Factors Controlling the Losses of Urea through Ammonia Volatilization

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Volatilization of ammonia from N fertilizer is the major mechanism of N losses that occur naturally in all soils and is influenced by numerous soils, environmental and N fertilizer management factors. Vegetables are often damaged by NH₃ gas volatilized from the high rates of N fertilizer. We determined the rate of NH₃ volatilization from urea applied to surface of the alluvial soil (coarse silty, mixed, mesic family of Dystric Fluventic Eutrochrepts, Ihyeon series) as affected by fertilizer management factors such as rate of urea application, irrigation schedule and temperature. The NH₃ volatilization was triggered about 3 d after urea application and reached at maximum level in general within 15 days. Cumulative amounts of 3.0, 4.4, and 8.0 kg of NH₃ N after 17 d were volatilized at application rates of 200, 400, and 600 kg N ha⁻¹, respectively, which were equivalent to the N losses of 15.0, 10.9, and 13.0% of N applied. Masses of N volatilization were 5, 21, 75 and 87 kg NH₃ N ha⁻¹ at 5, 8, 22, and 28, respectively. Total amounts of 21.3, 21.2, and 16.6 kg N ha⁻¹ were volatilized at control, 5 and 10 mm water irrigation before fertilization, respectively. However, those at 5 mm irrigation after fertilization were only 10.44 kg N ha⁻¹. Results showed that urea loss can be avoided by incorporating with the recommended level, applying when temperatures are low or irrigating immediately to carry the urea into soil.

Key words: Ammonia gas, Urea, Volatilization, Temperature, Irrigation

Introduction

Nitrogen is essential for plant growth and part of every living cell. Plants require large amount of N for normal growth. Plants take up most of their N as ammonium or nitrate ion. Also N is necessary for chlorophyll synthesis and, as a part of the chlorophyll molecule, is involved in photosynthesis. Nitrogen deficiency thus results in chlorosis of the leaves. Inadequate N leads to low protein in seed and plant vegetative parts (Havlin et al., 2005). On the other hand, excess N can increase vegetative growth, reduce fruit set and adversely affect quality (PPI, 2003). Therefore, adequate managements of soil and N fertilizers to meet the crop needs result in improved yield and water use efficiency while minimizing potentially negative effects on the environment (Brady and Weil, 2002; Khalil et al., 2005; Ro et al., 2003; Sommer et al., 2004).

Soil properties, environmental conditions, and N fertilization influence the loss of N from the soil. Losses

Received : 23 January 2007 Accepted : 16 February 2007 *Corresponding author: Phone : +82332506440, E-mail : yangjay@kangwon.ac.kr of available N from soil include crop removal, nitrate leaching, volatilization, denitrification, and runoff and erosion (Khalil et al., 2006; Rodríguez et al., 2005). The amount of N, which is removed by harvested crops, highly depends on variety and quantity of the crops. Although removal in crops is not usually considered as a loss, in reality it is. Nitrate leaching is of importance in groundwater contamination and loss of available N source from the rhizosphere (Brady and Weil, 2002). Denitrification, which is a phenomenon commonly found under anaerobic soil conditions, leads in general to the loss of nitrogen through gaseous losses of N₂O and N₂ (Freedman, 1992). The net effect of N removal from soil is lower soil N levels.

When N fertilizer materials such as urea, ammonium nitrate or ammonium sulfate are applied to the surface of calcareous or alkaline soils, a chemical reaction may cause the loss of N as ammonia (NH₃) gas through volatilization process (Havlin et al., 2005). The NH₃ volatilization ultimately depends on the quantity of ammonia or ammonium ions in soil solution, which is highly influenced by soil acidity. As shown in eq. 1, since

pKa value is 9.3, ammonia form is predominant at pH condition is greater than 9.3. Therefore, ammonia volatilization is favored by high soil pH or by reactions that in turn raise the pH temporarily (Havlin et al., 2005). When NH4⁺-containing fertilizers such as ammonium sulfate are applied to acidic or neutral soils, little or no NH3 volatilization occurs because soil solution pH is not significantly increased (Havlin et al., 2005). In this case, soil pH decreases slightly when ammonium is nitrified to nitrate. On the other hand, solution pH around the urea granule increases during urea hydrolysis when urea is applied to acidic or neutral soil (Havlin et al., 2005). Thus solution pH may increase above 7 and the equilibrium in eq. 1 shifts toward the right, resulting in a favorable condition for NH3 volatilization. Therefore urea is more subject to NH₃ volatilization than ammonium sulfate.

