N₂O EMISSIONS FROM SHIMAJIRI-MAJI (CALCARIC DARK RED SOIL) AFTER APPLYING TWO CHEMICAL FERTILIZERS

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Abstract. Nitrous oxide (N₂O) emissions from Shimajiri-maji (calcaric dark red soil) from Okinawa, Japan, were measured in the laboratory by a closed-chamber incubation method after applying two different chemical fertilizers (normal fertilizer, NF; controlled-release fertilizer, CF). The total nitrogen content was 45% in both NF and CF. At higher temperatures (30°C) CF had better potential to reduce N₂O emissions than at lower temperatures (20°C), with total N₂O emissions, from highest to lowest, following the pattern of NF at 30°C > CF at 30°C > CF at 20°C > NF at 20°C. Under alternately saturated and drained conditions, the highest peaks of N₂O fluxes tended to occur soon after drainage with both CF and NF, and nitrification was the primary source of N₂O emissions. Conversely, only slight N₂O emissions were detected during prolonged saturated conditions, and it was assumed that denitrification was the secondary source of N₂O. This suggests that replacing types of nitrogen fertilizers (replacing NF with CF) does not necessarily result in a direct reduction in N₂O emissions as some earlier studies have reported. It is therefore important to continuously monitor temperature and soil moisture content during fertilization and modify the fertilizer accordingly to achieve effective reduction of N₂O emissions and minimize environmental impacts.
Keywords: *nitrous oxide, global warming, nitrification, denitrification.*

Introduction

Nitrous oxide (N₂O) is an aggressive greenhouse gas that is associated with global warming and also contributes to the destruction of the stratospheric ozone layer (IPCC, 2006; Forster et al., 2007). Globally, agricultural soils constitute the major source of anthropogenic N₂O emissions (Bouwman, 1996; Akiyama, et al., 2000; Smith et al., 2002; Forster et al., 2007). N₂O is produced in soils through the microbial processes of nitrification and denitrification (Davidson, 1992; Murray et al., 2005). Nitrification is the aerobic microbial oxidation of ammonium (NH_4^+) to nitrate (NO_3^+); and denitrification is the anaerobic microbial reduction of nitrate (NO_3^+) to N₂O (EPA, 2013). N₂O is an intermediate gas that results from the denitrification process and leaks from microbial cells into the soil and then into the atmosphere (Akiyama et al., 2000).

The global warming potential of N₂O is about 300 times that of carbon dioxide (CO₂) (Reilly et al., 2003), and N₂O contributes 6.24% of the overall effect of greenhouse gases on radiative forcing (Butterbach-Bahl et al., 2013). Several studies have

confirmed that N_2O production in soils increases with nitrogen fertilizer application by stimulating microbes in the soil to convert nitrogen to N_2O (Pathak and Nedwell, 2001; Sanders, 2012). So far it is known that the amount of N_2O emission depends on the amount of fertilizer used, which suggests that more restrained use of fertilizers needs to be considered in order to reduce N_2O emissions (Crutzen et al., 2008).

During the 1990's, global nitrogen fertilizer application rose by 6%−7%, and application was expected to gradually increase due to the permanently increasing demand for food (Hou et al., 2000). However, restraining the use of fertilizers is not only associated with reducing N_2O emissions but is being considered to address many other aspects of agricultural sustainability. Akiyama (2006) argues that N_2O emissions from agricultural soils are influenced by climate, soil type, and the type of fertilizer.

Modern fertilizer management techniques aim to manage the duration and extent of nitrogen accumulation in soils and thereby influence the magnitude of N_2O emissions from fertilizer sources (Clayton et al., 1997; Forster et al., 2007). Improvements in nitrogen (N) fertilizer efficiency are oriented towards the use of slow-release products to minimize N_2O emissions and consequently reduce global warming effects (Hou et al., 2000; Akiyama et al., 2010). Controlled-release fertilizer (CF), also known as slow-release fertilizer, is a granulated coated fertilizer that releases nutrients gradually into the soil in order to optimize nutrient uptake efficiency (Minami et al., 1994; Mayer, 2010; Zebarth et al., 2012).

