JOURNAL OF ENVIRONMENTAL SCIENCES 38 (2015) 14–23

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JOURNAL OF ENVIRONMENTAL SCIENCES
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Ammonia volatilization from a Chinese cabbage field under different nitrogen treatments in the Taihu Lake Basin, China

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ARTICLE INFO

Article history:
Received 6 January 2015
Revised 25 April 2015
Accepted 30 April 2015
Available online 21 August 2015

Keywords:
Ammonia volatilization
Nitrogen fertilizer
Slow-release fertilizer
Vegetable soil

ABSTRACT

Ammonia (NH_3) volatilization is a major pathway of nitrogen (N) loss from soil-crop systems. As vegetable cultivation is one of the most important agricultural land uses worldwide, a deeper understanding of NH_3 volatilization is necessary in vegetable production systems. We therefore conducted a 3-year (2010–2012) field experiment to characterize NH_3 volatilization and evaluate the effect of different N fertilizer treatments on this process during the growth period of Chinese cabbage. Ammonia volatilization rate, rainfall, soil water content, pH, and soil NH_4^+ were measured during the growth period. The results showed that NH_3 volatilization was significantly and positively correlated to topsoil pH and NH_4^+ concentration. Climate factors and fertilization method also significantly affected NH_3 volatilization. Specifically, organic fertilizer (OF) increased NH_3 volatilization by 11.77%–18.46%, compared to conventional fertilizer (CF, urea), while organic–inorganic compound fertilizer (OIF) reduced NH_3 volatilization by 8.82%–12.67% compared to CF. Furthermore, slow-release fertilizers had significantly positive effects on controlling NH_3 volatilization, with a 60.73%–68.80% reduction for sulfur-coated urea (SCU), a 71.85%–78.97% reduction for biological Carbon Power® urea (BCU), and a 77.66%–83.12% reduction for bulk-blend controlled-release fertilizer (BBCRF) relative to CF. This study provides much needed baseline information, which will help in fertilizer choice and management practices to reduce NH_3 volatilization and encourage the development of new strategies for vegetable planting.

Introduction

Nitrogen (N) fertilizer is the most widely used fertilizer worldwide and the primary N input source in soil-crop systems. It plays an important role in increasing crop yields to meet the food demands of a growing global population. However, the excessive use of N fertilizer for crop production can cause substantial N losses through surface runoff, leaching, and gaseous emissions of ammonia (NH_3) and nitrous oxide (N_2O) (Alva et al., 2006; Duretz et al., 2011).

Ammonia volatilization is one of the major N loss pathways from N fertilizer application (Harrison and Webb, 2001). Agricultural activities reportedly contribute up to 90% of the total NH_3 emissions to the atmosphere (Boyer et al., 2002; Misselbrook et al., 2000), with the majority coming from livestock production and 12% resulting from N fertilizer application (Ferm, 1998). Approximately 15%–40% of farmland N application is lost through ammonia volatilization, equivalent to 20%–70% of total farmland N loss (Chien et al., 2009; Harrison and Webb, 2001). Ammonia volatilization negatively

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http://dx.doi.org/10.1016/j.jes.2015.04.028

affects environmental quality, whereby NH_3 that is dissipated into the atmosphere reacts with atmospheric acids to form fine aerosols (Huckaby et al., 2012), or deposits return to the ground to cause soil acidification (Van der Eerden et al., 1998). Emitted NH_3 also becomes a secondary production source of N_2O, a major greenhouse gas (Sutton et al., 2008).

Ammonia volatilization is influenced by environmental factors such as soil pH, moisture, and texture, as well as air temperature, light, wind speed, and precipitation (Bouwmeester et al., 1985; He et al., 1999; Sommer and Ersboll, 1996). Furthermore, planting and management factors also affect NH_3 emissions; for example, the use of different types of N fertilizer and application methods, irrigation, and crop rotation systems (Holcomb et al., 2011; Xu et al., 2012; Zaman et al., 2009).

Different types of fertilizer have different effects on NH_3 volatilization from crop-soil systems. Urea is one of the most widely used N fertilizers worldwide because of its high N concentration. Indeed, NH_3 volatilization from urea accounts for approximately 10–35% of N applied in field crop planting (Christianson, 1989; Fan et al., 2005; Soares et al., 2012). A previous study found that four different N fertilizers each resulted in differing levels of NH_3 volatilization loss (% of N applied) $(NH_4)HCO_3 > (NH_4)_2SO_4 > CO(NH_2)_2 > NH_4NO_3$ (He et al., 1999). The application of composted manure may promote NH_3 volatilization in crop-soil systems, mainly due to the high pH of compost manure (Matsushima et al., 2009; Paramasivam et al., 2009). In addition to the benefits of slow-release N fertilizers for increasing crop yield or N absorption and utilization, studies have begun to focus on the consequential environmental effects of such fertilization. Rao (1987) found that sulfur-coated urea was effective in reducing NH_3 volatilization losses from 16.9% to 3.4% of N applied in paddy fields. Knight et al. (2007) reported that NH_3 volatilization from slow-release sources (dehydrated sewage sludge, sulfur-coated urea, polymer-coated urea, and methylene urea) was significantly reduced compared with that observed from surface-applied urea on creeping bent grass. Blaise and Prasad (1995) indicated that NH_3 volatilization loss from polymer-coated urea accounted for 7.6% of N applied, which was 11.6% lower than that observed using commercial prilled urea in paddy fields.

The Taihu Lake region is one of the most densely populated and intensively farmed areas in China. Vegetable fields are among the most important agricultural land uses in the Taihu Lake region, and are distinguished by their short growth cycle, high multiple cropping index, large N fertilizer demand, and substantial nonpoint source pollution (De Neve and Hofman, 1998). The average N fertilizer application for vegetables in the Taihu Lake region ranges from 300 to 700 kg N/ha per growing season but can even reach 3000 kg N/ha, more than 10 times the actual crop demand (Wu et al., 2011; Yan et al., 2010). Besides causing NH_3 volatilization, excess N fertilizer also results in nutrient imbalance for crops, excess nitrate content, and other environmental problems (Zhang et al., 2004).

