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**Estimation of N₂O and CO₂ emissions from organic and N
fertilizers by coupling field measurements with modelling
analysis**

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Index

1.	General introduction	4
2.	Assessing soil GHG efflux: lysimetric experiment to compare different instruments for CO ₂ emissions.	10
2.1	Introduction.....	10
2.2	Materials and methods	12
2.2.1	Experimental site.....	12
2.2.2	Instruments description	14
2.2.2.1	Sassflux	14
2.2.2.2	Static chamber with gas analysis by gas chromatography (GC).....	15
2.2.2.1	Static chamber with photoacoustic spectroscopy (gas monitor Type 1302)	16
2.2.3	Statistical analysis.....	17
2.3	Results	18
2.3.1	Environmental conditions.....	18
2.3.2	CO ₂ concentration measurements.....	19
2.3.3	CO ₂ fluxes trend over the monitored period.....	22
2.3.4	Overall performance of the different instruments for soil flux measurements	25
2.3.5	Comparison of the different instrumental performances with respect to the environmental parameters	28
2.3.6	Comparison of the different flux calculation methodologies.....	35
2.4	Discussions.....	38
2.5	Conclusions.....	41
2.6	References.....	42
3.	Evaluation of DNDC and SPACSYS model simulations of GHG fluxes from lysimeter experiment.	44
3.1	Introduction.....	44
3.2	Materials and methods	47
3.2.1	Experimental site.....	47
3.2.2	CO ₂ and N ₂ O flux measurements.....	47
3.2.3	Models description.....	48
3.2.3.1	DNDC	49
3.2.3.2	Spacsys.....	50
3.2.4	Evaluation of the models performance.....	52
3.3	Results	54
3.4	Discussion	62
3.5	Conclusion	63

3.6	References	64
4.	Field evaluation combined to modelling analysis to study fertilizer and tillage as factors affecting N ₂ O and CO ₂ emissions: a case study in Po valley (Northern Italy)	67
4.1	Introduction	67
4.2	Material and methods	68
4.2.1	Case study	68
4.2.2	Experimental design	69
4.2.3	Sampling and analysis of gases	69
4.2.4	Lysimeter trial	70
4.2.5	Model description	73
4.2.6	Statistical analysis and evaluation of the model performance	74
4.3	Results	76
4.3.1	The field measurement of N ₂ O and CO ₂	76
4.3.2	N ₂ O measured and modeled emissions in the lysimeter trial	77
4.3.3	Model application to the field experiment	78
4.4	Discussion	83
4.4.1	N ₂ O emissions from mineral and manure N fertilizers	83
4.4.2	Tillage effects on N ₂ O emissions	84
4.4.3	Irrigation effects on N ₂ O emissions	85
4.4.4	Emissions factor estimation	85
4.4.5	Fertilizer and tillage effects on CO ₂ emissions	86
4.5	Conclusion	86
4.6	References	88
5.	General conclusion.	91

1. General introduction

In the last decades, a large number of studies about the effect of greenhouse gases (GHG) on climate change led many experts to consider the reduction of GHGs emissions as a crucial strategy to tackle the predicted global warming. In particular, atmospheric warming is known to be caused mainly by carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O). CH₄ and N₂O have 25 and 298 times higher Global Warming Potential (GWP) than CO₂ (IPCC, 2007), and their increasing concentrations exert a strong influence on atmospheric chemistry and the global climate (Tanaka et al., 2009). The atmospheric concentration of N₂O increased from approximately 275 ppb in pre-industrial times to a present day concentration of 314 ppb (Houghton et al., 1996; IPCC, 2007), while CO₂ concentration raised from 280 ppm to 380 ppm primarily because of fossil fuel burning and land use change (Keeling and Whorf, 2001); methane has been reported to have an increasing annual rate of 8 ppbv (IPCC, 2007).

In order to provide insights on GHG trends, in 1988 the World Meteorological Organisation (WMO) and the United Nations Environment Program (UNEP) established a scientific Intergovernmental Panel on Climate Change (IPCC) in order to evaluate the available scientific information on climate variations, to examine the social and economic influence on climate change, and to formulate suitable strategies for the prevention and the control of climate change. Since the end of 90s, European Union (EU) adopted the goal of stabilizing CO₂ atmospheric concentration by the year 2000 at the level of 1990 and asking EU Member States to plan and implement initiatives for environmental protection and energy efficiency. In 1997 Parties to the Convention on Climate Change (UNFCCC, New York 1992) adopted the Kyoto Protocol, which establishes emission reduction objectives (i.e. industrialised countries and countries with economy in transition) in the period 2008-2012. In particular, the European Union as a whole was committed to an 8% reduction within the period 2008-2012, in comparison with base year levels with different percentage for each country. For Italy, the EU burden sharing agreement established a reduction objective of 6.5% in the commitment period, in comparison with the base 1990 levels (ISPRA, 2014). For 2020, the EU has committed to cutting its emissions to 20% below 1990 levels, selecting a target . of reducing Europe's greenhouse gas emissions by 80-95% for 2050.

It is widely accepted that the main anthropogenic source of GHG (except CO₂) is due to agriculture activities. Accordingly, most N₂O originates from soil microbial process (nitrification and denitrification) as an intermediate product (Delwiche, 1981), contributing approximately by 52% to the global anthropogenic N₂O emissions (Mosier et al., 1998; Olivier et al., 1998; Kroeze et al., 1999; IPCC, 2007). The complex interaction of microbiological processes and soil conditions, such as water content, carbon (C) and nitrogen (N) content, temperature and pH regulates gas diffusion dynamics in the soil profile, and determines how and when N₂O, CO₂ and CH₄ are released from the soil surface (Granli and Bockman, 1994). CH₄ is produced in the soil in small quantities compared with CO₂ d, and under anaerobic condition as in the rice fields

(Matthews et al. 2000). Most biological and chemical soil processes are strongly dependent on temperature (Shaver et al., 2000) including decomposition (Shaw and Harte, 2001), N mineralization and nitrification (Stark and Firestone, 1996), nutrients uptake (BassiriRad, 2000), and consequently emissions of CO₂, N₂O and CH₄ (Malhi et al., 1990; Raich and Schlesinger, 1992; Abdalla et al., 2009) respond to temperature. At the same time, soils are the major terrestrial C stock (Batjes, 1996) and can be also a sink for CH₄ and N₂O (Butterbach-Bahl and Papen, 2002; Chapuis-Lardy et al., 2007). Soil and crop management practices, such as tillage, cropping system, N fertilization, and irrigation, can influence soil surface CO₂ emissions (Curtin et al., 2000; Sainju et al., 2008). The increase of soil water content can result in increasing CO₂ and N₂O emissions (Sainju et al., 2008) by creating the optimal condition for microbial activity (Calderon and Jackson, 2002). Moreover soil physical disturbance (tillage) can contribute to modify soil structure accelerating the decomposition of organic fraction (Paustian et al., 2000) by increasing aeration due to greater soil disturbance (Roberts and Chan, 1990), and by physical degassing of dissolved CO₂ from the soil solution (Jackson et al., 2003). In fact reduced tillage intensity decreases soil disturbance and microbial activity, which in turn induces lowers CO₂ emissions (Curtin et al., 2000). Tillage also causes N₂O emissions by influencing soil aeration and temperature enhancing exchange dynamics of N₂O between soils and the atmosphere (Vor et al., 2003).

National inventories of N₂O fluxes from agricultural soils are mainly derived from the use of the default IPCC Tier 1 method, that assumes 0.9–1.25% of applied inorganic nitrogen to agricultural soils to be released to the atmosphere as nitrous oxide (Bouwman, 1996; IPCC, 2006, 2007). The adoption of this standard value has advantages in collating annual inventories but may mask significant variations in emission factors (EFs) on a regional scale (Schmid et al., 2001; Lægneid and Aastveit, 2002). Italian National inventories reports are made by ISPRA that indicates annually the different GHG sources. Regarding N₂O, agriculture is the dominant source, accounting for 73% of national N₂O emissions (ISPRA, 2014). For the agriculture sector, the trend of GHG emissions from 1990 to 2012 shows a decrease by 16% due to the reduction of the farm activities resulting in a decreasing number of livestock and cultivated surface, and for the use of renewable energy sources (biogas).

The estimation of GHG emissions from agriculture sector at regional and field scale can be carry out by different methods, that can be applied to improve the knowledge on the real contribution and conditions that can determine the release of GHG from soil. Many studies have been done to asses GHG emission from different soil types, latitudes, fertilizations, weather conditions in order to increase the knowledge regarding this very complex aspect (Curtin et al. 2000, Lægneid M., Aastveit, 2002, Collier et al. 2014).

In order to get the overview of the emission a field sampling is required, and data collected need to be analyzed with particular analyzers or through laboratory analysis, and using software or complex calculation to get fluxes. A variety of greenhouse gas measurement techniques exists, each with its own strengths and weaknesses (Nefte, 2006). Mass balance techniques based on wind dispersion of gases are

suitable to measurement of flux from small sources (such as landfills or animal paddocks). Another approaches, based on micrometeorological real-time direct measurement of vertical gas flux such as eddy covariance, can provide direct measurements over large areas. However, the widely used method used by researcher is chamber-based methods focus on the increase of the gas concentration at the soil surface by sampling from a portion of soil. This technique allows measurements from small areas and numerous treatments, but are subject to a high variability due to spatial variation in soil gas flux (Collier et al. 2014). Given the considerable expense of establishing and maintaining relevant flux measurement sites, the use of simulation models to estimate N₂O fluxes from agricultural soils, using soil and climate data, has obvious benefits. Modelling also allows the complex links between soil physical, chemical and microbial processes that underpin nitrification, denitrification and decomposition to be examined. Agriculture models can simulate the processes responsible for production, consumption and transport of GHG in both the long and short term, and also allow spatial simulation (Williams et al., 1992). Several models have also been developed in the last years to estimate GHG emissions from fields (e.g., Huang et al., 1997). These models can be easy to use and set to drive at larger or field scale, and they can successfully predict GHG emissions. There are different categories of models: empirical/semi empirical model with simple dependencies derived from regressions between measured data on soil/ecosystem properties and GHG emissions (Cai et al., 2003), the so-called data-driven models (e.g., Smith et al., 1997, 1998, 2000) and mechanistic models with an exact description of the basic processes common for all ecosystems combined with a detailed description of site/ecosystem-specific factors (process-oriented models, e.g., Li et al., 2000; Grant, 2001). All the models require comprehensive input data but the mechanistic models give a deep understanding of emissions' mechanisms, describing the water, temperature, C and N related variables occurring in the soil, as long as they can be parameterized successfully and detailed data sets are available at the appropriate spatial and temporal scales as input to the models (Blagodatsky, 2012).

Most of the soil-plant-atmosphere models come as computer software linked to a database with information on environmental conditions (daily weather data, spatial soil data). They describe biological processes that determine how carbon and nitrogen are exchanged between soil and the atmosphere.

The balance of sources and sinks can help to determine the emissions profile of a site and thus the overall contribution towards climate change mitigation. The strategies that can be pursued included, in term of farm emissions (to the farm gate), from fuel consumption (spraying or spreading, irrigation, tillage operations and drilling, heating and lighting of livestock housing and glasshouses, crop drying), emissions from soil (CO₂, N₂O and CH₄), livestock (enteric fermentation, manures and their storage), and considered potential impacts on C in soil and plant biomass. It also included upstream emissions from product manufacture (pesticides, fertilizers, polyethylene for polytunnels and mulch, their packaging, storage and transport to the farm) and machinery manufacture (based on depreciation per operation) (Agriculture and Environment Research Unit Science and Technology Research Institute, 2010).

The purpose of this study was to help define concepts and tools to facilitate agricultural sector to reduce greenhouse gas emissions. This analysis aimed to define the best viable options 'tentative' model for integrated farm soil emission assessment that will decrease greenhouse gas emissions. Into the different chapters of the present work some of the main aspects regarding gas emission from soil have been considered. In particular we based our focus on the three crucial aspects:

- evaluation of three measuring systems for CO₂ emissions, in particular the aims was testing the performance of novel system developed by Università Cattolica del Sacro Cuore di Brescia (SASSFlux system) and its features in different environmental condition and test the differences and its capability to collect emission gas data from the soil in comparison with two widely used instruments and methods (Brue&Kjaer gas monitor and collecting air gas sampling and analyzing them by gas chromatography);
- testing two process-based models, DNDC and SPACSYS, evaluating their performance and the agreement between simulated and measured CO₂ and N₂O emissions, water content and soil temperature observed data from a 1-month experiment carried out on lysimeters applying different organic and mineral fertilizers;
- applying all the knowledge acquired from experimental trials on a field case study regarding the evaluation of CO₂ and N₂O emissions from different combination of organic and mineral fertilizers and tillage in a dairy farm in Po valley (Northern Italy).

The complete work of this thesis aims to provide a comprehensive view of the different aspects to be addressed in the assessment of GHG emissions from different scenarios of agricultural management. Observed data and model simulation of CO₂ and N₂O emissions were taken into account, and the analysis resulted in the definition of the best viable strategies to be adopted to reduce significantly GHG emissions at field scale.

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2. Assessing soil GHG efflux: lysimetric experiment to compare different instruments for CO₂ emissions.

2.1 Introduction

Gas exchange between soil and atmosphere has been studied by soil scientist for decades because the knowledge of GHG fluxes is essential for the understanding of biological phenomena such as evapotranspiration, soil respiration, microbial nutrient transformation and fertilizer use efficiency (Healy et al, 1996). Soil respiration is an important process of carbon cycling in terrestrial ecosystems and provides an useful index for heterotrophic metabolic activity in the soils. There are many methods for measuring soil CO₂ efflux, with large differences in accuracy, spatial and temporal resolution, and applicability.

The most common methods to estimate gas efflux from soil is placing a lid (chamber) over the soil surface and quantifying the amount of gases entering the chamber per unit area of soil per unit time (Nay, 1994). Accumulation of GHG in chambers method is widely used to measure soil respiration under field conditions because it is simple and has the advantage of integrating the flux over time (hours to days). Many factor causing under or over-estimations of CO₂ fluxes have been identified (Anderson 1973; Gupta and Singh 1977; Sharkov 1984). Chamber can alter the microclimate at the soil surface and remove part or all of the radiation, causing CO₂ releasing from the compacted soil pores (Matthias et al. 1980). In addition, chamber effects (Mosier, 1990) include temperature and moisture change in the soil and in the air under the chamber, alteration of the gas concentration gradient between the soil and the chamber headspace, influencing diffusion rates (Healy et al. 1996) elimination or alteration of ambient turbulent pressure fluctuations within the chamber. Moreover gas mass flow reducing (Rayment and Jarvis 1997) and sensitivity to pressure differences between the chamber headspace and the atmosphere (differences of 1 Pa or less have been found to induce significant mass flow of CO₂ into or out of the soil beneath the chamber, resulting in significant over or underestimation of the true fluxes) (Kanemasu et al. 1974, Fang and Moncrieff 1996, Rayment and Jarvis 1997, Lund et al. 1999).