Cumulative temperature has been identified as a factor influencing the release of N from CF in soils; therefore, temperature would determine the effectiveness of using CF to reduce N_2O emissions (Engelsjord et al., 1997; Akiyama, 2006). On the other hand, Zebarth et al. (2012) suggest the use of CF both to reduce N_2O emissions, as its main propose, and to reduce nitrate (NO_3^-) leaching into groundwater. According to Akiyama (2006), CF can reduce nitrogen losses by delaying the initial supply of nitrogen and providing it steadily to the crop; and use of CF is recommended in environmentally vulnerable areas or fields with high susceptibility to nitrogen losses (Zekri and Koo, 1991). Gillman et al. (2008) emphasizes the environmental risks when soil nitrate (NO_3^-) concentrations are increased. Likewise, closely monitoring nitrogen inputs in soils so that they do not exceed crop nitrogen requirements will be also important in reducing nitrogen leaching losses (IPNI, 2013).

In Japan, the reduction of N_2O emissions and nitrogen leaching during the growing season has become a major concern for sustainable agriculture (NGGI, 2014). Split applications of nitrogen fertilizer and use of CFs are under discussion since they reduce leaching of nitrogen, at least temporarily, and therefore reduce the availability of N leading to N_2O emissions during the processes of nitrification and denitrification (Akiyama et al., 2006; NGGI, 2014).

The aim of our study was to measure N_2O emissions from Shimajiri-maji (calcaric dark red soil) from Okinawa, Japan, following application of two different types of chemical fertilizers—controlled-release fertilizer (CF) and normal fertilizer (NF)—in a laboratory experiment. Our specific objectives were (i) to study the influence of temperature using the same fertilization conditions, and (ii) to evaluate the influence of different fertilizers under the same temperature conditions. This information on N_2O emissions from Shimajiri-maji soil will be useful because Okinawa's climate and soils differ from those in other parts of Japan, and data on N_2O emissions induced by nitrogen fertilizers under specific temperature conditions are not currently available for

Okinawan soils. Finally, our results are intended to contribute to informed decision-making by farmers who use chemical fertilizers.

Materials and Methods

A laboratory experiment was performed at the Faculty of Agriculture of the University of Ryukyus (26°14′N, 127°45′E) in 2013. We used Shimajiri-maji soil (pH 8; C/N ratio, 8.4; particle density, 2.8 g cm^{-3}; clay content, 73%) gathered from a non-irrigated field at the university. Four PVC cylinders (50 cm high, 14-cm inner diameter) were filled with Shimajiri-maji soil (3 kg tightly packed) previously passed through a 7-mm sieve, making sure that no aggregates were retained on the sieve. To control the temperature inside the cylinders of soil, the cylinders were placed in a water bath fitted with a thermostatically controlled heater and cooler (*Fig. 1*). Temperature and fertilizer conditions used are shown in Table 1. Nitrogen fertilization consisted of (a) normal fertilizer (NF), which was ammonium sulphate (NH$_4$)$_2$SO$_4$, and (b) controlled-release fertiliser (CF), which was LP-SS100 (JCAM AGRI.co., LTD., Tokyo, Japan) in which release of nitrogen is controlled by the thickness of a sulphur coating (sigmoidal release pattern: rate of release over 100 days, 25°C, 80% release). Two replicates of each cylinder were prepared with the top 20 cm consisting of a band of their respective fertilizer doses mixed beforehand with 200 g of soil (*Table 1*).
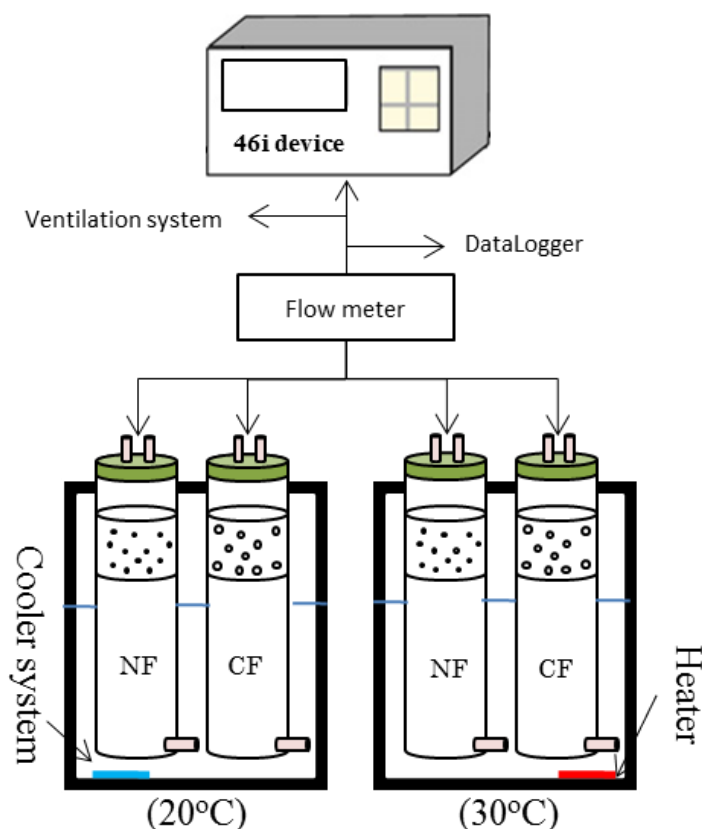

