ISSN 0367-6315 (Print) / ISSN 2288-2162 (Online)
Korean J. Soil Sci. Fert. 46(4), 288-295 (2013)
http://dx.doi.org/10.7745/KJSSF.2013.46.4.288

Article

Emission of NO_2 Gas Causing Damage to Plants in an Acid Soil under Conditions Favorable for Denitrification

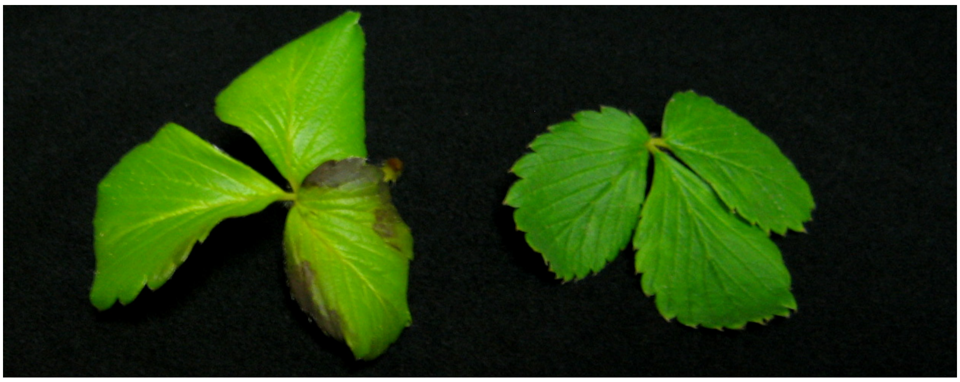
Sun-Young Suh, Il-Su Byeon, Yong-Se Lee, and Jong-Bae Chung*

Division of Life and Environmental Science, Daegu University, Gyeongsan 712-714, Korea

(Received: June 26 2013, Accepted: July 17 2013)

Nitrogen dioxide (NO_2) gas damage on vegetable crops commonly occurs in plastic film houses where relatively large amounts of NO_3^- are applied in acid soils. In acid soils, HNO_2 can be formed from the NO_2^- accumulated during denitrification, and NO_2 can be evolved from the chemical self-decomposition of HNO_2. In this study, NO_2 gas production and its detrimental effects on plants were investigated in soils of various conditions to elucidate the mechanisms involved in the gas production. A silty loam soil was amended with NO_3^- (500 mg N kg^{-1}) and glucose, and pH and moisture of the soil were adjusted respectively to 5.0 and 34.6% water holding capacity (WHC) with 0.01 M phosphate buffer. The soil was placed in a 0.5-L glass jar with strawberry leaf or NO_2 gas absorption badge in air space of the jar, and the jar was incubated at 30°C. After 4-5 days of incubation, dark burning was observed along the outside edge of strawberry leaf and NO_2 production was confirmed in the air space of jar. However, when the soil was sterilized, NO_2 emission was minimal and any visible damage was not found in strawberry leaf. In the soil where water or NO_3^- content was reduced to 17.3% WHC or 250 mg N kg^{-1}, NO_2 production was greatly reduced and toxicity symptom was not found in strawberry leaf. Also in the soil where glucose was not amended, NO_2 production was significantly reduced. In soil with pH of 6.5, NO_2 was evolved to the level causing damage to strawberry leaf when the soil conditions were favorable for denitrification. However, compared to the soil of pH 5.0, the NO_2 production and its damage to plants were much less serious in pH 6.5. Therefore, the production of NO_2 damaging plants might be occurred in acid soils when the conditions are favorable for denitrification.

Key words: Acid soil, Denitrification, Nitrogen dioxide, Nitrate, Nitrite self-decomposition



NO_2 was evolved to the level causing damage on strawberry leaf when the soil conditions were favorable for denitrification. In sterile soil, damage was not found (right).

*Corresponding author : Phone: +82538506755, Fax: +82538506759, E-mail: jbchung@daegu.ac.kr
§Acknowledgement: This research was supported by the Daegu University Research Fund in 2012.

