Universitat de Lleida

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Resum

L’emissió de gasos amb efecte d'hivernacle (GEH) procedent de l'agricultura depèn de la gestió del reg i dels fertilitzants. L'objectiu d'aquesta tesi va ser identificar les estratègies menys emissores –d` entre les següents- compatibles amb un rendiment òptim: (i) reg continu (CI)/intermitent (II) en un arrossar; (ii) fertilització de fons amb gallinassa (CM), purí porcí (PS), urea (U) o sulfat amònic (AS) en un arrossar amb AS en cobertora; (iii) incorporació/eliminació del rostoll de panís amb diferents dosis de N mineral, i (iv) reg enterrat (SDI)/superficial per degoteig (DI) combinat amb N mineral aplicat via fertirrigació amb i sense DMPP en un cultiu súper-intensiu d'olivera.

El CI minimitza significativament les emissions de l’arrossar alhora que permet atènyer el rendiment màxim. L'aplicació de purí porcí a dosis agronòmiques proporciona alts rendiments i minimitza els GEH. Considerant les emissions i el rendiment del panís, el tractament control va ser la millor opció, independentment de la gestió del rostoll. Pel sistema d'olivera súper-intensiva, l'aplicació de DMPP + 50 kg N ha^{-1} + DI va ser la millor opció.

Resumen

La emisión de gases con efecto invernadero (GEI) procedente de la agricultura depende de la gestión del riego y de los fertilizantes. El objetivo de esta tesis fue identificar las mejores estrategias -de entre las siguientes- para mitigar los GEI manteniendo un rendimiento máximo: (i) riego continuo (CI)/intermitente (II) en un arrozal, (ii) la fertilización de fondo con gallinaza (CM) , purín porcino (PS), urea (U) o sulfato amónico (AS) en un arrozal con AS en cobertera, (iii) la incorporación/eliminación del rastrojo con diferentes dosis de N mineral en el cultivo del maíz, (iv) el riego por goteo enterrado (SDI)/superficial (DI) en combinación con N mineral aplicado vía fertirrigación con y sin DMPP en un olivar súper-intensivo.

El CI mitiga significativamente las emisiones del arrozal al tiempo que garantiza el rendimiento máximo. La aplicación de purín porcino a dosis agronómicas proporciona altos rendimientos y minimiza los GEI. Considerando las emisiones de GEI y el rendimiento del maíz, el tratamiento control fue la mejor opción, independientemente de la gestión del rastrojo. La aplicación de DMPP + 50 kg N ha^{-1} + DI fue la mejor opción para el cultivo súper-intensivo de olivo.

Summary

Greenhouse gases emissions from agriculture depend on irrigation and fertilisation management. The objective of this thesis was to identify the less emitting management strategies among the following, compatible with a feasible yield: (i) continuous (CI)/intermittent irrigation (II) on rice, (ii) background fertilisation with chicken manure (CM), pig slurry (PS), urea (U) or ammonium sulphate (AS) and topdressing on rice, (iii) stover incorporation/removal with different doses of mineral N and, (iv) subsurface (SDI)/surface drip irrigation (DI) in combination with mineral N fertigation with and without DMPP on a super-intensive olive tree orchard.

Continuous irrigation significantly mitigated emissions from paddy fields while ensuring the highest yield. Pig slurry application at agronomic doses allowed high yields and minimized emissions. Based on emissions and maize yield, the control treatment was the best option regardless of stover management. Applying DMPP with 50 kg N ha^{-1}+ drip irrigation (DI) was the best option for the olive tree orchard.

Extended summary

Nitrous oxide (N_2O) is a potent greenhouse gas (GHG) directly linked to applications of nitrogen (N) fertilisers to agricultural soils. Identifying mitigation strategies for these emissions based on fertiliser management without incurring in yield penalties is of economic and environmental concern. With that aim, this Thesis evaluated: (1) to determine the effect of irrigation frequency on GHG and N_2 emission from a paddy soil at the Ebro Delta (NE Spain); (2) to compare the effect of different doses of urea, ammonium sulphate, chicken manure and pig slurry on GHG and N_2 emission during the seedling period, the rice crop season and the postharvest period under Mediterranean conditions from rice; (3) to compare the effect of maize (*Zea mays* L.) stover incorporation/removal with different ammonium nitrate doses, on the emission of GHG from a high mineral N soil; (4) to compare the effect of subsurface/surface drip irrigation in combination with mineral N fertigation with and without DMPP on the GHG emissions from a high density Arbequina olive tree orchard.

Water management is known to be a key factor on methane (CH_4), carbon dioxide (CO_2), and nitrous oxide (N_2O) emissions from paddy soils. A field experiment was conducted to study the effect of continuous irrigation (CI) and intermittent irrigation (II) on these emissions. Intermittent irrigation of rice paddies significantly stimulated (N_2O+N_2)–N emission, whereas no substantial N_2O emission was observed when the soil was re-wetted after the dry phase. The cumulative emission of (N_2O+N_2)–N was significantly larger from the II plots (0.73 kg N_2O–N ha^{-1} $season^{-1}$) than from the CI plots (-1.40 kg N_2O–N ha^{-1} $season^{-1}$). Draining prior to harvesting increased N_2O emissions. Draining and flooding cycles controlled CO_2 emission. The cumulative CO_2 emission from II was 8416.35 kg CO_2 ha^{-1} $season^{-1}$, significantly larger than that from CI (6045.26 kg CO_2 ha^{-1} $season^{-1}$). Lower CH_4 emission due to water drainage increased CO_2 emissions. The soil acted as a sink of CH_4 for both types of irrigation. Neither N_2O–N nor CH_4 emissions were affected by soil temperature. Global warming potential was the highest in II (4738.39 kg CO_2 ha^{-1}) and the lowest in CI (3463.41 kg CO_2 ha^{-1}). These findings suggest that CI can significantly mitigate the integrative greenhouse effect caused by CH_4 and N_2O from paddy fields while ensuring the highest rice yield.

Greenhouse gas fluxes from cultivated soil are affected by factors such as temperature, water and mineral nitrogen content. Furthermore, agricultural management such as the application of organic and inorganic fertilisation affects N_2O, CH_4 and CO_2 emissions

although it depends on the type of fertiliser used. In this context, a field experiment was realized in order to compared the effect of different fertilisation strategies on N_2O, CH_4, and N_2 emissions and on ecosystem respiration (CO_2 emission), during the different periods of rice cultivation (seedling, rice crop and postharvest period) under Mediterranean climate. At Site 1 background treatments were 2 doses of chicken manure (CM): 90 and 170 kg NH_4^+-N ha^{-1} (CM-90, CM-170), urea (U, 150 kg N ha^{-1}) and no-N (control). To all of them 50 kg N ha^{-1} ammonium sulphate (AS) were topdress applied. At Site 2, background treatments were 2 doses of pig slurry (PS): 91 and 152 kg NH_4^+-N ha^{-1} (PS-91, PS-152) and AS at 120 kg NH_4^+-N ha^{-1}. Sixty kg NH_4^+-N ha^{-1} as AS were topdress applied to AS and PS-91. There was an N control too. During seedling GWP was ~38-55% of rice crop season for the CM treatments, and (N_2O+N_2)-N emission from U was ~11% of the applied N. The postharvest period was a net sink for CH^4, and CO^2 boosted only from the CM-170 treatment (up to 2 Mg CO_2 ha^{-1}). Global warming potential (GWP) of the rice crop season reached 17 Mg CO_2-eq ha^{-1} for U, and was 14 for CM-170, and 37 for CM-90. The CM-170 treatment reduced CH4 emission. The application of PS at agronomic doses (~170 kg N ha^{-1}) allowed high yields (7.4 Mg ha^{-1}), the control of GWP (5.5 to 6.5 Mg CO_2-eq ha^{-1}), and a 25% reduction in greenhouse gas intensity (GHGI) to 0.75 kg CO_2-eq kg^{-1} when compared to AS (1.02 kg CO_2-eq kg^{-1}).

In order to improve the sustainability of the maize production system management practices that mitigate greenhouse gases (GHG) emission while keeping yield high are required. Application of crop residues is a cost-effective and sustainable alternative to increase organic matter contents and the fertility levels in the soil under Mediterranean conditions. However, these management practices may induce important changes in the N_2O emissions from these agroecosystems, with additional impacts on CO_2 emissions. In this context, a field experiment was realized in order to compared the effect of maize stover incorporation or removal along with different mineral N fertiliser doses (0, 200 and 300 kg N ha^{-1}) on the emission of greenhouse gases on a sprinkler irrigated maize (*Zea mays* L.) crop under Mediterranean conditions on a high nitrate-N soil.

Applying fertiliser tended to increase N_2O emissions and stover incorporation did not have any clear effect. Nitrification was probably the main process leading to N_2O which ranged from -0.11 to 0.36% of the applied N, below the IPCC (2007) values. Denitrification was limited due to low soil moisture content and limiting readily available carbon. Stover incorporation increased CO_2 emission. Nitrogen fertilisation tended to reduce CO_2 emission but only in 2011. The maize field acted as a net CH_4 sinks (in 2011) and mineral fertiliser application decreased CH_4 oxidation by the soil. Considering global warming potential, greenhouse gas intensity, as well as N_2O cumulative emissions and yield, it can be concluded that no fertilisation (control treatment) regardless of stover management was the best option combing productivity with keeping greenhouse gases emission under control. The application of nitrogen in many areas of the Ebro Valley (Spain) is not necessary due to the high N soil content (i.e. 200 g NO_3-N kg^{-1}) until the soil restores a normal mineral N content. This study indicates that efforts to mitigate greenhouse gases in this system should be focused in: (1) keeping an efficient irrigation with relatively low water filled pore space and (2) decreasing the soil mineral N content of the soil.

Drip irrigation combined with split application of N fertiliser dissolved in the irrigation water (i.e. drip fertigation) is commonly considered best management practice for water and nutrient efficiency. The emissions of GHGs (i.e. N_2O, carbon dioxide (CO_2) and methane (CH_4)) can easily be manipulated by drip fertigation without yield penalties. In this study, we tested management options to reduce these emissions in a field experiment from olive (*Olea europaea* L.) orchard. In the olive orchard, drip irrigation combined with nitrogen (N) fertigation can save water and improve nutrient efficiency. This system allows reducing production costs and increases crop yield. Spanish Arbequina is the most suited variety for super intensive olive groves. Moreover its oil has excellent sensorial features.

Nitrification inhibitors reduce greenhouse gas emissions. A field study was conducted to compare the emissions of N_2O, CO_2 and methane CH_4 associated with the application of N fertiliser through fertigation (0 and 50 kg N ha^{-1}), and 50 kg N ha^{-1} + nitrification inhibitor in a high tree density Arbequina olive orchard.

Subsurface drip irrigation markedly reduced N_2O and N_2O+N_2 emissions compared with surface drip irrigation. Fertiliser application significantly increased N_2O+N_2, but not N_2O emissions. Denitrification was the main source of N_2O. The N_2O losses (calculated as emission factor) ranging from -0.03 to 0.14% of the N applied, were lower than the IPCC (2007) values. The N_2O+N_2 losses were the largest, equivalent to 1.80% of the N applied, from the 50 kg N ha^{-1}+drip irrigation treatment which resulted in water filled pore space N60%most of the time (high moisture). Nitrogen fertilisation

significantly reduced CO_2 emissions in 2011, but only for the subsurface drip irrigation strategies in 2012. The olive orchard acted as a net CH_4 sink for all the treatments. Applying a nitrification inhibitor (DMPP), the cumulative N_2O and N_2O+N_2 emissions were significantly reduced with respect to the control. The DMPP also inhibited CO_2 emissions and significantly increased CH_4 oxidation. Considering global warming potential, greenhouse gas intensity, cumulative N_2O emissions and oil production, it can be concluded that applying DMPP with 50 kg N ha^{-1}+drip irrigation treatment was the best option combining productivity with keeping greenhouse gas emissions under control.

Contents

Chapter 1. General introduction

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1.1. Greenhouse gas emissions from fertilised agricultural systems

The causal relationship between anthropogenic increases in GHG concentrations and the modern problem of global warming is irrefutable (IPCC, 2014). The ability of the atmosphere to trap heat is augmented with increased concentrations of carbon dioxide (CO_2), methane (CH_4), and N_2O. It has been estimated that agriculture contributes about 84% and 52% of global antropogenic nitrous oxide (N_2O) and methane (CH_4) emissions, respectively (Smith et al., 2007), while it is only responsible for about 1% of carbon dioxide (CO_2) emissions (OECD, 2000).

Rising atmospheric concentrations of the greenhouse gases (CO_2, N_2O and CH_4) have caused an increase in radiative forcing of the earth's atmosphere. Agriculture plays an important role in the global flux of these gases. In intensively managed agro ecosystems, agricultural practices may offer a way to curb agricultural emission, in turn partially mitigating the enhanced greenhouse effect (Gregorich et al., 2005). Agricultural soils can constitute either a net source or sink of GHG. The ways in which these soils are managed can influence the flux of GHG by changing one or more of the following: the soil climate (i.e., temperature and water content), the physical/chemical environment of the soil, mineral fertilisers and the amount and chemical composition of organic fertilisers applied to soil. Changes in these variables control the rate and extent of microbial processes, which in turn control the stabilization of carbon (C) in soil and affect the production of greenhouse gas emission (Conrad, 1996). Changes in the soil physical environment affect the aeration and diffusion of these gases.

The production of N_2O in soil is a function of nitrification and denitrification mediated by soil microbes (Robertson and Groffman, 2007; Freing et al., 2012). Factors that regulate N_2O production include available carbon, inorganic N, and oxygen, all of which are affected by soil water, porosity, and aggregate structure (Robertson and Groffman, 2007). Management practices that can influence N_2O emissions include application of fertiliser N (amount, source, timing and placement) (Roberts, 2007), crop selection, tillage, stover management, soil water content and soil temperature (Parkin and Kaspar, 2006).

Within the soil, CO_2 is produced as a result of biological and chemical activities: the decomposition (oxidation) of soil organic materials by heterotrophic micro-organisms and the respiration of plant roots (Hanson et al., 2000; Mosier et al., 2006; Al-Kaisi et al., 2008; Smith et al., 2011). Factors including soil temperature, soil moisture, cropping system, and N availability can influence soil microbial activity (Al-Kaisi et al., 2008) and thus may impact the process of decomposition of soil organic matter and the production of CO_2. Application of nitrogenous fertiliser affects CO_2 emission (1) directly by providing nitrogen to crops and microbes, and (2) indirectly by influencing soil pH, which influences microbial activity (Rastogi et al., 2002).

In soil, CH_4 can be produced without being emitted to the atmosphere because soil is both a producer (source) and consumer (sink) for atmospheric CH_4 (Smith et al., 2011). The net balance of its flux depends on two counteracting processes in the soil: methanogenesis (production by methanogenic bacteria under anaerobic conditions) and methanotrophy (consumption by methanotrophic bacteria mainly under aerobic conditions) (LeMer and Roger, 2001). When the balance between methanogenesis and methanotrophy is positive, the soil is a net CH_4 source, and when the balance is negative, the soil is a net sink. Because the aerobic methane-utilizing bacteria (methanotrophs) are ubiquitous in soils (LeMer and Roger, 2001), upland soils are generally considered as net CH_4 sinks (Smith et al., 2000). Fertiliser N applications have influences on the atmospheric CH_4 uptake by soil (Steudler et al., 1989).

Irrigation is an important way to ensure water supply for crop production and to adapt agriculture to increasing water demand and scarcity due to climate change. On the other hand, irrigation itself might affect climate by altering the capacity of soils to act as sinks or sources of GHGs, in particular, CO_2, N_2O and CH_4 (Lal, 2004).

Many technical measures have been proposed already to mitigate GHGs emissions from agriculture. Among the strategies proposed to diminish N_2O emissions from arable soil, the utilization of N-fertilisers together with a nitrification inhibitor is proposed as a feasible measure to reduce N_2O emissions. The nitrification inhibitor 3,4-dimethylphirazole phosphate(DMPP) has some advantageous properties, namely high efficiency and low risk of translocation, compared to other nitrification inhibitors (Zerulla et al., 2001).

1.2 Importance of the studied crops

Rice is arguably one of the most important cereal crops feeding more than half of world's population. Globally, rice fields cover around 153 million hectares comprising approximately 11 % of the world's arable lands (FAOSTAT 2011). Rice fields are major sources of CH_4 and N_2O and can also be source or sink of CO_2. According to IPPC (2014), rice fields contribute about 30 and 11% of global agricultural CH_4 and N_2O emissions, respectively. Nitrous oxide is produced by the microbial transformation of nitrogen (N) in soils and manures and is often boosted where available N exceeds plant demands, especially under wet conditions (Smith and Conen, 2004). Production of CH_4 is derived by decomposition of organic materials in anoxic flooded rice cultures by the processes of production, oxidation, and transport (LeMer and Roger, 2001). In rice fields, CO_2 is emitted mainly from microbial decay (Janzen, 2004) and soil organic matter (Smith, 2004).

In the European Union about 475,000 ha are devoted to rice with a total production of 3.2 Mt of rice grain (1.8 Mt white rice). Italy is the largest producer, with 52% of the total, followed by Spain with 20%. In Spain, more than one third of the total rice cultivation, about 110,785 ha rice (MAGRAMA, 2013), is spatially concentrated in the Mediterranean eastern part of the country and covers about 3% of the Spanish irrigated area. In the Ebro Valley, the development of rice cultivation is related to the special climatic and soil characteristics of the area. Soil salinity and/or a water table close to the surface do not allow any other crop.

The irrigation system in rice cultivation is continuous flooding and nowadays, chemical fertilisers are the most often used. The autonomous regions of Aragon and Catalonia hold about 42% of Spanish pig herd (MAGRAMA, 2013). The use of pig slurry as fertiliser is the most common recycling method and it could be a strategic alternative to apply it to rice crops. In the Ebro Delta, the poultry sector is also relevant and it produces 51,786 t manure $year^{-1}$ (MAGRAMA, 2013).

The Ebro Valley is one of the most intensive agricultural areas in Spain, where 30% (72 000 ha) of the irrigated area is dedicated to maize (Villar et al., 2002). The maize stover produced in this area ranges from about 14 to 17 t dry matter ha^{-1} $year^{-1}$ (Lloveras et al., 2012) depending on total maize production. Average crop yields in the area range from 10 to 15 t maize grain ha^{-1} (14% moisture) under sprinkler irrigation (Cela et al., 2011).

Under good agronomical conditions, the most efficient farms can produce up to 20 t ha^{-1} (Biau et al., 2013). About 50 % of the farmers at the Ebro Valley incorporate crop stovers to the soil and the rest allot this by-product to animal consumption or any other purposes depending on the price (Biau et al., 2013). Half of the maize-producing lands located in the Ebro Valley, are being fertilised using mineral N where the rest receive organic fertilisers using mainly pig slurry (Sisquella et al., 2004). High yielding maize crops growing in the Spanish agro-systems require water but also a satisfactory input of available nitrogen (N) and a long growing season. In general, N is applied at doses of over 300 kg N ha^{-1} when fertilising only with mineral N (Sisquella et al., 2004). High pre-sowing soil N content is the result of excessive N application (from mineral fertilisers) to previous crops, which tends to accumulate in the soil (Berenguer et al., 2009).

Fruit tree orchards have a historical and economic importance for Mediterranean agriculture, notably in Spain. Fruit tree orchards have the potential to mitigate global warming by sequestrating carbon. In addition, cover crops can be established below the trees protecting the soil from erosion, contributing to soil carbon sequestration (Aguilera et al., 2013). Fruit tree orchards also supply a relevant fraction of the Spanish diet, representing nearly 20 % of dietary energy intake according to FAOSTAT (FAO 2014), mainly in the form of olive oil.

The olive tree (*Olea europapea* L.) is drought-resistant and is usually grown in Mediterranean areas with limited water resources and without irrigation, often with very low levels of productivity. In Mediterranean areas, where summer rainfall is a limiting factor, olive trees respond positively to irrigation, with improved vegetative growth and olive production (Rufat et al., 2014). The economic sustainability of olive tree cropping in Spain and other countries is linked to the ability to fully mechanize farming operations to reduce manpower and to diminish/decrease production costs, while maintaining high production standards, in terms of quantity and quality. A new olive growing system that could potentially allow further reduction in production costs is the super intensive olive grove (super-high-density system). In this system, trees are trained to form hedgerows, orchards can be brought into production within only a few years after planting and over-the row mechanical harvesters can be used (Tous et al., 2010). Therefore, it is essential that the cultivars used in super intensive olive groves have a very low vigour and excellent sensorial features of their oil (Tous et al., 2008, 2010).

On the basis of worldwide evaluations of olive cultivars, at the present time, three olive cultivars are considered to meet these requirements quite well. They are the Spanish Arbequina and Arbosana and the Greek Koroneiki. However, considering the vegetative and productive aspects it is currently widely accepted that among these cultivars, Arbequina is the best one for super intensive olive groves (De La Rosa et al., 2007; Tous et al., 2010; Rufat et al., 2014). Consequently, Arbequina is progressively being introduced into new environments in all olive-growing countries. However, recent trends to high and very high density orchards could lead to an increase on irrigation water and nutrient plant requirements. However, in many olive growing areas, irrigation is scarce and expensive to apply, with deficit irrigation strategies being required to optimize its use.

1.3. The main factors affecting greenhouse gas emission from soil

According to Mosquera et al. (2007), "The production and consumption of both N_2O and CH_4 from soils occurs as a result of different microbial processes, which in turn are controlled by factors that influence the growth of microorganisms (soil O_2 content, soil temperature, mineral N content in organic matter and pH). Soil management practices (land use, nutrient application via manure and N fertiliser, incorporation of either crops or crop residues, tillage, reduction of soil compaction), through their effect on these factors, can indirectly influence these fluxes."

1.3.1. Effect of fertiliser management on greenhouse gas emission

Fertiliser management is a critical element for reducing the environmental impacts of crop fields. Fertilisers applied to soil are not always efficiently used by the crops (Galloway et al., 2003; Cassman et al., 2003). Enhancing the fertiliser use efficiency can reduce GHG emissions especially N_2O and it can also indirectly minimize CO_2 emissions from manufacturing of nitrogenous fertiliser (Schlesinger, 1999). Practices that improve fertiliser use efficiency and decrease GHG emission include the following: precise adjustment of application doses according to crop needs (Zou et al., 2005; Pittelkow et al., 2013), using nitrification inhibitors or slow release fertilisers (Ghosh et al., 2003; Linquist et al., 2012), adjusting application timing and selecting appropriate source (Ali et al., 2012), precise placement of fertilisers into the soil (Linquist et al., 2012), avoiding over applications, or eliminating N applications where possible (Zhang et al., 2010).

1.3.1.1. Effect of nitrogen mineral fertiliser, adjusting fertilisation and matching N supply with demand on greenhouse gas emissions

Many types of fertilisers are used in agriculture, but the most common fertilisers are ammonium nitrate based fertilisers, nitrate based fertilisers, ammonium based fertilisers and urea, and urea based fertilisers. Statistical analyses on the database with measurements of N_2O emissions (Bouwman, 1996; Stehfest and Bouwman, 2006) showed no significant effect of fertiliser type on N_2O emission. However, several studies in which different mineral fertilisers are compared in one experiment often show large differences. In incubation studies, the N_2O emission from nitrate based fertiliser is much higher than from ammonium based fertiliser under wet conditions (e.g. Pathak and Nedwell, 2001). The studies of Clayton et al. (1997), Dobbie and Smith (2003), Velthof et al. (1997) and Jones et al. (2005, 2007) also point at much higher N_2O emissions from nitrate based fertiliser than from fertiliser only containing ammonium, especially during wet conditions. In a field experiment by Leick and Engels (2001) the N_2O emission was slightly higher for the nitrate based fertiliser compared to ammonium sulphate. Urea is considered as an ammonium based fertiliser, since hydrolysis of urea leads to the formation of ammonium. Urea and ammonium sulphate additions potentially affect N_2O emissions because they have different nitrification rates and can have opposite effects on soil pH (Burger and Venterea, 2011). In a meta-analysis of many different crops, Bouwman et al. (2002) reported that urea and ammonium sulphate use resulted in similar N_2O emissions

The dose of fertiliser controls GHG emission, and especially N_2O increases with increased N inputs (Gregorich et al., 2005; Pittelkow et al., 2013). The N_2O emissions by nitrification and denitrification depend on the soil N content (Akiyama et al., 2000), and also on the N-fertiliser applied to the soil (Signor et al., 2013). The use of N-fertilisers influences directly the amount of ammonium (NH_4^+) or nitrate (NO_3^-) available in the soil. The larger the amount of NH_4^+-N in the fertiliser, the larger the nitrification (Mosier et al., 2001; Liu et al., 2005). As a consequence, the emission of N_2O can also increase, because the nitrite (NO_2^-) formed during nitrification can be used as electron acceptor, if O_2 is limited, and also because denitrification can occur after nitrification, when soil conditions are favourable. Emissions of N_2O will also be greater when NO_3^- in the soil is high (Zanatta et al., 2010). When NO_3^- availability decreases, N_2O emissions also decrease, because denitrification is reduced (Hellebrand et al., 2008). On the other hand, N-fertilisation implies a higher plant biomass production, and then more crop residues (and carbon -C- sources) would be available in the soil, that could increase N_2O emissions for a long period, after the N-fertiliser application (Hellebrand et al., 2008).

A generic strategy to reduce N_2O emissions is to avoid excessive application of N in space and time leading also to less indirect emission of CO_2 during N fertiliser production. Huang et al. (2005) reported that N_2O emission increased linearly with the amount of N fertiliser especially at higher doses. Li et al. (2010) found that a reduction in N fertiliser dose had no significant effect on CH_4 emissions, but that 33% reduction in the current average N application dose could result in a 27% decrease in N_2O emission in a rice field.

Recent field studies reported that high N doses can roughly decrease net CH_4 emissions by 30 to 50% from the crop fields (Dong et al., 2011; Yao et al., 2012). Aulakh et al. (2001) reported that the increase in the application of N fertiliser decreased CH_4 emission and increased N_2O emission compared with a control treatment. Zou et al. (2005) also recorded a 75% decrease in CH_4 and a 58% increase in N_2O, when N application was increased from 150 to 400 kg N ha^{-1}. Recent meta-analyses indicate that CH_4 emissions may be N dose dependent, where N addition at low doses tends to stimulate CH_4 emissions but can potentially mitigate CH_4 emissions at high N doses (Banger et al., 2012).

Placement of N fertiliser into the soil near the active root uptake zone may decrease surface N emission and enhance plant N use efficiency resulting in less N_2O emissions. Hussain et al. (2015) pointed out that placing chemical fertiliser in the 6 to10 cm of the top soil layer can significantly increase the N use efficiency and decrease N_2O emissions. Furthermore, splitting N application in different growth stages of the crop can also enhance the N use efficiency and reduce N losses.

Application of N fertiliser to soil would impact decomposition of organic matter only if N is limiting in soil (Brady and Weil, 2008) relative to the amount of organic matter to be mineralized. The amount of N in previously existing organic matter in soil, which typically has a C/N ratio of 10:1, does not limit the occurrence of decomposition (Paustian et al., 1992); however, because newly added plant residues may have a high C/N ratio (larger than 20), short-term carbon dynamics may be affected by the addition of N fertiliser (Snyder et al., 2009). However, over a long period of time, the decomposition rates are likely to balance out. The addition of N fertiliser may just enhance the first steps of decomposition of soil organic matter to some extent or when there are changes in the way organic residues are applied to soil.

Previous research has demonstrated inconsistent results of the effect of N fertilisation on soil microbial biomass and CO_2 emission. Dick (1992) reported that N fertilisation may enhance soil microbial activity by increasing plant biomass production and thus boosting CO_2 emissions. Contrarily to this finding, Ladd et al. (1994) reported that N fertilisation can reduce microbial activity and therefore CO_2 emissions due to decreasing soil pH, depending on the fertiliser reaction. Other studies have also shown that soils fertilised with high N doses produce relatively low soil CO_2 emissions (Wilson and Al-Kaisi, 2008; Ramirez et al., 2010). On the other hand Al-Kaisi et al. (2008) and Ni et al. (2012) found no consistent significant effect of N fertilisation on soil microbial biomass and soil CO_2 emissions in a corn-soybean rotation.

The effects of N fertilisation on CH_4 emissions are complex and sometimes contradictory depending on the source, quantity and method of N application (Lindau, 1994). Although upland soils generally behave as CH_4 sinks, some soils can also behave as CH_4 sources depending on the source of N fertiliser used (LeMer and Roger, 2001). Bronson and Mosier (1993) reported higher CH_4 consumption in unfertilised dryland wheat than in fertilised, irrigated wheat. However, there are also reports that the dose of N application did not affect CH_4 emissions or oxidation from soils (Amos et al., 2005; Mosier et al., 2006).

Research on the effect of timing of N application on soil CO_2 and CH_4 emissions in corn production found greater emissions of CO_2 from soil and greater consumption of CH_4 by soil when N was applied in late spring compared to in early spring (Phillips et al., 2009). The higher level of inorganic N and higher water filled pore space (WFPS) in late spring compared to that in early spring may have contributed to larger soil organic matter mineralization and higher rates of microbial respiration which eventually led to higher CO_2 emissions. Consumption of CH_4 by methanotrophic microbes in soil is generally inhibited by N fertiliser addition, especially by ammonium based N fertiliser, through inhibiting methane monoxygenase enzyme in methanotrophs, the enzyme responsible for methane consumption (Dunfield and Knowles, 1995) both in upland and lowland soils (Bodelier and Laanbroek, 2004). However, Phillips et al. (2009) found that CH_4 consumption was enhanced when N was applied in late spring compared to in early spring. Higher soil CH_4 consumption with later application may have been related to stimulated microbial activity caused by N application at higher soil and air temperatures compared to those in early spring (Phillips et al., 2009).

1.3.1.2. The effect of organic fertilisers application on greenhouse gas emission

Organic fertilisers contribute to GHG emission directly through the release of CO_2, CH_4, and N_2O from C and N compounds present in these amendments, and indirectly through their effects on soil properties thereby inducing GHG emission from soil. Emission of N_2O in manured soils is variable (Lessard, et al., 1998). Most of the difference observed between studies is likely due to soil type and climate, as well as the type and composition of organic fertiliser when measurements are made in the same crop (Lessard, et al., 2000).

Emission of N_2O from soil applied organic fertiliser is controlled by the amount of applied N and C. The higher the amount of applied mineral N and easily mineralizable N, the higher the risk on N_2O emission. Application of total N can be much higher for solid (e.g. chicken manure) than for liquid manure, but much of the N in solid manure is unavailable (i.e., in organic compounds) in the short term for denitrification (Byrnes et al., 1993). With time, the organic N in solid manure would be mineralized and could eventually become available for denitrification. The lower N_2O emission following application of solid manure may result from the uptake of available N by growing plants, which precludes a large build-up of mineral N. Furthermore, short measurement periods (i.e., one year) following application of solid manure may not fully account for the total manure-induced emission of N_2O; hence a full accounting of N_2O from solid manure for a period of several years may be needed to explain the slower release of available N (Gregorich et al., 2005).

The similarity of N_2O emission from soils amended with mineral fertiliser (e.g. urea or ammonium sulphate) and liquid manure (e.g. pig slurry) agrees with the observation that NH_4^+-N constitutes a large fraction (50–70%) of liquid manure N. Liquid manure also contains labile soluble organic C that can stimulate N_2O production where C availability limits denitrification. In soils with low C content, liquid manure has often resulted in greater N_2O emission than mineral fertiliser (Rochette et al., 2000). The similarity in

N_2O emission from soils receiving liquid manure and mineral fertiliser suggests that available C was probably not limited in soils where mineral N was applied (Gregorich et al., 2005).

A meta-analysis of all studies available in Mediterranean climates shared additional insight into organic fertiliser management. Aguilera et al. (2013) found that solid organic fertiliser have determined lower N_2O emissions than even untreated fields and that pig slurries have determined the highest emissions.. Aguilera et al. (2013) suggested that these findings reflect comparatively high doses of N mineralization and high concentrations of NH_4^+. Switching to solid organic fertiliser could reduce emissions by 0.40, 0.56, 0.84, and 0.03 t CO_2-eq ha^{-1} yr^{-1} on synthetic, synthetic/organic mixtures, liquid organic and untreated fields, respectively (Aguilera et al., 2013).

Generally, emission of CH_4 increases by the addition of organic fertiliser and such an increment depends on the quantity and quality of material as well as the timing of its application (Denier van der Gon et al., 2002; Naser et al., 2007).

Organic manure has been widely used in agroecosystems due to their positive roles in soil fertility improvement and climate change mitigation via soil carbon sequestration (Gong et al., 2012). Previous studies have shown various responses of soil CO_2 emissions to applications of organic amendments (Ghidey and Alberts, 1993; Mapanda et al., 2011). The amount of soil CO_2 emissions is dependent on many factors, primarily the type and level of applied organic amendments (Diacono and Montemurro, 2010), as well as the quantity of carbon already in the soil (Six et al., 2002). In fact, soil management, plant cover and soil nutrient status can not only alter soil respiration, but also change the temperature sensitivity of this process (Paz-Ferreiro et al., 2012). Thus, the overall response of soil CO_2 emissions to organic amendments is a complex process and remains uncertain.

1.3.1.3. Effect of crop residues management on greenhouse gas emission

Crop residues may play multiple roles in mediating soil N_2O emissions. As an organic N fertiliser, they are subject to microbial N mineralization and nitrification, leading to N_2O production. In general, this function relies on the N content of crop residues (Toma and Hatano, 2007; Miller et al., 2008; Frimpong and Baggs, 2010). Crop residues also serve as an organic C substrate for microbial growth and therefore stimulate microbial

N assimilation (immobilization). This action often triggers a strong competition for NH_4^+ between heterotrophic microorganisms and autotrophic nitrifiers (Stark and Hart, 1997; Shi and Norton, 2000; Burger and Jackson, 2003), resulting in reduced N_2O production. Furthermore, crop residues can serve as an energy provider for denitrifiers, enhancing denitrification, and, accordingly, N_2O production under anaerobic conditions.

Via influences on relative C and N availability, crop residues also affect N_2O yield, i.e., the ratio of N_2O to N_2 produced. The N_2O yield has been documented to increase with increasing soil NO_3^- availability; N_2O production may account for up to nearly 100% of the total amount of NO_3^- reduction (Terry and Tate, 1980; Weier et al., 1993; Miller et al., 2008). Besides these direct impacts, crop residues can further modify soil aeration by enhancing soil aggregation as well as microbial O_2 demand, therefore increasing the level of soil microsite anaerobicity.

The effects of crop residues on soil N_2O emissions can also be affected by soil physical and chemical properties. For example, soil pH influences on the decay rate of crop residues and therefore N availability for nitrification and denitrification. Soil texture and structure affect pore size distribution, the movement of water through soil, and therefore the soil O_2 status for crop residue degradation and N transformation processes. The effects of crop residue incorporation on the N_2O emissions from soil have been extensively investigated both in the laboratory and on the field (Aulakh et al., 2001; Ma et al., 2010, Montoya-González et al., 2009; Muhammad et al., 2011; Zou et al., 2005), leading to debatable results because of several environmental factors (e.g., soil property, crop residue type, climate, and management practices) vary among different studies.

The incorporation of crop residues can substantially change the availability of soil NH_4^+-N and NO_3^--N, the major factors controlling nitrification and denitrification respectively, and therefore soil N_2O production. Normally, when their C: N ratios are 40, crop residues can provide sufficient N to meet the growth and proliferation of soil microbial community following crop residue amendment, leading to net N mineralization (Vigil and Kissel, 1991).

This extra N supply may stimulate nitrification and/or denitrification, depending on soil aeration conditions and thereby enhancing soil N_2O emissions compared with unamended controls. In contrast, N in crop residues cannot meet the N requirement of microbial growth induced by crop residue C when the C/N ratios of crop residues are

>45 (Vigil and Kissel, 1991). Thus, active microbes will assimilate indigenous soil N into their biomass, causing net N immobilization. Obviously, this N depletion can lessen nitrification and/or denitrification and hence soil N_2O emissions. Heterotrophic microbial growth-associated N assimilation following soil amendment of crop residues has been considered to be the basis for negative relations between soil N_2O emissions and C/N ratios of crop residues (Millar and Baggs, 2005; Garcia-Ruiz and Baggs, 2007; Frimpong and Baggs, 2010).

Li et al. (2013a, b) reported that even at C/N ratios of crop residues above 100, N_2O emissions in crop residue amended soils were significantly larger than the unamended controls under aerobic conditions. This suggests that crop residue addition may affect abiotic factors other than soil inorganic N. It is possible that active microbial growth following crop residue addition consumes sizable O_2 in soil pores, causing a shift in aeration to more anaerobic conditions. As a result, denitrification may replace nitrification and become a major process for N_2O production in some soil pores, thereby enhancing soil N_2O emissions compared with the unamended controls. This heterotrophic microbial growth-induced O_2 depletion should be positively related to the amount of crop residue addition (Millar and Baggs, 2005).

Furthermore, the magnitude of N_2O and CO_2 emissions varies with the types, quality or chemical composition of the residues added to soils (Curtin et al., 1998; Baggs et al., 2000). Usually, larger CO_2 and N_2O emissions were obtained in the soils to which residues of high N content and low lignin content had been incorporated (Millar and Baggs, 2004). Residue consists of many kinds of organic constituents such as cellulose, hemicellulose, lipids, proteins, lignin, etc., and the contribution of each constituent in increasing CH_4 emission is variable. Methane emission fluxes are very sensitive to the mode of straw management into the soil (Millar and Baggs, 2004).

In paddy soils, rice straw and root residues are the main inputs of crop residues to soils, which not only play important roles in nutrient supply and crop yields, but also promote C sequestration when organic C inputs from rice residues exceed CO_2 emissions (Witt et al., 2000; Lu et al., 2003).

Crop residue removal decreased the emission of all three gases as compared with straw incorporation (Baggs et al., 2000). Koga and Tajima (2011) also recorded less CH_4 and CO_2 emissions from residues removed treatments as compared with straw return ones.

Nayak et al. (2013) argued that crop residue addition stimulated CH_4 emission by 108% and inhibited N_2O emission by 21% compared to plots fertilised only with chemical fertiliser.

1.3.1.4. Effect of the use of the nitrification inhibitors (DMPP) on greenhouse gas emission

In order to decrease fertiliser-induced N losses and increase N use efficiency, several chemical compounds which depress nitrification (i.e., nitrification inhibitors: NI) have been developed. Some practical advantages of the use of NI like DMPP (3,4-dimethylpyrazole phosphate) are (i) a significant reduction in the risk of NO_3^- leaching and (ii) a decrease in N_2O emissions (Weiske et al., 2001; Majumdar et al., 2002; Menéndez et al., 2006, 2009; Cui et al., 2011; Pfab et al., 2012). The application of DMPP together with NH_4^+-based fertilisers, cow urine or cattle slurry has demonstrated efficient in reducing N_2O emission and NO_3^- leaching while increasing the yield and use efficiency of fertiliser N in croplands and grasslands (Weiske et al., 2001; Cui et al., 2011; Pfab et al., 2012).

This inhibitor delays the microbial oxidation of ammonium (NH_4^+) to nitrite (NO_2^-) by depressing the activity of *Nitrosomonas sp.* in soil (Weiske et al., 2001; Zerulla et al., 2001). In addition, the use of a NI would also mitigate the CO_2 and CH_4 emissions (Weiske et al., 2001; Maris et al., 2015).

The extent to which DMPP inhibits N_2O emission and NO_3^- leaching is primarily dependent on factors such as rate, time and method of NI application (Barth et al., 2008; Zaman and Nguyen, 2012); field management (irrigation, type, geometry and NH_4^+-based fertilisers application method, Sanz-Cobena et al., 2012); climate (precipitation and temperature, Shepherd et al., 2012); and soil properties (moisture, pH, texture, organic carbon and mineral N, Barth et al., 2001; Shepherd et al., 2012).

Regarding the effect of DMPP on yield, it was demonstrated that the application of DMPP is able to increase or at least maintain, the crop yield and quality parameters (Rufat et al., 2014) while reducing greenhouse gas emissions under Mediterranean conditions (Maris et al., 2015).

1.3.2. The main factors affecting greenhouse gas emission from soil

The addition of water, either by irrigation or rainfall, increases soil moisture content, which affects the soil emissions of all three GHGs. Nowadays, about 18% of the world's croplands receives supplementary water through irrigation (Millennium Ecosystem Assessment, 2005). There are wide variations between EU Member States with regard to water availability, climate and aridity, leading to a heterogeneous agricultural water demand. In arid and semi-arid areas of the EU, including much of Spain, Portugal, Italy, Greece and southern France, irrigation allows crop production where water would otherwise be a limiting factor. In more humid and temperate areas including Denmark, the Benelux states, north and central France, Germany, southern Sweden, south-eastern UK and eastern Austria, irrigation provides a way of regulating the local amount and seasonal availability of water to match agricultural needs. It thus reduces the risks to crops which can arise from unexpected climatic events. In the Mediterranean regions, water has been used for agricultural purposes and today, irrigation is the principal user of water. Irrigation today represents 80% of the total water demand in Spain and nearly 90% of actual water consumption. Most of the water used for irrigation comes from surface water sources (68%). Another important share of water used in agriculture comes from aquifers (28%). Crop types irrigated include a wide variety, from permanent crops (olives, citrus) through annual crops (wheat, maize, rice) to a large number and area of horticultural crops, including a substantial area of glasshouse horticulture in the coastal regions (Magrama, 2014).

The most popular irrigation systems for crops are: sprinkler irrigation, furrow irrigation, continuous flooding (for rice), intermittent flooding, surface drip irrigation and subsurface drip irrigation. The water–use efficiency varies between irrigation systems and it taken into consideration, among other factors, when determining the best irrigation system for a particular field. The choice of irrigation type will then have a different influence on soil moisture and the associated GHG emissions.

The important influence of irrigation on GHG emission can be explained by the fact that in Mediterranean agroecosystems this type of management activity is usually applied during the dry summer period, which leads to optimal moisture and temperature conditions for N_2O, CO_2 and CH_4 production. The typical Mediterranean climate pattern includes a very marked drought period during summer and usually has mild temperatures and an erratic distribution of rainfall over the rest of the year; this contributes to the existence of several wetting and drying cycles.

The application of water through irrigation or rainfall causes increases in GHG emission. The amount of the emissions depends on the amount of water applied and the subsequent soil moisture (Dobbie and Smith, 2001). The N_2O emissions from surface drip irrigation are up to 70% lower than those observed from furrow irrigation in melon crops (Sánchez-Martín et al., 2008). Kallenbach et al. (2010), in California, found N_2O emissions in the growing season from subsurface drip irrigation to be half of those from furrow irrigated tomatoes. Differences between furrow and subsurface irrigation likely resulted from the high denitrification rates caused by furrow irrigation. Kallenbach (2010) and Kennedy (2012) suggest that subsurface drip irrigation could reduce N_2O emissions, but complex interactions among multiple crop management factors make it difficult to quantify precisely how much of the emission reduction is due to the irrigation treatment alone. Future studies should address this limitation and also examine the possible N_2O reductions from drip irrigation systems (both subsurface and surface) if applied in other agro ecosystems. Conversely, CO_2 emissions from furrow and subsurface drip irrigation were similar with no significant difference (Kallenbach et al., 2010). To our knowledge, emission differences between the two types of drip irrigation have not yet been assessed.

Under rainfall or sprinkler irrigation, infiltration is mainly vertical, and water distribution is quite homogeneous onto the soil (Mualem and Assouline, 1996).

Very few studies conducted in Spain have specifically examined the effect of different irrigation practices and technologies on GHG emissions (Sánchez-Martín et al., 2008, Abalos et al., 2014, Vallejo et al., 2014). In all these studies N_2O and CO_2 emission were affected by the type of irrigation. While, emissions of CH_4 were negligible, and no significant differences between the irrigation treatments were found.

1.3.2.1. Effect of irrigation on greenhouse gas emissions from rice paddy soils

When a rice field is flooded, the soil becomes progressively more anaerobic as the O_2 content and redox potential (Eh) both decline through time. In the absence of O_2, decomposition of crop residues and other organic materials is facilitated by anaerobic bacteria that generate CH_4 rather than CO_2 (Horwath, 2011). Gaseous CH_4 is released to the atmosphere either through the rice plant itself (e.g., transported through aerenchyma), direct emission from soil via ebullition, and degassing during drainage. Various soil properties such as temperature, texture, chemical content (e.g., C, $Fe^{3+/2+}$, NH_4^+), and redox status can also affect CH_4 fluxes (Kirk, 2004).

A recent review of emissions from global rice systems suggests that approximately 89% of the systems' total global warming potential (GWP) is attributed to CH_4 of rice fields continuously flooded; the remaining 11% comes from N_2O (Linquist et al., 2012). Practices such as mid-season drainage or flooding period reduction can reduce CH_4 emissions from rice but also promote higher N_2O emissions that offset some of the total emissions reductions (Hou et al., 2000; Johnson-Beebout et al., 2009). However, most studies that consider both CH_4 and N_2O have found that some form of mid-season drainage still yields a net reduction in GHG emissions (Zou et al., 2005; Linquist et al., 2012).