Figure 1. Schematic diagram of the closed chamber system.

Table 1. *Fertilizer and temperature conditions*

Cylinder	Fertilizer	Treatment	Temp.
#	type	g-N cm^{-3}	°C
1	NF[a]	0.75	20
2	CF[b]	0.38	20
3	NF[a]	0.75	30
4	CF[b]	0.38	30

[a] Normal fertilizer (NF) treatment calculated based on 40% of nitrogen content

[b] Controlled-release fertilizer (CF) treatment calculated based on 40% of nitrogen content

Fluxes of N$_2$O were measured by using a closed-chamber method (*Fig. 1*). The lids of the four cylinders described above were closed to isolate the air inside from the atmosphere, and the airflow was controlled by solenoid valves operating at defined time intervals (*Table 1* and *Fig. 1*).

Emissions of N$_2$O were measured by a Thermo Scientific Model 46i Nitrous Oxide Analyzer (Thermo Fisher Scientific, Waltham, MA, USA) that utilizes non-dispersive infrared spectrometry to measure ambient nitrous oxide concentrations (*Fig.2*).
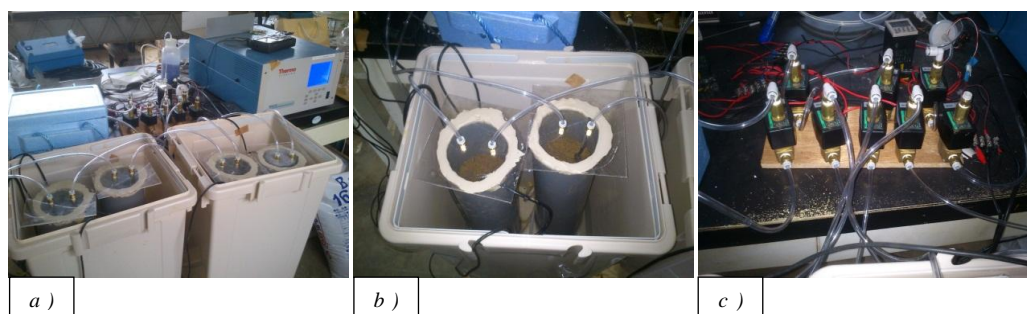
Figure 2. *Closed chamber system installed*

a) Upper right, the Thermo Scientific Analyzer 46i; installed cylinders in the foreground;
b) Installation of soil moisture sensor (EC-5) and temperature sensor (5TE);
c) Solenoid valves attached to inflows and outflows of each cylinder.