Therefore, chambers should be closed only for the shortest time as possible, typically 10 to 30 min for static chamber. Normally, the air is ventilated within the chamber by a fan. Measurement of GHG flux with static chambers collected in vials and then analyzed by gas chromatography (CG) is a standard method: gas samples are collected over a interval of time and GHG flux is calculated as a result of concentration increase over time (Hutchinson and Mosier, 1981; Liebig et al., 2010).

In many studies (Ball *et al.*, 1999; Du *et al.*, 2006; Jantalia *et al.*, 2008) fluxes of trace gases such as N₂O and CO₂ were measured using chamber methods and involved CG analysis. Nay et al. (1994) suggest that static chamber techniques, in particular to measure CO₂ fluxes, tend to overestimate small fluxes (under 6.5 kg C ha⁻¹ d⁻¹) and underestimate large fluxes due to suppression of the gas concentration gradient at the soil surface following chamber deployment and the microclimate effect inside the chamber that alter the flux

(Healy et al., 1996; Rochette and Bertrand, 2007; Venterea, 2010). Moreover these techniques are time consuming, complex, and expensive (Sainju et al. 2012).

In other studies (De Kleine et al., 1994; Akiyama et al., 2000; Dobbie and Smith, 2003), a trace gas analyzer (TGA), which is based on photo-acoustic infrared (IR) spectrometry or other system (Neftel et al. 2006) has been used in conjunction with chamber methods for flux measurements.

The variability of CO₂ flux measurements depends to variations in chamber size, chambers placement (in the crop row vs. between rows), soil properties (e.g. soil temperature, water content, organic matter, and texture), vegetation, and landscape position (Parkin et al., 1987; Livingston and Hutchinson, 1995).

An aspect very important in the measurement of GHG fluxes is sampling. Ideal sampling does not change the conditions of the ecosystem under consideration and it should not affect the flux. Frequent problems are condensation of water in connecting tubes, gas losses and/or contamination from walls (Neftel 2006).

In order to estimate the release of GHG for experimental trials, Università Cattolica del Sacro Cuore of Piacenza together with Ecometrics, (spin-off of Università Cattolica del Sacro Cuore of Brescia), developed a novel static and diffusional sampler to measure fluxes at soil level (SASSFlux). This automatic instrument meets the needs to detect soil fluxes continuously and rapidly through different analyzer installed, IRGA Carbocap 343, Vaisala, SF, is used to measure CO₂ concentration, while a rotative gas-filter photometer (IRGA T320U, Teledyne, CA) measures N₂O concentration) managing four Plexiglas automatic chambers by a software.

The present experiment aims to evaluate the performance of SASSFlux automatic sampler system to measure carbon dioxide (CO₂) fluxes in comparison with two static technique to detect gas from soil as photo acoustic infrared spectroscopy (Gas Monitor Type 1302, Bruel&Kjaer, B&K) and air sampling collected and analyzed by gas chromatography (GC). Both systems need static chambers because they are not able to take samples straight from the soil. The experiment has been carried out on controlled condition portion of soil using the lysimeters with different soil type and different nitrogen (N) fertilizations.

In particular the aims was testing the performance of SASSFlux system and its features in different environmental condition and test the differences against the others instruments and its easiest capability to collect emission gas data from the soil.

Our hypothesis is that fluxes measured by SASSFlux system are comparable to those measured by low time resolution techniques (B&K and GC), placed in same conditions of kind and size of chamber, soil properties.

2.2 Materials and methods

2.2.1 Experimental site

A lysimetric experiment was carried out to compare the three different monitoring systems (SASSFlux, Bruel&Kjaer Gas Monitor Type 1302) and air sampling to analyze in gas chromatography, using the same static chamber for collect CO₂ flux measurement from soil. The trial was carried out from April to May 2013 at Vittorio Tadini Experimental Station (44° 58' N 9° 41' E; 118 m a.s.l.) in Gariga di Podenzano (Piacenza). Eight lysimeters of polyethylene(HDPE) with a cross section area of 1m² and a height of 0.5-0.6 m were loaded with repacked soil (two different soil type: silt-loam and sand-loam texture). Each group of lysimeters (four lysimeter per type of soil) were host a different treatment (digestate, compost and chemical fertilizer) considering a nitrogen demand for this crop of 100 Kg ha⁻¹ of nitrogen livestock effluents, digestate and chemical fertilizer were applied accordingly. One of them for each group did not host any treatment and it was considered as control.

Measurements were carried out with three different methods (GC, B&K and Sassflux)and 9 sampling days along in for 4 weeks were carried out.

In order to evaluate the three methods, measurements were performed using static chambers made of a PVC ring (0.4 m diameter X 0.3 m height), so removing the automatic chambers from SASSFlux system. A cylindrical stainless steel frame (0.45 m diameter and 0.2m height) was positioned a week before into the lysimeter. The outside of the cylinder was coated with reflective paint. The frames were installed immediately after treatment application and were positioned in a 0,10 m deep in the soil.

These chambers were adapted to have six air sampling ports, to allow simultaneous sampling by different instruments. Four ports were dedicated to Bruel&Kjaer (B&K) and SASSFlux samplings. The other two ports were used to sample the air into evacuated glass vials. This procedure allowed direct comparison of measurement systems minimizing the variability due to sampling from different areas (Neftel, 2006) of the lysimeter. After closing each chamber, gas samples for GC were collected at 0, 6, 12 and 18 min interval by injecting a needle attached to a syringe in the vial, SASSFlux and B&K systems run continuously until the end of each sampling time. During the sampling period we collected 200 flux data for each type of instrument; SASSFlux CO₂ sensor is able to collect one concentration data for second, while B&K can take samples more or less each 2 minutes, depending the setting.

Data for the database were collected during the sampling period by different instrument, sampling manually for the GC, using 4 vials per measurement cycles, instead B&K and SASSFlux performed their sampling automatically taking air from the chamber and reading in the respective analyzers (one data each 2 minute for B&K and one datum per second for SASSFLUX)(**Errore. L'origine riferimento non è stata trovata.**).

Table 1: Instruments sampling details.

	Sampling days	N° of sampling	N° of sampling per day	Type of sampling
Gas-Cromatograph	9	200	3	Manually
B&K	9	200	3	Automatic
Sassflux	9	200	3	Automatic

The soil at each experimental lysimeter were also be assessed in terms of the bulk density, soil organic carbon content, total N, microbial biomass carbon (a measure of the size of the microbial community), texture (sand , silt, clay) and pH.

For calculating GHG flux, the concentration data were analyzed by using the HMR package of R software. The HMR function analyses the data series sequentially, and starts each analysis by fitting the nonlinear function (Hutchinson and Mosier, 1981):

$$C_t = \varphi + f_0 e^{-kt} \quad [2]$$

using a single-parameter (k) criterion (concentrated least squares; Seber and Wild, 1989). In this equation (C_t is the concentration at t time) f_0 denotes the initial flux, φ denotes the new chamber equilibrium concentration, and $K > 0$ is an adaption rate that depends on soil, gas, and chamber characteristics (K values are calculated by HMR corresponding estimated values of φ and C_0 are positive or negative)(Pedersen, 2015).

Moreover further flux calculation has been carried out using a tool (named by ourselves GER) developed by Ecometrics researcher usually used for data from SASSFlux, in order to compare this aspect as well. This software calculates the fluxes using the linear regression function allowing to manage a big amount of concentration data as SASSFlux use to collect (one for second), taking into account more parameters (chamber temperature) compared to HMR, having the chance to select the best range of concentration data as well.

This last feature has been included because although molecular diffusion theory states that chamber feedback will lead to declining gradients of the relationship between concentration and time (Hutchinson & Mosier, 1981; Livingston et al., 2006), linear concentration data often predominate (Forbrich et al., 2010) the flux. User selecting a particular range of data, is possible to apply the linear regression just for the appropriate linear increasing concentration in the graph, avoiding fluxes over estimation, getting in this way a comparable flux data with HMR non linearity approach. In our case we decided to compare the fluxes calculated with both method, taking all the data available (ALL) and selected 70" (from 50" to 120") as the better fitting for linear regression, in order to understand the different between them, and which is the most comparable solution with HMR.

Daily rainfall and mean air temperature data were measured by a weather station (WatchDog, Spectrum technology, USA). Soil water content was measured throughout the course of the experiment using Spectrum technology SM100 Waterscout Soil moisture sensors connected to a weather station and placed at 0.1m depth. Soil temperature was also measured in one lysimeter.

Detailed description of the fertilization or other aspects about this experiment are detailed on chapter 3.

2.2.2 Instruments description

2.2.2.1 *Sassflux*

The SASSFLUX system consists of four transparent Plexiglas automatic chambers (base-lid type of 20 l volume) that are automatically (by motors controlled by a computer) closed over a metal collar (35x35 cm basal area and 7 cm height) that bounds the soil surface (inserted into the soil to a depth of 5 cm), very important feature because avoid soil disturbance. The end positions for opening and closing the lids is controlled by two limiting switches for chamber, that operate a small fan for mixing the air within the chamber when the lid is closed during the flux measurement. When the chamber is closed a 3 l min⁻¹ membrane pump takes an air sample and directs it (through a Teflon tube) to the control unit that contains an Infrared Gas Analyzer (IRGA Carbocap 343, Vaisala, SF) which is used to measure CO₂ concentration. In order to avoid pressure alterations the air is then returned to the chamber through a second Teflon tube. A dedicated software manages data acquisition, the control of chambers' opening and closure, air sampling time, and chambers' "washing out" (deployment time) time to allow gas concentration to return to environmental values before each new sampling. A solenoidal-valve system is used to shift the air sampling from one chamber to next one and to cyclically analyze air from different chambers. IRGA's concentration measures are registered every second and saved in a file.

When a soil portion is covered with one of the enclosures the gas concentration in chamber headspace can (1) increase, if gas is emitted from soil, (2) decrease, if gas is absorbed by vegetation or (3) remain constant, if gas does not interact with the soil or emissions and absorption compensate each other .

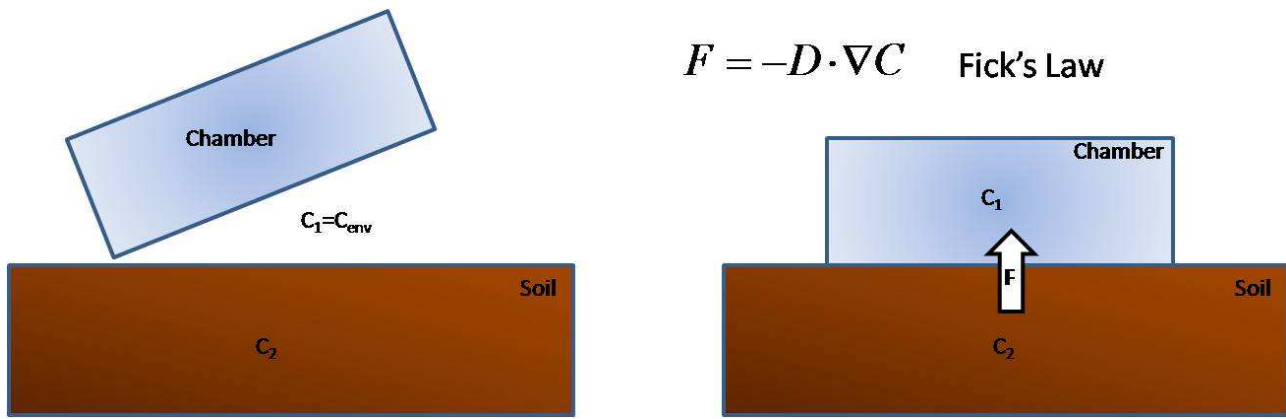


Figure 1: When the enclosure is open (left) CO₂ concentration in the chamber is equal to the environmental value. If soil concentration C₂ is higher than atmospheric value C₁, when the enclosure is closed an effusive flux F is activated by CO₂ gradient concentration in accordance with Fick's law.

In case of net emission of CO₂ from plant-soil system the open chamber CO₂ concentration is equal to environmental value, but after the closure it progressively increases, first linearly, then it tends to an asymptotic value.

Soil CO₂ flux is the quantity of gas that pass through a unit of volume per unit time and it can be represented as the scalar variation on time (dCO₂/dt) related to chamber volume (V) and area of soil surface (A) as described in the following formula (Figure 1).

$$F_{CO_2} = \frac{dCO_2}{dt} \frac{P}{RT} \frac{V}{A} \quad [1]$$

where P is the atmospheric pressure, T is the temperature and R is the universal gas constant. For the previously explained reasons, the zero-time (dCO₂/dt) value is needed.

The benefits of this method are continuous, fast measurements of CO₂ or N₂O flux without soil disturbance, resulting in accurate determinations of GHG flux dynamics. The IRGA analyzers part of the SASSFlux system immediately analyze CO₂ or N₂O concentration and the software coupled to the system provides a rapid estimate of GHG fluxes. Due to the size of the chambers, their use is only possible in situation where the vegetation present a very small growth (grass) or in the space of soil between the plants.

2.2.2.2 Static chamber with gas analysis by gas chromatography (GC)

The chambers taken into account for our experiment consist in a PVC ring-shape lid (0.4 m diameter and 0.3 m height) and a cylindrical stainless steel frame (0.45 m diameter and 0.2m height) used to facilitate the positioning of the static chamber into the soil (45 l volume).

The chamber have six air sampling valves, to allow simultaneous sampling by different instruments. Two ports are dedicated to Bruel&Kjaer (B&K), the other two ports are used to inject the air into evacuated

glass vials (23 mL), with a syringe system (450 ml) and PTFE tubing (6 mm internal diameter). Inside the chamber a small fan mix the air inside in order to avoid gas stratification during the sampling. The frames of each chamber were inserted 5 cm into the soil, after tillage operation. Flux was measured by placing the chamber on the frame manually by the operator. Gas samples were collected by injecting a needle attached to syringe (300 ml) in a evacuated headspace vials (23 ml) through a PTFE/SI septum. Each chamber was closed consecutively for a period, during which the concentration of the gas within the headspace was measured.

The CO₂ concentration in the vials was measured with a gas chromatography in the laboratory of the department of Agricultural and Environmental Chemistry performed with a TRACE GC ULTRA (Thermo Electron Corporation) gas chromatograph interfaced to a POLARIS Q mass-selective detector operating in the low-resolution selected-ion monitoring SIM and in tandem mass spectrometry MS/MS modes.

The instrument was equipped with a sample-introduction system TRIPLUS (Thermo Electron Corporation) interfaced to the GC-MS. Helium was used as a carrier gas at a flow rate of 1.5 mL min⁻¹.

