Short communication

Effects of rare-earth fertilizers on the emission of nitrous oxide from agricultural soils in China

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Abstract

Rare-earth fertilizers have long been used in agriculture in China. The consequences of these applications are of more recent concern. In our study, an experiment was carried out to identify the effects of applying rare-earth fertilizers on emission of nitrous oxide from paddy and dryland soils in northern China. Normal dosage of rare-earth fertilizers only, normal dosage of urea only, normal dosage of urea plus rare-earth fertilizers, and a normal urea application plus a 10-fold increase in the dosage of rare-earth fertilizers were applied to the soils in pots, prepared for our experiment. A static closed-chamber technique was used to measure nitrous oxide emission flux from the soil in the pots before and after fertilization during the experiment. The results show that the application of only rare-earth fertilizers did not have any visible effect on the emission of nitrous oxide from both paddy and dryland soils. Applying a normal dosage rare-earth fertilizers plus urea led to greater emission of nitrous oxide from the soils than only applying the normal dosage of urea. When a 10-fold increase of rare-earth fertilizers dosage was added to a normal dosage of urea, the emission of nitrous oxide from the soils increased even further. We speculate that the application of rare-earth fertilizers leads to an increase of available NH$_4^+$-N from urea hydrolysis and activate bacteria and enzymes in nitrification and de-nitrification.

Keywords: Rare-earth fertilizer; Nitrous oxide emission; Agricultural soils

1. Introduction

Nitrous oxide (N$_2$O) is a greenhouse gas (Wang and Sze, 1980) and involved in the destruction of stratospheric ozone (Crutzen, 1970). Long-term global measurements of atmospheric N$_2$O show an annual growth rate of 0.3%. During the 1990s, the concentration of N$_2$O was about 311 ppbv in the atmosphere (Bouwman, 1990; Battle et al., 1996). Agricultural soils are significant sources of N$_2$O (Iserman, 1994; Harrison et al., 1995). The emission of N$_2$O from the application of nitrogen fertilizer to agricultural soils is currently estimated to be 2–3 Tg yr$^{-1}$ N$_2$O-N (1 Tg = 10$^{12}$ g), which accounts for about 21–46% of total emission from global anthropogenic sources (FAO and IAEA, 1992). Therefore, the emission of N$_2$O from agricultural soils has generated considerable attention.

Rare-earth elements (REEs) are members of Group IIIA in the periodic table and all have similar physical and chemical properties. Fertilizers containing REEs (REE fertilizers) have been applied as microelement fertilizers in agriculture since the 1980s. Subsequently, physiological effects of REE fertilizers have been reported in such...
instances as the improvement of membrane stabilization and hormone effectiveness, growth response to coleoptile segments, better nitrogen fixation efficiency and reduction in water loss by plants (Guo, 1998; Brown et al., 1990). Currently, compound fertilizers such as urea, organic compounds and carbon ammonium mixed with REEs are widely used by Chinese farmers (Guo, 1998; Huo and Xiao, 1998). It is estimated that application of REE fertilizers in China covered approximately \(3.7 \times 10^6\) hm\(^2\) in 1993 and \(1.6-2.0 \times 10^7\) hm\(^2\) in 1995 (Peng and Wang, 1995). Other studies also pointed out that exterior rare earth has an effect on the activities of microbes and enzymes and therefore affected nitrogen transformation in soils (Chu et al., 2000a, 2001; Xu and Wang, 2001; Ozaki et al., 2006). \(\text{N}_2\text{O}\) is primarily emitted into the atmosphere as a result of microbiological activities through the nitrogen cycle in soils (Bouwman, 1990). Consequently, the application of REE fertilizers to agricultural soils might also affect the process of \(\text{N}_2\text{O}\) generation and further increases the uncertainty of emission estimates of \(\text{N}_2\text{O}\) from agricultural soils. In this study we carried out an experiment to test the effect of applying rare-earth fertilizers on \(\text{N}_2\text{O}\) emission from agricultural soils in northern China.