Previous studies on the environmental effects of excessive N fertilizer application have focused on field crops (*e.g.*, rice, wheat, and corn), rather than vegetables, particularly when studying NH_3 volatilization. However, vegetable crops comprise a large percentage of agricultural production, and in China, the Chinese cabbage (*Brassica rapa* L. subsp. *pekinensis* (Lour.)) is one of the most important cultivated vegetables, reaching a planting area of 2.67×10^6 ha in 2010 (Zhang and Li, 2011). Thus, understanding the interaction of N fertilizer treatments and NH_3 volatilization in a vegetable-soil system is crucial for agronomic output.

We therefore conducted this study to evaluate and characterize NH_3 volatilization in a Chinese cabbage field subjected to different N fertilizer treatments over a 3-year period. Our results should prove useful in reducing NH_3 volatilization and improving fertilizer application strategies for vegetable planting.

1. Materials and methods

1.1. Site description

The experimental site was situated in the Taihu basin of China, at a vegetable production base of Hangzhou Yuhang Mengyuan Agricultural Science and Technology Co., Ltd. (30°21.57″, 119°54.19″E), which has been used for vegetable production since 2006. Experiments were conducted from September to December (Chinese cabbage growth period) of 2010–2012. The region has a subtropical monsoon climate, with an average annual air temperature of 15.8°C, and an annual precipitation of approximately 1200–1500 mm, mostly occurring between June and September. The cultivated soil for this study is classified as yellow-brown soil. The main properties of the soil in the top 20 cm layer at the start of the experiment were as follows: pH, 5.45 (1:5, soil/water); total N, 1.67 g/kg; total P, 2.39 g/kg; organic matter (OM), 25.73 g/kg; and bulk density, 1.29 g/cm^3.

1.2. Experimental design

Seven different fertilizer treatments were applied for comparison: (1) no fertilizer (CK); (2) organic fertilizer (OF; Chn-agri Jiangsu Fertilizer Co., Ltd., Nanjing, China), a commercial organic fertilizer, granulated, containing 1.53% N (pH, 8.53), with poultry litter as the main component; (3) conventional fertilizer (CF; Chn-agri Jiangsu Fertilizer Co., Ltd., Nanjing, China), using urea as an N fertilizer, containing 46% N; (4) organic–inorganic compound fertilizer (OIF; Zhejiang University and Zhejiang Academic of Agricultural Sciences, Hangzhou, China), a specific fertilizer for leaf vegetables, granulated, containing 13% N, composed of urea (46% N), diammonium phosphate (DAP, 16% N), potassium chloride, and organic fertilizer (1.5% N), with 90% inorganic N and 10% organic N; (5) sulfur-coated urea (SCU; Hanfeng Slow-release Fertilizer Co., Ltd., Taizhou, China), with sulfur-coated and microcrystalline wax acting as surface sealant, containing 37% N; (6) biological Carbon Power® urea (BCU; Hanfeng Slow-release Fertilizer Co., Ltd., Taizhou, China), a new type of slow-release urea covered with Carbon Power synergistic agents (CP), which is extracted from natural plants, contains more than 2000 types of Carbon Power active agents, and has 46% N; (7) bulk-blend controlled-release fertilizer (BBCRF; Hanfeng Slow-release Fertilizer Co., Ltd., Taizhou, China), a specific slow-release fertilizer for leaf vegetables, N supplied by SCU and BCU, containing 17% N. A randomized complete block design, including all seven treatments and three replications, was established in 21 plots of 21 m^2 (3.5 × 6 m) each.

The plots were planted with the Chinese cabbage cultivar 'Qingza No. 3,' which is commonly planted on local vegetable croplands. This cultivar has a growth period of approximately 100–120 days from September to December or January of the following year. The planting density is typically 60,000–70,000 plants per ha, and the row spacing of the plants is 0.3–0.4 m. Nitrogen was applied to each plot equivalent to 300 kg N/ha for one planting season. According to the practice of the local farmers, OF, CF, and OIF were applied three times: 60% for basal dressing, 20% for the first top dressing (at the rosette stage), and 20% for the second top dressing (at the anterior folding stage). The slow-release fertilizers (SCU, BCU, and BBCRF) were applied only once as basal fertilization. Basal fertilization involved surface tillage after fertilizer broadcasting, whereas the fertilizer for the two top dressings was spread by hand only over the surface of the fields. To avoid damaging plant roots, fertilizer was spread a short distance away from the roots when applying the two top dressings and the field was irrigated in a timely fashion afterwards. The experiment was repeated for 3 years (2010–2012) with the same experimental setup.

1.3. Sampling and measurements

We recorded daily meteorological data, including precipitation and air temperature using an automatic HOBO-U30 weather station (Onest Computer Corporation; MA, USA). For every year of the experiment, we collected soil samples from the 0–5 cm surface layer (1) on the day before each fertilization, (2) on days 3, 7, and 14 post-fertilization, and (3) on the day of cabbage harvest. Soil samples were used to monitor soil pH, soil water content, and soil NH_4^+ concentration. Volumetric soil water content was measured using the gravimetric method (Lampurlanes et al., 2001). Soil pH was determined by mixing 5 g moist soil with 25 mL de-ionized water as described by Zaman et al. (2009). Soil NH_4^+ concentration was determined using 5 g soil, which was shaken with 50 mL 0.5 mol/L K_2SO_4 solution for 1 hr, and then filtered through Whatman #1 filter paper. The soil extracts were immediately analyzed for NH_4^+ using a flow injection analyzer (FIA, AA3; Bran + Luebbe; Norderstedt, Germany) (Zaman et al., 2009).