The GC system was fitted with a 30 m by 0.32 mm (I.D.) fused silica capillary coating CP Poraplot Q-HT (Varian). The injection mode was split, the split flow being 10 ml min⁻¹ and the split ratio was 7. The oven temperature will be maintained at 40 °C for 2,5 minutes, increased from 40 to 240°C at 40°C min⁻¹, and then the oven temperature was held at 240°C for 2 min. The injector temperature was maintained at 200°C, and the transfer line at 200°C. For calculating GHG flux, data obtained from CG can be analyzed by different or software, that analyses the data series sequentially fitting the function using a single-parameter (k) criterion (concentrated least squares; Seber and Wild, 1989).

2.2.2.1 Static chamber with photoacoustic spectroscopy (gas monitor Type 1302)

The gas monitor Type 1302 (Brüel & Kjær) photoacoustic spectroscopy is an instrument used to detect different type of gases. In photoacoustic spectroscopy (PAS) the gas to be measured is irradiated by intermittent light of pre-selected wavelength, the gas molecules absorb some of the light energy and convert it into an acoustic signal which is detected by a microphone. The light source used in the Brüel & Kjær gas monitors is a heated black body emitting broad-band infrared light. A large range of optical filters are available for use with Brüel & Kjær gas monitors. Multi-gas Monitor Type 1302 can be equipped with up to 6 optical filters from this range of 23 optical filters. Carbon dioxide filter (UA 0983) is dedicated to the measurement of carbon dioxide at concentrations ranging from 340 ppmv (normal concentration in outdoor air) up to 5000 ppmv in badly ventilated, crowded rooms. Water Vapour (SB 0527) filter is always installed in the Type 1302. This filter measures the concentration of water vapour in the analysis cell and thus makes it possible for the 1302 to compensate for water vapour influence on the gas to be measured (The Brüel & Kjær Photoacoustic Transducer System and its Physical Properties, 2005).

2.2.3 Statistical analysis

The differences of the CO₂ fluxes gathered with the three different measuring techniques were analyzed by regression techniques against the fertilizer treatments and the air and soil temperature, water content and wind speed. The goodness of fit was assessed by means of the R² parameter and the statistical significance of each regression was assessed by mean of the F test. The relative agreement of the instruments was assessed by looking at the departure of the slope from the bisector of the 1st quadrant and to the departure of the intercept from the origin of the x-y plan.

2.3 Results

2.3.1 Environmental conditions

During the sampling period the air temperature range was between 6.2 and 25.8 °C (26/5/13 at 5 AM and 9/5/13 at 4 PM respectively), corresponding to the seasonal average temperature (min 12 to max 23°C), with a total amount of 29.5 mm of rain (most rainy day was 29/4/13). Wind speed has been within 1.11 m s⁻¹ for all the period except on 19/5/13 where it was over 1.38 Km h⁻¹. Soil temperature increased in the first four days due to high temperature, dry condition and for the movement of soil for the installation of the instrumentation, then decreased twice rapidly because of rainy days and decreasing of air temperature.

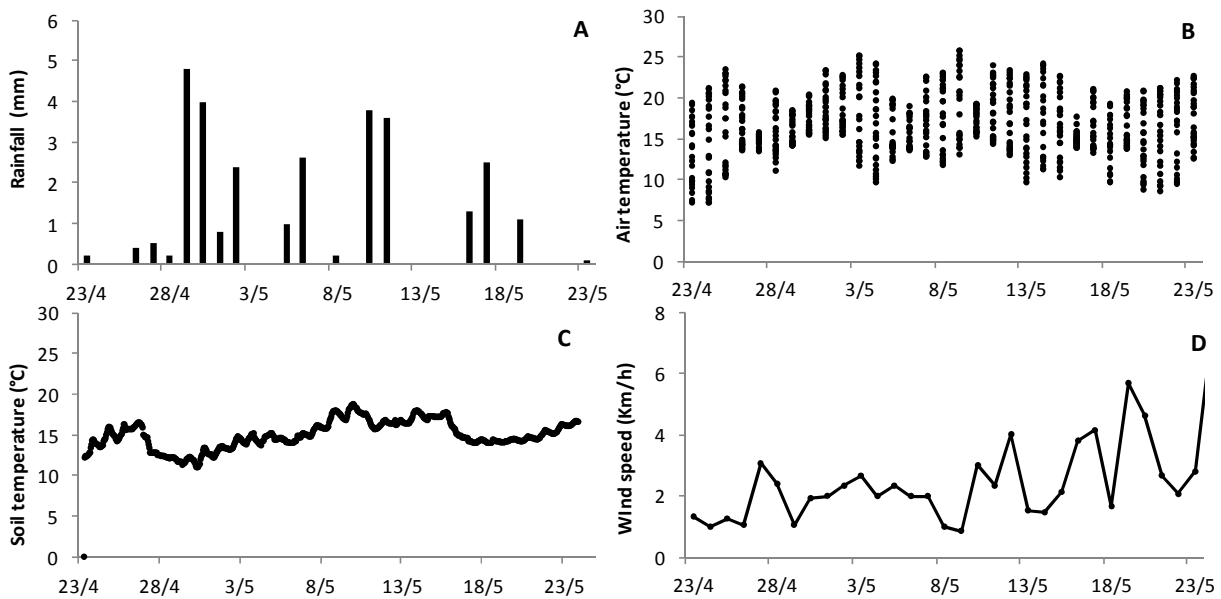


Figure 2: Daily total of precipitation (A), air and soil temperature (B and C respectively), and the trend of wind speed (D) in experimental site.

2.3.2 CO₂ concentration measurements

Figure 3 reports an example of CO₂ accumulation during a measurement cycle into a lysimeter after the closure of the sampling chamber. The accumulation dynamic clearly do not follows a linear increase, as expected from the physic of the closed static chambers. On the contrary the non-linear regression HMR better follows the accumulation dynamic for the data of all the techniques.

As is possible to see in the figure 4 raw concentration data of the three instruments showed different trends, and it can be observed that, in some cases the three curves are matching (Figure 4a), one of the instrument is in discrepancy with the other two (Figure 4b, Figure 4c) or all of them showed different trends (Figure 4 it should be remembered that all the instruments have been calibrated before their deployment in the field against a cylinder CO₂ standard as a span gas and a cylinder of N₂ was used for zero injecting the difference gases through separate cylinder containing standard concentration of that gas. Thus their different behavior in the field is quite surprising. Evidently there are influences of some environmental factors which have to be detected.

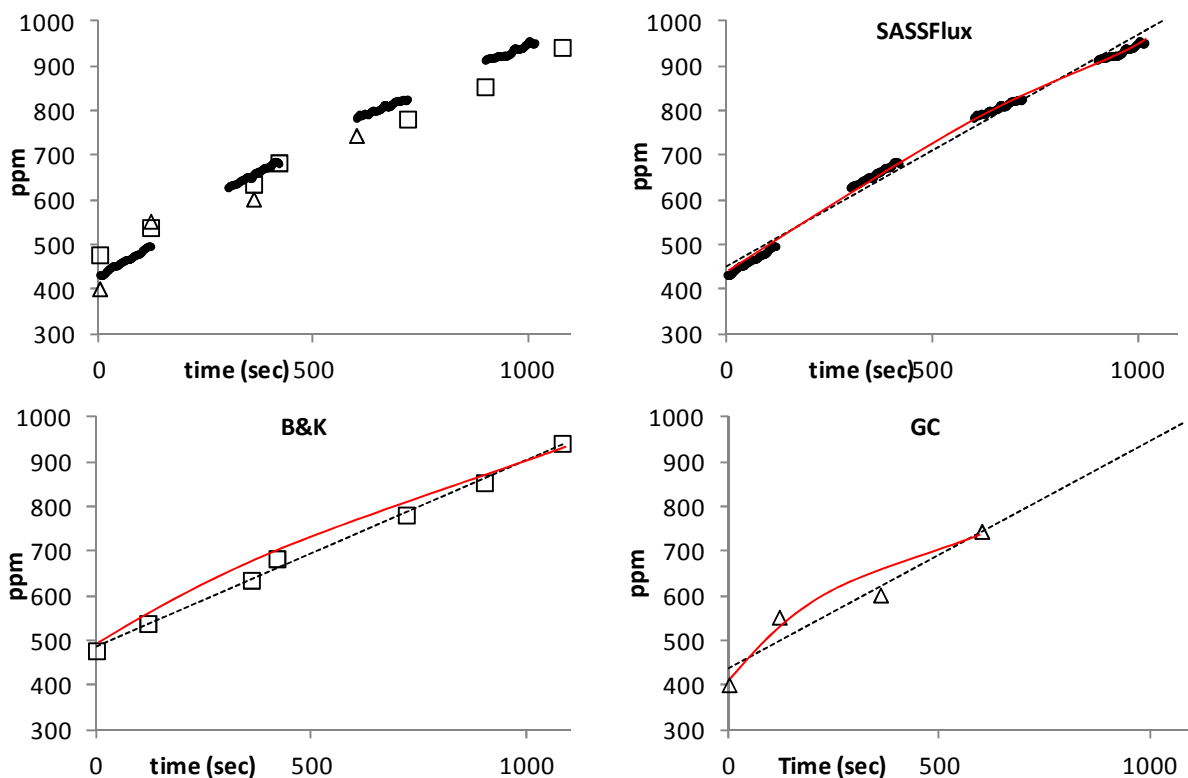


Figure 3: a) Example of static chamber raw data for different instrument, SASSFlux (points), B&K (square) and GC (triangle.). b) Linear fitting (dashed line) and non linear fitting with HMR (red line) of the b) SASSFlux data, c) Bruel-Kjaer data and d) Gas Chromatograph data.

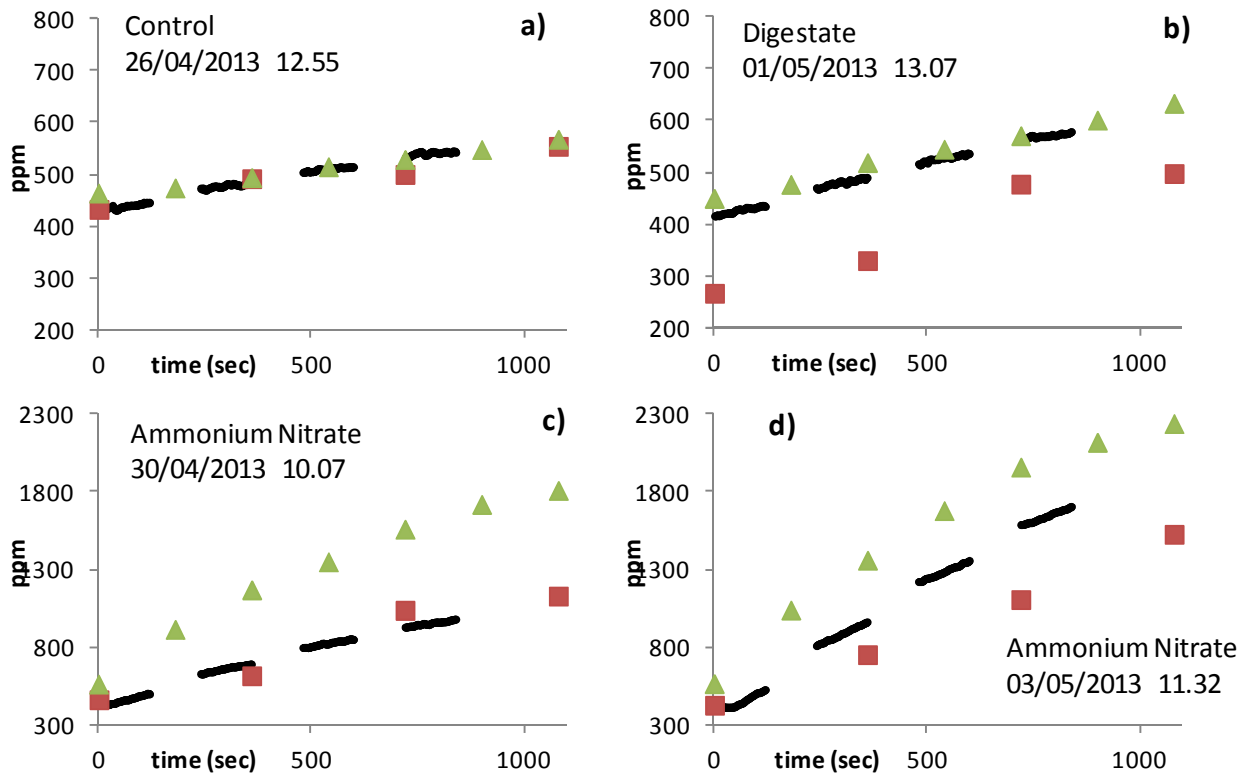


Figure 4: Examples of CO₂ accumulation for the different instruments. The black dotted line is for SASSFlux data, red squares are GC data and green triangle B&K. Please note the different scales for a) and b) of the graphs above and c) and d) below.

The precision of the CO₂ measurements of the three instruments was tested by comparing the concentrations measured during the first seconds after the closure of the chambers (a proxy of the atmospheric CO₂ concentrations). This is the only possible direct comparison of the instruments allowed by the experiment set-up because of the alternate sampling of the continuous analyzers (B&K and SASSFlux). As it can be observed from Table 2 the average atmospheric CO₂ concentration revealed by the gas chromatographer is the lowest one (393.9 ppm) but with the greatest standard deviation among all the measurements (92.3 ppm); also B&K showed a significantly great standard deviation (70.1 ppm) but with the greatest average value (472.8 ppm), while the SASSFlux measurements showed the lowest standard deviation (21.3 ppm) and then the greatest precision.

Again it is worth noticing that the minimum CO₂ concentration detected by GC is quite unrealistic because it is well away from the average CO₂ concentration of the atmosphere, thus confirming a greater erraticism of this techniques compared to the other two.

Deepening the analysis for the different soil types and treatments (Table 3, Table 4, Table 5) it appears that the SASSFlux system gave the most stable measurements of the atmospheric CO₂ concentration regardless of soil type and treatments (from a minimum average of 416 ± 18 ppm in sand+ ammonium nitrate to a maximum of 437.6 ± 22.3 ppm in silt+compost). On the contrary both GC and B&K were affected by the soil type and treatment, generally showing higher CO₂ concentrations above the silty soil (417.6 ppm the

GC and 512.2 ppm the B&K) and lower ones above the sandy soil (370.1 ppm the GC and 433.4 ppm the B&K), and higher absolute concentrations in the digestate treatment (429.2 ± 107.7 ppm the GC and 538.6 ± 96.2 ppm the B&K).

The best partial agreement was between SASSFlux and B&K measurements over the sand soil (10 ppm of difference), while over the silt soil the best partial agreement was between GC and SASSFlux (18 ppm of difference).