Intermittent irrigation involves alternate flooding and aeration (drying) of the soil throughout the crop rice. It possess the advantage of ameliorating soil oxidative conditions by enhancing root activity, higher soil capacity, and ultimately minimizing water inputs that result in anaerobic conditions. It enhances diffusion of oxygen into the soils increasing the aerobic area and reducing CH_4 production (Linquist et al., 2012). Yagi et al. (1996) stated that intermediate drainage can minimize CH_4 emission by 44% compared with continuous flooding. Adhya et al. (2000) also found a 15% reduction in CH_4 emissions by intermittent drainage with respect to permanent flooding. Methane emissions in intermittent irrigation are generally very low, but N_2O emissions from this system vary in a broad range (250 g N_2O ha^{-1} to 12.4 kg N_2O ha^{-1} according to Kumar et al., 2000; Aulakh et al., 2001; Maris et al., 2015). The countervailing differences in the CH_4 and N_2O fluxes during wetting and drying cycles must be considered when examining how agricultural management might affect overall emissions from rice cultivation.

Intermittent drainage can have a marked effect on soil CO_2 emissions, increasing them considerably (Miyata et al., 2000; Saito et al., 2005). However, the mechanism of CO_2 exchange between rice paddies and the atmosphere is not fully understood (Miyata et al., 2000). Miyata et al. (2000) found a significantly larger net CO_2 flux from rice paddy soils to atmosphere when the field was drained compared to when it was flooded. These differences in the CO_2 flux were mainly due to increased CO_2 emissions from the soil surface under drained conditions resulting from the removal of the diffusion barrier caused by floodwater. The existence of floodwater, anaerobic soil, and changes in the micrometeorological environment influence root activity, photosynthesis, and respiration of the rice plant (Liu et al. 2013). Therefore, it is necessary to investigate soil CO_2 evolution from paddy soils to better understand the mechanisms that regulate carbon storage and loss in extensively cultivated paddy fields.

Various water saving irrigation management modes are currently practiced in paddy fields in the world, including intermittent irrigation, controlled irrigation, flooding-midseason drainage frequent water logging with intermittent irrigation, and flooding-midseason drainage flooding-moist intermittent irrigation but without water logging (Belder et al., 2004; Mao, 2002). Water saving irrigation management modes is not currently practiced in paddy fields in Spain. In the present thesis, testing the intermittent irrigation has proven effective in reducing water input, but has caused yield reduction compared with continuous irrigation. Moreover, the global warming potential was the highest in intermittent irrigation (4738.39 kg CO_2 ha^{-1}) and the lowest in continuous irrigation (3463.41 kg CO_2 ha^{-1}) (Maris et al., 2015). These results suggest that the application of good practice in paddy fields in Spain: applying a suitable intermittent irrigation can result in a good yield. It also implies the saves water and may possibly reduce GHG emissions. Avoiding water saturation when rice is not grown and shortening the duration of continuous flooding during the rice growing season are effective options for mitigating GHG emissions from rice fields. The implications of shifting from a permanent flooding to an intermittent irrigation system on rice environment and productivity will be assessed through monitoring of water consumption, soil salinity, plant x soil x microbial community interactions, GHG emission, soil chemistry. In addition, it should be identified the rice cultivars varieties that maintain high yield under this system irrigation.

The wet–dry cycles of water saving irrigation changes the agro-ecosystem, including the soil properties, soil water cycle and soil N transfer, transformation and losses (Yang et al., 2015). Therefore, further studies on N use efficiency and loss from paddy fields with joint application of controlled release N fertiliser and water saving irrigation are necessary to identify water and N management practices that can minimize environmental pollution while maintaining rice yield.

Moreover, the "Climate Smart" Agriculture sourcebook sugests that use the efficiency of a Alternate Wetting and Drying rice production system (AWDS) consisting in flooding the fields with a water layer 2-5 cm deep and then leaving the water level to drop below the soil surface before the fields are reflooded again. It is estimated that, if done properly, this system may reduce water input by 15-30% and GHG emission reduced by up to 48% without yield penalty. For this reason the present study can be considered a large opportunity to understand how the intermittent irrigation affects greenhouse gases emission from a paddy soil under Mediterranean conditions. Under these condition the present study can be included or considered in the context of a “Climate Smart Agriculture”, which relates production increase in future agriculture to both adaptation to climate change and mitigation of greenhouse gas emissions.

1.3.3.2. Effect of soil moisture on greenhouse gas emissions from soil

Alternating wetting and drying cycles that permit nitrification to progress, and water filled pore space WFPS above about 60% but below saturation, are conditions for the largest potential for N_2O emissions (Granli and Bøckman, 1994). The magnitude of N loss is controlled by the interaction of soil moisture and N availability, principally NO_3^- availability (McSwiney and Robertson, 2005). Proper irrigation practices to improve water use efficiency, and to avoid moisture excesses associated with reductions in air-filled pore space, may help minimize the potential for N_2O emissions.

Maximum CO_2 emission from soils has been found at intermediate soil moisture contents when WFPS is between 20 and 60%, and vary depending on crop type and location (Schaufler et al., 2010). In both very wet and very dry soils, soil respiration is restricted which limits CO_2 emissions (Smith et al., 2003). Wetting of a dry soil tends to increase CO_2 emissions due to the fact that there are increases in the respiration rate (Orchard and Cook, 1983). The relationship between CO_2 emissions and soil moisture also depends on the type of crop. For instance, Lee et al. (2009) observed that the CO_2 fluxes increased with increases in soil moisture for soils planted with maize but not sunflower or chickpea, due to differences in management practices. Similarly Gillam et al. (2008) found that denitrification was primarily controlled by soil O_2 supply, WFPS and C availability, and the $N_2O/(N_2O+N_2)$ ratio was generally high where there was abundant moisture, but not saturated conditions.

Methane uptake, in cultivated soils, shows a strong negative correlation with increasing soil moisture, which is likely due to the decreasing aeration in the soil (Lessard et al., 1994; Flessa et al., 1995). Emissions of CH_4 are most noted under waterlogged conditions (Smith et al., 2003). The contradicting effects of soil moisture and temperature on the simultaneous production and oxidation of CH_4 could counteract each other (Schaufler et al., 2010).

1.4. References

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Chapter 2. Objectives

Chapter 2. Objectives

The main hypothesis of this study is that the use of different types of fertiliser (organic or mineral) and irrigation systems have a significant impact on greenhouse gases (N_2O, CO_2 and CH_4) and there is wide scope to reduce the amount of N_2O, CO_2 and CH_4 emitted, controlling direct and indirect factors associated with N fertilization and irrigation. Therefore, **the broad objective of this thesis is**: "To evaluate how nitrogen and irrigation management practices influence on greenhouse gas (CO_2, CH_4 and N_2O) and N_2 emissions from rice and irrigated maize and super-intensive olive trees"

The specific objectives of this thesis are:

(1) To determine the effect of irrigation frequency (continuous irrigation and intermittent irrigation) on the emission of greenhouse gases (CH_4, CO_2, N_2O), and N_2 from a paddy soil at the Ebro Delta (NE Spain);

(2) To compare the effect of urea, ammonium sulphate, chicken manure and pig slurry applied at different doses on the emission of N_2O, N_2, CH_4 and the ecosystem respiration (CO_2) during the seedling period, the rice crop season and the postharvest period under Mediterranean conditions in a rice field;

(3) To compare the effect of two contrasting maize (*Zea mays* L.) stover management practices (incorporation or removal) combined with different ammonium nitrate fertiliser doses, on the emission of greenhouse gases (N_2O, CH_4 and CO_2) in a soil with a high mineral N (200 g N kg^{-1} on average) content.

(4) To compare the effect of applying two different irrigation strategies (subsurface drip irrigation (SDI) and, surface drip irrigation (DI)) in combination with mineral N applied via fertigation with and without DMPP on the GHG emissions from a high density Arbequina olive tree orchard.

This document consists of four independent chapters presented in the format of a journal article. For this reason, some parts, such as the material and methods section, may contain a certain degree of repetition.
Some of the chapters have already been accepted for publication in scientific journals, while others are currently under revision.

Chapter 3. Material and methods

Chapter 3. Material and methods

3.1. Localisation of the experimental sites

- The effect of irrigation frequency on the greenhouse gases (GHG) emission was studied at the Institute for Food and Agricultural Research and Technology (IRTA), in its Amposta station, Catalonia, Spain. (Fig 3.2.1).
- Effect of organic and mineral fertilisers on greenhouse gases emission from Mediterranean rice paddy soils: the experiment was carried out at two rice paddies located at two different sites in the Mediterranean Ebro Valley (NE Spain), representative of the agricultural practices in the Valley. Site 1 is located at the Institute for Food and Agricultural Research and Technology (IRTA), at its Amposta station in the Ebro River Delta. Site 2 is located at Villanueva de Sigena (Fig 3.2.1).
- Effect of stover management and nitrogen fertilization on greenhouse gases emission from irrigated maize in a high nitrate-N soil was carried out at a maize field (*Zea mays* L.) located at Almacellas (NE Spain) (Fig 3.2.1).
- Effect of irrigation, nitrogen application, and a nitrification inhibitor on nitrous oxide, carbon dioxide and methane emissions from an olive (*Olea europaea* L.) orchard: was carried out at a commercial high tree density (1010 trees ha^{-1}) adult olive tree plantation (*O. europaea* L. cv. Arbequina) located at Torres de Segre (Lleida, Catalonia, Spain) (Fig 3.2.1).

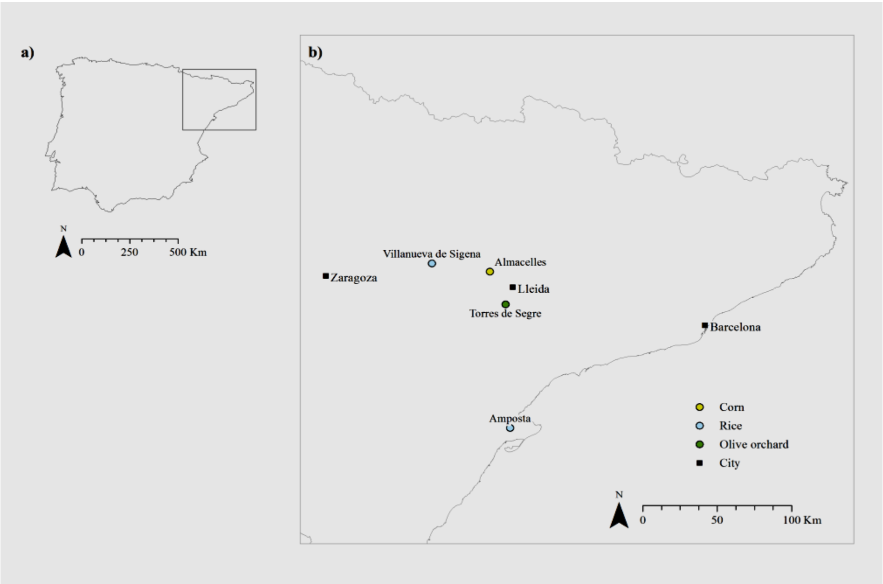

Fig 3.2.1 Localisation of the experimental sites

3.2. Gas sampling and analysis

The N_2O, N_2O+N_2, CO_2 and CH_4 emissions were always sampled weekly using the closed chamber method and the gas samples were quantified by means of the photoacoustic technique (Innova 1412 Photoacoustic Multigas Monitor; Fig. 3.2.1). The closed chamber method and the acetylene (C_2H_2) inhibition method were applied in the field for rice and in the laboratory for the super-intensive olive tree orchard.

Fig. 3.2.1 Photoacoustic analyser (Innova 1412 Photoacoustic Multigas Monitor)

On the rice and maize crops the N_2O, N_2O+N_2, CO_2 and CH_4 emissions were sampled weekly directly in the field using the cylindrical static chamber. For sampling on the waterlogged rice crop cylindrical (20 cm diameter and 60 cm high) static chambers were made of polyvinyl chloride (PVC) coated with an epoxy resin and was inserted 18 cm into the soil. While, on the maize crop the cylindrical static chambers were only 19 cm diameter and 22 cm high, and were inserted only 5 cm into the soil (Fig. 3.2.2 a and b).

Fig. 3.2.2 Views of the gas sampling chambers used on maize (a) and on rice (b)

This cylinders were closed with a vented screwed lid with a three-way key. Air samples from inside the chamber were taken in duplicate immediately after closing the chamber, and 20 and 40 min later. Samples were taken through a Teflon® tube connected to the three-way key and into 100 ml plastic syringes adapted with a valve (Fig. 3.2.3).

Fig. 3.2.3 Taking samples of air inside the closed chamber

Before sampling, air within the chamber was mixed by filling and emptying the syringe six times before withdrawing the sample. After taking the gas sample the syringes were closed by the valve. After 40 min of sampling the three-way keys were left open until the sampling with acetylene.

The acetylene (C_2H_2) inhibition method (Balderson et al. 1976; Yoshinari and Knowles, 1976) was used to inhibit the last step of denitrification (N_2O to N_2) and it was applied only on the rice crop. Ten percent (v/v) of the air enclosed in the chamber was replaced by C_2H_2 (Fig. 3.3.3).

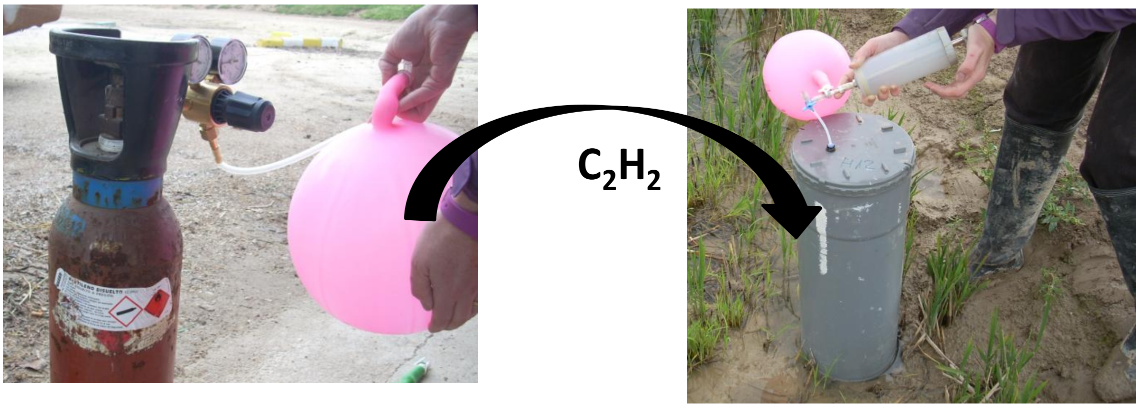

Fig. 3.3.3 Ten percent (v/v) of the air enclosed in the chamber was replaced by C_2H_2

After C_2H_2 was allowed to diffuse into the soil for 20 min, samples were taken as described in the previous paragraph. After 40 min of sampling the three-way keys were left open until the following sampling and the chambers were removed from the field and cleaned properly with water.

The syringes were transported to the laboratory and the concentrations of N_2O, CO_2 and CH_4 in the sampled air were analyzed using the photoacoustic technique (Innova 1312 Photoacoustic Multigas Monitor) (Fig. 3.3.4).

Fig. 3.3.4 Analysing the samples of N_2O, CO_2, CH_4 and N_2O+N_2 using the photoacoustic technique

The N_2O, CO_2 and CH_4 emission fluxes were determined from the linear increase of gas concentration at each sampling time (0, 20 and 40 min) during the time of chamber closure. The cumulative emission throughout the study period was calculated by integrating the emission curve through time. During N_2O, CO_2 and CH_4 emission monitoring, soil temperature at a depth of 5 cm was determined by means of a thermometer.

In the super-intensive olive tree orchard undisturbed soil cores, which were 15 cm long and 7 cm in diameter, were taken weekly, using PVC tubes. The soil cores were placed on a lid immediately after withdrawing them from the soil. This lid was kept on place until the samples were weighted to gravimetrically determine their water content (Fig. 3.3.5).

Fig. 3.3.5 The PVC tubes used to take undisturbed soil cores from the super-intensive olive tree orchard

The undisturbed soil cores were taken from the wet topsoil of the bulb generated by the irrigation system and immediately brought to the laboratory (Fig. 3.3.6).

Fig. 3.3.6 The undisturbed soil cores were taken from the wet bulb

The total time spent every sampling day to withdraw the soil cores was about 1 h. The samples were immediately taken to the laboratory (inside an insulated closed cage) which was only 15 min drive away from the field. This procedure began one week before the start of irrigation and continued until irrigation finished. Nitrous oxide, CO_2 and CH_4 fluxes were measured in the laboratory using the closed chamber method.

Each soil core collected in the PVC cylinder was placed in a glass jar (1.5 L) with an air-tight glass lid. Each of these lids was equipped with a three-way key which was directly connected to a photoacoustic analyser via a Teflon® tube (Fig. 3.3.7).

Fig. 3.3.7 The glass jars (1.5 L) with air-tight glass lids, containing the undisturbed soil cores collected in the PVC cylinders (a) and the connection between the glass jars and the photoacoustic analyser (Innova 1412 Photoacoustic Multigas Monitor) via Teflon® tubing (b)

The glass jars were hermetically closed for 40 minutes during which the photoacoustic analyser withdrew and analyzed gas samples at times 0, 20 and 40 minutes after closing. The glass jars lids' were left open to allow the inside and outside gases concentrations and pressures to equilibrate before proceeding with the acetylene inhibition method.

The acetylene (C_2H_2) inhibition method (Balderston et al., 1976; Yoshinari et al., 1976) was used to inhibit the last step of denitrification (N_2O reduction to N_2). Ten percent (v/v) of the air enclosed in the chamber was then replaced by C_2H_2. This replacement inhibited the reduction of N_2O to N_2 (Federova et al., 1973). After the C_2H_2 had been allowed to diffuse for 20 min, the gas inside the jars was analysed for N_2O as described in the previous paragraph. Forty min after sampling, the glass jars were emptied and left open.

Surface soil temperature (at a depth of 10 cm) was recorded always during sampling in the field. The photoacoustic analyser refers the gases concentration to 20ºC and 1 atm; the concentration was corrected to be referred to the actual field temperature and atmospheric pressure of each sampling day. Sampling was done at the time of the day when soil temperature was about the average soil temperature of the day in order to minimize over or underestimation of the emission caused by daily soil temperature fluctuation.

A value for molecular nitrogen emission was obtained by substracting N_2O emissions without acetylene from N_2O emissions with acetylene (Ryden et al., 1979).

3.3. Soil moisture and soil temperature

After the gas analysis, the soil samples were dried at 105ºC to a constant weight in order to gravimetrically determine moisture content. Water-filled pore space (WFPS) was then calculated by dividing the volumetric water content by the total soil porosity. Total soil porosity was determined by measuring the bulk density of the soil according to the following relationship: soil porosity = (1 - soil bulk density)/PD), with PD representing the particle density, which for this soil texture was assumed to be 2.65 g cm^{-3} (Porta et al., 2008).

Actual rainfall and temperature data were obtained from the closest meteorological station to each experimental site (Meteorological Service of Catalonia and of Aragon http://www.ruralcat.net/web/guest/agrometeo.estacions and www.aragon.es/Clima_Datos_climatologicos

Chapter 4. Influence of irrigation frequency on greenhouse gases emission from a paddy soil

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ARTICLE

Influence of irrigation frequency on greenhouse gases emission from a paddy soil

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Abstract Water management is known to be a key factor on methane (CH_4), carbon dioxide (CO_2), and nitrous oxide (N_2O) emissions from paddy soils. A field experiment was conducted to study the effect of continuous irrigation (CI) and intermittent irrigation (II) on these emissions. Methane, CO_2, and N_2O emissions from a paddy soil were sampled weekly using a semi-static closed chamber and quantified with the photoacoustic technique from May to November 2011 in Amposta (Ebro Delta, NE Spain). Intermittent irrigation of rice paddies significantly stimulated ($N_2O + N_2$)–N emission, whereas no substantial N_2O emission was observed when the soil was re-wetted after the dry phase. The cumulative emission of ($N_2O + N_2$)–N was significantly larger from the II plots (0.73 kg N_2O–N ha^{-1} $season^{-1}$, $P < 0.05$) than from the CI plots (-1.40 kg N_2O–N ha^{-1} $season^{-1}$). Draining prior to harvesting increased N_2O emissions. Draining and flooding cycles controlled CO_2 emission. The cumulative CO_2 emission from II was 8416.35 kg CO_2 ha^{-1} $season^{-1}$, significantly larger than that from CI (6045.26 kg CO_2 ha^{-1} $season^{-1}$, $P < 0.05$). Lower CH_4 emission due to water drainage increased CO_2 emissions. The soil acted as a sink of CH_4 for both types of irrigation. Neither N_2O–N nor CH_4 emissions were affected by soil temperature. Global warming potential was the highest in II (4738.39 kg CO_2 ha^{-1}) and the lowest in CI (3463.41 kg CO_2 ha^{-1}). These findings suggest that CI can significantly mitigate the integrative greenhouse effect caused by CH_4 and N_2O from paddy fields while ensuring the highest rice yield.

Keywords Water management · Intermittent irrigation · Continuous irrigation · Ammonium sulfate

Introduction

Global warming induced by increasing greenhouse gases (GHG) concentration in the atmosphere is a matter of great environmental concern. Methane (CH_4), carbon dioxide (CO_2), and nitrous oxide (N_2O) are important long-living GHG, which have attracted considerable attention during the last decades because of their contribution to global warming. The agroecosystem plays a significant role in the global budget of GHG (Hou et al. 2012). Agriculture is responsible for about 50 % of the global anthropogenic CH_4, and for 60 % of N_2O (IPCC 2007), and can be an important source of trace gases or can act as a major sink. Agricultural CH_4 and N_2O emissions have increased by nearly 17 % from 1990 to 2005 (IPCC 2007), and agricultural N_2O emissions are predicted to increase between 23 and 60 % by 2030 due to increased chemical and manure nitrogen inputs (FAO 2010). Paddy fields are considered to be an important source of anthropogenic CH_4, N_2O (Hou et al. 2012), and CO_2 (Liu et al. 2013). Atmospheric CH_4 from rice fields will further increase with the increasing rice harvested area in the years to come (Cai et al. 2007).

Rice is the staple food of nearly 50 % of the world's population. Rice planting areas account for about 20 % of the world total. In Spain, rice covers about 3 % of the Spanish irrigated area (about 11,0785 ha rice) (http://www.magrama.gob.es/es/estadistica/temas/estadisticas-agrarias/

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agricultura/esyrce/, accessed 12 January 2015). Hence, it is interesting to study CH_4 and N_2O emissions from Spanish paddy fields.

Water management has been recognized as one of the most important practices that affect CH_4, CO_2, and N_2O emission from paddy fields (Xiong et al. 2007; Liu et al. 2010; Hadi et al. 2010; Hou et al. 2012). In Spain, the most typical water management of paddy fields involves continuous flooding to improve rice growth and increase yields. The influence of water management on CH_4 and N_2O emission from paddy fields under continuous flooding and intermittent irrigation has been well documented in the climatic conditions of China, Japan, and India (Panthak et al. 2003; Zheng et al. 2004; Zheng et al. 2006; Hadi et al. 2010; Hou et al. 2012; Suryavanshi et al. 2013) but not in the Mediterranean climate, especially in the Ebro Delta (Spain). Continuously flooded rice fields have a high potential for CH_4 emission, while N_2O emissions are negligible. However, Nugroho et al. (1994) reported that intermittent drainage did not affect CH_4 emission or, inversely, sometimes resulted in higher CH_4 emission than continuously flooded soil in Indonesia. Nitrous oxide emissions during intermittent irrigation depend greatly on whether or not water logging is present in paddy soils (Zou et al. 2005). Intermittent drainage has been proposed as a water management technique to reduce CH_4 emission from paddy soils; it is also useful for the removal of hazardous organic components in rice rhizosphere and to increase the availability of some nutrients (Hadi et al. 2010). Intermittent irrigation has been shown to mitigate CH_4 emissions compared with continuous flooding (Zou et al. 2009; Liu et al. 2010). Draining a paddy soil prior to harvesting increased N_2O emissions (Hadi et al. 2010).

Intermittent drainage can have a strong effect on soil CO_2 emissions, increasing them considerably (Miyata et al. 2000; Saito et al. 2005). However, the mechanism of CO_2 exchange between rice paddies and the atmosphere is not fully understood (Miyata et al. 2000). For example, using eddy covariance measurements, Miyata et al. (2000) found a significantly larger net CO_2 flux from rice paddy soil to atmosphere when the field was drained compared to when it was flooded. These differences in the CO_2 flux were mainly due to increased CO_2 emissions from the soil surface under drained conditions resulting from the removal of the diffusion barrier caused by floodwater. The existence of floodwater, anaerobic soil, and changes in the micrometeorological environment influence root activity, photosynthesis, and respiration of the rice plant (Liu et al. 2013).

Soil properties (such as soil moisture, soil oxygen status, soil redox potential, and soil temperature) and microbial activity in continuous irrigation (CI) paddy fields are very different from those in intermittent irrigation (II) rice fields, and induce changes in CH_4, CO_2, and N_2O emissions. To our knowledge, very few studies have been made on the quantification of CH_4, CO_2, and N_2O emissions from CI and II paddy fields in Spain. In the present study, the CH_4, CO_2, and N_2O–N and ($N_2O + N_2$)–N emissions from paddy fields with two types of water management (CI and II) were measured during one cropping season (from May to November 2011). The aim of this study was to determine the effect of irrigation frequency (continuous irrigation and intermittent irrigation) on the emission of greenhouse gases (CH_4, CO_2, N_2O–N), N_2, and the global warming potential (GWP) from a paddy soil at the Ebro Delta (NE Spain) to know the environmentally sound irrigation practice.

Materials and methods

Experimental design

The experiment was conducted in 2011 on experimental plots at the Institute for Food and Agricultural Research and Technology (IRTA), in its Amposta station (40°39′19.02″N, 00°47′01.2″W), Catalonia, Spain. This region has a Mediterranean climate with an average annual temperature of 17 °C and a mean annual precipitation of 550 mm. Soil texture in the experimental site is silty clay loam (3.5 % total sand, 61.7 % total silt, and 34.8 % total clay), which is representative of the soil type in this region. The main (0–20 cm depth) properties of this soil are 2.34 % organic matter, 3 mg NO_3^-–N kg^{-1}, 6 mg NH_4^+–N kg^{-1}, 44 mg total P-Olsen kg^{-1}, 158 mg total K kg^{-1}, and pH 8.1. The experiment involved two irrigation treatments: continuous irrigation (CI) and intermittent irrigation (II). Each treatment had three replicates established in a randomized block design in six plots of an approximate size of 30 m^2 (5 × 6 m) each. Irrigation started on 15th March and the field was flooded until 1st June.

In the CI treatment, a water layer of 10 cm was kept until 12th September when the field was drained. Harvesting took place on 20th September. In the II treatment, soil was flooded as in the continuous flooding system (10 cm water layer), but the irrigation was suspended until the water layer disappeared, at that moment it was irrigated again. Ten irrigations were done during the growing season to the II treatment, and each irrigation lasted for approximately 1 day. The final drainage was applied on 12th September and harvesting took place on 16th September. In Spain, rice is permanently flooded for most of the growing season, although short drainage periods may be needed to correct specific crop disorders dependent on herbicide application, etc. Rice (*Oryza sativa* L.) cultivar *Gleva* was sown directly on site on 9th May in both treatments (II and CI) at a density of 170 kg ha^{-1}. Fertilizers, herbicides, and pesticides were applied in accordance with local conventional practice. To minimize the impact of weeds on yield, Molinate and Bentazona herbicides combined with cultural practices were used. Puddling before sowing and weeding by hand (until the rice plant has become so tall that cannot be weeded without damage) were performed, especially for the so-called wild rice, red rice or "crodo" as it is called in Italy. Two applications of fungicide (Benzotiazol at a dose of 300 g ha^{-1}) were done on 26th July and on 19th August. Nitrogen fertilizer was applied at a rate of 170 kg N ha^{-1} as ammonium sulfate (21 % N richness). To improve N utilization, N was applied 33 % on the 6th May, 33 % on the 10th June, and 33 % on the 12th July. Phosphorous and K were applied on 6th May to all the plots, at 57 kg P_2O_5 ha^{-1}, and 57 kg K_2O ha^{-1}.

Sampling and measurements

Gas samples were collected using the closed chamber method at an interval of 7 days throughout the period of rice growth (Peng et al. 2011; Hou et al. 2012). The cylindrical (20-cm diameter and 60-cm high) static chamber was made of polyvinyl chloride (PVC) coated with an epoxy resin and was inserted 18 cm into the soil each sampling day on the 6 plots. This cylinder was closed with a vented screwed lid with a three-way key. Air samples from inside the chamber were taken in duplicate immediately after closing the chamber, and 20 and 40 min later. Samples were taken through a Teflon tube connected to the three-way key and into 100-ml plastic syringes adapted with a valve. Before sampling, air within the chamber was mixed by filling and emptying the syringe six times before withdrawing the sample. After taking the gas sample, the syringes were closed by the valve. After 40 min of sampling, the three-way keys were left open until the sampling with acetylene.

The acetylene (C_2H_2) inhibition method (Balderston et al. 1976; Yoshinari and Knowles 1976) was used to inhibit the last step of denitrification (N_2O–N_2). Ten percent (v/v) of the air enclosed in the chamber was replaced by C_2H_2. After C_2H_2 was allowed to diffuse into the soil for 20 min, samples were taken as described in the previous paragraph. After 40 min of sampling, the three-way keys were left open until the following sampling and the chambers were removed from the field and cleaned properly with water.

The syringes were transported to the laboratory and the concentrations of N_2O, CO_2 and CH_4 in the sampled air were analyzed using the photoacoustic technique (Innova 1312 Photoacoustic Multigas Monitor). The N_2O, CO_2, and CH_4 emission fluxes were determined from the linear increase of gas concentration at each sampling time (0, 20, and 40 min) during the time of chamber closure. The cumulative emission throughout the study period was calculated by integrating the emission curve through time. During N_2O, CO_2, and CH_4 emission monitoring, soil temperature at a depth of 5 cm was determined by means of a thermometer. In this study, water-filled pore space (WFPS) was calculated according to the following equation (Peng et al. 2011):

$$\text{WFPS}\ (\%) = (\text{Gravimetric water content}\ (\%)) \\ /\text{Total soil porosity} \times \text{Soil bulk density} \times 100,$$

where total soil porosity = (1 − soil bulk density)/2.65, with 2.65 g cm^{-3} as the assumed particle density of the soil (Porta et al. 2008).

Nitrogen gas emission was obtained by subtracting N_2O emission without acetylene from N_2O emission with acetylene (Ryden et al. 1979), and then the N_2O–N/(N_2O + N_2)–N ratio was calculated.

Since the chambers were not transparent, it cannot be assumed that the CO_2 flux was the net flux, as photosynthesis was ignored.

Global warming potential (GWP)

Global warming potential (GWP) is an index defined as the cumulative radiative forcing between the present and some chosen later time "horizon" caused by a unit mass of gas emitted now. In GWP estimation, CO_2 is typically taken as the reference gas, and an increase or reduction in emission of CH_4 and N_2O is converted into "CO_2-equivalents" through their GWPs. The GWP for CH_4 (based on a 100-year time horizon) is 25, whereas that for N_2O is 298, when the GWP value for CO_2 is taken as 1 (IPCC 2007). GWP of CH_4, N_2O, and CO_2 emissions was calculated using the following equation (IPCC 2007): GWP = cumulative CO_2 emission + cumulative CH_4 emission × 25 + cumulative N_2O emission × 298.

Statistical analysis

Statistical analyses of data were carried out using the JMP ver. 10 (SAS Institute Inc., Cary, USA). Daily emission fluxes, as well as the estimated seasonal emission data, were checked for normal distribution. A *t* test was used to examine the statistical significance of the parameter estimates. An analysis of variance (ANOVA) *F* test partitioned the total variation of the results. A one-way ANOVA was used to test whether the cumulative emissions depended on the water regime.

Results and discussion

The coefficients of variation (CV%) of N_2O–N and ($N_2O + N_2$)–N ranged from 199 to 477 %. Such high uncertainties are unfortunately common in this kind of study.

Grant and Pattey (2003) obtained coefficients of variation from 30 to 100 %. Our CV was in the same range as that reported by Flessa et al. (1995) and Thornton et al. (1996) (CV > 150 %), but lower than described by Teira-Esmatges et al. (1998). A review on N_2O studies with a much greater number of replicates than the one reported here was done by Mosier et al. (1996), revealing that it is not the measurement technique that provides most of the uncertainty in N_2O flux values in the literature but rather the diverse combination of physical and biological factors that control gas fluxes.

Nitrous oxide and molecular nitrogen emission

The measured N_2O fluxes differed considerably from day to day, probably due to the changes in soil temperature and water content. The measured emission fluxes ranged from −71 to 384 g ($N_2O + N_2$)–N ha^{-1} day^{-1} in CI, and from −113 to 526 g ($N_2O + N_2$)–N ha^{-1} day^{-1} in II (Fig. 1), which is broader than many of the ranges reported in the literature (Peng et al. 2011; Hou et al. 2012).

Emission from the soil depends on (Teira-Esmatges et al. 1998) (i) the formation of N_2O during denitrification and nitrification and its diffusion to the headspace, and (ii) the consumption of N_2O through its reduction to N_2 during denitrification and the diffusion rate of N_2O from the headspace into the soil. When N_2O consumption was larger than its emission, the N_2O concentration in the headspace decreased resulting in negative fluxes of N_2O. Negative fluxes indicate that the soil acted as a sink for N_2O.

The evolution of the daily ($N_2O + N_2$)–N fluxes from the CI is quite parallel to that from the II treatment (Fig. 1). The ($N_2O + N_2$)–N emission fluxes from the II paddy plots were higher than those from the CI plots for most of the rice-growing season. The average daily flux of ($N_2O + N_2$)–N in the II fields (178.2 g ha^{-1} day^{-1}) was 1.5 times higher than in the CI fields (115.18 g ha^{-1} day^{-1}). The highest peak of ($N_2O + N_2$)–N emission flux from the II paddy fields (526.44 g ha^{-1} day^{-1}, 1.72 times that from the CI paddy fields) was observed on measurement day 91 in the physiological maturity period, which coincides with the day when the soil temperature was the highest (27.0 °C in the CI plots and 27.8 °C in the II plots). Other four peaks of ($N_2O + N_2$)–N emission flux from the II fields were observed (Fig. 1). In the CI plots, another three peaks of ($N_2O + N_2$)–N emission were observed (Fig. 1). The peaks in II are mainly due to mineral fertilizer application (days 14 and 62 of sampling) and to the high soil water content, while peaks in CI are mainly due to the application of mineral fertilizer (day 62 of sampling) and to draining (days 42, 91 and 118 of sampling).

After fertilization, on measurement days 14 and 48, the ($N_2O + N_2$)–N flux increased along with soil temperature, probably because the concentration of NH_4^+–N and of NO_3^-–N in soil solution increased. Toshiaki et al. (2007) reported that the development of denitrifying bacteria activity along with the rise of soil temperature might account for the high N_2O emissions.

Under CI, the ($N_2O + N_2$)–N flux was lower than under II. One possible reason for this may be the dissolution of N_2O in the flooding water. Toshiaki et al. (2007) reported that the N_2O concentration in flood water was as high as between 0.65 and 10.4 µg l^{-1}. He proposed that the

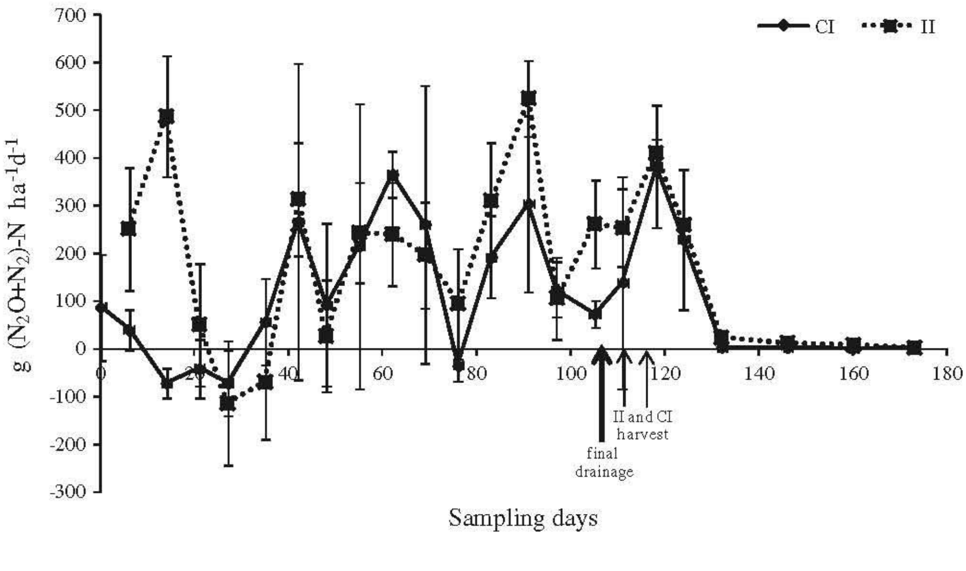

Fig. 1 Daily flux of ($N_2O + N_2$)–N from the paddy soils under different water management practices through the sampling season. The *vertical arrow* on day 112 of measurement indicates the harvest of rice in the II treatment, and that on day 116 indicates the harvest of rice in the CI treatment. *II* intermittent irrigation, *CI* continuous irrigation. *Vertical lines* indicate the standard error of the average ($n = 3$)

$(N_2O + N_2)$–N emission can be mitigated considerably by a thin film of flooding water on paddy soils, which is already common practice in the Ebro Delta.

Intermittent irrigation clearly increased the $(N_2O + N_2)$–N fluxes from the rice paddy. Smith and Patrick (1983) observed that alternate anaerobic and aerobic conditions considerably increased N_2O fluxes relative to continuous anaerobic and aerobic conditions, and that the net N_2O flux increased when the duration of both the anaerobic and aerobic periods was increased from 7 to 14 days.

In this experiment, the time between the disappearance of the floodwater layer and reflooding was usually about 1 week. The results are consistent with those reported by Cai et al. (1997) and Toshiaki et al. (2007) who showed that the soil water content associated with maximum N_2O emissions was normally close to field capacity. At about this soil water content, either nitrifiers or denitrifiers may be N_2O generators. Yagi et al. (1996) showed that water management with very short anaerobic–aerobic cycling induced a very low N_2O emission in a Japanese paddy field.

The results of the present study suggest that II of rice paddies significantly stimulated $(N_2O + N_2)$–N emission. The cumulative emissions during the sampling period were 25.05 kg $(N_2O + N_2)$–N ha^{-1} $season^{-1}$ in CI and 34.12 kg $(N_2O + N_2)$–N ha^{-1} $season^{-1}$ in II (Table 1). The cumulative $(N_2O + N_2)$–N emission from the II plots was 1.36 times greater than that from the CI plots. Felber et al. (2012) estimated that the total denitrification loss of nitrogen $((N_2O + N_2)$–N) is in the range of 6–26 kg N ha^{-1} $year^{-1}$, albeit with uncertainties close to 100 %.

The measured daily N_2O–N emission fluxes cover a shorter range of emissions than the $(N_2O + N_2)$–N emissions though broader than many of the ranges reported in the literature (Aulakh et al. 2001; Ma et al. 2012). They ranged from −119.66 to 116.07 g N_2O–N ha^{-1} day^{-1} in CI, and from −114 to 79 g N_2O–N ha^{-1} day^{-1} in II (Fig. 2). Ma et al. (2012) and Hadi et al. (2010) also reported negative N_2O–N fluxes. In CI, 48 % of the N_2O–N flux measurements were negative, and 8.3 % were >100 g of N_2O–N ha^{-1} day^{-1}. In II, 27 % of the N_2O–N flux measurements were negative and 6.25 % were >50 g of N_2O–N ha^{-1} day^{-1}. The drain applied before harvest determined increased N_2O–N in both treatments, though this was much clearer in II (Fig. 2).

The cumulative $(N_2O + N_2)$–N and N_2O–N emissions from the studied irrigation types were significantly different. The cumulative N_2O–N emissions during the sampling period were 0.73 kg N_2O–N ha^{-1} $season^{-1}$ from II and −1.40 kg N_2O–N ha^{-1} $season^{-1}$ from CI (Table 1). The cumulative N_2O–N ha^{-1} emissions with similar management practices found by Hadi et al. (2010) were between −50.3 and −14.8 kg N_2O–N ha^{-1} $season^{-1}$. Aulakh et al. (2001) reported cumulative emissions between 2 and 36.8 kg $(N_2O + N_2)$–N ha^{-1} $season^{-1}$.

Ratio of N_2O–N:$(N_2O + N_2)$–N

The N_2O–N:$(N_2O + N_2)$–N ratio is an indicator of the extent to which denitrification proceeds to N_2. In general, this ratio varied a lot indicating that the production of the two gases reacted differently to changes in conditions and that their production is partly independent. This is in agreement with what Ciarlo et al. (2007) reported.

The total N_2O produced in the presence of acetylene may be a good indicator of total denitrification; the production of N_2O in the absence of acetylene may not be solely a product of denitrification but may include nitrification and other aerobic processes as well. In the II plots, WFPS ranged between 73 and 93 % (Fig. 3), suggesting complete reduction of N_2O–N_2.

The cumulative N_2O–N:$(N_2O + N_2)$–N ratio was 0.055 for CI and 0.021 for II. The low N_2O–

Table 1 Cumulative emission of N_2O–N, $(N_2O + N_2)$–N, CO_2, CH_4, GWP, rice yield and the statistical significance of the effect of soil temperature, irrigation type, and their interactions ($P < 0.05$; $n = 3$)

Treatment	N_2O–N (kg ha^{-1} $season^{-1}$)	$(N_2O + N_2)$–N (kg ha^{-1} $season^{-1}$)	CO_2 (kg ha^{-1} $season^{-1}$)	CH_4 (kg ha^{-1} $season^{-1}$)	GWP (kg CO_2 ha^{-1})	Rice yield (kg ha^{-1})
II	0.73 ± 0.08a	34.14 ± 0.35a	8416.35 ± 178.56a	−155.82 ± 1.81b	4738.39	6291.12 ± 682.14b
CI	−1.40 ± 0.1a	25.05 ± 0.67b	6045.26 ± 416.57b	−87.09 ± 6.69a	3463.41	9572.23 ± 156.08a
ANOVA results						
Soil temperature	n.s.	0.0006	0.0001	n.s.		
Irrigation (CI/II)	n.s.	0.0019	0.0150	0.0062		
Soil temp × irrigation	n.s.	n.s.	n.s.	n.s.		

Different letters, per column, indicate significantly different emissions using a *t* test ($P < 0.05$)

II intermittent irrigation, *CI* continuous irrigation, *ns* not significant

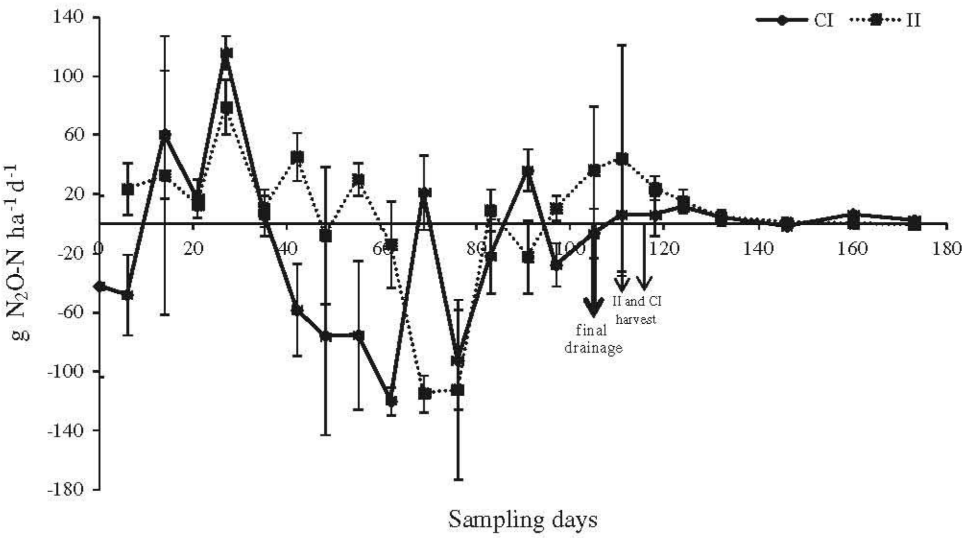

Fig. 2 Daily flux of N_2O–N from the paddy soils under different water management practices through the sampling season. The *vertical arrow* on day 112 of measurement indicates the harvest of rice in the II treatment, and that on day 116 indicates the harvest of rice in the CI treatment. *II* intermittent irrigation, *CI* continuous irrigation. *Vertical lines* indicate standard errors of three replications for each treatment

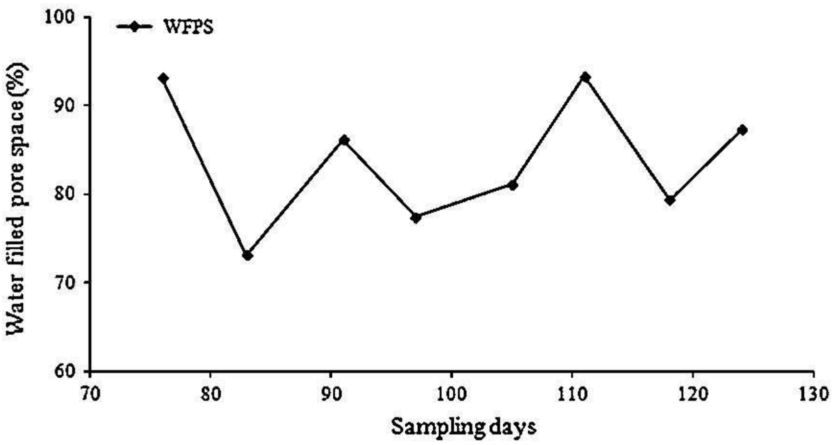

Fig. 3 Average water-filled pore space through the sampling season in the intermittent irrigation treatment (II)

N:(N_2O + N_2)–N ratio is probably due to stronger anaerobic conditions created by the presence of a surface water layer, which promoted N_2O reduction to N_2, as suggested by Xu et al. (2004). In addition, the surface water layer probably limited N_2O upward diffusion, as suggested by Yan et al. (2000), and this probably stimulated N_2O reduction to N_2. Another possible explanation would be the greater sensitivity of the N_2O reductase than the other denitrifying enzymes to oxygen (Knowles 1982). Ciarlo et al. (2007) found an average N_2O–N:(N_2O + N_2)–N ratio of 0.051–0.17 when WFPS was between 70 and 120 %. Other researchers have also noted that in continuously wet soil denitrification proceeds rapidly to N_2 and little N_2O is released (Abdirashid et al. 2003).