Introduction

In crop fields, especially in greenhouses, gaseous NH_3 frequently produced from soils and it causes damage to plants. Gaseous emission of NH_3 is most likely to take place when soils are moist, warm, and alkaline, and when the source of fertilizers or manures are on or near the soil surface (Gasser, 1964; Nelson, 1982). Also nitrogen dioxide (NO_2) can be produced from nitrogen fertilized soils, and at μM levels has resulted in visible symptoms of injury in some vegetables (Nouchi, 2002). Nitrogen dioxide damages plants by destroying cellular membranes and inhibiting photosynthesis and respiration (Lea, 1998; Wellburn, 1990).

Nitrogen dioxide gas is known to be produced through the action of ammonium oxidizing bacteria in acid soils amended with incompletely decomposed organic residues (Smith and Chalk, 1980a, 1980b). Recently chlorosis and necrosis were found along the outer edge of the bottom leaves of strawberry plants growing in plastic film houses in Chungdo, Gyeongbuk. Those injuries are supposed to be the toxicity of NO_2 gas produced in soils. In those plastic film houses of strawberry cultivation, soil pH was around 5.0 and soil beds amended with compost and basal chemical fertilizers were covered with dark plastic sheeting before planting. During the plant growing period, water and nutrients including nitrogen were supplied using inline drip irrigation systems. The nutrient solution contained 60 and 7.5 mg N L^{-1} in the form of NO_3^- and NH_4^+, respectively. Also NO_2 gas injury was found in fig trees grown in containers with application of nutrient solution containing 200 mg N L^{-1} of NO_3^-, and pH of the artificial soil in the containers was 5.5 (Kim et al., 2010). Kim et al. (2012) reported NO_2 gas injury in cucumber plants grown in acid soil (pH 4.8) of plastic film house where soil NO_3 content was 500 mg L^{-1}.

Considering those incidences of NO_2 gas damage to crop plants, NO_2 emission is closely related to the NO_3^- applied as a nitrogen fertilizer and also to the acidic soil pH. Since water evaporation and aeration are quite limited in the soil beds that were covered with plastic sheeting, the soil conditions may be favorable for denitrification. Therefore, NO_2 gas is supposed to be produced during the reduction process of NO_3^- in the soil, especially biological denitrification. However, NO_2 is not included in the gaseous intermediates of current models of biological denitrification (Alexander, 1977). Nitrogen dioxide gas can be produced by the spontaneous chemical decomposition of HNO_2 in acid solutions containing NO_2^-, where the equilibrium between NO_2^- and HNO_2 shifts towards HNO_2 (pK_a=3.38) (Nelson and Bremner, 1970; Van Cleemput and Baert, 1978; Reuss and Smith, 1965). Therefore NO_2 gas might be produced in acid soils where NO_2^- is accumulated through soil microbial processes of denitrification.

Production of NO_2 gas damaging crops is limited mostly to the acid soils of plastic film house fertigated with nutrient solutions containing relatively large amounts of NO_3^- as a N source. Thus, the toxic level of NO_2 gas production can be associated with denitrification processes in the soils. Although the detail mechanisms responsible for the emission of NO_2 from soil is not clearly understood, previous studies have shown that NO_2 gas can be produced in soils under various conditions (Kim, 1973; Nelson and Bremner, 1970; Reuss and Smith, 1965; Slemr and Seiler, 1984; Van Cleemput and Samater, 1996).

In this study, NO_2 gas production and its damaging effect on plants were investigated in soils under the conditions favorable to high rates of denitrification, and the mechanisms involved in the NO_2 gas production were discussed.

Materials and Methods

Soil Soil was collected from 0-20 cm layer of a vegetable farm in Geumho, Yeongcheon. The soil was classified as Jungdong series (coarse loamy, mixed, mesic family of Typic Udifluvents), and soil sample was sieved through a 5-mm screen and refrigerated (4℃) until used. Selected soil properties are shown in Table 1.