Water treatment used in the experiment consisted of allowing water to enter the cylinders from the bottom until the soil was saturated to the upper surface of the cylinder and then allowing the water to drain (this cycle was repeated several times). Sensors to measure soil moisture were installed in cylinders 1 and 3 (EC-5; Decagon, Pullman, WA, USA), and sensors to measure soil moisture and temperature were installed in cylinders 2 and 4 (5TE; Decagon). Every 80 minutes, N$_2$O emissions were measured for 15 min followed by 5 min of ventilation to the atmosphere; this procedure was repeated for each cylinder in sequence. N$_2$O fluxes were calculated from the change in concentration and expressed in mol min^{-1} using the ideal gas law:

$$N_2O = P \cdot (V \cdot C) / (RT) \tag{Eq. 1}$$

where P is the pressure (101325 Pa), V is the total volume (L) of the chamber system; C is the change in greenhouse gas concentration over time (slope in ppm min^{-1}), R is the gas constant (Pa L mol^{-1} K^{-1}), and T is the soil temperature inside the cylinders.

Results and Discussion

N₂O emissions and soil moisture were measured for two trials with different flooding/draining regimens (*Fig. 3* and *Fig. 4*). Cumulative fluxes of N₂O in the second trial together with soil moisture content are presented in *Figure 5*. Under all of the conditions tested, the N₂O measurements were consistent in that the same emission trends occurred soon after the start of drainage: at the start of drainage high peaks in N₂O flux were observed, and the peaks tended to decrease rapidly (*Fig. 3* and *Fig. 4*). Our results agree with those of a field study on N₂O emissions over humid tropical soils in Costa Rica, which found that N₂O emissions increased only after rainfall had increased the soil moisture content (Weitz et al., 2001).
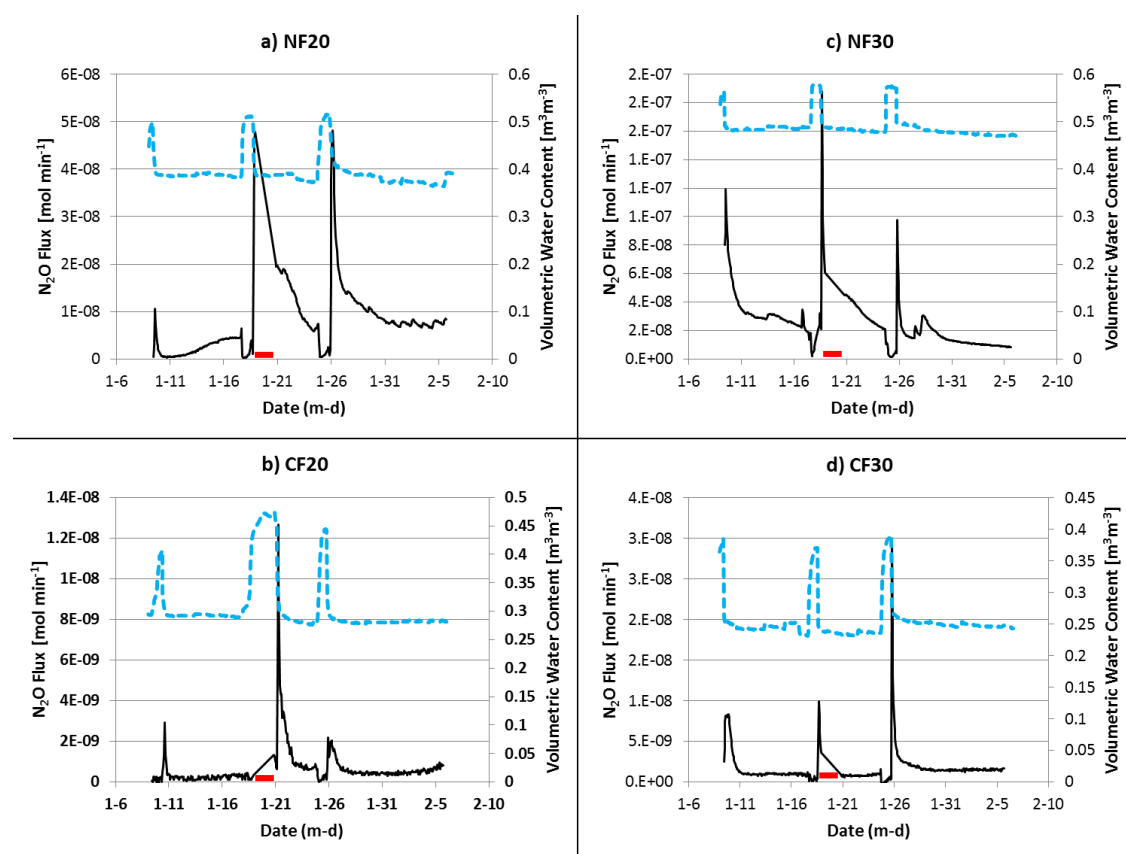