Little differences in environmental CO₂ measurements are expected over different soil types and treatments. However the differences displayed by the GC and B&K systems appears to be quite excessive (83 and 117 ppm on average for GC and B&K respectively) compared to the difference displayed by SASSFlux (21 ppm on average).

Table 2: Statistical summary of the environmental concentration of CO₂ (ppm) measured by the three instrumental systems at the beginning of each measurement cycle (average of the whole period)

	Average	Maximum	Minimum	Standard deviation	Median
Gas-Cromatograph	393.9	683.3	74.7	92.3	397.7
B&K	472.8	781.0	373.0	70.1	450.0
Sassflux	429.5	558.1	380.1	21.3	425.5

Table 3: Statistical summary of the environmental concentration of CO₂ (ppm) measure by GC for at the beginning of each measurement cycle in sandy and silty soil and for the different treatments

GC				
	Average ambient CO ₂	Max ambient CO ₂	Min ambient CO ₂	Standard dev. ambient CO ₂
Sand				
Ammonium Nitrate	376,6	539,3	233,0	69,8
Compost	372,0	527,6	153,7	80,3
Control	356,6	506,1	74,7	91,5
Digestate	375,4	550,3	190,2	88,1
Silt				
Ammonium Nitrate	421,8	683,3	253,4	109,2
Compost	414,2	671,7	242,3	85,6
Control	405,3	566,5	274,3	83,6
Digestate	429,2	679,8	243,2	107,7

Table 4: Statistical summary of the environmental concentration of CO₂ (ppm) measure by SASSFlux for at the beginning of each measurement cycle in sandy and silty soil and for the different treatments

SASSFlux				
	Average ambient CO ₂	Max ambient CO ₂	Min ambient CO ₂	Standard dev. ambient CO ₂
Sand				
Ammonium Nitrate	416,6	466,3	380,1	18,0
Compost	423,8	457,5	401,3	13,6
Control	424,6	458,0	401,1	13,7
Digestate	429,7	558,2	403,6	31,2
Silt				
Ammonium Nitrate	434,9	480,4	386,1	25,0
Compost	437,6	510,8	402,7	22,3
Control	436,6	471,5	408,5	14,2
Digestate	433,5	485,0	402,3	18,5

Table 5: Statistical summary of the environmental concentration of CO₂ (ppm) measure by B&K for at the beginning of each measurement cycle in sandy and silty soil and for the different treatments

B&K				
	Average ambient CO ₂	Max ambient CO ₂	Min ambient CO ₂	Standard dev. ambient CO ₂
Sand				
Ammonium Nitrate	422,1	470,0	373,0	27,7
Compost	430,8	479,0	379,0	26,9
Control	432,4	470,0	383,0	22,0
Digestate	448,2	601,0	403,0	41,5
Silt				
Ammonium Nitrate	513,7	691,0	378,0	73,9
Compost	508,5	675,0	399,0	72,9
Control	488,0	598,0	395,0	48,7
Digestate	538,6	781,0	408,0	96,2

2.3.3 CO₂ fluxes trend over the monitored period

The CO₂ fluxes estimated by the HMR methodology on all the available CO₂ concentration data per sampling cycle are reported in Table 6. At a first glance the overall CO₂ flux averages do not differ too much (from 3.05 up to 3.49 gCO₂ m⁻² d⁻¹), and the best agreement was observed between GC and B&K measurements. However considering the different soil types the best agreements were between SASSFlux and B&K in the sand soil (from 0.88 up to 0.91 gCO₂ m⁻² d⁻¹; F= 5.65, P=0.01) and between B&K and GC in the silt soil (from 4.96 up to 5.39 gCO₂ m⁻² d⁻¹; F= 6.29, P=0.01).

Despite the average values were not so different among the three instruments, the agreement between two of them varied with the treatment. For example SASSFlux and B&K showed very similar values for ammonium nitrate and digestate over sand, while B&K and GC agreed for their measurements over silt treated with ammonium nitrate and compost.

In general the average fluxes measured by B&K and SASSFlux agreed in the 50% of the cases, while B&K and GC agreed in the 25% of the cases, and in the remaining 25% of the cases there was no agreement among all the instruments.

Table 6: CO₂ fluxes average for all instrument (SASSFlux, B&K and GC) calculated with HMR method in sandy and silty soil and for the different treatments

	Avarege SASS_HMR_All (gCO ₂ m ⁻² d ⁻¹)	Avarege BK_HMR_all (gCO ₂ m ⁻² d ⁻¹)	Avarege GC_HMR_all (gCO ₂ m ⁻² d ⁻¹)
Sand	0.9 ^b	0.9 ^b	1.1 ^a
Ammonium Nitrate	0.8	0.8	1.0
Compost	1.0	0.9	1.2
Control	0,6	0,7	0.9
Digestate	1.2	1.1	1.5
Silt	6.1 ^a	5.4 ^{ab}	5.0 ^b
Ammonium Nitrate	6.1	5.3	5.3
Compost	5.2	4.3	4.4
Control	3.8	3.5	2.5
Digestate	9.1	8.4	7.6

All the CO₂ fluxes measured with the three instruments in the lysimeter experiment are also presented in Figure 5.

However the implications of the use of different soil matrix on the CO₂ soil effluxes will be discussed in the chapter 3 (Evaluation of DNDC and SPACSYS model simulations of GHG fluxes from lysimeter experiment). Here we better focus on flux measurement methods, by comparing the differences of the measurements got with the three instrumental techniques during the experiment.

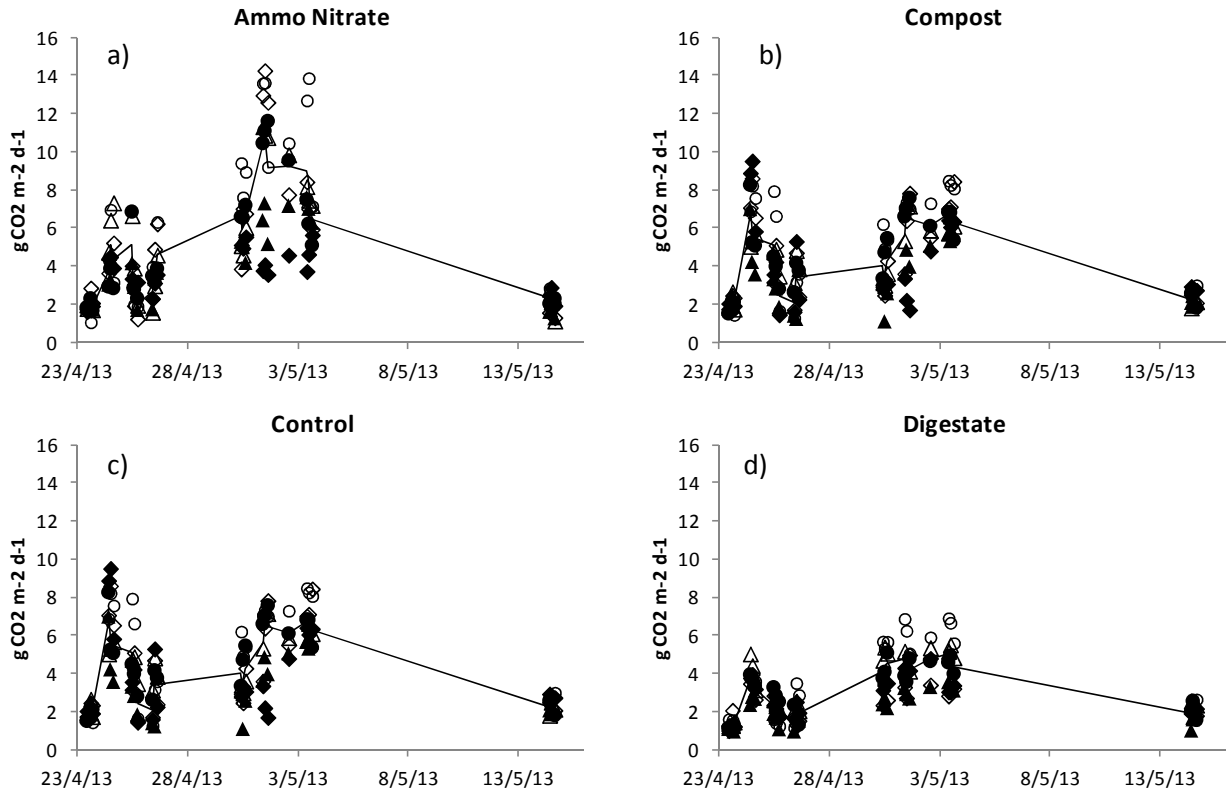


Figure 5: Measurements of CO₂ fluxes done with SASSFlux (point), B&K (triangle) and GC (rhombus) during the lysimeter experiment with various fertilization treatments: a) NH₄-NO₃, b) Compost, c) Control, d) Digestate. In the plots two flux calculation methods are presented: GER (black figure) and HMR (uncolored figure)

2.3.4 Overall performance of the different instruments for soil flux measurements

For the following instrumental comparisons, the flux calculation method named HMRall was used.

A direct comparison of all the available simultaneous flux measurements made by the different instruments is shown in Figure 6, where the SASSFlux and B&K fluxes are reported as a function of the GC fluxes. SASSflux measurements (Figure 6a) were 12% higher than GC ones (slope=1.1207, R^2 0.8313, $p < 0.0001$) while the B&K measurements were more aligned with the GC ones (slope=0.9992, R^2 0.8893, $p < 0.0001$).

The soil type greatly influenced the performance of the SASSFlux and the B&K systems with respect to GC, as shown in Figure 7. In the sandy soil, where CO_2 fluxes were low, both SASSFlux and B&K recorded CO_2 fluxes that were about a half of the fluxes recorded by the GC (respectively -47% and -39% of GC, $p < 0.05$). On the contrary the agreement between the three instruments was good on the silty soil (SASSFlux +4% and B&K-6.5% of GC, $p < 0.001$).

Nevertheless the performance of the two SASSFlux and B&K systems were very similar in both soil types, thus suggesting a possible distortion of the GC system in sandy soils. This distortion could be attributed, at first glance, to the inherent difficulty of the GC sampling system to measure low CO_2 effluxes, such as those occurred at the sandy soil.

However, the agreement between the SASSFlux and the B&K measurement methodologies with the CG show a marked variation with the treatment. The following analysis take into account all the measurements without distinguishing them by soil type.

The agreement of SASSFlux and GC measurements (Figure 8) was better for the ammonium nitrate treatment (+ 8%, $p < 0.01$) and for the compost treatment (+8%, $p < 0.01$) than in all the pooled data, while the agreement between SASSFlux and CG was substantially the same as for the pooled data in the digestate treatment (+ 13%, $p < 0.05$). However the SASSFlux measurements were significantly higher than GC ones (+ 55%, $p < 0.01$) in the control treatment.

Despite the better overall agreement between GC and B&K, the B&K system measured lower fluxes than GC in the ammonium nitrate (-11%, $p < 0.01$) and in the compost (-18%, $p < 0.01$) treatments (Figure 9), and higher fluxes in the control (+39%, $p < 0.01$) and in the digestate (+7.8%, $p < 0.01$) treatments.

The greater fluxes measured by both SASSFlux and B&K systems in the control treatment rises some doubts on the capability of the GC system (considering sampling as well) to detect low CO_2 fluxes from soils.

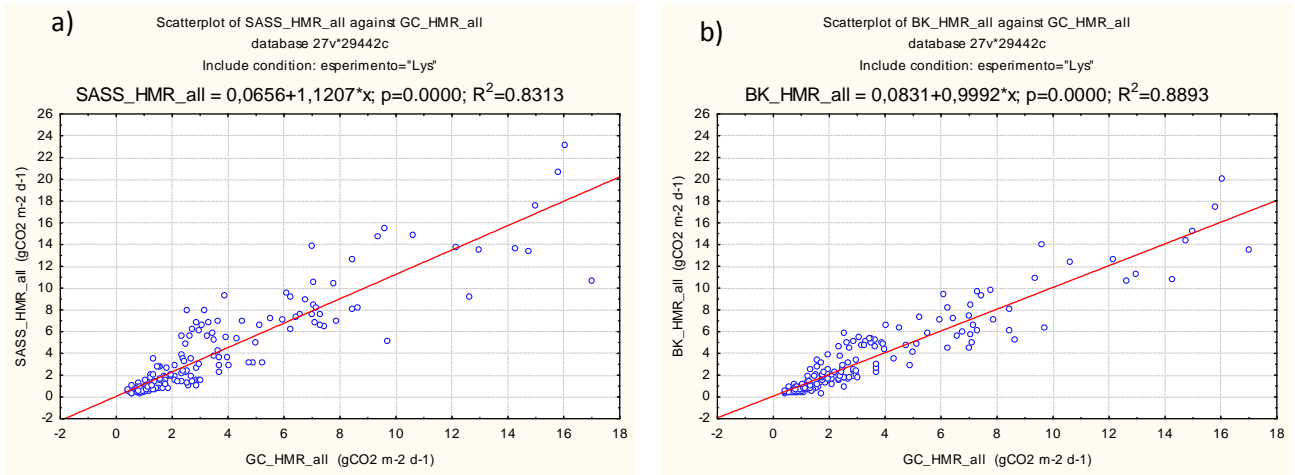


Figure 6: Comparison between all the fluxes measured a) by the SASSFlux and the GC systems, and b) by the B&K and the GC systems.

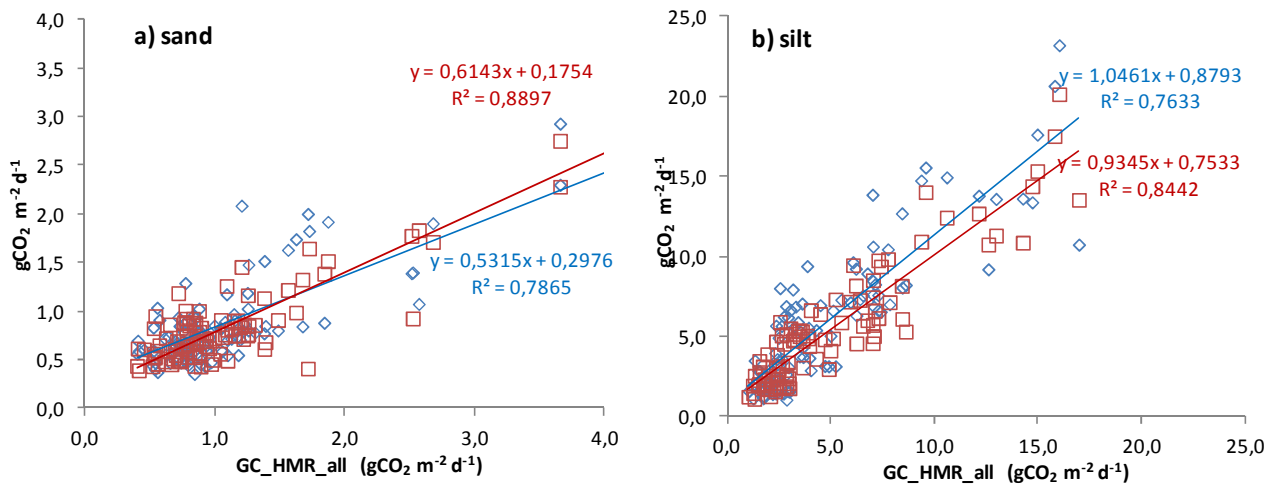


Figure 7: Comparison between all the fluxes measured by the SASSFlux and the B&K systems against the GC system in a) sandy soil and in b) silty soil. Blue rhombus are SASS HMR ALL (blu line) and red square are B&K HMR ALL (red line) regression line.