Soil conditions favorable for NO_2 emission Emission of NO_2 gas and its damaging effect on plants were investigated in soils under four different conditions including those favorable to high rates of denitrification as shown in Table 2. Soil pH was adjusted to 5.0 by adding 0.01 M phosphate buffer solution (pH 5.0) required to maintain water content of soil at 17.3 or 34.6% WHC. The soil was amended with $NaNO_3$ to adjust the required concentration of NO_3^-. For each treatment, about 200 g of the prepared soil was placed in a 0.5 L glass jar, and a small glass beaker filled with 20 mL of distilled water was

Table 1. Characteristics of the soil used in the experiment.

pH	Organic matter	Total N	NH_4-N	NO_3-N	CEC	Texture
	g kg^{-1}		mg kg^{-1}		$cmol_c$ kg^{-1}	
6.2	23.0	1.3	9.7	254.0	8.1	Silt loam

Table 2. pH and contents of ammonium, nitrate, glucose and moisture in the prepared soils of four treatments.

Treatment	pH	NH_4-N	NO_3-N	Glucose	Moisture
		---------------- mg kg^{-1}	----------------	g kg^{-1}	% WHC†
1	5.0	9.7	500.4	5	17.3
2	5.0	9.7	500.4	5	34.6
3	5.0	9.7	254.0	5	34.6
4	5.0	9.7	500.4	-	34.6

† Water holding capacity

placed on the soil. A strawberry leaf was placed in the beaker with keeping the lower part of leafstalk dipping in the water. In the experiment for detection of NO_2 gas production in the soil, NO_2 gas filter badge (Toyo Roshi Kaisha, Ltd., Tokyo, Japan) was installed on the top of small beaker placed in the glass jar filled with about 200 g of the prepared soil. Direct contact between soil and strawberry leaf or NO_2 absorption filter badge was completely eliminated during the experiment. The prepared experimental systems were placed in a growth chamber for 5 days at 30°C with the cap of glass jars loosely closed. During the incubation, NO_2 gas production was evaluated by daily monitoring of the development of toxicity on the strawberry leaves. After the incubation experiment, NO_2 gas absorbed on the filter badge and NH_4^+, NO_3^-, and NO_2^- in the soil were determined.

Effect of sterilization on NO_2 emission from acid soil Using soil of pH 5.0 amended with NO_3^- and glucose (Treatment 2 in Table 2), the effect of soil sterilization on NO_2 emission was investigated. Water content of the soil was adjusted to 47.6% WHC using 0.01 M phosphate buffer solution (pH 5.0). Half of the soil was sterilized twice at 134°C at intervals of 24 hours. The sterile and non-sterile soils were placed in individual 0.5 L glass jars, and strawberry leaf or NO_2 absorption filter badge was installed in air space of the jars using a small beaker to eliminate direct contact with soil. For the treatment of sterile soil, strawberry leaves and other materials were also sterilized before placing in the glass jar. The prepared experimental systems were incubated for 5 days at 30°C with the cap of glass jars loosely closed. During the incubation period, NO_2 production was evaluated by daily monitoring of the development of toxicity on the strawberry leaf. After the incubation period, NO_2 gas absorbed on the filter badge and NH_4^+, NO_3^-, and NO_2^- in the soil were determined.

Effect of pH on NO_2 emission from soil Effect of soil pH on NO_2 gas emission from soils was investigated under the conditions favorable for denitrification. Content of NO_3^- in the soil was adjusted to 500 mg N kg^{-1} with $NaNO_3$, and glucose was also added in the rate of 5 g kg^{-1} soil. Soil pH was adjusted to 5.0 and 6.5 by adding the required volume of 0.01 M phosphate buffer solution of respective pH to maintain water content of the soil at 43.3% WHC. About 200 g of each soil prepared was placed in 0.5 L glass jars, and as described in detail earlier in this section, strawberry leaf or NO_2 gas filter badge was installed in air space of the jar using a small beaker to eliminate direct contact with soil. The prepared experimental systems were placed in a growth chamber for 5 days at 30°C with the cap of glass jars loosely closed. During the incubation, NO_2 gas production was evaluated by daily monitoring of symptoms of NO_2 toxicity appeared on the strawberry leaves. After the incubation experiment, NO_2 gas absorbed on the filter badge and NH_4^+, NO_3^-, and NO_2^- in the soil were determined.