NH_3 volatilization from experimental plots was measured using the venting method (Hu et al., 2010; Paramasivam et al., 2009; Wang et al., 2002), which was designed based on the traditional enclosure method (Kissel et al., 1977) and the sponge-trapping and KCl extraction method (Cabrera et al., 1994). The venting method was performed using polyvinyl chloride (PVC) collector tubes (10 cm in height and 15 cm in diameter) and two phosphoglycerol-soaked sponges, which were placed in the top and middle of the tube as absorbents. The top sponge served to isolate and absorb the air outside the tube, and the middle sponge was used to absorb NH_3 volatilized from the soil. The tube was inserted into the center of the soil plot to a depth of 1 cm, and every plot contained one tube. The samples were collected daily in the first week after fertilizer application, and then once every 2–3 days until the next fertilization, or until no differences were observed in the volatilization rate compared with the control treatment. The samples collected from the cabbage soil using the phosphoglycerol-soaked sponge were immediately sealed and transported to the laboratory. The sponges that absorbed NH_3 were immersed in 300 mL of 1.0 mol/L KCl solution in 500-mL containers and shaken for 1 hr. The NH_4^+ concentration of the solution was determined using a continuous-flow injection analyzer (FIA, AA3; Bran + Luebbe; Norderstedt, Germany). The NH_3 volatilization rate was calculated using Eq. (1):

$$R_{AV} = M/(A \times D) \times 10^{-2} \quad (1)$$

where R_{AV} (kg N/(ha·day)) is the NH_3 volatilization rate, M (mg) is the NH_3–N collected using the PVC collector, A (m^2) is the cross-sectional area for the capturer, and D (day) is the continuous capture time for NH_3 volatilization. The cumulative NH_3 volatilization rate was determined as the sum of daily volatilization rates during the measurement period.

1.4. Statistical analysis

The experiment was established as a completely randomized design with three replications. All statistical analyses were performed using SPSS 17.0 (SPSS Inc., Chicago, IL, USA). We tested for significant differences in means across fertilizer treatments *via* a one-way analysis of variance (ANOVA) with Duncan's multiple range test ($p < 0.05$). The cumulative NH_3 volatilization (% N applied) and rate of NH_3 volatilization reduction were each combined across 3 years and assessed with a generalized linear model (GLM). We ran two Pearson's correlations to test the relationships between (1) NH_3 volatilization rate and soil pH, and (2) NH_3 volatilization rate and soil NH_4^+ concentration.

2. Results

2.1. Temperature, rainfall, irrigation, and soil water content

Air temperature during the experimental period is shown in Fig. 1. The average temperature during the growth period was 16.97°C, 10.39°C, and 13.20°C in 2010, 2011, and 2012, respectively. Rainfall varied widely during the 3 years of the experiment, totaling 337.82 mm in 2010, 190.40 mm in 2011, and 236.20 mm in 2012. Irrigation in 2011 was relatively higher than in the other 2 years, mainly because of the lower rainfall (Fig. 2). Soil water content varied along with the changes in rainfall and irrigation, with 2010 being more variable than 2011 and 2012 (Fig. 2).

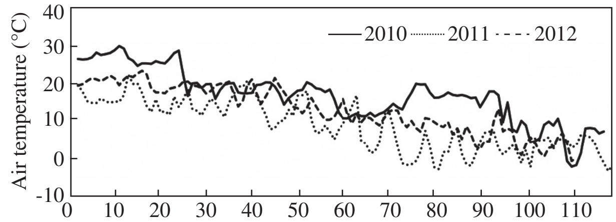

Fig. 1 – Air temperature during the experimental period in 3 different years.

2.2. Soil pH

Soil pH increased significantly within 3 days after fertilization in the OF, CF, and OIF treatments, and then began to decrease approximately 7 days after fertilization, until the next top dressing (Fig. 3). The OF treatment resulted in the highest pH peak across all treatments, and pH remained higher than the control until harvest (Fig. 3). Soil pH variations were similar across the two top dressings and the basal dressing. Finally, soil pH in the three slow-release fertilizer treatment groups, SCU, BCU, and BBCRF, gradually increased until approximately 25–35 days after fertilization, and then decreased slowly to approach control values (Fig. 3).

2.3. Soil NH_4^+–N concentration

Patterns in soil NH_4^+–N concentration were similar throughout the experiment in each year (Fig. 4). Compared to the control, NH_4^+ concentrations in the topsoil layer (0–5 cm) of the OF, CF, and OIF treatments increased sharply within 3 days after fertilization and decreased thereafter (until the next fertilization), with the highest peaks occurring in the CF treatment. Variation in NH_4^+ concentration over the years was similar across the two top dressings and the basal dressing. In the three slow-release fertilizer treatments, soil NH_4^+ concentrations increased gradually after fertilization, peaking at approximately 2 weeks after fertilization, and then slowly decreased, although concentrations remained higher than control for 60 days after fertilization (Fig. 4).

2.4. NH_3 volatilization rate

Across all 3 years, NH_3 volatilization in the OF, CF, and OIF treatments mainly occurred within the first week after fertilization, and the peaks of NH_3 volatilization rate occurred on day 3 or day 4 for both basal and top dressings, except during 2010, when the rate for basal dressing peaked slightly later (Fig. 5). NH_3 volatilization rates decreased rapidly post-days 3 or 4 until there was no difference from control rates by approximately 2 weeks after fertilization. In each year, the peaks of NH_3 volatilization rate in the basal dressing period were prominently higher than those in the two top dressing periods (Fig. 5). Within the same fertilizer application period, OF treatments exhibited the highest peaks per year.