It is known that high soil nitrate content inhibits N_2O reduction to N_2 (Ciarlo et al. 2007). Knowles (1982) explained this phenomenon by stating that nitrate is preferred as an electron acceptor with respect to nitrous oxide. However, neither N_2O nor the N_2O–N:(N_2O + N_2)–N ratio was related to soil nitrate contents, probably because of the strong control that moisture exerted on these variables.

Carbon dioxide emission

The daily CO_2 flux is shown in Fig. 4. The measured emission fluxes ranged from −5664.0 to 104140.8 g CO_2 ha^{-1} day^{-1} in CI, and from −1574.4 to 158923.2 g CO_2 ha^{-1} day^{-1} in II, exhibiting a wide fluctuation during the rice-growing season. The results are consistent with those reported by Li et al. (2004), who found that rice fields may act as a sink for CO_2, with net CO_2 fluxes of −2191.8 to 6849.3 kg CO_2 ha^{-1} day^{-1}. Liu et al. (2008) found a range of CO_2 emission fluxes from 6571.2 to 443760.0 mg CO_2 ha^{-1} day^{-1}. The cumulative CO_2 emissions during the sampling period were 8416.3 kg CO_2 ha^{-1} season^{-1} from II and 6045.2 kg CO_2 ha^{-1} season^{-1} from CI.

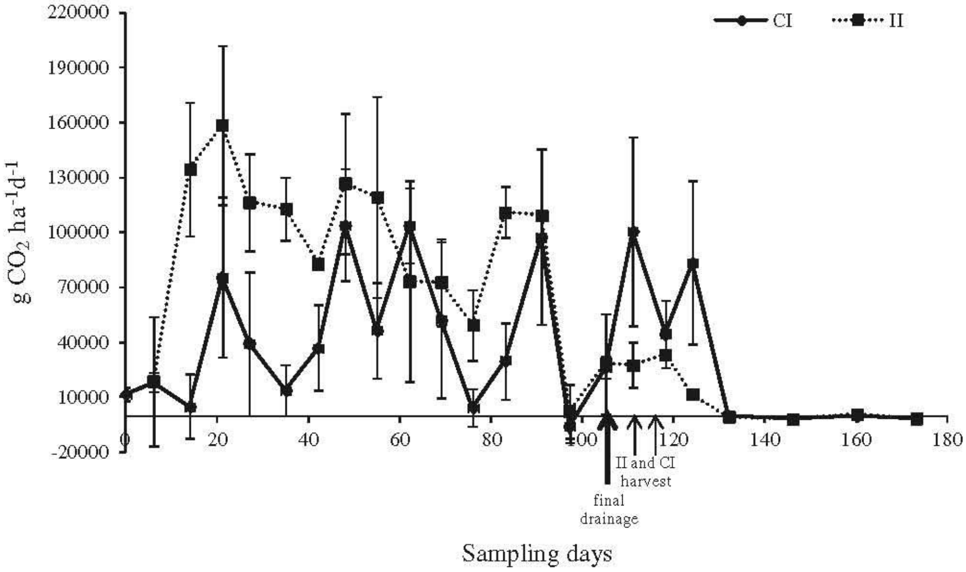

Fig. 4 Daily flux of CO_2 from the paddy soils under different water management practices through the sampling season. The *vertical arrow* on day 112 of measurement indicates the harvest of rice in the II treatment, and that on day 116 indicates the harvest of rice in the CI treatment. *II* intermittent irrigation, *CI* continuous irrigation. *Vertical lines* indicate standard errors of three replications for each treatment

The CO_2 fluxes during the rice seedling stage ranged from 5241.6 to 18403.2 g CO_2 ha^{-1} day^{-1} in CI, and from 17841.3 to 19012.8 g CO_2 ha^{-1} day^{-1} in II. The first drainage in II plots took place on 1st June (day 6 of sampling), until which every field had remained flooded. In both treatments, fluxes of CO_2 increased gradually until the mid-seedling stage when two peaks were clearly observed (on day 21). In II plots, the peak appears due to draining and mineral fertilization (ammonium sulfate), while in the CI plots the peak appears due only to the application of ammonium sulfate. In the first part of the tillering stage, two other peaks were observed (Fig. 4), associated also to fertilization (II and CI) and drainage (II).

Fertilization has shown contradictory effects on soil CO_2 flux: enhancement (Fisk and Fahey, 2001; Iqbal et al. 2009; Bhattacharyya et al. 2012), or no effect (Lee et al. 2007). Fertilizer application enhances biomass production and C input. Many experiments have shown a positive effect of N additions on soil organic carbon content, a consequence of the higher biomass generated which, in turn, returns the C in the form of CO_2 to the atmosphere (Iqbal et al. 2009). The results of this experiment are in agreement with those of Xiao et al. (2005) who reported an increased soil CO_2 flux in response to N fertilization from rice paddies in suburban Shanghai, China. The higher CO_2 flux as a response to fertilization can be interpreted in two ways. One interpretation is that the microbial use of C increases when applying nitrogen fertilizer (Fisk and Fahey 2001). Another is that microbial biomass assimilates carbon less efficiently and so respires a greater proportion of C when applying nitrogen fertilizers (Iqbal et al. 2009).

In II plots, the soil CO_2 fluxes increased immediately after flooding and exceeded pre-flooding values by two-thirds. This increase was abrupt (Fig. 4). Replacement of soil air by water must have caused an enriched CO_2 pulse. Subsequently, the CO_2 flux rapidly decreased after the water pulse. In the following days, CO_2 remained at minimum levels (about 2875.2 g CO_2 ha^{-1} day^{-1}) during flooding. As standing water declined and eventually disappeared, the CO_2 fluxes gradually increased and finally reached maximum levels (about 158923.2 g CO_2 ha^{-1} -day^{-1}). This indicates that draining and flooding cycles play vital roles in controlling CO_2 emissions in paddy soils.

Average soil CO_2 daily flux under flooded conditions was 38651.66 g CO_2 ha^{-1} day^{-1} whereas under drained conditions it was 6382.16 g CO_2 ha^{-1} day^{-1}. It is likely that floodwater decreased topsoil diffusivity and may have decreased soil CO_2 fluxes (Maier et al. 2010). Reduction of oxidizing activity under anoxic conditions may be another reason for low soil CO_2 fluxes during the flooding period (Kogel-Knabner et al. 2010). Miyata et al. (2000), Cai et al. (2003), and Liu et al. (2013) found that that the water content of paddy soils had a strong effect not only on CH_4 emissions but also on CO_2 emissions. Lower CH_4 emissions due to water drainage may increase CO_2 emission. However, during the submerged period of paddy rice cultivation, CO_2 production in the soil is severely restricted. This effect can be explained with two basic mechanisms (Liu et al. 2013). Firstly, when flooding biological activity reduction under anoxic conditions slows down rather than completely inhibits CO_2 production. Secondly, when flooding a field for subsequent rice cultivation, water replaces the gaseous phase in the soil pores. Since the CO_2 diffusion rate in water is four orders of magnitude lower than that in air, part of the produced CO_2 is stored in the soil. Hence, the soil CO_2 fluxes can be dramatically reduced by flooding during rice cultivation (Miyata et al. 2000; Campbell et al. 2001; Saito et al. 2005). Results from the present study provide indirect support for this conclusion, since the soil CO_2 flux rates under flooded conditions were significantly lower than those observed under drained conditions.

The soil CO_2 fluxes from both treatments were generally low during the post-harvest period and reached their maximum negative values at the end of the sampling period (Fig. 4). Low or negative fluxes of CO_2 in the post-harvest period coincide with the period of drainage and a low temperature. This indicates that draining (when included as an integral part of the irrigation treatment) and temperature play vital roles in controlling CO_2 emissions in a paddy soil.

Methane emission

The daily fluxes of CH_4 emission from paddy soils under continuous and intermittent irrigation are shown in Fig. 5. The measured emission fluxes ranged from −4810.93 to 8041.06 g CH_4 ha^{-1} day^{-1} in CI, and from −5082.06 to 3285.86 g CH_4 ha^{-1} day^{-1} in II, exhibiting a wide seasonal fluctuation during the rice-growing season. The negative fluxes indicate that the soil acts as a net sink. Negative fluxes have also been found by Muhr et al. (2008), Yao et al. (2012), and Feike et al. (2013).

The average daily flux of CH_4 in the II fields was −1063.87 and −63.05 g ha^{-1} day^{-1} in the CI fields. The first CH_4 efflux peak in continuous flooding (6432.6 g CH_4 ha^{-1} day^{-1}) was very high and was observed at the end of the vegetative phase (day 42 of sampling). In the CI, a second CH_4 efflux peak (8041.06 g CH_4 ha^{-1} day^{-1}) during the reproductive phase (day 69 of sampling) was observed. Near flowering, high CH_4 efflux probably occurs due to large root exudation serving as a source of carbon (C) (Wassmann and Aulakh 2000). In addition, at this stage, aerenchymas are fully mature throughout the entire plant, working as continuous channels transporting CH_4 into the atmosphere (Wassmann and Aulakh 2000). The decrease in CH_4 flux during maturation and until harvest is due to the adverse conditions for CH_4 production caused by the end of irrigation and plant senescence, when labile organic C compounds are no longer released by roots (Cai et al. 1997). In the post-harvest period, the daily fluxes of CH_4 emissions were very low. Water management in the field is one of the determinants for CH_4 production in paddy soils, because methanogenesis takes place under strict anaerobic reducing conditions. Methane emission under CI was significantly higher than under II. The results of this study are consistent with the results obtained by Moterle et al. (2013) and Suryavanshi et al. (2013), who observed that there was a pronounced difference in CH_4 production between paddy soils under intermittent irrigation and continuous flooding. The relationship between the period of drainage and the change of CH_4 flux is important to evaluate how long the fields should be drained to mitigate CH_4 emission (Yagi et al. 1996). Draining lasting at least 10 days was needed to reduce CH_4 flux appreciably in the field studied by Yagi et al. (1996). This is probably due to the fact that longer drainage allows oxygen to diffuse into deeper layers of the soil column, in which the redox components are converted from their reduced form to their oxidized form (Fe^{2+} to Fe^{3+}, Mn^{2+} to Mn^{4+}, NH_4^+ to NO_3^-), as shown by Patrick and Jugsujinda (1992). Once the redox components in soil are converted to their

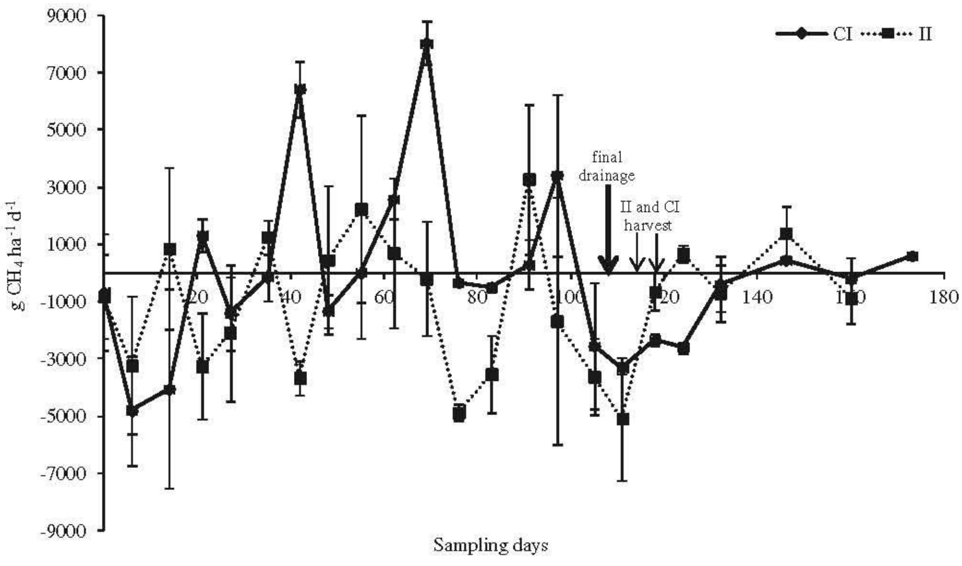

Fig. 5 Daily flux of CH_4 from the paddy soils under different water management practices through the sampling season. The *vertical arrow* on day 112 of measurement indicates the harvest of rice in the II treatment, and that on day 116 indicates the harvest of rice in the CI treatment. *II* intermittent irrigation, *CI* continuous irrigation. *Vertical lines* indicate standard errors of three replications for each treatment

oxidized form, it takes a certain period to reduce these oxidized components and to decrease soil Eh to a level suitable for CH_4 production after the field is reflooded.

Although some authors such as Dong et al. (2011) argue that the already high N applications to paddy fields will have to increase, because this is the most limiting factor in rice productivity, this is not the case in the Ebro Delta, as fertilizer doses are already well optimized. Low emissions of CH_4 in the two treatments may be due to the use of ammonium sulfate and soil salinity. Linquist et al. (2012) summarized that sulfate can reduce overall CH_4 emissions by both suppressing methanogenesis as well as contributing to anaerobic CH_4 oxidation. Nitrogen fertilization may directly or indirectly affect the processes involved in the CH_4 budget of rice paddies, i.e., the production, oxidation, and transport of CH_4. However, studies investigating N fertilizer effects on these processes have yielded contradictory results. For example, after fertilization with urea or $(NH_4^+)_2SO_4$, lower CH_4 emissions were detected and this was attributed to the direct inhibition of methanogenesis by these fertilizers (Lindau et al. 1990; Cai et al. 1997; Ma et al. 2007). However, higher CH_4 emissions were also observed from paddy fields after applications of ammonium-based non-sulfate fertilizers (e.g., urea, $(NH_4^+)_2HPO_4$, which may increase plant growth and carbon supply and thus provide more methanogenic substrates and enhance the efficiency of CH_4 transport to the atmosphere (Singh et al. 1996; Schimel, 2000; Zheng et al. 2006). Dan et al. (2001) and Cai et al. (2007) reported no difference in CH_4 emissions between N fertilized and unfertilized rice paddies. These conflicting findings regarding CH_4 emissions as affected by N fertilizer underscore the need for more research, especially for non-sulfate, non-nitrate N fertilizers, because CH_4 production is generally inhibited by sulfate, as described in previous studies (Schütz et al. 1989; Minami 1995; Scheid et al. 2003), and also because nitrate-based fertilizers are not recommended for use in paddy rice production in order to avoid intensive N_2 loss by denitrification. The above contrasting effects of N fertilizer on CH_4 emissions from paddy fields indicate that soil N availability interacts with other site-specific factors when controlling CH_4 production processes.

The negative cumulative emissions of CH_4 (soil acts as a sink) in both treatments may be due to soil salinity and to a high sulfate (SO_4^{2-}) content in irrigation water. In this study, the soil salinity was 4.65 dS m^{-1} (measured in the soil saturated paste extract). In the study area (Ebro Delta) groundwater is highly salty, sometimes more than sea water. Over extensive areas the groundwater electrical conductivity at 5 m depth varies from 16 to 60 dS m^{-1} with maximum values over 100 dS m^{-1} (Casanova 1998). It is possible that salinity caused a reduction in the total microbial activity, thereby reducing CH_4 production (Pattanaik et al. 2000). Biswas et al. (2006) have studied CH_4 emission from the saline rice fields of Sunderban mangroves of the Indian East coast and reported a significant reduction of CH_4 emission from the rice fields reclaimed from mangrove swamp compared to upland rice fields and mangrove forest area. In the present study, the high concentrations of sulfate in the irrigation water (about 150 ppm SO_4^{2-}, Casanova 1998) may lead to the suppression of CH_4 emission. In natural systems, Pennock et al. (2010) found that annual CH_4 emissions from a freshwater wetland declined when the concentration of sulfate in the water increased. Segers (1998) summarized that sulfate can reduce overall CH_4 emissions by both suppressing methanogenesis as well as contributing to anaerobic CH_4 oxidation. Three possible mechanisms as to how sulfate (and other electron acceptors) could suppress methanogenesis were proposed. First, the reduction of electron acceptors could reduce substrate concentrations to a value that is too low for methanogenesis. Second, the presence of electron acceptors could result in a redox potential that is too high for methanogenesis. Third, electron acceptors could be toxic for methanogens. In a supra-optimal concentration of sulfate, this element could possibly decrease CH_4 emission, which is presumably due to saturation of the relevant enzyme surfaces, competition for electrons between methanogens and sulfate reducers, and the development of toxicity (Banik et al. 1995). So, the soil salinity together with a high sulfate concentration in the irrigation water could inhibit CH_4 emission.

Global warming potential

The integrative GWP of CO_2, CH_4, and N_2O on a 100-year horizon for the CI treatment was 3463.41 kg CO_2-eq ha^{-1}, which was 26.9 % lower than that for the II paddy fields. The soil acted as a sink for N_2O which resulted in the reduction of the GWP for the CI treatment. In addition, the mean rice yield of the CI paddy fields was 9572.23 kg ha^{-1}, which was higher than that of II paddies by 34.2 % and the difference was significant ($P > 0.05$) (Table 1). These results suggest that CI can significantly mitigate the integrative greenhouse effect caused by CH_4 and N_2O from paddy fields while ensuring the highest rice yield.

Conclusions

From this study, it can be concluded that (1) intermittent irrigation (II) led to significantly higher ($N_2O + N_2$)–N (1.36 times greater) and CO_2 emissions than continuous irrigation (CI); (2) draining prior to harvesting increased

N_2O–N emissions; (3) draining and flooding cycles controlled CO_2 emissions; (4) lower CH_4 emissions due to water drainage (II) may increase CO_2 and $(N_2O + N_2)$–N emission, and (5) the soil acted as a CH_4 sink for both types of irrigation.

The integrative GWP of CO_2, CH_4 and N_2O on a 100-year horizon decreased by 34.2 % in the CI paddy fields compared with the II fields. These results suggest that CI can significantly mitigate the integrative greenhouse effect caused by CH_4 and N_2O from paddy fields while ensuring the highest rice yield.

The present study makes it clear how flooding and drainage affect the exchanges of $(N_2O + N_2)$–N, CO_2 and CH_4 from rice paddies in the short term. Further measurements throughout rice cultivation to assess the long-term effect of an intermittent drainage practice on the exchange of these gases from rice paddies are needed.

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Chapter 5. Effect of organic and mineral fertilisers on greenhouse gases emission from Mediterranean rice paddy soils

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Abstract

Soil fertilisation affects greenhouse gas emissions. The objective of this study was to compare the effect of different fertilisation strategies on N_2O, CH_4, and N_2 emissions and on ecosystem respiration (CO_2 emission), during the different periods of rice cultivation (seedling, rice crop and postharvest period) under Mediterranean climate. Emissions were quantified weekly by the photoacoustic technique at two sites. At Site 1 background treatments were 2 doses of chicken manure (CM): 90 and 170 kg NH_4^+-N ha^{-1} (CM-90, CM-170), urea (U, 150 kg N ha^{-1}) and no-N (control). To all of them 50 kg N ha^{-1} ammonium sulphate (AS) were topdress applied. At Site 2, background treatments were 2 doses of pig slurry (PS): 91 and 152 kg NH_4^+-N ha^{-1} (PS-91, PS-152) and ammonium sulphate (AS) at 120 kg NH_4^+-N ha^{-1}and no-N. Sixty kg NH_4^+-N ha^{-1} as AS were topdress applied to AS and PS-91. There was an N control too. During seedling GWP was ~38-55% of rice crop season for the CM treatments, and (N_2O+N_2)-N emission from U was ~11% of the applied N. The postharvest period was a net sink for CH_4, and CO_2 boosted only from the CM-170 treatment (up to 2 Mg CO_2 ha^{-1}). Global warming potential (GWP) of the rice crop season reached 17 Mg CO_2-eq ha^{-1} for U, and was 14 for CM-170, and 37 for CM-90. The CM-170 treatment reduced CH_4 emission. The application of PS at agronomic doses (~170 kg N ha^{-1}) allowed high yields (7.4 Mg ha^{-1}), the control of GWP (5.5 to 6.5 Mg CO_2-eq ha^{-1}), and a 25%

reduction in greenhouse gas intensity (GHGI) to 0.75 kg CO_2-eq kg^{-1} when compared to AS (1.02 kg CO_2-eq kg^{-1}).

Keywords: pig slurry, chicken manure, urea, ammonium sulphate, seedling period

1. Introduction

Globally, agriculture accounts for 60%, 50% and 1.1% of total anthropogenic N_2O, CH_4 and CO_2 emissions, respectively (Liu et al., 2012). Greenhouse gas (GHG) fluxes from cultivated soil are affected by factors such as temperature, water and mineral nitrogen content (Zou et al., 2005). Emissions are also related to soil microbial activity (Conrad, 1996). Furthermore, agricultural management such as the application of organic and inorganic fertilisation affects N_2O, CH_4 and CO_2 emissions (Gogoi and Baruah, 2012) although it depends on the type of fertiliser used. Urea and ammonium sulphate account for about 90% of the total N fertiliser applied to rice cultivation in the world (Food and Agriculture Organization, 2011).

In most circumstances, paddy soils are a net source of N_2O to the atmosphere, as reported in both instantaneous and annual estimates (Brumme et al., 1999; Groffman et al., 2000). However, periods of N_2O consumption have been reported in many field studies (Chapuis-Lardy et al., 2007; Van Groenigen et al., 2015). Nitrous oxide is consumed in several reactions of nitrification (Wrage et al., 2004), and in suboxic conditions, N_2O entering the soil is consumed by denitrification, producing N_2. Owing to microbial transformations in soils, the gross production of N_2O in soils is larger than its net emission, and in some periods there may be a net flux into the soil from the atmosphere (Brumme et al., 1999).

The GHG emission from rice (*Oryza sativa* L.) and the subsequent global warming potential (GWP, 3757 kg CO_2-eq ha^{-1} $season^{-1}$) is roughly four fold that from wheat (*Triticum aestivum* L.; 662 kg CO_2-eq ha^{-1} $season^{-1}$) or maize (*Zea mays* L.; 1399 kg CO_2-eq ha^{-1} $season^{-1}$) (Linquist et al., 2012). Flooded rice emits both N_2O and CH_4 due to the negative soil redox potential and different bacterial communities (Kógel-Knabner et al., 2010; Arends et al., 2014). Anaerobiosis favours the activity of methanogens which in the presence of organic matter substantially contribute to CH_4 emission (Banik et al., 1996). Fertilisation management, mainly the type of N fertilisers, is a key point for N losses to the atmosphere and GHG emissions from paddy fields (Gogoi and

Baruah, 2012; Maris et al., 2015). Urea is prone to large gaseous losses, particularly by ammonia volatilization (Mikkelsen et al., 1978) and denitrification to N_2O and N_2, though reports on N_2O emission are contradictory (Lindau et al., 1991; Zou et al., 2005), possibly due to the influence of location and management practices (Zhao et al., 2011). Ammonium based fertilisation can influence CH_4 emissions (Cai et al., 2007). Recent rice field studies suggest that high NH_4^+-N concentration may stimulate methanotrophic activity and CH_4 oxidation, thereby reducing CH_4 emissions (Bodelier and Laanbroek, 2004; Banger et al., 2012) by roughly 30 to 50% (Xie et al., 2010; Yao et al., 2012). It has been stated that when fertilising with ammonium sulphate the competition of sulphate-reducing bacteria for hydrogen reduces CH_4 emission. Nitrogen fertilisation may also increase CH_4 emissions due to increased rice biomass which can facilitate gas transport through rice plants (Singh et al., 1999), as well as enhance carbon substrate availability for methanogens (Lu et al., 2000; Schimel, 2000). Lindau et al. (1991) found that urea addition increased CH_4 emissions by approximately 40 to 75% compared to control.

Although chemical N is the main source of N in rice crops (Food and Agriculture Organization, 2011), organic fertilisers are of interest in areas with large animal herds. The addition of fresh organic fertiliser with readily available C enhances CH_4 emission (Zou et al., 2005; Sass, 2007).

According to Hou et al. (2000) efforts to reduce the overall GWP of rice should focus on reducing CH_4 emissions. However, both CH_4 and N_2O need to be considered, as many strategies that reduce CH_4 emissions tend to increase N_2O emissions and vice-versa (Cai et al., 1998; Ma et al., 2007; Zou et al., 2005). Many studies have failed to account for the combined effects of management practices on both gases (Linquist et al., 2012).

Fertilisation also enhances CO_2 flux (Xiao et al., 2005; Bhattacharyya et al., 2012). The effect of organic fertilisers and mineral fertiliser on soil CO_2 flux is due to the decomposition processes that transform plant-derived carbon (C) to soil organic matter and CO_2 (Franzluebbers et al., 1995). Soil CO_2 emission is increasingly important as it integrates all the components of soil CO_2 production, including rhizosphere respiration and soil microbial respiration (Iqbal et al., 2009), one of the primary fluxes of C between soil and atmosphere.

Field measurements of GHG emissions are typically limited to the rice crop season. Some authors have pointed out the need to quantify annual rather than seasonal emissions (Fitzgerald et al., 2000; Liang et al., 2007) because of the importance of emissions during fallow periods. Furthermore, according to some Chinese studies (Ma et al., 2012) the rice seedling period (SP) had a GWP (of N_2O and CH_4) equivalent to the GWP of the entire rice crop, though there are few such studies (Ma et al., 2013). The cumulative N_2O emission of the rice SP ranged from 0.24 to 0.62 kg N_2O-N ha^{-1} and, that of CH_4 from 21.8 to 162.2 kg CH_4 ha^{-1} in Chinese systems (Liu et al., 2012, Ma et al., 2013). In China the rice seedlings are generally grown in nursery patches for 30-40 days before they are transplanted on to paddy fields, while in Mediterranean areas rice is mainly sown on site. Other substantial technological differences in rice cropping systems relative to the Chinese ones, including the dose and type of fertiliser applied, make it worth studying GHG emissions from Mediterranean rice systems as this information is very scarce or lacking. Greenhouse gas emission estimates should reflect the specific conditions of the different countries and the agricultural practices involved (IPCC, 2007).

Rice (*Oryza sativa* L.), a very important food in many parts of the world, is a semi-aquatic species and is mostly grown under flooded low-land conditions in paddies: floodable fields in which the rice seedlings are sown or planted out and grown until harvest. In the European Union about 475,000 ha are devoted to rice with a total production of 3.2 Mt of rice grain (1.8 Mt white rice). Italy is the largest producer, with 52% of the total, followed by Spain with 20%. In Spain, more than one third of the total rice cultivation, about 110,785 ha rice (MAGRAMA, 2013), is spatially concentrated in the Mediterranean eastern part of the country and covers about 3% of the Spanish irrigated area. In the Ebro Valley, the development of rice cultivation is related to the special climatic and soil characteristics of the area. Soil salinity and/or a watertable close to the surface do not allow any other crop. This is also the case in some other Mediterranean areas such as Valencia (Spain) or the Camargue (France) regions.

In Spain, from mid-October to the end of February, uncultivated rice fields are kept dry. However, if avoiding the rise of salts by capillarity on saline soils is necessary and water availability during those months is not limiting, fields are kept flooded. Sodic and low permeability soils drain very slowly remaining flooded after harvest. Another reason for winter flooding at the Ebro Delta Natural Park is the existence of agro-environmental subsidies for waterfowl. After the winter rains, when the remaining straw is slightly decomposed, water is drained from the field and the straw is incorporated into the soil between November and January or somewhat later. In inland areas this can be delayed until April. Once this primary work is done, the soil is dried; windy days favour the dry up process. From mid-March to the first week of May, land is prepared for sowing: levelled and fertilised, mainly with N, phosphorous (P) and potassium (K). Sowing density ranges from 160 to 200 kg seed ha^{-1}. On site (rice is not transplanted) mechanical sowing takes place from April 15th to May 15th. The seed may be previously soaked in water for 12 to 36 h and dried for 24 h. A water layer of 3 to 5 cm is kept of the field after sowing. Later on it is increased to 10 to 15 cm. Flooding is constant throughout the rice cycle (with water running in and out the fields at all times), except for the time when some agricultural practices (fertiliser side-dressing, pesticide treatments) require a drain. In early September water is drained and rice can be harvested up to middle October.

The irrigation system in rice cultivation is continuous flooding and nowadays, chemical fertilisers are the most often used. The autonomous regions of Aragon and Catalonia hold about 42% of the Spanish pig herd (MAGRAMA, 2013). The use of pig slurry (PS) as fertiliser is the most common recycling method and it could be a strategic alternative to apply it to rice crops. In the Ebro Delta, the poultry sector is also relevant and it produces 51,786 t manure $year^{-1}$ (MAGRAMA, 2013). The objective of this study was to compare the effect of organic N fertilisers (pig slurry and chicken manure) with urea and ammonium sulphate on the emission of N_2O, CH_4, N_2O+N_2 and the ecosystem respiration (CO_2) from the rice paddy soil. The emission of N_2O, CH_4, N_2O+N_2 and the ecosystem respiration (CO_2) has been studied for the entire rice crop and for the postharvest (fallow) period as well as for the seedling period (separately from the entire rice crop period).

Two contrasted sites in the Ebro valley were studied, with different organic fertilisers available (CM or PS) and with different mineral N applied at sowing time (urea or ammonium sulphate). Both management strategies (with mineral or organic fertilisers) were designed to include a similar background applied NH_4^+-N dose (in the range from 90 to 170 kg NH_4^+-N ha^{-1}) but to differ widely in the organic-C application (CM had a high C/N ratio and PS a low one).

2. Materials and methods

2.1. Site description and experimental design

The experiment was carried out at two rice paddies located at two different sites in the Mediterranean Ebro Valley (NE Spain), representative of the agricultural practices in the Valley. Site 1 is located at the Institute for Food and Agricultural Research and Technology (IRTA), at its Amposta station (coordinates: 40°42′30″N, 00°37′56″W, altitude: 3 m a.s.l.) in the Ebro River Delta. Site 2 is located at Villanueva de Sigena (coordinates: 41°45′32″N, 0°2′18″W, altitude: 297 m a.s.l.). The main soil properties and climatic characteristics of these sites are summarized in Table 1. Site 1 was sampled in 2011 and 2012. Site 2 was sampled in 2012 (Table 2). Rainfall and air temperature during the sampling period (Figs. 1a, 1b) were obtained from the meteorological stations located at the experimental sites (Meteorological Service of Catalonia: http://www.ruralcat.net/web/guest/agrometeo.estacions and of Aragon: http://eportal.magrama.gob.es/websiar/Inicio.aspx). Additionally, soil temperature (10 cm depth) was measured when soil samples were taken.

In both sites, during the seedling period (the first 35 days after sowing) a water layer of 3 to 5 cm was kept on the field and of 10 cm from the end of the seedling period to harvest. Water was continuously flowing in and out the plots at both sites. The dates of the main field labours and of the sampling periods are detailed in Table 2.

At Site 1, rice (*Oryza sativa* L.), cultivar Gleva was sown directly on site in 2011 and 2012 at a density of 182 kg ha^{-1}. The background treatments were (Table 3): urea (U) 150 kg N ha^{-1} and 2 different doses of chicken manure (CM) containing 90 (CM-90), and 170 kg NH_4^+-N ha^{-1} (CM-170). The dose of organic-N applied each year with the CM is shown on Table 3. The main properties of the applied CM are shown on Table 4. In both years, the topdressing fertilisation was applied as ammonium sulphate (AS) at a dose of 50 kg N ha^{-1} except to the control (Table 3). The control treatment was not sampled in 2011. The fertiliser treatments were randomly distributed in three blocks (replicates). The blocks were distributed in the direction of the waterflow. The area of each individual plot was 20.25 m^2 (4.5 m $*$ 4.5 m). Sampling began in May 2011 and finished in January 2013, including both the rice crop season and the postharvest period of 2012 and partly that of 2013 (Table 2).

At Site 2, rice (*Oryza sativa* L.) cultivar Guadiamar was sown directly on site in 2012 at a density of 150 kg ha^{-1}. The background treatments were (Table 3) ammonium sulphate (AS) at a dose of 120 kg NH_4^+-N ha^{-1}, 2 doses of pig slurry (PS) equivalent to 91 (PS-91), and 152 kg NH_4^+-N ha^{-1} (PS-152) plus a control (no nitrogen applied). Topdressing at a dose of 60 kg NH_4^+-N ha^{-1} was applied only to the AS and PS-91 treatments. The main properties of the applied PS are shown on Table 4. The fertilisation treatments were randomly distributed in four blocks (replicates). The area of each individual plot was 36 m^2 (6 m * 6 m) for PS-91 and PS-152 and 18 m^2 (3 m * 6 m) for AS and the control treatments. The water was moving from one block to the following one. Sowing was earlier on the coast (Site 1) with respect to inland (Site 2) (Table 2) as this favours yield (Casanova et al., 2000). In both sites, weeds and pests were controlled in accordance to local conventional practice.

2.2. Gas sampling and quantification

Gas samples were collected weekly using the closed chamber method throughout the rice crop season, at both sites. The cylindrical (20 cm diameter and 60 cm high) static chambers were made of polyvinyl chloride (PVC) coated with an epoxy resin. They were inserted 18 cm into the soil. This cylinder was closed with a vented screwed lid with a three-way key. Air samples from inside the chamber were taken in duplicate immediately after closing the chamber, and 20 and 40 min later. Samples were taken through a Teflon® tube connected to the three-way key and into 100 ml plastic syringes, adapted with a valve. Air inside the chamber was mixed by filling and emptying the syringe six times before withdrawing the sample. After taking the air sample the syringes were closed by the valve. After the last sampling (40 min from closing the chamber) the three-way keys were left open until sampling with acetylene.

The acetylene (C_2H_2) inhibition method (Balderston et al., 1976; Yoshinari et al., 1977) was used to inhibit the last step of denitrification (N_2O reduction to N_2). Ten percent (v/v) of the air enclosed in the chamber was replaced by C_2H_2. After that, C_2H_2 was allowed to diffuse for 20 min, and samples were taken as described above. After 40 min of sampling the chambers were left open. The syringes were transported to the laboratory and the concentrations of N_2O, CH_4 and CO_2 in the sampled air were quantified using the photoacoustic technique (Innova 1412 Photoacoustic Multigas Monitor).

Surface soil temperature was always recorded during sampling. The photoacoustic analyser refers the gases concentration to 20ºC and 1 atm; the concentration was corrected to be referred to the actual field temperature and atmospheric pressure of each sampling day. Sampling was done at the time of the day when soil temperature was about the average soil temperature of the day in order to minimize over or underestimation of the emission caused by daily soil temperature variation.

Since the chambers were not transparent, it can be assumed that the CO_2 flux was the ecosystem respiration including plant autotrophic respiration. Since the plants were inside the closed chambers it was assumed that the stomata were closed in the darkness.

2.3. Calculations and statistical analysis

Gas samples were collected weekly using the closed chamber method throughout the rice crop season, at both sites. The cylindrical (20 cm diameter and 60 cm high) static chambers were made of polyvinyl chloride (PVC) coated with an epoxy resin. They were inserted 18 cm into the soil. This cylinder was closed with a vented screwed lid with a three-way key. Air samples from inside the chamber were taken in duplicate immediately after closing the chamber, and 20 and 40 min later. Samples were taken through a Teflon® tube connected to the three-way key and into 100 ml plastic syringes, adapted with a valve. Air inside the chamber was mixed by filling and emptying the syringe six times before withdrawing the sample. After taking the air sample the syringes were closed by the valve. After the last sampling (40 min from closing the chamber) the three-way keys were left open until sampling with acetylene.

The acetylene (C_2H_2) inhibition method (Balderston et al., 1976; Yoshinari et al., 1977) was used to inhibit the last step of denitrification (N_2O reduction to N_2). Ten percent (v/v) of the air enclosed in the chamber was replaced by C_2H_2. After that, C_2H_2 was allowed to diffuse for 20 min, and samples were taken as described above. After 40 min of sampling the chambers were left open. The syringes were transported to the laboratory and the concentrations of N_2O, CH_4 and CO_2 in the sampled air were quantified using the photoacoustic technique (Innova 1412 Photoacoustic Multigas Monitor).

Surface soil temperature was always recorded during sampling. The photoacoustic analyser refers the gases concentration to 20ºC and 1 atm; the concentration was

corrected to be referred to the actual field temperature and atmospheric pressure of each sampling day. Sampling was done at the time of the day when soil temperature was about the average soil temperature of the day in order to minimize over or underestimation of the emission caused by daily soil temperature variation.

Since the chambers were not transparent, it can be assumed that the CO_2 flux was the ecosystem respiration including plant autotrophic respiration. Since the plants were inside the closed chambers it was assumed that the stomata were closed in the darkness.

2.4. Global warming potential (GWP) and greenhouse gas intensity (GHGI)

Global warming potential (GWP) is an index defined as the cumulative radiative forcing between the present and some chosen later time ''horizon'' caused by a unit mass of gas emitted now. In GWP estimation, CO_2 is typically taken as the reference gas, and an increase or reduction in emission of CH_4 and N_2O is converted into ''CO_2-equivalents'' through their GWPs. Therefore, in the present study, the global warming potential (GWP) of N_2O and CH_4 emissions was calculated in units of CO_2 equivalents (CO_2-eq.) over a 100-year horizon (Forest et al., 2007). A radiative forcing potential relative to CO_2 of 298 was used for N_2O and of 25 for CH_4 (Forest et al., 2007). Although soil CO_2 fluxes also represent a source of GHG emissions, on a global scale, they are largely offset by high rates of net primary productivity and atmospheric CO_2 fixation by crop plants, and are therefore estimated to contribute <1% to the GWP of agriculture (Smith et al., 2008; Linquist et al., 2012). Therefore, CO_2 as a contributor to GWP was not included in this analysis. The GWP of N_2O and CH_4 emissions were calculated using the following equation (IPCC, 2007): GWP (kg CO_2-eq ha^{-1}) = cumulative N_2O emission * 298 + cumulative CH_4 emission * 25.

At physiological maturity rice ears were harvested (1 to 4 m^2) and grain humidity was determined after drying it to a constant weight at 65°C in order to calculate the rice yield adjusted to 14% grain moisture content.

The greenhouse gas intensity (GHGI) was calculated as follows: GHGI (kg CO_2-eq kg^{-1} grain yield) = GWP kg^{-1} grain yield.

3. Results

All fertilisation treatments resulted in high and similar yields (7 to 10 Mg ha^{-1}). The exception was the yield of AS-top-11 and that of CM-170-12 which were half of the maximum one attained each year (Table 5).

3.1. Nitrous oxide and molecular nitrogen emission of the rice crop season

At Site 1, as shown in Figs. 2a and 2b, all treatments had a similar pattern of N_2O emission during the rice crop season. The N_2O fluxes ranged from -370 (in 2011) to 318 g N_2O-N ha^{-1} d^{-1} (in 2012) and some high peaks occurred after AS was topdress applied (day 42 of sampling in 2011 and day 70 of sampling in 2012). The average of the measured N_2O fluxes was: -15, -9, 2 and 5 g N_2O-N ha^{-1} d^{-1} for AS-top-11, U-11, CM-170-11 and CM-90-11. In 2012, they were 2 g N_2O-N ha^{-1} d^{-1} from control and ranged from 9 to 11 g N_2O-N ha^{-1} d^{-1} for the rest of treatments.

The N_2O emission factor (EF) ranged from 0.83 to 7.3% of the applied N and was maximum for AS-top-12 and it was 2% for the CM-90-12 and U-12 treatments (Site 1; Table 5).

In 2011, the average of the measured N_2O+N_2 fluxes ranged from 51 (AS-top-11) to 59 g (N_2O+N_2)-N ha^{-1} d^{-1} (CM-90-11). These records indicate that in 2011, and for the rice crop season, N_2O-N losses for the CM treatments, and N_2O+N_2 losses for the U treatment were underestimated. During the first 20 days of sampling, the soil acted as a sink for N_2O+N_2 for all treatments (Fig. 3a) until the topdress application of AS (day 42 of sampling). In 2012, the daily fluxes of N_2O+N_2 exhibited less fluctuation (Fig. 3b) than in 2011 and included some peaks, mainly for U during the first 35 days of sampling. The cumulative N_2O–N/(N_2O+N_2)–N ratio was between 0.04 to 0.58 (Table 5).

In 2011, the daily N_2O and N_2O+N_2 fluxes observed in all the treatments were correlated with soil temperature and air mean temperature. The highest fluxes of N_2O were generally observed when the air temperature ranged between 22 and 24ºC (soil temperature ranged between 23 and 25ºC). In 2012 no correlation was observed (Table 6).

At Site 2, high fluxes of N_2O were observed after background fertilisation with the high dose of PS and with AS, but they were lower (than the control) from the low PS dose (Fig. 4a). Nevertheless, the average of the N_2O fluxes during the rice crop season was close to 2 g N_2O-N ha^{-1} d^{-1} for all treatments, and the cumulative N_2O emissions did not differ among treatments (Table 5).

The EF was negligible for AS-12 and PS treatments (Site 2). Overall, the cumulative N_2O-N emission during the rice crop season ranged from 0.6% (CM-170-11) to 11.3% (AS-top-12) of the applied N.

The N_2O+N_2 flux the day after fertilisation was up to between 10 to 18 times higher for PS-152-12 than for the other treatments (Fig. 4b). However, the average of the sampled fluxes of N_2O+N_2 during the rice crop season was kept between 8 to 11 g (N_2O+N_2)-N ha^{-1} d^{-1}.

The N losses as N_2O+N_2 (Table 5) ranged from 1.1% (CM-170-12) to 79.6% (AS-top-11) of N applied. The cumulative N_2O–N/(N_2O+N_2)–N ratio was between 0.16 and 0.25 (Table 5).

3.2. Methane emission of the rice crop season

At Site 1, the average of the daily CH_4 fluxes in the two years varied from -7.19 to 24.62 kg CH_4 ha^{-1} d^{-1}. In 2011, the emission fluxes were lower than in 2012. The fluxes of CH_4 from the CM-90-12 treatment showed very clear peaks during the seedling stage (days 14 and 19 of sampling), during the reproductive phase (days 77 and 91 of sampling) and during the ripening phase (day 120 of sampling) (Fig. 5b). The cumulative CH_4 emission was increased by U and CM fertilisers (Table 5). In 2012, a negative and significant correlation between the daily CH_4 flux and the redox potential (Eh) was found (Table 6). Soil Eh during the rice crop season ranged from -445 to -109 mV (Fig. 5d).

At Site 2, the average of the daily CH_4 fluxes was between 0.2 and 0.3 kg CH_4 ha^{-1} d^{-1} and no difference in cumulative CH_4 between treatments was found (Table 5). The daily CH_4 flux was maximum when air temperature was approximately 24°C and soil temperature ranged between 23 and 25°C. Soil temperature, air mean temperature and CH_4 flux were positively correlated (Table 6).

