (h), and S is the chamber area (m^2). The cumulative NH_3 losses were the sum of NH_3 volatilization fluxes on sampling days.

The NH_3 loss proportion was calculated as following equation:

$$E_N = \frac{C_{NH_3} - C_0}{N} \times 100\% \quad (2)$$

where E_N is the NH_3 loss proportion (%), C_{NH_3} is the NH_3 volatilization at every non-zero N application rate (kg N ha^{-1}), C_0 is the NH_3 volatilization at the zero N application rate (kg N ha^{-1}), and N is N fertilizer application rate (kg N ha^{-1}).

The total amount of NH_3 volatilization for rice fields across China was calculated as following equation:

$$T_N = \sum_{n=1}^{n} \left(C_{F_{iNH_3}} \times S_i \right) \quad (3)$$

where T_N is the total amount of NH_3 volatilization (kg N), i represents an individual province, $C_{F_{iNH_3}}$ is the NH_3 volatilization of ith province at farm's N practice (kg N ha^{-1}), S_i is the growing rice area of the ith province (ha). If there was no monitor site in a certain province, the total NH_3 volatilization in this province was calculated using the monitored data of neighboring provinces.

The air temperature was determined using a mercury thermometer or a potentiometer when the NH_3 volatilization was measured. The precipitation and wind speed were obtained from the China Meteorological Forcing Dataset (CMFD).

2.4. Sample analysis

Soil samples at a depth of 0–20 cm were collected at the beginning of the trial using a 5-cm internal diameter auger. For each site, five replicate soil samples were randomly taken and mixed together to produce a composite sample. Average soil texture was determined for all fields using a mixed bulk sample from all samples across a field. Bulk density of soil samples was measured after being dried in an oven at 105 °C for 24 h. The soil pH (1:5 soil/water) and floodwater pH were determined using a potentiometer. The soil organic matter (SOM) was analyzed with dichromate oxidation, while total N (TN) was determined using the Kjeldahl digestion method (KDY-9830, Beijing) (Peng et al., 2011).

2.5. Statistical analysis

Spearman's correlation coefficients and multiple linear regression were used to test for significant correlations between NH_3 volatilization rates and influencing factors using SPSS 19.0 statistical software (SPSS Inc., Chicago, IL). A p values less than 0.05 was considered statistically significant.

3. Results

3.1. Temporal and spatial variations

The temporal variations indicated that NH_3 volatilization rate peaked 1–3 days after fertilization, followed by a rapid decline (Fig. 2a). For the three types of rice cultivation, the trends of NH_3 volatilization exhibited similar patterns, but the peak values for the single-rice were far lower than those for the double-rice and rice-upland rotation (Fig. S2), which had a lower N application rate. The average peak values for the single, double and rice-upland after basal fertilizer application were 4.2, 11.5 and 8.1 kg N ha^{-1} d^{-1}, respectively, for which the N application rates were 108, 149.2 and 117.9 kg N ha^{-1}. NH_3 volatilization rates dropped to a low level (<2 kg N ha^{-1} d^{-1}) from the peak value after 7–10 days.

The NH_3 volatilization for single rice, double cropping rice and rice-upland were 40.1, 54.9, and 57.9 kg N ha^{-1}, respectively, for typical farmers' practice (average rate of 269.0 kg N ha^{-1}). The average cumulative NH_3 volatilization was 56.0 kg N ha^{-1}, which represented 17.7% (14.4–21.0%) of the total N input. The average NH_3 volatilization in 2013 was 57.2 kg N ha^{-1}, slightly higher than that found in 2012 (55.1 kg N ha^{-1}) with no significant difference ($p > .05$). The proportion of the applied N lost as NH_3 from the double cropping rice was the highest, up to 19.1% (Fig. 2b). In this system, the NH_3 loss from the late rice was 1.4 times that of the early rice (Fig. S3). The NH_3 emission per unit of grain N production (NPGN) for the double cropping rice was the highest, followed by rice-upland and single rice (Fig. 2c).