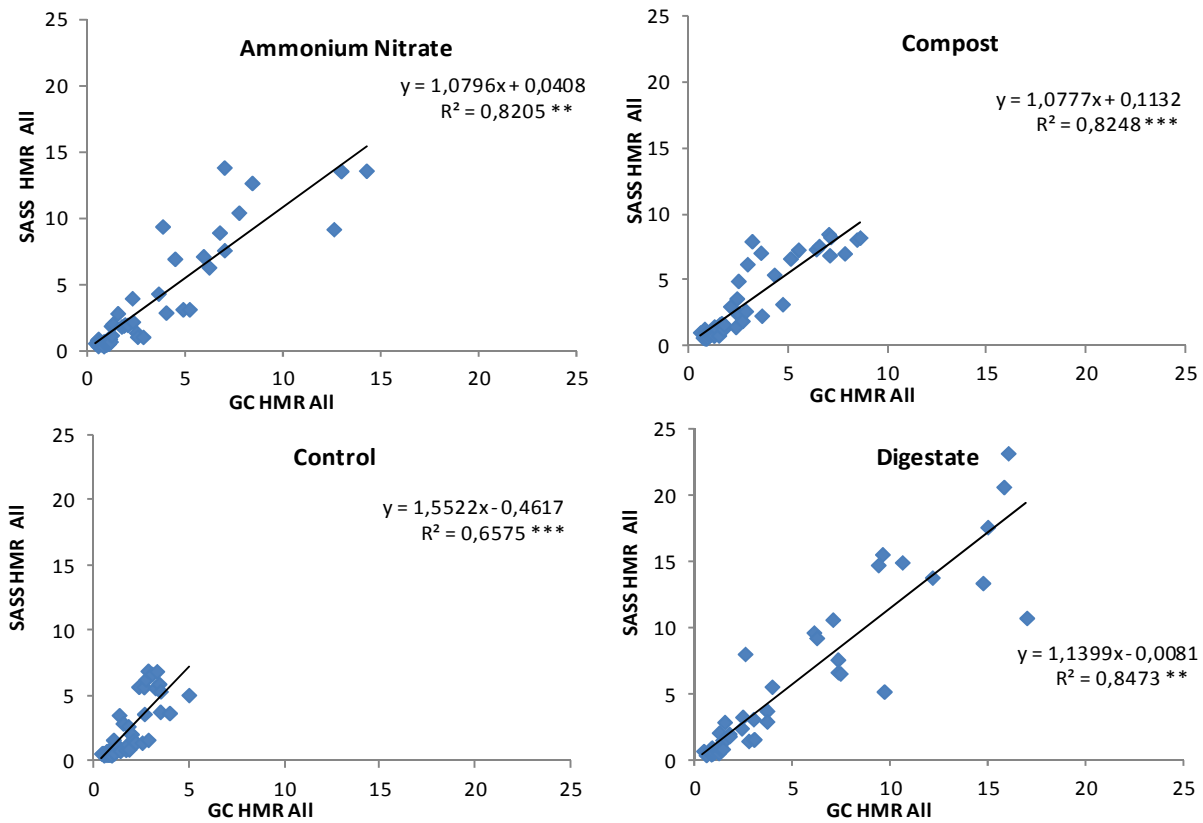


Figure 8: Comparison between the fluxes measured by the SASSFlux and the GC systems in the four different treatments. Significant * at $P \leq 0.05$, ** at $P \leq 0.01$ and *** at $P \leq 0.01$.

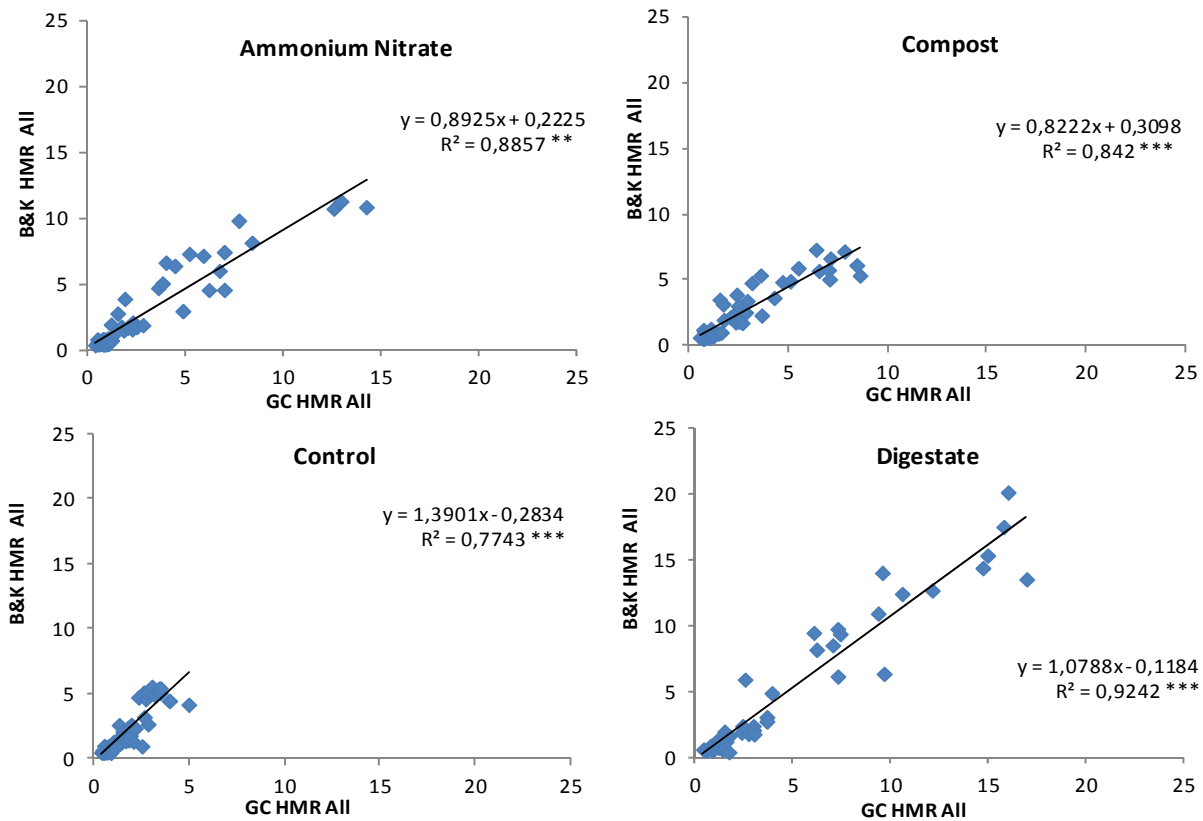


Figure 9: Comparison between the fluxes measured by the B&K and the GC systems in the four different treatments. Significant * at $P \leq 0.05$, ** at $P \leq 0.01$ and *** at $P \leq 0.01$.

2.3.5 Comparison of the different instrumental performances with respect to the environmental parameters

Figure 9 reports the differences between the CO₂ fluxes derived from the SASSFlux and GC measurements at increasing air temperature in the four soil treatments. With the only exception of the digestate treatment, the differences between the SASSFlux system and the GC are only slightly affected by the air temperature. These differences, all not statistically significant, increased by 0.01 gCO₂ m⁻² d⁻¹ every °C in the ammonium nitrate treatment, 0.035 gCO₂ m⁻² d⁻¹/°C in the compost treatment and 0.075 gCO₂ m⁻² d⁻¹/°C in the control treatment. On the contrary, the differences between the two methods were more evident in the digestate treatment (+0.327 gCO₂ m⁻² d⁻¹/°C), $p < 0.01$, even though the R² is poor.

The same pattern was found for the dependence between the B&K and GC differences (Figure 10), with a slightly lower increase of the differences at increasing temperature in the digestate treatment compared to the SASSFlux system.

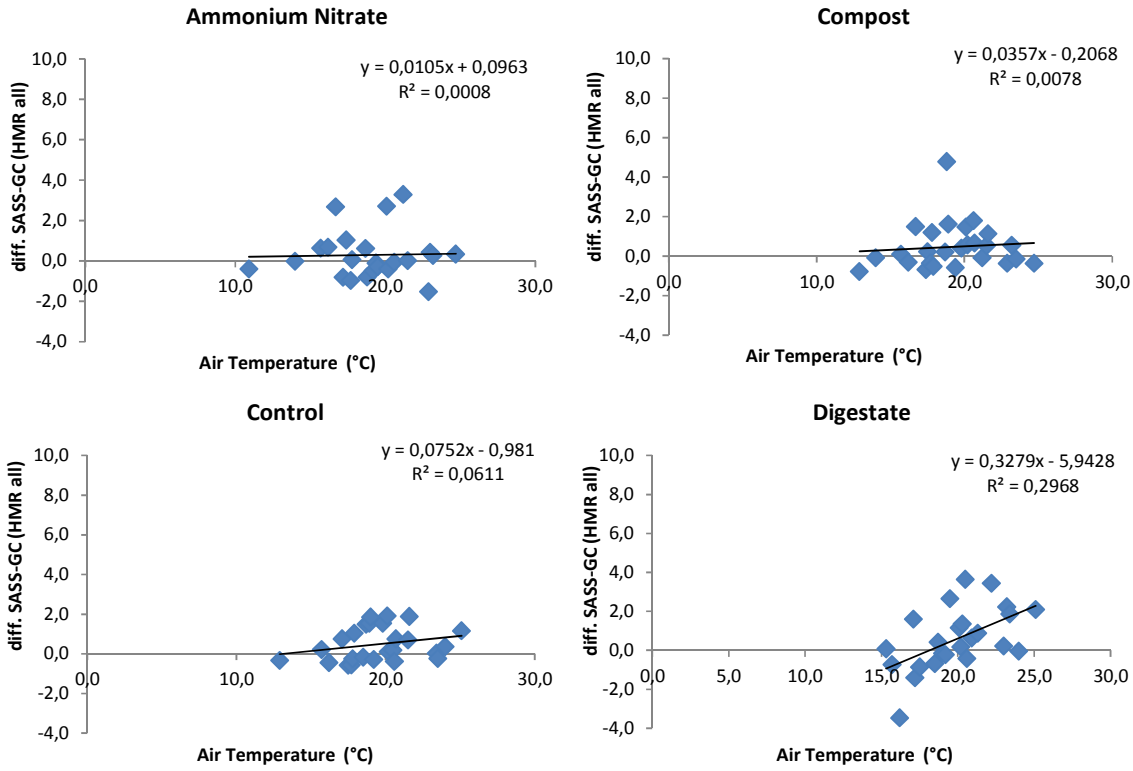


Figure 9: Differences between the CO₂ fluxes derived from the SASSFlux and GC measurements at increasing air temperature in the four soil treatments. The units of the differences are gCO₂ m⁻² d⁻¹.

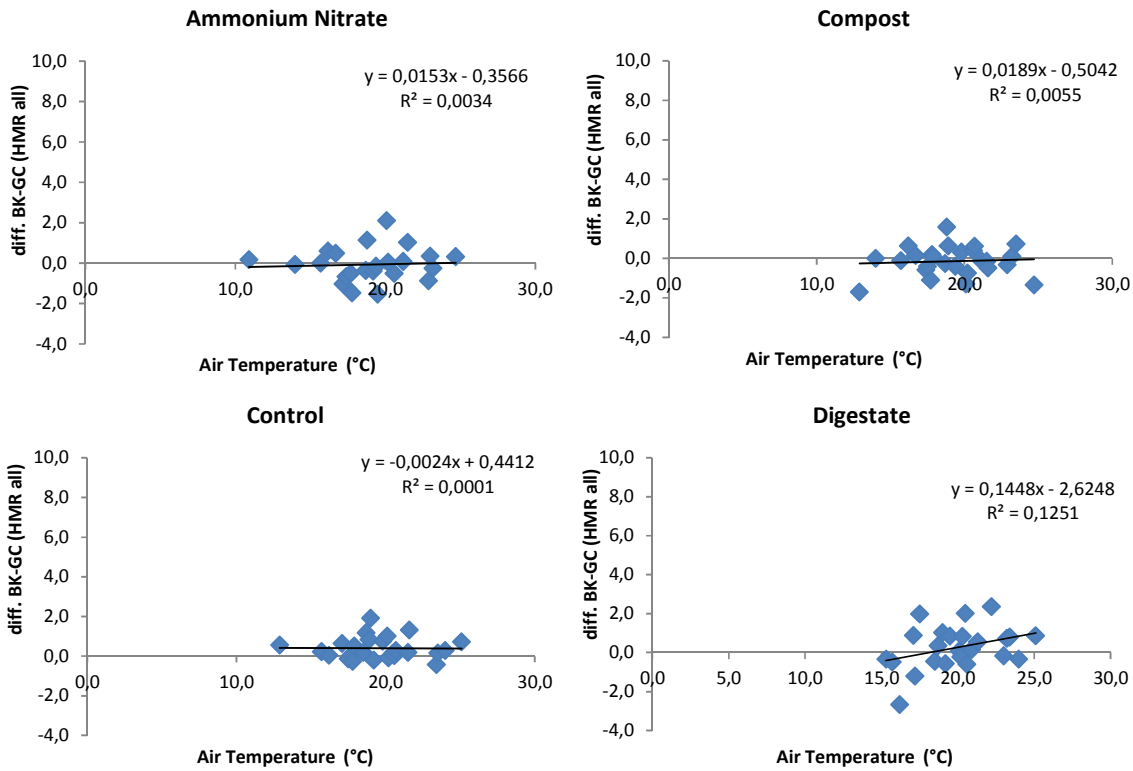


Figure 10: Differences between the CO₂ fluxes derived from the B&K and GC measurements at increasing air temperature in the four soil treatments. The units of the differences are gCO₂ m⁻² d⁻¹.