3.3. Carbon dioxide flux (ecosystem respiration) of the rice crop season

At Site 1, in 2011, the fluxes of CO_2 reached a maximum during the reproductive stage of rice (days 45 to 80 of sampling), and then declined until the final drainage (Fig 6a). The average of the daily CO_2 fluxes differed among treatments and varied from 12 to 19 kg CO_2 ha^{-1} d^{-1} as the total N dose increased. In 2012, the daily flux of CO_2 increased gradually during the seedling period (SP) and reached a maximum during the ripening phase (days 100 to 120 of sampling), while the lowest occurred at the end of the vegetative phase (Fig. 6b). The average of the daily flux of CO_2 increased from 6 up to 16 kg CO_2 ha^{-1} d^{-1} as N dose increased. Differences in the cumulative CO_2 respiration were only recorded in 2012 (Table 5), being larger in CM-170-12 than in the U-12 and C-12 treatments. In both years, the daily CO_2 flux was positively correlated with soil temperature and air mean temperature (Table 6).

At Site 2, in 2012, the average of the daily fluxes of CO_2 respiration ranged from 7 to 10 kg CO_2 ha^{-1} d^{-1}; without differences between treatments in the cumulative CO_2 ecosystem respiration (Table 5). The daily respiration flux of CO_2 markedly increased during the reproductive phase (days 35 to 70 of sampling) and the ripening phase (days 70 to 100 of sampling; Fig. 6c). A significant and positive correlation between soil temperature, air mean temperature and daily CO_2 flux was found (Table 6).

In both sites and years, the daily CO_2 respiration flux was maximum at air temperatures ranging between 21 and 26°C which corresponded to soil temperatures ranging between 22 and 27°C.

3.4. Global warming potential (GWP) and greenhouse gas intensity (GHGI) of the rice crop season

The contribution of CH_4 to total GWP was always much larger than that of N_2O throughout the rice crop season. At Site 1, the maximum GWP was calculated for U-12 (17 Mg CO_2-eq ha^{-1}) and CM where it ranged from 14 (CM-170-12) to 37 (CM-90-12) Mg CO_2-eq ha^{-1}. At Site 1, the GWP was negative for the AS-top-11, U-11 and C-12 treatments (Table 5). At Site 2, the maximum GWP reached only 6 to 8 Mg CO_2-eq ha^{-1} from the AS-12, PS-91-12 and PS-151-12 treatments (Table 5). A negative GWP value indicates that the soil acted as a net sink for GWP, which is similar to soil C sequestration. In contrast, a positive GWP value indicates that the soil acted as a net source for GWP.

The highest GHGI (~ 5 kg CO_2-eq kg^{-1}) were calculated for Site 1 and they were associated, in 2012, with CM treatments (Table 5).

3.5. Greenhouse gas emissions during the postharvest period

In both years, at Site 1, during the postharvest (fallow) period no notable N_2O emission was observed (Figs. 2a and b). In 2012, high N_2O+N_2 fluxes were recorded (Fig. 3b) which ranged from 6 to 24 kg (N_2O+N_2)-N ha^{-1}, which represent half of the emission of the rice crop season. Urea always recorded the highest emissions, which were double than those from the CM treatments (Table 7). In both years, the CH_4 flux dropped rapidly, within a few days, after the final drainage before harvest (Figs. 5a and 5b). The cumulative CH_4 fluxes were negative, from -416 to -23 kg CH_4 ha^{-1} (Figs. 5a and 5b), without differences between treatments (Table 7). Soil Eh during the postharvest period ranged from -109 to +112 mV (Fig. 5d). The ecosystem respiration (CO_2 flux) ranged from -13 (in 2011) to 2001 kg CO_2 ha^{-1} (in 2012), which is lower than from the rice crop season. The highest values were recorded in the CM-170-12 treatment (Table 7).

3.6. Greenhouse gas emissions during the seedling period

At Site 1, the cumulative N_2O emission during the rice seedling period was significantly affected by the fertilisation treatment (Table 8). It was significantly larger (roughly four times) from CM (~3 kg N_2O-N ha^{-1}) than from U, while U did not differ from the control. The opposite was observed for the cumulative N_2O+N_2 emission (Table 8), where for U it accounted for 53% (~17 kg (N_2O+N_2)-N ha^{-1}) of the emission during the rice crop season while in the rest of treatments it did not surpass 10% (<2 kg (N_2O+N_2)-N ha^{-1}). Nitrogenous gas emission ((N_2O+N_2)-N) was dominated by N_2 in the U treatment and in the control, while in CM treatments it only appeared as N_2O. Application of CM significantly increased CH_4 emission, although it decreased as the dose of CM increased (Table 8). It ranged from -19 kg CH_4 ha^{-1} for U to 418 kg CH_4 ha^{-1} for CM-90-12. For manures, it accounted between 38% (CM-90-12) and 55% of the total CH_4 emission during the rice crop season (Table 8).

The GWP did not differ between the control and U (where GWP was negligible) treatments, but it was significantly higher for CM which ranged from 5.5 (CM-170-12) up to 11.5 Mg kg CO_2-eq ha^{-1} (CM-90-12). The cumulative ecosystem respiration (CO_2 flux) tended to increase with the CM dose, being higher for the CM-170 treatment (2.4 Mg CO_2-eq ha^{-1}) than for the U treatments and the control (~460 kg CO_2 ha^{-1}). The cumulative CO_2 emission accounted for 12% and up to 16% of that recorded for the rice crop season for the treatments with CM and for just 5 and 6% for the control and U rice crop season emission, respectively (Table 8).

At Site 2, fertilisation treatments only affected the cumulative N_2O emission (Table 8). The PS-152 treatment (0.9 kg N_2O-N ha^{-1}) was the only one with an emission higher than the control (0.4 kg N_2O-N ha^{-1}). The cumulative N_2O+N_2 emissions (~1-2 kg (N_2O+N_2)-N ha^{-1}) accounted for 8 (AS) to 26% (PS-152) of the cumulative emission for the rice crop season. The GWP varied from 987 (PS-91) to 1996 kg CO_2-eq ha^{-1} (AS-12 in Site 2; Table 8). The ecosystem respiration (~114-197 kg CO_2 ha^{-1}) was less than 3% of that of the rice crop season (Table 8).

4. Discussion

4.1. Nitrous oxide and molecular nitrogen emission during the rice crop season

Both nitrification and denitrification are known to occur in tandem in flooded rice soil (DeDatta, 1995; Kyaw and Toyota, 2007) since flooded soils have an aerobic surface layer and a subsurface anaerobic layer. In the present study, some oxygen exchange existed as water was running into and out the plots continuously. For this reason it may be hypothesized that N_2O emission was due to other processes than denitrification.

It was expected that there might be an increase of N_2O emission from the fertilised treatments with respect to the control as has been reported for different fertilisers (organic and mineral) in previous studies (Williams et al., 1998; Del Prado et al., 2010; Bergstermann et al., 2011), but the increment was observed only in the CM treatments and at high PS dose, though not significantly. The low soil organic matter content in the present study (~2%) could have been a limiting factor for denitrification in the control and mineral treatments, and with the addition of PS due to its low organic matter content (Table 3). This constraint was also pointed out by Teira-Esmatges et al. (1998) and Menéndez et al. (2008). Vallejo et al. (2005) reported that Mediterranean agricultural soils often have organic contents below 2%, which is a limiting factor for denitrifying activity. However, an important increase in N_2O emission (relative to the control) occurred in the present study from CM-90-11 and -12. In addition, the cumulative N_2O-N emission from CM-90-12 was twice that from CM-90-11, mainly because more than 5 times more organic-N had been applied in 2012 (Table 3), although some N may have been immobilized (Pathak et al., 2002). When applying CM containing a high amount of organic-N the processes taking place were mineralization in the first place, followed by nitrification and most probably denitrification (due to waterlogged conditions) though not complete (i.e. not to N_2; Table 5).

In 2012, the cumulative N_2O+N_2 emissions from the U treatments were higher than from the CM treatments (Table 5) since U may have facilitated the start of denitrification during the rice crop season. There was no difference in the emission from AS and from the control, in agreement with what Menéndez et al. (2008) also found.

The soil acted as a net sink of N_2O during the first days of sampling and during the postharvest period, in both years. Negative fluxes of N_2O (i.e. soil acted as a sink) have previously been documented under various edaphoclimatic conditions for different crops (Teira-Esmatges et al., 1998; Chapuis-Lardy et al., 2007; Cardenas et al., 2010; Abalos et al. 2012; Van Groenigen et al., 2015). However, the origin of net negative N_2O fluxes is often unclear (e.g. Donoso et al., 1993; Goldberg and Gebauer, 2009). Past experiments have linked negative fluxes to soil properties such as moisture content, temperature, pH, oxygen and available nitrogen (Heincke and Kaupenjohann, 1999; Khalil et al., 2002). However, the influence of these factors seems to vary between experiments and no clear set of conditions that would favour negative fluxes from different soil types has been established yet (Chapuis-Lardy et al., 2007). Based on recent evidence from the literature the following possible pathways for N_2O consumption (negative fluxes of N_2O) have been identified (Van Groenigen et al. 2015): (1) first, in addition to the "typical" nitrous oxide reductase (nosZ I) that reduces N_2O during denitrification, (2) second, a microbial nondenitrifier, "atypical" N_2O reductase (nosZ II) which play a significant role in N_2O consumption in soil was identified; (3) third, some bacteria that perform dissimilatory nitrate reduction to ammonia (DNRA) are capable of N_2O reduction to N_2 as they carry a nos gene encoding for N_2O reductase (N_2OR) (Simon et al., 2004); (4) fourth, direct assimilatory N_2O fixation via nitrogenase (Vieten et al., 2008; Ishii et al., 2011; Farías et al., 2013) or (5) fifth, indirect N_2O fixation via a combination of N_2O reduction and N_2 fixation can account for N_2O consumption.

The background N_2O emission has become one of the most sensitive factors for developing an inventory of agricultural N_2O emissions (Yan et al., 2003; Akiyama et al., 2005). In the present study, background emission of N_2O was only noticeable in 2012 (Table 5) where it achieved 1.95 kg N_2O-N ha^{-1}, which is higher than the background emissions from paddy fields in literature (0.2-1.38 kg N_2O-N ha^{-1}, average: 0.79 kg N_2O-N ha^{-1}; Zou et al., 2007, 2009**)** and it is most likely to be a consequence of mineralization of previously incorporated rice straw (Gu et al., 2007).

The cumulative N_2O emission from the fertilised treatments ranged from 1.9 to 10 kg N_2O-N ha^{-1} (Table 5), which is somewhat higher than the range reported by Akiyama et al. (2005) based on 113 measurements from 17 continuously flooded sites worldwide (1.0 to 6.2 kg N_2O-N ha^{-1}).

The N_2O emission factor (EF) of the applied N was negligible for AS and PS, but for the other treatments it was higher (up to 7.3%) than the IPCC (2007) reference (i.e. 1% regardless of the N source, location, climate and soil type).

The cumulative N_2O+N_2 emission during the rice crop season ranged from 1.1 to 79.6% of the applied N. The highest relative N losses were found for the treatments with AS-top-11 and -12 at a dose of 50 kg N ha^{-1} (Table 5). In general, the readily available NH_4^+-N topdress applied increased N_2O and N_2O+N_2 emissions (Figs. 2 and 3) as Pathak et al. (2002) and Zou et al. (2005) also found. Topdressing fertilisers are often recommended to improve N use efficiency; however, if they do not improve N use efficiency they can result in high N_2O fluxes (Linquist et al. 2003). Zou et al. (2005), Pathak et al. (2002) and Linquist et al. (2003) found that the N_2O emission increased by 3, 43 and more than 60% when mineral fertiliser was topdress applied as compared to the control. Other studies (Lindau et al., 1991; Buresh et al., 1993; Phongpan and Mosier, 2003; Nishida et al., 2004, Bandyopadhyay and Sarkar, 2005) also shown high losses from the applied N, report emissions between 5 to as high as 73% of the applied N as N_2O+N_2 over the rice crop season independently of the type (mineral or organic) of fertiliser. Also, the field denitrification losses can amount to 60–70 kg N ha^{-1} $year^{-1}$ on poorly drained soils (Van Cleemput 1998).

The N_2O-N/(N_2O+N_2)-N ratio is an indicator of the extent to which denitrification proceeds to N_2. The low N_2O-N/(N_2O+N_2)-N ratios obtained (0.1 to 0.58; Table 5) were due to the strong anaerobic conditions created by continuous flooding (10 cm water layer) which promoted N_2O reduction to N_2 (Xu et al., 2004) and probably limited N_2O upward diffusion (Yan et al., 2000) further favouring N_2O reduction to N_2.

Since the loss of N due to denitrification was higher than by nitrification during the rice crop season, denitrification losses must be taken into account in these rice systems in order to obtain an accurate assessment of the N balance (Hofman and Van Cleemput, 2001).

4.2. Methane emission during the rice crop season

The cumulative CH_4 emissions in the present study (ranging from 98 to 1346 kg CH_4 ha^{-1}; Table 5) is well in agreement with the review of Minami (1995) and Yan et al. (2009), who found that the seasonal CH_4 emissions ranged from 48 to 1830 kg CH_4 ha^{-1} for paddy fields around the world.

Urea and AS tended to increase CH_4 emission (decreased its oxidation) and seemed to be affected by the dose of fertiliser (Table 5). These results are consistent with the results of Lindau et al. (1991). In contrast, Cai et al. (1998) found that CH_4 emission decreased with urea application, while Wang et al. (1993) reported no change in emission with urea application.

Furthermore, the high dose of CM did not result in a further increase in CH_4 emission and there was even a tendency to reduce CH_4 emission. The reason for this is unclear; it may be due to the formation of phytotoxic substrates in the soil at high organic-C contents (Schütz et al., 1989; Kludze and DeLaune, 1995) which also inhibit plant development (Schütz et al., 1989). The same effect was observed by Khalil et al. (1998), who attributed it to a saturation effect for the production and release of CH_4, so increments in fertiliser doses did not further increase CH_4 emissions. In the present study, this phenomenon was more evident in 2012 where more organic-N and C were applied, although the emitted CH_4-C as percentage of the applied organic-C was almost the same in both years. This finding suggests that at the tested CM doses, the applied organic-C is not limiting CH_4 emission. In mass, the cumulative CH_4 emission was inversely proportional to the CM dose and in both years significantly higher than from the U and control treatments (Table 5).The higher soil NH_4^+ concentents for the CM-170 than for the CM-90 treatments (both years), resulted in the stimulation of methanotrophic activity and CH_4 oxidation as Bodelier and Laanbroek (2004) and Noll et al. (2007) also described.

When applying PS the emitted CH_4-C was much higher than the applied organic-C and almost the same for both doses. Therefore, CH_4 must have consumed some soil-C (about 1% of the soil organic-C of the 18 cm top soil layer) as the previous crop remains had been thoroughly removed.

In 2012, the high CH_4 emissions were negatively correlated with the Eh (Figs. 5b and d; Table 6) as already reported in previous studies (Cai et al., 1997; Yu et al., 2004). As reported by Minami (1995) and Wang et al. (1993) CH_4 emission began to increase as the soil Eh decreased, and decreased rapidly after the drainage as soil Eh increased. Methane usually forms only after the soil Eh has been lowered to sufficiently negative values, typically less than -100 mV (Masscheleyn et al., 1993).

4.3. Carbon dioxide flux (ecosystem respiration) during the rice crop season

Application of N fertiliser increases plant biomass production stimulates soil biological activity, and consequently, CO_2 emission (Dick, 1992; Wilson and Al-Kaisi, 2008; Iqbal et al., 2009). By contrast, DeForesta et al. (2004) indicated that reduced extracellular enzyme activities and fungal populations resulting from N fertiliser application, decreased soil CO_2 emissions. Almaraz et al. (2009) did not observe any significant effect of mineral fertiliser application on cumulative CO_2 emissions.

In this study, the cumulative ecosystem respiration tended to increase with increasing doses of organic-C (Table 5). The highest CM-170-12 dose tripled the emissions of the control. Although the amount of organic-C applied was higher in 2012 than in 2011, the emitted CO_2-C as percentage of the applied organic-C was lower in 2012, indicating that these high organic-C doses probably caused a “saturation” effect on methanogeness. In mass, the recorded respiration was proportional to the CM dose, but not significant difference between treatments was found (Table 5).

In both years, after the final drainage, a large peak of CO_2 was observed in all the treatments (Figs. 6a and b). One possible reason for this may be that the 10 cm water layer prevented oxygen diffusion into the saturated soil, resulting in limited aerobic respiration activity in the soil (Chimner and Cooper, 2003).

When applying PS the emitted CO_2-C was also much larger than the applied organic-C, leading to almost the same cumulative mass of CO_2 for both PS doses. The application of organic-C promotes a priming effect on carbon oxidation (Singh et al., 2008), resulting into higher CO_2 emission which continues with the oxidation of native soil organic-C.

Research on the dose of organic fertiliser to be applied to specific soils is lacking and further work is needed to quantify the effect of long term applications of mineral and organic fertilisers on CO_2 emissions.

4.4. Greenhouse gas emissions during the postharvest period

In 2011, after harvest, the field was non-flooded (drained and dried) most of the time, and rainfall was lower than in 2012 (Fig. 1a). In 2011, after the winter rains, when the remaining straw was slightly decomposed, water was drained from the field and the straw was incorporated into soil during February or March. From mid-March to the first half of April, land was prepared for sowing (levelled and fertilised). Unlike this pattern, in 2012, the field was drained for harvest on the 12th September and flooded again on the 28th September until the 29th November when it was drained until the end of the last sampling (3rd January 2013), meaning that the soil was flooded during two of the three months of the postharvest period due to rainfall (Fig. 1a) and irrigation.

In both years, the cumulative N_2O emissions were very low or negative and did not differ among treatments (Table 7). Several other studies have also found negative N_2O fluxes from field measurements during the postharvest period, which could be associated with the reduction of N_2O to N_2 (Lardy et al., 2007).

In both years, the measured cumulative N_2O+N_2 emissions were high, equivalent to half of the N_2O+N_2 emitted during the rice crop season, despite in 2012 only half of the postharvest period was sampled. The measured cumulative N_2O+N_2 emission ranged from 6.29 to 23.72 kg (N_2O+N_2)-N ha^{-1} (Table 7). A possible explanation for this result can be that in 2012 the inundation lasted for enough time for denitrification to take place or the soil conditions were more favourable for denitrification as Blackmer et al. (1982) also described. Soil moisture during the rice crop season (continuous flooding) could result in a subsequent accumulation of organic-C and nitrate in winter, favouring denitrification (Byrnes et al., 1993). Also, the measured cumulative N_2O+N_2 emission was stimulated by U (Table 7). These results are in line with those of Bronson et al. (1998), who also found that during the postharvest period more N_2 than N_2O was produced. In both years, the mineral N remaining in the soil after harvest (September) was very low in all N fertilisation treatments (Figs. 7a and b). Therefore, must have been nitrification during the postharvest period.

In both years, CH_4 fluxes decreased and remained low or even negative after harvest, with the cumulative emission being negative (Table 7), in agreement with Wang et al. (1998). The absence of plant-mediated transport, lower temperatures than those of the rice crop season, and the absence of a sufficiently reducing environment (Table 7) can explain this fact. The paddy soil during the postharvest period became aerobic with higher Eh (Fig, 5d), which inhibited the growth of methanogenic bacteria and CH_4 production (Jiao et al., 2006). In the present study this happened after the final drainage (day 131 of sampling) when Eh increased from -207 to 122 mV (Fig. 5d). From day 131 of sampling onwards, the soil acted as a net sink of CH_4, due to the aerobic condition of the soil (Fig. 5b). Methanogenic bacteria populations can build up after the soil is flooded during land preparation, but there would be a delay until the methanogens recover in population and their activity to the high levels that are found in continuously flooded soil (Pavlostathis and Giraldo, 1991).

It is considered that CO_2 emission comes mostly from organic (soil organic matter, litter and dead roots) decomposition and root respiration (Bowden et al., 1993). In both years, the cumulative ecosystem respiration during the postharvest period ranged from -13 to 2001 kg CO_2 ha^{-1} which was 87 to 98% lower than the respiration corded during the rice crop season (Tables 5 and 7). Therefore, the postharvest period was not an important source of CO_2 with the exception of CM-170-12 to which high doses of C had been applied.

4.5. Greenhouse gas emissions during the seedling period

4.5.1. Nitrous oxide and molecular nitrogen emission during the seedling period

The paddy soils were a small source of N_2O during the rice seedling period (SP; <0.85 kg N_2O-N ha^{-1}) when applying mineral fertiliser (U and AS) or PS (< 0.9 kg N_2O-N ha^{-1}), in line with the emissions obtained from Chinese rice paddies (e.g. Liu et al., 2012), but they were much higher when CM was applied (3-4 kg N_2O-N ha^{-1}; Table 8) due to the large amount of organic-C applied and to the weak initial anaerobic conditions (Fig.5d). Emissions were enhanced in the days following organic fertilisation which is in accordance with other authors (Chadwick et al., 2000; Rochette et al., 2004; Vallejo et al., 2006), and tended to increase with the dose of NH_4^+ from the PS and AS treatments (in the order: PS-91, AS, PS-152). As Vallejo et al. (2006) explained, although the amount of N_2O coming from nitrification is generally small, it can be large when NH_4^+-N is applied, as in pig slurry where it is the main form of N. The cumulative N_2O emissions from CM and from the PS-152 treatment were significantly larger relative to control, but they accounted for only 0.21 to 1.12% of the applied N (Table 8).

When using U, 11% of the applied N was emitted, probably because U facilitates the onset of denitrification (Sampanpanish, 2012). The N_2 emission from the CM treatments was negligible (Table 8) because the initial conditions in the SP were not anaerobic enough to allow reduction to N_2 (Fig.5d). Also, some N immobilization could exist since the amount of C applied with CM was high (4588 kg C ha^{-1} were applied in CM-90, and 8663 kg C ha^{-1} in CM-170).

The PS application did not increase (N_2O+N_2) emission (Table 8). The low denitrification from PS (0.70-1.12% of the applied N was lost as (N_2O+N_2)-N during the SP) may be due to the low soil organic-C content, limiting denitrification.

The increase in CM dose tended to decrease N_2O and N_2O+N_2 emissions, while the increase in PS dose tended to increase them (Table 8). It is documented that N_2O emissions were closely associated with the C/N ratio of the incorporated organic materials (Ma et al., 2009), a high C/N ratio (e.g. chicken manure) often decreases N_2O emission, while N_2O emission is generally facilitated by organic material with low C/N ratio (e.g. pig slurry) (Zou et al., 2005; Ma et al., 2009).

In addition, other measurements could be applied to improve fertiliser N use efficiency in paddy fields, especially during the seedling period. For example, deep placement of urea, applying slow-release and controlled release N fertiliser would be effective in minimize N losses. Also, nitrification or urease inhibitors could have effect on improving nitrogen use efficiency (Sun et al. 2015).

4.5.2. Methane emission during the seedling period

In both sites, the cumulative CH_4 emissions during the SP were about half the cumulative CH_4 emissions during the rice crop season. This differs from other records, as in China, Ma et al. (2012) found that the emission during the SP was the same as that during the rice crop season, probably because of the intensive nursery patch system.

Urea has been described as an inhibitor of CH_4 emission (Schütz et al., 1989). Methane emissions were only increased in CM treatments. Obviously, organic fertiliser provided methanogenic substrates, and could promote CH_4 production during the rice SP period (Liu et al., 2012).

When applying CM (high organic-C and at agronomic NH_4^+-N doses), the cumulative CH_4-C emission was 7% of the applied organic-C for CM-90-12 and 2% of it for CM-170-12. When applying PS (relatively low organic-C and agronomic NH_4^+-N doses), CH_4-C emission was about 230% of the applied C and the percentage did not increase with the PS dose. Therefore, CH_4 formation must have consumed some soil-C as the previous crop remains had been thoroughly removed.

4.5.3. Carbon dioxide flux (ecosystem respiration) during the seedling period

In both sites, no significant effect of U, AS or PS application on the cumulative ecosystem respiration was found (Table 8). When applying PS, the CO_2-C emission was 428% of the applied organic-C for PS-91, and 242% for PS-152; in mass it was the same from both treatments indicating that the main C source was the soil organic matter.

When applying CM, the cumulative CO_2-C emission was 7.5% of the applied organic-C for both CM doses; twice (CM-90) or five times (CM-170) that from the control. This is in concordance with the results of Hossain and Puteh (2013) who found that the application of chicken manure increased the cumulative CO_2 emission by 121% compared to control as also stated for manures by Moore and Dalva (1993).

4.6. Global warming potential (GWP) and greenhouse gas intensity (GHGI)

4.6.1. Global warming potential and greenhouse gas intensity during the rice crop season

The global warming potentials (GWP) of the present study (Table 5) are in the same range as those found by Ma et al. (2013) and Wang et al. (2013). One key aspect here is that PS did not increase the GWP with respect to the control as AS did, while maintaining high yields (Table 5).

The soil acted as a net sink of CH_4 and N_2O for AS-top-11, U-11 and the control (2012) resulting in a negative GWP during the rice crop season (Table 5). Negative GWP values suggest that the C sequestration exceeded the CO_2-eq emission (Table 5).

Overall, the GWPs were high for the treatments with CM, since CM application increased CH_4 and N_2O emission (Table 5). Previously published field measurements of CH_4 and N_2O emissions from rice systems with different types of organic fertilisers applied also demonstrated that this practice increases the GWP (Ma et al., 2013; Wang et al., 2013).

The yields obtained indicate that the different fertilisation options are feasible with the exception of AS-top-11 and CM-170-12 which were affected by different agronomic constraints. In AS-top-11 there was a lack of available N (N losses reached 80% of the applied N). In the CM-170-12 treatment plants were damaged by a very serious attack of the fungus *Pyricularia oryzae*, which reveals excessive N fertilisation (Yanni and Sehly, 1991).

As a consequence, the GHGI relating GWP to grain yield was significantly higher for the CM treatments than for the mineral fertiliser and control treatments (Table 5). Overall, high N fertiliser doses are not recommended here for rice production. In the future, the N use efficiency in intensively managed rice crops should be improved.

The GHGI ranged from -1.57 to 5.18 kg CO_2-eq kg^{-1} grain yield (Table 5). A negative GHGI (consequence of the negative GWP) indicates equilibrium among yield, carbon sequestration into the soil and GHG emission (Mosier et al., 2006, IPCC, 2013).

With the exception in of the CM-90-12 (5.18 kg CO_2-eq kg^{-1} grain yield) and CM-170-12 (4.63 kg CO_2-eq kg^{-1} grain yield) treatments (Table 5), the rest of the GHGI of the present study (ranged from -1.57 to 1.97 kg CO_2-eq kg^{-1} grain yield) are lower than those reported by Qin et al. (2010) and Shang et al. (2011) under continuous flooding conditions (2.06 to 3.22 kg CO_2-eq kg^{-1} grain yield).

In order to achieve the goals of high yield and low GWP over the long-term it an optimum dose of N fertiliser and a proper amount of organic matter should be applied especially when organic fertilisers are used.

4.6.2. Global warming potential during the seedling period

In the present study, the average GWP of GHG emission during the rice SP was as high as in the study of Linquist et al. (2015) during the rice crop season when urea was the N fertiliser. However, in Site 1 the U application remarkably decreased the GWP since

N_2O and CH_4 emissions were significantly low (Table 8). In Site 2, PS applied at agronomic doses (~170 kg N ha^{-1}) kept the GWP to a minimum. Overall, the GWP was high for the treatments with CM as they significantly increased CH_4 and N_2O emission (Table 8). To achieve the goal of GHG reduction during the rice SP, the negative impact of organic fertiliser (e.g., CM in this study) should be considered.

4.7. Influence of temperature on greenhouse gas emissions

A significant correlation between soil temperature, mean air temperature and daily N_2O fluxes was found: negative in Site 1 in 2011 and positive in 2012 and Site 2 (2012) (Table 6). A positive correlation agrees with those of Livesley et al. (2008) and Scheer et al. (2008) who observed that high N_2O emissions coincide with high air and soil temperatures. Thus, the differences between years can be explained by the higher temperatures in 2012 than in 2011 (Fig.1) and because in 2012 measurements started when the soil was not yet anaerobic (Table 6). Many studies found significant effects of temperature on N_2O emissions (Conrad et al., 1983; Skiba and Smith, 2000). Temperature directly affects the activity of bacteria and controls biological oxygen consumption and this may also affect the emission of N_2O (Lesschen et al., 2011).

A significative positive correlation between soil temperature, mean air temperature and daily CH_4 flux was found in Site 2 (Table 6), despite some previous studies showing that the effect of temperature on CH_4 emissions was not consistent (Dijkstra et al., 2012). However, Huang et al. (2001), Kögel-Knabner et al. (2010) and Das and Adhya (2012) indicated that under permanent flooding, the seasonal variation of CH_4 emission from rice was mainly attributable to soil temperature and mean air temperature. The variability of the temperature response from one location to another and the interactions of temperature with other factors that affect CH_4 emissions are still not well understood (Schaufler et al., 2010) and this may explain the lack of correlation in Site 1.

Although CO_2 fluxes were not considered in the GHG evaluation, soil CO_2 flux has been described as influenced by temperature (Keller et al., 2004). A significant correlation between soil temperature, mean air temperature and daily respiration (in both years and both sites) was found too (Table 6). Soil temperature significantly influences respiration fluxes by inducing the acceleration of soil organic carbon decomposition, root respiration, and microbe respiration. Song et al. (2003) also found evidence of the influence of temperature on CO_2 emission both in the field and in laboratory experiments.

5. Conclusions

Under the tested Mediterranean conditions, the background application of U and AS, with an AS topdress led to the maximum rice yields (8-10 Mg ha^{-1}). Background fertilisation with organic fertilisers (CM or PS) at 90 kg NH_4^+-N ha^{-1} led to similar yields than the mineral fertilisers treatments.

During the rice SP, mineral fertilisers such as AS (120 kg N ha^{-1}) and the application of PS at an agronomic dose (91 kg NH_4^+-N ha^{-1}) did not increase GHG emissions relative to control. Overall during this period the chicken manure (high C/N ratio) applied at similar NH_4^+- N doses to PS, increased N_2O, N_2O+N_2 and CH_4 emissions with respect to the control, which was not the case when applying PS (low C/N ratio). Thus, the introduction of PS could be an interesting fertiliser, keeping GHG emissions under control and ensuring feasible yields. However, CM did, increasing both emissions (CH_4 and N_2O) to an equivalent of 11 Mg CO_2-eq ha^{-1} (CM-90) as well as ecosystem respiration to 2 Mg CO_2 ha^{-1} (CM-170).

Nitrogen mineral fertiliser such as AS and U had no effect on cumulative N_2O emission during the rice crop, while increasing the dose of CM (high C/N fertiliser) the cumulative N_2O and N_2O+N_2 emissions tended to decrease. Denitrification was the dominant process in N_2O and N_2O+N_2 emissions, and must be taken into account to obtain an accurate assessment of the N balance. Chicken manure significantly increased CH_4 emission.

The postharvest period was a significant source of (N_2O+N_2)-N for the U treatment and acted as sink of CH_4 for all the treatments. The ecosystem respiration increased with high soil C application to soil (CM-170).

The GWP during the SP was low for AS and organic fertilisers with low C/N ratio (PS).

During the rice crop season, application of CM tends to increase GWP, although not significantly different between chicken manure treatments and urea treatment was observed. Maximum GWP values were observed in 2012 at CM-90 dose (37 Mg CO_2-

eq ha^{-1}) and tend to be halved at higher dose (CM-170), probably due to some microbial toxicity of the applied ammonium.

The results of the present study suggest the need to reconsider if a 1% EF for N_2O emissions (as suggested by IPCC in the 2007 guidelines) is universally applicable, or if different standards should be considered depending on the management practices.

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Table 1. Main soil properties of the rice paddy soils at Site 1 and Site 2. Annual averages of precipitation and air temperature[†]

Site	Site 1	Site 2
USDA textural class of the cultivated horizon	silty clay loam	silty loam
Organic matter (% d.m., Walkley-Black)	2.21	1.01
Calcium carbonate eq. (% d.m.; potenciometry)	37	29
Kjeldahl N (% d.m., volumetric titration)	0.15	0.08
NH_4^+-N (mg/kg d.m., UV-VIS spectrophotometry)	6.0	6.6
NO_3^--N (mg/kg d.m.; colorimetry)	3.0	6.7
P (mg/kg d.m.; Olsen; UV-VIS spectrophotometry)	44	6
K (mg/kg d.m.; ammonium acetate extract; ICP-OES spectrophotometry)	158	81
Na (mg/kg d.m.; ammonium acetate extract; ICP-OES spectrophotometry)	248	27
C/N	9.1	-
pH (1:2.5 water extract)	8.1	8.5
Electrical conductivity of the saturated soil-paste extract (EC_e) (dS m^{-1})	4.61	0.77
Precipitation (mm)	550	350
Temperature (°C)	17.0	14.6

[†]Meteorological Service of Catalonia and Aragon, http://www.ruralcat.net/web/guest/agrometeo.estacions

Table 2. Timing of the field main labours and gas sampling per year and site

Site	Year	Background fertilisation (dd/mm/yy)	Flooding (dd/mm/yy)	Sowing (dd/mm/yy)	Start of sampling (dd/mm/yy)	Topdress fertilisation (dd/mm/yy)	Drainage (dd/mm/yy)	Harvest (dd/mm/yy)	Rice crop season (days)	End of sampling (dd/mm/yy)	Postharvest sampling period (days)
Site 1	2011	14/04/11	26/04/11	27/04/11	27/05/11	07/07/11	05/09/11	15/09/11	111	12/04/12	210
	2012	18/04/12	24/04/12	25/04/12	26/04/12	04/07/12	04/09/12	13/09/12	141	03/01/13	111
Site 2	2012	15/05/12	16/05/12	16/05/12	23/05/12	05/07/12	11/09/12	17/10/12	152	23/10/12	-

Table 3. Fertilisation treatments applied annually at each site

Site	Year	Treatments	Background		Topdress	kg organic-C ha^{-1}
			kg NH_4^+-N ha^{-1}	kg organic-N ha^{-1}	kg NH_4^+-N ha^{-1} (as AS)	
1	2011	AS-top-11	0	-	50	-
		U-11	150	-	50	-
		CM-90-11	90 (9.5 t CM ha^{-1})	82	50	746
		CM-170-11	170 (19.1 t CM ha^{-1})	167	50	1500
1	2012	Control-12	0	-	0	-
		AS-top-12	0	-	50	-
		U-12	150	-	50	-
		CM-90-12	90 (15.2 t CM ha^{-1})	424	50	4588
		CM-170-12	170 (28.7 t CM ha^{-1})	800	50	8663
2	2012	Control	0	-	0	-
		AS-12	120	-	60	-
		PS-91-12	91 (30 t PS ha^{-1})	37	60	12
		PS-152-12	152 (51 t PS ha^{-1})	62	0	22

AS: ammonium sulphate; U: urea; CM: chicken manure; PS: pig slurry

Table 4. Main properties of the applied chicken manure and pig slurry

	Chicken manure		Pig slurry
Year	2011	2012	2012
pH	8.5	6.9	-
Dry matter (%)	29.2	77.2	3.74
Organic matter (%, d.m.)	59.7	78.2	60.59
Organic N (%, d.m.)	2.99	3.61	3.31
NH_4^+-N (%, d.m.)	3.10	0.76	7.49
Organic C (%, f.m.)	17.78	46.22	1.14
C/N	10	13.70	2.85

f.m.: fresh matter basis; d.m.: dry matter basis

Table 5. Average cumulative emission of N_2O-N, (N_2O+N_2)-N, CH_4, and ecosystem respiration (CO_2) over the entire rice crop. Percentage that the N_2O-N and the (N_2O+N_2)-N emission represent of the applied N and emission factor (EF). The ratio between the N_2O-N and (N_2O+N_2)-N emission is shown too. Global warming potential (GWP) of each treatment, rice yield and, greenhouse gas intensity (GHGI) per site and year

Site	Treatment -year	Cumulative N_2O-N (kg ha^{-1})	Cumulative (N_2O+N_2)-N (kg ha^{-1})	$\frac{N_2O-N}{\%\ N\ applied}$	EF (%)	$\frac{(N_2O+N_2)-N}{\%\ N\ applied}$	$\frac{N_2O-N}{(N_2O+N_2)-N}$	Cumulative CH_4 (kg ha^{-1})	GWP (kg CO_2-eq ha^{-1})	Yield[a] (kg ha^{-1})	GHGI (kg CO_2-eq kg^{-1} yield)	Cumulative CO_2 (kg ha^{-1})
1	AS-top-11	-11.91b	39.81	-	-	79.62	-	-222b	-9114c	5187b	-1.57b	9316
	U-11	-3.13ab	40.86	-	-	20.43	-	-125b	-4077b	9990a	-0.41b	10304
	CM-90-11	4.76a	43.46	3.61	-	32.92	0.11	181a	5965a	7547ab	0.79a	10975
	CM-170-11	1.38ab	33.49	0.63	-	15.43	0.04	98a	2876a	8096a	0.35a	13412
	Significance	*	ns	-	-	-	-	*	*	*	*	ns
1	C-12	1.95b	19.69	-	-	-	0.10	-130c	-2684c	7518a	-0.36c	5504b
	AS-top-12	5.63ab	23.72	11.26	7.3	47.44	0.24	292b	8980b	8482a	1.06b	8627ab
	U-12	5.74ab	31.32	2.87	1.87	15.66	0.18	632ab	17513ab	8859a	1.97b	8187b
	CM-90-12	10.05a	18.88	2.12	1.71	2.12	0.53	1346a	36660a	7068a	5.18a	10638ab
	CM-170-12	9.31ab	16.08	1.09	0.86	1.10	0.58	465ab	14333ab	3092b	4.63a	15366a
	Significance	*	ns	-	-	-	-	*	*	*	*	*
2	C-12	1.93	7.82	-	-	-	0.25	126	3609b	3715b	0.97ab	6798
	AS-12	1.72	10.88	0.96	-0.11	6.04	0.16	319	8475a	8287a	1.02a	10099
	PS-91-12	1.73	9.08	1.35	-0.14	6.87	0.19	203	5580ab	7385ab	0.75b	8275
	PS-152-12	2.10	9.17	0.98	0.08	4.22	0.23	283	6577ab	7364ab	0.89ab	8470
	Significance	ns	ns	-	-	-	-	ns	*	*	*	ns

[a] Yield was adjusted to 14% of water content; C: control; AS: ammonium sulphate; U: urea; CM: chicken manure; PS: pig slurry; *: significant at the 0.05 probability level. ns: not significant; Within columns, means followed by the same letter are not significantly different according to Tuckey's test (α=0.05).

Treatments: Site 1: C: Control: no N applied; AS-top-11 and -12: ammonium sulphate (AS) at 50 kg NH_4^+-N ha^{-1} (applied topdress); U-11 and -12: urea at 150 kg N ha^{-1} (applied background) + AS at 50 kg NH_4^+-N ha^{-1} (applied topdress); CM: chicken manure, numbers behind indicate the applied rate as kg NH_4^+-N ha^{-1} (CM-90-12: 90 kg NH_4^+-N ha^{-1} and CM-170-12: 170 kg NH_4^+-N ha^{-1} was applied background) + AS at 50 kg NH_4^+-N ha^{-1} (applied topdress); Site 2: C: Control: no N applied; AS: ammonium sulphate at 120 kg NH_4^+-N ha^{-1} (applied background)+ AS at 50 kg NH_4^+-N ha^{-1} (applied topdress) ; PS: pig slurry, numbers behind indicate the applied rate as kg NH_4^+-N ha^{-1} : PS-91-12: 91 kg NH_4^+-N ha^{-1} (applied background) + 50 kg NH_4^+-N ha^{-1} (applied topdress); and PS-152-12: 152 kg NH_4^+-N ha^{-1} (applied background).

Table 6. Spearman rank correlation coefficients between soil temperature, air mean temperature, redox potential (Eh), and N_2O-N, (N_2O+N_2)-N, CO_2 and CH_4

Variables	N_2O-N			(N_2O+N_2)-N			CO_2			CH_4		
	Site 1		Site 2	Site 1		Site 2	Site 1		Site 2	Site 1		Site 2
	2011	2012	2012	2011	2012	2012	2011	2012	2012	2011	2012	2012
Soil T	-0.153*	0.030	0.197*	0.251*	0.043	-0.027	0.178*	0.341*	0.303*	0.091	0.079	0.269*
Air mean T	-0.138*	0.031	0.191*	0.341*	0.079	-0.046	0.189*	0.454*	0.313*	0.093	0.101	0.328*
Eh	-	-0.049	-	-	-0.004	-	-	-0.015	-	-	-0.171*	-

Eh: redox potential; *: significant at the 0.05 probability level

Table 7. Cumulative emissions of N_2O-N, (N_2O+N_2)-N, CH_4, CO_2 and global warming potential (GWP) from each treatment, at both sites during the rice seedling period (SP) of 2012. Nitrogen losses are related to the applied total N. Also, N, CH_4, and CO_2 emissions are related to the cumulative emissions during the rice crop season (RC). The ratio between the N_2O-N and (N_2O+N_2)-N emission during the SP is shown too

Site	Treatments	Cumulative N_2O-N (kg ha^{-1})	Cumulative (N_2O+N_2)-N (kg ha^{-1})	$\frac{(N_2O+N_2)\text{-}N}{\%\ N\ applied}$	$\frac{(N_2O+N_2)\text{-N}}{(N_2O+N_2)\text{-N}_{RC}}$ (%)	Cumulative CH_4 (kg ha^{-1})	$\frac{CH_4}{CH_{4\ RC}}$ (%)	Cumulative CO_2 (kg ha^{-1})	$\frac{CO_2}{CO_{2\ RC}}$ (%)	GWP (kg CO_2-eq)
Site 1	C-12	0.15 b	0.87 b	-	4.40	0.01 c	0.003	458 b	5.3	44 c
	U-12	0.81 b	16.64 a	11.00	53.12	-19.07 c	-	465 b	6.0	-236 c
	CM-90-12	3.71 a	3.21 b	1.80	9.50	417.81 a	37.61	1281 ab	12.0	11497 a
	CM-170-12	2.85 a	2.67 b	0.27	5.78	187.35 b	54.66	2397 a	16.0	5532 b
	Significance	*	*	-	-	*	-	*	-	*
Site 2	C-12	0.43 b	1.01	-	12.24	56.83	44.56	177	2.6	1544
	AS-12	0.52 ab	0.89	0.74	8.08	73.65	23.07	114	1.1	1996
	PS-91-12	0.25 b	0.84	0.70	9.57	36.49	17.82	190	2.3	986
	PS-152-12	0.87 a	1.91	1.12	25.95	65.04	22.91	197	2.3	1885
	Significance	*	ns	-	-	ns	-	ns	-	ns

RC: the rice crop season was, at site 1, from 26/04/2012 to 12/09/2012, and at site 2 from 23/05/2012 to 23/10/2012. C: control; AS: ammonium sulphate; U: urea; CM: chicken manure; PS: pig slurry; *: significant at the 0.05 probability level. ns: not significant; Within columns, means followed by the same letter are not significantly different according to Tuckey's test (α=0.05).
Treatments: Site 1: C: Control: no N applied; U: urea at 150 kg N ha^{-1} (applied background); CM: chicken manure, numbers behind indicate the applied rate as kg NH_4^+-N ha^{-1} (CM-90-12: 90 kg NH_4^+-N ha^{-1} and
CM-170-12: 170 kg NH_4^+-N ha^{-1} was applied background); Site 2: C: Control: no N applied; AS: ammonium sulphate at 120 kg NH_4^+-N ha^{-1} (applied background); PS: pig slurry, numbers behind indicate the applied rate as kg NH_4^+-N ha^{-1} (PS-91-12: 91 kg NH_4^+-N ha^{-1} and PS-152-12: 152 kg NH_4^+-N ha^{-1} was applied background).

Table 8. Average cumulative emission of N_2O-N, (N_2O+N_2)-N, and CH_4 and the ecosystem respiration (CO_2) during the postharvest period at Site 1 in years 2011 and 2012

Year	Treatments	Cumulative N_2O-N (kg ha^{-1})	Cumulative (N_2O+N_2)-N (kg ha^{-1})	Cumulative CH_4 (kg ha^{-1})	Cumulative CO_2 (kg ha^{-1})
2011 (210 days)	AS-top	-0.06	17.84ab	-97.95	492.72a
	U	1.25	24.06a	-67.48	680.42a
	CM-90	0.87	10.56b	-23.25	-13.14b
	CM-170	0.26	10.67b	-52.21	842.07a
	Significance	ns	*	ns	*
2012 (111 days)	C	-3.53	6.29b	-335.99	92.09b
	AS-top	-3.33	9.44b	-416.50	433.08b
	U	-1.35	23.72a	-197.98	360.99b
	CM-90	-1.93	9.13b	-399.11	501.96b
	CM-170	-2.61	18.72ab	-152.59	2000.63a
	Significance	ns	*	ns	*

AS: ammonium sulphate; U: urea; CM: chicken manure; ns: not significant; *: significant at the 0.05 probability level. Within column means followed by the same letter are not significantly different according to the Tuckey's test (α=0.05).

