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Greenhouse Gas Emissions from Agricultural Activities

–measuring and modeling of N_2O emissions–

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Preface

This thesis is submitted in partial fulfilment of the requirements for the Doctor of Philosophy (Ph.D.) degree at the United Graduate School of Agricultural Sciences, Kagoshima University, Japan. The PhD program was financed by the World Bank – Robert S. McNamara Fellowship Program.

The PhD study consisted of laboratory experimental work and experimental fieldwork, including modeling experiments, conducted at the Department of Resource and Environmental Science of Agriculture, Forestry and Fisheries, Faculty of Agriculture, University of Ryukyus.

This thesis is based on two manuscripts entitled:

I. Simulation of N_2O emissions from a sugarcane field in Okinawa, Japan.

II. N_2O emissions from shimajiri-maji (calcaric dark red soil) after applying two chemical fertilizers.

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May 2015

Okinawa, Japan

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Summary

The greenhouse gas emissions from agricultural activities constitute a major problem that influences on global warming. Since significant proportion of greenhouse gases are either emitted during cultivation or during agricultural activities, describing characteristics of greenhouse gases is essential. Nitrous oxide (N_2O) is reported as one of the most powerful gases contributing to global warming effects. The characteristics of N_2O gas exposed to different climate conditions are however not clear-cut. This study investigated the emissions of N_2O measured from soil during exposure to different conditions of fertilization, temperature and soil moisture (laboratory experiment). Additionally, for the experimental fieldwork, N_2O emissions from a sugarcane field were measured and two computational models (DNDC and APSIM) were performed for N_2O simulations.

Conditions of temperature and soil moisture, resulting from using two different chemical fertilizers, had significant influences on N_2O emissions. The trend of N_2O emissions was mainly associated with the water treatment applied within the experiment (from saturated condition to drained condition). Under conditions of high soil moisture over short periods, nitrification was the primarily source of N_2O emissions; and during prolonged saturated conditions nitrification was assumed as secondary source of N_2O. Similar conditions can be observed during rainfall events in upland fields. Regarding to the fertilizer use, our results suggest that by replacing types of nitrogen fertilizers does not necessarily result in a direct reduction of N_2O emissions.

When measuring N_2O in a sugarcane field, the fluxes were considerably larger in the daytime than in the night time, assuming they vary synchronously with the air temperature changes. Where nitrification was the main source of N_2O emissions and nitrifier denitrification occurred under high soil moisture conditions after rainfall.

Afterwards, simulations conducted using DNDC and APSIM showed specific points of divergence. The trend of N_2O emissions simulated by DNDC model was closely similar to that of the field data. In contrast, the N_2O emissions simulated by APSIM were smaller than field observation data. By comparing the characteristics of both DNDC and APSIM focusing on nitrification and denitrification, examined separately; the nitrification rate was larger than the denitrification rate in both models. However, in APSIM model, the nitrification rate was highest soon after the fertilization, whereas in DNDC, the nitrification rate occurred after rainfall events. This shows that the nitrification calculated by DNDC involves the effect of soil moisture, whereas that in APSIM model does not. Simulations of N_2O emissions associated with nitrification can be improved by modifying and validating more accurate coefficients within their equations.

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1. Introduction

Agricultural activities involve greenhouse gas emissions causing global warming effects. Greenhouse gas emissions from agriculture mostly come from the management of agricultural soils, livestock, rice production, and biomass burning (EPA, 2000).

1.1. Agricultural activities linked to greenhouse gas emissions

Agricultural activities represent the largest land use and the most widespread set of environmental impacts (Smith et al., 2007; EPA, 2012; Steinfeld et al., 2006). Agriculture consists in cultivating crops, animals and other products used to sustain and enhance human life (EPA, 2012). In the case of crops, the biomass is usually harvested; hence, carbon and nitrogen removed from agricultural systems. To maintain biomass productivity and soil fertility, carbon and nitrogen, have to be inserted back in soils. A common practice for this purpose is the application of organic or chemical fertilizers as well as planting of N-fixing crops. Galloway et al. (2004), reports that within the microbial processes occurred in agricultural soils, carbon and nitrogen components release gases such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O); well known as greenhouse gas (hereafter, referred as GHG) emissions. From an agricultural management perspective, fertilization is considered the major source of nitrous oxide emissions (N_2O) to the atmosphere (Pathak and Nedwell, 2001; Sanders, 2012); contributing to global warming effects. It is generally reported that considerable anthropogenic emissions of N_2O arise from agricultural soils (Bouwman, 1996; Akiyama, et al., 2000; Smith et al., 2002; Foster et al., 2007). Therefore, substantial reductions of greenhouse gas emissions are essential to mitigate global warming.

By looking at thermodynamic theory, a study on entropy and sustainability has explained that agricultural ecosystems exchange both energy and matter under production of entropy, indicating that degradation of complex molecules into simple forms involves GHG emissions (Addiscott, 1995). Therefore activities involved on agricultural systems such as: land use changes, fertilizer application, harvesting and tilling influence the release of GHGs (Richter and Roelcke, 2000). GHG emissions are found naturally in the atmosphere as part of the ecosystem and they allow to keeping balance on air temperature (EPA, 2013). However, since industrial revolution (1760-1850) emissions of GHGs have increased by the intensive use of fossil fuels in industrial and domestic processes; as a consequence of energy consumption. Therefore, high GHG emissions have accumulated in the atmosphere causing unbalance on climate. Trenberth et al. (2007) reports that global mean surface temperature increased for 0.74°C +/- 0.18°C during the past 100 years. Agricultural soils, globally, contribute 10-12% of anthropogenic GHGs, where the net CO_2 exchange is assumed as neutral for croplands (Smith et al. 2007). In the 1990's 20% of anthropogenic CO_2 emissions were originated from land use changes mainly through deforestation (Denman et al., 2007). Nowadays, agricultural activities are reported as contributor raising approximately 1/3 of global GHG emissions (IPCC, 2001); being one of the main drivers of climate change (IPCC, 2007). In contrast, in the case of accumulated CO_2 in the atmosphere there are two different effects expected. The negative effect due to the increased CO_2 concentrations is linked with increase in global temperatures. The positive effect is referred to stimulating the biomass by high CO_2 concentrations which are used as substrate in the process of photosynthesis in plants (Hansen et al., 2006; Prasad et al., 2008).

1.2. Climate change and greenhouse gas effect

Climate change, is a complex interacting system –atmosphere, land surface, snow and ice, oceans and other water bodies, and living things– recognized as the major environmental problem facing the globe (Le Treut et al., 2007; UNEP, 2014). Evidences on climate change have reported rise of global temperatures, warming oceans, shrinking ice sheets, declining artic sea ice, glacial, ocean acidification and extreme events (NASA, 2013). The global climate system involves changes over time which are influenced by its own internal dynamics known as ‘climate forcing’, the major cause of climate change (NOAA, 2015). Climate forcing data consist of natural events such as volcanic eruptions and solar radiations as well as human-induced changes in atmospheric compositions (Le Treut et al., 2007; IPCC, 2007). Solar radiation influences on climate system. So far, there are three pathways to change the radiation balance within the earth: (1) by changing the incoming solar radiation (changes on earth’s orbit or in the sun itself); (2) by changing the fraction of solar radiation that is reflected and known as albedo (changes on cloud cover, atmospheric particles or vegetation); and (3) by altering the longwave radiation from earth surface backwards space (changes on greenhouse gas concentrations).

The figure 1 shows an estimation of the earth's global energy balance. The amount of incoming solar radiation absorbed by the earth and atmosphere is balanced releasing the same amount of outgoing radiation. Nearly half of the incoming solar radiation is absorbed by the earth. Solar radiation is released to the atmosphere by warming the air in contact with the surface (thermals), trough evapotranspiration and outgoing longwave radiation (Fig. 1).

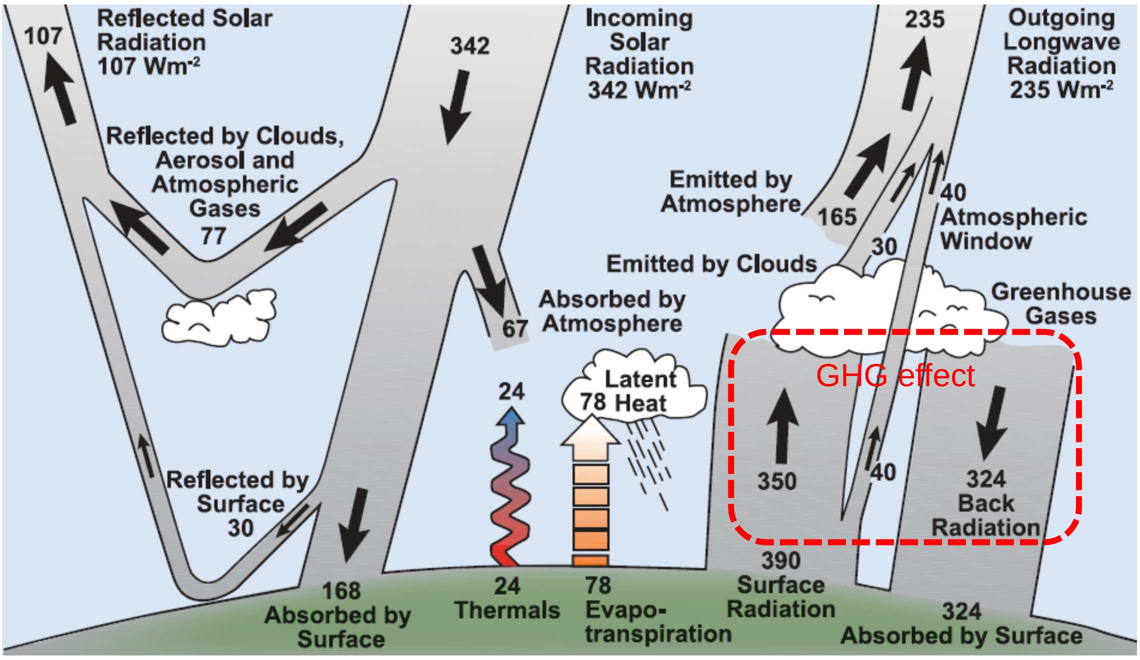


Figure 1: Estimation of the earth's annual and global mean energy balance (Based on Kiehl and Trenberth, 1997).

Studies on thermal environment and surface have reported that the solar irradiance received by the earth is about 1370 $Wm^{-2}s^{-1}$ (Stramaccioni, 2006). The amount of energy averaged over the entire planet is 342 $W.m^{-2}$, equivalent to 1/4 of the total received (Fig. 1). The energy absorbed by the earth's surface is about 168 Wm^{-2} and 67 Wm^{-2} absorbed by the atmosphere. About 30 Wm^{-2} of the sunlight is reflected back to the atmosphere and the 77 Wm^{-2} remaining is reflected through clouds, aerosols and atmospheric gases.

The term GHG is understood as a gas into the atmosphere that absorbs and emits radiation within the thermal infrared range. GHG emissions affect the temperature of the earth; without them, earth's surface would average about 33 °C colder, below the present average of 14 °C (Karl and Trenberth, 2003; Le Treut, 2007). The problem consists in the increased heat trapped in the atmosphere by greenhouse gases like: carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4) which reflect the sun's rays back down to the earth (IPCC, 2006; Murray et al., 2005); originating the well know greenhouse gas effect.

The greenhouse gas effect is originated from molecules that absorb the terrestrial infrared radiation, typically wavelengths from 5 μm to 15.4 μm (Feldman et al., 2014). The figure 2 shows the GHG effect explained in four sequential phases: (1) first, the radiation from sun passes through the atmosphere; (2) the earth absorbs the radiation, warms up, and heat is reflected back; (3) some of this radiation is absorbed by GHG in the atmosphere; (4) the earth keeps warm.

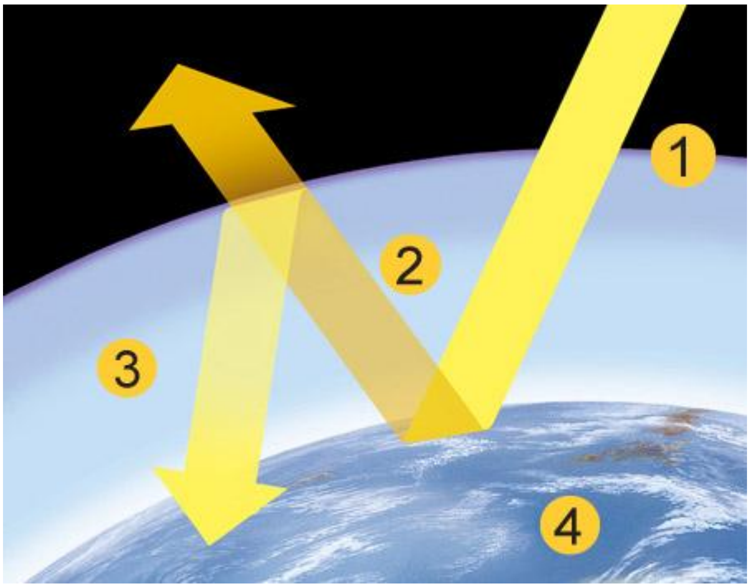


Figure 2: Greenhouse gas effect. Phases of the radiative forcing (Based on EPA, 2012).