Figure 3. First trial: N₂O fluxes (black lines) for two N fertilizer treatments—normal fertilizer (NF) and controlled-release fertilizer (CF)—under different temperature conditions: a) NF at 20°C; b) CF at 20°C; c) NF at 30°C; d) CF at 30°C. Volumetric water content (blue lines) is included for each observation. Red segments represent missing data.

By looking at N₂O emissions and their correlation with temperature and fertilizer type, we observed that the peak N₂O emissions flux, from highest to lowest, had the following pattern in the first trial: NF30 > NF20 > CF30 > CF20 (*Fig. 3*). On the other

hand, we obtained a different pattern in the second trial: NF30 > CF30 > CF20 > NF20 (*Fig. 4*). Akiyama et al. (2010) argues that the timing of nitrogen release from chemical fertilizers might depend on temperature conditions, moisture, and soil properties. N_2O emissions from NF were higher than those from CF because the release of nitrogen from NF was faster than from CF, and the higher temperature also caused higher emissions in the same fertilizer application. In this sense, it was difficult to establish whether N_2O emissions were larger from NF or from CF when the temperature conditions were clearly different.
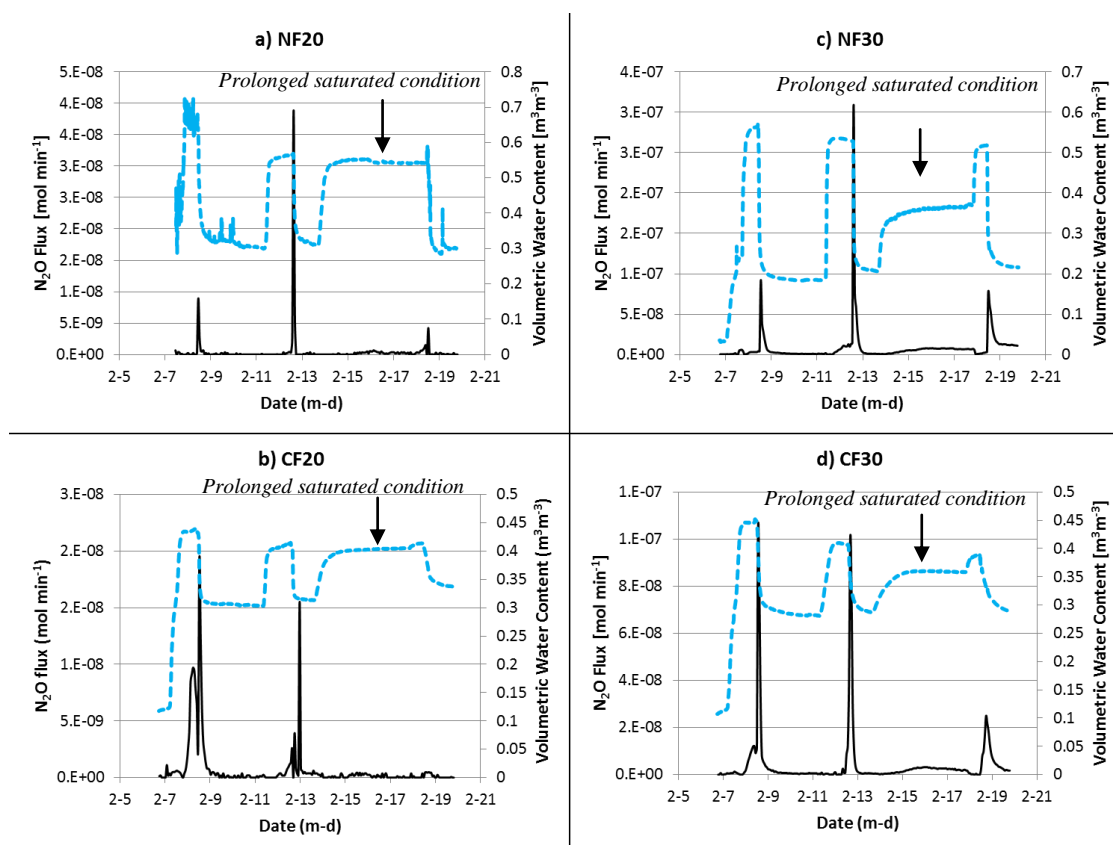