2. Materials and methods

2.1. Soil and REE fertilizers

Two types of agricultural soil from the north of Beijing (39°60’N, 116°30’E) were used in this experiment. On one of these soils rice had been cultivated for more than 20 years (hereafter called paddy soil) and on the other wheat had been grown for about 15 years (hereafter called dryland soil). Both soils are typically luvisolic cinnamon soils found in the temperate monsoon climate of the region. Soil from the first 20 cm of the surface layer was collected. The basic characteristics of soils were analyzed according to the methods described by Kim (1995) and are presented in Table 1. The REE fertilizers used in this study was supplied by the Research Center for Agriculture Application of Rare Earth Elements in China. The concentration of REE fertilizers is 212.4 mg L\(^{-1}\), identified as a rare-earth oxide. Individual rare-earth oxide components, as percentages, are listed in Table 2.

2.2. Experiment

Both types of soils that we had collected were thoroughly mixed and then 20 kg (fresh weight) soil was placed in pots for treatment. Five treatments were prepared for both paddy and dryland soils. All treatment soils were stabilized for 2 weeks before REE fertilizers and urea were applied. According to the information from the Research Center for Agriculture Application of Rare Earth Elements in China, the recommended dosage of REE fertilizers for agricultural soil ranged between 0.7 and 3.6 kg h m\(^{-2}\). In our study the normal dosage of 1.35 kg REE fertilizers per hm\(^2\), corresponding to 0.6 mg REE fertilizers per kg experimental soil (0.6 mgRE kg\(^{-1}\)), was used. We also applied a 10-fold dosage of REE fertilizers (6.0 mgRE kg\(^{-1}\)) to investigate the consequences of excessive application of REE fertilizers. The application dosage of urea was 0.15 g per kg of soil (0.15 gurea kg\(^{-1}\)) following the recommendation of the fertilization manual (Pang, 1994), which corresponds to 3.0 g urea per treatment.

A pre-treatment test was conducted to investigate the intrinsic difference in experimental pots of \(\text{N}_2\text{O}\) emission from the paddy soil and dryland soil. Each treatment applied 3 g urea, and five replicates were set for each of the soils.

<table>
<thead>
<tr>
<th>Component</th>
<th>La(_2)O(_3)</th>
<th>CeO(_2)</th>
<th>Pr(<em>6)O(</em>{11})</th>
<th>Nd(_2)O(_3)</th>
<th>Sm(_2)O(_3)</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage</td>
<td>28.0</td>
<td>50.8</td>
<td>5.2</td>
<td>15.8</td>
<td>0.1</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

Table 1

<table>
<thead>
<tr>
<th>Soil</th>
<th>Total N (g kg(^{-1}))</th>
<th>Total P (g kg(^{-1}))</th>
<th>Organic matter (g kg(^{-1}))</th>
<th>pH(_{\text{H}_2\text{O}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paddy soil</td>
<td>11.1</td>
<td>5.6</td>
<td>21.3</td>
<td>7.40</td>
</tr>
<tr>
<td>Dryland soil</td>
<td>9.8</td>
<td>8.6</td>
<td>14.5</td>
<td>7.25</td>
</tr>
</tbody>
</table>
The detailed treatments in the experiment are listed in Table 3. The treatments included the normal dosage of only rare-earth fertilizer, a normal dosage of only urea, a normal dosage of urea plus rare-earth fertilizer, urea plus the 10-fold dosage of rare-earth fertilizer and a control without any fertilizer application.

Two successive fertilizations were carried out on 13 May 2003 (the first fertilization) and 27 May 2003 (the second fertilization) for the paddy soil and on 9 June 2002 (the first fertilization) and 18 June 2003 (the second fertilization) for the dryland soil. It is to be noted that the 0.6 mgRE kg\(^{-1}\) dosage was applied in the first fertilization and the 6.0 mgRE kg\(^{-1}\) dosage in the second fertilization only for the REE fertilizers treatment applications. Both the REE fertilizers and urea were dissolved in distilled water and then applied to the soils, bringing the soil moisture content to about 35% (W/W).