Analytical procedures Nitrogen dioxide absorbed on filter badges, in which triethanolamine was spread in absorption layer, was extracted and color developed using coloring solution. The coloring solution was prepared as follows: 5 g of sulfanilic acid was dissolved in 700 mL distilled water and mixed well after adding of 50 mL of 85% phosphoric acid solution, and then 50 mL of 0.1% N-(1-naphthyl) ethylenediamine dihydrochloride solution was added, and the final volume was adjusted to 1 L with distilled water. Absorption layer removed from the inner frame of the badge case was put in a mass cylinder, and 50 mL of coloring solution was added. The coloring was completed in 40 min at 25℃, and absorbance was measured at 545 nm using a spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan). Blank absorbance was measured using unexposed filter badge following the same procedure above. Soil NH_4^+, NO_3^-, and NO_2^- were determined by extraction of fresh soil in a 2 M KCl solution followed by flow-injection analysis (FIASTAR-5000 system, FOSS Tecator, Höganäs, Sweden).

Results

Emission of NO_2 gas during denitrification in acid soil Among the treatments (Table 2), dark brown burning of NO_2 toxicity symptom was observed along the outside edge of strawberry leaf after 4-5 days of incubation at 30°C in the wet acid soil of treatment 2 (Fig. 1). The treatment 2 was prepared to provide the most favorable soil environment for denitrification by adding excessive nitrate and water along with glucose. In soils where water content was reduced to 17.3% WHC (Treatment 1) or NO_3^- content was reduced to 250 mg N kg^{-1} (Treatment 3), NO_2 toxicity symptom was not observed in the strawberry leaf during the incubation. Also in the soil of treatment 4, where glucose was not amended, NO_2 toxicity symptom was not found in the strawberry leaf.

Emission of NO_2 gas from soils was qualitatively measured using NO_2 gas absorbing filter badge installed in the air-space of experimental system. The amount of NO_2 gas absorbed on the filter badge can represent the relative concentration of NO_2 gas in the air above the soil in glass jar. The filter badges were extracted by a coloring solution after incubation, and the measured absorbances are presented in Table 3. The highest absorbance was found in treatment 2, in which soil condition was most favorable for denitrification. In other treatments, where NO_2 toxicity symptom was not observed in the strawberry leaf during the incubation, the absorbance was much lower compared to that found in treatment 2. The dark brown burning along the outer edge of strawberry leaf observed in treatment 2 could be due to the relatively higher concentration of NO_2 gas accumulated in the airspace above the soil. The less production of NO_2 gas in treatment 1, 3, and 4 can be attributed to the lower contents of water, NO_3^-, and organic carbon, respectively, in soil. Under those conditions denitrification activity in

Table 3. NO_2 gas productions in the soils of different treatments during the 5 days of incubation. The absorbance was measured at 545 nm using a spectrophotometer after extracting NO_2 gas absorbed on the filter badge with coloring solution.

Treatment†	Absorbance
1	0.101
2	0.427
3	0.138
4	0.205

† For the details of each treatment, see Table 2 in Materials and Methods section.