3.2. Influencing factors

The NH_3 volatilization was positively correlated with N input rate ($p < .01$, $R^2 = 0.52$) increasing with N application rate following a quadratic or exponent function (Fig. 3a and Figs. S4–5). This suggests that the NH_3 loss proportion was larger under higher N input compared to that under the lower N input (Fig. S6). It seems that soil properties (soil organic matter, soil total N, and soil bulk density), climate conditions (air temperature, precipitation, and wind speed) and water pH did not have a significant impact on NH_3 volatilization ($p > .05$, Fig. 3b–h).

Interestingly, multiple linear regression indicated that soil organic matter had a significant negative effect while wind speed had a significant positive effect on total NH_3 volatilization ($p < .05$, Table 1 and Table S4). However, the different rice cropping systems responded differently to.3.2(tal)3

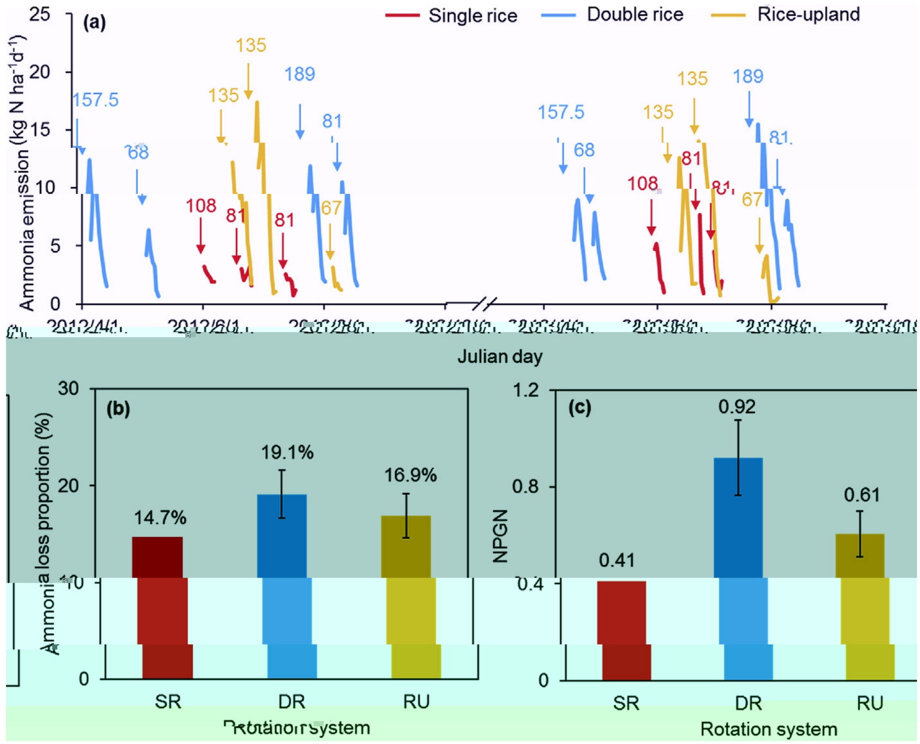

Fig. 2. NH_3 loss from paddy soil. (a) The temporal variation of NH_3 volatilization in three typical monitoring sites of single rice, double rice and upland rice crop rotation with wheat: Jilin (43.9°N, 124.3°E), Fujian (26.2°N, 119.1°E) and Anhui (31.7°N, 117.7°E), respectively; (b) the total NH_3 loss proportion in the different rice cropping systems; (c) the NH_3 emission per unit of grain nitrogen production. The arrows in (a) represent fertilizer application, and the number above represents the N application rate (kg N ha^{-1}). SR, DR and RU in (b) and (c) represent single rice, double rice, and rice-upland, respectively, and NPGN in (c) represents the NH_3 emission per unit of grain N production. Data are shown as mean ± SEM (standard error of mean).