According to the IPCC (2013), human influence on the climate system is evident in most regions of the planet. Observations of changes in the climate system are based on regional evidences. Several reports on climate change highlighted that the atmosphere and ocean have warmed, the amount of snow and ice has diminished; therefore, the global mean sea level has risen and the concentrations of greenhouse gases have increased. It is expected that continued emissions of greenhouse gases may cause further warming and changes in all components of the climate system. In this sense, limiting climate change effects will require substantial and sustained reductions of GHG emissions.

1.2.1. Global warming

The global warming is one of the most serious problems facing the world today. Demographic expansion and industrialization are considered major factors causing global warming and consequentially climate change. These factors have influenced the land use patterns. For instance, the use of fossil fuels for energy (coal, oil, etc.) or agricultural practices produces CO_2 emissions that have exacerbated in the atmosphere. According to the Intergovernmental Panel on Climate Change (1997), since the early 20th century, a net increase in atmospheric GHG concentrations has been evidenced being the mean surface temperature raised 0.8°C since 1980. Currently, high atmospheric GHG concentrations are counted as GHG contributors. The figure 3 shows the sequential trend of human activities which conducted to influence the climatic conditions, globally.

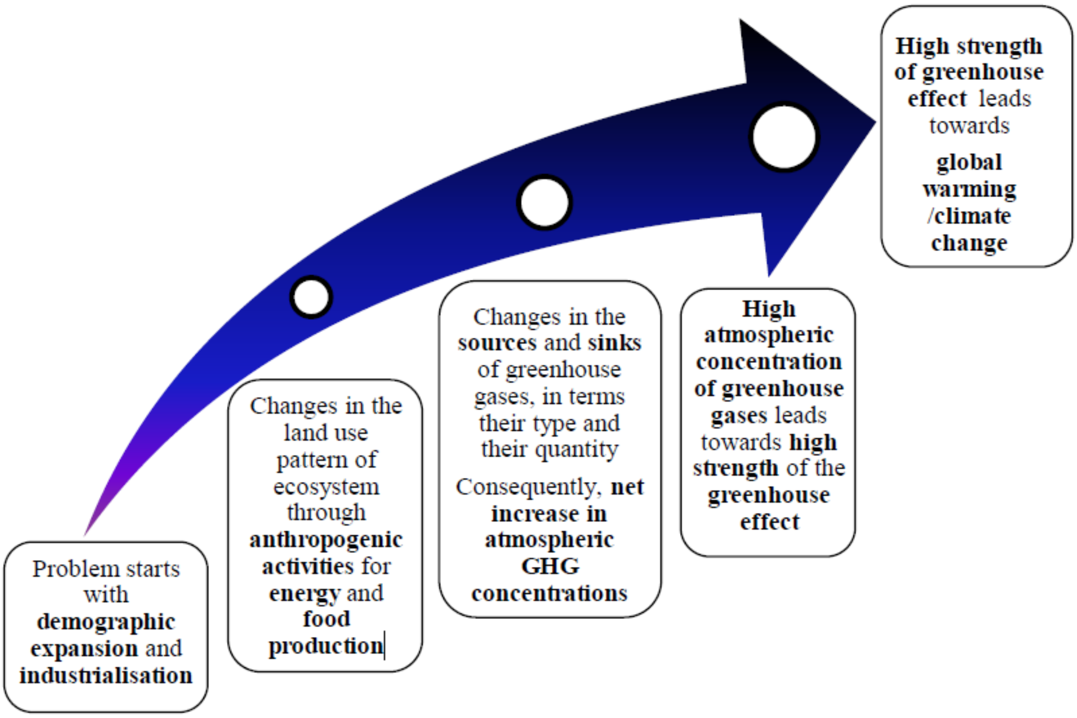


Figure 3: Effect of demographic expansion and industrialization on global warming

1.2.2. Major greenhouse gases

The major three greenhouse gases considered being responsible for global warming are: carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). Anthropogenic sources are sources of these gases. CO_2 emissions mainly come from fossil-fuel combustion, land-use conversion, and cement production. CH_4 emissions come from rice paddies and waste dumps. N_2O emissions come mainly from fertilizer use. The table 1 shows the concentrations of these gases at pre-industrial and contrasting with concentration data for 2013. On the other hand, the Global Warming Potential (GWP) data indicates the warming effect as GHG. The atmospheric lifetime expresses the total effect of a specific greenhouse gas after taking into account global sink availability. While the lifetime indicates how long the gas remains in the atmosphere and increased radiative forcing quantifies the contribution to additional heating over an area.

Table 1: Major greenhouse gases

GHG	**Pre-industrial concentration** [a]	**Concentration in 2013** [b]	**Global Warming Potential (GWP)** [c]	**Atmospheric life time** [d]
	-- ppb --	-- ppb --	-- yr --	-- yr --
Carbon dioxide (CO_2)	280 000	395 400	1	100-300
Methane (CH_4)	772	1 893	28	12
Nitrous oxide (N_2O) [c]	270	326	265	121

[a] Pre-1975 concentrations. IPCC (2001)
[b] IPCC (2013)
[c] CCES (2014)
[d] IPCC (2007)

Regarding to global warming effects occurred as a result of the greenhouse effect, most scientists have agreed that taking actions oriented to reduce the amount of air pollutants is essential. By doing so would reduce air pollution and save energy at the very least. Some recommended actions include: reducing the use of fossil fuels; increasing the use of air pollution control devices; stopping deforestation; planting more trees; reducing water pollution; and slowing human population growth. Following is described the trend of the major GHGs collected from 1979 to 2013 showing their variations over time.

1.2.2.1. Carbon dioxide (CO_2)

Fossil fuel combustion (coal, oil, natural gas) and increased deforestation (destruction of forests for other uses) have reported as main sources of CO_2 in the atmosphere (Trenberth et al., 2007). Carbon dioxide (CO_2) emissions have increased by about 40% up in comparison with pre-industrial concentrations (Fig. 4). The IPCC (2001), reports that CO_2 is a responsible gas for 50-55% percent of the global warming trend. Global data of CO_2 emissions estimated from 1979 to 2014 shown that CO_2 emissions have constantly increased over time (NOAA, 2015).

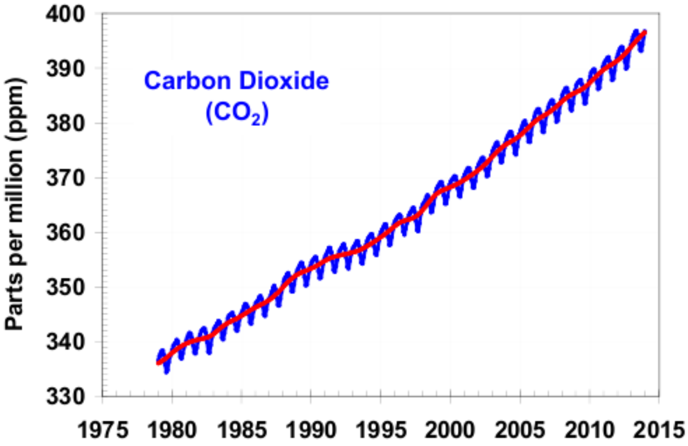


Figure 4: Carbon dioxide emissions (NOAA, 2015).

It is estimated that the increased emissions of CO_2 were 1.4 ppm per year before 1995 and 2 ppm per year thereafter. Plants consume CO_2 for its growth and humans need oxygen for life; therefore fewer plants would mean less CO_2 removed from the air.

1.2.2.2. Methane (CH4)

Methane (CH_4) emissions represent approximately 12% of the global warming trend (IPCC, 2001). CH_4 emissions in the atmosphere arise from both natural and anthropogenic sources. Natural CH_4 sources (wetlands, termite activity, oceans) are considered responsible for about 30 % of total emissions. About 70 % of CH_4 emissions from anthropogenic sources (agricultural livestock, rice cultivation, waste practices, biomass burning and so on). The tendency of CH_4 is shown in Figure 5.

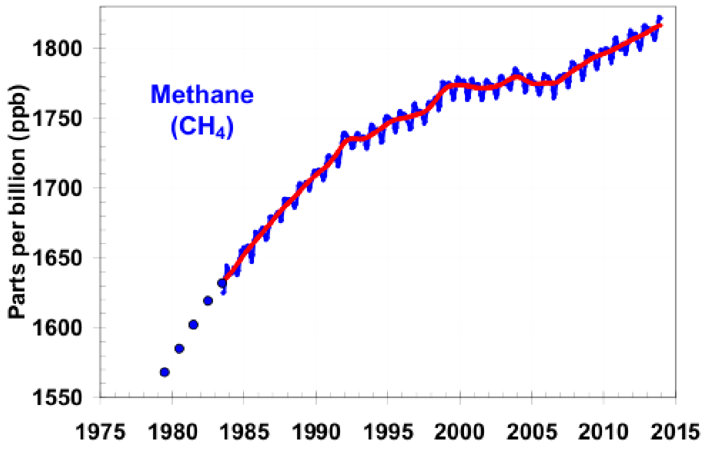


Figure 5: Methane emissions (NOAA, 2015).

Although the trend of CH_4 has increased, during 1983-1999 the growth rate of CH_4 has slightly declined. The economic collapse of the former Soviet Union associated with the reduction of fossil fuel use is attributed as explanation why CH4 emissions were decreased. From 2007, CH_4 emissions have begun to increase again. It is thought that this increasing trend is caused by global changes on temperatures and precipitation events during 2007 and 2008 (Dlugokencky et al., 2009).

1.2.2.3. Nitrous dioxide (N_2O)

Nitrous oxide (N_2O) is responsible for about 6% of global warming (IPCC, 2001). N_2O is produced by microbial processes using nitrogen substrate such as ammonium (NH_4^+) and nitrate (NO_3^-). Nitrogen fertilizer use (organic or chemical), crop residues, and sewage sludge are sources of N_2O emissions; and the most significant source in regard to environmental impacts is the fertilization activity (Bockmann and Olfs, 1998). Since industrialization period, N_2O emissions have constantly increased due to nitrogen fertilizer use as part of agricultural practices. According to Montzka (2011), the emissions of N_2O would increase in 0.26% annually and it is predicted that N_2O emissions might be maximized in tropical regions. The figure 6 shows the increasing concentrations of N_2O.

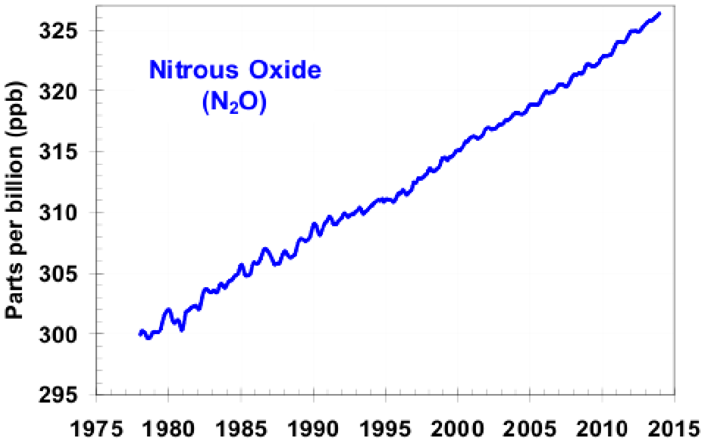


Figure 6: Nitrous oxide emissions (NOAA, 2015).

1.3. Emissions of N_2O from agricultural soils

Agricultural soils usually have large pools of ammonium (NH_4^+) and nitrate (NO_3^-) especially over fertilized fields using manure and synthetic fertilizers; where microbial transformation rates are high predominantly after fertilization (Dandie et al., 2008). The microbial activity in soils increases as temperature increases. By increasing the microbial activity in soils a higher production of N_2O is expected. Agricultural soils are exposed to continuous changes on its temperature and its moisture content (Akiyama et al., 2000; Sylvia et al., 2005). A study on N_2O emissions conducted in a grassland region during freezing and thawing has reported that during freezing there was an accumulation of ammonium (NH_4^+) and nitrate (NO_3^-); and emissions of N_2O were detected after the thawing period (Muller et al., 2002). Soil moisture content is also considered an important factor influencing N2O emissions due to the movement of nutrients and oxygen flow (Pathak, 1999).