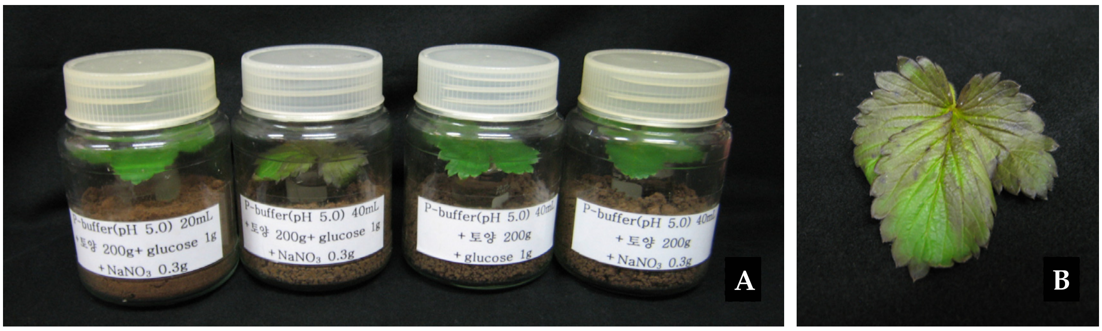


Fig. 1. Photograph showing the effect of various soil treatments on the damage to strawberry leaf caused by NO_2 gas produced from the soil during denitrification. A: (from left to right) Treatment 1, 2, 3, and 4. B: Strawberry leaf damaged by NO_2 gas produced from the soil in treatment 2. For the details of each treatment, see Table 2 in Materials and Methods section.

Table 4. Changes in concentration of inorganic nitrogens in the soils of different treatments of nitrate, glucose, and water content during 5 days of incubation at 30℃.

Treatment†	NH_4-N	NO_3-N	NO_2-N
	----------	mg kg^{-1}	----------
		Before incubation	
1, 2, 4	9.7	500.4	-
3	9.7	254.0	-
		After incubation	
1	6.4	507.3	0.6
2	6.4	60.5	36.4
3	3.6	28.8	0.7
4	11.1	411.5	5.8

† For the details of each treatment, see Table 2 in Materials and Methods section.

the soils can be lower in comparison to the soil in treatment 2.

Inorganic nitrogen concentrations measured at the end of incubation are presented in Table 4. In treatment 1, where soil moisture content was adjusted to 17.3% WHC, the NO_3^- in soil before incubation was hardly removed during the incubation. However, with moisture content of 34.6% WHC, nearly 90% of the initial NO_3^- in soil was removed during the incubation in treatment 2 and 3. And a large amount of NO_2^- was found to be accumulated along with loss of NO_3^- (about 440 mg N kg^{-1}) in wet acid soil of treatment 2. Only 20% of the initial NO_3^- was removed in treatment 4, where glucose was not amended, and this result could be due to the treatment where the soil environment was not anoxic enough for active denitrification.

Table 5. NO_2 gas productions in the sterile and non-sterile soils during the 5 days of incubation. The absorbance was measured at 545 nm using a spectrophotometer after extracting NO_2 gas absorbed on the filter badge with coloring solution.

Treatment	Absorbance
Non-sterile	0.309
Sterile	0.015

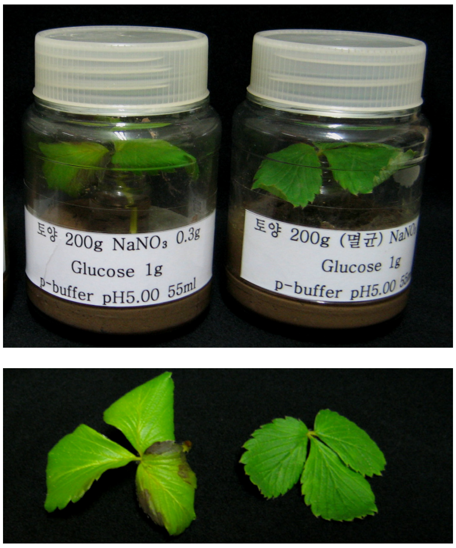


Fig. 2. Photograph showing the effect of soil sterilization on NO_2 gas-induced damage in strawberry leaf. In sterile soil, damage was not found on the strawberry leaf (right), but NO_2 gas-induced damage was observed on strawberry leaf in non-sterile soil (left) during the 5 days of incubation at 30℃.