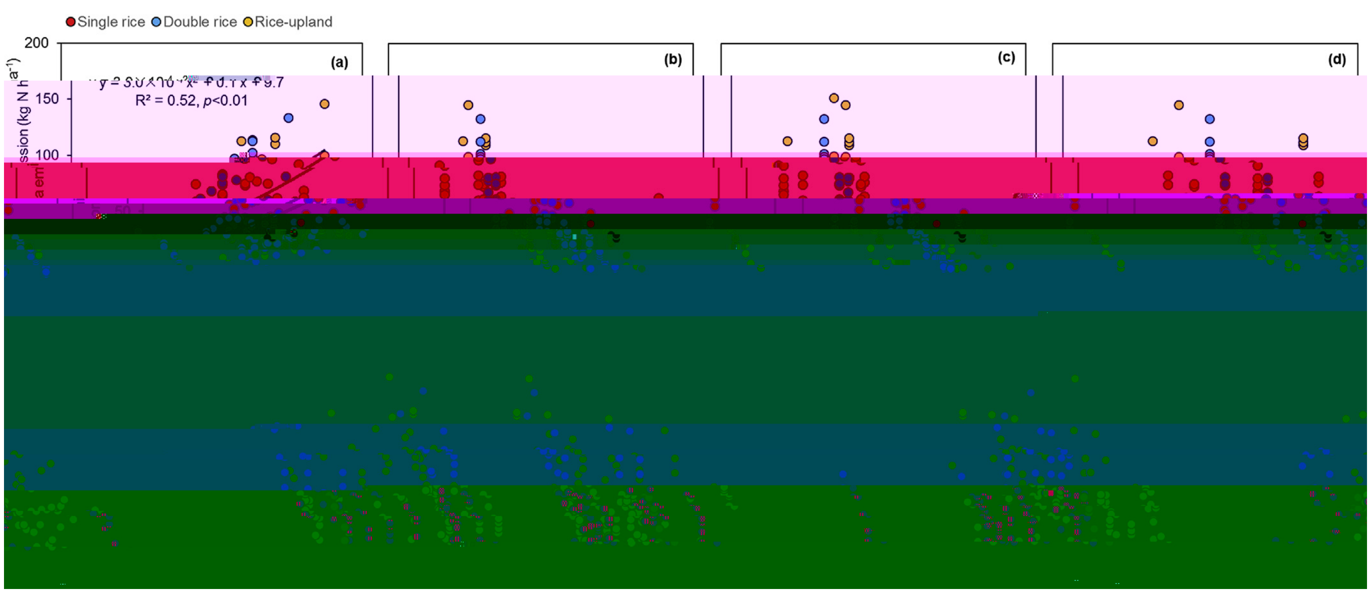

Fig. 3. Relationship between NH_3 volatilization and associated influencing factors.

farmer's N application rate. The spatial pattern of NH_3 emission was illustrated in Fig. 4. High emission rates were found in Hunan, Anhui and Jiangxi provinces, all of which have large growing areas, accounting for 16.5%, 14% and 13.3% of the total NH_3 emission in China, respectively. For Liaoning, Jilin, Guizhou and Hainan provinces, the NH_3 emissions were all less than 30 Gg N yr^{-1}.

4. Discussion

4.1. Non-linear response of NH_3 emissions to N rate

N fertilizer rate directly impacts NH_3 volatilization, and an elevated N concentration in soil accelerates the loss of NH_3 to the atmosphere (Ju et al., 2009; Jiang et al., 2017). Most previous estimates have found that the response of NH_3 emission to N application rates is linear (Cui et al., 2013, 2014; Chen et al., 2014). Recently, several studies using data synthesis analysis have suggested that NH_3 emission response to N addition could be non-linear (Zhou et al., 2016; Jiang et al., 2017). By controlling for the differences resulting from different methodologies and measurement timing, our study suggests that NH_3 volatilization increases with N application rate following a quadratic function, rather than a linear relationship. There could be several reasons for the observed non-linear response. Firstly, as a dominant factor affecting NH_3 emissions in paddy fields, NH_4^+ concentration in the surface water of paddy fields increases with N inputs (Sommer et al., 2004; Rochette et al., 2013; Shang et al., 2014), and the instantaneous rate of NH_3 emission is exponentially correlated with NH_4^+ concentration (Chen et al., 2015a). Secondly, crop N use efficiency decreases dramatically with N application rate, particularly when N input exceeds crop needs (Peng et al., 2006). Therefore, more NH_4^+