1.3.1. Process of N_2O production

Emissions of N_2O in soils result from microbial transformation (nitrification and denitrification) of nitrogenous compounds that act together to produce a cumulative flux of N_2O. While their individual effects vary under specific field conditions, the combined contributions from both nitrification and denitrification are important to understanding the GHG balance of crops. According to Bouwman (1996) and Sylvia et al. (2005) the most significant factors in the processes of N_2O are: organic carbon, ammonium (NH_4^+) and nitrate (NO_3^-) in the soils. Organic carbon and NH_4^+ are the substrates used by the denitrifying and nitrifying bacteria respectively, so without these there is nothing to drive the reaction. Nitrate is a terminal electron acceptor in the denitrification process. Carbon is often an important constraint to biological activity in soil systems and has been shown to limit denitrification (Miller et al., 2008). While the presence of nitrifiers and denitrifiers in the soil is critical to the process of nitrification and denitrification, seldom do their numbers limit these processes in agricultural soils. Nitrifying bacteria are less common in the soil than denitrifying bacteria; however there are usually sufficient levels of nitrifying and denitrifying bacteria in the soil so as not to pose a constraint to the processes (Sylvia et al., 2005).

The figure 7 shows the main processes involved in producing N_2O: nitrification, denitrification and nitrifier denitrification. The overlapping boxes illustrate the processes of nitrification and denitrification. As nitrifier denitrification is a pathway of nitrification (Wrage et al., 2001); the box of nitrification is overlapped to the box of nitrifier denitrification including their own outflows of N2O.

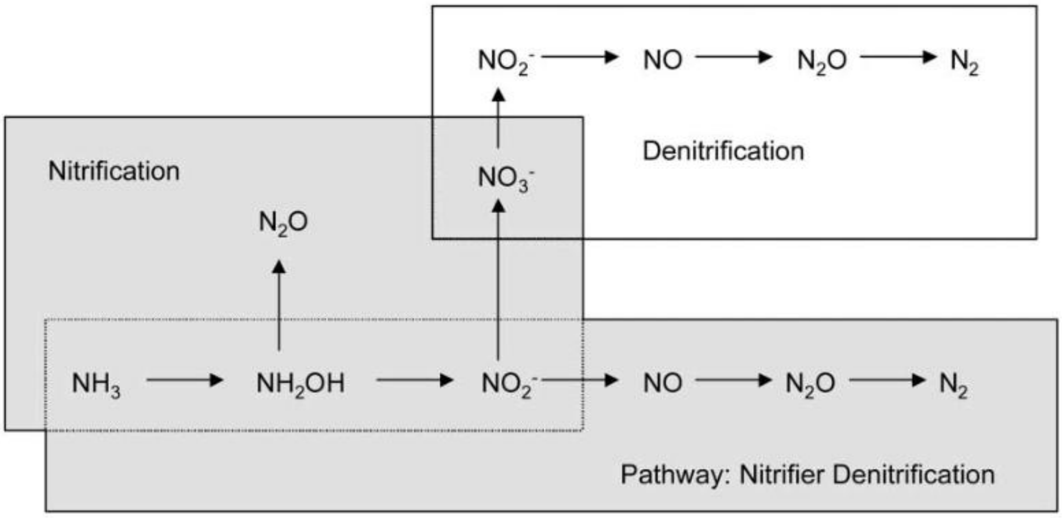


Figure 7: Biochemical transformations of mineral nitrogen in soil

1.3.1.1. Nitrification

Nitrogen fertilization is the major source of N_2O emissions from agricultural soils (Bouwman, 1996). Nitrification is the oxidation of ammonium (NH_4^+) or ammonia (NH_3) to nitrate (NO_3^-) via hydroxylamine (NH_2OH); and next via nitrite (NO_2^-) performed by bacteria and archaea (Yoshida and Alexander, 1970; Bremner, 1997; Wrage et al., 2001; Leininger et al., 2006) as shown in the figure 7. Nitrification occurs in soils when the oxygen content is relatively high (Bremner and Blackmer, 1980; Akiyama et al., 2000); a temperature between 25°C and 35°C (Bargsten, 2010); and approximately 60% of water content (Abduosalam, 2009). Therefore nitrification is predominantly an aerobic process; however when the oxygen content decreases, the N_2O emissions also tend to decrease (Poth and Focht, 1985). According to Wezermal and Gannon (1967), the nitrite

(NO_2^-) is the electron donor within the nitrification processes indicating that microorganisms obtain their carbon from carbon dioxide (CO_2) available in the atmosphere.

1.3.1.2. Denitrification

Denitrification is the biological reduction of nitrate (NO_3^-) to dinitrogen (N_2), as shown in the figure 7; where nitrite (NO_2^-), nitric oxide (NO) and nitrous oxide (N_2O) are intermediates steps within the process (Payne, 1973; Russow et al., 2009). Denitrification is an anaerobic process that means in absence of oxygen, where the microorganisms can switch to this condition and grow normally (Bremner and Shaw, 1958; John, 1977). Denitrification generally requires nitrate (NO_3^-) and organic matter and usually occurs at temperatures ranging between 5°C and 75°C (Russow et al., 2009); and decay at temperatures of 75°C to 85°C (Keeney et al., 1979). However, such high temperatures are not considered as accurate indicators, since most of soil temperatures are below 60°C, at least in cases water is available (Malhi et al., 1990).

1.3.1.3. Nitrifier-denitrification

Nitrifier-denitrification is performed only by nitrifiers, whereas nitrifiers and denitrifiers are involved in nitrification and denitrification, respectively (Wrage et al., 2001). In nitrifier-denitrification, nitrifiers oxidize ammonia (NH_3) to nitrite (NO_2^-) then reduce the nitrite NO_2^- N_2O and dinitrogen (N_2); as shown in the figure 7. Nitrifier-denitrification may be the predominant source of N_2O fluxes when soil moisture conditions are low. (Webster and Hopkins, 1996). Wrage et al. (2005) have shown that nitrifier-denitrification contributed 37% of N_2O emissions after 6 hours of applying ammonium nitrate (NH4NO3) in an arable soil. Russow et al. (2009) have reported that nitrifier-denitrification occurred when soil oxygen contents were between 2% and 5%, concluding that specific studies on nitrifier-denitrification vs N2O fluxes are essential.

1.3.2. Factors controlling N_2O emissions

The factors controlling soil N_2O emissions are complicated due to the many processes involved. Controlling factors of N_2O emission can be listed as follows: substrate supply and availability, soil temperature, soil moisture, interactions between temperature and moisture, and finally other controlling factors related (soil bulk density, soil texture, soil pH, soil nutrients, plants, and atmospheric concentration). The following section discusses the factors above mentioned.

1.3.2.1. Substrate supply and availability

To produce N_2O emissions soil organic matter acts as a carbon source and as a hydrogen donor. Generally, N_2O production is significantly enhanced upon the addition of soil organic carbon (Skiba et al., 1994). Studies on sources of N_2O in soils have reported by adding glucose enhances the denitrification rate in soils under anaerobic condition (Jacobson and Alexander, 1980; Azam et al., 2002). A study over pastoral ecosystems reported that available organic carbon is supplied via plant roots which has influenced in increasing denitrification rates (Bailey, 1976). In contrast, a study on N_2O emissions from a bermudagrass pasture has reported that soil inorganic nitrogen uptake by plants occurred during winter-spring season reducing consequently N_2O emissions (Sauer, 2009). Although contradicting results about the relation between plants and N_2O emissions were reported, there is a classic study conducted by Burford and Bremner (1975) that demonstrates a strong relationship between denitrification and temperature with a strong linear correlation (r=0.99). Therefore, those factors who affect the magnitude and quality of the carbon pools in soils such as plants have the potential to control the carbon substrate supply available for induced N_2O emissions.

1.3.2.2. Soil temperature

The effect of temperature on N_2O emissions is complex due to multiple processes are involved within N_2O emissions from soils (Li et al., 1992). The optimum temperature to producing nitrification is 35°C (Hadas et al., 1986); while the optimal temperature for denitrification is 60°C (Bremner and Shaw, 1958). However, N_2O emissions may not always respond positively to temperature. Gödde and Conrad (1999) have revealed that N_2O emissions from soils might be higher under low temperature conditions (4°C) compared to a higher temperature (15°C); indicating that microorganisms are able to adapt to low temperatures. Likewise, a study on gaseous emissions from denitrification has shown that N_2O emissions were becoming smaller as temperature was increased; confirming that that N_2O emissions generally represent the smaller fraction (<25%) of denitrification process (Avalakki et al., 1995). Another study on denitrification conducted in wet forests by sampling two different seasons has confirmed that microbial populations had greater activity when increasing temperature rather than when exposed to low temperatures; consequently higher N_2O emissions (Struwe and Kjøller, 1991).

1.3.2.3. Soil moisture

Soil moisture has a strong influence on soil N_2O emissions, since it controls the level of aeration (Smith et al., 2003). When soil moisture contents is high, the air permeability declines, reducing soil aeration, and thus the denitrification occurs under conditions of limited oxygen (Grable, 1971; Azam et al., 2002). Generally, N_2O gas is emitted under high soil moisture conditions, since microbial activity in dry soil conditions is low (Weitz et al., 2001). High N_2O emissions are commonly observed when an abrupt change in soil moisture is produced (Müller et al., 1997); making the carbon content of soil is dissolved to feed heterotrophic microbes (Rudaz et at., 1991). However, when soils are fully saturated and anaerobic conditions are given, is expected that N2O emissions can be reduced to dinitrogen (N_2) through denitrification (Letey et al., 1980; Wrage et al., 2001). Therefore several studies report that N_2O emissions from soils may peak at soil water-filled pore space (WFPS) between values of 75% to 90% (Khalil and Baggs, 2005; Klemedtsson et al., 1988). On the other hand, N_2O production by nitrifiers is also affected by soil moisture. Various studies on N_2O emissions have found that the optimal soil water content for nitrification occurs when WFPS is 60% and 70% (Skopp et al., 1990; Bateman and Baggs, 2005). Clayton et al. (1997) found 65% WFPS to be a critical threshold above which N_2O emissions from a fertilized grassland soil increased significantly. The effect of soil moisture linked to N_2O emissions may vary according to soil structure and texture (Weitz et al., 2001). Therefore, an increase in the soil moisture content linked to N_2O emissions can have a more significant impact in fine textured soils where microbial activity occurs normally and not short due to high infiltration.

1.3.2.4. Interaction between soil moisture and temperature

The soil temperature is closely related to soil moisture (Schindlbacher et al., 2004). A study has confirmed that the rewetting of dry soil exposed to a constant temperature of 14°C caused increase of N_2O emissions, concluding that the interaction between soil moisture and soil temperature is a determining factor for N_2O emissions (Ruser et al., 2006). Dobbie and Smith (2001) have shown that the magnitude of N_2O emissions increases with increasing water-filled pore space (WFPS). Emission factor (EF), defined as a representative value that relates the quantity of a pollutant with an activity associated to the release of that pollutant (EPA, 2014); is usually calculated considering the relation between water-filled pore space (WFPS) and soil temperature. Flechard et al.

(2007) have reported that the EF for individual fertilization events had increased with soil temperature and were generally higher for WFPS values in the range 60–90% (Fig. 8); though precipitation onto dry soils also showed nitrogen losses of the nitrogen fertilizer applied.

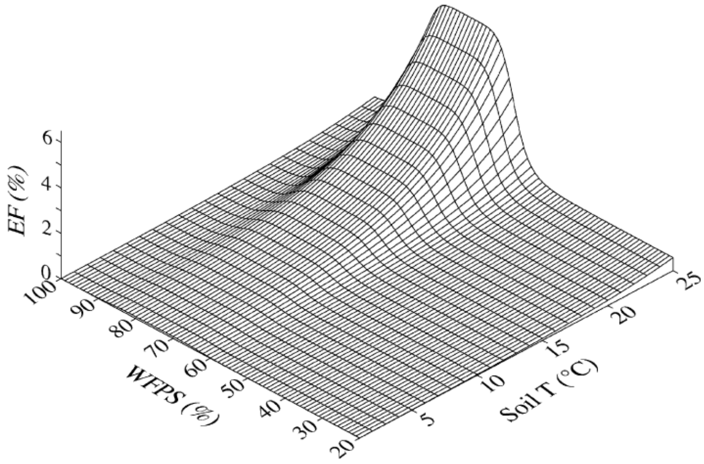


Figure 8: Response of the emission factor (EF) from fertilized soil relating soil temperature and WFPS; assuming a monthly rainfall of 50 mm (Flechard et al., 2007).