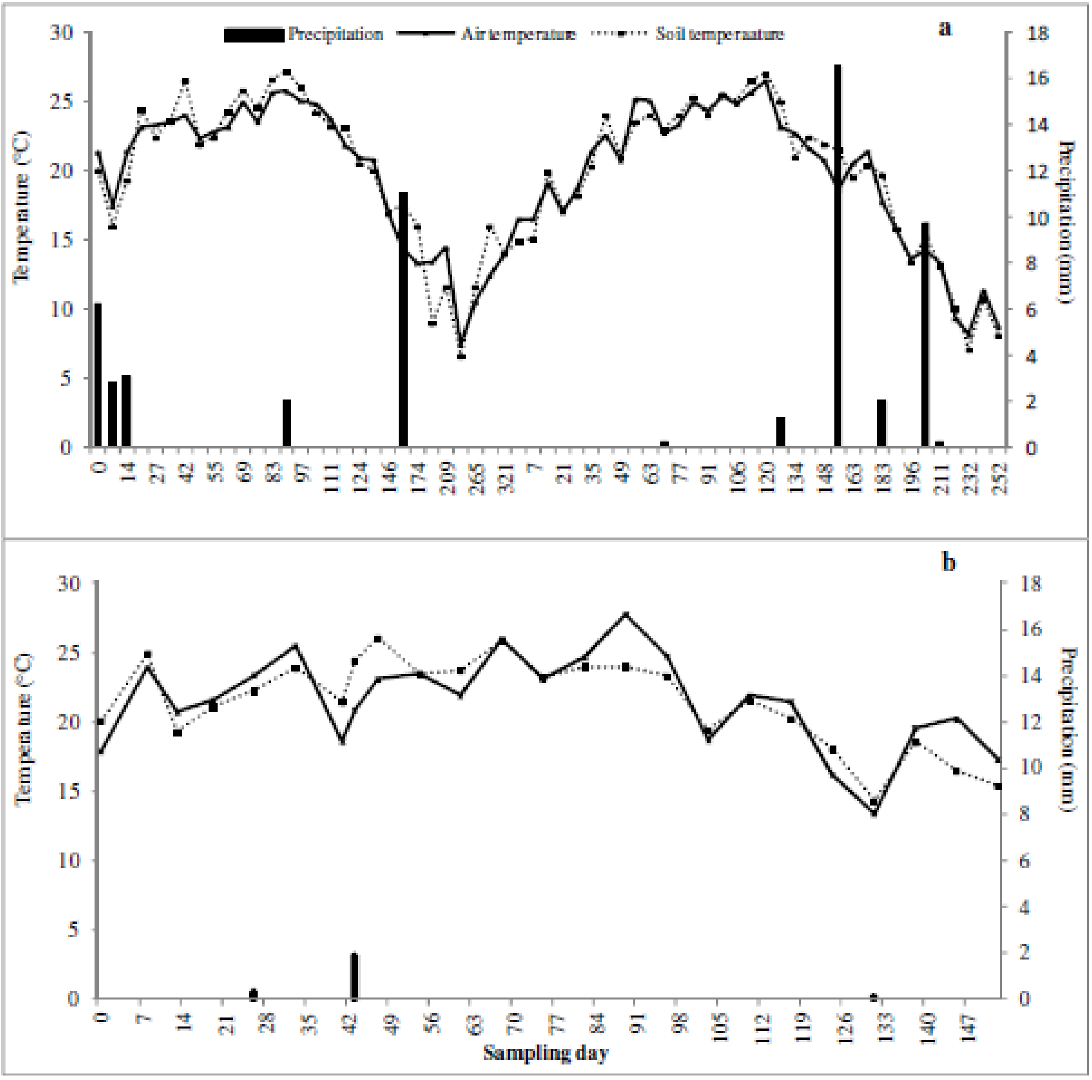

Fig. 1. Evolution of the actual precipitation, air temperature and soil temperature during the rice cropping seasons of 2011 and 2012 at Site 1 (a), and during 2012 at Site 2 (b)

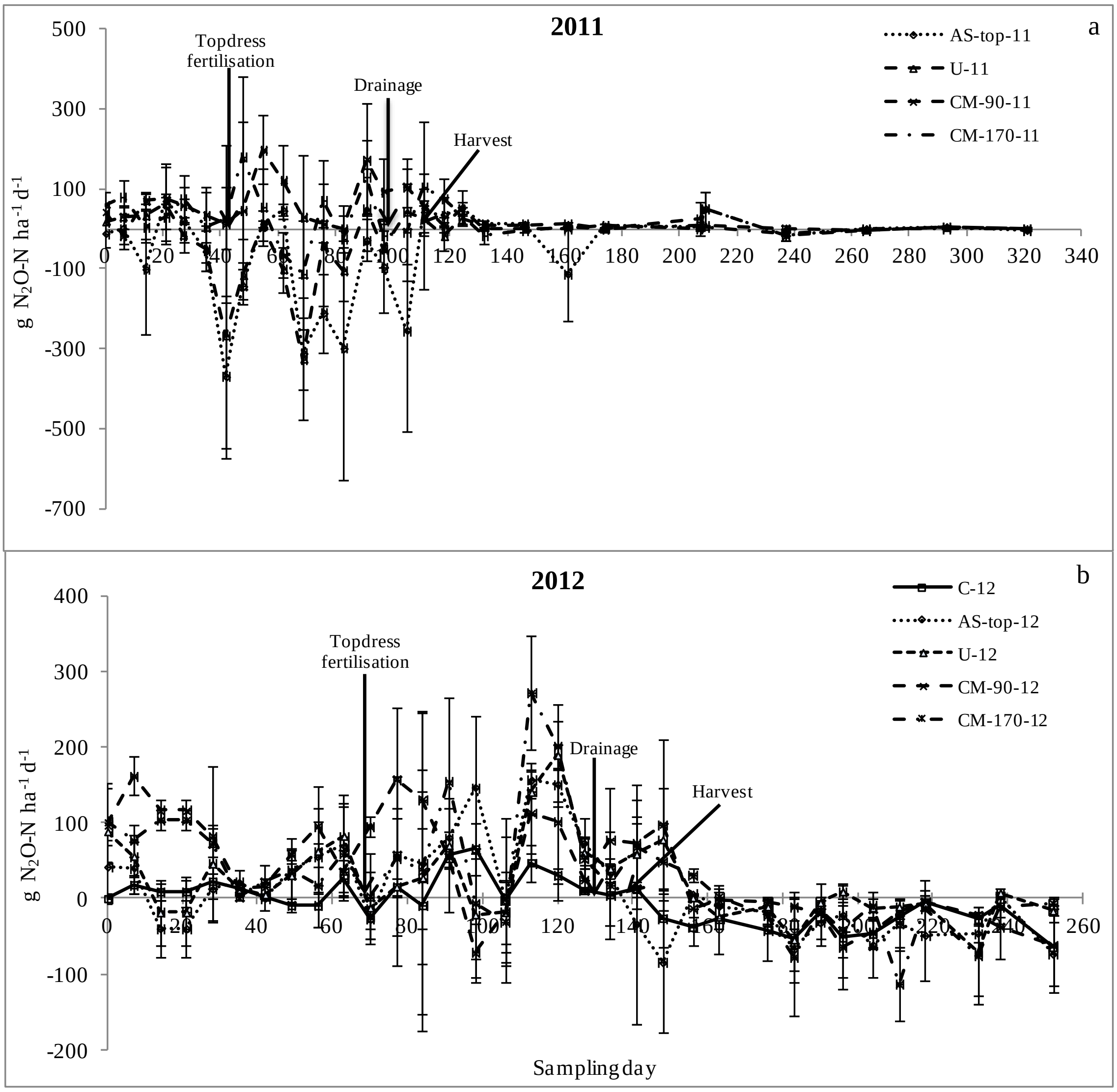

Fig. 2. Evolution of the sampled daily fluxes of N_2O-N from Site 1 during the rice crop season of 2011 (a) and 2012 (b)

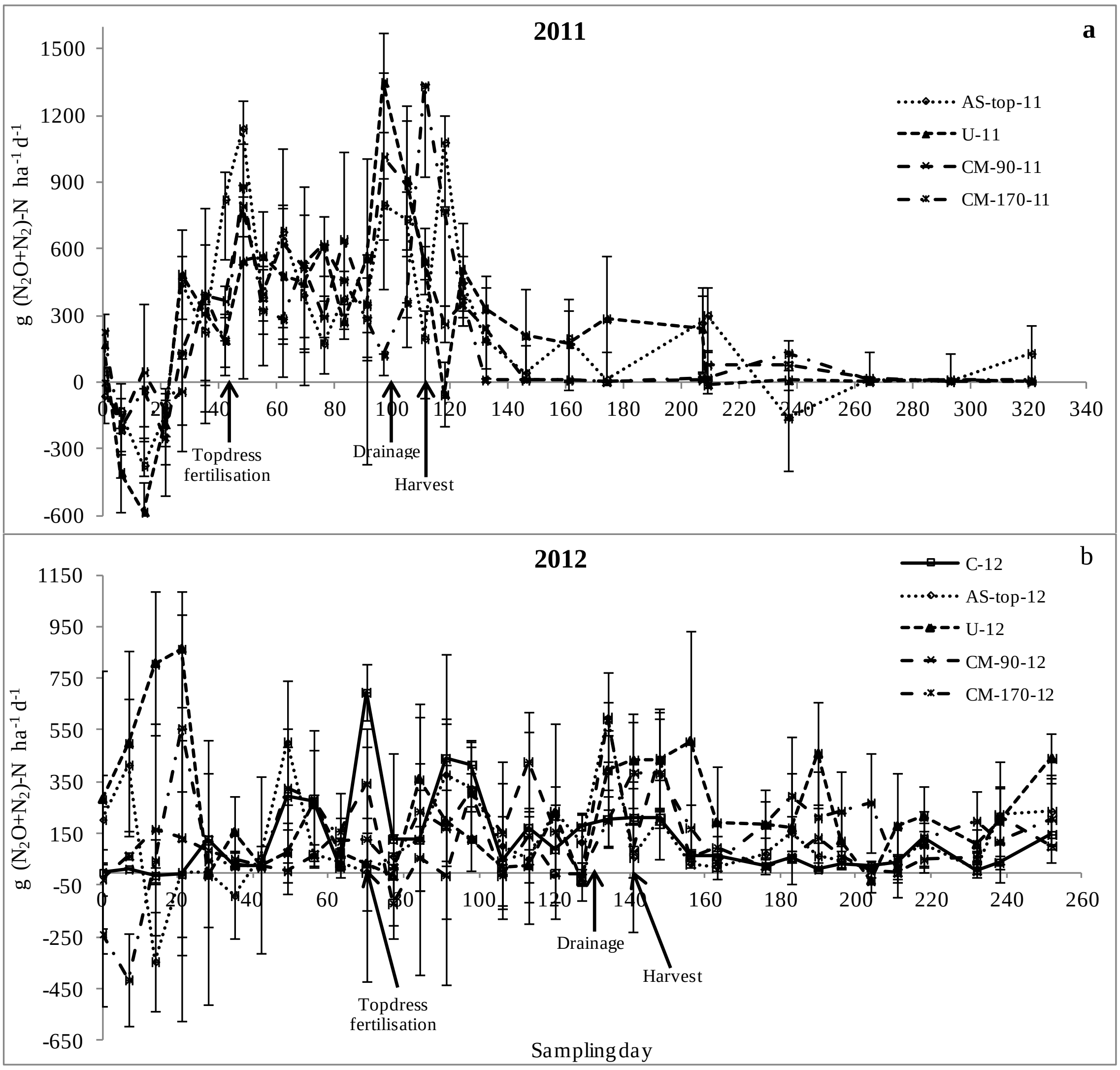

Fig. 3. Evolution of the sampled daily fluxes of (N_2O+N_2)-N from Site 1 during the rice crop season of 2011 (a) and 2012 (b)

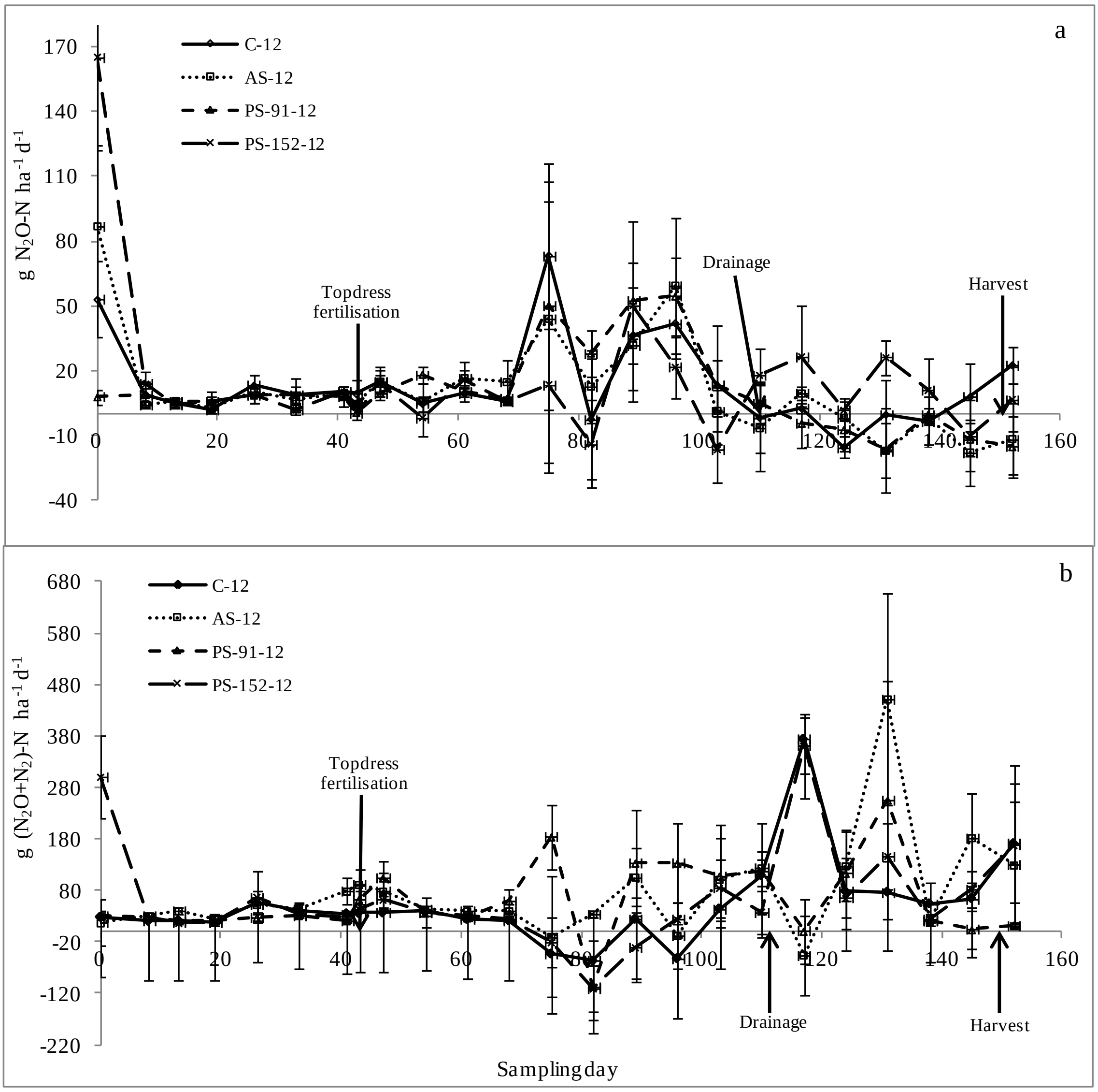

Fig. 4. Evolution of the sampled daily fluxes of N_2O-N (a) and (N_2O+N_2)-N (b) from Site 2 during the rice crop season of 2012.

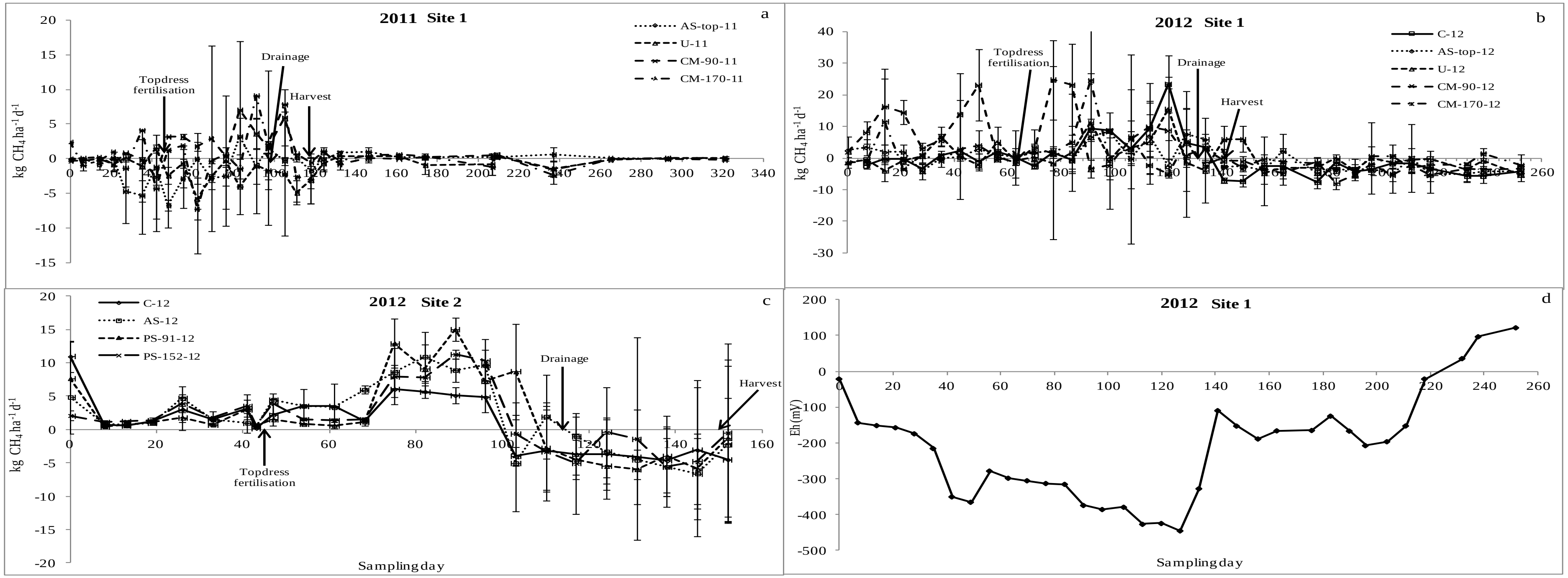

Fig. 5. Evolution of the sampled daily fluxes of CH_4 at Site 1 in 2011 (a), CH_4 at Site 1 in 2012 (b), CH_4 at Site 2 in 2012 (c), and redox potential (Eh) evolution at Site 1 in 2012 (d)

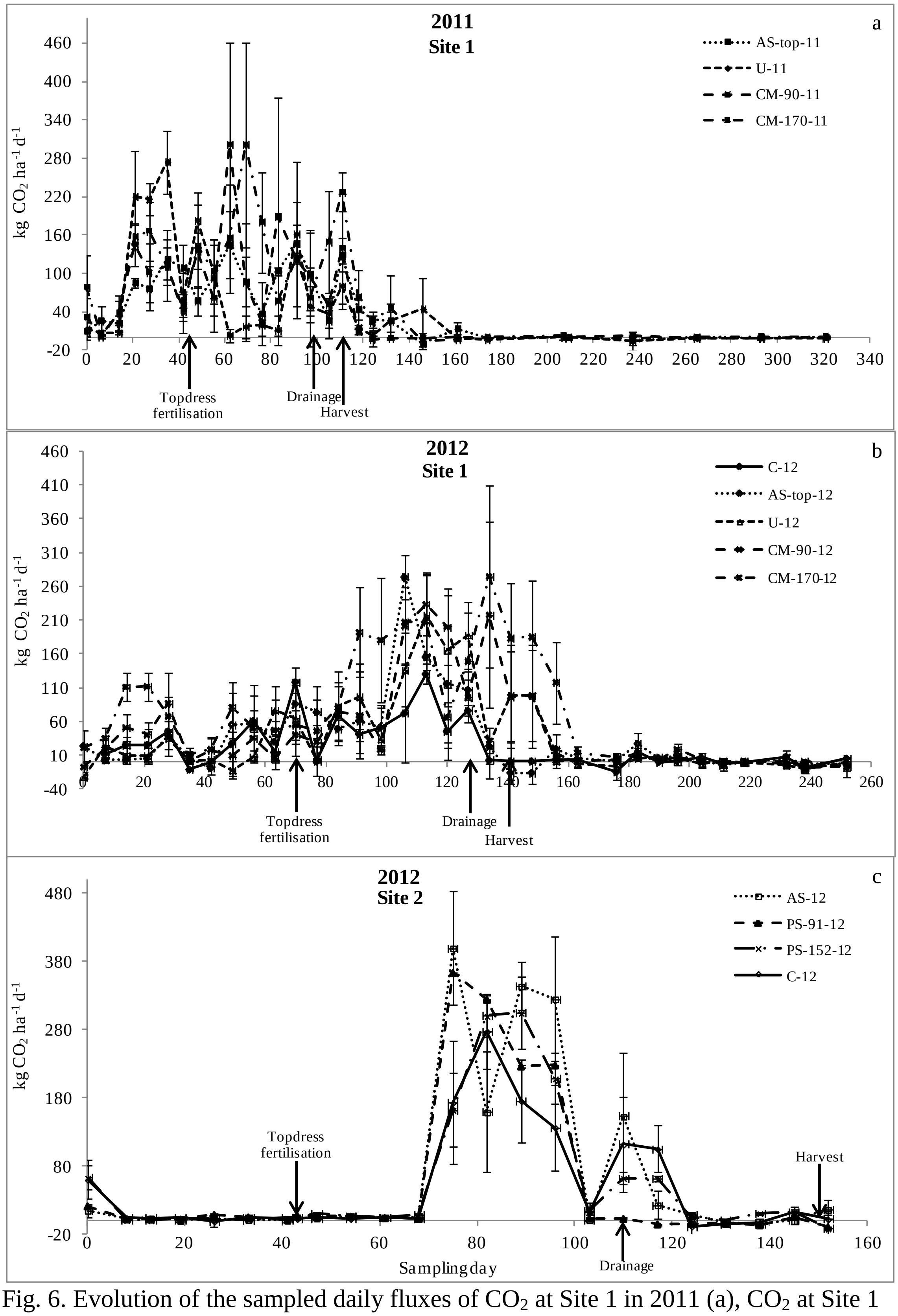

Fig. 6. Evolution of the sampled daily fluxes of CO_2 at Site 1 in 2011 (a), CO_2 at Site 1 in 2012 (b), and CO_2 at Site 2 during 2012 (c)

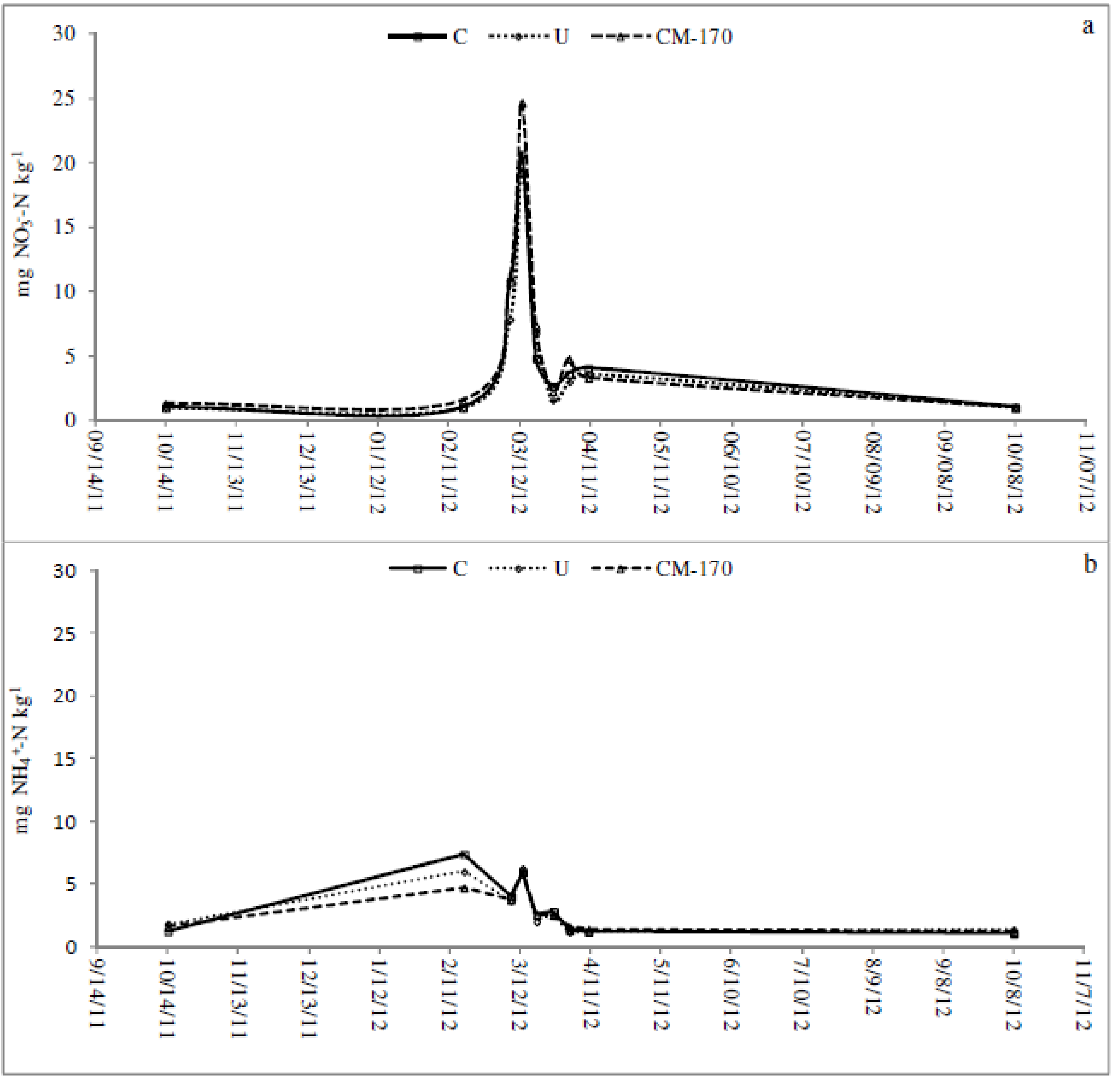

Fig. 7. Evolution of soil (a) NO_3^--N content and (b) NH_4^+-N content during the postharvest period at Site 1 in 2012 in 2011 and 2012

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Chapter 6. Effect of stover management and nitrogen fertilization on greenhouse gases emission from irrigated maize in a high nitrate-N soil

Chapter 6. Effect of stover management and nitrogen fertilisation on greenhouse gases emission from irrigated maize in a high nitrate-N soil

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Abstract

In order to improve the sustainability of the maize production system management practices that mitigate greenhouse gases (GHG) emission while keeping yield high are required. This study compared the effect of maize stover incorporation or removal along with different mineral N fertiliser doses (0, 200 and 300 kg N ha^{-1}) on the emission of greenhouse gases on a sprinkler irrigated maize (*Zea mays* L.) crop in the Ebro Valley. Nitrous oxide (N_2O), carbon dioxide (CO_2), and methane (CH_4) emissions were sampled weekly using a semi-static closed chamber and quantified with the photoacoustic technique during two years under Mediterranean conditions on a high nitrate-N soil. Applying fertiliser tended to increase N_2O emissions and stover incorporation did not have any clear effect. Nitrification was probably the main process leading to N_2O which ranged from -0.11 to 0.36% of the applied N, below the IPCC (2007) values. Denitrification was limited due to low soil moisture content and limiting readily available carbon. Stover incorporation increased CO_2 emission. Nitrogen fertilisation tended to reduce CO_2 emission but only in 2011. The maize field acted as a net CH_4 sinks (in 2011) and mineral fertiliser application decreased CH_4 oxidation by the soil. Considering global warming potential, greenhouse gas intensity, as well as N_2O cumulative emissions and yield, it can be concluded that no fertilisation (control treatment) regardless of stover management was the best option combing productivity with keeping greenhouse gases emission under control. The application of nitrogen in

many areas of the Ebro Valley (Spain) is not necessary due to the high N soil content (i.e. 200 g NO_3-N kg^{-1}) until the soil restores a normal mineral N content.

Keywords: nitrous oxide, carbon dioxide, methane, nitrification, WFPS

1. Introduction

Agricultural production practices play an important role in the global fluxes of methane (CH_4), nitrous oxide (N_2O) and carbon dioxide (CO_2). These greenhouse gases (GHG) contribute each 6.5%, 5.5% and 0.1% to the total anthropogenic greenhouse gas emissions, respectively (Sänger et al., 2011). The production or consumption of these gases is mainly due to biological processes which are strongly affected by natural conditions and agricultural management (Snyder et al., 2009).

Soils commonly produce N_2O during both nitrification and denitrification processes (Bremner, 1997), with the possibility of both processes to coexist within the same soil aggregate due to microsite variability (Kremen et al., 2005). In addition, N_2O can also be formed in soils by nitrifier-denitrification, chemodenitrification, and co-denitrification (Wrage et al., 2001, 2005). Therefore the magnitude of fluxes between soil and atmosphere depends largely on soil temperature, soil water content, oxigen (O_2) availability, nitrogen (N) availability (nitrate and ammonium), and organic carbon (C) availability (Davison, 1991; Farquharson and Baldock, 2008; Seungdo and Bruce, 2008). In addition, the above regulators are strongly influenced by weather, vegetation, soil properties (bulk density, organic matter, pH and clay content), and soil management (Firestone and Davidson, 1989; Dobbie and Smith, 2003; Seungdo and Bruce, 2008). Nitrous oxide emission often indicates an inefficient use of nitrogen (N) in agricultural soils (Bouwman et al., 2002).

Although soils are usually considered as net sources of atmospheric N_2O, they can also act as sinks, at least temporarily (Ryden, 1981; Minami, 1997; van Groenigen et al., 2015). Consumption of N_2O is enzymatically and energetically feasible van Groenigen et al., 2015). The sink strength depends on the potential for N_2O reduction to N_2, the ease of N_2O diffusion within the soil profile and its dissolution in soil water (Chapuis-Lardy et al., 2007). Rosenkranz et al. (2006) found that N_2O consumption occurred not only at relatively high soil moisture content (from 25 to 80% WFPS), but also at relatively low soil moisture content (from 15 to 25% WFPS). Soil was even found to be an N_2O sink under very dry and oxic soil conditions (Donoso et al., 1993; Flechard et al., 2005; Goldberg and Gebauer, 2009a,b). One of the reasons may be that atmospheric N_2O diffuses into the soil when the N_2O concentration in the soil profile is low (Clough et al., 2005; Heincke and Kaupenjohann, 1999). Another reason for N_2O consumption under dry conditions may be aerobic denitrification by heterotrophic nitrifiers (Robertson et al., 1989) or nitrifier denitrification by autotrophic ammonia oxidizers (Wrage et al., 2001). Most scientists assume that aerobic denitrification is the main process for N_2O consumption in dry soil with relatively high O_2 concentrations (Bateman and Baggs, 2005; Chapuis-Lardy et al., 2007; Morley and Baggs, 2010). However, there is still a lack of experimental evidence to support this assumption.

An environment is a source of CH_4 when its production (methanogenic Archaea) exceeds its consumption (methanotrophic bacteria) and it leads to CH_4 emission. If the opposite happens, the environment is a CH_4 sink (Le Mer and Roger, 2001). In general, aerobic conditions do not favor CH_4 production because CH_4 is usually formed in soils by the microbial breakdown of organic compounds in strictly anaerobic conditions (Smith et al., 2003). Methane is eliminated from the soils by microbial oxidation (Le Mer and Roger, 2001). Although arable soil has been identified as one of the main CO_2 sources in agro-ecosystems due to inappropriate management practices, it can also serve as a net sink for atmospheric CO_2 through appropriate agricultural management (Paustian et al., 1997; Forest et al., 2007; Patiño-Zúñiga et al., 2009).

Crop stover's incorporation is an important resource of carbon (C) and N, as well as other nutrients (Kumar and Goh 1999), improving soil fertility and increasing soil organic C (Singh et al., 2008). Crop stover incorporation also influences denitrification rate, abundance of denitrifiers, and N_2O emission from soil (Henderson et al., 2010). It may have effects on soil moisture, temperature, dissolved organic carbon (DOC) content, inorganic N concentration, microbial activity, and redox potential (Kumar and Goh, 1999), thus regulating N_2O release from soil. The C/N ratio of the incorporated stover into soil is an important determinant not only of the magnitude of inorganic N dynamics but also for N_2O emissions (Millar and Baggs, 2004; Toma and Hatano, 2007). Nitrous oxide production has been found to be high following the incorporation of crop residues with low C/N ratio rather than that of high C/N ratio ones (Baggs et al., 2000, Huang et al., 2004) due to mineralization promotion, resulting in high NH_4^+ availability for nitrification and organic C release to allow denitrification in the presence of NO_3^- (Baggs et al., 2000). In contrast, addition of high C/N ratio residues might decrease the available N for nitrification and denitrification due to microbial N immobilization, thereby lowering N_2O production at least in the short term. Results from the few available empirical studies show that the crop stover removal impacts on soil GHG emission, however, are inconsistent. According to Johanson and Barbour (2010) maize stover removal did not alter soil CO_2 nor N_2O emissions compared to stover retained treatments. In other studies, removing crop stover decreased soil N_2O emissions (Singh et al. 2008). Baggs et al. (2003) and Abalos et al. (2012) reported a stimulation of N_2O emission when incorporating crop stover to soil.

In Spain, more than 99 000 ha are devoted to intensive maize produced under irrigation (Ministerio de Agricultura Pesca y Alimentación, 2014). The Ebro Valley is one of the most intensive agricultural areas in Spain, where 30% (72 000 ha) of the irrigated area is dedicated to maize (Villar et al., 2002). The maize stover production in this area ranges from about 14 to 17 t dry matter ha^{-1} $year^{-1}$ (Lloveras et al., 2012). Average crop yields in the area range from 10 to 15 t maize grain ha^{-1} (14% moisture) under sprinkler irrigation (Cela et al., 2011). Under good agronomical conditions, the most efficient farms can produce up to 20 t ha^{-1} (Biau et al., 2013). About 50% of the farmers at the Ebro Valley incorporate crop stover to the soil and the rest allot this by-product to animal consumption or any other purposes depending on the price (Biau et al., 2013). Half of the maize-producing land located in the Ebro Valley, is being fertilised using mineral N where the rest receives organic fertilisers mainly pig slurry (Sisquella et al., 2004). High yielding maize growing in the Spanish agro-systems requires water but also adequate input of available nitrogen (N) and a long growing season. It is common practice to apply alone N mineral at above 300 kg N ha^{-1} (Sisquella et al., 2004). High pre-sowing soil N content is the result of excessive N application to previous crops, which can accumulate in the soil (Berenguer et al., 2009). Meaning that successive crops can not efficiently utilize the residual nitrate available in the soil profile and often led to substantial accumulation of residual nitrate in the soil profile (Ju et al., 2009; Wan et al., 2009). Nitrate can leach into deeper soil layers after high irrigation rates or heavy rainfall, this can result in pollution of shallow groundwater (Ju et al., 2003; Ju et al., 2007). Thus, nitrate accumulation and leaching may be an important pathway for N fertiliser losses in the cropping systems. It is well documented by Wan et al. (2009) that the persistence of much nitrate available in the soil profile can determine low denitrification rates due to insufficient readily available C and by low soil moisture limitation. Moreover, the high organic matter mineralization detected in the Ebro Valley (Badia, 2000) also contributes to high pre-planting soil N contents (Cela et al., 2007). Villar et al. (2002) quantified an excess of N in the system which was sufficient to produce above 11 to 12 t ha^{-1} of maize yield without N fertilisation.

It has been well documented that the application of mineral fertilisers does not only increase the N_2O but also the CO_2 and CH_4 emissions (Ruser et al., 2001, 2006; Scheer et al., 2008). However, few studies exist on GHG emission from maize crop soils with a high mineral N content (200 g N kg^{-1} on average) under Mediterranean conditions. The objective of this study was to compare the effect of two different maize stover management (incorporation or removal) combined with different doses of mineral N fertiliser on the emission of greenhouse gases (N_2O, CH_4 and CO_2) in a high mineral N (200 g N kg^{-1} on average) maize (*Zea mays* L.) system under Mediterranean conditions.

2. Materials and methods

2.1. Site and soil characteristics

The study was carried out at a maize field (*Zea mays* L.) located at Almacellas (NE Spain, 41º43'N, 0º26'E) under sprinkler irrigation during 2011 and 2012. The location is characterized by a semiarid climate, with an average annual temperature of 14.8°C and an average (last 10 years) annual rainfall of 350 mm, with summer being the driest and hottest season of the year (rainfall below 13 mm and temperature sometimes above 30°C). The average relative (last 10 years) humidity is 65% and the average wind speed is 1.45 m s^{-1}. Rainfall and air temperature during the sampling period (Figs. 1a, 1b) were obtained from the Almacelles meteorological station. Additionally, soil temperature (10 cm depth) was measured while soil samples were taken.

The soil is well drained without salinity problems and classified according to the USDA soil taxonomy system (Soil Survey Staff, 1992), as a Gypsic Haploxerept. Some physico-chemical properties of the top layer were: 3.47% organic matter content; pH_{H2O} 8.4; a bulk density of 1.4 g cm^{-3}; a sand content of 28%; silt of 42%; clay of 30%; 122 mg P (Olsen) kg^{-1}; and 420 mg K (NH_4^+ Ac) kg^{-1}. Soil nitrate content (NO_3^--N) was determined before sowing and fertilising (initial NO_3^--N) and after harvesting (residual NO_3^--N; Table 1).

The soil ammonium content (NH_4^+-N) was considered negligible (Villar et al., 2002; Berenguer et al., 2009; Biau et al., 2013) and was only measured at the onset of the experiment in 2010 (0-30 cm depth). This NH_4^+-N content was 16 kg ha^{-1} (Biau et al., 2013). The N mineralization potential in the soil was determined by method used by Bosch et al., (2009).

2.2. Experimental design, treatments and crop management

The experimental plots were established and arranged in a completely randomized split-plot design with three N doses under two crop stover managements in three blocks (replicates). The elemental plot dimensions were 18 by 17 m. The applied crop stover management treatments were: i) stover removal (-R) from the field after harvesting each year and, ii) stover incorporation (+R) with conventional tillage (with disk ploughing) to a depth of 25-30 cm. The applied N treatments were (1) N0: no N application; (2) N200: 200 kg N ha^{-1} year^{-1} and (3) N300: 300 kg N ha^{-1} year^{-1}. As previously mentioned, these two treatments were applied with both (-R and +R) crop stover treatments (Table 2). The N fertiliser (ammonium nitrate [AN]; 33.5% N) was applied in two side dressing using a small drop-type hand driven fertiliser spreader; 50% at growth stage V3–V4 and 50% at V5–V6 (Table 2). Each year prior to sowing all plots were fertilised with phosphorus (P) (150 kg P_2O_5 ha^{-1} year^{-1}) and potassium (K) (250 kg K_2O ha^{-1} year^{-1}) (Table 3) to avoid deficits of these nutrients.

In both years, maize (*Zea mays* L.,) was sown in early April (Table 3) at a rate of 80,000 seeds ha^{-1} with 75 cm spacing between rows. Plots were sprinkler-irrigated with approximately 700 to 1000 mm of water (nitrate-free) per year during the maize growing period. Irrigation began in the first days of April and lasted until mid-September, every 7 to 12 d depending on the weather condition and crop development.

The field was treated with 3.3 L ha^{-1} of pre-emergence herbicide Trophy (Acetochlor 40% + Dichlormid 6%) and 1 L ha^{-1} of the post-emergence herbicide Fluoxypyr 20% (to control *Abutilon theophrasti* M.) plus 1.5 L ha^{-1} of Nicosulfuron to control *Sorghum halepense* L. Maize was harvested in the second week of September of each year. Grain moisture was determined using 300 g sample of each plot and the grain yield was adjusted to 14% moisture (GAC II, Dickey-John, Auburn, IL, USA).

The whole maize plant biomass except the grain (maize stover) was either incorporated into or removed from the soil using commercial machinery.

2.3 .Gas sampling and quantification

Gas samples were collected weekly using the closed chamber method throughout the maize crop season, in 2011 and 2012. Three replicates were taken in 2011 and 4 in 2012. The cylindrical (19 cm diameter and 22 cm high) static chambers were made of polyvinyl chloride (PVC) coated with an epoxy resin. They were inserted 5 cm into the soil. This cylinder has a vented screw lid with a three-way key. Air samples from inside the chamber were taken in duplicate immediately after closing the chamber, and 20 and 40 min later. Samples were taken through a Teflon® tube connected to the three-way key and into 100 ml plastic syringes, adapted with a valve. Air inside the chamber was mixed by filling and emptying the syringe six times before withdrawing the sample. After taking the air sample the syringes were closed by the valve. After the last sampling (40 min from closing the chamber) the three-way keys were left open. The syringes were transported to the laboratory and the concentrations of N_2O, CH_4 and CO_2 in the sampled air were quantified using the photoacoustic technique (Innova 1412 Photoacoustic Multigas Monitor).

Surface soil temperature was recorded during sampling. The photoacoustic analyser refers the gases concentration to 20ºC and 1 atm; the concentration was corrected to be referred to the actual field temperature and atmospheric pressure of each sampling day. Sampling was done at the time of the day when soil temperature was about the average soil temperature of the day in order to minimize over or underestimation of the emission caused by daily soil temperature variation.

2.4. Soil moisture and soil temperature

After the gas analysis, the soil samples were dried at 105ºC to a constant weight to gravimetrically determine moisture content. Water-filled pore space (WFPS) was then calculated by dividing the volumetric water content by the total soil porosity. Total soil porosity was calculated by measuring the bulk density of the soil according to the following relationship: soil porosity = 1 – (soil bulk density/PD), with PD representing the particle density, which for this soil texture was assumed to be 2.65 g cm^{-3} (Porta et al., 2008).

Soil temperature (at a depth of 10 cm) was also measured while the gas samples were taken.

2.5. Calculations and statistical analysis

The daily N_2O, CO_2 and CH_4 emission was determined from the linear increase of gas concentration at each sampling time and replicate during chamber closure. The average of 3 replicates in 2011 and 4 in 2012 was calculated every sampling day. The cumulative emission throughout the study period was calculated by integrating the emission curve through time. The direct N_2O emission factor (EF) was calculated according to the IPCC (2001) as the difference between the N_2O emitted from fertilised soil and that from the control divided by the N applied as fertiliser.

The normal distribution of the flux data (N_2O, CO_2 and CH_4) was verified using the Shapiro-Wilk test. When necessary, in order to fulfil the assumption of normality, data were log transformed prior to analysis. Cumulative emission of N_2O, CO_2 and CH_4 was examined using data from all plots with an ANOVA model (JMP version 10, SAS Institute, USA) that included terms for maize stover (R), fertiliser treatment (N), and interactions (R x N). Significant differences among treatment's means were further examined by the Tukey's multiple range test at the 0.05 probability level. Multivariate correlation analysis was used to analyse the relationship between GHG emission and the measured conditions (i.e. soil temperature, air mean temperature and WFPS). The correlations were assessed using the non-parametric Spearman rank coefficient (ρ). A p value of 0.05 was used as the threshold for statistical significance.

2.6. Global warming potential (GWP) and greenhouse gas intensity (GHGI) calculation

Global warming potential (GWP) is an index defined as the cumulative radiative forcing between the present and some chosen later time ''horizon'' caused by a unit mass of gas emitted now. In GWP estimation, CO_2 is typically taken as the reference gas, and an emission or an inmission of CH_4 and N_2O is converted into ''CO_2-equivalents''. In the present study, the global warming potential (GWP) of N_2O and CH_4 emission was calculated in units of CO_2 equivalents (CO_2-eq) over a 100-year horizon (Forest et al., 2007). A radiative forcing potential relative to CO_2 of 298 was used for N_2O and 25 for CH_4 (Forest et al., 2007). Although soil CO_2 fluxes also represent a source of GHG emission, on a global scale, they are largely offset by high rates of net primary productivity and atmospheric CO_2 fixation by crop plants, and are therefore estimated to contribute <1% to the GWP of agriculture (Smith et al., 2008; Abalos et al., 2012; Linquist et al., 2012). Therefore, CO_2 as a contributor to GWP was not included in this analysis. The GWP of N_2O and CH_4 emission were calculated using the following equation (IPCC, 2007): GWP (kg CO_2-eq ha^{-1}) = cumulative N_2O emission * 298 + cumulative CH_4 emission * 25.

The greenhouse gas intensity (GHGI) was calculated as follows: GHGI (kg CO_2-eq kg^{-1} grain yield) = GWP/kg grain yield.