$$NH_4^+ \leftrightarrow NH_3 + H^+ (pK_a = 9.3) \tag{1}$$

Volatilization of NH₃ is a mechanism of N loss that occurs naturally in all soils. However, compared with NH₃ volatilization from N fertilizers, NH₃ loss from N mineralized from organic N (mineralization) is relatively small (Havlin et al., 2005). Many factors involved in soil, environment and fertilizer influence the quantity of NH₃ volatilization from fertilizers. Understanding these factors which interact among one another is driven from comprehension of the chemical reactions of N fertilizers with soil gas (Beyrouty et al., 1988; Brady and Weil, 2002; Cameron, 1992; Havlin et al., 2005; Haynes, 1992).

As for agricultural fields, it has been widely accepted that the losses of nitrogen can account for about 50-60% of added fertilizer nitrogen (Jung et al., 1996). The N use efficiency in an cultivated alpine soil for vegetable crops was estimated to be as low as only 7 to 11% (Cho, 1999) due to the severe soil erosions at the steep slopes which lower the depth of top soil and resultantly soil fertility. In the Northeastern part of Kangwon Province, especially in the mountainous areas with elevation higher than 600 m above sea level, the alpine agriculture is commonly practiced to grow the Chinese cabbage. In this case, the application level of N fertilizer as urea have been commonly far exceeded the recommendation (Cho, 1999). Due to the geographic and climatic conditions, the Chinese cabbage is cultivated during summer under high precipitation condition. Diurnal variations of temperatures at the alpine regions are generally quite high even in the same season. In general, NH3 volatilization is known to increase as increasing temperature up to 45°C due to the higher kinetic reaction rates and urease activities (Havlin et al., 2005). The NH₃ volatilization from urea in this area might vary accordingly by temperature variations.

Ammonia volatilization at surface soil under dry condition is in general low because microbial and chemical reactions involved in volatilization do not readily take place. It is known that maximum ammonia volatilization occurs when soil surface is at or near field capacity of soil moisture contents and when slow drying conditions exist for several days (Havlin et al., 2005). Water evaporation from the surface soil accelerates the ammonia volatilization. Application of urea to the soil surface thus converts rapidly to NH₃ or NH₄⁺ with adequate moisture, proper temperature, and the presence of urease. This NH₃ can be released to the atmosphere through volatilization or damage vegetables causing wilting under high temperature and humid conditions with exceeded N application in the alpine regions. Thus judicious management strategies for soil and N fertilizers in this region are needed.

The amount of ammonia release through volatilization into the atmosphere is known to be depending upon such factors as NH4⁺ concentration in the surface soil solution, soil pH, soil temperature, soil moisture, and wind speed above the soil (Beyrouty et al., 1988; Havlin et al., 2005). By the way, concentration of ammonia gas at higher than 60 ml m^{-3} in the atmosphere is known to be toxic to plant development and growth (Brady and Weil, 2002). Concentrations of ammonia were higher at near the surface of the soil, as reported by Mengel and Kirkby (2001), and they decreased with increasing height in the air above the soil surface. However, no guideline for the fertilizer management in this respect is recommended. In this study, the volatilized ammonia from the surface of the soil, treated with urea, was measured in order to assess the factors that favorably lead to the NH₃ volatilization.