The figure 8 shows the fitted response of the EF values of up to 6.5% for 25°C of soil temperature and highest peaks of WFPS between 70% and 80% were detected (Fig. 8). A study conducted with soils of low temperature and varying different levels of soil moisture content has concluded that N_2O emissions were relatively low (Maag and Vinther, 1996). Although N_2O emissions might occur at high temperatures and high soil moisture conditions, in the practice, such conditions are not common in agricultural fields where soil moisture is generally lower than the soil temperature (McKenzie et al., 1999). Likewise, a field experiment performed in a pastoral system in Switzerland has reported that soil water content was the main factor controlling soil N_2O emissions (Rudaz et al., 1999).

1.3.2.5. Other controlling factors

Other controlling factors involved in N_2O emissions are:

- Soil nutrients,
- Soil texture,
- Soil bulk density,
- soil pH,
- plants, and
- atmospheric concentration.

Soil nutrients such as ammonium (NH_4^+) and nitrate (NO_3^-) are closely related to nitrous oxide (N_2O) emissions because these compounds serve as a substrate for nitrifying and denitrifying microorganisms. Skiba et al. (1994) and Ludwig and Meixner (1994) showed that differences of the NO_3^- content in soil that accounted the major part for nitric oxide (NO). Soil texture influences on physical variations of air and water properties, which determine the water infiltration rate and gas emissions. Soil bulk density controls the gas exchange because the compaction of soils influence the oxygen flow, thus when the bulk density value is high usually the emissions of N_2O tend to decrease. Soil pH for nitrification and denitrification; and their respective N_2O emissions generally depend on NO_3^- concentrations and microorganisms involved in soils. The optimum soil pH reported for nitrification varies from 3.0 to 9.5 (Kyveryga et al., 2004; Ste-Marie and Paré, 1999); whereas for denitrification varies between 7.0 and 8.2 (Delwiche and Bryan, 1976). Although the processes are slightly favored under alkaline soil pH levels, they also take place in acidic soils. Clough et al. (2005) showed that N_2O emissions from a urine patch increased with soil pH of 4.7; however, when soil reached its field capacity with a pH of 6.6 the N_2O emissions were decreased. Although several studies indicate that soil pH may influence the rates of N_2O emissions; Simek et al. (2002) have reported that there is not clear relationship between denitrifying enzyme activity and soil pH, indicating that soil denitrifiers might be able to adapt to soils into different pH values. Plants influence the emission of N_2O by affecting nitrate (NO_3^-) and carbon content of the soil as well as partial pressure of oxygen. Plants can directly affect the availability of NO_3^- through uptake and assimilation making it unavailable to denitrifiers. However, mineralization of roots and other plant material to NH_4^+ and nitrification of NH_4^+ to NO_3^- can potentially provide more NO_3^- for denitrification and conversely immobilization can reduce NO_3^-in the soil. Finally, atmospheric concentration of N_2O determines whether the soil acts as a sink or source for N_2O emissions, since both production and consumption of N_2O occur simultaneously in the soil. The fluxes of N_2O are commonly considered bi-directional assuming that production and consumption of is equal, thus this theoretical difference is known as compensation point mixing ratio. Some studies discuss about the compensation of the point mixing ratio in regard to the atmospheric concentration, indicating that soil are generally considered as source from which N_2O emissions come from.

1.4. Measurement of greenhouse effect

The impact of the greenhouse effect is usually estimated by calculating the difference between the actual global surface temperature and the temperature that the planet would be without any atmospheric absorption, considering the same planetary albedo of 33 °C for both calculations (NOAA, 2015). Although this is an assumption it is useful as referential data. Another way of measuring the GHG effect consists in calculating the difference between the radiation that is emitted to the earth's surface and the amount of radiation emitted to the atmosphere. If there would not greenhouse effect the value would be zero. The surface emits about 150 Wm^2 which is a higher value than the reflected to the atmosphere. The complexity in estimating gases consists in determining individually their capability to absorb radiation associated with its dispersed distribution in the atmosphere. The greenhouse gases absorb differentially the infrared radiation (heat radiation). Also different parts of the planet differ wildly in how much infrared radiation is emitted as well as how much of cloud and water vapor are available. This because of some wavelengths of infrared radiation can be absorbed by water vapor and clouds.

1.4.1. Concentration of greenhouse gases

Concentrations of gases in the atmosphere can be expressed in parts per million (ppm) or billion (ppb). For ppm, this can be visualized as 1 cubic centimeter (cm^3) of gas per cubic meter of air. One ppm means that there is one molecule of the gas in question per 1 000 000 molecules of all gases present. Some greenhouse gases are more effective at absorbing radiation than others because they absorb radiation at different wavelengths and some overlap with others. The figure 9 shows various greenhouse gases indicating their capacity of absorption.

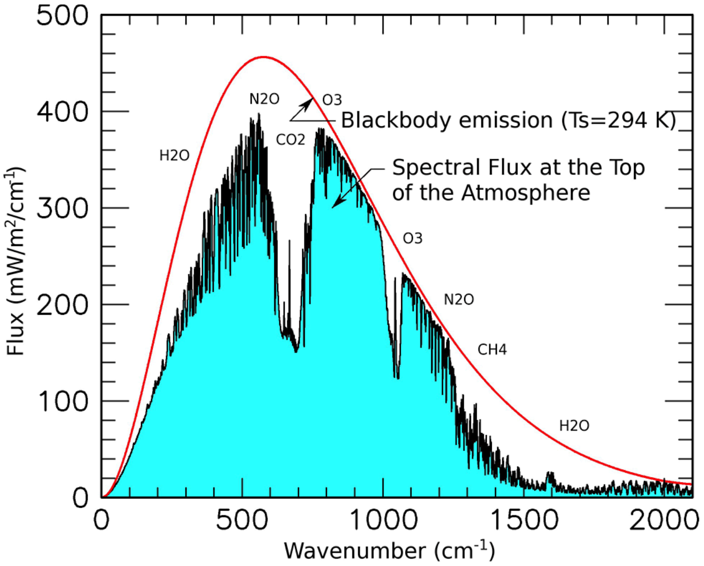


Figure 9: Absorption of greenhouse gases (IPCC, 1996).

To account for the differences in absorption, the concept of global warming potential has been introduced in which all gases are compared with CO_2, which has a global warming potential of 1. For instance, over a period of 100 years the global warming potential of methane is 23 times than CO_2; and N_2O represents 300 times stronger than CO_2 (IPCC, 1996). It is important that the global warming potential is set in relation to a time period since the atmospheric lifetime of greenhouses gases varies greatly. CO_2 can stay in the atmosphere for 50-200 years depending on how it is recycled back to land or the oceans; methane has a lifetime in the atmosphere of 10 to 15 years, while some of the fluorinated greenhouse gases have lifetimes of several thousand years.

1.4.1.1. Gas chromatography

Gas chromatography is a measurement technique for most greenhouse gases such as CO_2, CH_4, SF_6, N_2O, CO and so on. The principle of gas chromatography consists in the separation of a compound into its molecular constituents. A gas chromatograph has two inlets: an inert carrier flow (usually nitrogen) and a sample injector (Fig. 10).

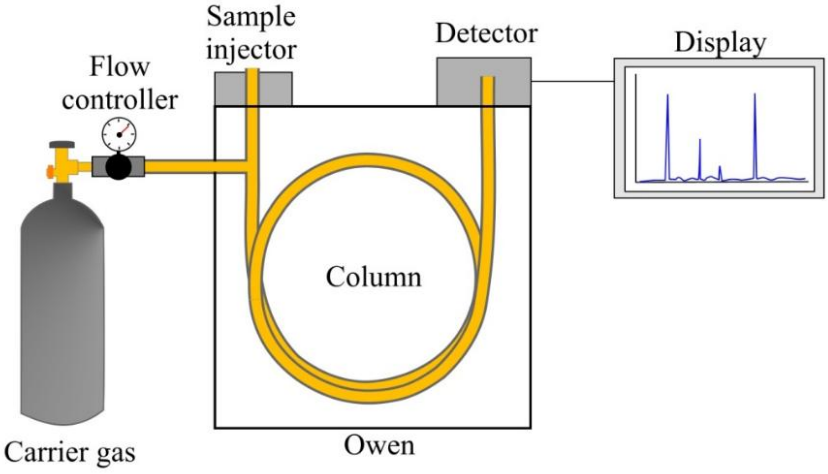


Figure 10: Schematic diagram of a gas chromatograph

To measure greenhouse gases, the sample is injected through a sample loop (typically 0.25–1 ml) into a carrier gas stream of the specific gas intended to measure fitted with an electron capture detector (Wang et al., 2010, Kelliher et al., 2013). The volume of sample injected should be at least two times larger than the size of the sample loop. Analysis takes 2–10 min and in near background conditions (around 310 $\mu l l^{-1}$) an accuracy of 0.2 $\mu l l^{-1}$ can be obtained (Jones et al., 2011). Periodical calibration of the system is required in order to avoid inconsistences of data (Loftfield et al., 1997, Smith et al., 2003). However, the accuracy of measurements using a gas chromatograph varies between laboratories, instruments and operators (Kelliher et al., 2013). Usually, users should perform regular tests and conduct calibration in scheduled periods. Zheng et al. (2008) mentioned the importance in conducting previous tests in order to avoid possible sources of contamination.

1.4.1.2. Infrared technics

Infrared techniques consist in analyzing the ability of most of the greenhouse gases to absorb infrared light at unique wavelengths. The sample gas is either pumped into a measurement cell where the infrared radiation illuminates the sample (closed path system) or the infrared radiation can be used outside air (open path system). To measure N_2O emissions, a closed measurement system is largely utilized. The most common infrared detectors are: (1) Fourier transform infrared spectrometer (FTIR) that use a broadband thermal system to scan though the infrared spectrum to measure simultaneously gases (Galle et al., 1994); (2) Photo-acoustic instrument that combines opto-acoustics with a broadband infrared source (Iqbal et al., 2013); (3) Laser-based systems aim to achieve a unique absorption line of a specific trace gas (Mammarella et al., 2010).

1.4.2. Flux measurement methods

The estimation GHG emissions consist in measuring gas concentrations above atmospheric levels. Based on these data available N_2O flux rates can be derived using different flux methods. Sensors and methodologies are introduced below.

1.4.2.1. Closed chamber method

Closed chamber method consists in amplifying significantly the concentration signal, thus, smaller emissions can be monitored. Gas chromatographs are utilized attached to the chamber system to measure soil respiration rates of gases such as CH_4 or N_2O fluxes (Flechard et al., 2005). The term flux describes both emission and uptake. Generally, chamber system installations are simple and do not require much cost (Fig. 11).

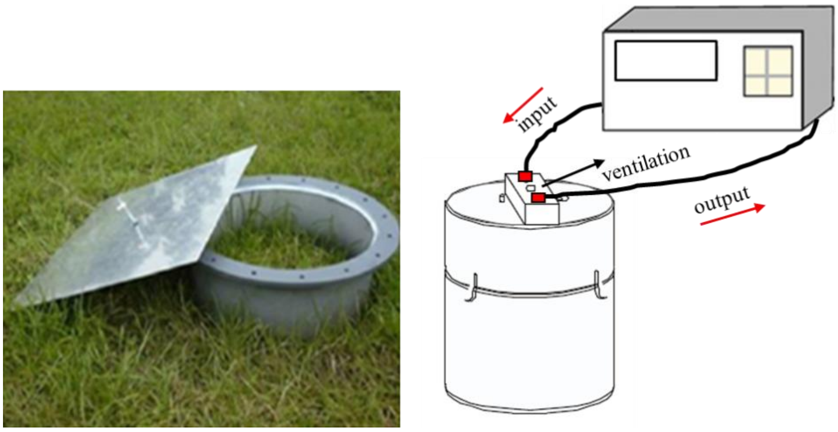


Figure 11: Closed chamber method

When installing a closed chamber method, essential aspects need to be considered: (i) mixing the air inside the chamber using a ventilation system; (ii) installing a vent hole or tube to avoid effects of pressure differences between inflow and outflows; (iii) using lids for chambers used in order to isolate the air inside from the atmosphere; (iv) the temperature and humidity inside the chamber should be closely controlled in order to avoid insulation or water trapping by the whole air flow within the monitored system.