Comparison of NO_2 emission in sterile and non-sterile soils Emission of NO_2 was identified in acid soils containing NO_3^- under the conditions favorable to high rates of denitrification (Fig. 1). It was further confirmed whether the activities of denitrifying bacteria are directly involved in the processes related to the emission of NO_2 gas in acid soils. In the sterile soil of pH 5.0 and moisture content of 47.6% WHC, even though the soil contained NO_3^- (500 mg N kg^{-1}) and glucose, NO_2 emission was minimal and any visible damage was not found in the strawberry leaf during the 5 days of incubation at 30°C (Table 5 and Fig. 2). On the contrary, NO_2 toxicity symptom was observed on strawberry leaf in non-sterile soil of the same treatment after 4-5 days of incubation. Although the content of NO_3^- was reduced from 500.4 to 60.5 mg N kg^{-1} in non-sterile soil during the incubation, denitrification was supposed to be completely suppressed in sterile soil and the final content of NO_3^- in the soil was even slightly higher than the initial NO_3^- content (Table 6). These results indicate that NO_2 gas emission cannot be occurred in the soil without biological denitrification. And NO_2 emission in wet acid soils containing NO_3^- can be primarily attributed to the accumulation of NO_2^- produced as the first reaction intermediate in the process of biological denitrification.

Effect of pH on NO_2 emission from soil amended with NO_3^- and glucose The incidence of NO_2 gas toxicity on plants generally occurs in acid soils with a pH of 5.0-5.5. The effect of soil pH on NO_2 gas emission from soils was investigated under the conditions favorable

Table 6. Changes in concentrations of inorganic nitrogen in sterile and non-sterile soils during the 5 days of incubation at 30℃. Before incubation, $NaNO_3$ and glucose was added in the soils and pH and water content was adjusted to 5.0 and 47.6% WHC with 0.01 M phosphate buffer solution.

Treatment	NH_4-N	NO_3-N	NO_2-N
	----------	mg kg^{-1}	----------
		Before incubation	
	9.7	500.4	-
		After incubation	
Non-sterile	6.5	60.5	36.4
Sterile	14.7	512.4	0.3

for denitrification.

As shown in Fig. 3, toxicity symptom was observed on strawberry leaf in soils of both pH 5.0 and 6.5 after 4-5 days of incubation. Compared to the soil of pH 5.0, the NO_2 gas production and its damage on the strawberry leaf were much less serious in pH 6.5 soil (Fig. 3 and Table 7). Amount of NO_2 gas absorbed on the filter badge in pH 5.0 soil was more than twice the value measured in pH 6.5 soil. The amount of NO_2 gas absorbed can represent the relative concentration of NO_2 gas in the air above the soil in glass jar. The difference in severity of NO_2 gas toxicity symptom between soils of pH 5.0 and 6.5 seems to directly reflect the difference of NO_2 emission in the two soils. During the 5 days of incubation, 85 to 90% of the initial soil NO_3^- were removed through denitrification, and the removal rate was slightly higher in pH 5.0 soil (Table 8), where NO_2 emission was higher and NO_2 toxicity was more severe. Nitrite accumulation in the soil was not much different between the two pHs. Although NO_2 gas production was less than that found in acid soil, these results indicate that NO_2 gas can be formed during denitrification to the levels inducing damages on plants even in near-neutral pH soil environments.

Fig. 3. Photograph showing the effect of soil pH on NO_2 gas-induced damage in strawberry leaf during denitrification. Damage was found on strawberry leaf in both soils of pH 5.0 (A) and 6.5 (B) during the 5 days of incubation at 30℃.

Table 7. NO_2 gas productions in the soils of pH 5.0 and 6.5 during the 5 days of incubation. The absorbance was measured at 545 nm using a spectrophotometer after extracting NO_2 gas absorbed on the filter badge with coloring solution.