Materials and Methods

Study site and fertilization The experimental site was a field located in Woodu-dong, Chuncheon, Kangwon. The soil on the field is of Ihyeon soil series (coarse silty, mixed, mesic family of Dystric Fluventic Eutrochrepts) (Alluvial soils). The Ap horizon of a typical pedon has chemical characteristics determined

Texture	pH	Organic matter	P2O5	K^+	Ca ²⁺	Mg ²⁺	CEC
	(1:5)	g kg ⁻¹	$mg kg^{-1}$	cmol ⁺ kg ⁻¹			
Coarse silty	6.77	24.63	1,286.53	0.26	5.75	0.33	10.35

Table 1. Chemical properties of the soil (Ihyeon series. coarse silty, mixed, mesic Dystric Fluventic Eutrochrepts).

using standard methods (NIAST, 2000a), as shown in Table 1. The nitrogen fertilizer used was urea [(NH₂)₂CO, MW: 60.06 g].

Experimental device and treatments A vinyl film chamber with a lid on top was built on the surface of the soil in the field as shown in Fig. 1. The ammonia gas trapped and collected in beakers filled with boric acid (H₃BO₃) solution was analyzed according to the Kjeldahl distillation method (NIAST, 2000b). The trapping beakers were placed at the rings on the supporting stand at heights of 0, 10, 20, and 30 cm above the soil surface.

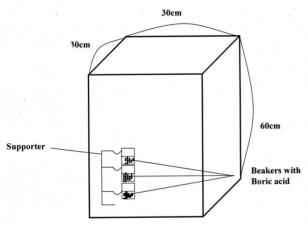


Fig. 1. The vinyl film chamber with a lid on top.

Rates of urea application to soil surface were 0, 200, 400, and 600 kg N ha⁻¹ at 22°C. The recommended level of N for cabbage is 240 kg ha⁻¹. The effects of the ambient temperature on the volatilization of urea were determined at 5, 8, 22, and 28°C at urea application of 400 kg ha⁻¹. Since soil moisture contents might make some changes for the volatilization of urea, different irrigation practices were introduced; no irrigation, irrigation of 5 and 10 mm before urea application and irrigation of 5 mm after urea placement at rate of 400 kg ha⁻¹ at 22°C. Concentrations of ammonia trapped at 10, 20 and 30 cm above the soil surface were analyzed for N by Kjeldahl distillation method. Amounts of NH₃ N volatilized from urea were assessed based on ammonia concentration trapped in the beaker and converted to the rate of volatilization at each level of urea application.

Results and Discussion

Rates of urea application Volatile ammonia gas [NH3 (g)] was triggered to detect about 3 days after surface application of urea to soil under field condition as shown in Fig. 2. No ammonia gas was trapped until 3 d after urea application, indicating the conversion of urea to ammonia was mediated by a biochemical process with a lag period of about 3 days. A maximum amount of NH₃ (g) was obtained in general within 15 d after fertilization. Afterwards, a slight increase in total amount of NH₃ (g) was observed until 17 d after urea application. Ferguson et al. (1984) reported that NH₃-N volatilized as kg ha⁻¹ basis was stabilized after 12 to 16 d after N fertilization, which varied with soils' buffering capacity. The volatilization was higher at lower buffering capacity. The initial soil pH of 6.5 was increased to 7 to 8.5 after 3 to 6 days of N fertilizer application, depending on the buffering capacity of the soils. The higher pH increases, the lower buffering capacity. However, pHs were decreased to be stabilized at initial pH after 10 to 14 d after N application. Thus buffering capacity of the soil influences NH3 volatilization loss. Soil pH and subsequent NH₃ loss is much higher with lower buffering capacity. Havlin et al. (2005) reported that buffering capacity of soil influences on NH3 volatilization in two different manners: (1) to resist the increase in pH with fertilizer application and (2) to remove part of ammonium and ammonia from soil solution.