Chamber fluxes (F) are calculated from the increase in concentration (dC) during chamber closure (dt) and the volume of the chamber (V) enclosing surface area (A).

$$F = dC/dt \ V/A \qquad \text{(Eq. 1)}$$

Most chamber studies have assumed a linear increase in concentration over time (Kutzbach et al., 2007). According to Kroon et al. (2008) assuming a linear correlation may underestimate fluxes by 20–40%; therefore, calculating fluxes from 3–5 different chambers might help to reduce some uncertainties (Smith and Conen, 2004; Venterea et al., 2009). When using chamber method a square meter of the surrounding area can be considered without interference from other sources (Dobbie and Smith, 2001). Measurements can be linked to environmental data collection at the same time, for instance, soil temperature, nitrate availability, soil water content, pH and so on. However, one of the disadvantages reported on chambers method consists in the risk of missing main peak measurements after rainfall or fertilization if the experiment is set up after these events. This suggest that chambers need to be prior sealed and installed in order to avoid altering the microclimate inside if arrangements are planned after the mentioned events. According Grace et al. (2013) this kind of incidents can be minimized by using automated chamber systems previously programmed to measure flux measurements continuously within defined periods of time.

1.4.2.2. Micrometeorological methods

Micrometeorological methods have some advantages in comparison with closed chamber systems explained before. Micrometeorological measurements are designed for larger scale observations without interfering with the micro-environment system and they have a very high temporal resolution. These methods integrate fluxes 10 m^2 up to regional scales. Likewise, micrometeorological methods require large and uniform surfaces; as well as fast response infrared sensors which are costly. The data collection for these methods is also constrained by the atmospheric stability that sometimes might influence negatively field data observations (Fowler and Duyzer, 1989).

Among the micrometeorological methods, the most common ones are described below:

- Eddy covariance method,
- relaxed eddy accumulation method,
- aerodynamic gradient method,
- mass balance method, and
- boundary layer budget approach method.

The eddy covariance method consists in quantifying molecules that move up and down over time and how fast they move; thus the method represents the vertical fluxes as covariance between measurements of vertical velocity and the investigated concentration (Kirschbaum et al., 2001; Burba and Anderson, 2013). The relaxed eddy accumulation method consists in slow response concentration analysis that uses a sonic anemometer to measure the vertical wind speed, additionally sampling air into updraft and downdraft reservoirs (Pattey et al., 2006). The aerodynamic gradient method, consists in a slower sensor than the used on both previous methods, where additionally to the wind speed and gas concentration, temperature profiles are included as part of the calculation. The mass balance method uses concentration measurements versus height, in combination with the vertical gradient of wind; and is commonly applied for finite sources that only stretch out about 4–5 times the height of the measurement tower in the upwind direction (Denmead et al., 1998). Finally, the boundary layer budget approach method consists in collecting air samples during the flight of an airplane where fluxes are calculated using inverse modeling techniques.

1.5. Modeling N_2O emissions

When modeling C and N transfer in ecosystems, many processes have to be addressed. Ecosystems are complex and inherit various interactions, feedbacks, etc., which are challenging to capture by simulations: (1) exchange of nutrients between biosphere and soil environment; (2) biomass growth and uptake of N and water; (3) CO_2 released by respiration, and consumed in photosynthesis; (4) litter input into the soil and root exudations; (5) decomposition by microbial processes, nitrification and denitrification (Fig. 12).

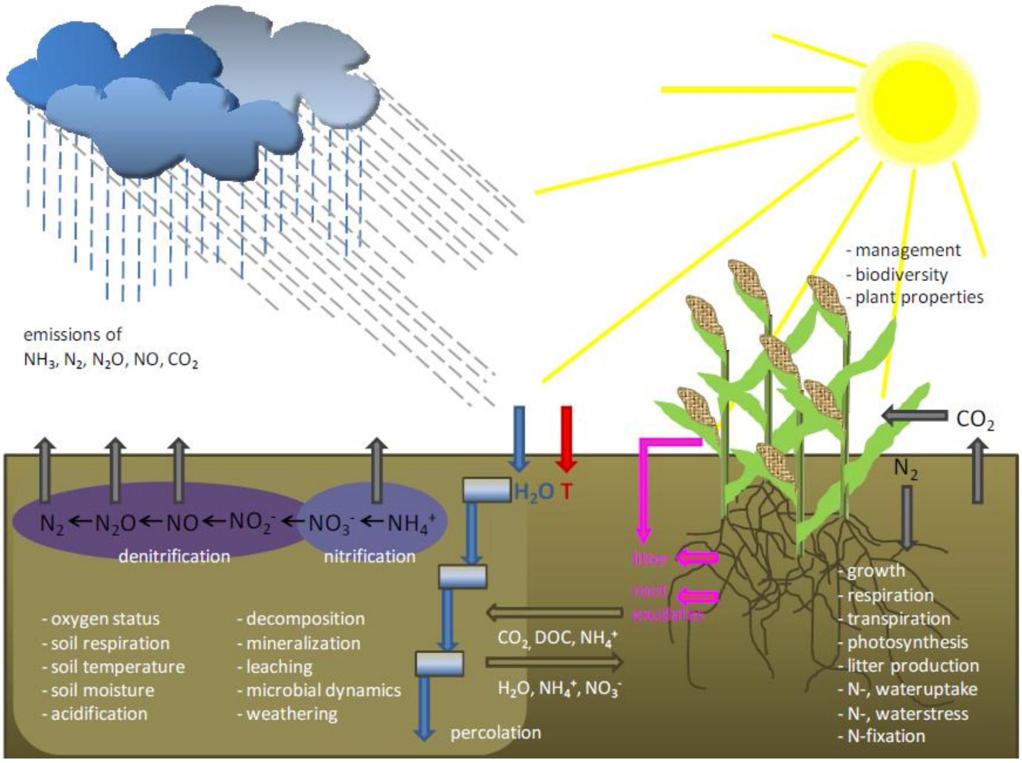


Figure 12: Scheme of relevant process and interactions in ecosystems (Bremner, 1997)

Interactions and processes should be taken into account to have a comprehensive understanding of an ecosystem. Therefore models are essentially based on internal interactions within the agricultural system. Soil climatic conditions like water content and temperature are dependent on physical properties of the soil and on rainfall, air temperature and radiation. These factors as well as other information regarding biodiversity of plants and human impact have to be considered via input files or linkage to other models.

Nowadays, only field measurements are not enough to significantly reduce these uncertainties associated with global estimates of greenhouse gases. The most promising strategy to overcome these problems is the development of models. Models are largely used to estimate greenhouse gases from small scales up to global scales. However, most of them highlight that models need to be parameterized and validated in different conditions in order to be universally used at global scale (Fuentes, 2013). In the field of agricultural science, simulation models capable to predict greenhouse gas emissions and environmental effects have become increasingly recognized as potential tool to support field research work. Following are presented some of the models currently used to simulate greenhouse gas emissions such as: DNDC, APSIM and DEYCENT

1.5.1. DNDC

DNDC (version 9.5) is a process-oriented model consisting of four sub-models: soil, climate, crop, and decomposition and denitrification (Ri et al., 2003; Vogeler et al., 2013). Three sets of data are input: (1) climatic conditions (temperature, precipitation, wind speed, irradiation), (2) soil parameters (texture, organic matter content), and (3) farming parameters (crop, fertilization, management). A generic agro-ecosystem modeling framework is used to predict carbon and nitrogen cycling from the input parameters. Model output consists of daily water balance, carbon balance, nitrogen balance, and crop yield. This study focused exclusively on N_2O emissions, and we calculated the total nitrogen flux by summing the calculated daily fluxes of each simulated year.

1.5.2. APSIM

APSIM is a modeling framework developed to simulate biological and physical processes of cropping systems in response to climate and management (Keating et al., 2003; Delve and Probert, 1998). We used version 7.6, which consists of three components: (1) a set of management modules that allow the user to specify the initial characteristics of the simulation, including data entry options, as well as the format of the output data; (2) a set of biophysical modules to simulate the biological and physical processes of the selected farming system; and (3) the simulation engine, which drives the whole simulation process and facilitates communication among the modules. In addition to the modular framework, APSIM provides generic simulations tested for several cropping systems in temperate and tropical regions, including a strong framework for simulating sugarcane crops.

1.5.3. DAYCENT

DAYCENT is a daily time series biogeochemical model used in agro ecosystems to simulate fluxes of carbon and nitrogen between the atmosphere, vegetation and soil (Del Groso et al., 2006). DAYCENT is a 1-dimensional model that uses daily data to modeling decomposition, nutrient flows, soil water, and soil temperature and has increased spatial resolution for soil layers. Key sub-models include plant growth with dynamic C allocation among plant components, soil organic matter decomposition and nutrient mineralization, and N_2O emissions from nitrification and denitrification. The main inputs of the DAYCENT model are: (1) soil texture; (2) daily weather data such temperature and precipitation; (3) plant type; (4) management practices like irrigation system and amount and timing of fertilizer applied.

1.6. Objectives

Rising global temperatures have been accompanied by changes in weather and climate. It is therefore important to reduce net greenhouse gases (GHG) as global major objective. Although fertilizer use is known as determining factor of N_2O emission in agricultural soils, specific characteristics and conditions will define regional impacts. Hence, this current study was carried out with the main aim of investigating the characteristics of N_2O emissions from agricultural soils. The objectives are presented as part of two main activities (activity 1 and activity 2).

Activity 1

The activity 1 consisted in a field experiment and modeling:

I. Field experiment:

> **Objective 1: To measure N_2O emissions from a sugarcane field by examining the characteristics**: *timely change, influence of soil moisture, spatial dispersion, and emission factor.*

II. Modeling:

> **Objective 2: To simulate N_2O emissions by examining the applicability of models for field observations:** *DNDC and APSIM.*

Activity 2

The activity 2 consisted in a laboratory experiment:

I. Laboratory experiment:

> **Objective 3: To measure N_2O emissions by examining the influence of different fertilizers** under same temperature.

> **Objective 4: To measure N_2O emissions by examining the influence of temperature** using same fertilizer condition.

2. Materials and methods

2.1. Measurement and simulation of N_2O emissions from a sugarcane field

The first part consisted in conducting a field experiment to collect data on N_2O emissions from a sugarcane field in Okinawa; and in the second part consisted in running simulations of N_2O emissions with the DNDC and APSIM models.

2.1.1. Measurement of N_2O emissions from a sugarcane field

The field experiment was carried out in a sugarcane field at the University of the Ryukyus, Okinawa Island, Japan (26°14′N, 127°45′E). Meteorological data collected from 1981 to 2010 at the Naha weather station of the Japan Meteorological Agency (10 km southwest of the study site) show that the research site receives an average rainfall of 2000 mm. The mean annual humidity is 79%, and the average annual temperature is 23.3°C. January is the coldest month (average temperature, 14.5°C), and July is the warmest month (26.7°C).

The experimental work was conducted in a lysimeter (3.5 m × 2.1 m) filled with Shimajiri-maji (dark red calcareous soil: USDA soil taxonomy), a local soil in Okinawa. The Japanese sugarcane cultivar NORIN-8 (Okinawa Prefectural Agricultural Research Center; Itoman, Okinawa, Japan) was grown. Seeds were sown and germinated in pots, and then the seedlings were transplanted to two ridges in the lysimeter. The distance between plants was 0.25 m, and the distance between the two ridges was 1.25 m. Ammonium sulfide $(NH_4)_2S$ fertilizer (0.083 kg-N, equivalent to 110 kg-N ha–1), was applied in two doses. The sugarcane cultivation schedule is shown in Table 3.

Table 1: Schedule of sugarcane cultivation and N_2O measurement

Date (dd/mm/yyyy)	Transplanting	Fertilization dose	N_2O measurement	Harvest
13/05/2011	X			
10/07/2011		110 kg-N ha-1		
12/07/2011			X	
04/08/2011			X	
25/08/2011		110 kg-N ha-1		
28/02/2012				X

Two PVC cylinders (15 cm high, 10 cm inner diameter) were installed, one on a ridge and the other between the ridges, on 10 July (Fig. 13). The tops of the cylinders were covered to isolate the air inside the cylinder from the atmosphere, and the airflow was controlled by solenoid valves at defined time intervals. N_2O fluxes were measured by the closed-chamber method, by connecting the closed cylinders to a Thermo Scientific Model 46i Nitrous Oxide Analyzer (Thermo Fisher Scientific, Waltham, MA, USA), which measures ambient N_2O concentrations by non-dispersive infrared spectrometry. N_2O emissions were measured for 30 min every hour, followed by 30 min of ventilation to the atmosphere, alternately in the two cylinders. This procedure was repeated continuously from 13 July to 4 August 2011.