Figure 4. *Second trial: N₂O fluxes (black lines) for two N fertilizer treatments—normal fertilizer (NF) and controlled-release fertilizer (CF)—under different temperature conditions: a) NF at 20°C; b) CF at 20°C; c) NF at 30°C; d) CF at 30°C. Volumetric water content (blue lines) is included for each observation*

Several studies of fertilized systems have shown that the magnitude of N_2O emissions increases with increasing water-filled pore space (WFPS) (Dobbie and Smith, 2001; Akiyama et al., 2000; Abbasi and Adams, 2000). Bateman and Baggs (2005) reported that denitrification occurs when WFPS is between 60% and 70%, which is a range covering the 65% WFPS during the irrigation periods in our experiments. However, in the first trial (*Fig. 3*), we could not confirm N_2O emissions during the irrigation period, even when the soil moisture was at near saturation. Therefore, we assumed that nitrification was the main biological process of N_2O emission under the conditions of the first trial and that the duration of the high soil moisture conditions might have been too short for denitrification. A study about denitrification in suburban

lawn soils reported that denitrification rates were the highest in saturated and fertilized soils in comparison with all of the other conditions tested (Raciti et al., 2011). Therefore, in order to find out the characteristics of N₂O emissions during denitrification, the duration of the near-saturated conditions over the third cycle in the second trial was intentionally prolonged (*Fig. 4*). We observed that the slope of the cumulative N₂O fluxes started to become steeper in second half of the third cycle (*Fig. 5*). We assume that the duration of the saturated conditions was long enough to identify denitrification as the source of N₂O emissions.
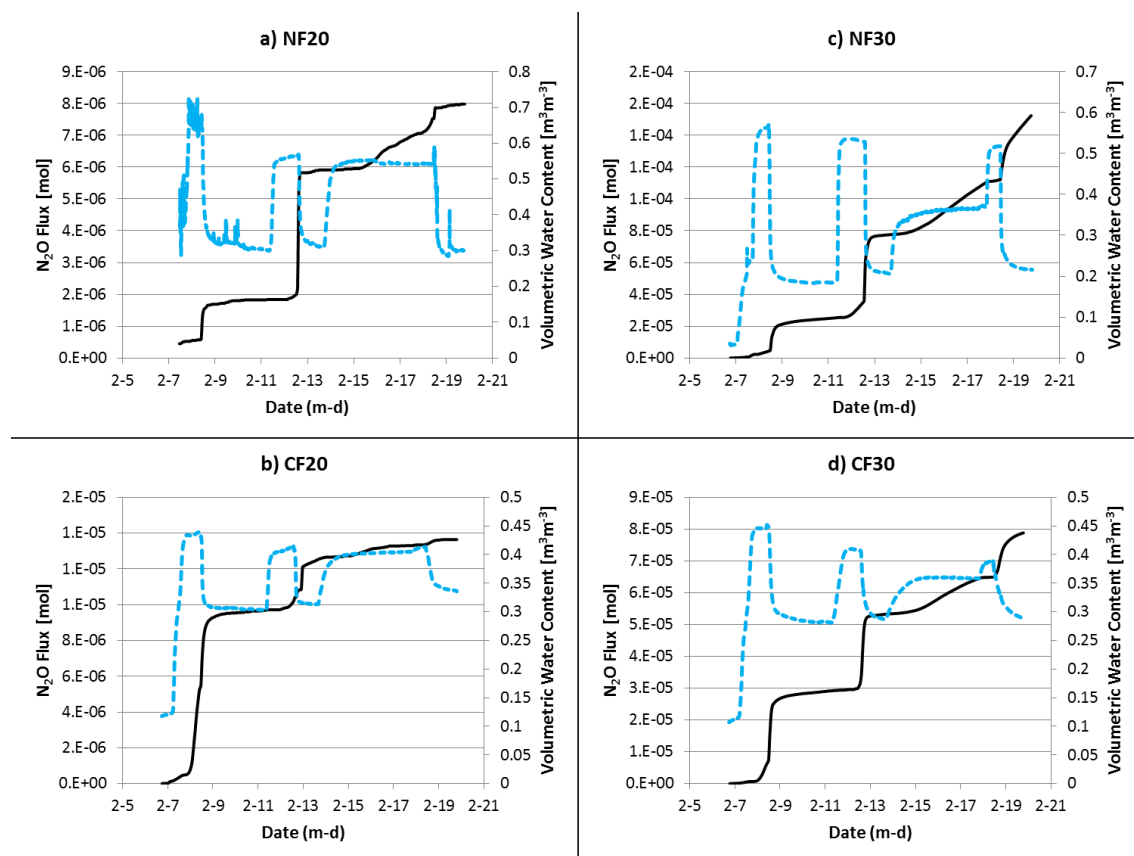