satellite observations, which implies that NH_3 emissions may be substantially underestimated in China (Zhang et al., 2017). The underestimation of NH_3 emissions could be an integrated result of the following reasons: (i) variation in methodology; (ii) lower N application rate used by farmers in the past; and (iii) non-linear response of NH_3 emissions to N rate.

In this study, we used a continuous airflow enclosure (CAE) method to estimate NH_3 emission, which is widely used in field scale studies (Cao et al., 2013; Chen et al., 2015b; Zhao et al., 2015). Besides the CAE method, another commonly used method for the determination of NH_3 emission is a high-resolution micrometeorological (HRM) method. Compared to the open HRM method, the closed CAE method may result in uncertainty due to the fact that the chamber can't accurately simulate the natural wind conditions above the soil surface (Li, 2013). However, it is still the most suitable method for comparing multiple treatments at field scale (Jantalia et al., 2012; Yang et al., 2013). The deviation of CAE from the HRM method has been found to be less than 5% (Pacholski et al., 2006).

Previous national scale studies have normally collected data on NH_3 emission factors that were determined using different measuring methods at different times (Chen et al., 2014; Pan et al., 2016; Zhou et al., 2016). Different methods (e.g., dynamic chamber, closed chamber and micrometeorological method) may result in systematic variations in the measured NH_3 emissions, which cannot be accounted for in an inventory study. Additionally, many experiments were conducted decades ago (e.g. in 1990s), when the typical N application rate used by farmers was much lower and soil N level was also lower. Based on our non-linear regression, a low N application rate would suggest a low NH_3 emission proportion. With an increase in N fertilizer application rate, the NH_3 emission proportions are likely to be higher. Zhou et al. (2016) suggested that NH_3 emission response to N addition could be non-linear using data synthesis analysis of historical measurements. Chen et al. (2014) calculated that NH_3 lost from paddy fields accounted for approximately 16% of N input (209 kg N ha^{-1}), and non-linear response was the main reasons causing underestimation.

A “zero increase of fertilizer use” policy has been introduced in China, however, the total amount of N fertilizer use will be still be increasing until 2020. Therefore, the total NH_3 emission from paddy soil in China previously calculated is likely to be an underestimate. China consumed 31.1 Mt of synthetic N fertilizers in 2014, accounting for 28.5% of global total (FAO, 2017). The underestimate of NH_3 emission factors would result in a large underestimate of the total NH_3 emissions in China. Thus, refining the estimate of NH_3 emission factors, as found in this study, is vital for the accuracy of the national scale inventory of total NH_3 emissions, which is important for developing strategies to improve the air quality in China.

4.3. Policy implications

Approximately 20% of global NH_3 emissions originate from China (Klimont et al., 2001; Yamaji et al., 2004), in particular from intensive N fertilizer application to croplands (Yan et al., 2003; Wang et al., 2005). Compared to reactive N (Nr) loss through other pathways, such as N leaching and runoff (Gao et al., 2016; Hou et al., 2016), the amount of Nr loss through NH_3 volatilization is much larger and plays a more important role in the environment. Previous policy regulations mainly focus on the reduction of Nr loss from agricultural non-point-source pollution to water bodies to mitigate eutrophication. For example, to balance food security and environmental protection, several policies have been implemented, including “Water Pollution Prevention and Control Action Plan” (WPPCAP), “Soil Pollution Prevention and Control Action Plan”