Figure 11 show the effects of the soil humidity on the differences between the measurements made with the SASSFlux and the the GC instruments. Each point represents the average CO₂ flux of all the measurements made with the same soil water content, and bars represent the standard deviations. It appears that in no case the differences in CO₂ fluxes depends on soil humidity (all regression are n.s.). However, even though not significant, a very slight decrease of the differences appeared in the ammonium nitrate (-0.03 gCO₂ m⁻² d⁻¹/%FC) and in the digestate (-0.037 gCO₂ m⁻² d⁻¹/%FC) treatments. The same pattern is confirmed for the differences between B&K and GC (Figure 12), but with a remarkable scatter in the digestate treatment at high level of soil water content.

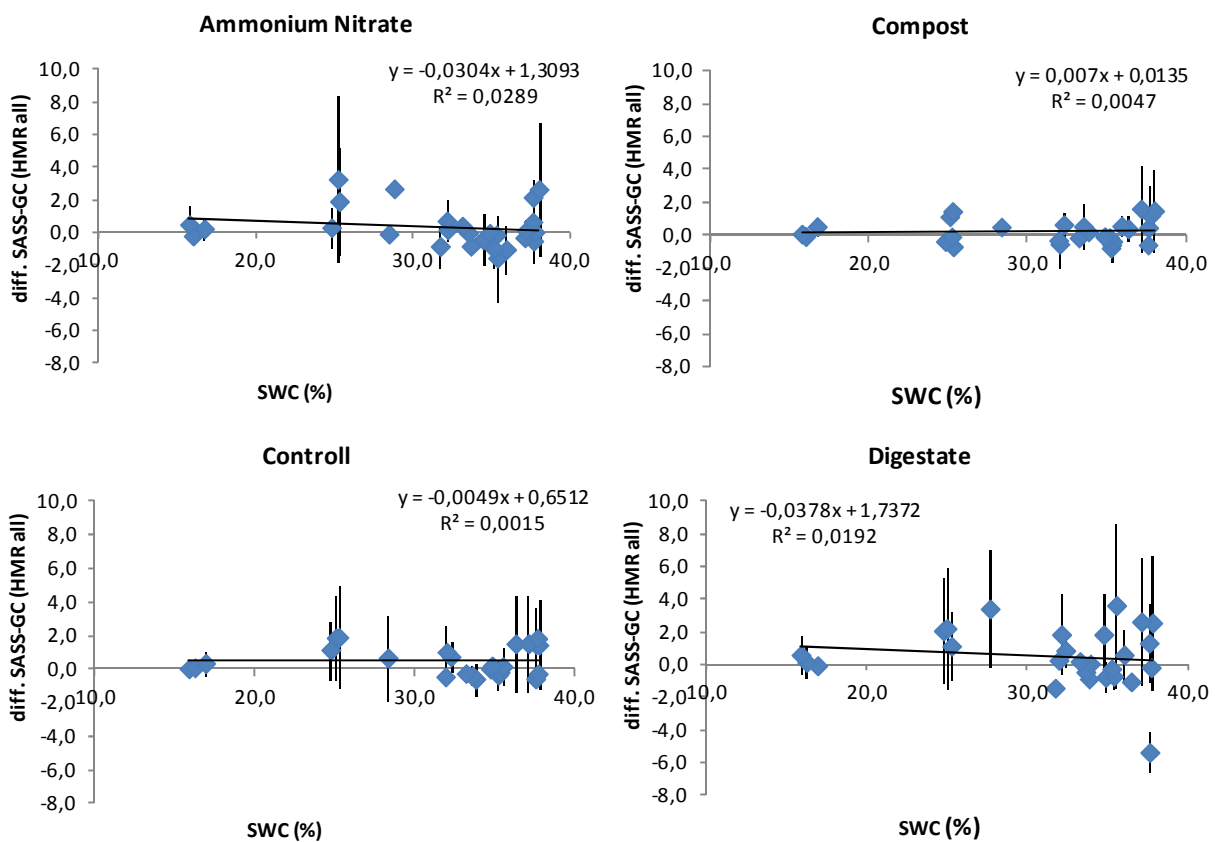


Figure 11: Differences between the CO₂ fluxes derived from the SASSFlux and GC measurements at increasing soil water content in the four soil treatments. The units of the differences are gCO₂ m⁻² d⁻¹.

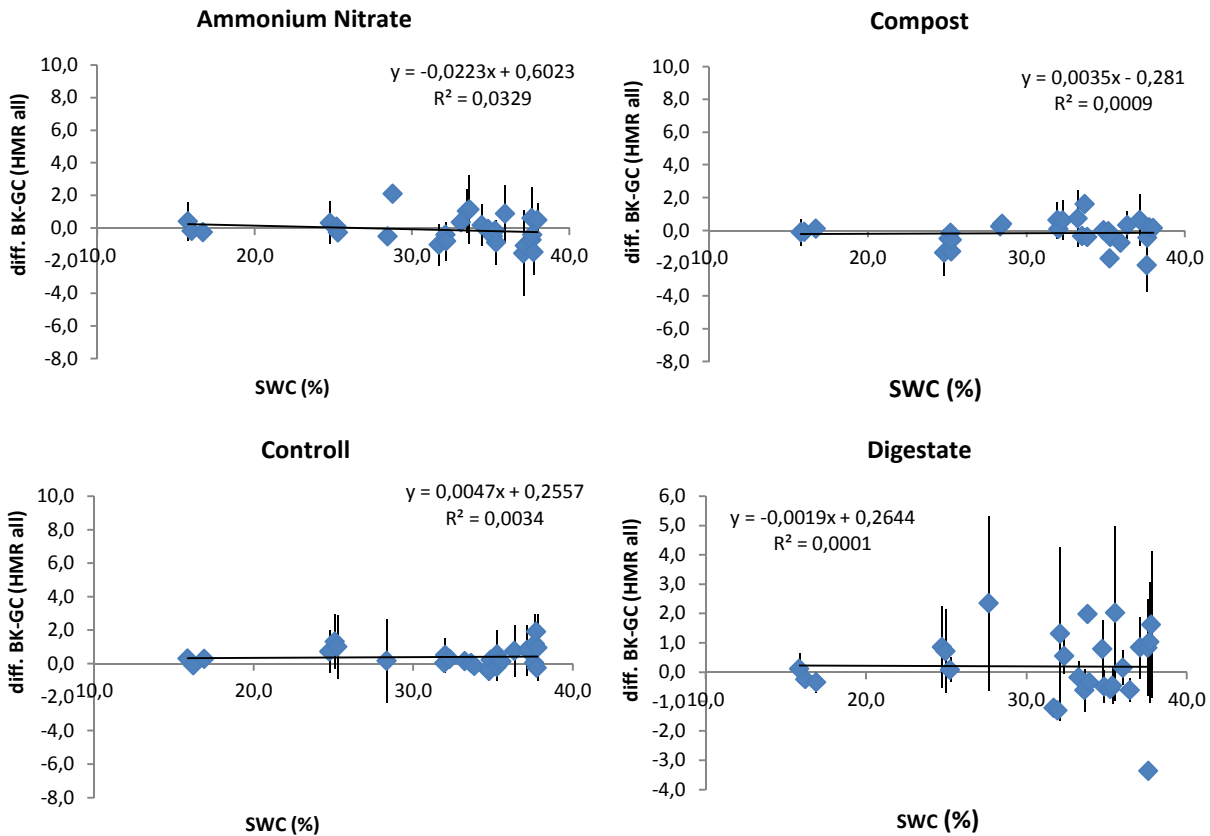


Figure 12: Differences between the CO₂ fluxes derived from the SASSFlux and GC measurements at increasing soil water content in the four soil treatments. The units of the differences are gCO₂ m⁻² d⁻¹.

Figure 1 shows the effect of wind intensity on the differences between the CO₂ fluxes derived from the SASSFlux and B&K in the four soil treatments. Each point represents the average CO₂ flux of all the measurements made with the same wind speed classes, and bars represent the standard deviations.

Apart from the ammonium nitrate treatment, all the other treatments show a positive influence of the differences of the measured fluxes on wind speed. However only in the digestate treatment the regression is statistically significant ($p < 0.05$). In this treatment the differences increased by 0.31 gCO₂ m⁻² d⁻¹ every 1 km/h of wind speed.

The same pattern has been observed for the differences between B&K and GC (Figure 4), even though the dependence of the differences on the wind speed in the digestate treatment was less pronounced (0.31 gCO₂ m⁻² d⁻¹ every 1 km/h of wind speed, $p < 0.05$).

The explanation of this phenomena is not clear. Increased wind speed could have resulted in increased turbulence on the lysimeter soil around the measuring chambers. The turbulence, in turn, could have acted as a pumping force on the extraction of CO₂ from the soil. A similar phenomenon have been described in hystosols by Takle et al. (2004) who highlighted that the rapid fluctuations in the static pressure fields introduced by wind interactions with terrain may lead literally to pressure pumping of CO₂ at the surface.

But the explanation could also be, simply, a greater air leaking induced by the wind speed on the sampling system of the GC. In fact, an air leaking would lead to a lower CO₂ concentration in the trapping vials, and thus to a lower flux.

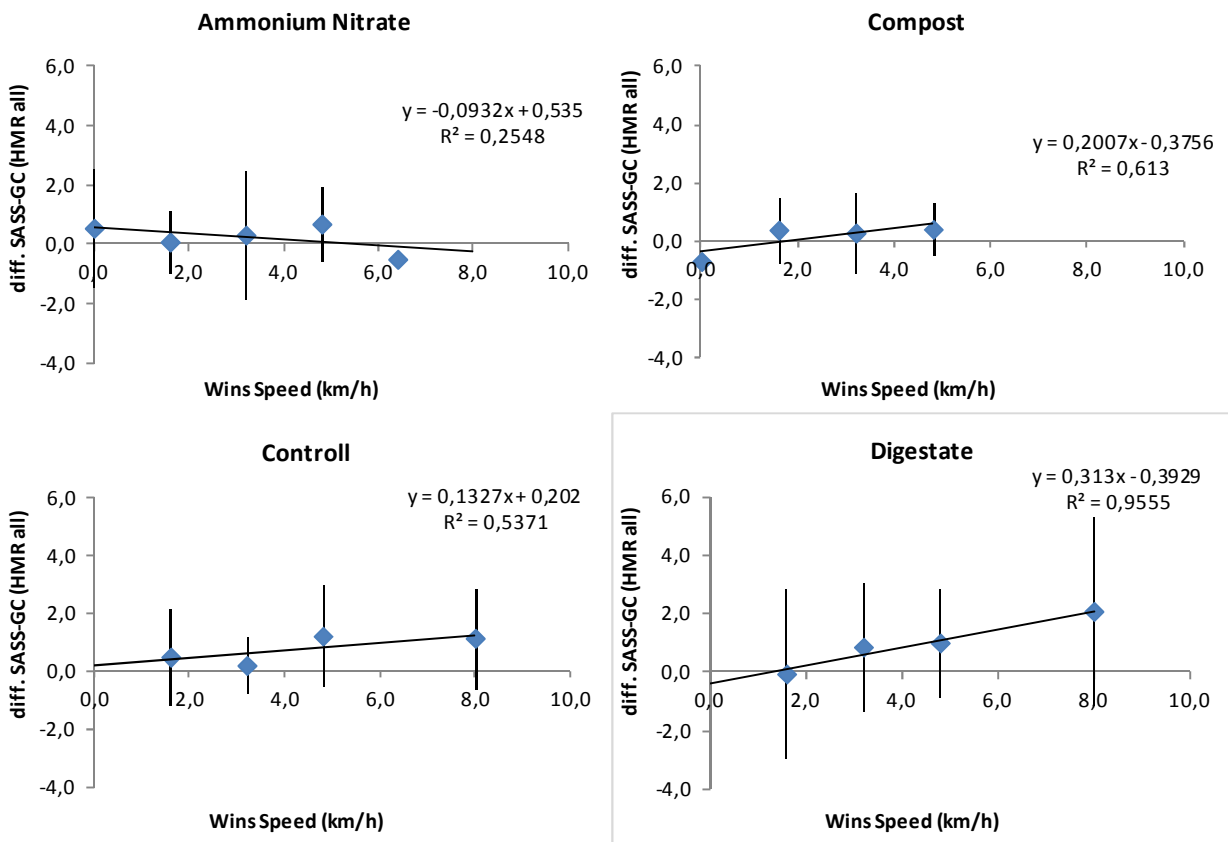


Figure 13: Differences between the CO₂ fluxes derived from the SASSFlux and GC measurements at increasing wind speed in the four soil treatments. The units of the differences are gCO₂ m⁻² d⁻¹.

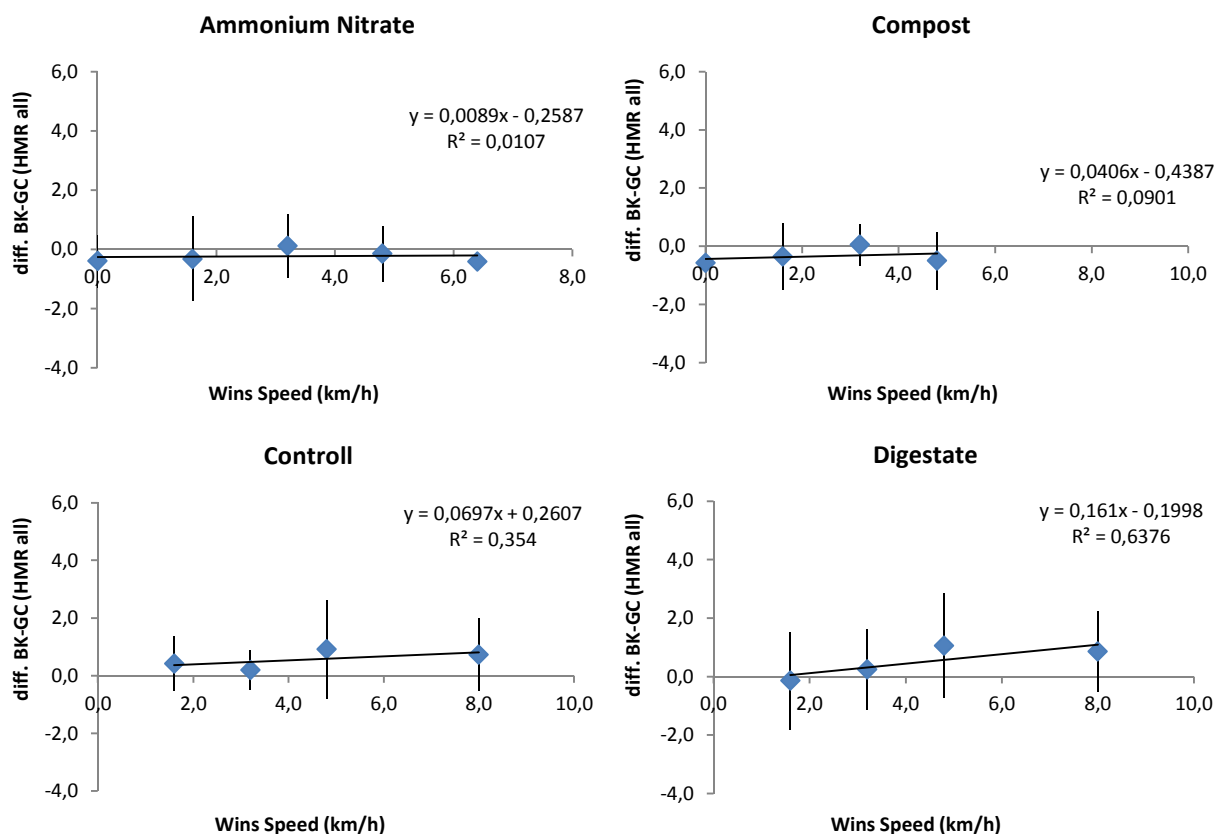


Figure 14: Differences between the CO₂ fluxes derived from the B&K and GC measurements at increasing wind speed in the four soil treatments. The units of the differences are gCO₂ m⁻² d⁻¹.