3. Results

3.1. Environmental conditions and water filled pore space

The measured average daily soil temperature ranged from 19.5 to 30.1°C and 7.8 to 28.8°C during 2011 and 2012 respectively (Fig. 1a). In 2011, the average air temperature during the sampling period was 22.1°C (ranging from 14.8 to 28.1°C) and in 2012 was 20.1°C (ranging from 8.4 to 29.3°C) (Fig. 1a). In 2011, the average soil temperature was 4.5°C higher than in 2012, the average air temperature was 2°C higher than in 2012, and the total rainfall during the sampling period was 3 times lower than in 2012. Therefore, an influence of soil temperature, average air temperature and the total rainfall during the sampling period on the WFPS was expected.

In 2011, during the crop maize season, the WFPS ranged from 12 to 42%, while in 2012, the WFPS ranged from 17 to 54% (Fig. 1b and d). In 2011, the total rainfall during the sampling period was 63 mm, while in 2012 was 198 mm (Fig. 1c).

In 2011 the average annual relative humidity was 65% and the average annual wind speed was 1.25 m s^{-1}, while in 2012, the average annual relative humidity was 61% and the average annual wind speed was 2.10 m s^{-1} (Almacelles Station; Meteorological Service of Catalonia, http://www.meteo.cat/observacions/xema).

3.2. Nitrous oxide emission

In 2011, the measured fluxes of N_2O were large between days 11 and 40 after the start of sampling for all the +R treatments. This period coincided with a sharp increase in WFPS (11 d after sampling started; Fig. 1b) and with the second side dress fertilisation (35 d after sampling started; Table 3). From day 99 of sampling until harvest (119 d after sampling started) emission peaks were observed in all the treatments (Fig. 2a and

b) coinciding with a period of relatively higher WFPS (ranging from 35 to 42%; Fig. 1b). The N_2O fluxes from the +R treatments were higher than from the -R treatments, with the highest peaks measured for N300 (+R) (70.9 kg N_2O-N ha^{-1} d^{-1}; Fig. 2a). For the -R treatments, the highest N_2O emission fluxes were measured at the end of the crop (Fig. 2b).

In 2012, the measured fluxes of N_2O were the largest the first 55 days after sampling started; with higher N_2O fluxes from the +R treatments. In this period, large fluxes coincided with the first side dress fertilisation (day 20 after sampling started) and the second side dress fertilisation (day 53 after sampling started; Table 3). From day 56 until harvest the average fluxes of N_2O remained low for all the treatments (Fig. 2c and d).

The average of the measured daily N_2O fluxes per treatment ranged between -9.77 and 107.28 g N_2O-N ha^{-1} d^{-1} in 2011 and between -4.14 and 106.87 in 2012, indicating that both years the soil acted both as a source and as a sink of N_2O.

In both years, the cumulative N_2O emission tended to increase with the dose of mineral N fertiliser applied (Table 4). The cumulative N_2O emission was significantly influenced by stover management in 2011, but not in 2012 (Table 4). In 2011, a larger cumulative emission (1.83 kg N_2O-N ha^{-1}) during the maize crop season from the N300 (+R) than from the other treatments was registered. In 2012, the largest cumulative emission was measured for the N300 (-R) treatment (2.41 kg N_2O-N ha^{-1}; Table 5), although this increase was not significant ($p > 0.05$). The year had a significant effect on N_2O emission (Table 5).

In both years, the N_2O emission factor (EF) ranged from -0.11 to 0.36% of the applied N (Table 5).

The measured daily N_2O fluxes in all the treatments were correlated with soil temperature, average air temperature and WFPS in 2011, and only with soil temperature and average air temperature in 2012 (Table 6).

3.3. Carbon dioxide flux (ecosystem respiration)

The CO_2 fluxes were generally high between day 57 and 71 after sampling started in 2011 (Fig. 3a and b). In 2012, the fluxes of CO_2 were the highest for days 50 and 119 after sampling started (Fig. 3c and d). In both years, +R and -R treatments showed the highest CO_2 fluxes (Fig. 3).

In both years, the cumulative CO_2 emission was significantly lower from the -R than from the +R treatments (Table 4). Cumulative CO_2 emission was larger in 2012 than in 2011 (Table 4).

In both years, there were significant correlations between CO_2 emission and soil temperature and average air temperature (Table 6).

3.4. Methane emission

In 2012, the fluxes of CH_4 were mostly positive (Fig. 4c and d), while in 2011 the soil acted as a sink for CH_4 throughout the sampling period (Fig 4a and b). The maximum measured emission flux was 891.31g CH_4 ha^{-1} d^{-1} from N0 (-R) in 2012, while the maximum oxidation flux was -7097.31 g CH_4 ha^{-1} d^{-1} from N300 (+R) in 2011. In 2011, the cumulative CH_4 oxidation significantly decreased when increasing the N dose. On the contrary, in 2012 the cumulative CH_4 emission decreased when increasing the N dose (Table 4). In both years, the cumulative CH_4 emission (or methane oxidation) tended to decrease with the dose of fertiliser (Table 4).

In both years, the daily CH_4 fluxes observed in all the treatments were correlated with soil temperature and average air temperature (Table 6).

3.5. Global warming potential (GWP) and greenhouse gas intensity (GHGI)

In both years, the global warming potential (GWP) calculated with the N_2O and CH_4 emission ranged from -3420.45 to 1579.48 kg CO_2-eq ha^{-1} for the sampling period (Table 5). In 2011 the maize field acted as a net sink of CH_4 for most treatments (except for N300 (-R)) and this, in turn, reduced the overall GWP (Table 5). In 2012, the N200 (-R) treatment showed the highest GWP, although not statistically different ($p > 0.05$) from the other treatments (Table 5).

The greenhouse gas intensity (GHGI) was negative for all the treatments except for N300 (-R) during 2011 (Table 5). While, in 2012 the GHGI was low for all the treatments (Table 5).

4. Discussion

4.1. Nitrous oxide emission

In both years, high peaks of N_2O were observed after rain or irrigation, when WFPS ranged between 35 and 40%. Bateman and Baggs (2005) reported that nitrification was the main process producing N_2O when WFPS is between 35 and 60%. Values around 40 to 60% are considered as the optimal conditions for nitrifiers because the diffusion of neither substrates nor oxygen (O_2) is restricted (Paul and Clark, 1996). Similarly Liu et al. (2006) and Perdomo et al. (2009) report large N_2O fluxes after rain or irrigation. It must be kept in mind that the amount of water applied with irrigation was the same (850 mm on average) in both years. Since during the sampling period the total rainfall was higher (more frequent rainfalls and of higher intensity) in 2012 than in 2011 this explains the higher WFPS in 2012 (Fig. 1b and d) though never above 54% (Fig. 1b and d). Therefore it may be speculated that the N_2O emission from this soil at 35 to 55% WFPS was dominated by nitrification, since at <60% WFPS nitrification becomes more important than denitrification as other authors also described (Lin et al., 2010; Jahangir et al., 2011; Laville et al., 2011). Similar results were found under conditions similar to those of the present study, with a minimum threshold for denitrification recorded at WFPS >55% (Zou et al., 2006). Also, Linn and Doran (1984) and Abbasi and Adams (2000) measured a significant N_2O production by nitrification in soils up to 60% WFPS. The high correlation found between N_2O emission and WFPS in both years, also may indicate the predominance of nitrification (Table 6). The influence of soil moisture on N_2O emission is more prominent after rewetting of an extremely dry soil (Jorgensen et al., 1998) which may explain the sharp increase in the N_2O flux during the first days of sampling in 2012 since nearly 25 mm fell when the soil was very dry (WFPS <25%, Fig. 1b and 1d). In 2011, during the same period, the fluxes of N_2O from all the treatments were lower (Fig. 2a) or almost nonexistent (Fig. 2b). This might be explained by the less frequent rainfall and of lower intensity (not surpassing 13 mm) (Fig. 1c). Probably, the N_2O production at 20% WFPS (or below 20% WFPS) was limited by substrate diffusion and water availability for microbial activity, as Stark and Firestone (1995) already mentioned. This limitation did not occur from 35% WFPS on, at which N_2O emission attributed to nitrification became evident. By means of an empirical model, Lu et al. (2006) found that precipitation was the key factor stimulating N_2O emission from agricultural soils. The results of the present study provide further evidence that WFPS is a key factor determining N_2O emission under Mediterranean conditions.

High fluxes of N_2O were also observed after side dressing with ammonium nitrate which stimulates nitrifier's activity. Studies conducted during the past decade show that hydrolysis and nitrification of applied NH_4-based N fertilisers synchronize mostly within the two weeks following application to maize (e.g. Liu et al., 2003), and this indicates that nitrification is the main process leading to N_2O emission from the soil (Ju et al., 2004; Wan et al., 2009).

The average of the measured daily N_2O fluxes per treatment ranged between -9.77 and 107.28 g N_2O-N ha^{-1} d^{-1} in 2011 and between -4.14 and 106.87 in 2012, indicating that soil acted as a small source of N_2O. Negative fluxes of N_2O (i.e. soil acted as a sink) have previously been documented in agricultural systems and under various edaphoclimatic conditions (Teira-Esmatges et al., 1998; Chapuis-Lardy et al., 2007; Cardenas et al., 2010; Abalos et al. 2012). Net negative N_2O fluxes have been found in a range of conditions, but not always connected to low N and low O_2 (Wagner- Riddle et al., 1997; Khalil et al., 2002). The rate of N_2O consumption (reduction to N_2 plus absorption by water) primarily depends on soil properties, such as the availability of mineral N (substrate for nitrification and denitrification), soil oxygen and water content, soil temperature, pH and redox conditions, and the availability of labile organic C and N (Stevens et al., 1998; Glatzel and Stahr, 2001; Wzodarczyk et al., 2005; Mathieu et al., 2006). The diverse conditions stimulating N_2O consumption, including the enigma of uptake in dry soil, hint at various processes responsible for the uptake.

Based on recent evidence from the literature the following possible pathways for N_2O consumption (negative fluxes of N_2O) have been identified (Van Groenigen et al. 2015): (1) first, in addition to the "typical" nitrous oxide reductase (nosZ I) that reduces N_2O during denitrification, (2) second, a microbial nondenitrifier, "atypical" N_2O reductase (nosZ II) which play a significant role in N_2O consumption in soil was identified; (3) third, some bacteria that perform dissimilatory nitrate reduction to ammonia (DNRA) are capable of N_2O reduction to N_2 as they carry a nos gene encoding for N_2O reductase (N_2OR) (Simon et al., 2004; Van Groenigen et al. 2015); (4) fourth, direct assimilatory N_2O fixation via nitrogenase (Vieten et al., 2008; Ishii et al., 2011; Farías et al., 2013) or (5) fifth, indirect N_2O fixation via a combination of N_2O reduction and N_2 fixation can account for N_2O consumption,

Denitrification is usually the main source of N_2O emission in soils with high water content (>70% WFPS), while nitrification increases linearly with increasing the water content in soil up to a maximum of 60% WFPS and decreases thereafter (Bagg and Bateman, 2005).

Another condition to stimulate denitrification in soil with a high mineral N content is the existence of a readily available C source (Ju et al., 2011). In the present study additional C substrate in the form of maize stover was supplied which was not readily decomposable and probably was not available for N_2O production through denitrification. In the present study denitrification was likely to be limited not only by low soil moisture content but also by lack of a readily decomposable C source. Over the last twenty years or more large amounts of nitrate have been found to accumulate at different depths in soil profiles (Ju et al., 2004, 2006 ; Zhao et al., 2006), and these can remain roughly constant for several years (Zhao et al., 2006). The source of this nitrate is the very large surplus of N applied in conventional fertiliser regimes in the long term and the high capacity of the soils to nitrify ammonium based fertilisers (Ju et al., 2009; Wan et al., 2009). These authors attributed the persistence of this nitrate to low denitrification rates due to low availability of readily decomposable C and to limitation by low soil moisture.

In this study as in other previous assays (Zhang et al. 2004; Wang et al. 2009) increasing doses of mineral N fertiliser led to increasing N_2O emission, though not significantly different neither in 2011 nor in 2012 (Table 4). These results could be explained by the high initial mineral N content in the soil profile due to the previous management (Biau et al., 2013).

In both years, the high residual N (Table 1) indicates a high N mineralization potential in this fertile soil, which was estimated to be approximately 150 kg N ha ha^{-1}. This is in agreement with Sio et al. (1990), who estimated the N mineralization potential to be 120 kg N ha^{-1}. This high N mineralization potential should be considered when setting a N fertiliser recommendation in the area.

Application of stover is a cost-effective and sustainable alternative to improve the organic matter content of soils (Abalo et al., 2012). However, as pointed out in this study, this management practice may have induced changes in the extent to which mineralization or immobilization has taken place. In general, stover incorporation has been described to affect soil N content, soluble organic carbon content, and microbial activity; and therefore regulate the soil N_2O emission in a complex manner (Miller et al., 2008). In this study, stover incorporation in 2011 significantly increased the cumulative N_2O emission (Table 4). In 2012; the lowest N_2O emission was registered for the +R treatments (Table 4). These results might be due to the fact that in 2012 a higher amount of stover (37 Mg ha^{-1} on average) with a higher C/N ratio (C/N=63) than in 2011 was incorporated (C/N=46). Moreover, the Nini was 38% higher on average in 2011 than in 2012 (Table 1). In 2011 stover incorporation, may have resulted in a more rapid mineralization, N release and, hence, increased N availability (Baggs et al., 2000; Verschot et al., 2006) for nitrification and denitrification and, consequently, enhanced N_2O emission (Table 1 and 5). On the contrary, in 2012, a net N immobilization may have occurred. In the conditions of this study, the threshold for the predominance of N immobilization above mineralization might be above a stover C/N ratio of 46. This speculation could be verified if data on mineral N evolution were available or if a laboratory based mineralization experiment had been performed. Previous authors (e.g. Heal et al., 1997; Myers et al., 1994) stated that the residue C/N threshold above which net N immobilization occurs is 20–25. Cayuela et al. (2009) found that wheat straw (C/N = 198) and cotton cardigans (C/N = 30.5) led to a rapid immobilization of N. Abalos et al. (2013) found that maize stover (C/N = 127) incorporation led to an immobilization of N under Mediterranean conditions. Similarly, Hadas et al., (2004) described that sorghum stover (C/N = 72) and maize stover (C/N = 32) resulted in N immobilization.

Emission factors (EF) express the direct N_2O emissions as a percentage of the applied N fertiliser (Cardenas et al., 2010). In the present study, N_2O emission factors (EF) ranged from -0.11 to 0.36% of the applied N (Table 5), lower than the default IPCC values (2007 i.e. 1% regardless of the N source, location, climate and soil type). The EF% of this study was also below those reported by Abalos et al. (2012) in maize under Mediterranean climate. A negative EF was found for the N300 (-R) treatment in 2011 and for the N200 (+R) treatment in 2012, implying that the cumulative N_2O emission from these treatments was smaller than from the control, which was also encountered by Toma et al. (2007) and Maris et al. (2015). The relative low N_2O EF in these Mediterranean soils with a high organic matter content (3.47%) and high mineral N content (200 g N kg^{-1} on average) could likely be explained by the low availability of readily available C and the WFPS not being high enough to stimulate N_2O production by denitrification during the sampling period.

In the present study, it was clearly observed that the year had a significant effect on N_2O emission (Table 5).This is attributed to the differences in soil temperature, the average air temperature and WFPS between the two years. The average soil temperature in 2011 (27.5°C) was 4.5°C higher than in 2012, the average air temperature in 2011 (22.1°C) was 2°C higher than in 2012 and, the WFPS was between 12% and 42% in 2011 and somewhat higher, between 17% and 54%, in 2012.

A significant correlation between soil temperature, average air temperature and daily N_2O fluxes was found (in both years; Table 6). Many researchers reported significant effects of temperature on N_2O emissions (Conrad et al., 1983; Skiba and Smith, 2000). Temperature directly affects the activity of nitrifying and denitrifying bacteria. Generally N_2O fluxes increase with rising temperature (Granli and Bøckman 1994; Smith 1997), but this relationship is not straightforward, as many different processes are involved. Temperature increase stimulates microbial respiration, i.e. O_2 consumption, the volume of the anaerobic fraction of the soil increases, enhancing denitrification activity (Lesschen et al., 2011; Parkin and Tiedje 1984; Smith 1997). Nevertheless, Castaldi (2000) found that only at high rates of O_2 consumption (58 mg O_2 g^{-1} h^{-1}), which occurred at about 34°C, did the production of N_2 outweigh that of total N_2O. Since in the present study (in both years) the soil temperature did not rise above 30°C it can be confirmed that nitrification was the dominant source of N_2O.

4.2. Carbon dioxide emission (ecosystem respiration)

On Table 4 one can see the contradictory results obtained among the two years when applying different doses of mineral fertiliser on CO_2 emission. In 2011, the cumulative CO_2 emission decreased with increasing N doses (by 5% in the N200, and by 31% in the N300; Table 4), while in 2012, increasing N doses lead to increasing cumulative CO_2 emission. One possible explanation for these results might be the very high mineral N content in the soil in 2011 (approximately 38% higher than in 2012) which in combination with mineral N application could inhibit CO_2 emission. Fogg (1988), DeForest et al. (2004), and Burton et al. (2004) suggested a decrease in extracellular enzyme activity when the application of N increases. These studies did not cite any specific mechanism for this decrease, so the process is relatively unclear. Fogg (1988), DeForest et al. (2004) and Burton et al. (2004) also found that CO_2 emissions from the soil were reduced by 15 to 41% when applying N compared to control.

In the present study, stover management significantly increased the cumulative CO_2 emissions (Table 4), which were the double in 2012 than in 2011. Incorporation of maize stover may have increased the organic C content of the soil leading to larger CO_2 emission. Also, increasing the organic C content in the soil increases microbial activity which may have favored N immobilization in 2012. The C/N ratio of maize stover is high so application of ammonium nitrate must have stimulated its decomposition contributing to larger CO_2 emissions from the +R treatments. On the other hand, stover removal led to significantly lower CO_2 emission. Maize stover served as a C substrate for soil microorganisms so removing it reduced CO_2 emission.

Temperature is an important factor that influences soil CO_2 flux (Keller et al., 2004). A significant correlation between soil temperature, average air temperature and daily CO_2 flux (in both years) was found (Table 6). It has often been reported that temperature is the factor that is best correlated with CO_2 emission (Almaraz et al., 2009). Increasing soil temperature generally stimulates microbial processes related with the production of CO_2 and N_2O (Kirschbaum, 1995). In addition, increasing soil temperature may increase gas diffusivity (Smith et al., 2003). Data from previous studies (Chan and Parkin, 2001; Venterea et al., 2005) support the direct impact of soil temperature on the GHG transport.

4.3. Methane emission

In 2011, the soil acted as a net CH_4 sink, while in 2012 the soil acted as a net source of CH_4. In 2011, the cumulative CH_4 oxidation was high when WFPS was low (from 12 to 42%). The magnitude of CH_4 oxidation by soils is largely controlled by the diffusion of atmospheric CH_4 into the soil (Koschorreck and Conrad, 1993), which in turn is strongly influenced by soil moisture (Shrestha et al., 2004). This is in agreement with the studies by Guo and Zhou (2007) and Wang et al. (2012). A higher WFPS in 2012 than in 2011 (Figs. 1b and d) may have been responsible for the soil acting as a source of CH_4 (Table 4). High soil moisture can limit O_2 diffusion from atmosphere and to the soil, causing a reduction in CH_4 oxidation (Wang et al., 2012).

In both years it was clear that an increase in total applied N decreased CH_4 oxidation, though this was significant only in 2011 (Table 4). It has been shown that the application of N fertiliser inhibits CH_4 oxidation in soil (Kravchenko et al., 2002; Jassal et al., 2011), and several studies noted that non amended soils act as a CH_4 sink (Flessa and Beese, 2000).

In 2012 a positive correlation between soil temperature, average air temperature and daily CH_4 flux was found. However, in 2012 the correlation was negative (Table 6). This unexpected difference in the sign of the correlation among years can be explained by two counteracting processes which occur simultaneously: methane production and methane oxidation. Dunfield et al. (1993) reported that CH_4 oxidation and production fluxes show a significant dependence on temperature in the range of 20 to 35°C whith no obvious response at lower temperatures (0–15°C). In the present study, the measured average daily soil temperature ranged from 19.5 to 30.1°C and 7.8 to 28.8°C during 2011 and 2012 respectively (Fig. 1a). While, in 2011 the average air temperature during the sampling period was 22.1°C (ranging from 14.8 to 28.1°C) and in 2012 was 20.1°C (ranging from 8.4 to 29.3°C) (Fig. 1a).

4.5. Global warming potential (GWP) and greenhouse gas intensity (GHGI)

Discovering the main sources of net GWP in specific cropping systems is very useful for mitigating GHG emissions in the future. In 2011, the negative CH_4 emission (Table 5) resulted in negative GWP values. In 2012 all the treatments had a positive GWP ranging from 1141.10 to 1579.48 kg CO_2 ha^{-1}. A negative GWP indicates that the soil acted as a net sink for GWP, which is similar to soil C sequestration. In contrast, a positive net GWP value indicates that the soil acted as a net source for GHG.

By definition, the GHGI of each treatment depends on the net GWP and the grain yield. The GHGI ranged from -0.24 to 0.11 kg CO_2-eq kg^{-1} grain yield (Table 6). In 2012, the GHGI was higher for the -R treatments than for the +R (Table 5). In 2011, the GHGI was negative for all the treatments except for N300 (-R) (Table 5). A negative GHGI (as the consequence of the negative GWP) indicates an equilibrium among yield, carbon sequestration into the soil and GHG emissions (Mosier et al., 2005; IPCC, 2013).

In both years, the grain yield did not increase with increasing N fertiliser doses (Table 5). This was likely due to the high application of N to soil as well as to the high initial mineral N content (200 g N kg^{-1} on average) (Biau et al., 2013). Numerous studies have also shown that above a certain N application dose there is no yield response, but that the residual nitrate increases sharply (e.g. Porter et al., 1996, Bhogal et al., 2000). Overall, high doses of N fertiliser are not recommended here for maize production. Alternating maize with another N demanding crop without fertiliser application until the soil mineral N content becomes normal could be a strategy to reduce the GWP of the system.

In the present study denitrification must have been less important than nitrification for N_2O emission. This indicates that an efficient irrigation was applied, preventing favorable conditions for denitrification. Increasing soil WFPS would most probably determine high emissions by denitrification.

Efforts to mitigate greenhouse gases emission in this system should, therefore, be focused on: (1) keeping an efficient irrigation with relatively low WFPS and, (2) decreasing the soil mineral N content of the soil.

5. Conclusions

The present study showed that nitrification was the main process of N_2O production in this highly intensive cropping system. Denitrification was probably limited by low soil moisture and lack of a readily available C source. The losses of N_2O (calculated as emission factor) ranged from -0.11 to 0.36% of the applied N, lower than the IPCC (2007) reference. Although, the N_2O emission was low, creating favorable conditions for denitrification could determine high emissions.

Crop stover management produced contradictory effects on N_2O emission (mineralization and immobilization of mineral N in soil) due to the C/N ratio of stovers incorporated. Stover incorporation increased CO_2 emission. The high grain yield and the fact that all the treatments except N 300 (-R) acted as net CH_4 sink in 2011 explain the low or negligible GWP and GHGI obtained for the fertilised treatments. Considering the "Climate Smart Agriculture" objective of maintaining a high yield in future together with mitigating of greenhouse gases emission, the management of the studied high nitrate-N content system should be focused on: (1) keeping an efficient irrigation with relatively low WFPS and, (2) decreasing the soil mineral N content of the soil.

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Table 1 Soil mineral N (mg kg^{-1}) before sowing and fertilising (Nini), residual nitrogen after harvest (Nresi) (depth 0-30 cm), incorporated stover (Mg ha^{-1}) and stover N content per treatment

Treatments	mg N kg^{-1}						Incorporated stover		Stover N content	
	2010		2011		2012		Mg stover ha^{-1}		g N kg^{-1} stover	
	N ini	N resi	N ini	N resi	N ini	N resi	2010	2011	2010	2011
N0 (+R)		63.0	127.0	58.0	86.0	47.0	29.4	27.6	11.8	9
N200 (+R)		226.0	228.0	273.0	159.0	237.0	26.2	41.7	12.8	9.9
N300 (+R)		225.0	334.0	375.0	254.0	269.0	30.7	41.3	12.5	9.7
	98.1	171.3	229.6	235.3	166.3	184.3	28.7	36.8	12.3	9.5
N0 (-R)		117.0	138	116	151.0	93.0	-	-	-	-
N200 (-R)		199.0	314	230	185.0	250.0	-	-	-	-
N300 (-R)		269.0	354	328	220.0	175.0	-	-	-	-
		195.0	268.6	224.6	185.3	172.6	-	-	-	-

+R: stover incorporation; -R: stover removal. Treatments: N0(+R): no N applied and stover incorporation; N200(+R): 200 kg N ha^{-1} applied (ammonium nitrate) and stover incorporation; N300(+R): 300 kg N ha^{-1} applied (ammonium nitrate) and stover incorporation; N0(-R): no N applied and stover removal; N200(-R): 200 kg N ha^{-1} applied (ammonium nitrate) and stover removal; N300(-R): 300 kg N ha^{-1} applied (ammonium nitrate) and stover removal.

Table 2 Fertilisation applied to each treatment

Treatment	First sidedress fertilisation (AN 33.5% N) kg N ha^{-1}	Second sidedress fertilisation (AN 33.5% N) kg N ha^{-1}
N0 (-R)	0	0
N200 (-R)	100	100
N300 (-R)	150	150
N0 (+R)	0	0
N200 (+R)	100	100
N300 (+R)	150	150

+R: stover incorporation; -R: stover removal. Treatments: N0(+R): no N applied and stover incorporation; N200(+R): 200 kg N ha^{-1} applied (ammonium nitrate) and stover incorporation; N300(+R): 300 kg N ha^{-1} applied (ammonium nitrate) and stover incorporation; N0(-R): no N applied and stover removal; N200(-R): 200 kg N ha^{-1} applied (ammonium nitrate) and stover removal; N300(-R): 300 kg N ha^{-1} applied (ammonium nitrate (AN) 33.5% N) and stover removal.

Table 3 Timing of field labours and gas sampling per year and Site

Year	Stover incorporation/ removal) (dd/mm/yy)	Sowing (dd/mm/yy)	Start of sampling (dd/mm/yy)	First side dress fertilisation (dd/mm/yy)	Second side dress fertilisation (dd/mm/yy)	End of sampling (dd/mm/yy)	Harvest (dd/mm/yy)	Duration of the sampling period
2011	19/11/10	06/04/11	16/05/11	20/05/11	22/06/11	12/09/11	29/09/11	176
2012	24/11/11	03/04/12	27/04/12	17/05/12	20/06/12	03/10/12	02/10/12	182

Table 4 Cumulative emission of N_2O-N, CO_2 and CH_4 during the maize crop seasons of 2011 and 2012

	Cumulative emissions (kg ha^{-1})					
	N_2O-N		CO_2		CH_4	
Crop residue	2011	2012	2011	2012	2011	2012
-R	0.99b	2.14a	1590.78b	4811.18 b	-97.12a	32.03a
+R	1.56a	1.91a	2862.51a	5518.12 a	-109.62a	28.61a
Fertiliser						
N 0	1.22a	1.77a	2539.08a	4942.31a	-141.47b	34.51a
N 200	1.27a	1.98a	2406.45a	5048.17a	-88.15ab	31.46a
N 300	1.32a	2.24a	1734.40a	5503.48a	-80.49a	24.98a
Residue (R)	*	n.s.	*	*	n.s.	n.s.
Fertiliser (F)	n.s.	n.s.	n.s.	n.s.	*	n.s.
R x F	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
Year	*		*		*	

Within columns, means followed by the same letter are not significantly different according to Tuckey's test (p=0.05); * Significant at the 0.05 probability level; ns: not significant.

Table 5 Cumulative N_2O-N, CO_2 and CH_4 emissions, emission factor (EF), global warming potential (GWP), maize yield and greenhouse gas intensity (GHGI) per treatment and year

[a]: data published in Biau et al. (2013)

Treatments	Cumulative N_2O-N (kg ha^{-1})		Cumulative CO_2 (kg ha^{-1})		Cumulative CH_4 (kg ha^{-1})		EF (%)		GWP (kg CO_2-eq ha^{-1})		Yield[a] (kg ha^{-1})		GHGI (kg CO_2-eq kg^{-1} yield)	
	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012
N0 (-R)	1.05a	1.70a	1465.12a	4368.55a	-144.79b	32.04a			-3306.85b	1292.30a	18300	16700	-0.19b	0.08ab
N200 (-R)	1.10a	2.32a	1422.97a	4776.38a	-149.93b	36.36a	0.03	0.31	-3420.45b	1579.48a	18800	14100	-0.24b	0.11a
N300 (-R)	0.83a	2.41a	1884.25a	5288.62a	3.34a	27.70a	-0.11	0.36	330.84a	1388.99a	18800	14100	0.02a	0.09ab
N0 (+R)	1.41a	1.85a	3613.04a	5516.07a	-138.16b	36.96a			-3033.82b	1458.65a	13900	16606	-0.18b	0.08ab
N200 (+R)	1.45a	1.65a	3389.93a	5319.96a	-26.37a	26.57a	0.02	-0.10	-227.15ab	1141.10a	18600	16400	-0.01ab	0.06b
N300 (+R)	1.83a	2.08a	1584.54b	5718.34a	-42.01a	22.28a	0.21	0.12	-504.91ab	1158.12a	18600	17100	-0.03ab	0.06b

Table 6. Spearman rank correlation coefficients between soil temperature, main air temperature with N_2O-N, CO_2 and CH_4 cumulative emissions per year. Significant correlations are denoted by an asterisk ($p<0.05$)

	N_2O		CO_2		CH_4	
Variables	2011	2012	2011	2012	2011	2012
soil T	0.12*	-0.12*	0.45*	0.27*	-0.26*	0.28*
mean air T	0.18*	-0.16*	0.13*	0.37*	-0.13*	0.33*
WFPS	0.14*	0.11*	0.03	0.22	0.01	0.02

WFPS: water filled pore space; Eh: redox potencial

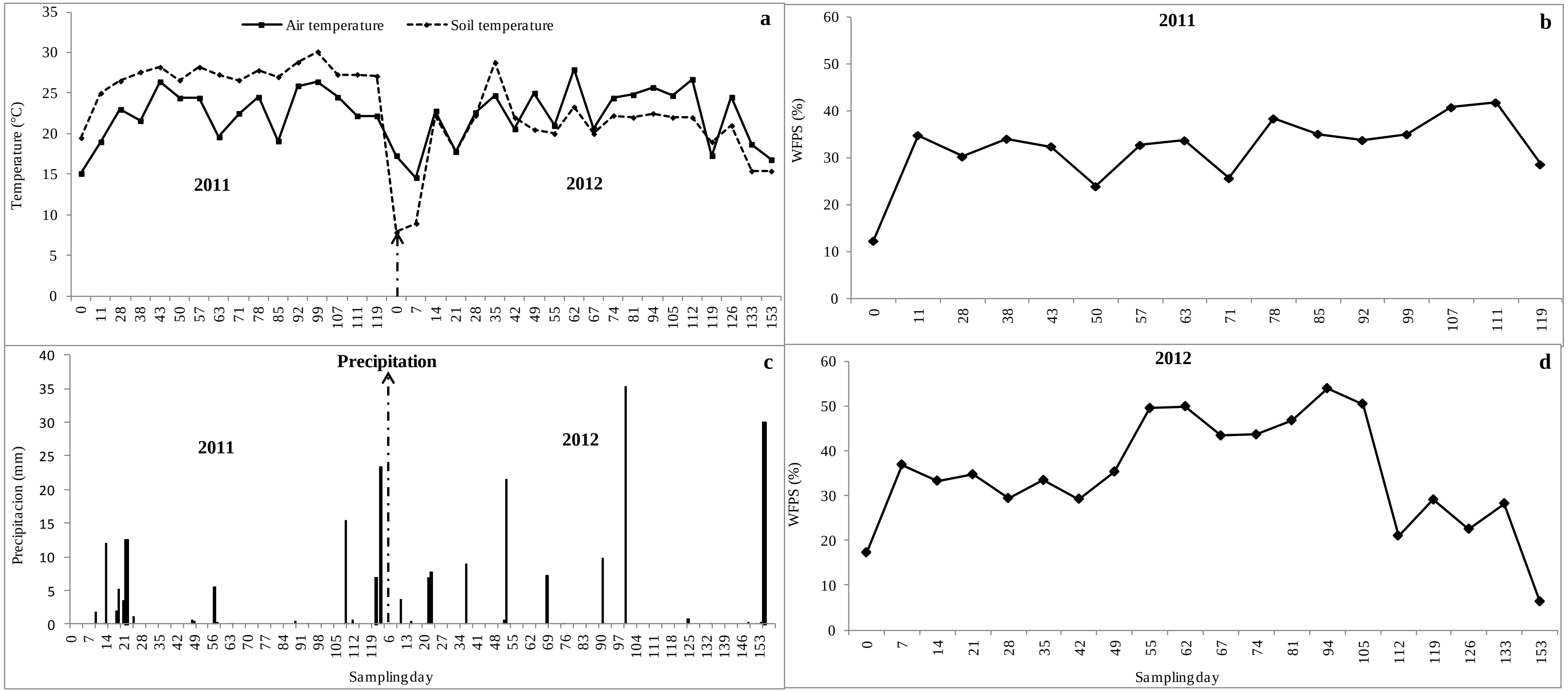

Fig. 1. Evolution of air and soil temperatures (a), and of precipitation (b) during the maize cropping seasons of 2011 and 2012, as well as of the soil water filled pore space (WFPS, %) in 2011 (c) and in 2012 (d)

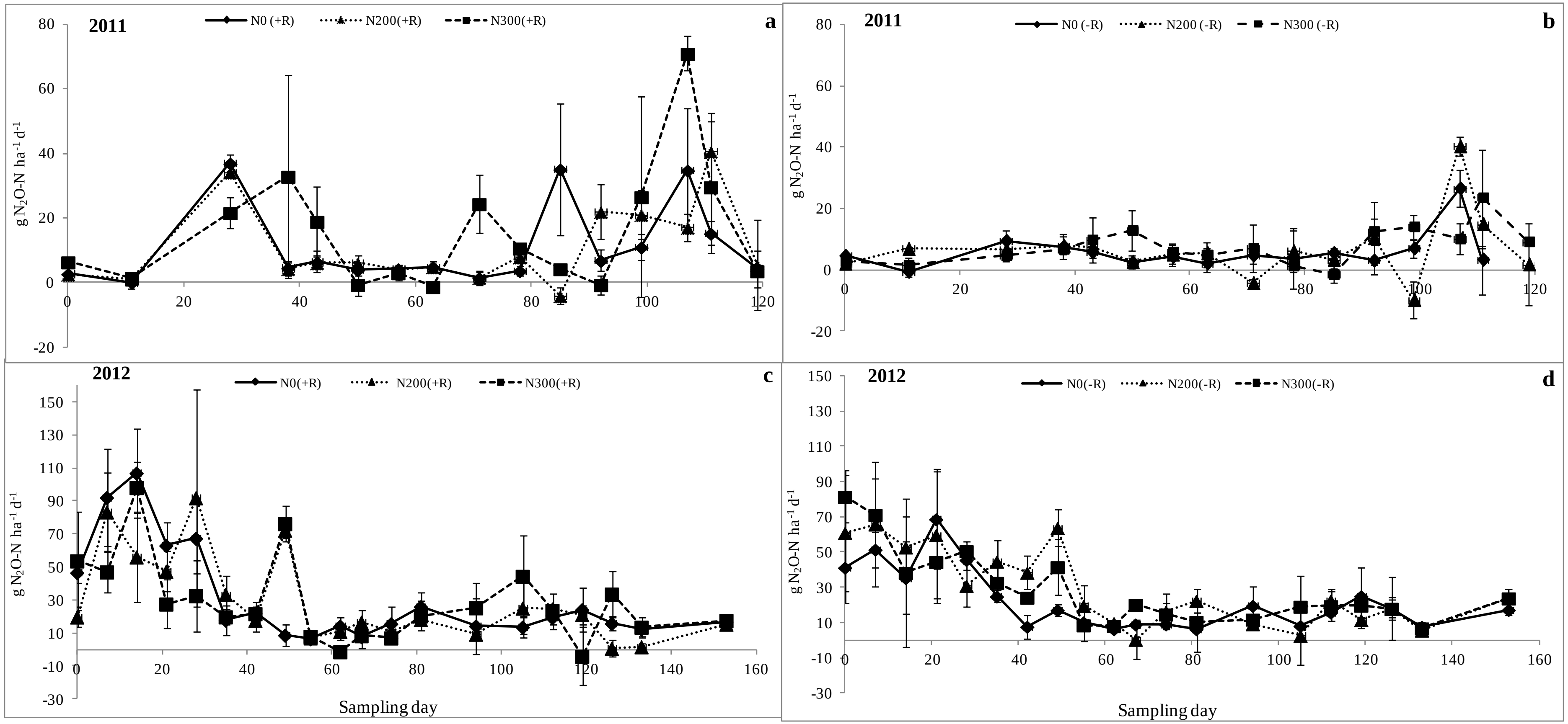

Fig. 2. Measured flux of N_2O-N with crop residue incorporation during the sampling period of 2011 (a), with crop residue removed during the sampling period of 2011 (b), with crop residue incorporation during the sampling period of 2012 (c) and, with crop residue removed during the sampling period of 2012 (d)

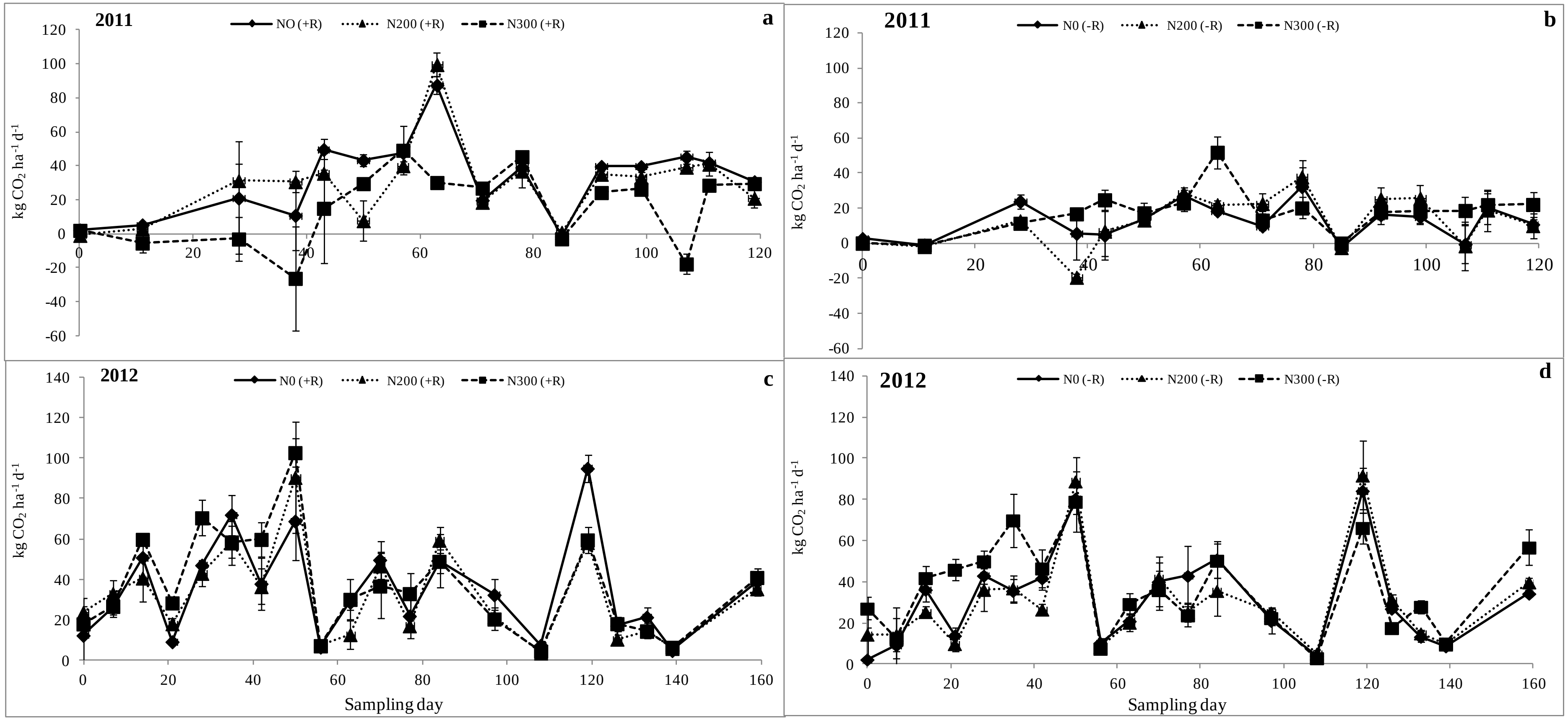

Fig. 3. Measured flux of CO_2 with crop residue incorporation during the sampling period of 2011 (a), with crop residue removed during the sampling period of 2011 (b), with crop residue incorporation during the sampling period of 2012 (c), and with crop residue removed during the sampling period of 2012 (d)

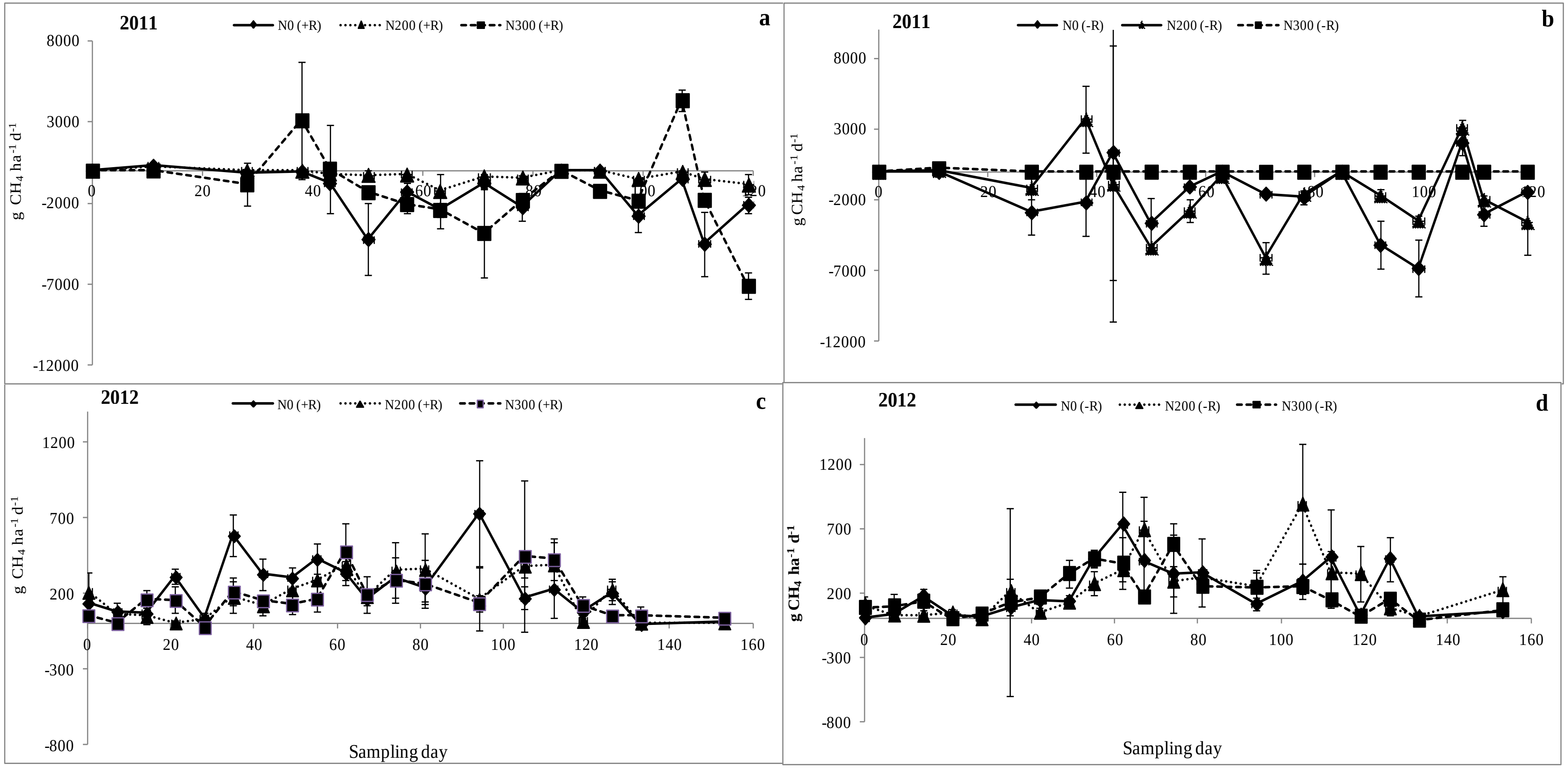

Fig. 4. Measured flux of CH_4 with crop residue incorporation during the sampling period of 2011 (a), with crop residue removed during the sampling period of 2011 (b), with crop residue incorporation during the sampling period of 2012 (c), and with crop residue removed during the sampling period of 2012 (d)

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Chapter 7. Effect of irrigation, nitrogen application, and a nitrification inhibitor on nitrous oxide, carbon dioxide and methane emissions from an olive (*Olea europaea* L.) orchard

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Review

Effect of irrigation, nitrogen application, and a nitrification inhibitor on nitrous oxide, carbon dioxide and methane emissions from an olive (*Olea europaea* L.) orchard

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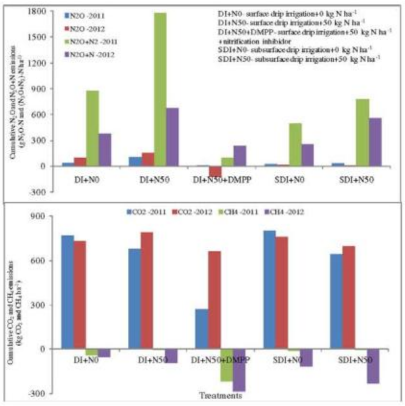
HIGHLIGHTS

- Subsurface drip irrigation mitigated N_2O emission compared with drip irrigation.
- Nitrogen application didn't increase N_2O–N nor $(N_2O + N_2)$–N emissions.
- The olive orchard acted as a net CH_4 sink for all the treatments.
- DMPP reduced the cumulative N_2O, $N_2O + N_2$ and CO_2 emission compared to the control.
- The N50 + DI + DMPP treatment reduced emissions at a high yield (2737 kg oil ha^{-1}).