Patterns of NH_3 volatilization rates in the SCU, BCU, and BBCRF treatments were very similar (Fig. 5). Peaks of NH_3 volatilization rates occurred on days 7–9, and NH_3 loss was much slower and decreased significantly less compared to the non-slow-release fertilizer treatments. About 20 days after fertilization, the NH_3 volatilization rate had approached control

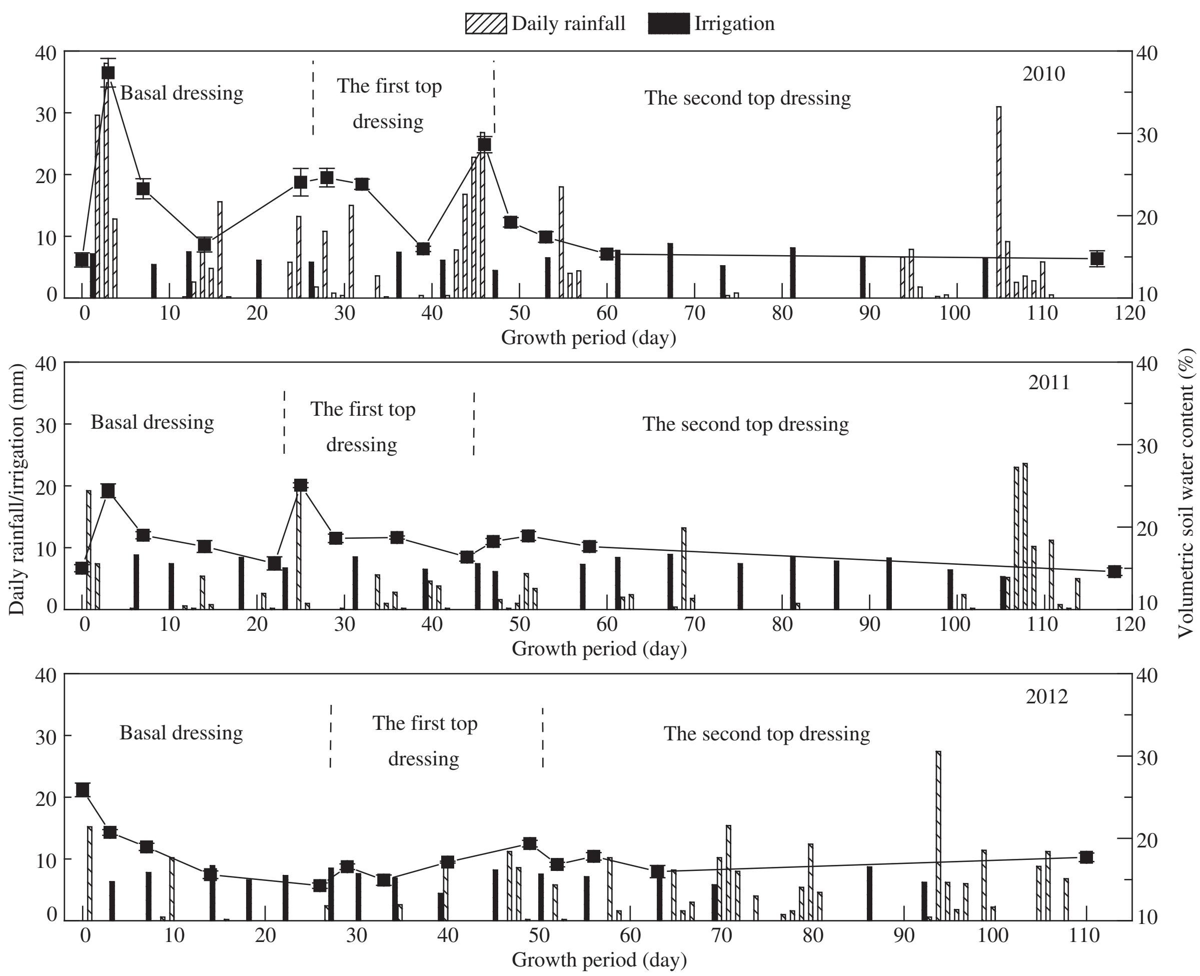

Fig. 2 – Daily rainfall, irrigation, and soil water content during the experimental period in 3 different years.

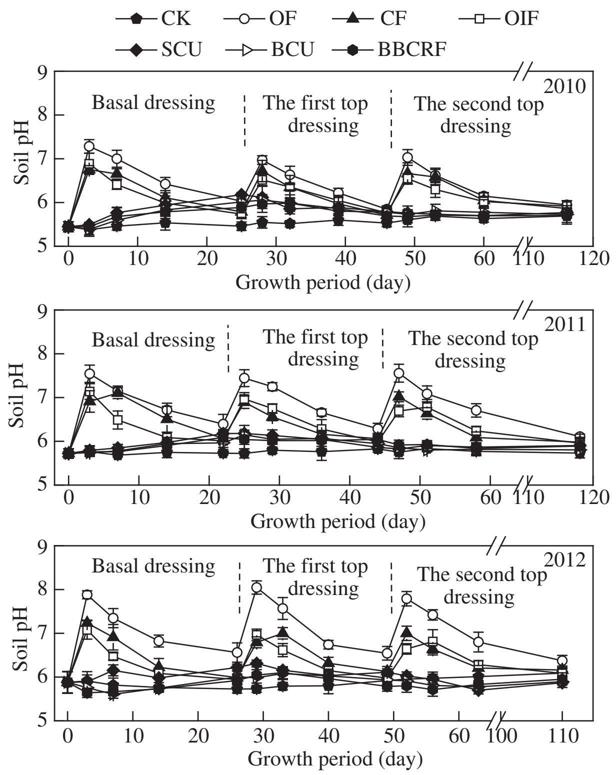

Fig. 3 – Soil pH of the different treatments during the cabbage growth period in 3 different years. Vertical bars are standard errors of the means (n = 3). OF: organic fertilizer; CF: conventional fertilizer; OIF: organic–inorganic compound fertilizer; SCU: sulfur-coated urea; BCU: biological Carbon Power urea; BBCRF: bulk-blend controlled-release fertilizer.