Figure 15 shows the effect of the CO₂ flux intensity on the differences between the CO₂ fluxes derived from the SASSFlux and the GC systems in the four soil treatments. It is clear that the differences between the two instruments increase at increasing flux intensity recorded by SASSFlux. In all the treatments but the control one (Ammonium nitrate, Compost and Digestate) the SASSFlux CO₂ flux measurements are about 25% higher than those of the GC (all statistically significant with $p < 0.01$, even though with a poor R^2). In the control treatment the difference between the two instruments increases even with a double rate of 57% with a significant relationship ($p < 0.001$) with a R^2 of 0.78.

Evidently the GC measuring system is less able to detect little soil fluxes than the SASSFlux system. When the effluxes of CO₂ from the soil are weak, a rapid equilibrium is reached between the CO₂ concentrations in the soil pores and in the chamber headspace. The longer is the measurement time the lower is the measured flux because when the concentration equilibrium is reached the flux tend to zero.

The differences between B&K and GC (Figure 16) was on the contrary insensitive to flux intensity in the ammonium nitrate and compost treatments, while they were dependent on the flux intensity in the control ($p < 0.05$) and in the digestate (n.s.) treatments.

These results confirmed, from another point of view, what found by directly comparing the fluxes recorded by SASSFlux and GC (Figure 6), i.e. that the SASSFlux measurements are systematically higher than those of GC, and that the B&K measurements are greatly dependent on the soil substrate.

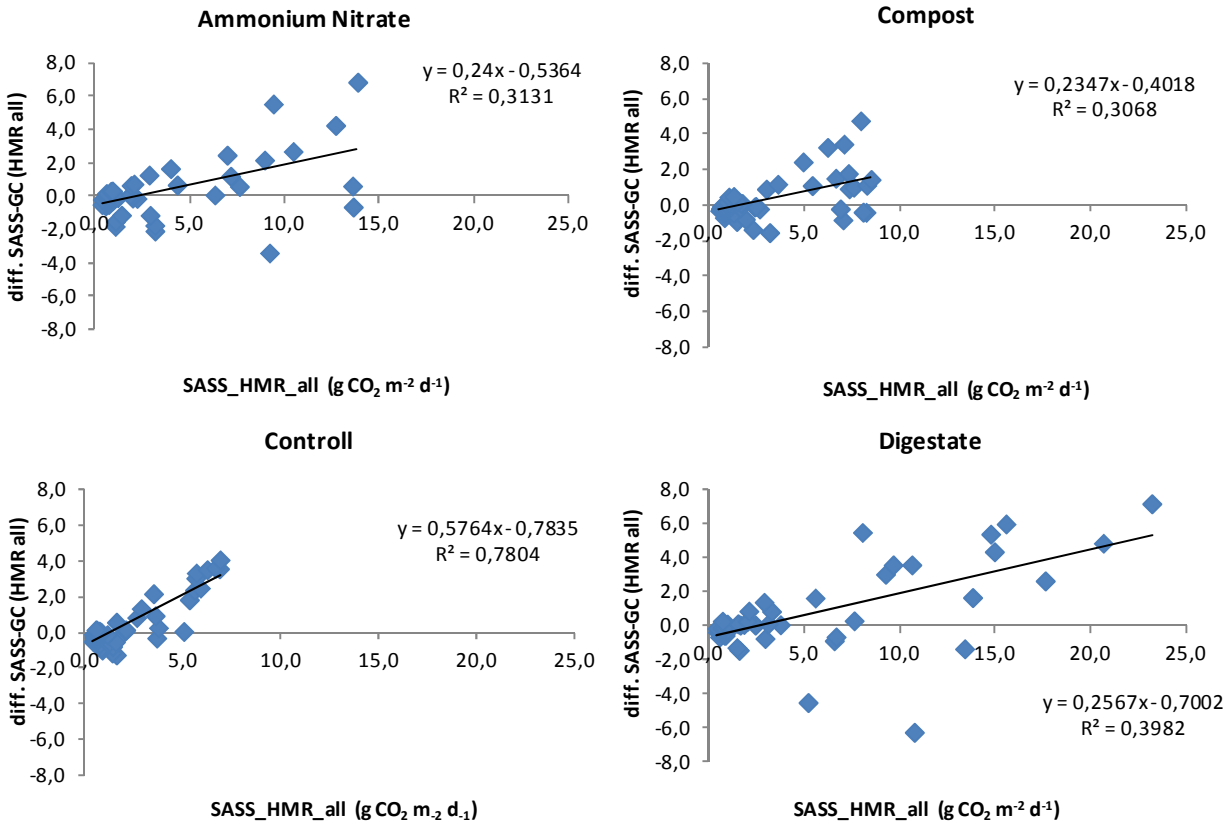


Figure 15: Differences between the CO₂ fluxes derived from the SASSFlux and GC measurements at increasing CO₂ flux intensities in the four soil treatments. The units of the differences are gCO₂ m⁻² d⁻¹.

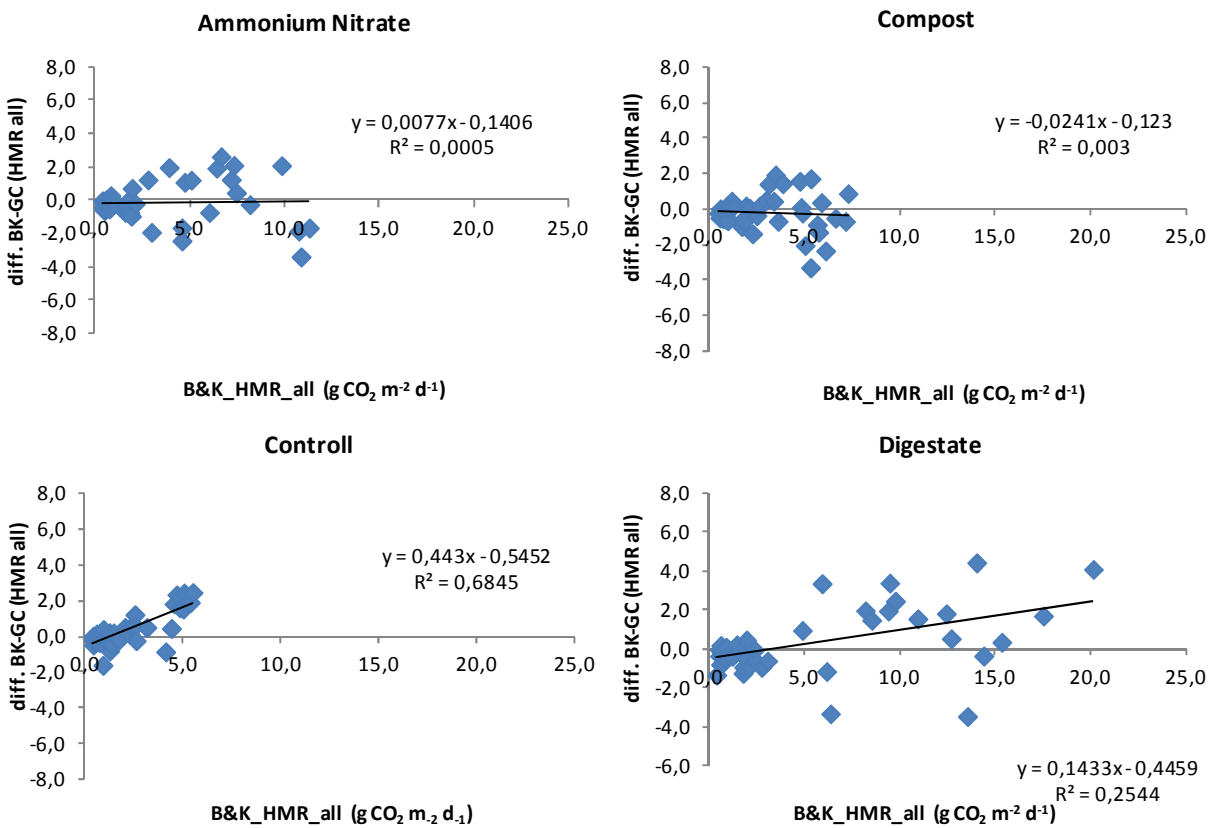


Figure 16: Differences between the CO₂ fluxes derived from the B&K and GC measurements at increasing CO₂ flux intensities in the four soil treatments. The units of the differences are gCO₂ m⁻² d⁻¹.

2.3.6 Comparison of the different flux calculation methodologies

Even the flux calculation methods could have affected the final flux value. In order to assess the effect of the flux calculation methods on the estimated fluxes a comparison of the different methods have been done with the same instrument. For this comparison the SASSFlux instrument has been chosen because it has a high number of data due to its high temporal resolution.

Figure17 and Figure18 show the comparison between fluxes calculated with the HMR methodology but by using all data for HMR or data from a shorter interval (70 s). The agreement between these two approaches varies significantly in the different treatments. HMR 70s calculated fluxes resulted 10% lower than HMR made on all data in the ammonium nitrate treatment and 40% higher than HMR all in the digestate treatment. The other treatments were in between.

Overall the HMR70 methods gives out 9% higher fluxes than HMR all, with a R² of 0.6228.

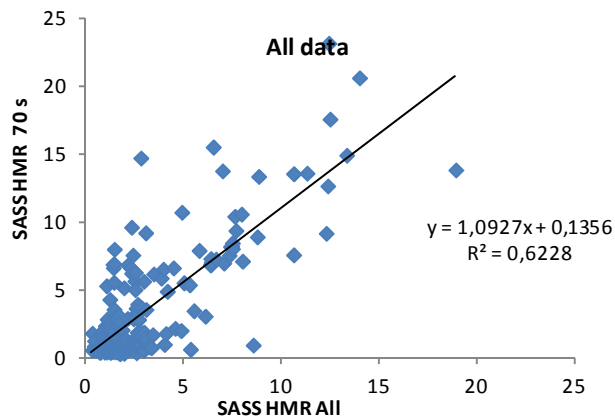


Figure 17: Comparison between fluxes calculated with the HMR method limited to the first 70 s of data gathered by the SASSFlux system (HMR_70s) and the HMR method with all the 839 s data available for each cycle (HMR_All).

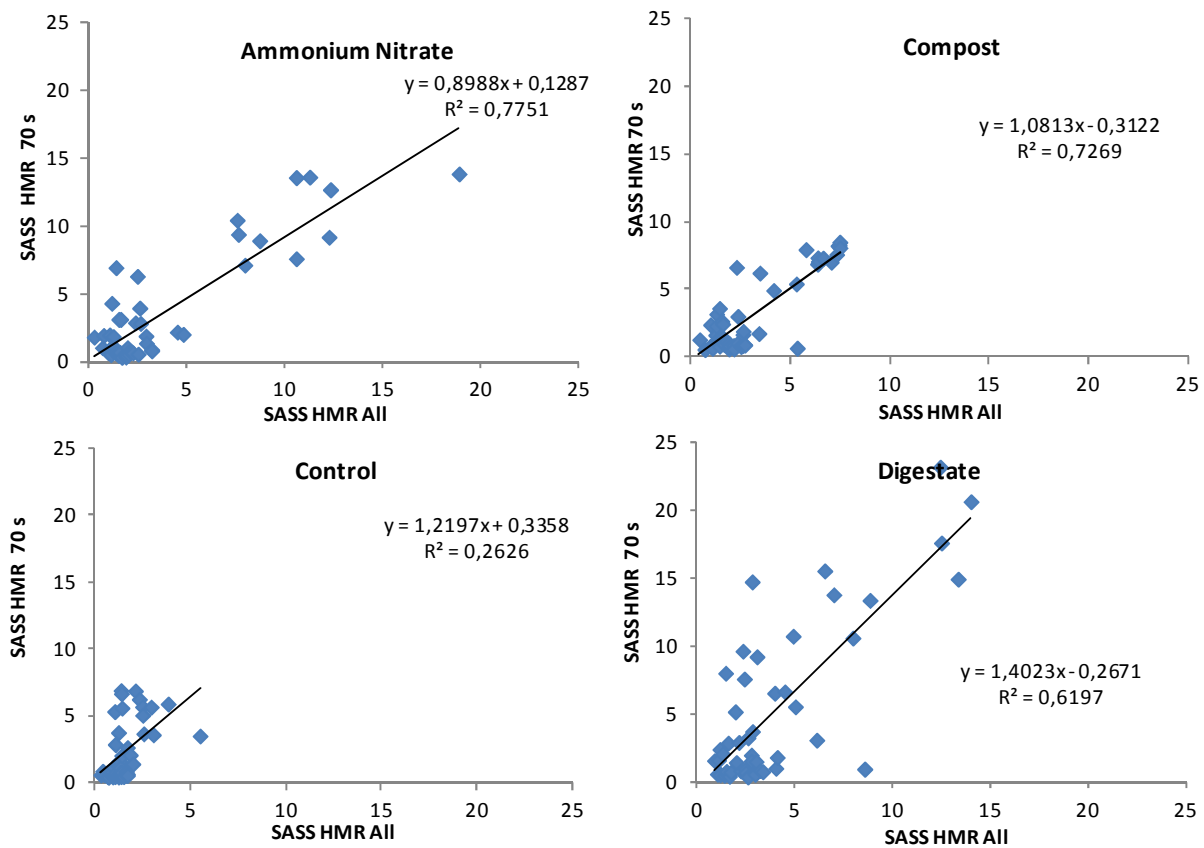


Figure 18: Effect of the treatment on the agreement between the HMR_All and the HMR_70s calculation methods in the SASSFlux system

Another comparison was performed between GER 70s methodology, which calculates the fluxes using a shorter time interval (70 s) and a linear regression, and the HMR methodology on all concentration data. In general the GER 70 s methodology had higher fluxes (+12%, $R^2=0.91$, $p<0.001$; Figure 9). The same result is confirmed for each treatment included between the two extremes represented by the digestate (+9%) and the control treatment (+26%). The agreement between these two methodologies is better than the two previous ones (HMR 70 s vs HMR all) as it can be observed from higher R^2 coefficient and the statistical significance ($p<0.001$) of all the regressions.