Treatment	Absorbance
pH 5.0	0.649
pH 6.5	0.352

Discussion

A major loss mechanism of NO_3^- in soil is biochemical denitrification, and in this process NO_3^- is reduced to NO_2^- followed by the reduction of NO_2^- to N_2, via the gaseous intermediates NO and N_2O (Alexander, 1977). Nitrogen dioxide is not included as a gaseous intermediate in the current biochemical models of denitrification. However, NO_2 was produced in soils amended with NO_3^- under favorable conditions for denitrification in this study. And also there was a strong positive correlation between NO_2 gas production and the loss of NO_3^- from the soil (Table 6 and 7). Therefore, it can be suggested that NO_2 gas causing injury to strawberry leaves might be produced by some other ways than the biological NO_3^- reduction processes during the denitrification.

Nitrogen dioxide can be produced by abiotic processes, and several mechanisms have been proposed to explain the NO_2 gas emission from soils. Nelson and Bremner (1970) found that most of the NO_2 gas evolved in treatment of soils with NO_2^- is formed by self-decomposition of HNO_2 ($2HNO_2 \rightleftharpoons NO + NO_2 + H_2O$) and by atmospheric oxidation of NO produced by this reaction. Smith and Chalk (1980b) showed that NO and NO_2 were formed by self-decomposition of NO_2^-. Van Cleemput and Baert (1984) also suggested that, whatever NO_2^- is formed in a soil, the NO_2^- decomposition occurs under acid conditions. Indeed, several other experiments have shown that NO_2^-

Table 8. Changes in concentrations of inorganic nitrogens in the soils of pH 5.0 and pH 6.5 during the 5 days of incubation at 30℃. Before incubation, $NaNO_3$ and glucose was added in the soils and water content was adjusted to 25% with pH 5.0 phosphate buffer solution to promote denitrification.

Treatment	NH_4-N	NO_3-N	NO_2-N
	----------	mg kg^{-1}	----------
		Before incubation	
	10.2	500.4	-
		After incubation	
pH 5.0	8.3	50.6	27.6
pH 6.5	8.7	75.3	28.5

is rapidly decomposed in acidic or mildly acidic soils (Burns et al., 1995; Van Cleemput and Samater, 1996). Considering these results, NO_2^- seems to be a key compound in the emission of NO_2 as well as the production of NO, N_2O, and N_2 by biological reduction processes in soil.

Though concentrations of NO_2^- in soils are usually low, NO_2^- can be accumulated in soils as an obligate intermediate in aerobic nitrification as well as in the anaerobic denitrification process (Alexander, 1997). In this study, in the acid soil prepared for high rate of denitrification, 36.4 mg N kg^{-1} of NO_2^- was found even after the 5 days of incubation (Table 4). Thomsen et al. (1994) also reported that during the denitrification NO_3^- was converted to NO_2^- and the NO_2^- accumulated until NO_3^- became undetectable in soil at pH 5.5. Therefore, the self-decomposition of HNO_2 by chemical pathways may be the common source of NO_2 in acid soils, where NO_2^- is accumulated as an intermediate during the denitrification process. In the present study, most of the inorganic N in soil was present in the form of NO_3^- with a small amount of *in situ* NH_4^+ (9.7 mg N kg^{-1} soil) as shown in Table 1. Incidences of NO_2 toxicity in plants are mostly reported in acid soils where NO_3^- was applied as a nitrogen fertilizer (Kim et al., 2010, 2012).

Although NO_2 emission and its damaging effect were identified in the wet acid soils containing NO_3^-, NO_2^- accumulation and NO_2 production were completely inhibited when the soil was sterilized (Table 5 and 6). Nelson and Bremner (1969) found that soil sterilization had little effect on NO_2^- decomposition. Smith and Chalk (1980a) also found that gaseous N evolution was similar in γ-irradiated and non-irradiated soils treated with NO_2^-. From these results, it can be further confirmed that emission of NO_2 gas in the acid soil containing NO_3^- can be attributed to the chemical self-decomposition of HNO_2 formed by protonation of NO_2^- which can be accumulated as an obligate intermediate in the denitrification pathway. Therefore, for the production of NO_2 gas to the level causing injury to plants, a relatively large amount of NO_2^- should be accumulated in soils and then the NO_2^- should be decomposed through self-decomposition and other possible mechanisms.