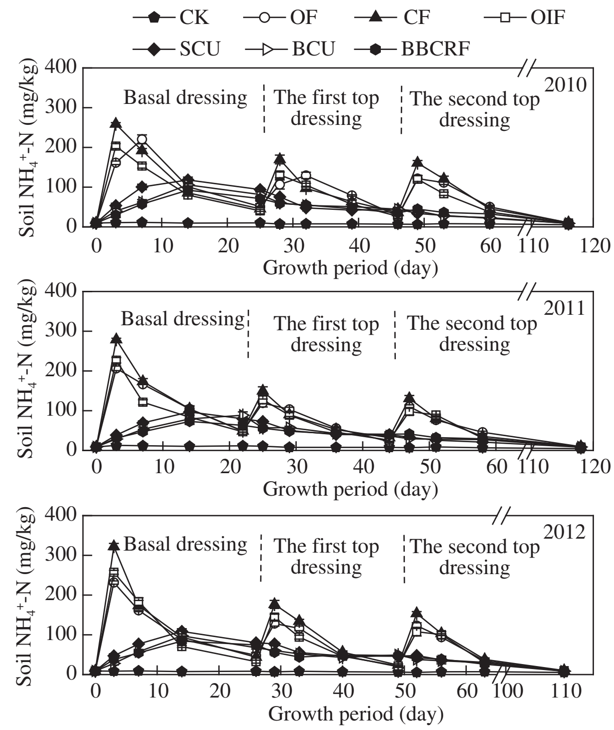

Fig. 4 – Soil NH_4^+–N concentration of the different treatments during the cabbage growth period in 3 different years. Vertical bars are standard errors of the means (n = 3).

levels. Therefore, slow-release fertilizers result in longer periods of NH_3 volatilization but far lower NH_3 loss rates compared to chemical and organic fertilizers. For all three fertilizers, the highest peaks occurred in 2012.

During the entire growth period of each year, the NH_3 volatilization rate of the seven different treatments was positively correlated with soil pH in the topsoil layer (Table 1). However, the correlation disappeared by 14 days after fertilization, indicating that while an increase in soil pH can promote NH_3 volatilization, it does so significantly only during the initial phase of fertilization, gradually decreasing thereafter.

We observed a significant positive correlation between NH_3 volatilization rate and soil NH_4^+ concentration in the topsoil layer during each year of the experiment (Table 1). This correlation remained strong over time when assessed 3, 7, and 14 days after fertilization (Table 1). Thus, NH_4^+ concentration in the soil appears to continuously and intensively influence the rate of NH_3 volatilization.

2.5. *Cumulative NH_3 volatilization*

In each year, the cumulative NH_3 volatilization of the entire growth period consistently followed the order: OF > CF > OIF > SCU > BCU > BBCRF > CK (Fig. 6). Differences between treatments were statistically significant, except for BBCRF and BCU in 2012 (Table 2). Moreover, the cumulative NH_3

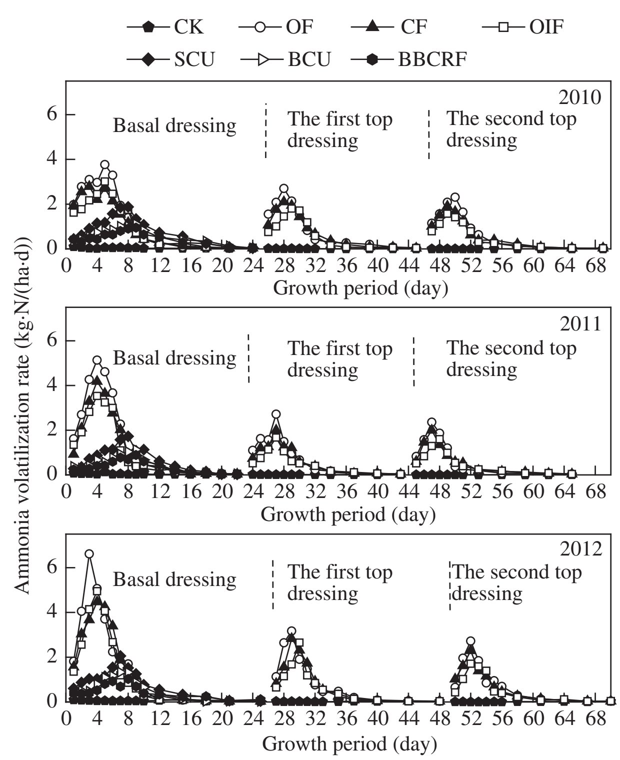

Fig. 5 – Ammonia volatilization rate of the different treatments during the cabbage growth period in 3 different years.

Table 1 – Relationships between NH_3 volatilization rate and soil pH, NH_3 volatilization rate and soil NH_4^+ concentration during the Chinese cabbage growth period in 3 different years.

Time		Relationship of NH_3 volatilization rate and soil pH [a]	Relationship of NH_3 volatilization rate and soil NH_4^+ concentration [b]
Year	2010	$y = -16.13x^2 + 1.40x + 46.58$ $r^2 = 0.684$, $p < 0.01$, $n = 56$	$y = 0.0074x^2 + 1.87x - 0.12$ $r^2 = 0.623$, $p < 0.01$, $n = 56$
	2011	$y = -14.30x^2 + 1.19x + 43.09$ $r^2 = 0.585$, $p < 0.01$, $n = 56$	$y = 0.0072x^2 + 2.86x - 0.12$ $r^2 = 0.729$, $p < 0.01$, $n = 56$
	2012	$y = -9.63x^2 + 0.83x + 28.29$ $r^2 = 0.491$, $p < 0.01$, $n = 56$	$y = 0.0093x^2 + 2.36x - 0.19$ $r^2 = 0.640$, $p < 0.01$, $n = 56$
Days after fertilization	3 days	$y = -9.19x^2 + 0.87x + 24.56$ $r^2 = 0.927$, $p < 0.01$, $n = 45$	$y = 0.032x^2 - 6.03x - 0.45$ $r^2 = 0.781$, $p < 0.01$, $n = 45$
	7 days	$y = 6.49x^2 - 0.45x - 21.55$ $r^2 = 0.447$, $p < 0.01$, $n = 45$	$y = 0.025x^2 - 7.95x - 0.15$ $r^2 = 0.723$, $p < 0.01$, $n = 45$
	14 days	$y = 3.61x^2 - 0.29x - 10.93$ $r^2 = 0.040$, $p > 0.05$, $n = 45$	$y = -0.035x^2 + 5.583x + 0.064$ $r^2 = 0.549$, $p < 0.01$, $n = 45$