### 2.3. Sample collection and measurement

A static closed-chamber technique was used to investigate N\(_2\)O flux. The closed-chambers, with radius of 13.5 cm and height of 60 cm, made of polyvinyl chloride, were placed on each pot used in the experiment and sealed with water. The concentrations of N\(_2\)O in the closed-chamber were linearly correlated (\(r = 0.998\)) with time over an 80 min period. Four samples, at intervals 15 min each, were collected by using a 50 mL glass syringe from enclosed interspaces. The pressure changes (the four samples accounted for only 0.5% of the total volume of each chamber) caused by sampling were negligible. Temperature and atmospheric pressure were recorded simultaneously.

A gas chromatograph (Hewlett Packard 5890), fitted with a 4 mm \(\times\) 3 m stainless steel column packed with Porapack Q (80–100 mesh) and an electron capture detector (ECD), was used for measurement of N\(_2\)O concentrations. High-purity N\(_2\) (99.999%) was used as carrier gas and the flow rate was maintained at \(~20.0\) mL min\(^{-1}\). The column and the detector temperatures were set at 60 and 330 °C, respectively. The volume of injection was 1 mL. The standard N\(_2\)O gas was supplied by the National Research Center for CRM's.

### 2.4. Calculations and statistics

Fluxes of N\(_2\)O were calculated from the linear increase of gas concentrations in the chamber as a function of time (Nykänen et al., 1995). Statistical analyses were performed using SPSS 12.0 for Windows. The non-parametric Kendall's \(W\) and Wilcox tests were used to establish the intrinsic difference from the experimental treatments for the two soils and the effect of application of REE fertilizers on N\(_2\)O emission fluxes. Least significant difference (LSD) tests were used for the comparison of daily N\(_2\)O fluxes among treatments during the two successive fertilizations.

### 3. Results

The results of pre-treatment tests are presented in Fig. 1. There were no statistically significant differences in the five replicates for both paddy soil and dryland soil (Kendall's \(W\) test: \(p_{\text{paddy soil}} = 0.866\); \(p_{\text{dryland soil}} = 0.425\)). Therefore the intrinsic difference in N\(_2\)O flux emissions from different experimental pots could be neglected.

Fig. 2 shows the emission fluxes of N\(_2\)O in the treatments (see Table 3). The fluxes of N\(_2\)O in the treatment of only REE fertilizers application always remained at a low level during the two successive fertilizations. No significant differences were found between the treatment of the REE fertilizers application only and the control for the two soils, even when applying the 10-fold REE fertilizers.
(Wilcoxon test: $p_{\text{paddy soil}} = 0.29_{\text{(control, 0.6 mgRE kg}^{-1})}$ and $0.11_{\text{(control, 6.0 mgRE kg}^{-1})}$ and $P_{\text{dryland soil}} = 0.33_{\text{(control, 0.6 mgRE kg}^{-1})}$ and $0.73_{\text{(control, 6.0 mgRE kg}^{-1})}$).

The peaks of $\text{N}_2\text{O}$ fluxes (Fig. 3) were the results of fertilizing urea and the urea plus REE fertilizers for paddy soil (A) and dryland soil (B). The peaks of $\text{N}_2\text{O}$ fluxes in the treatment of urea fertilization showed that the application of nitrogenous fertilizer clearly increased $\text{N}_2\text{O}$ emission from agricultural soils. This is entirely consistent with results from previously reported field studies (Iserman, 1994; Harrison et al., 1995). However, the peaks of $\text{N}_2\text{O}$ fluxes in the treatments of applying urea plus REE fertilizers were much higher than those from the urea only application, especially for the 10-fold REE fertilizers treatment.