Amounts of NH₃-N volatilized from urea were significantly increased with increasing levels of urea applications from 200 to 600 kg ha⁻¹. Total amounts of 3.0, 4.4, and 8.0 kg of NH₃-N were volatilized at application rates of 200, 400, and 600 kg N ha⁻¹, respectively. These NH₃-N volatilized were equivalent to the losses of 15.0, 10.9, and 13.0% of the N applied at the respective rates of 200, 400, and 600 kg ha⁻¹. These values are relatively smaller than previous study (Jung et al., 1996). A very little amount of gaseous ammonia was also detected even from the control plot where no fertilizer urea was added. It was well anticipated that the

organic matter of the soil might contribute to NH₃ volatilization. Results demonstrated that the recommended level of N fertilizer should be practiced in order to avoid of N losses through volatilization.

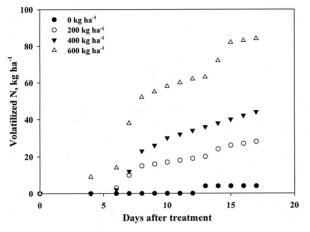


Fig. 2. Total amounts of ammonia volatilization from urea in 17 d after application at 22° C at different application levels.

Effects of temperature As shown in Fig. 3, there was practically no ammonia gas was detected at the ambient temperature of 5°C, which is sometimes called a "biological zero temperature" (Brady and Weil., 2002). The losses of urea as ammonia volatilization were 5, 21, 75, and 87 kg NH₃-N ha⁻¹ at 5, 8, 22, and 28°C after 10 d urea application, respectively. At 28°C, about 15% of the applied N was lost. Drastic increases in ammonia gas evolution with increase in temperature confirmed the biochemical nature of urea hydrolysis, because the reaction rates of urea decomposition far exceeds those of ordinary chemical reactions. The temperatures, 22°C and 28°C, must be given a special attention, because these are

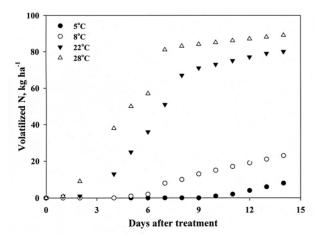


Fig. 3. Effects of temperature on the ammonia volatilization from urea at 400 kg ha⁻¹.

the prevalent ambient temperatures for actively developing and growing crops during summer. Results suggest that urea fertilization during the high temperature seasons might accelerate the N loss through volatilization.

Effects of irrigation The effects of various irrigation practices on the ammonia volatilization before or after urea application were shown in Fig. 4. The amount of NH₃-N volatilized at 5 mm irrigation after fertilization was only 10.44 kg N ha⁻¹. However, irrigation prior to urea fertilization significantly increased N volatilization showing the amounts of NH₃-N volatilized were 21.2, 21.3, and 16.6 kg N ha⁻¹, for control, 5 and 10 mm of irrigation, after 16 d. Ammonia volatilizations were decreased as increasing the level of irrigation.

Result showed that irrigation to the soil surface after urea application greatly suppressed ammonia volatilization. This was because of facilitating urea diffusion into soils and thus helping urea to be converted into ammonium in the soil. Another possible reason for this would be that water added after fertilization will actively hold ammonia gas in soil solution as aqueous form, thus effectively prevent the gaseous escape into the atmosphere.

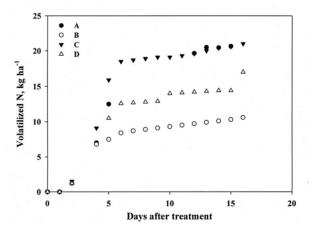


Fig. 4. Effects of irrigation practices on the ammonia from urea at 400 kg ha⁻¹ at 22°C. [A, fertilizer \rightarrow no irrigation; B, fertilizer \rightarrow irrigation (5mm); C, irrigation (5mm) \rightarrow fertilizer; D, irrigation (10mm) \rightarrow fertilizer].