[a] x represents soil pH, and y represents NH_3 volatilization rate.
[b] x represents soil NH_4^+ concentration, and y represents NH_3 volatilization rate.

volatilization per year followed the order 2012 > 2010 > 2011 using the non-slow-release fertilizers, and 2010 > 2012 > 2011 using the slow-release fertilizers (Table 2).

The OF treatment resulted in significantly higher cumulative NH_3 volatilization than the other treatments (Tables 2 and 3). In contrast, the OIF treatment appears to have played an active role in reducing NH_3 volatilization, decreasing NH_3 loss up to approximately 13% compared to CF levels (Tables 2 and 3). Moreover, slow-release fertilizer application significantly decreased the cumulative NH_3 volatilization compared with the non-slow-release fertilizers (Fig. 6). Specifically, BBCRF decreased NH_3 volatilization by the highest percentage among the three treatments, resulting in up to 84.77% reduction compared to the CF treatment in 2011 (Tables 2 and 3). In terms of year-by-year patterns, 2010 saw the highest cumulative NH_3 volatilization for the slow-release fertilizers.

The OF, CF, and OIF were applied three times (basal dressing plus the first and second top dressings) during the cabbage growth period. Cumulative NH_3 volatilization was highest in the basal dressing and lowest in the second top dressing across all 3 years (Fig. 6). However, the percentage of NH_3 volatilization relative to N applied was highest in the first top dressing and lowest in the basal dressing across all 3 years (Table 2).

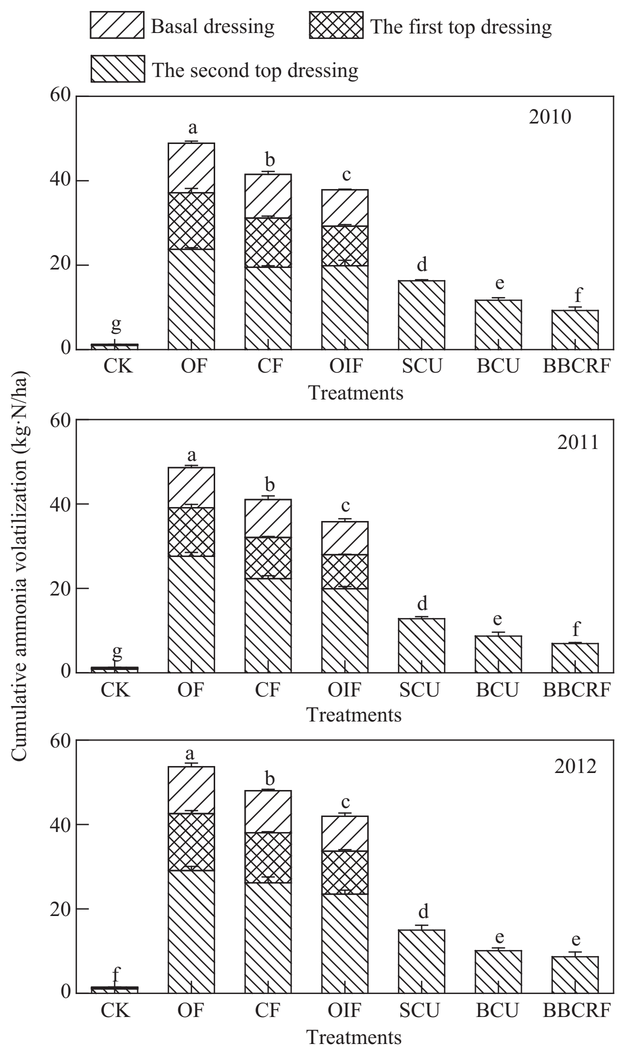

Fig. 6 – Cumulative ammonia volatilization of the different treatments during the cabbage growth period in 3 different years. Vertical bars are standard errors of the means (n = 3). Columns with the same letter are not significantly different at $p < 0.05$ for each year.

3. Discussion

3.1. Effect of climate factors on NH_3 volatilization

We found that the cumulative NH_3 volatilization of all fertilizer types was lower in 2011 than in 2010 and 2012 (Fig. 6). The primary cause of these differences was the markedly lower temperature during the 2011 growth period (Fig. 1). Increasing temperature promotes the rate of NH_4^+ conversion to NH_3, and increases NH_3 diffusion rate, urea hydrolysis, and organic N mineralization (Fenn and Kissel, 1974; Koivunen and Horwath, 2004).

Although the temperature during the basal dressing period in 2010 was slightly higher than that in 2012, the peaks of NH_3 volatilization rate and total cumulative NH_3 volatilization in

Table 2 – Net cumulative NH_3 volatilization for different treatments during the cabbage growth period in 3 different years, expressed as the percentage of N applied.