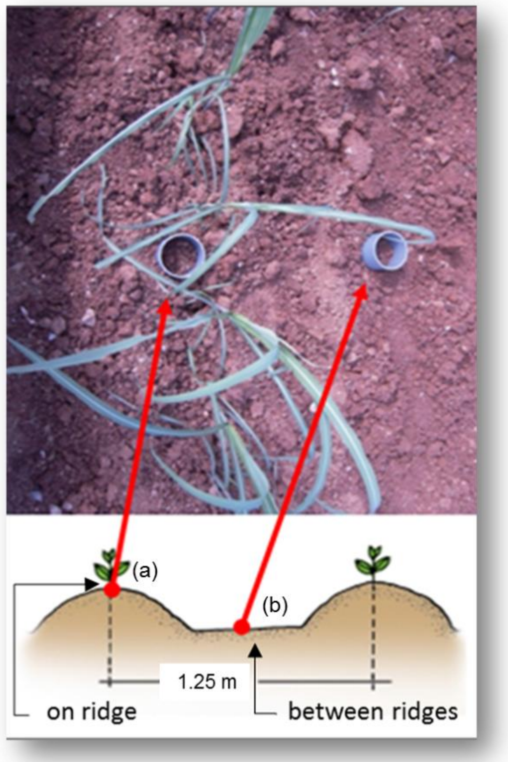


Figure 13: Installation of chambers in the lysimeter. Chambers were places in two different locations: (a) on ridge; (b) between ridges

The change in the N_2O concentration, expressed as ppm min^{-1}, was calculated by linear regression using data from the last 7 min of each measurement period. The N_2O flux was then calculated by using the ideal gas law as follows:

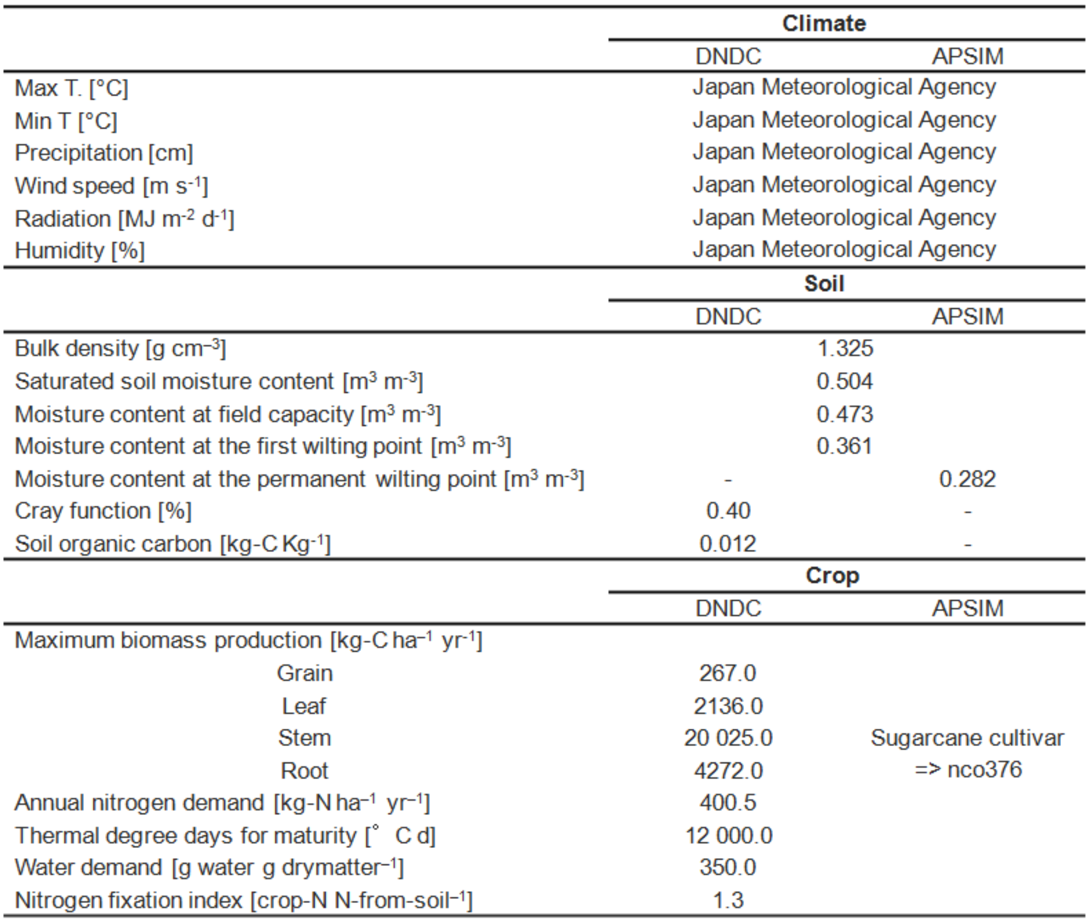
$$q = 60 \cdot N \cdot 10^6 \cdot \frac{PV}{RT} \cdot a \cdot \frac{1}{A} \qquad \text{(Eq. 3)}$$

where q is the N_2O flux (µg-N·m^{-2}·h^{-1}), N is molecular weight, P is standard atmospheric pressure (101325 Pa), V is the total volume of the closed chamber system (L); R is the gas constant (Pa L mol^{-1} K^{-1}), T is the soil temperature inside the cylinders, a is the change in the gas concentration per minute (ppm min^{-1}), and A is the area of soil surface within the cylinder (m^2).

2.1.2. Simulation of N_2O emissions using DNDC and APSIM models

We performed simulations with the DeNitrification and DeComposition (DNDC) and Agricultural Production Systems Simulator (APSIM) models to estimate N_2O emissions and compared the results with the observed data from the field experiment. DNDC (version 9.5) including its four sub-models (soil, climate, crop, and decomposition and denitrification) were used for N_2O simulations. The input data consisted in: climatic conditions (temperature, precipitation, wind speed, irradiation); soil parameters (texture, organic matter content); and farming parameters (crop, fertilization, management). On the other hand, the APSIM (version 7.6) was used exploring its three main modules on management control, biophysical components, simulation engine; driving the whole simulation process for N_2O emissions. For both simulations (DNDC and APSIM) the period of simulation was from 1 January 2011 to 31 December 2012. Table 3 shows the input parameters for modeling DNDC and APSIM models. The schedule of sugarcane cultivation shown in Table 2 was also used for model simulations as input data.

Table 2: Input parameters for the DNDC and APSIM models



	Climate	
	DNDC	APSIM
Max T. [°C]	Japan Meteorological Agency	
Min T [°C]	Japan Meteorological Agency	
Precipitation [cm]	Japan Meteorological Agency	
Wind speed [m s^{-1}]	Japan Meteorological Agency	
Radiation [MJ m^{-2} d^{-1}]	Japan Meteorological Agency	
Humidity [%]	Japan Meteorological Agency	
	Soil	
	DNDC	APSIM
Bulk density [g cm^{-3}]	1.325	
Saturated soil moisture content [m^3 m^{-3}]	0.504	
Moisture content at field capacity [m^3 m^{-3}]	0.473	
Moisture content at the first wilting point [m^3 m^{-3}]	0.361	
Moisture content at the permanent wilting point [m^3 m^{-3}]	-	0.282
Cray function [%]	0.40	-
Soil organic carbon [kg-C Kg^{-1}]	0.012	-
	Crop	
	DNDC	APSIM
Maximum biomass production [kg-C ha^{-1} yr^{-1}]		
Grain	267.0	
Leaf	2136.0	
Stem	20 025.0	Sugarcane cultivar => nco376
Root	4272.0	
Annual nitrogen demand [kg-N ha^{-1} yr^{-1}]	400.5	
Thermal degree days for maturity [° C d]	12 000.0	
Water demand [g water g drymatter^{-1}]	350.0	
Nitrogen fixation index [crop-N N-from-soil^{-1}]	1.3	

Note: APSIM does not allow users to set crop parameters, but the cultivar can be chosen from a list.

2.2. Measurement of N_2O emissions from shimajiri-maji soil

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. 14). Temperature and fertilizer conditions used are shown in Table 4. Nitrogen fertilization consisted of (a) normal fertilizer (NF), which was ammonium sulphate $(NH_4)_2SO_4$, and (b) controlled-release fertilizer (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 4).

Table 3: Fertilizer and temperature conditions

Cylinder	Fertilizer	Treatment	Temperature.
-- # --	-- 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_2O were measured by using a closed-chamber method (Fig. 14). 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 (Fig. 15).

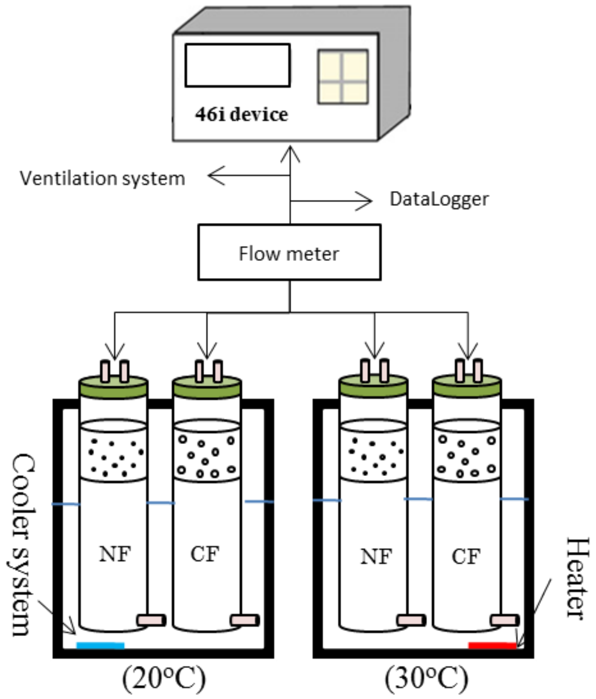


Figure 14: Schematic diagram of the closed chamber system

Emissions of N_2O 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.

Figure 155: 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_2O 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_2O fluxes were calculated from the change in concentration and expressed in mol min^{-1} using the ideal gas law:

$$N_2O = P \cdot (V \cdot C) / (RT) \qquad \text{(Eq. 2)}$$

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.

3. Results and discussion

3.1. Characteristics of N_2O emissions from a sugarcane field-experiment

Following are presented: the measurement of N_2O emissions in the field; the comparison of the DNDC and APSIM model estimations with experimental results; and the characteristics of modeling simulations of N_2O emissions.

3.1.1. Measurement of N_2O emissions in the field

N_2O emissions were clearly detected in the chamber on the ridge during the observation period (Fig. 16). Fluxes were relatively larger in the daytime than in the nighttime; and we inferred that they varied synchronously with air temperature changes. N_2O emissions increased from 13 July, when rainfall occurred occasionally, and emissions were highest on 20 July; thereafter, the emissions decreased gradually. We assumed that the decrease in N_2O emissions was due to a decrease in the ammonium content of the soil caused by nitrification. Morimoto et al. (2008) also reported that, in an experiment conducted at a lettuce farm, N_2O emissions were highest soon after the application of fertilizer and then gradually decreased, and they concluded that nitrification was the dominant process affecting N_2O emissions during their experiment. Likewise, Watanabe et al. (2000) reported that the main process affecting N_2O emissions from a maize field in northeastern Thailand was nitrification. Wrage et al. (2001) showed convincingly that nitrifier denitrification, the process by which ammonia (NH_3) is first oxidized to nitrite (NO_2^-) and then the NO_2^- is reduced to nitric oxide (NO), nitrous oxide (N_2O), and molecular nitrogen (N_2), contributes to N_2O emissions. Subsequently, Kool et al. (2011) showed that nitrifier denitrification is a significant cause of N_2O emissions from soil under high soil moisture conditions. On the basis of these previous results, we concluded that nitrification was the dominant process responsible for N_2O emissions in our sugarcane field, and that nitrifer denitrification occurred under high soil moisture conditions after rainfall in our experiment.

In contrast, N_2O emissions measured between ridges were mostly zero during the observation period; N_2O emissions were detected between ridges only after a rainfall (Fig. 16). Because the fertilizer was applied only on the ridges, there was little nitrogen from the fertilizer between the ridges. Therefore, we inferred that N_2O emissions occurred between the ridges only after rainfall had washed nitrogen (as ammonium) from the ridges.