Ambient distribution of ammonia It was revealed that under field conditions the concentrations of ammonia in the air rarely reach this level of toxicity with exceptions of very high rates of fertilizer applications as shown in Fig. 5. After passing the lag period of about 6

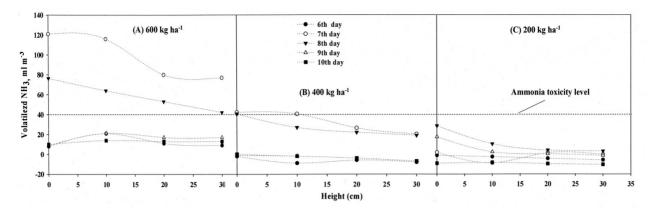


Fig. 5. Distribution of volatilized ammonia in the ambient of chamber at 22°C.

days under field conditions, maximum quantities of ammonia gas were detected in 7 and 8 d after fertilizer urea applications at all designated heights above the soil surface. The ammonia concentrations showing less than 20 ml m⁻³ after 9 d were far below the ammonia gas toxicity level as shown in Fig. 5. But unusually high rates of fertilization such as 600 kg ha⁻¹ may cause ammonia gas damage on plants possibly within several days.

Conclusions

Volatilization of ammonia from N fertilizer is the major mechanism of N losses that occur naturally in all soils and is influenced by numerous soil and environmental factors and N fertilizer management factors. It has been reported that vegetables are often damaged by NH₃ gas volatilized from the high rates of N fertilizer. The NH3 volatilization was started about 3 d lag time after urea application and reached at maximum level in general within 15 to 17 days. After 17 d, 13.0% of N applied was lost through volatilization, which was considered to be very high in view of N fertilizer economy and N use efficiency. Masses of N volatilization were significantly increased with temperatures. Results suggest that urea fertilization during the high temperature should be avoided to prevent N loss through volatilization. Irrigation practice influenced significantly the rate of N volatilization. Irrigation after urea application was better management practice to prevent the ammonia volatilization, as compared to irrigation before N fertilization. Concentrations of ammonia volatilized were highest right above the soil surface and decreased as increasing level in the air. In conclusion, urea loss can be minimized by practicing fertilizer management such as incorporating urea with soil at the recommended level, applying when temperatures are low or irrigating

immediately to carry the urea into soil.

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암모니아 휘산에 의한 요소비료의 손실에 미치는 요인

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질소비료로부터 암모니아의 휘산은 자연적으로 존재하는 모든 토양에서 일어나는 질소 손실의 주된 기작이다. 암모니아 휘산은 다양한 토양과 환경의 조건 및 비료관리 방안에 의해 영향을 받는다. 질소비료 의존도가 높은 채소들도 휘산된 암모니아 가스에 의해 피해를 받는 사례가 종종 보고되고 있다. 본 연구에서는 표토에 시용된 요소비료로부터 암모니아 휘산량을 측정하였고, 이에 미치는 요소비료 시용량, 관개시기, 및 온도 등의 비료관 리요인들의 영향을 조사했다. 암모니아 휘산은 요소를 시용한 뒤 약 3일 후에 시작되었으며, 약 2주 후에 최대 에 도달하였다. 17일 후, 휘산된 암모니아태 질소의 양은 200, 400, 600 kg N ha⁻¹ 의 시용량에서 각각 3.0, 4.4, 그리고 8.0 kg 이었다. 이들 휘산량은 시용된 질소가 15.0, 10.9, 및 13.0% 가 손실된 것과 상응한다. 온도가 5, 8, 22, 28°C 일때 휘산된 질소의 양은 각각 5, 21, 75, 87 kg N ha⁻¹ 이였다. 요소비료를 시용한 뒤 0, 5, 10 mm 의 물을 관개한 경우, 휘산된 질소의 양은 각각 21.3, 21.2, 16.6 kg N ha⁻¹ 이었다. 한편, 요소를 시용한 후 5 mm를 관수한 경우의 질소 휘산량은 10.44 kg N ha⁻¹ 로 감소하였다. 그러므로 요소비료를 권장량을 표토와 혼 합, 온도가 낮을 때 그리고 요소비료를 시용후 즉시 관개하는 방안이 암모니아 휘산에 의한 질소 손실을 최소 화 하는 비료관리 방안이었다.