Treatment [a]	Net cumulative NH_3 volatilization (% of N applied) [b]											
	Basal dressing			1st top dressing			2nd top dressing			Total		
	2010	2011	2012	2010	2011	2012	2010	2011	2012	2010	2011	2012
OF	12.64 a [c]	14.86 a	15.57 a	22.06 a	18.68 a	22.04 a	19.41 a	15.66 a	18.20 a	15.88 a	15.79 a	17.39 a
CF	10.30 b	11.92 b	13.95 b	19.12 b	15.83 b	19.29 b	17.07 b	14.71 ab	16.40 a	13.42 b	13.26 b	16.00 b
OIF	10.48 b	10.58 c	12.48 c	15.39 c	13.03 c	16.51 c	14.15 c	12.80 b	13.47 b	12.20 c	11.51 c	13.48 c
SCU										5.10 d	3.98 d	4.64 d
BCU										3.56 e	2.61 e	3.01 e
BBCRF										2.76 f	2.02 f	2.54 e
F value	N fertilizer treatment (N)				801.64 **							
	Fertilization period (FP)				294.88 **							
	Year (Y)				51.74 **							
	N × FP				7.82 **							
	N × Y				2.23 *							
	FP × Y				22.34 **							
	N × FP × Y				1.85 ns							

[a] OF organic fertilizer; CF: conventional fertilizer; OIF: organic–inorganic compound fertilizer; SCU: sulfur-coated urea; BCU: biological Carbon Power urea; BBCRF: bulk-blend controlled-release fertilizer.
[b] Net cumulative NH_3 volatilization (% of N applied) = (cumulative NH_3 volatilization from a given nitrogen treatment − cumulative NH_3 volatilization from control treatment)/total amount of N application × 100%.
[c] Each value is the mean of three replicates. Means in each column followed by the same letter are not significantly different at $p < 0.05$ for each year and each fertilization period.
* Significant at $p < 0.05$.
** Significant at $p < 0.01$.
ns Not significant.

the OF, CF, and OIF treatments of 2010 were all significantly lower than those of 2012, and the peaks were delayed (Figs. 5 and 6). The reason for these differences is that after basal dressing in 2010, continuous high-intensity rainfall persisted from day 2 to day 4 (80.41 mm in total) in the experimental area (Fig. 2). High-intensity rainfall after fertilization can improve fertilizer infiltration, which causes a reduction in topsoil N concentration, resulting in a beneficial effect by inducing deeper application of N fertilizer, and consequently controlling NH_3 volatilization (Black et al., 1987; Fan et al., 2005). In addition, we found that heavy rainfall after fertilization can also weaken the range of increase in topsoil pH (Fig. 3), and this may be another reason for the reduction in NH_3 volatilization. Conversely, a smaller amount of rain and irrigation occurring after fertilization might promote NH_3 volatilization through an increase in soil water content (Fig. 2), which can promote urea hydrolysis, and cause a rapid increase in NH_4^+ in the topsoil (Edwards and Daniel, 1993). However, heavy rainfall can promote NH_3 volatilization of slow-release fertilizers (Figs. 5, 6 and Table 2). In this case, heavy rain might promote the rate of erosion of the coating material and increase the probability of contact between urea and soil water, thus accelerating the rate of urea hydrolysis.

Table 3 – Reduction rate of NH_3 volatilization in different treatments during the cabbage growth period in 3 different years.

Treatment	Reduction rate (%) [b]		
	2010	2011	2012
OF	−18.35 f [c]	−19.05 f	−12.14 e
CF	0 e	0 e	0 d
OIF	9.09 d	13.16 d	13.07 c
SCU	61.98 c	69.96 c	70.08 b
BCU	73.44 b	80.29 b	80.57 a
BBCRF	79.44 a	84.77 a	83.64 a
F value	N fertilizer treatment (N)	3685.97 **	
	Year (Y)	26.24 **	
	N × Y	3.19 ns	

OF organic fertilizer; CF: conventional fertilizer; OIF: organic–inorganic compound fertilizer; SCU: sulfur-coated urea; BCU: biological Carbon Power urea; BBCRF: bulk-blend controlled-release fertilizer.
[b] Reduction rate is the percentage of NH_3 volatilization reduction compared to conventional fertilizer (CF) treatment.
[c] Each value is the mean of three replicates. Means in each column followed by the same letter are not significantly different at $p < 0.05$ for each year.
** Significant at $p < 0.01$.
ns Not significant.

3.2. Effect of soil pH and NH_4^+–N on NH_3 volatilization

NH_3 volatilization rates for the seven fertilizer treatments were positively correlated with soil pH during the entire growth period. However, the effect of soil pH on NH_3 volatilization was gradually reduced over time (Table 1). Several studies have shown that an increase in soil pH promotes NH_3 volatilization (Duan and Xiao, 2000; Fan et al., 2011; Gonzatto et al., 2013), and that is mainly because the higher pH directly influences the equilibrium between NH_4^+ and NH_3 (Gil et al., 2008).

Topsoil NH_4^+ is the source of NH_3 volatilization, and therefore the topsoil NH_4^+ concentration directly affects the NH_3 volatilization rate (Harrison and Webb, 2001; Soares et al., 2012). Our results showed that a highly significant, positive correlation existed between NH_3 volatilization rate and soil NH_4^+ concentration during all three experimental periods, and that this effect continuously influenced the entire process of NH_3 volatilization (Table 1). A positive correlation between soil NH_4^+ and NH_3 volatilization rate also occurred in the application of urea to two vegetable fields in Nanjing suburbs (He et al., 2005).

3.3. *Effect of different N treatments on NH_3 volatilization*

In our study, the CF treatment caused a sharp rise in soil pH and NH_4^+ concentration compared to the control treatment (Figs. 3 and 4). We attributed this outcome to the high levels of hydroxyl (OH^-) and NH_4^+ ions produced by the rapid hydrolysis of urea and ammonification, respectively (Zaman et al., 2007). Soil pH and NH_4^+ then decreased, the former due to hydrogen (H^+) production during nitrification (Zaman et al., 2009) and the latter due to uptake by plants, nitrification, microbial immobilization, NH_4^+ leaching, and runoff losses (Zaman et al., 2009; Zhao et al., 2012). In response, a sharp decline in NH_3 volatilization rate also occurred (Fig. 5).