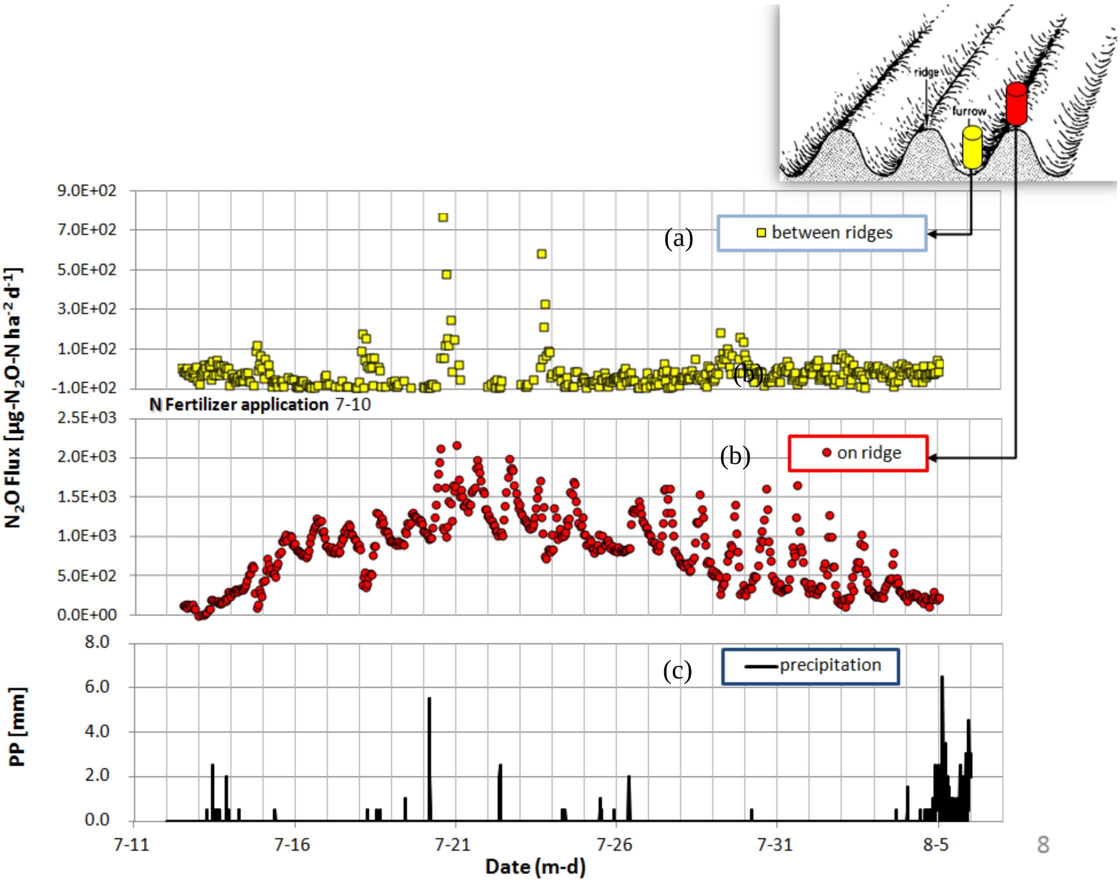


Figure 166: Field measurement results: (a) between-ridges N_2O emissions; (b) on-ridge N_2O emissions; (c) precipitation.

These results show that there was large spatial difference in emissions even in the same field. Therefore, to estimate total N_2O emissions from the field, it was necessary to take dispersion into account. Therefore, we calculated EFs (i.e., the percentage of nitrogen in the N_2O emissions attributable to the added nitrogen in fertilizer) for three cases. Because N_2O emissions from between the ridges were mostly zero, we considered the N_2O emissions from the field without fertilizer to be zero. We then calculated N_2O emissions for three different cases: Case 1, ridge width = 10 cm; Case 2, ridge width = 20 cm; and Case 3, the average of on-ridge and between-ridge emissions. The EFs calculated for the chamber placed on-ridge, for the chamber placed between-ridge and for the Cases 1–3 are shown in Table 5. The NIR EF for upland fields is 0.62% (NGGI, 2012). The calculated between-ridge and Case 1 EFs were lower than the NGGI value of 0.62%. Because the diameter of the chamber in our experiment was 10 cm, we assumed that Case 1 represented the minimum width of the fertilized area. Therefore, we inferred that the actual width of the fertilized area might be close to or wider than the Case 2 width and that the actual EF for this sugarcane field was larger than the NIR value.

Table 4: Value of the emission factor (EF) for each case

Emission factor	On-ridge	Between-ridge	Case 1	Case 2	Case 3
EF (%)	4.43	0.065	0.481	0.897	2.25

3.1.2. Comparison of the DNDC and APSIM model estimations with the experimental results

The observed N_2O emissions data and the values calculated by the DNDC and APSIM models are shown in Figure 17. Because the output of both models is given on a daily basis, we calculated the total daily N_2O emissions from the measured data and then compared the simulated emissions with the observed values. Considering the spatial dispersion mentioned above, we compared the simulation results with the N_2O emissions of Cases 1–3 as well as with the observed on-ridge and between-ridge emissions. The observed data collected from 13 July to 4 August were compared against the simulation for the period from 10 July to 19 August. The pattern of N_2O emissions simulated by the DNDC model was similar to that of the field data, although a time lag was slightly detected in the simulation. In contrast, the N_2O emissions simulated by APSIM were smaller than the observed emissions, and the emissions peak was simulated soon after the 10 July fertilizer application.

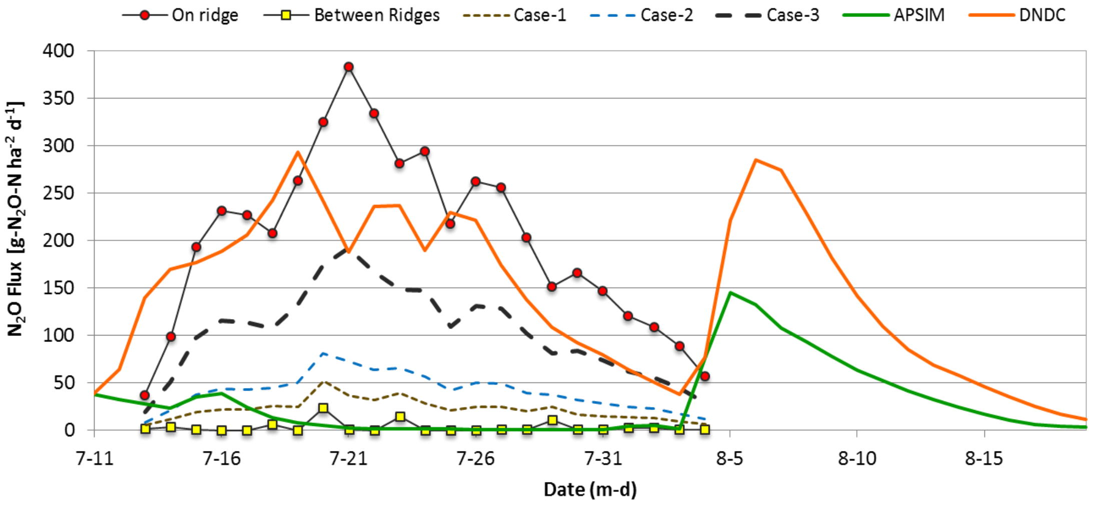


Figure 17: Comparison of observed N_2O emissions with values calculated by the DNDC and APSIM models.

Total N_2O emissions for on-ridge chamber, between-ridge chamber, and for each of the three cases (Case 1, ridge width = 10 cm; Case 2, ridge width = 20 cm; and Case 3, the average of on-ridge and between-ridge emissions) were then calculated from the sum of each N_2O emission, separately, during 23 days (from 13 July to 4 August). Similarly, total N_2O emissions simulated by two models over the same time period, are shown in Table 6.

Table 5: Total measured and simulated N_2O emissions

N_2O emission	On-ridge	Between-ridge	Case 1	Case 2	Case 3	DNDC	APSIM
Total (kg)	4655.3	68.7	550.5	897.5	2249.5	3778.6	246.0

The emissions simulated by DNDC were between the Case 3 and on-ridge values. We considered that the most realistic N_2O emissions value was probably close to the Case 2 value or between the Case 2 and Case 3 values. Therefore, we thought that the DNDC model overestimated actual N_2O emissions. In contrast, the emissions simulated by APSIM were smaller than the Case 1 emissions. Thus, we considered that APSIM underestimated N_2O emissions. Vogeler et al. (2011) showed that N_2O emissions simulated by the DNDC model from a urine patch in a pasture were larger than the emissions simulated by the APSIM model. Considering that N_2O emissions from agricultural soils are influenced by many factors, including soil moisture, soil temperature, and inorganic nitrogen and organic carbon contents (Akiyama et. al., 2010), it is clear that the DNDC and APSIM models must be validated to determine the most appropriate model for simulating N_2O emissions from sugarcane fields in Okinawa Prefecture.

3.1.3. Characteristics of the DNDC and APSIM models in the simulation of N_2O emissions

We showed above that the DNDC model overestimated and the APSIM model underestimated N_2O emissions. Next, we examined the characteristics of the two models in the simulation of N_2O emissions, focusing on nitrification and denitrification processes. Daily changes in the nitrification and denitrification rates calculated by the DNDC and APSIM models are shown in Figure 18.

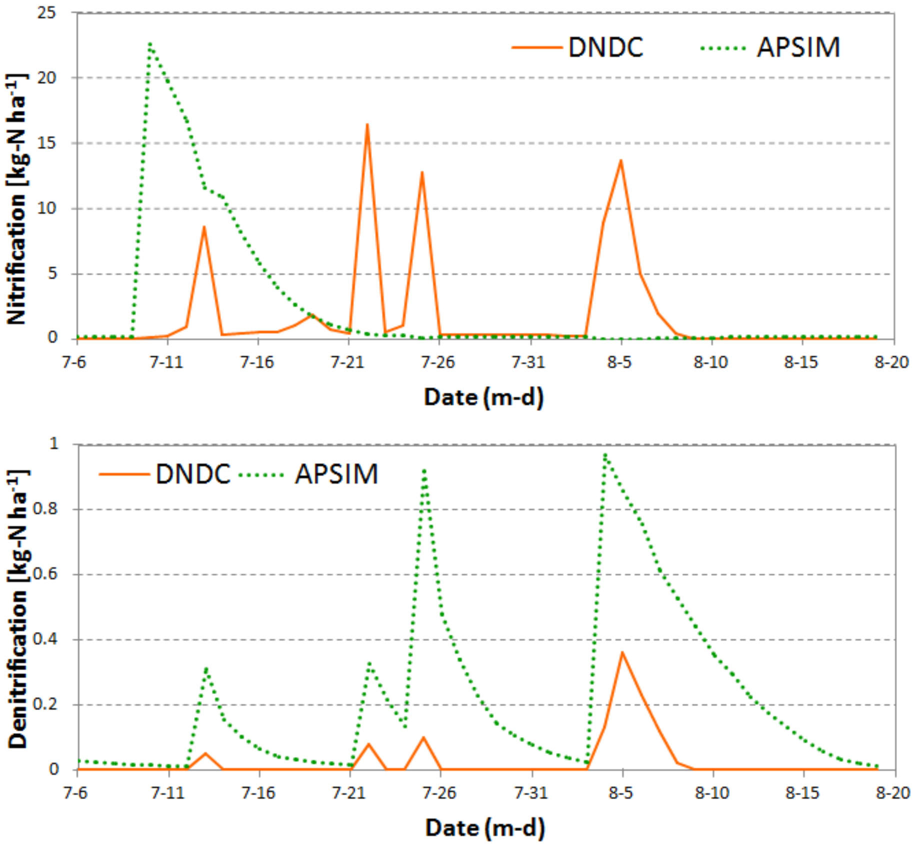


Figure 18: Daily changes of the (a) nitrification rate and (b) denitrification rate calculated by the DNDC and APSIM models.

Comparison of the ranges of the nitrification and denitrification rates confirmed that in the simulation results of both models the nitrification rate was larger than the denitrification rate. Moreover, in both models, the denitrification rate was influenced by precipitation events. Some differences in the nitrification rate were detected in the two models. In the APSIM model, the nitrification rate was highest soon after the fertilization, whereas in the DNDC model nitrification rate peaks occurred after rainfall events. This difference reflects that fact that the nitrification equation in the DNDC model takes into account the effect of soil moisture, whereas that in the APSIM model does not. N_2O production during nitrification is simulated in the two models by using the following equations:

$$\text{DNDC}: \mathrm{N_2O_{ni}} = 0.006 \cdot R_{ni} \cdot W_{fps} 2.72^{34.6-9615/(T_s+273.15)} \quad \text{(Eq. 4)}$$

$$\text{APSIM}: \mathrm{N_2O} = k_{ni} \cdot R_{ni} \quad \text{(Eq. 5)}$$

where N_2O_{ni} is the N_2O production during nitrification; R_{ni} is the nitrification rate (kg ha–1 d–1); Wfps is the water-filled pore space (%); Ts is the soil temperature (°C); and kni is a coefficient for estimation of N_2O production.

The DNDC model also takes into account the fraction of N_2O emitted to the atmosphere. As a result, in the simulation, nitrification rate peaks and rainfall events are synchronous with each other and with N_2O emissions.

In the APSIM model, we used 0.002 as the default value of k_{ni}, following Li et al. (2007). However, this value may be soil-specific, so a larger value might have been a more appropriate value in our study. In future studies, different k_{ni} values should be evaluated.