Figure 5. *Cumulative N₂O fluxes (black lines) and volumetric water content (blue lines) in the second trial with different chemical fertilizers (NF and CF) under different temperature conditions: a) NF at 20°C; b) CF at 20°C; c) NF at 30°C; d) CF at 30°C.*

According to Signor (2013), the highest N₂O emissions are clearly emitted during the first and second week after application of nitrogen fertilizer to the soil. Our observations do not include the entire duration of nitrogen release until its completion, because in the first and second trials we emphasized identifying the trend of N₂O emissions (*Fig. 3* and *Fig. 4*). Nevertheless, from the relationship between soil moisture conditions and the cumulative N₂O emissions we could deduce that N₂O emissions tend to become smaller after drainage. We can say that after each drainage condition N₂O emissions showed a certain period of stabilization that tended to gradually increase over time (*Fig. 5*). When comparing emissions in terms of temperature, the cumulative emissions of NF30 at day 13 were 19.1 times that of NF20, while cumulative emissions of CF30 were 5.8 times that of CF20. When comparing emissions in terms of fertilizer type, cumulative

emissions from NF20 were 1.7 times that of CF20, while cumulative emissions from NF30 were 0.52 times that of CF30.

Our results showed that N$_2$O emissions were lower when using CF than when using NF over the same number of days. Previous studies on CF products commonly report benefits in terms of N$_2$O reduction or NO$_3^-$ leaching losses (Wilson, 2009). Total amount of N$_2$O emissions was the largest in NF30. Although N$_2$O emissions were strongly related to fertiliser exposure, the slope of the relationship varied depending on the temperature. This suggests that even under high temperatures CF has a greater potential to reduce N$_2$O emissions that does NF. A study on the effects of slow-release fertilizers in Andosols reported a 20% reduction in N$_2$O emissions by using CF (Minami et al., 1994). In contrast, in our experiment, the total reduction of N$_2$O emissions by using CF as compared to using NF was 48%.

Conclusions

We confirmed that conditions of temperature and fertilization had significant influences on N$_2$O emissions. The trend of N$_2$O emissions was associated primarily with the water treatment applied within the experiment (from saturated conditions to drained conditions). Under conditions of high soil moisture over short periods, we assumed that nitrification was the main source of N$_2$O emissions. In upland fields, the same conditions can be observed soon after rainfall. On the other hand, we considered that denitrification could be observed when the duration of high soil moisture was prolonged over the second trial. By comparing ranges of N$_2$O emitted under NF and CF, we confirmed that emissions from CF were smaller than those from NF under both temperature conditions. Thus, we conclude that N$_2$O emissions may be reduced by using CF for crops such as sugarcane that are widely cultivated on Shimajiri-maji soil in Okinawa. Finally, we recommend using the same experimental setup over cultivated fields under natural environmental conditions to validate the main findings of this research.

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APPENDIX

Electronic Appendix: Original Data