OF application promoted NH_3 volatilization more so than the CF treatment. Three characteristics of the OF likely contributed to this pattern: high pH (8.53), ammonia content, and a high poultry litter component. First, the OF probably increased the topsoil basicity a good deal, which directly influences the NH_4^+ and NH_3 equilibrium (Gil et al., 2008), especially when the soil was originally acidic (Whalen et al., 2000). Next, the presence of ammonia is likely to increase topsoil NH_4^+ more rapidly than the other treatments, particularly if rainfall or irrigation occurs after fertilization. Finally, a previous study found that using poultry litter as fertilizer caused higher NH_3 volatilization than using urea (Paramasivam et al., 2009). Taken together, these results demonstrated that organic fertilizer is generally disadvantageous for reducing NH_3 volatilization.

The OIF used in this experiment actively reduced NH_3 volatilization compared to the CF treatment. One reason for this is the presence of DAP in the OIF, which causes less NH_3 volatilization than urea. Indeed, Bayrakli (1990) reported that under the same experimental conditions, total NH_3 volatilization for urea and DAP were 32.6% and 2.3% of the N applied to the soil, respectively. Another reason is that when an organic–inorganic compound fertilizer is applied, inorganic N is released first and subsequently generates a certain amount of NH_3 volatilization, while the released organic N needs to be mineralized by soil microorganisms (Hu et al., 2010).

The applications of the three slow-release fertilizers (SCU, BCU, and BBCRF) had significantly positive effects on reducing NH_3 volatilization, extended the NH_3 volatilization process, and delayed the peaks of the NH_3 volatilization rate (Fig. 5). Of the three, SCU exhibited the worst performance, although our results using this fertilizer still generally corroborated previous, field crop-focused studies indicating the successful decrease of NH_3 volatilization (do Nascimento et al., 2013; Gu et al., 2013; Malakouti et al., 2008; Rao, 1987). SCU likely has this effect because the sulfur-coat and microcrystalline wax in this fertilizer effectively prevent the direct contact of urea and soil water. This slows down the rate of urea hydrolysis, which changes soil pH and NH_4^+ concentrations to eventually result in NH_3 volatilization.

The second-best performer of the three slow-release fertilizers was BCU. Here, the CP synergistic agent was key to controlling urea hydrolysis, soil pH, and NH_4^+ concentrations (Figs. 3 and 4), thus reducing NH_3 volatilization. In general, the effect of BCU warrants further research, especially as the CP synergistic agent is extremely complex, containing more than 2000 types of Carbon Power active agents, and we do not fully understand the potential interactions that can occur.

In our study, the application of BBCRF was the most effective in reducing NH_3 volatilization across all treatments. Mainwhile, BBCRF had better performance in controlling soil pH and NH_4^+ than SCU and BCU (Figs. 3 and 4). The result indicated that using BBCRF was certainly more effective in controlling NH_3 volatilization than using SCU or BCU separately. Because BBCRF is a new slow-release fertilizer, the mechanisms behind its effectiveness are not entirely clear. Possibly, BBCRF enhances the slow-release effect and promotes N uptake to a greater extent than either of the other two slow-release fertilizers. While this explanation is intriguing, more studies are required to verify the effect of this new fertilizer on NH_3 volatilization.

Lastly, different fertilizer application methods also affect NH_3 volatilization. In the results, NH_3 volatilization mainly occurred within one week after non-slow-release fertilization, so increasing fertilization frequency must increase the risk of NH_3 volatilization. In our study, the non-slow-release fertilizers (OF, CF and OIF) were applied three times during the growth period every year, but the slow-release fertilizers (SCU, BCU and BBCRF) were applied only once. This is also an important reason for the better performance of the slow-release fertilizer treatments in controlling NH_3 volatilization. In addition, cumulative NH_3 volatilization (% of N applied) in the OF, CF, and OIF treatments were lower in the basal dressing period than during the two top dressings (Table 2). We suggest that this result is mainly because the basal fertilizer received surface tillage after broadcasting, whereas for the two top dressings, fertilizer was only spread over the field surface. Huijsmans et al. (2003) reported that surface incorporation and deep placement reduced NH_3 volatilization by 75% and 95%, respectively, compared with surface spreading. Volatilization is increased when fertilizer is surface-applied due to decreased fertilizer infiltration into the soil and an increase in the area of contact with the ambient air (Sogaard et al., 2002; Vandermolen et al., 1990).

4. Conclusions

NH_3 volatilization was significantly and positively correlated to topsoil pH and NH_4^+ concentration. Differences in fertilizer type significantly affected the variation in topsoil pH and NH_4^+ concentration, which caused significant differences in NH_3 volatilization across treatments. OF application resulted in the highest NH_3 volatilization, while OIF application reduced NH_3 volatilization, but to a lesser degree than the reduction observed with the three slow-release fertilizers, which showed highly significant effects on controlling NH_3 volatilization. Among the three slow-release fertilizers, BBCRF was more effective in controlling NH_3 volatilization than either SCU or BCU. Furthermore, climate factors and fertilization method also significantly affected NH_3 volatilization. In sum, the use of organic–inorganic compound fertilizers and slow-release fertilizers should be considered as a preferred fertilization strategy for vegetable crops, resulting in both agronomic and environmental benefits.

Acknowledgments

This study was supported by the National Key Science and Technology Project on Water Pollution Control and Treatment (Nos. 2008ZX07101-006 and 2012ZX07506-006). The authors thank the Hangzhou Yuhang Mengyuan Agricultural Science and Technology Co., Ltd. for the use of the field site. The authors are extremely grateful to the reviewers and editor for helping to improve this manuscript.

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