Our results suggest that the simulation of N_2O emissions associated with nitrification by the DNDC model might be improved by modifying the coefficients in Eq. 4 such that total simulated N_2O emissions agreed with the total observed N_2O emissions.

3.2. Characteristics of N_2O emissions, influence of fertilizer and temperature conditions

N_2O emissions and soil moisture were measured for two trials with different flooding/draining regimens (Fig. 19 and Fig. 20). Cumulative fluxes of N_2O in the second trial together with soil moisture content are presented in Figure 21. Under all of the conditions tested, the N_2O measurements were consistent in the same emission trends occurred soon after the start of drainage; detecting high peaks of N_2O which tended to decrease rapidly (Fig. 19 and Fig. 20). Our results agree with those of a field study on N_2O emissions over humid tropical soils in Costa Rica, which found that N_2O emissions increased only after rainfall had increased the soil moisture content (Weitz et al., 2001).

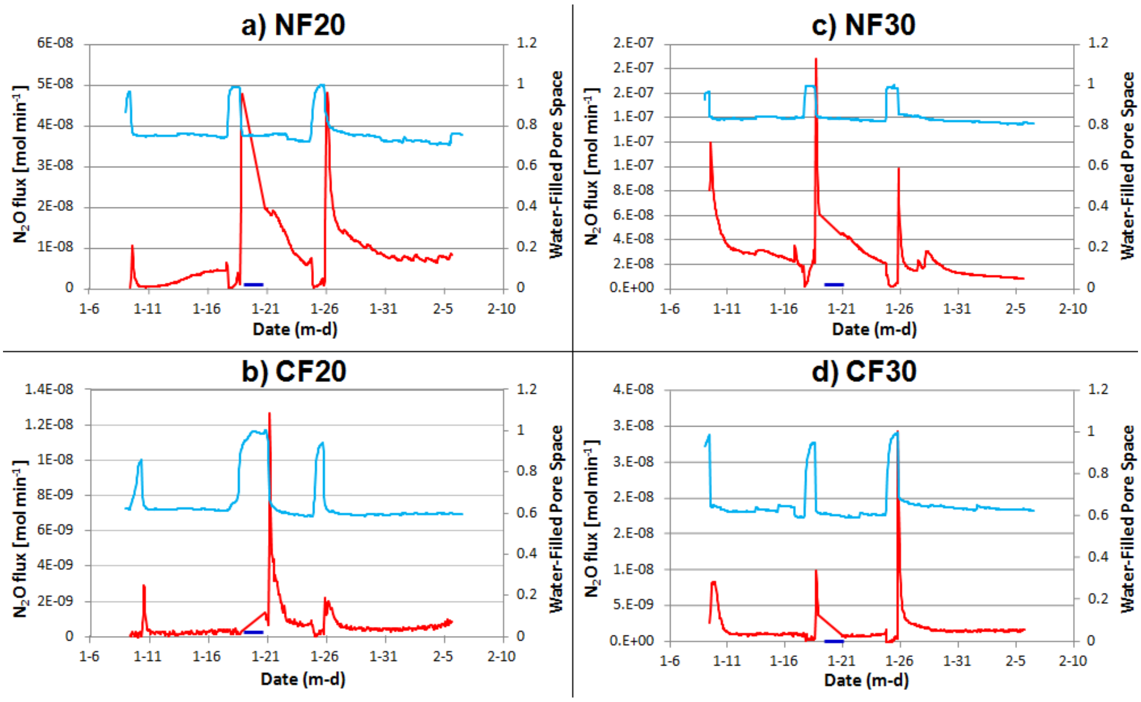


Figure 19: First trial: N_2O fluxes (black lines) for two N fertilizer treatments—normal fertilizer (NF) and controlled-release fertilizer (CF)—under different temperature conditions: a) NF at 20°C; b) CF at 20°C; c) NF at 30°C; d) CF at 30°C. Volumetric water content (blue lines) is included for each observation. Dark blue segments represent missing data.

By looking at N_2O emissions and their correlation with temperature and fertilizer type, we observed that the peak N_2O emissions flux, from highest to lowest, had the following pattern in the first trial: NF30 > NF20 > CF30 > CF20 (Fig. 19). On the other hand, we obtained a different pattern in the second trial: NF30 > CF30 > CF20 > NF20 (Fig. 20). 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.

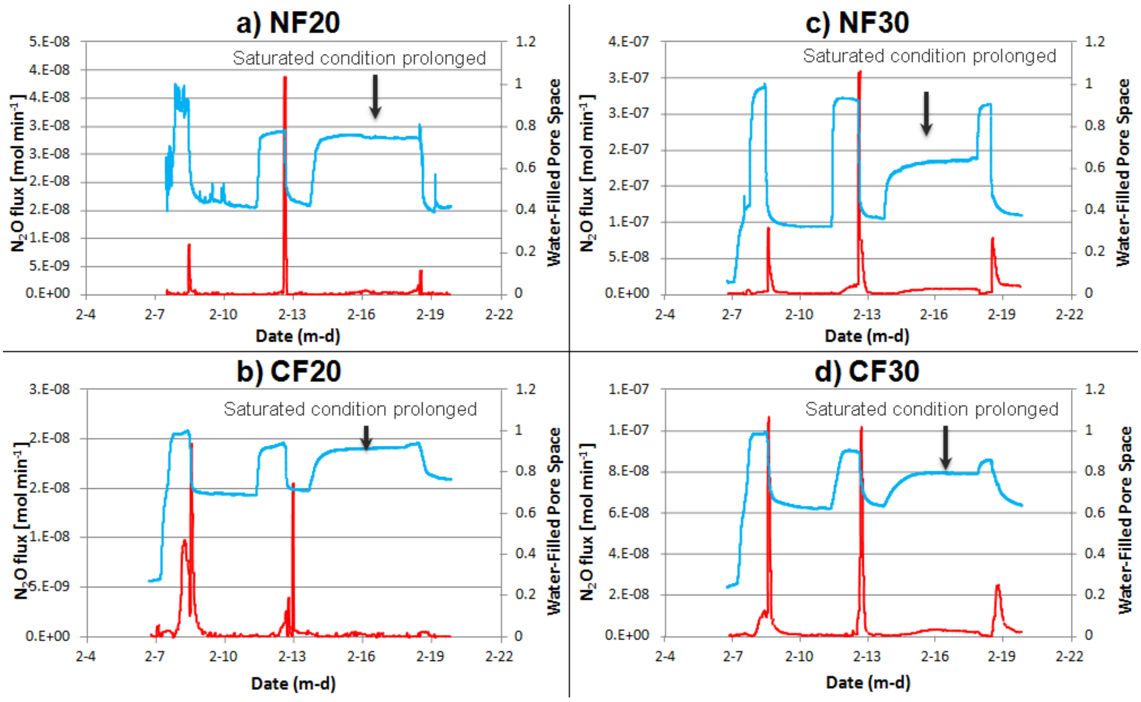


Figure 20: Second trial: N_2O fluxes (black lines) for two N fertilizer treatments—normal fertilizer (NF) and controlled-release fertilizer (CF)—under different temperature conditions: a) NF at 20°C; b) CF at 20°C; c) NF at 30°C; d) CF at 30°C. Volumetric water content (blue lines) is included for each 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. 19), 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 N_2O emissions during denitrification, the duration of the near-saturated conditions over the third cycle in the second trial was intentionally prolonged (Fig. 20). We observed that the slope of the cumulative N_2O fluxes started to become steeper in second half of the third cycle (Fig. 21). We assume that the duration of the saturated conditions was long enough to identify denitrification as the source of N_2O emissions.

According to Signor (2013), the highest N_2O 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 N_2O emissions (Fig. 19 and Fig. 20). Nevertheless, from the relationship between soil moisture conditions and the cumulative N_2O emissions we could deduce that N_2O emissions tend to become smaller after drainage. We can say that after each drainage condition N_2O emissions showed a certain period of stabilization that tended to gradually increase over time (Fig. 21). 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 the cumulative emissions from NF20 were 1.7 times that of CF20, while cumulative emissions from NF30 were 0.52 times that of CF30.

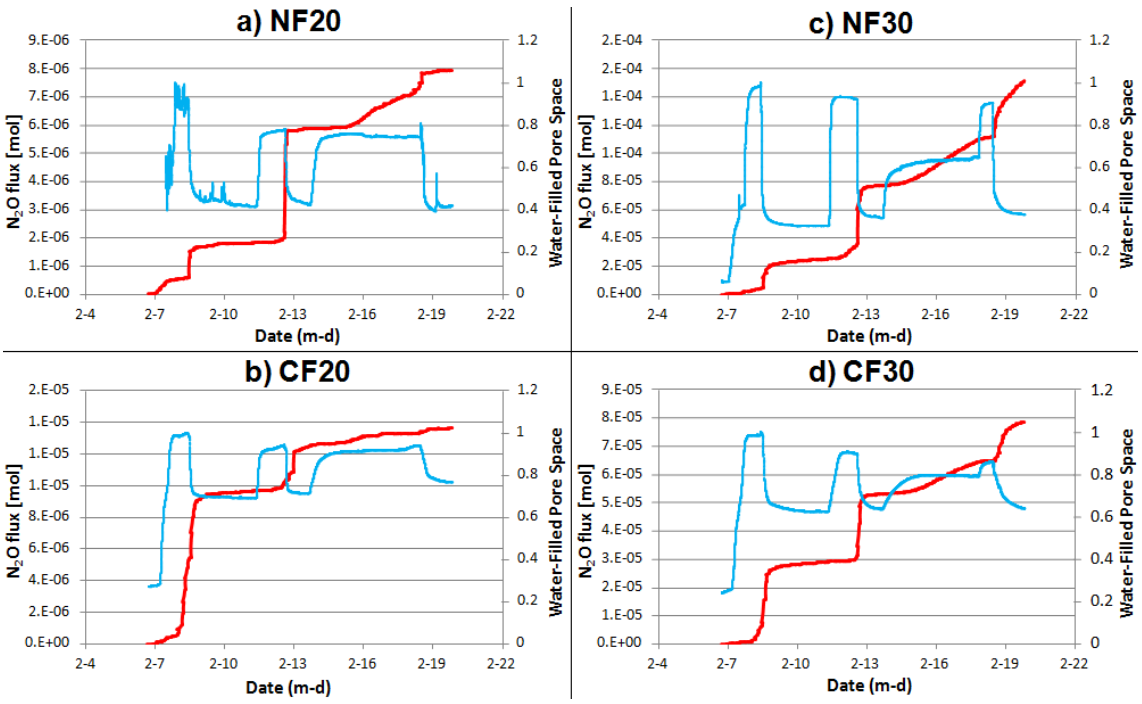


Figure 21: Cumulative N_2O fluxes (black lines) and volumetric water content (blue lines) in the second trial with different chemical fertilizers (NF and CF) under different temperature conditions: a) NF at 20°C; b) CF at 20°C; c) NF at 30°C; d) CF at 30°C.

Our results showed that N_2O 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_2O reduction or NO_3^- leaching losses (Wilson, 2009). Total amount of N_2O emissions was the largest in NF30. Although N_2O emissions were strongly related to fertilizer 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_2O emissions that does NF. A study on the effects of slow-release fertilizers in Andosols reported a 20% reduction in N_2O emissions by using CF (Minami et al., 1994). In contrast, in our experiment, the total reduction of N_2O emissions by using CF as compared to using NF was 48%.

4. Conclusions

This study examined greenhouse gas emissions from agricultural activities with highlighting: the characteristics of N_2O emissions, the applicability of models, the influence of different fertilizers, and the influence of temperature. Conclusions of this study are presented below:

1. **The characteristics of N_2O emissions** were clearly detected soon after the rainfall (activity 1) as well as after simulated drainage (activity 2); revealing a dominant influence of soil moisture which facilitates the nitrification as main process.
2. **The applicability of models**, DNDC and APSIM; requires to consider sensitivity analysis focused on default coefficients assumed by models within biochemical process (nitrification and denitrification).
3. **The influence of different fertilizers** has been demonstrated when compared the CF30 with the NF30; achieving a reduction of 48% in N_2O emissions.
4. **The influence of temperature** is important to consider, because at higher temperatures (summer planting) there is high potential to reduce N_2O emissions than at lower temperatures (spring planting) over sugarcane fields in Okinawa

5. Perspectives

In this study, the qualitative and quantitative characteristics of N_2O emissions were investigated. Because the study was conducted in Okinawa, the results have the potential for use in other sub-tropical regions where sugarcane is cultivated. Sugarcane fields may be guided by the results obtained in regard to the variations of soil moisture content and soil temperatures influencing on N_2O emissions. It is recommended further research on N_2O emission from sugarcane fields in Okinawa considering annual climate variations.

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