GRAPHICAL ABSTRACT



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ABSTRACT

Drip irrigation combined with nitrogen (N) fertigation is applied in order to save water and improve nutrient efficiency. Nitrification inhibitors reduce greenhouse gas emissions. A field study was conducted to compare the emissions of nitrous oxide (N_2O), carbon dioxide (CO_2) and methane (CH_4) associated with the application of N fertiliser through fertigation (0 and 50 kg N ha^{-1}), and 50 kg N ha^{-1} + nitrification inhibitor in a high tree density Arbequina olive orchard. Spanish Arbequina is the most suited variety for super intensive olive groves. This system allows reducing production costs and increases crop yield. Moreover its oil has excellent sensorial features. Subsurface drip irrigation markedly reduced N_2O and $N_2O + N_2$ emissions compared with surface drip irrigation. Fertiliser application significantly increased $N_2O + N_2$, but not N_2O emissions. Denitrification was the main source of N_2O. The N_2O losses (calculated as emission factor) ranging from −0.03 to 0.14% of the N applied, were lower than the IPCC (2007) values. The $N_2O + N_2$ losses were the largest, equivalent to 1.80% of the N applied, from the 50 kg N ha^{-1} + drip irrigation treatment which resulted in water filled pore space >60% most of the time (high moisture). Nitrogen fertilisation significantly reduced CO_2 emissions in 2011, but only for the subsurface drip irrigation strategies in 2012. The olive orchard acted as a net CH_4 sink for all the treatments. Applying a nitrification inhibitor (DMPP), the cumulative N_2O and $N_2O + N_2$ emissions were significantly reduced

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with respect to the control. The DMPP also inhibited CO_2 emissions and significantly increased CH_4 oxidation. Considering global warming potential, greenhouse gas intensity, cumulative N_2O emissions and oil production, it can be concluded that applying DMPP with 50 kg N ha $^{-1}$ + drip irrigation treatment was the best option combining productivity with keeping greenhouse gas emissions under control.

Contents

1. Introduction

Agricultural practices such as irrigation and fertilisation improve plant growth but increase greenhouse gas emissions from the soil to the atmosphere; this, in turn, influences the biogeochemical carbon (C) and nitrogen (N) cycles in the soil (Davidson, 1992). Greenhouse gas emissions from crop land have been estimated to account for 13.5% of anthropogenic emissions worldwide (IPCC, 2007). Improving agricultural practices is a recommended strategy for mitigating GHG emissions from agricultural soils without incurring losses in yield (IPCC, 2007). However, this strategy is highly dependent on crop species (Bouwman et al., 2001). The olive tree (*Olea europaea* L.) is drought-resistant and is usually grown in Mediterranean areas with limited water resources and without irrigation, often with very low levels of productivity. In Mediterranean areas, where summer rainfall is a limiting factor, olive trees respond positively to irrigation, with improved vegetative growth and olive production (Rufat et al., 2014). The economic sustainability of olive tree cropping in Spain and other countries is linked to the ability to fully mechanize farming operations to reduce manpower and to decrease production costs, while maintaining high production standards, in terms of quantity and quality. A new olive growing system that could potentially allow further reduction in production costs is the super intensive olive grove (super-high-density system). In this system, trees are trained to form hedgerows, orchards can be brought into production within only a few years after planting and over-the row mechanical harvesters can be used (Tous et al., 2010). Therefore, it is essential that the cultivars used in super intensive olive groves have a very low vigour and excellent sensorial features of their oil (Tous et al., 2008, 2010).

On the basis of worldwide evaluations of olive cultivars, at the present time, three olive cultivars are considered to meet these requirements quite well. They are the Spanish Arbequina and Arbosana and the Greek Koroneiki. However, considering the vegetative and productive aspects it is currently widely accepted that among these cultivars, Arbequina is the best one for super intensive olive groves (De La Rosa et al., 2007; Tous et al., 2010; Rufat et al., 2014). Consequently, Arbequina is progressively being introduced into new environments in all olive-growing countries. However, recent trends to high and very high density orchards could lead to an increase on irrigation water and nutrient plant requirements. However, in many olive growing areas, irrigation is scarce and expensive to apply, with deficit irrigation strategies being required to optimize its use.

Drip irrigation is designed to increase water-use efficiency, reduce salinisation, and maintain, or even increase, crop yields (Li et al., 2003; Tilman et al., 2002). In Spain drip irrigation is typically used in olive trees and vineyards, while furrow irrigation is used in horticulture and represents only 5% of the total irrigated area. Drip irrigation represents approximately 49% of the total irrigated area and is more common in the region of Andalucía. In Spain, olive trees occupy 2, 593, 523 ha, of which the 28.55% (740 511 ha) are irrigated (20.54% of the total irrigated area) almost exclusively by drip irrigation (ESYRCE, 2014). Drip irrigation makes it possible to apply small amounts of N fertiliser and water directly to the tree rooting zone; this leads to improved nutrient use efficiencies (Tilman et al., 2002) and leaves less N available for transformation into N_2O by microorganisms. This has also been proposed as a way to reduce N_2O emissions by spatially limiting the quantity of water available to microorganisms and thus restricting their ability to produce N_2O (Kennedy et al., 2013; Steenwerth and Belina, 2010). To date, there is little available information assessing GHG emissions from drip irrigation and from deficit irrigation systems, such as Subsurface Drip Irrigation (SDI), which could potentially mitigate GHG emissions (compared to Surface Drip Irrigation (DI)) by delivering water directly to tree roots. Maintaining a smaller water filled pore space (WFPS) in SDI compared to DI may limit denitrification. The adoption of SDI technology has so far been slow, but certain benefits have already been demonstrated, including water savings and a reduction in GHG emissions (Kallenbach et al., 2010). The upfront costs and maintenance requirements of SDI may, in part, explain its slow rate of adoption. The cost of installing surface drip irrigation is approximately 5000 € ha^{-1} in Catalonia, but could vary depending on the type of crop. The subsurface drip irrigation involves additional costs as: (I) costs to bury the pipeline (approximately 300 € ha^{-1}); the depth of burying the pipe depends on the soil characteristics and cultivation techniques; (II) the level of automation of the irrigation system; (III) if irrigation is installed on a large number of hectares the price is lower (scale factor).

A mitigation strategy that has so far proven highly effective for reducing N fertiliser losses and increasing N use efficiency and yields in some cropping systems involves the application of nitrification inhibitors (Cui et al., 2011; Moir et al., 2012). Nitrification inhibitors can delay the microbial oxidation of NH_4^+ to nitrite (NO_2^-), often for several weeks or even months, and are therefore very effective at reducing subsequent denitrification (Weiske et al., 2001). Although hundreds of nitrification inhibitors are known, to date, only a few have attained commercial importance for practical use; these include dicyandiamide and 3,4-dimethylpyrazol phosphate (DMPP). The application of DMPP in combination with NH_4^+-based fertilisers, such as cattle or pig slurry, has proved efficient for reducing N losses in the forms of N_2O emissions and NO_3^- leaching, while also increasing yields and improving N use efficiency on croplands and grasslands (Weiske et al., 2001; Villar and Guillaumes, 2010; Moir et al., 2012; Pfab et al., 2012).

However, at present, little is known about GHG and N_2 emissions from fertigated high tree density olive crops under Mediterranean climatic conditions.

The objectives of this study were to compare the GHG emissions from an adult high tree density Arbequina olive orchard (i) applying two different irrigation strategies (subsurface drip irrigation (SDI) and, surface drip irrigation (DI)) in combination with mineral N applied via fertigation and, (ii) applying the DMPP nitrification inhibitor.

2. Materials and methods

2.1. Site characteristics

The study was carried out at a commercial high tree density (1010 trees ha^{-1}) adult olive tree plantation (*O. europaea* L. cv. Arbequina) located at Torres de Segre (Lleida, Catalonia, Spain) (Fig. 1) in 2011 and 2012. The location is characterized by a continental Mediterranean climate, with an average annual temperature of 14.8 °C and an average annual rainfall (over the last 10 years) of 350 mm, with summer being the driest and hottest season of the year (rainfall below 13 mm and temperatures sometimes higher than 30 °C). The average relative humidity is 65% and the average wind speed is 1.45 m s^{-1}. In 2011 the average annual relative humidity was 65% and the average annual wind speed was 1.25 m s^{-1}, while in 2012, the average annual relative humidity was 61% and the average annual wind speed was 2.10 m s^{-1} (Meteorological Service of Catalonia, http://www.meteo.cat/observacions/xema/dades?codi=X7). The soil was moderately deep, calcareous, silty loam with a pH of 8 and an electrical conductivity (EC 1:5) of 1.4 dS m^{-1} (due to the presence of gypsum); it had an organic matter content of 1.5% and was non-saline. The initial nutrient content was 23 mg NO_3^-–N kg^{-1}, 50 mg Olsen-P kg^{-1} and 131 mg K kg^{-1} (Rufat et al., 2014). At the beginning and end of each growing season, a composite soil sample was taken from each elementary plot to a depth of 0.25 m to determine the soil NO_3^-–N content (Fig. 2).

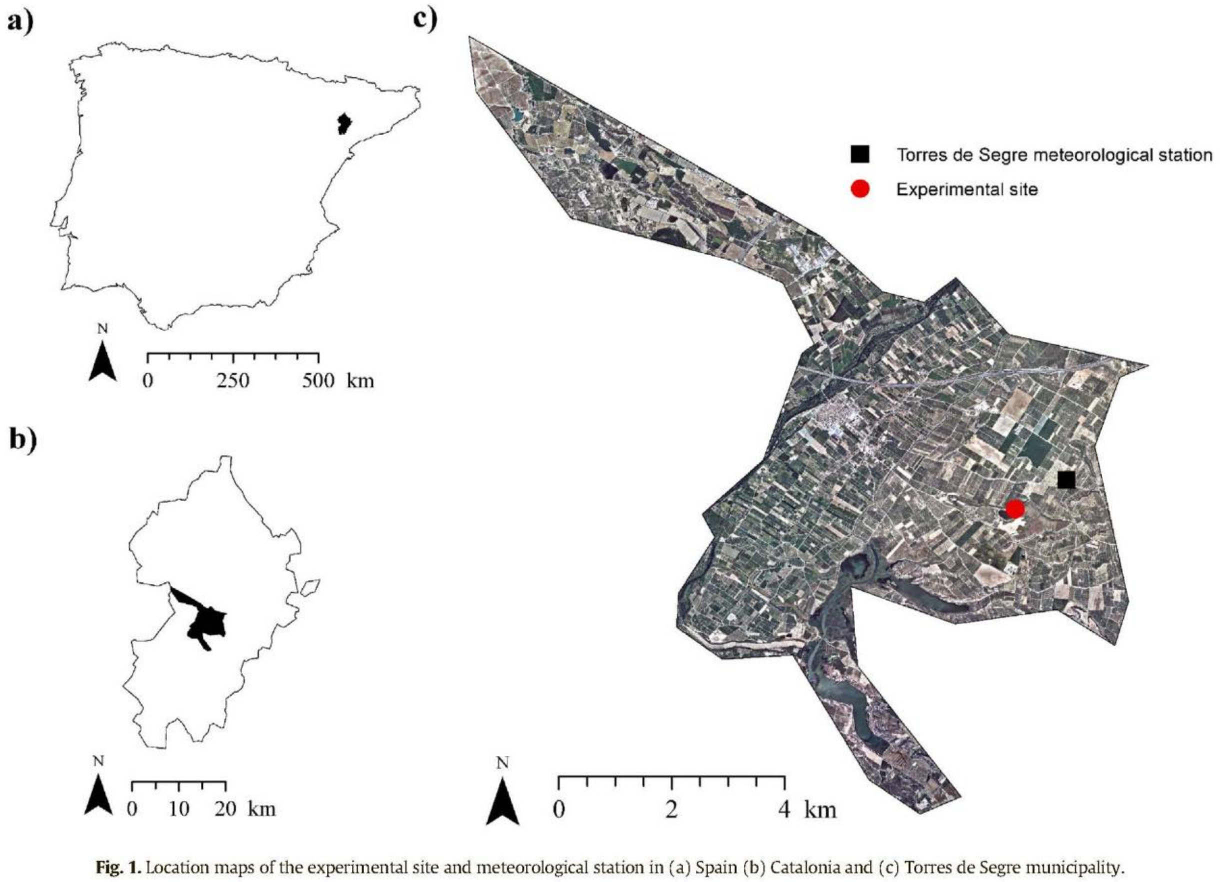

Fig. 1. Location maps of the experimental site and meteorological station in (a) Spain (b) Catalonia and (c) Torres de Segre municipality.

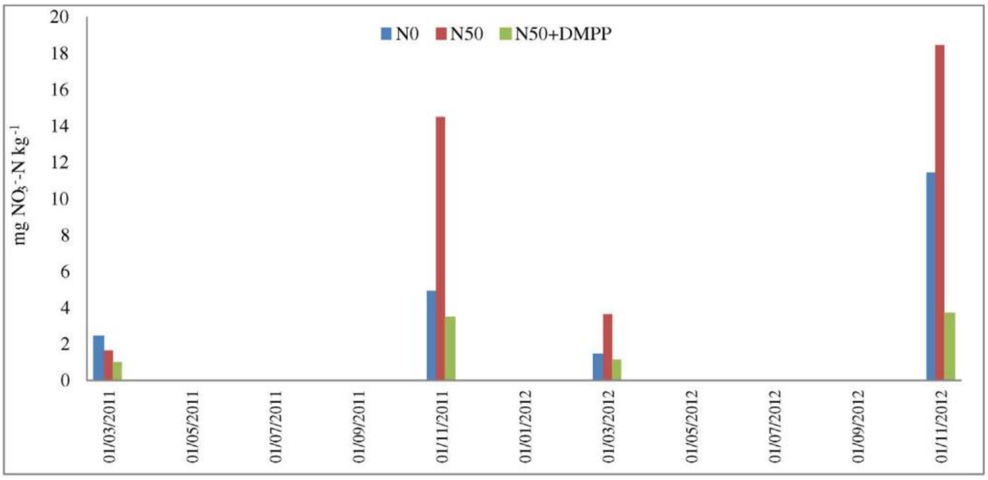

Fig. 2. Evolution of soil NO_3^-–N content through time for the three nitrogen treatments.

2.2. Experimental design

The trees had been planted in the summer of 2002 at a spacing of 4.5 m × 2.2 m, resulting in a density of 1010 trees ha^{-1}. The experimental plots were established and arranged in a randomized block design with three N treatments under two different irrigation treatments and with three blocks (replications) (Rufat et al., 2014). Each plot included three rows with six trees per row. The research project had a duration of three years, but greenhouse gases could be measured only on two of them (2011 and 2012). In 2013 (the 3-year project 2010–2012 was enlarged), the treatments were changed: the N dose was increased from 50 to 100 kg N ha^{-1} in both irrigation systems (surface/subsurface drip irrigation) since a positive response of yield to N had been found. The irrigation treatments applied were (1) DI: "Surface Drip Irrigation" to which 100% of the water requirements were applied, calculated according to the FAO methodology (Allen et al., 1998) and the crop coefficient (Kc) values of Girona et al. (2002); this was applied through surface drip irrigation (according to Table 1), with water being applied on a daily basis; and (2) SDI: "Subsurface Drip Irrigation" to which less than 100% of water requirements were applied according to the following scheme: April, May and June, 70% of requirements; July to September 10th, 25% of requirements; 11th September to the end of October, 70% of requirements. This crop coefficient (Kc) value can help establishing the annual amount of water needed to irrigate olive trees in most of the areas where "Arbequina" cultivar is grown. Girona et al. (2002) established that the optimal Kc for vegetative growth was 0.74, while the optimal Kc to produce olive oil was about 0.68. It is well studied that oil yield and the percentage of oil extraction from fresh fruits are significantly dependent on the applied Kc. Using a higher Kc than the optimal estimated values could have a negative effect on parameters such as vegetative growth, fruit yield and oil yield (Girona et al., 2002).

Table 1
Typical ETo, rainfall, and applied irrigation and fertilisation per year.

Year	Month	ETo (mm)	Rainfall (mm)	Irrigation (mm)		Fertilisation (kg N ha^{-1})	
				DI	SDI	N50	N50 + DMPP
2011	April	110	15	37	20		
	May	147	45	58	46	22	22
	June	157	6	83	63	17	17
	July	171	21	90	25		
	August	166	0	111	33		
	September	114	6	63	46	16	16
	October	73	11	34	29		
	Total	938	104	476	262	55	55
2012	April	96	52	12	8		
	May	151	13	77	52	8	8
	June	173	16	61	44	24	24
	July	170	6	88	32	14	14
	August	166	4	103	29		
	September	102	38	69	46	9	9
	October	54	92	12	10		
	Total	912	221	422	221	55	55

DI: surface drip irrigation; SDI: deficit subsurface drip irrigation.

In this study, SDI reduced the total amount of water applied by approximately 45% with respect to DI. The irrigation system consisted of 2.3 L h^{-1} applied via auto-compensated drip emitters located at 60 cm intervals in both the surface and subsurface systems. The different irrigation lines were placed 30 cm from the tree trunks. The subsurface irrigation lines were buried 20 cm beneath the soil surface and at a distance of 50 cm from the tree trunks. Irrigation water was taken from the River Segre and managed by the irrigation district of Carrassumada. The water conductivity was 0.9 dS m^{-1}, the chloride content was 2.25 meq L^{-1} and the sodium content was 2.14 meq L^{-1}; boron content was below 0.15 ppm and nitrate content was 9 ppm (Rufat et al., 2014).

The N treatments applied were (1) N0: no N application; (2) N50: 50 kg N ha^{-1}. As previously mentioned, these two treatments were applied with both the DI and SDI irrigation treatments. A third fertiliser treatment was also applied, (3) N50 + DMPP: 50 kg N ha^{-1} applied with the DMPP nitrification inhibitor (http://entecfertilisers.com.au/ENTEC/ENTEC%20Fertilisers/What%20is%20ENTEC), but only with the DI irrigation treatment. Nitrogen was applied once a week through fertigation, according to a monthly plan (Table 1). In the first year (2011) a N-32 solution (16% urea, 8% ammonium, and 8% nitrate) was used; in the second year (2012) a N-20 solution (10% ammonium and 10% nitrate) was used. In both years, DMPP was applied as a fertiliser marketed as Entec® 26 (facilitated by Compo Expert Spain S.L. http://www.interempresas.net/Horticola/Articulos/76288-Compo-Agricultura-presenta-una-nueva-tecnica-de-abono-con-ENTEC.html). All the plots were fertigated with 100 kg K_2O ha^{-1} (potassium solution 0-0-15) (Table 1). No phosphoric fertilisation was applied due to the high initial soil phosphorus content (41.33 mg Olsen-P kg^{-1}).

2.3. Gas sampling and analysis

Undisturbed soil cores, which were 15 cm long and 7 cm in diameter, were taken on a weekly basis, using PVC tubes. The soil cores were placed on a lid immediately after withdrawing them from the soil. This lid was kept on place until the samples were weighted to gravimetrically determine their water content. These were taken from the wet topsoil of the bulb generated by the irrigation system and immediately brought to the laboratory. The total time spent every sampling day to withdraw the soil cores was about 1 h. The samples were immediately taken to the laboratory (inside an insulated closed cage) which was only 15 min drive away from the field. This procedure began one week before the start of irrigation and continued until irrigation finished. Nitrous oxide, CO_2 and CH_4 fluxes were measured in the laboratory using the closed chamber method.

Each soil core collected in the PVC cylinder was placed in a glass jar (1.5 L) with an air-tight glass lid. Each of these lids was equipped with a three-way key which was directly connected to a photoacoustic analyser (Innova 1412 Photoacoustic Multigas Monitor) via a Teflon® tube. Air samples from inside the glass jar were taken immediately after closing the glass lid and then after 20 and 40 min. After the 40 min sample, the glass jars were left open. The glass jars were hermetically closed for 40 min during which the photoacoustic analyser withdrew and analyzed gas samples at times 0, 20 and 40 min after closing. The glass jars lids' were left open to allow the inside and outside gases concentrations and pressures to equilibrate before proceeding with the acetylene inhibition method.

The acetylene (C_2H_2) inhibition method (Balderston et al., 1976; Yoshinari et al., 1977) was used to inhibit the last step of denitrification (N_2O reduction to N_2). Ten percent (v/v) of the air enclosed in the chamber was then replaced by C_2H_2. This replacement inhibited the reduction of N_2O to N_2 (Federova et al., 1973). After the C_2H_2 had been allowed to diffuse for 20 min, the gas was analysed as described in the previous paragraph. Forty min after sampling, the glass jars were emptied and left open.

Surface soil temperature and atmospheric pressure were recorded always during sampling. The photoacoustic analyser refers the gases concentration to 20 °C and 1 atm; the concentration was corrected to be referred to the actual field temperature and atmospheric pressure of each sampling day. Sampling was done at the time of the day when soil temperature was about the average soil temperature of the day in order to minimize over or underestimation of the emission caused by daily soil temperature variation.

A value for molecular nitrogen emission was obtained by subtracting N_2O emissions without acetylene from N_2O emissions with acetylene (Ryden et al., 1979).

2.4. Soil moisture and soil temperature

After the gas analysis, the soil samples were dried at 105 °C to a constant weight in order to gravimetrically determine moisture content. Water-filled pore space (WFPS) was then calculated by dividing the gravimetric water content by the total soil porosity. Total soil porosity was determined by measuring the bulk density of the soil according to the following relationship: soil porosity = 1 − (soil bulk density) / PD, with PD representing the particle density, which for this soil texture was assumed to be 2.65 g cm^{-3} (Porta et al., 2008).

Actual rainfall and temperature data were obtained from the meteorological station located at Torres de Segre (Fig. 1). Soil temperature (at a depth of 10 cm) was also measured while the soil samples were taken.

2.5. Calculations and statistical analysis

The N_2O, CO_2 and CH_4 emission fluxes were determined from the linear increase of the gas concentration at each sampling time (0, 20 and 40 min) during the time of chamber closure. The average GHG flux for each treatment presented in the figures is the arithmetic mean of three replications per treatment in 2011 and nine replications per treatment in 2012.

The cumulative emission throughout the study period was calculated by integrating the emission flux curves over time.

All the results are expressed as mass of each gas emitted during the sampling period (or day for the fluxes) and per hectare. One must keep in mind that only 1/15 (6.66%) of the hectare was wet.

The $N_2O/N_2O + N_2$ ratio was also calculated.

According to Forster et al., 2007 albedo could contribute to an assessment of global warming. However, it has not been considered in this study because of the lack of information (e.g. local data on cloud cover), and the need to obtain local data on surface albedos, either by means of field measurements or remote sensing. With regard to initial and final albedo, substantial uncertainty can be expected if the values used do not come from measurements; otherwise, they should be substantially lower. Literature albedo values are sometimes given as ranges with rather broad limits. The CO_2-eq. emissions are very sensitive to small changes in albedo. Therefore, in the present study, the global warming potential (GWP) of N_2O and CH_4 emissions was calculated in units of CO_2 equivalents (CO_2-eq.) over a 100-year horizon (Forster et al., 2007). A radiative forcing potential relative to CO_2 of 298 was used for N_2O and 25 for CH_4 (Forster et al., 2007). Although soil CO_2 fluxes also represent a source of GHG emissions, on a global scale, they are largely offset by high rates of net primary productivity and atmospheric CO_2 fixation by crop plants, and are therefore estimated to contribute <1% to the GWP of agriculture (Smith et al., 2008; Linquist et al., 2012; Abalos et al., 2014). Therefore, CO_2 as a contributor to GWP was not included in this analysis.

The greenhouse gas intensity was calculated as follows: GHGI (CO_2-eq kg^{-1}) = GWP / oil production.

The direct N_2O emission factor (EF) was calculated according to the IPCC (2001) method as the difference between the N_2O emitted from the fertilised soil and that from the control, divided by the N applied as fertiliser.

The data distribution normality of the fluxes (N_2O, $N_2O + N_2$, CH_4 and CO_2) was verified using the Sharpiro–Wilk test. In some cases, the data were log transformed before analysis. The cumulative emission of N_2O, CO_2 and CH_4 was examined with an ANOVA model (JMP, Version 10. SAS Institute Inc., Cary, NC, 1989–2010) that included terms for irrigation type (I), fertiliser treatment (N), and interactions (I × N). Cumulative emissions of N_2O, CO_2 and CH_4 for the DMPP treatment were also examined with an ANOVA model, which included only the term for the fertiliser treatment (N). The Tukey's Honestly Significant Difference (THSD) post hoc test was used for multiple comparisons between means ($p < 0.05$) (Ma et al., 2012; Abalos et al., 2014). Multivariate correlation analysis was used to analyse the relationship between GHG emissions and the studied driving factors (i.e. soil temperature, air mean temperature and WFPS). The correlations were assessed using the non-parametric Spearman rank coefficient (ρ). A p value of 0.05 was used as the threshold for statistical significance.

3. Results

3.1. Environmental conditions and water filled pore space

The average daily soil temperature ranged from 17 to 29 °C during the sampling period in 2011 and from 14 to 27.5 °C in 2012. In 2011, the average air temperature during the sampling period was 15.6 °C, the total ETo was 938 mm, and the total rainfall was 104 mm. In 2012, the corresponding values were: 15.1 °C, 912 mm and 221 mm (Table 1).

In 2011, during the irrigation period, the WFPS ranged from 36 to 86% under the DI treatment and from 40 to 67% under the SDI treatment. In 2012, the corresponding ranges were from 22 to 55% and from 15 to 49% (Fig. 3a and b). In both years, the summers were not warmer nor wetter than the previous 10 year average. Therefore, no influence of ambient relative humidity on WFPS differences among years was expected.

3.2. Nitrous oxide and molecular nitrogen emissions from the 0 (N0) and 50 kg N ha^{-1} (N50) treatments

Figure 4a and b show the daily fluxes of N_2O sampled in 2011 and 2012 respectively. In both years high peaks of N_2O were observed during fertiliser application (Fig. 4a and b). In 2011, the highest N_2O

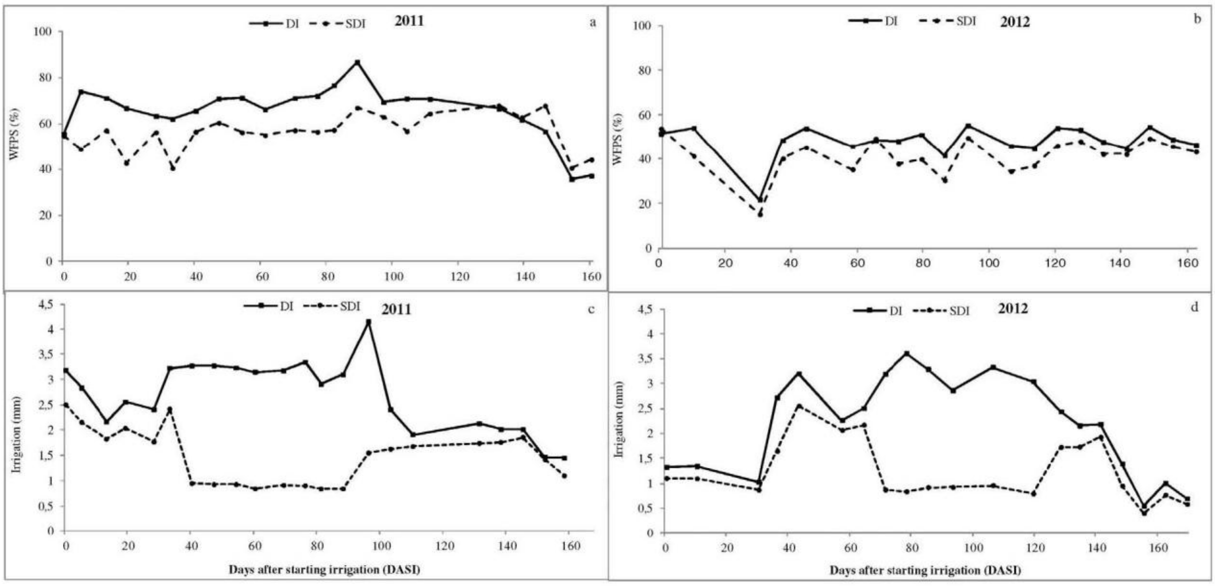

Fig. 3. (a) Soil water filled pore space (%) in 2011, and (b) in 2012, (c) irrigation water applied to each irrigation treatment (mm) in 2011 and (d) in 2012.

peak (9.16 g N_2O-N ha^{-1} d^{-1}) was recorded at 13 DASI (days after starting irrigation) for N50 + DI. In 2012, the highest N_2O peaks (7.54 g N_2O-N ha^{-1} d^{-1}) were observed at 58 DASI and 127 DASI (7.06 g N_2O-N ha^{-1} d^{-1}), for the same treatment (Fig. 4a and b). The largest cumulative N_2O emission was from the N50 + DI treatment (Table 3). In both years, fertiliser applications produced an increase in cumulative N_2O emissions, as did the DI treatment, but only significantly in 2012 (Table 3).

Figure 4c and d show the daily fluxes of $N_2O + N_2$ sampled in 2011 and 2012 respectively. In 2011, $N_2O + N_2$ peaks were observed on all the plots following the start of irrigation. The highest $N_2O + N_2$ peaks were recorded at 82 DASI (Fig. 4c), coinciding with a period of relatively high WFPS (57% for SDI and 77% for DI) (Fig. 3a). In 2012, $N_2O + N_2$ peaks were observed on all plots throughout the experiment, though these were much smaller than in 2011.

In 2011, $N_2O + N_2$ emissions correlated with WFPS ($\rho = 0.640$, $p < 0.05$) (Table 2). In 2012, $N_2O + N_2$ emissions did not correlate with any variable (Table 2). In both years, the cumulative $N_2O + N_2$ emissions were significantly larger ($p < 0.05$) for the N50 + DI treatment than for the others (Table 3). In both years, the cumulative emissions increased with N fertilisation, though only significantly ($p < 0.05$) in 2012 (Table 3). Irrigation significantly affected total cumulative $N_2O + N_2$ emissions, but only in the first year.

In both years, the N_2O emission factors (EF) ranged from −0.03 to 0.14% of the total quantity of N applied, while the $N_2O + N_2$ EF ranged from 0.57 to 1.80% of applied N (Table 4).

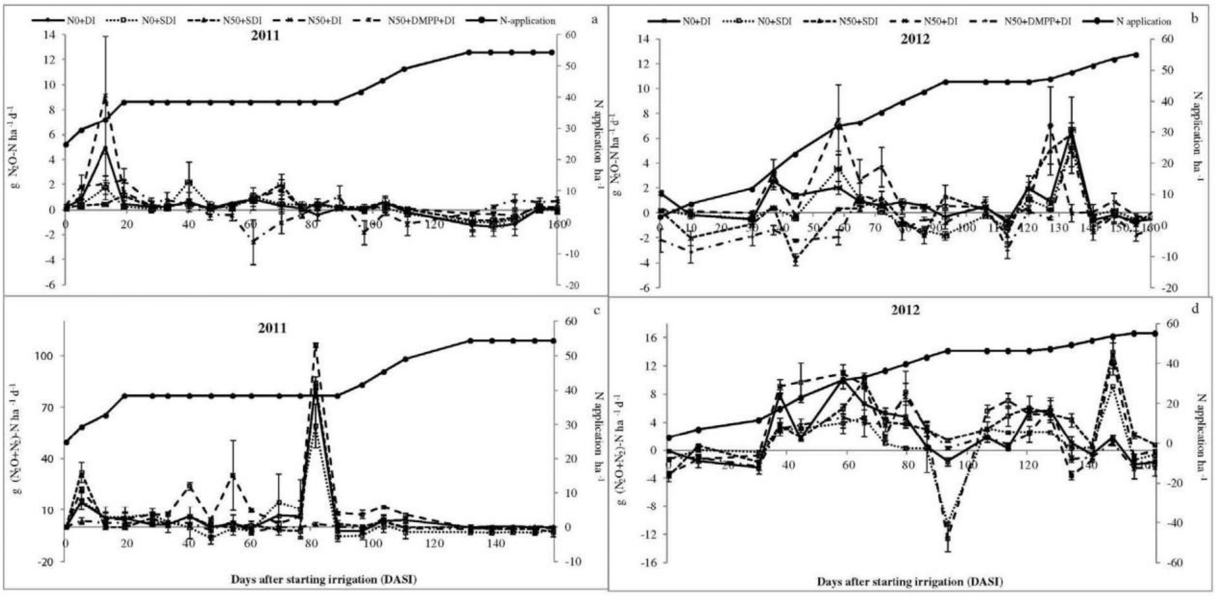

Fig. 4. Average daily flux of N_2O–N during the sampling period 2011 (a) and 2012 (b); average daily flux of ($N_2O + N_2$)–N during the sampling period 2011 (c) and 2012 (d). Vertical lines indicate the standard error of the average.

Table 2
Spearman rank correlation coefficients between measured soil/environmental parameters and N_2O–N, $(N_2O + N_2)$–N, CO_2 and CH_4 cumulative emissions per year. Significant correlations are denoted by an asterisk ($p < 0.05$).

Variables	N_2O–N		$(N_2O + N_2)$–N		CO_2		CH_4	
	2011	2012	2011	2012	2011	2012	2011	2012
Soil T	0.21	0.04	−0.47	0.16	−0.10	0.23	0.42	0.02
Air mean T	0.07	−0.16	0.43	0.18	−0.30	−0.17	0.36	0.21
WFPS	0.30	0.33*	0.64*	0.22	−0.08	0.14	−0.15	0.10

DI: drip irrigation; SDI: deficit subsurface drip irrigation; WFPS water filled pore space.

3.3. Carbon dioxide emissions from the 0 (N0) and 50 kg N ha^{-1} (N50) treatments

The evolution of CO_2 fluxes in 2011 and 2012 can be observed in Fig. 5a and b.

The maximum CO_2 emission was recorded in 2011, with 13.73 kg CO_2 ha^{-1} d^{-1} for the N0 + SDI treatment (Fig. 5a). The cumulative CO_2 emission was significant ($p < 0.05$) and highest from the N0 + SDI (2011) treatment (Table 3). In both years, fertilisation seemed to have an inhibitory effect on CO_2 emissions, with this effect being significant in 2011 (Table 3). In both years, there were no significant correlations between CO_2 emissions and soil and air temperature and WFPS (Table 2). No significant interaction between irrigation and nitrogen was found in either of the test years (Table 3).

3.4. Methane emissions from the 0 (N0) and 50 kg N ha^{-1} (N50) treatments

In both years, the soil acted as a sink for CH_4 for all the treatments (Table 3), although positive fluxes were also registered on some sampling dates (Fig. 6a and b). The cumulative CH_4 emission was negative and significantly larger for the fertilised plots in 2011 (−1 kg CH_4 ha^{-1} for DI and for SDI) (Table 3).

3.5. Effect of nitrification inhibitor (DMPP) on greenhouse gas emissions and molecular nitrogen

The effect of DMPP was only tested for N50 and DI. In both years, the cumulative N_2O and $N_2O + N_2$ losses were significantly ($p < 0.05$) smaller for N50 + DMPP than for the control and N50 + DI treatments (Table 5). In both years, DMPP had a significant effect on N_2O and $N_2O + N_2$ emissions (Table 5).

The daily fluxes of CO_2 ranged from −1.66 kg CO_2 ha^{-1} d^{-1} to 10.31 kg CO_2 ha^{-1} d^{-1} for the N50 + DMPP treatment (Fig. 5a and b). In both years, applying DMPP reduced cumulative CO_2 emissions with respect to the control (by 35% in 2011) and the N50 treatment (by 39% 2011), although only significantly in 2011 ($p < 0.05$) (Table 5).

Methane fluxes ranged from 2.21 to −10.32 kg CH_4 ha^{-1} d^{-1} (Fig. 6a and b). In both years, the cumulative CH_4 emission from the N50 + DMPP treatment was significantly smaller ($p < 0.05$) than from the control and the N50 treatment (Table 5). In both years, applying DMPP had a significant effect on CH_4 oxidation (Table 5).

3.6. Global warming potential and greenhouse gas intensity

In both years, the global warming potential (GWP) calculated with the N_2O, and CH_4 emissions ranged from −5848 to 8 kg CO_2-eq ha^{-1} for the sampling period (Table 4). In both years, the olive orchard acted as a net sink for CH_4 for all the treatments and this, in turn, reduced the overall GWP. Applying the irrigation treatments and nitrogen had a significant effect on the total GWP ($p < 0.05$) (Table 4).

The GWP for the N50 + DMPP treatment was significantly smaller than for those of N0 and N50 (both in DI) (Table 5).

The greenhouse gas intensity (GHGI) was significantly ($p < 0.05$) the lowest for the N50 + SDI (2012) treatment, followed by the N50 + DMPP + DI (2012) treatment (Tables 4 and 5). In both years, irrigation treatments had a significant effect on GHGI, while nitrogen had a significant effect in 2011 only ($p < 0.05$) (Table 4).

In 2011 (on-year), N50 + DI led to the highest oil production, while in 2012 (off-year) the highest oil production was for the N50 + DMPP + DI treatment (Tables 4 and 5). Further details on the productive and vegetative response to different irrigation and fertilisation strategies of this Arbequina olive orchard are published in Rufat et al. (2014).

4. Discussion

4.1. Nitrous oxide and molecular nitrogen emissions

In irrigated agroecosystems, water and N fertiliser management have an important influence on N_2O emissions (Vallejo et al., 2005). Applying N fertiliser increased the soil NH_4^+ and NO_3^- contents. The action of these ions in the nitrification and denitrification processes produced larger N_2O emissions from these plots under both of the irrigation strategies applied. Since the fertiliser applied contained both NH_4^+–N and NO_3^-–N, both nitrification and denitrification could have been involved in the production and emission of N oxides. The significantly larger $N_2O + N_2$ emissions recorded suggest that denitrification was a major source of N_2O.

The WFPS and mineral N in the wet bulb have a significant influence on nitrification and denitrification (Abalos et al., 2014). In the present study, the $N_2O + N_2$ fluxes peaked when the WFPS ranged from 66 to 86% (Figs. 3a and 4c). Above the critical threshold value (65% WFPS) denitrification sharply increased. Similar results were observed by Abalos et al. (2014), who reported that soil N_2O fluxes peaked when

Table 3
Cumulative N_2O–N, $(N_2O + N_2)$–N, CO_2, CH_4 emissions, and N_2O–N/$(N_2O + N_2)$–N ratio per year and treatment (excluding the DMPP treatments).

Irrigation	Nitrogen	Cumulative N_2O–N (g ha^{-1})		Cumulative $(N_2O + N_2)$–N (g ha^{-1})		$\frac{N_2O\text{–}N}{(N_2O+N_2)\text{–}N}$ (%)		Cumulative CO_2 (kg ha^{-1})		Cumulative CH_4 (kg ha^{-1})	
		2011	2012	2011	2012	2011	2012	2011	2012	2011	2012
DI	0	42 a	103 ab	872 ab	374 ab	0.04	0.27	771 a	735 a	−39 b	−56 a
	50	112 a	154 a	1774 a	678 a	0.06	0.22	681 ab	793 a	−1 a	−94 a
SDI	0	24 a	22 ab	502 b	254 b	0.04	0.08	801 a	762 a	−8 ab	−118 ab
	50	34 a	8 b	785 ab	558 ab	0.04	0.01	645 b	698 a	−1 a	−234 b
Irrigation (I)		ns	*	*	ns	–	–	ns	ns	ns	*
Nitrogen (N)		ns	ns	ns	*	–	–	*	ns	*	ns
IxN		ns	ns	ns	ns	–	–	ns	ns	ns	ns

DI: drip irrigation; SDI: deficit subsurface drip irrigation. Within columns means followed by the same letter (a or b) are not significantly different between treatments according to the Tuckey's test ($p = 0.05$). While, within columns means followed by the different letter (a and b) are significantly different between treatments according to the Tuckey's test ($p = 0.05$). ns: not significant; *: significant at the 0.05 probability level.

Table 4
Emission factor (EF%), global warming potential (GWP), and greenhouse gas intensity (GHGI) per year and treatment (excluding the DMPP treatments).

Irrigation	Nitrogen	EF (%)				GWP ($kg\ CO_2$-eq ha^{-1})		†Oil production ($kg\ ha^{-1}$)		GHGI ($kg\ CO_2$-eq kg^{-1} yield)	
		N_2O–N		($N_2O + N_2$)–N		2011	2012	2011	2012	2011	2012
		2011	2012	2011	2012						
DI	0	–	–	–	–	−963 b	−1369 a	2655 ab	1632 a	−0.36 b	−0.8 a
	50	0.14	0.10	1.80	0.61	8 a	−2304 a	3300 a	1198 a	0.002 a	−1.92 a
SDI	0	–	–	–	–	−193 ab	−2943 a	2956 ab	1439 a	−0.07 a	−2.05 a
	50	0.02	−0.03	0.57	0.61	−15 a	−5848 b	2338 b	1270 a	−0.006 a	−4.60 b
Irrigation (I)	–	–	–	–	–	*	*	*	ns	*	*
Nitrogen (N)	–	–	–	–	–	*	ns	ns	ns	*	ns
IxN	–	–	–	–	–	ns	ns	ns	ns	ns	ns

DI: drip irrigation; SDI: deficit subsurface drip irrigation. Within columns means followed by the same letter (a or b) are not significantly different between treatments according to the Tuckey's test ($p = 0.05$). While, within columns means followed by the different letter (a and b) are significantly different between treatments according to the Tuckey's test ($p = 0.05$). ns: not significant; *: significant at the 0.05 probability level. †data published in Rufat et al., 2014.

the WFPS ranged from 60 to 80% in a melon crop field with drip irrigation. These authors also observed that denitrification was limited when WFPS was below 60%. In the present study, the measured increase in N_2O emissions at between 60 and 80% WFPS supports the hypothesis of a WFPS threshold for N_2O production by denitrification of the type proposed by Davidson (1992). Davidson (1992) and Teira-Esmatges et al. (1998) also found that nitrification was the dominant source of N_2O in the 30–70% WFPS range. A similar WFPS threshold for major increases in N_2O emissions from soils was reported by De Klein and Van Logtestijn (1996) and by Dobbie and Smith (2001).