Although the production of NO_2 damaging crops is limited mostly to the acid soils (Kim et al., 2010; Van Cleemput and Baert, 1984), it is noteworthy that a substantial amount of NO_2 can be produced from soil with pH value of 6.5 in this study (Table 7). In other studies, though the amount of NO_2 formed by decomposition of NO_2^- increased with decrease in soil pH, NO_2 production was still found in soils having pH values of 6.0-7.0 (Reusss and Smith, 1965; Nelson and Bremner, 1969, 1970; Slemr and Seiler, 1984; Van Cleemput and Baert, 1984). The chemical self-decomposition is known to be the dominant process of NO_2^- loss and NO_2 production in soils at pH≦5 (Van Cleemput and Samater, 1996). The critical pH for chemical self-decomposition of HNO_2 into NO and NO_2 is known to be 5.47, and the spontaneous decomposition does not occur above this value (Van Cleemput and Baert, 1978). Then the emission of NO_2 in soils with pH values of 6.0-7.0 could be attributed to other processes than the self-decomposition of HNO_2.

Some of the NO_2 formed by decomposition of NO_2^- in soils might be produced by reaction of NO_2^- with organic or inorganic soil constituents (Nelson and Bremner, 1969; Van Cleemput and Samater, 1996). Nelson and Bremner (1969) found that at pH values above 5, where self-decomposition of NO_2^- is very slow, soil organic matter promoted volatilization of NO_2^-. In the study of Blackmer and Cerrato (1986), when various amounts of soil were added to identical samples of NO_2^- solution, the amounts of NO found increased with amounts of soil added. These findings indicate that NO is formed by reactions of NO_2^- with the organic fraction of soils as well as by self-decomposition of nitrous acid. In the study of Van Cleemput and Baert (1984), NO_2^- concentration decreased very rapidly following addition of 40 mg NO_2-N kg^{-1} to a silt loam soil (pH 6.0) preincubated with amorphous iron. Islam et al. (2008) also reported that the large quantity of DTPA-extractable Fe was in accordance with the catalysis of NO_2^- self-decomposition by metal ions in acidic soils. Although soil conditions favoring the formation of Fe^{2+} increased the decomposition of NO_2^- even under slightly acidic conditions (pH 6.0), the most important decomposition product was NO, and NO_2 was very small. Nitrogen dioxide could be further produced by atmospheric oxidation of NO produced by this reaction. Although a significant amount of NO_2 gas production was not reported in the various studies of NO_2^- decomposition by reactions with soil organic matter and Fe compounds, those reactions could be a possible process involved in NO_2 gas production during denitrification in soils of slightly acidic to neutral pH.

Conclusions

The results obtained by this research suggest that NO_2 gas damaging crops in acid soils of plastic film house is able to be produced through chemical self-decomposition of HNO_2 when the soil conditions are favorable for denitrification that produces NO_2^- which is the precursor of HNO_2. In plastic film houses of vegetable farming, soil beds amended with compost and basal chemical fertilizers are covered with plastic sheeting before planting. During the plant growing period, water and nutrients including nitrogen are mostly supplied using inline drip irrigation system. Therefore, in soils beneath the plastic sheeting, conditions favorable for denitrification can be created by overly wet condition due to the reduced water lost to evaporation and limited air exchange between soil and its surrounding atmosphere. Thus, proper selection of N fertilizer and its input rate and maintaining higher levels of available soil oxygen by avoiding excessive irrigation are expected to effectively reduce denitrification and the NO_2 toxicity problems in acid soils of plastic film house. But, most of all, acidic pH needs to be ameliorated to reduce the possibility of NO_2 gas emission from soils.

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