From Fig. 3 it can be seen that total emission of $\text{N}_2\text{O}$ in the treatments of applying urea plus REE fertilizers were always higher than those of applying only urea and increased with the rise of REE fertilizers dosage in both paddy and dryland soils. The percentage increases were 21% and 19% for low dosage REE fertilizers treatment ($0.6 \text{mgRE kg}^{-1} + 0.15 \text{gurea kg}^{-1}$) and 104% and 60% for the 10-fold REE fertilizers treatment ($6.0 \text{mgRE kg}^{-1} + 0.15 \text{gurea kg}^{-1}$) for paddy soil and dryland soil, respectively. LSD tests were used for comparison of daily $\text{N}_2\text{O}$ fluxes among treatments during the two successive fertilizations. Significant differences were found among all treatments at
p<0.05 except for the difference at between the treatment of the REE fertilizers only application and the control for both paddy and dryland soils (Fig. 3).

4. Discussion

The results from this study indicated that the effect of applying the REE only fertilizer was not obtrusive in N₂O emissions from the two soils. However, the fluxes of N₂O in the treatments of the urea plus REE fertilizers application were much higher than those in the urea only application and significantly increased with an increase in the REE fertilizers dosage. N₂O emissions from soils are the major consequences of biological nitrification and de-nitrification (Groffman, 1991; Conrad, 1996). NH₄⁺-N is the essential substance of nitrification and de-nitrification. Xu et al. (2001) reported that rare earth significantly affected the hydrolysis of urea and its hydrolyzed production in soil. The concentration of urea-derived exchangeable NH₄⁺-N in the soil significantly increased and appeared to be dose dependent when the dosage of applied REE fertilizers was more than 10 mg kg⁻¹ dw (dry weight). Bremner et al. (1981) observed that N₂O fluxes from well-aerated soils were clearly correlated with NH₄⁺ concentrations but not with NO₃⁻ concentrations. In our study the NH₄⁺-N available for nitrification from urea hydrolysis may have been increased due to the application of urea plus REE fertilizers.

On the other hand, Chu et al. (2000a, 2001) reported that the exterior REE lanthanum stimulated the microbial biomass nitrogen and respiration at low concentrations in red soil. As well, the processes of nitrification and de-nitrification are controlled by specific enzymes in soils. Studies showed that exogenous rare earth stimulates enzyme activity in soils (Liu and Wang, 2001; Xu et al., 2001; Chu et al., 2000b). REEs may serve as coenzymes for catalysis in soils (Ozaki et al., 2006). Hence, we may conclude from our study that bacteria and enzymes for nitrification and de-nitrification processes may be stimulated with the application of urea plus REE fertilizers. In addition, Zhu et al. (2002) evaluated the effect of lanthanum on nitrification in three Chinese soils by an incubation experiment and showed that the stimulation rate of soil nitrification reached about 20% in a red soil and 14% in a fluvo-aquatic soil at low concentrations of lanthanum. This is consistent with the percentage increase of total emissions of N₂O from the urea plus low dosage REE fertilizers application in our study.

It is estimated that the area of REE fertilizers application accounts for about 5% of the total agricultural land in China (Liu, 2007). In fact, compound fertilizers such as urea, and carbon ammonium compounds, mixed with rare earth are,
at present, the main part of rare-earth application in agriculture. In recent years, agricultural use of REE fertilizers has become widely extended in countries such as Korea, Japan and Australia. Therefore, it is important to take this wide application of REE fertilizers on greenhouse effects into account.

5. Conclusions

From our experiment we may conclude that the application of REE fertilizers can increase the emission of N2O from the soils fertilized by urea in northern China. This result indicates that the environmental consequences of the addition of rare earth to fertilizers should be of far reaching concern given the wide use of rare-earth fertilizers in agricultural activities in China. Our results also imply that the use of rare-earth fertilizers could lead to an increase of NH4+-N available from urea hydrolysis and activate bacteria and enzymes in nitrification and de-nitrification.

Acknowledgment

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