The reduced water supply to the SDI treatment affected WFPS, which was smaller for SDI than for DI (Fig. 3a and b). The highest WFPS was registered in 2011 for the DI treatment (with a WFPS of up to 86.6% and of >60% in 90% of the measurements and of >65% in 71%). The other treatments (DI in 2012 and SDI in both 2011 and 2012) had smaller WFPS; these ranged from only 42 to 67.8% and were >60% in only 38% of the measurements (Fig. 3a and b). In both years, the cumulative $N_2O + N_2$ emissions from both fertilised treatments were larger for DI than for SDI (Table 3). This predominance of denitrification seems to be confirmed by the high correlation observed between $N_2O + N_2$ emissions and WFPS (Table 2). The cumulative $N_2O + N_2$ emissions were smaller when the WFPS was below 55% (Fig. 3a, b and Table 3). Under these conditions both nitrification and denitrification would have been responsible for a significant fraction

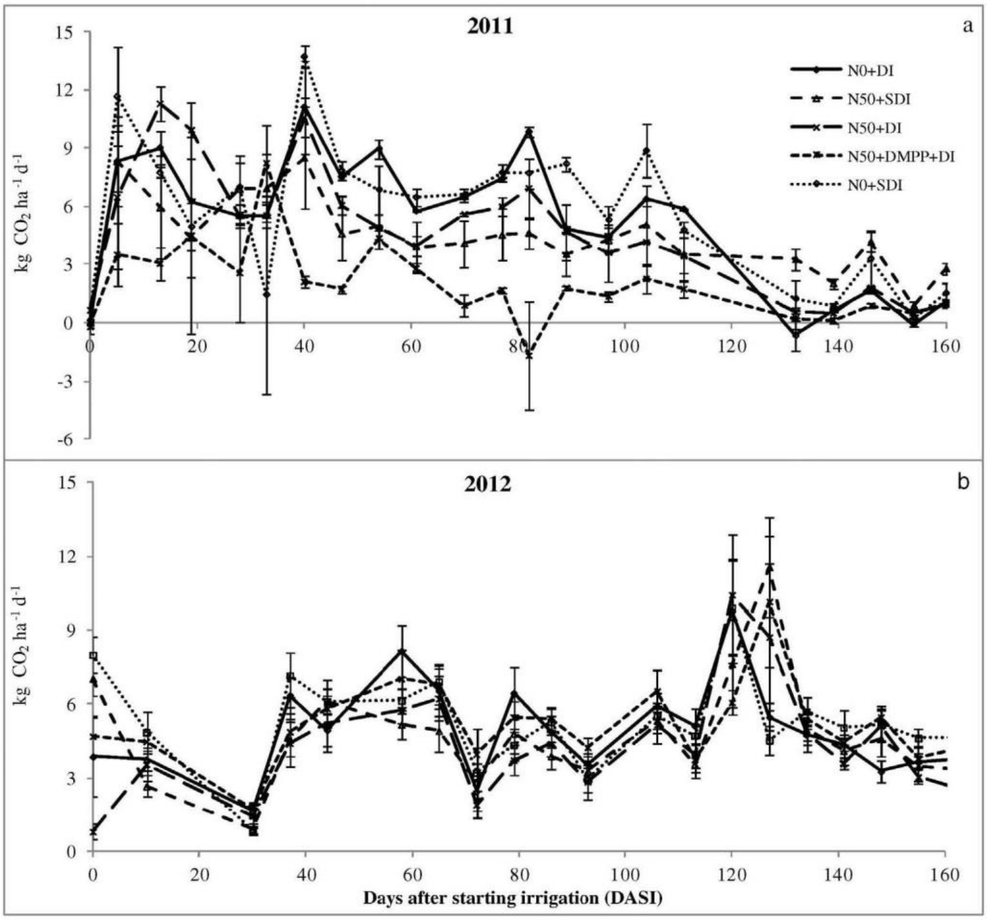

Fig. 5. Average daily flux of CO_2 during the sampling period (2011 and 2012). Vertical lines indicate the standard error of the average.

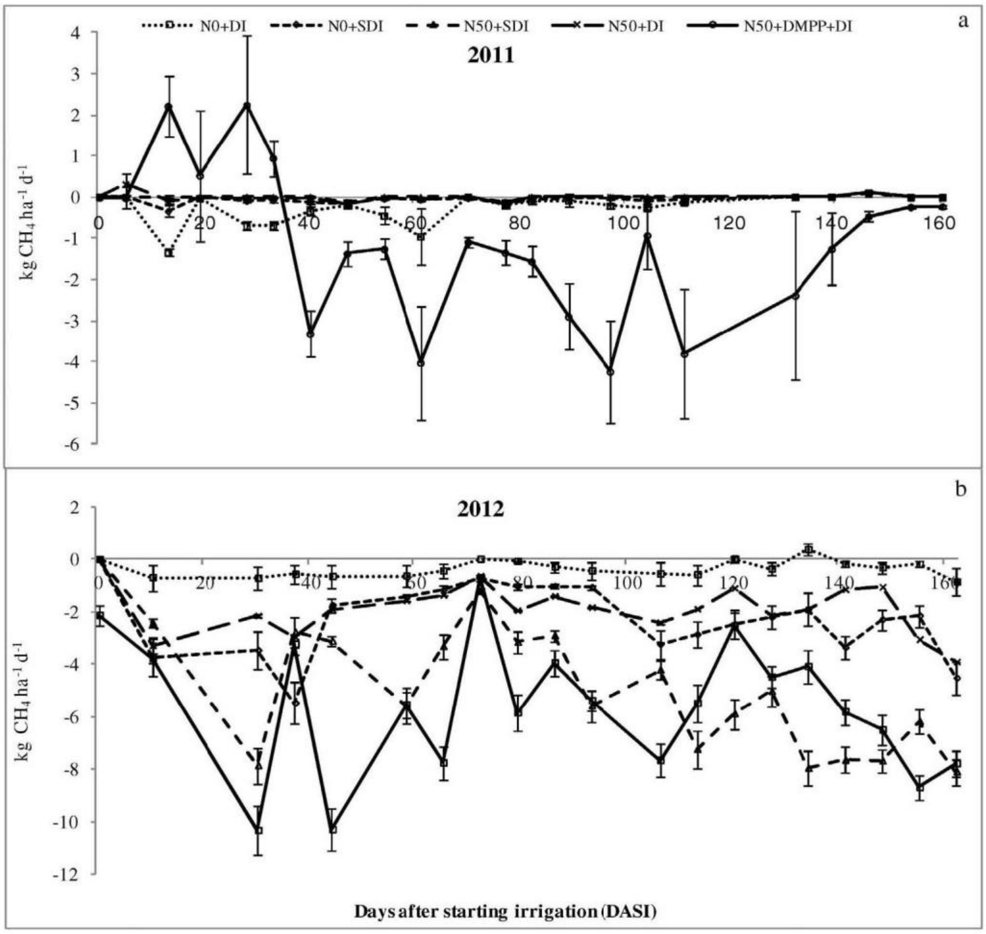

Fig. 6. Average daily flux of CH_4 during the sampling period (2011 and 2012). Note the differences in scale between the figures. Vertical lines indicate the standard error of the average.

of N_2O emissions since these moisture conditions were sub-optimal for denitrification, as previously noted by Kool et al. (2011). Other studies have also identified soil moisture as a major factor for controlling denitrification rates in irrigated systems (Duxbury and McConnaughey, 1986; Teira-Esmatges et al., 1998; Mahmood et al., 2005; Ruser et al., 2006; Sánchez-Martín et al., 2008a; Abalos et al., 2014; Vallejo et al., 2014).

As expected, high peaks of N_2O and $N_2O + N_2$ were observed close to fertilisation (Table 1 and Fig. 4) since the N readily available for microbial activity regulates N_2O emissions. The N_2O peaks may have been caused by the production of NO_3^- by nitrification, which is subsequently available for denitrification. The lack of available oxygen (O_2), as a consequence of the low solubility of O_2 in water combined with its rapid consumption by root and microbial respiration, enhances denitrification activity when WFPS is >60% (Khalil et al., 2004). On the other hand, when the soil was irrigated without preceding fertilisation, the N_2O and $N_2O + N_2$ emissions stayed generally low, which demonstrated that under these conditions mineral N availability could be the limiting factor for emission.

In the present study, with N_2O emission factors (EF) ranging from −0.03 to 0.14% of the applied N (Table 4), smaller values were registered than the IPCC (2007) default one (i.e. 1% regardless of the N source, location, climate and soil type). A negative EF implies that the cumulative N_2O emission from the treatment (in this case for N50 + SDI in 2012) was smaller than that from the control. Similar results were reported by Toma et al. (2007). One reason for this result might be a low N_2O emission. Another reason may be the large standard deviation, which is mainly attributable to the spatial temporal variability of N_2O

Table 5
Cumulative N_2O–N, $(N_2O + N_2)$–N, CO_2 and CH_4 emissions, global warming potential (GWP), and greenhouse gas intensity (GHGI) from the DI treatments per year.

Irrigation	Nitrogen	Cumulative N_2O–N (g ha^{-1})		Cumulative $(N_2O + N_2)$–N (g ha^{-1})		Cumulative CO_2 (kg ha^{-1})		Cumulative CH_4 (kg ha^{-1})		GWP (kg CO_2-eq)		†Oil production (kg ha^{-1})		GHGI (kg CO_2-eq kg^{-1} yield)	
		2011	2012	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012
DI	0	42 ab	103 ab	872 ab	374 ab	771 a	735 a	−39 a	−56 a	−963 a	−1369 a	2655 a	1632 a	−0.36 a	−0.80 a
	50	112 a	154 a	1774 a	678 a	681 a	793 a	−1 a	−94 a	8 a	−2304 a	3300 a	1198 a	0.002 a	−1.92 a
	N50 + DMPP	6 b	−116 b	101 b	237 b	270 b	662 a	−220 b	−285 b	−5498 b	−7160 b	2737 a	1674 a	−2.01 b	−4.28 b

DI: drip irrigation. Within columns means followed by the same letter (a or b) are not significantly different between treatments according to the Tuckey's test ($p = 0.05$). While, within columns means followed by the different letter (a and b) are significantly different between treatments according to the Tuckey's test ($p = 0.05$). ns: not significant; *: significant at the 0.05 probability level. †data published in Rufat et al., 2014.

emission. Nitrous oxide emission factors (EF) represent the first report of this metric for a perennial crop, for this reason further studies with more sampling intensity are needed.

For the N50 + SDI treatment in 2011 and the N50 − DI and N50 + SDI treatments (the DMPP treatments are not considered here) in 2012, the $N_2O + N_2$ loss from the N applied (calculated as the EF) was approximately 0.6% in all three cases. These results are within the range reported in the literature by Dhondt et al. (2004), Mahmood et al. (2005) and Šimek et al. (2004), who cited $N_2O + N_2$ losses ranging from 0.4 to 20% of the applied N. The highest measured EF of 1.80%, for the N50 + DI treatment in 2011 (Table 4), correlates with the highest WFPS.

The $N_2O/N_2O + N_2$ ratio was low and ranged from 0.04 to 0.27 for all the treatments (Table 3). Ruser et al. (2006) also observed that higher soil moisture contents reduced the $N_2O/N_2 + N_2O$ ratio.

Choosing between irrigation strategies is considered a critical way to save water in arid and semiarid regions and to maintain optimal crop yields. Studies comparing subsurface drip and furrow irrigation published by Kallenbach et al. (2010) and Kennedy et al. (2013) demonstrate that subsurface drip irrigation reduced N_2O emissions by 50% compared with furrow irrigation. Sánchez-Martín et al. (2008b, 2010), Vallejo et al. (2014) and Abalos et al. (2014) found that surface drip irrigation also reduced N_2O emissions compared with furrow irrigation. However, in Spain drip irrigation is typically used in olive trees and vineyards, while furrow irrigation is used in horticulture.

The results for the 2 years studied must be interpreted considering that 2011 was an "on-year" and that 2012 was an "off-year" in terms of alternate bearing. The olive tree exhibits a peculiar behaviour, named alternate bearing (biennial bearing or periodicity), defined as the tendency of some fruit trees not to bear a regular and similar crop year after year. Thus, a high-yield crop year ("on-year") is followed by a low-yield or even a no-crop year ("off-year"), which severely affects the fruit yield (Lavee, 2007). The alternate bearing is so pronounced in the olive tree, that it has been considered that this crop shows a biennial developmental cycle. For this reason the results of two consecutive years must always be considered for the proper determination of the production parameters. Furthermore, the WFPS was smaller in 2012 than in 2011 for all the treatments (Fig. 3a and b) and was judged to be a limiting factor for production. Olive production results showed that DI applied in combination with N50 produced the highest yield (3300 kg oil ha^{-1}) and also the highest GWP. This makes it necessary to evaluate other GHG mitigation strategies that would not jeopardize either the environmental quality or the productivity of this area.

4.2. Carbon dioxide emissions

In 2011, N fertilisation significantly reduced CO_2 emissions with respect to the control by 11.6% for the N50 + DI treatment and by 19.5% for the N50 + SDI treatment (Table 3). In 2012, an inhibitory effect on CO_2 emissions was observed, but only for the SDI treatments. This was probably because N application could reduce extracellular enzyme activity and the fungal population, resulting in a reduction in the CO_2 flux (Fogg, 1988; DeForest et al., 2004; Burton et al., 2004). Similar results were obtained by Burton et al. (2004), who found that, on average, N fertilised plots produced 15% less CO_2 emissions than unfertilised ones. Until now, fertilisation has exhibited contradictory effects with respect to soil CO_2 fluxes: suppression (Ding et al., 2006), enhancement (Fisk and Fahey, 2001; Xiao et al., 2005), or no effect at all (Lee et al., 2007).

The results of the present study of CO_2 emissions fall within the ranges reported by Kallenbach et al. (2010), who measured CO_2 fluxes from a sub-surface drip-fertigated crop in a semi-arid Mediterranean climate with fluxes ranging from 48.00 to 120.00 kg CO_2 ha^{-1} d^{-1}.

Abalos et al. (2014) are about the only authors to have published cumulative CO_2 emissions associated with DI applied to a melon crop over 90 days, with values ranging from 908.83 to 1192.08 kg CO_2 ha^{-1} for the application of 150 kg N ha^{-1}. In the present study, the highest cumulative CO_2 emissions recorded in either year were registered for the N0 + SDI (2011) treatment (801 kg CO_2 ha^{-1}) (Table 3).

Since the super intensive olive grove (1010 trees ha^{-1}) had a grass cover between the rows, it could be considered that the soil CO_2 fluxes measured in the present study were offset by atmospheric CO_2 fixation by the trees and grass cover between rows. It is well studied that the forests and the grassland cover increase surface albedos and reduce radiative forcing (Breuer and Eckhardt, 2003). The super intensive olive tree orchard could be considered to work as a forest, and to therefore have a positive effect in mitigating greenhouse gases and reducing radiative forcing.

4.3. Methane oxidation

Soil methane emissions result from the balance between anaerobic methanogenic CH_4 production and aerobic methanotrophic CH_4 consumption. The two processes tend to occur simultaneously and the rate of CH_4 and O_2 diffusion into soil microsites determines the final flux (Keller and Reiners, 1994). In the present study, the olive orchard acted as a net CH_4 sink for all of the treatments (Table 3). This was consistent with the results of previous studies with drip irrigation conducted in melon plantations (Vallejo et al., 2014; Abalos et al., 2014). In 2011, the cumulative CH_4 emission was significantly affected by the N fertiliser dose, while in 2012 it was significantly affected by irrigation (Table 3). In the literature there are reports of NH_4^+ or NH_4^+-generating compounds reducing the oxidation capacity of the soil after N application (Steudler et al., 1998; Hütsch et al., 1996). This has been attributed to an inhibitory effect of NH_4^+ at the cellular level due to the competitive inhibition of the enzyme CH_4 monooxygenase by NH_4^+ monooxygenase (Dunfield and Knowles, 1995; Le Mer and Roger, 2001; Bodelier and Laanbroek, 2004; Liu and Greaver, 2009; Vallejo et al., 2014).

In 2012, the cumulative CH_4 emissions were significantly affected by irrigation. Methane oxidation was larger for the SDI than for the DI treatments (Table 3), due to the relatively smaller WFPS for SDI (Fig. 3b). In 2012, all of the treatments were associated with a larger CH_4 oxidation due to the fact that the WFPS was relatively smaller than in 2011 during most of the growing season (Fig. 3a and b). A decrease in soil moisture enhanced CH_4 oxidation through improved CH_4 diffusion from the atmosphere into the soil pore spaces and through improved gas diffusivity, which allowed increased microbial CH_4 oxidation, which varies inversely with soil moisture (Ball et al., 1997; Brumme and Borken, 1999; Smith et al., 2003; Wu et al., 2014; Tate, 2015).

4.4. The effect of nitrification inhibitor (DMPP) application on nitrous oxide, molecular nitrogen, carbon dioxide and methane emission

The soil NO_3^-–N content registered in the plots with DMPP was slightly smaller than on the N0 and N50 plots (Fig. 2). The N_2O and $N_2O + N_2$ emissions from the N50 + DMPP treatment were also smaller than those from the N0 and N50 treatments. This shows that nitrification was inhibited by adding DMPP and that the products and by-products of nitrification and denitrification, including N_2O, were thereby reduced. In 2011, applying DMPP reduced the cumulative N_2O and $N_2O + N_2$ emissions by 5% and 6%, respectively, compared with the N50 treatment. In 2012, the soil acted as a net sink for N_2O for the N50 + DMPP treatment (Table 5). The $N_2O + N_2$ emissions were 35% lower for the N50 + DMPP treatment than for the N50 treatment. In a previous study undertaken under Mediterranean conditions, DMPP (applied as Entec® 26) also proved effective in reducing N_2O losses by 58%, whereas applying calcium ammonium nitrate caused a reduction of 26% (Macadam et al., 2003). Merino et al. (2005) and Menéndez et al. (2012) suggested that under semi-arid Mediterranean conditions, Entec® should be applied either in early spring (temperatures are still low and soil water content is high) or in summer (high temperatures and limited rainfall), in order to minimize N_2O emissions. In the present study, a reduction in N_2O emissions was obtained when applying DMPP (Table 1) during spring and autumn, when temperatures were smaller and the soil water content was high (WFPS >60%) (Fig. 3a and b).

The results of the present study suggest that the application of DMPP inhibited CO_2 emissions. In both years, the cumulative CO_2 emissions were smaller for the N50 + DMPP treatment than for the N0 and N50 treatments (Table 5). This result is consistent with that of Weiske et al. (2001) who reported a decrease in CO_2 emissions following the use of DMPP in field experiments involving summer barley, maize, and winter wheat after fertilisation with DMPP + ammonium nitrosulphate. Bowden et al. (2000) and Menéndez et al. (2006) also described a decrease in CO_2 emissions after using DMPP + mineral fertiliser on a forest soil and on a grassland. These authors thought that this might have been due to the nitrification inhibitor affecting carbon (C) mineralization. However, other literature shows that CO_2 emissions were not affected by DMPP (Müller et al., 2002; Menéndez et al., 2012).

Methane oxidation was significantly larger when DMPP was applied (Table 5). However, there are few results in the literature on the effect of DMPP on CH_4 emissions and these are contradictory. Weiske et al. (2001) reported a reduction in CH_4 emissions when DMPP was applied. On the other hand, Hatch et al. (2005) reported that under aerobic conditions, DMPP could increase CH_4 emissions.

The present study shows that applying DMPP together with drip fertigation (SDI or DI) reduced GHG emissions, obtaining a good yield and providing an opportunity for climate change mitigation in Mediterranean conditions.

4.5. Global warming potential and greenhouse gas intensity

From this study, several key findings emerged that elucidate the GWP for this agroecosystem. First, the only positive GWP was observed for the N50 + DI treatment (2011) and could be explained by the irrigation strategies employed (DI) and by N fertilisation (50 kg N ha^{-1}), which resulted in a higher N_2O emission factor, representing 0.14% of the applied N (Table 4). The percentage of applied N lost as N_2O ranged between 0.02 and 0.14% in 2011 and between −0.03 and 0.10% in 2012, in both irrigation systems (Table 4), which is substantially lower than the factors reported in a broad range of agricultural systems (Bouwman et al., 2001; Schellenberga et al., 2012). The low N_2O emissions observed may be related to the applied irrigation and fertilisation which matches water and N supply with tree demand. Of the different treatments compared with DMPP, the lowest GWP was that of N50 + DMPP (Table 5). This result is consistent with previous studies, in which nitrification inhibitors (such as DMPP) reduced GWP (Bremner, 1997; Halvorson et al., 2010). The present study shows an increase in the cumulative yield induced by fertilisation (with the exception of N50 + SDI, which was not significantly different from N0 + SDI) (Tables 4 and 5), and that in most of the treatments (with the exception of N50 + DI in 2011) the soil acted as a net sink of CH_4 and N_2O (N50 + DMPP + DI treatment in 2012), resulting in a negative GWP (and negative GHGI) during the sampling period (Tables 4 and 5). A negative GHGI (consequence of the negative GWP) indicates a balance among yield, carbon sequestration into the soil and GHG emission (Mosier et al., 2006; IPCC, 2013).

5. Conclusions

The present study showed that appropriate management of drip irrigation and fertigation may provide an opportunity to mitigate climate change in a Mediterranean olive orchard. Subsurface drip irrigation reduced N_2O (by 69.69% in 2011 and by 94.47% in 2012) and $N_2O + N_2$ (by 55.74% in 2011 and by 17.70% in 2012) emissions compared with surface drip irrigation. Denitrification was a major source of N_2O. The largest N_2O production by denitrification occurred at between 60 and 80% water filled pore space, the threshold for denitrification. The N_2O losses (calculated as emission factor) ranged from −0.03 to 0.14% of the applied N, lower than the IPCC (2007) reference. Applying the nitrification inhibitor (DMPP) mitigated N_2O, $N_2O + N_2$, CO_2 emissions and significantly increased CH_4 oxidation.

The yield increase induced by fertilisation and the fact that all of the treatments acted as net sink for CH_4 explain the low or even inexisting greenhouse gas intensity registered for the fertilised treatments. Based on global warming potential, greenhouse gas intensity as well as N_2O cumulative emissions, it was concluded that applying the nitrification inhibitor (DMPP) in combination with 50 kg N ha^{-1} + drip irrigation is the best tested option to combine oil productivity with greenhouse gas emission mitigation.

This work supports the concept that good yield can be achieved with lower greenhouse gas intensity matching water and nitrogen supply with crop demand through time, and that greenhouse gas intensity can be lowered with the nitrification inhibitor (DMPP) application strengthening the economic and environmental sustainability of this agroecosystem.

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Chapter 8. General discussion

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Agriculture is responsible for a large share of the emitted greenhouse gases (GHG). Agricultural soils in semiarid Mediterranean areas are characterized by low organic matter contents and low fertility. In the last few decades the doses of N fertiliser application have tremendously increased because the application of mineral fertilisers is relatively cheap and it is an easy and fast way to increase crop yields.

However, this management practice induces drastic changes in the soil environment which are associated with the availability of nutrients for plants but also for soil microorganisms. However, there exists a lack of knowledge about how the different types of nitrogen fertiliser (mineral and organic), different irrigation strategies and crop residues management affect GHG emissions (N_2O, CO_2 and CH_4). Emission factors (EF) from more northern countries are used to estimate the agriculture-based emission of nitrogenous gases of environmental concern from Mediterranean conditions. There was no alternative if an estimation of N_2O emissions had to be made, but the use of EF from other countries is questionable because the soil characteristics, the weather conditions and the management practices in the area under study differ notably from those at more northern latitudes.

The aim to propose effective mitigation strategies for GHGs motivated the performance of a series of experiments on three important and agronomically different crops (rice, maize and olive trees) of the Ebro Valley, with the objectives of gathering data on these emissions and of gaining insight on the factors and processes influencing them while keeping yield as profitable as possible.

8.1. Fertiliser effects on greenhouse gases emission

Mineral and organic fertilisers are well-known drivers of N_2O emissions which determine the relative importance of the different soil processes involved in these emissions. In this thesis, the application of different doses of mineral N (Chapters 5 and 6) had no significant effect on N_2O and N_2O+N_2 emissions, although, high N_2O and N_2O+N_2 emissions were obtained by increasing the dose of mineral N to the maize and olive tree crops (Chapters 5 and 6). This result is in line with those of Bouwman (1996) and Halvorson et al. (2008).

Urea application induced the highest N_2O+N_2 emission (Chapter 4). In both studied years, the N_2O+N_2 emission induced by urea application was in the same range as that obtained from chicken manure (CM) application to flooded rice.Urea applied to rice may have indirectly and locally affected soil reaction (Serrano-Silva et al., 2011), facilitating the onset of denitrification (Sampanpanish, 2012). Pathak et al. (2002) also observed high peaks of N_2O after urea application. When applying CM (also to rice) containing a high amount of organic-N the processes taking place were mineralization in the first place, followed by nitrification and most probably denitrification (due to waterlogged conditions) though not complete (not to N_2); all these processes were slower than when applying mineral fertiliser. Not always an increased C availability generates higher N_2O+N_2 fluxes, as shown by others in studies where organic versus mineral fertilisation have been compared.

Also in Chapter 4 it is shown that no differences were found between ammonium sulphate or pig slurry application at the same dose on the average N_2O and N_2O+N_2 daily fluxes, when applied to a paddy soil. This result was due to the fact that pig slurry displays a similar behaviour to that of mineral fertilisers (ammonium sulphate in this case). It is known that pig slurry tends to show a similar behaviour to mineral fertilisers due to its low organic-C content and high NH_4^+ (Sánchez-Martín et al., 2010), which can be rapidly nitrified in well aerated soils. Some studies have suggested, however, that liquid manure can activate the denitrifying soil microbial community due to the readily oxidizable C and sufficient mineralizable N they provide (Johnson et al., 2007).

Chicken manure application tended to decrease N_2O and N_2O+N_2 emissions, while pig slurry tended to increase them, though the differences were not significant (Chapter 4). It is documented that N_2O emissions are closely associated with the C/N ratio of the incorporated organic materials (Ma et al., 2010) in the following way: high C/N materials (e.g. chicken manure) often decrease N_2O emission, while N_2O emission is generally facilitated by low C/N ratio organic materials (e.g. pig slurry) (Zou et al., 2005, Ma et al., 2009).

Generally, incorporation of N into the soil or fertigation minimizes N emissions (Chapter 6), while application of N-fertiliser into floodwater (Chapter 4) can significantly increase N losses as Linquist et al. (2012) reported too. This can be clearly seen in this thesis when comparing the emission from the olive tree fertigated treatment with the paddy soil. The olive tree orchard was fertilised with a N-32 solution (16% urea, 8% ammonium, and 8% nitrate) in the first year and a N-20 solution (10% ammonium and 10% nitrate) in the second year (2012) at a dose of 50 kg N ha^{-1}, and the N_2O+N_2 losses ranged from 0.57 to 1.80% of the applied N (Chapter 6). Applying the same dose of N as ammonium sulphate-topdressing to rice lead to much higher N_2O+N_2 emissions ranging from 47.44 to 79.44% of the applied N (Chapter 4).

Also, in Chapter 5 and 8 a good indication of the extent of the denitrification processes in the soil is provided by the N_2O-N/(N_2+N_2)-N ratio. A decrease of this ratio implies a decrease in N_2O and/or an increase in N_2 emissions. In more reducing conditions (less O_2), nitrous oxide reductase could act more effectively in the use of N_2O as an electron acceptor, completing the process of denitrification (Wever et al., 2002).

Given that the soil C and N cycles are closely related, fertiliser application had a significant role on the emission of other GHGs such as CO_2 and CH_4. In Chapters 5 and 6, contradictory results were obtained during field studies with maize and olive trees when applying different doses of mineral N fertiliser on CO_2 emission. Fogg (1988), DeForest et al. (2004), and Burton et al. (2004) suggested a decrease in extracellular enzyme activity when the dose of N increases causing a CO_2 emission decrease. Conversely, it is known that microbial activity is often stimulated by the application of N fertiliser (Mendoza et al., 2006) and therefore CO_2 emission too. Moreover, N fertilisation stimulated plant growth and also the root respiration rate.

The type of N fertiliser used (organic; i.e. chicken manure (CM)) had a significant effect on CO_2 emission. The highest CO_2 emission was obtained always from the treatments with chicken manure (Chapter 4). The cumulative CO_2 emission increased with the dose of applied organic-C. In 2012, the high dose (CM-170) tripled the emissions from the control. On the contrary, when fertilising with ammonium sulphate or pig slurry no difference on CO_2 emission was observed (Chapter 4). Research on the dose of organic fertiliser to be applied to specific soils is lacking. Further work is needed to quantify the effect of long term applications of mineral and organic fertilisers on CO_2 emissions, especially in rice fields.

Mineral fertilisers as urea and ammonium sulphate (Chapter 4), N-32 solution (16% urea, 8% ammonium, and 8% nitrate) (Chapter 5) and ammonium nitrate (Chapter 6) tended to increase CH_4 emission (decreased its oxidation) and this seemed to be affected by the dose in the case of urea and ammonium nitrate. The partial inhibition of CH_4 uptake by well-drained soils in response to N application may be explained by two mechanisms: competitive inhibition of CH_4 monooxigenase (MMO) (Dunfield and Knowles, 1995) and toxic inhibition by hydroxylamine and nitrite produced via NH_4^+ oxidation (Schnell and King, 1994). The application of NH_4^+ to the soil has a higher inhibition effect than NO_3^- on CH_4 oxidation (Steudler et al., 1989).

In Chapter 4, the highest dose of CM reduced CH_4 emissions. The reason for this is unclear; it may be due to the formation of phytotoxic substances in the soil at high organic-C contents (Schütz et al., 1989, Kludze and DeLaune, 1995) which also inhibit plant development, or to the appearance of a saturation effect for the production and release of CH_4. So increments in fertiliser doses did not further increase CH_4 emissions. Probably after applying CM, the soil NH_4^+ concentration was higher for the CM-170-11 and CM-170-12 treatments than for the CM-90-11 and CM-90-12 ones, which resulted in the stimulation of metanotrophic activity and CH_4 oxidation as Bodelier and Laanbroek (2004) and Noll et al. (2008) also described.

The results of this thesis about how N fertilisers affect CH_4 emission are contradictory (Chapters 5 and 6), even within the same ecosystem. Maybe the types of fertiliser (mineral and organic) applied have produced changes on the CH_4 oxidizing bacterial community (this has not been studied in this thesis) (Bodelier and Laanbroek, 2004). Schimel and Gulledge (1998) suggested that many of these discrepancies regarding fertiliser effects on CH_4 emission may be explained assuming that not all community members are affected in the same way, making CH_4 oxidizing bacteria diversity an explanatory variable in methane dynamics. The nature of the effect (i.e., stimulation or inhibition) obviously depends on the community composition and hence on the biodiversity of the CH_4 oxidizing bacteria present (Bodelier and Laanbroek, 2004). This may be what happened in this study. With respect to the effects of N fertilisers on CH_4 consumption, also no generalizations can be made (Bodelier and Laanbroek, 2004). Nitrogenous fertilisation has different effects on CH_4 oxidation (inhibition and stimulation, both long-term and short-term) of which the mechanisms are far from clear (Bodelier and Steenbergh, 2014).

As in the case of CO_2 emissions, when ammonium sulphate and pig slurry were applied no difference was observed between fertiliser types in CH_4 emission (Chapter 4).

Therefore, in the Mediterranean studied crops, the impact of ammonium sulphate and pig slurry application on GHG emissions were minimal. In this context the question is: should ammonium sulphate and pig slurry be recommended in Mediterranean agroecosystems? Although this thesis results point in this direction, several confounding variables must be analysed before general recommendations can be made. Environmental controls, such as rainfall and temperature, and management factors such as irrigation, tillage and N fertiliser placement play key roles in determining the proportion of N_2O emitted due to nitrification and denitrification, and therefore best fertiliser practices depend on these variables too.

8. 2. Effect of crop stover management on greenhouse gases emission

The incorporation of crop residues as an amendment has significant roles in improving physical and chemical soil properties that are essential in protecting soil and a sustainable alternative to improve the organic matter content of semiarid Mediterranean soils. Generally, it is accepted that incorporating larger amounts of crop residues in the soil will increase mineralization, thus promoting CO_2 and N_2O production.

However, as demonstrated in Chapter 6, this management practice may increase GHG emissions. In the first year, the incorporation of crop residues increased N_2O emissions, while, in the second year, N_2O emissions were reduced in the same plots. This different result has been attributed to net mineralization in the first year and to net immobilization in the second year, due to the higher amount of stover and to the higher C/N ratio of the stover incorporated in the second year. In both years, the CO_2 emissions were affected by stover incorporation leading to an increase in CO_2 emission since maize stover served as a C substrate for soil microorganisms.

8.3. Nitrification inhibitor (3,4-dimethylpyrazol phosphate (DMPP)) effect on greenhouse gases emission

The 3,4-dimethylpyrazol phosphate (DMPP) nitrification inhibitor was developed as a means to reduce N fertiliser leach ate and increasing N use efficiency and yields in some cropping systems. Indeed, in Chapter 6 yield increase has been confirmed in the studied olive tree crop. An interesting finding of this thesis was that DMPP can also be used to reduce N_2O+N_2, CO_2 and CH_4 emissions. In the first year, applying DMPP reduced the cumulative N_2O and N_2O+N_2 emissions by 5% and 6%, respectively, compared with the same treatment without DMPP. In the second year, the soil acted as a net sink for N_2O for the N50+DMPP treatment and the N_2O+N_2 emissions were 35% lower for the N50+DMPP treatment than for the N50 treatment. This was explained by the nitrification inhibition by DMPP which lead to a reduction in the products and by-products of nitrification and denitrification, including N_2O.

Applying DMPP mitigated CO_2 emissions. This might have been due to the nitrification inhibitor affecting carbon mineralization. Methane oxidation was significantly larger when DMPP was applied. Unfortunately this result is not conclusive, as there are few results in the literature on the effect of DMPP on CH_4 emissions and these are contradictory.

8.4. Irrigation effects on greenhouse gases emission

8.4.1. Irrigation effects or water filled pore space effects on greenhouse gases emission from and olive tree orchard and a maize field

Sustainability requires the preservation of water in all countries, especially in arid and semi-arid areas. Good agricultural practices have emerged in these areas from the need to provide exactly the right amount of water for each crop, avoiding, as much as possible, over-watering, which is also associated with environmental problems such as leaching.

Drip irrigation is designed to increase water-use efficiency, reduce salinization, to improve nutrient efficiency and maintain, or even increase, crop yields (Tilman et al., 2002). Drip irrigation has also been proposed as a way to reduce N_2O emissions.

To date, there is a lack of data on GHG emissions from surface drip irrigation (DI) and from deficit irrigation systems, such as subsurface drip irrigation (SDI) from fertigated high tree density olive crops under Mediterranean climatic conditions. Subsurface drip irrigation could potentially mitigate GHG emissions (compared to DI) by delivering water directly to tree roots.

Water is one of the key factors controlling biologically produced trace gas emissions. According to the model proposed by Davison et al. (1991), denitrification is the dominant process when the soil is at WFPS >65%, while for WFPS <65% it is nitrification. The results of Chapter 4, 6 and 7 of this thesis do confirm this.

In Chapter 6 (in the olive orchard) it was shown that SDI markedly reduced N_2O and N_2O+N_2 emissions compared with DI. The reduced water supply to the SDI treatment affected water filled pore space (WFPS), which was lower than for DI. Denitrification was the main source of N_2O, when the WFPS >60% most of the time (high moisture). The largest N_2O production by denitrification occurred at between 60 to 80% WFPS, which was considered the threshold for denitrification in those conditions. It has also been clearly demonstrated that SDI reduced N_2O (by 69.69% in 2011 and by 94.47% in 2012) and N_2O+N_2 (by 55.74% in 2011 and by 17.70% in 2012) emission compared with DI for the type and dose of N fertiliser applied at this site. Adequate management of drip-fertigation, contributing to the attainment of water and food security (Tilman et al., 2002), may provide an opportunity for climate change mitigation.

In Chapter 5 (maize crop) it was shown that the highest N_2O emission occurred also when soil WFPS was >55%. In this case, it can suggest that nitrification had a determinant role on these emissions.

In Chapter 3 (on rice), under wet conditions (near-saturation) produced by continuous irrigation (CI) or intermittent irrigation (II) (WFPS between 73 and 93%) the main N_2O emission was produced by denitrification

In Chapter 5 and 6 the irrigation systems (WFPS) had not a significant effect on CO_2 emissions, nor on CH_4 emission.

The predicted effect of climate change in the semiarid and arid areas is influenced by its erratic rainfall. This effect is predicted for Mediterranean areas, especially for Spain, by the most of the climate simulation models.

The need to save water in arid and semiarid regions has led to the development of new irrigation systems for agricultural crops. The choice of the best irrigation system should take into account the effect of each irrigation practice on the GHG emissions.

8.4.2. Irrigation effects on greenhouse gases emission from a paddy soil

Methane and N_2O emissions from rice fields are very sensitive to water management and are often affected in opposite ways. The amount of water present in the soil pores dictates the emission mechanism of the gases. Water management is one of the most important factors that affect CH_4, CO_2, and N_2O emission from paddy fields. The influence of water management on CH_4 and N_2O emission from paddy fields under continuous flooding and intermittent irrigation has been well documented in the climatic conditions of China, Japan, and India but not in the Mediterranean climate, especially in the Ebro Delta (Spain). Wet and dry seasons also have an important role because very intense pulses occur with the first rainfall following the dry season. Countries with this kind of climate have a different pattern of GHG emission to other climates. Climatic conditions, therefore, play an important role in gas emissions. Indeed, in Chapter 3 the effect of continuous irrigation (CI) and intermittent irrigation (II) on GHG during a rice crop season was confirmed.

In chapter 3, the II led to higher CO_2 emissions than CI. This indicated that draining and flooding cycles play vital roles in controlling CO_2 emissions in paddy soils. Lower CH_4 emissions due to water drainage (II) may increase CO_2 and N_2O+N_2 emission.

An interesting finding of this thesis was that the soil acted as a sink of CH_4 for both types of irrigation probably due to the use of ammonium sulphate fertiliser, soil salinity (4.65 dS m^{-1}) and to a high sulphate (SO_4^{2-}) content in irrigation water (about 150 ppm SO_4^{2-}, Casanova 1998).

The irrigation water applied during the rice growing season was 2330 mm for II, 59.2% less than to CI. However, the application of II decreased rice yield by 34.3% compared to CI.

Continuous irrigation (CI) can significantly mitigate the GWP caused by CH_4 and N_2O from paddy fields while ensuring the highest rice yield.

8.5. Best management practices for nitrogen fertilisation

Best management practices should be based in maximizing crop productivity and minimizing N_2O emissions. In this sense, yield-scaled N_2O emissions are an effective tool in order to propose good management practices associated with N fertilisation. The following best management practices stem from this thesis:

- *Use of nitrification inhibitors.* In Chapter 7, it was identified that DMPP had a high potential to mitigate GHG emission. Its use can therefore be recommended when N fertiliser is applied for irrigated systems when irrigation is applied efficiently according to crop requirements.

- *Use of drip-fertigation*. This technique to supply irrigation water and fertilisers can be recommended as shown in Chapter 7. Although, environmental information regarding this technique is still scarce.

- *Residue management*. Application of crop residues is a cost-effective and sustainable alternative to improve the organic matter content of semiarid Mediterranean soils. However, as demonstrated in Chapter 6, these management practices may increase trace gas emissions from already N-rich soils. Based on mineralization rates, incorporation of residues should be made in such a way that the release of nutrients from the residue occur after N fertiliser applications.

1. Although, it has been seen that in our soil it is preferable to apply organic fertiliser with low C/N ratio (e.g. pig slurry) rather than organic fertiliser with high C/N ratio (e.g. chicken manure) or minerals fertiliser, if the latter are used properly, they can be equally beneficial. According to the results of Chapter 5 and 6 the N application dose was another very important factor.

In this way, Chapter 7 has shown that drip irrigation reduced water use, as well as decreased gas emissions. For these reasons, the drip irrigation system is especially recommended.

2. One of the strategies to mitigate emissions is the use of nitrification inhibitors. The use of a nitrification inhibitor e.g. DMPP could be very useful for irrigated crops and could also become a very effective strategy for reducing emissions in dryland crops provided the application timing is carefully controlled.

8.5. References

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Chapter 9. General conclusions

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According to the discussion of the results, one can come to the following conclusions:

1. Intermittent irrigation (II) significantly increased N_2O+N_2 and CO_2 emissions compared to continuous irrigation (CI) from paddy soils. Lower CH_4 emissions due to water drainage (II) increase CO_2 and N_2O+N_2 emission. The soil acted as a CH_4 sink for both types of irrigation probably due to soil salinity and to high sulphate content in irrigation water. Continuous irrigation can significantly mitigate the integrative greenhouse effect caused by CH_4 and N_2O from paddy soil while ensuring the highest rice yield.

2. The application of chicken manure (CM; high C/N ratio) to the rice paddy increased N_2O, N_2O+N_2, CO_2 and CH_4 emission during the rice crop season and also during the seedling period. Urea increased N_2O+N_2 emissions. The rice postharvest period was a significant source of N_2O+N_2, it acted as an important sink of CH_4 and was not an important source of CO_2.

3. Similar yields to those from mineral fertiliser can be obtained when background fertilisation is done with animal manure (CM or pig slurry –PS-) applied at adjusted N rates. The application of PS (low C/N ratio) at agronomic doses allowed high yields, the control of the global warming potential (GWP), and a reduction in greenhouse gas intensity (GHGI) when compared to AS. The introduction of organic fertilisers in paddy fields is a promising option.

4. Stover incorporation to maize increased CO_2 and N_2O (only one year) emissions. Different doses of ammonium nitrate (AN) didn’t affect greenhouse gases (GHG) emission, probably because the soil mineral N content was already high. The soil acted as a net CH_4 sink (in 2011) and AN decreased CH_4 oxidation. Considering the global warming potential (GWP) and yield, the control treatment regardless of stover incorporation or removal was the best option. The N_2O emission was low thanks to the low water filled pore space (WFPS) contents. Therefore, the efforts to mitigate greenhouse gases emission in this system should be focused on: (1) keeping an efficient irrigation with relatively low WFPS (as it is already done nowadays) and (2) decreasing the soil mineral N content of the soil.

5. On the olive tree orchard, the largest N_2O production by denitrification occurred at between 60 and 80% WFPS, the threshold for denitrification. The orchard acted as a net CH_4 sink for all the treatments. Applying a nitrification inhibitor (DMPP), the cumulative GHG emission was significantly reduced with respect to the control. Considering GWP, and oil production, applying DMPP with 50 kg N ha^{-1}+surface drip irrigation was the best option.

6. Selection of the correct irrigation system is extremely important from an environmental point of view. Surface drip-irrigation combined with split application of nitrogen fertiliser dissolved in the irrigation water (i.e. drip-fertigation) is considered an efficient strategy for water and nutrient application during crop production. The present study showed that the appropriate management of drip irrigation and fertigation may provide an opportunity to mitigate climate change in a Mediterranean olive orchard without yield penalties.

7. Finally, consistently with the "Climate Smart Agriculture" FAO's integrative approach, it can be concluded that on the studied intensive crops the proper management of irrigation and the application of N in form of pig slurry or mineral fertiliser (alone or together with the DMPP nitrification inhibitor, in certain conditions) at agronomic doses can be effective to control GHG emissions and increase crop productivity at farm scale in the semi-arid Mediterranean area.

Chapter 10. Further research

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Thanks to the results and conclusions of this thesis, new questions have been posed, pointing the way towards future challenges:

1. The study undertaken in paddy soil made it clear how flooding and drainage affect the exchanges of N_2O+N_2, CO_2 and CH_4 from rice paddies in the short term. Future studies could investigate the long term effect of an intermittent drainage practice on the exchange of these gases from rice paddies.

2. It would be interesting to quantify the effect of the C/N ratio of organic fertilisers and in particular of pig slurry and chicken manure on greenhouse gases emission. Is the C/N ratio the most important factor or the dose of organic fertiliser applied is more important? Research on the dose of organic fertiliser to be applied to specific soils from rice field in Mediterranean conditions is lacking. Moreover, further work is needed to quantify the effect of long term applications of mineral and organic fertilisers on GHG emissions.

3. It has been studied how irrigation systems affect emissions. A proposal for the future is to evaluate surface drip irrigation and the subsurface drip irrigation (SDI) in combination with different types and doses of fertilisers that would not jeopardize either the environmental quality or the productivity of the studied area. Nevertheless, more years of data would be beneficial to strengthen the conclusion that SDI with fertigation is effective in reducing GHG emissions compared to DI.

4. Given that use of the nitrification inhibitor (DMPP) represents an additional cost for farmers, understanding the best management practices to maximize their effectiveness is paramount to allow comparison with other cost-effective practices that increase crop productivity and nitrogen use efficiency.

5. The residual effect of nitrification inhibitors should be evaluated in longer experiments (>2 years); studies are also needed to evaluate the effect of inhibitors on non-target microbiological processes; the physiological effect of these inhibitors on plants requires further study. Upcoming studies should clearly report information on other potential factors that can affect the inhibitor's effectiveness such as soil temperature, organic matter content, cation exchange capacity and wind velocity.

6. Many operational factors with regard to drip-fertigation systems can be manipulated affecting the overall effect of these systems on GHG emissions. For subsurface systems, the depth and distance from the irrigation line with respect to the tree may be a key factor affecting both crop yields and emissions. Also, the distance between emitters as well as their nominal discharge may affect the wet bulb and thus the GHG fluxes.

7. Further studies should be conducted for a mechanistic understanding of the potential effects of different management practices and identify exactly the main regulatory factors for GHGs emissions from soils with very high mineral N (NO_3^--N) content.

8. The incorporation of stover to soil did not have a clear effect on N_2O emission during the maize crop season. Long-term field experiments are therefore needed to increase our understanding of the effect of stover incorporation on gaseous N losses. Taking into account the possible long-term soil carbon sequestration, which has both agricultural and climate change mitigation aspects, caution must be exercised establishing general recommendations for farmers based on the incorporation of maize residues. Integral life cycle analysis would be needed for a full assessment of whether or not is the incorporation of crop residues to soil beneficial.