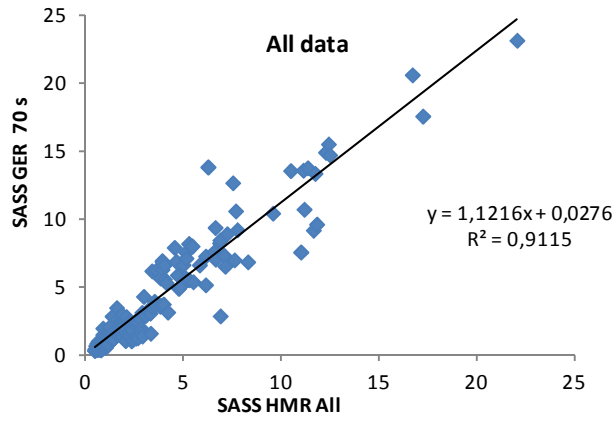


Figure 19: Comparison between fluxes calculated with the GER method limited to the first 70 s of data gathered by the SASSFlux system (GER_70s) and the HMR method with all the 839 s data available for each cycle (HMR_All)

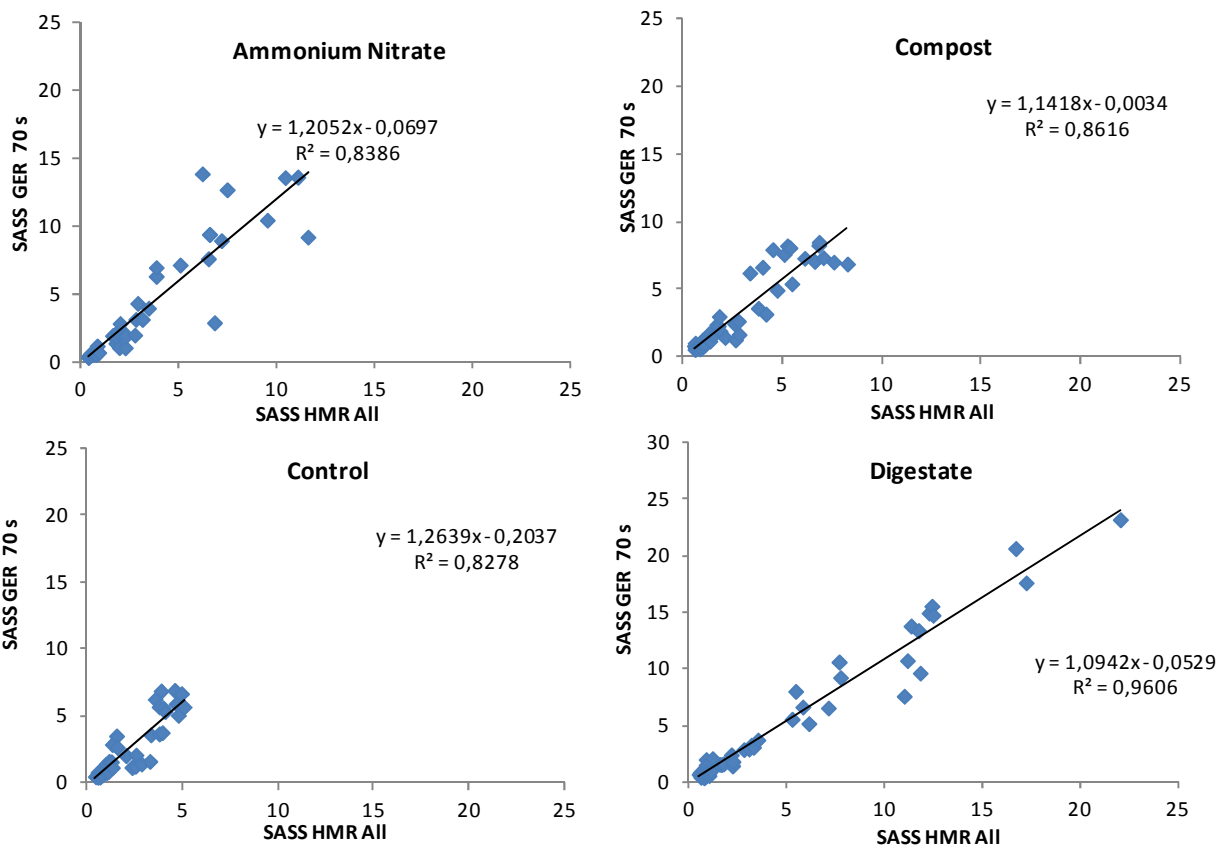


Figure 20: Effect of the treatment on the agreement between the HMR_All and the GER_70s calculation methods in the SASSFlux system

2.4 Discussions

Even though the final flux averages obtained by all the measurements with the three instruments were similar (Table 2), the three instruments clearly produced different flux results in simultaneous measurements with the same calculation methodology (Figure 5).

In general SASSFlux fluxes were the highest and GC fluxes were the lowest, with B&K in between and closer to GC ones. However GC and B&K revealed a great variability among the treatments and the soil type.

SASSFlux presented the best repeatability as confirmed by the lowest standard deviation of the CO₂ concentration measurements, while the other two instruments revealed to be less precise and more influenced by the treatment (Table 5).

At a first sight, the influence of the treatment on the instruments could be attributed to an interference of other gaseous compounds on the CO₂ detectors. However the most significant deviations from GC measurements were observed only in the control treatment, thus suggesting a simple artifact due to an underestimation of CO₂ fluxes by GC for low CO₂ fluxes, results in contrast with De Kleine (1999), even if studies described problems due to complex of this type of sampling (Sainjuet *al* 2012).

The differences among the instruments do not seem to be influenced by environmental factors such as air temperature (Figure 9 and 10) and soil water content (Figure 11 and 12), and only weakly influenced by wind (Figure 13 and 14) as confirmed by De Klein (1999).

The greater fluxes measured by SASSFlux compared to GC (and in lesser extent to B&K) could be attributed to different factors. One hypothesized factor could be the influence of the high humidity on the GMT343 CO₂ detector which is implemented into the SASSFlux. This influence is well known as described in the user manual (Vaisala, 2013) and the sensor implements a humidity correction which is usually set to a given humidity value. The correction is around 0.02% of CO₂ ppm reading per gH₂O m⁻³. In our case the humidity was set to 50%, but it is worth noticing that after 20 minutes of chamber closure the walls of the chambers were covered by dew and thus the air was water saturated (100%). With a temperature inside the chambers of 30°C, the saturated air would contain around 30 gH₂O m⁻³, and the correction for a CO₂ reading of 1000 ppb would be just around 6 ppm. So this factor could be excluded.

A second hypothesized factor could be the pressure fluctuations inside the chambers due to the air sampling systems. The structure of the sampling unit, for both methods, provide a reintroduction of the air after sampling (excluding the amount took for vials collecting). The GMT343 manual refers an influence of 1% of the CO₂ reading per hPa. Assuming an internal air pressure of 1050 hPa inside the GMT343, the effect on the accuracy of a 1000 ppm reading would be just around 10 ppm. Again also this factor seem to be not significant.

Other instrumental failures excluded, the flux calculation methodology used for SASSFlux data was considered as a possible cause of the deviations.

Special attention should be paid to the mixing of air in the chamber since it can be a major source of error. Excessive turbulence inside the chamber can cause mass flow of CO₂ between the soil and the chamber (Pumpanen et al, 2004)

The number of data used to estimate the CO₂ fluxes from the CO₂ accumulation curves may affect the final flux value. Since the flux value is extrapolated from the slope of the CO₂ accumulation curve just after the closure of the measuring chamber (exactly 0 s after the chamber closure), the shape of the fitted accumulation curve is crucial, particularly near the origin (at t=0s).

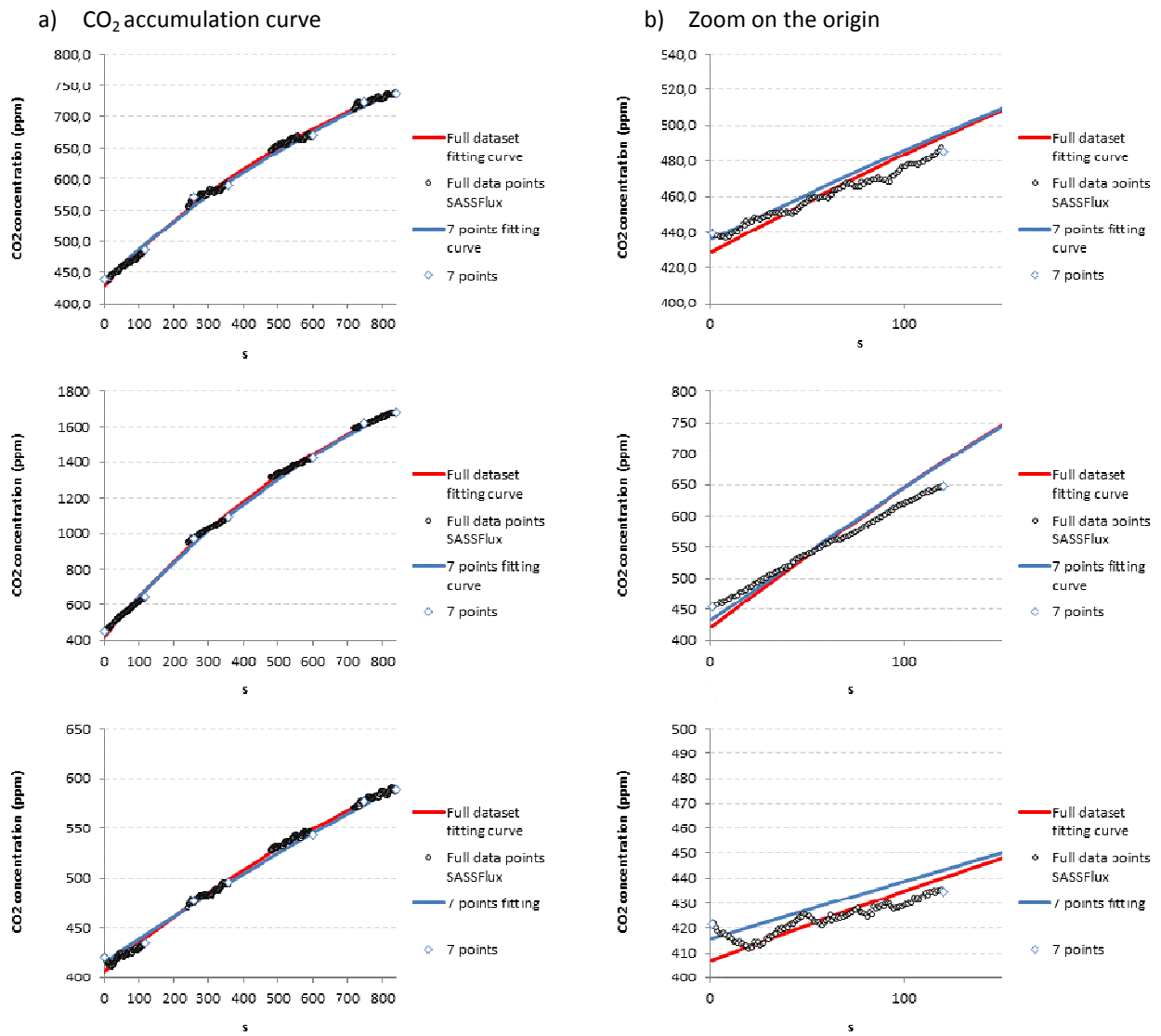
The linear fitting methods (like GER 70s) are very sensitive to the number of data used (see e.g. the Figure 3): the longer is the time series, the lower is the slope and then the resulting flux. 70 s was chosen for the SASSFlux system as a good compromise between rapidity and accuracy (Gerosa et al., 2014)

But even the HMR method which implies a non linear relationship between CO₂ concentration and time revealed to be sensitive to the number of data used for the curve estimation.

Figure reports three examples of accumulation curves estimated by the HMR_all method starting from a full set of SASSFlux concentration data (839 s) and from a subset of 7 CO₂ concentration data. Three sample relative to three different flux intensities have been taken: 6.7, 28.5 and 2.9 $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$, respectively from the top to the bottom, calculated with the HMR_all methodology.

It clearly appears that the slopes in the origin of the two fitting curves obtained from the full dataset and from 7 selected points are different (see the zooms on the second column of the Figure). In the first case (top graphs) the flux estimated with the full dataset is 45% lower than the one estimated with the 7 points dataset, in the second case (middle graphs) the full HMR flux is 6% higher than the 7 points one, and in the third case (bottom graphs) the flux estimated with the full dataset is 150% higher than the one estimated with the 7 points dataset.

It is remarkable that the greater differences are observed with fluxes of low intensities. But the lowest flux intensities have been recorded over the control plots, just where the SASSFlux system displayed the greater differences with the GC method. It is thus possible that these differences could be explained by the high temporal data density of SASSFlux compared to the other systems. It is worth noticing, in fact, that SASSFlux took a concentration data per second while the other two methods took only from 4 to 7 concentration data in 20 minutes.



2.5 Conclusions

The comparison of instruments with such a different temporal resolution (ranging from 4 to 480 measurements in 18 minutes) cannot be easily done because the data density, in particular just after the closure of the chamber, influences the values of the estimated fluxes.

The two instruments (GC and B&K), which have a very similar temporal sampling resolution, appear obviously closer each other with respect to the measured fluxes. However both of them had a much greater variability (i.e. less precision or repeatability) compared to the SASSFlux system. Moreover the GC methodology widely used in the literature revealed some weaknesses, particularly in measuring lower fluxes.

The SASSFlux system appears to be more stable and less influenced by the soil type and the soil treatments. However the SASSFlux requires that some cares should be devoted to the flux calculation methodology to be chosen in order to improve the comparability with the other systems. A simple linear regression on the data of first 70 seconds will be preferable with respect to the HMR method based on all the collected data.

The SASSFlux system performed satisfactorily even though it was employed with longer closure chamber time than those for which it was developed. A great temporal resolution and rapidity of the measurements is desirable, especially just after the closure of the chambers, could contribute to a better estimation of the instantaneous CO₂ flux at time zero, and thus explaining the relative difference observed between SASSFlux and the other two methods.

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3. Evaluation of DNDC and SPACSYS model simulations of GHG fluxes from lysimeter experiment.

3.1 Introduction

Greenhouse gas (GHG) emission from agriculture soil has become major concern due to its impact on global warming (Desjardins et al., 2007).

Agricultural soils can act as a source or a sink for the three main greenhouse gases, nitrous oxide (N₂O), carbon dioxide (CO₂) and methane (CH₄), deriving from biological processes and depend on many factors that have complex feedbacks and interactions (Giltrap et al, 2010).

These gases emitted from soil exhibit a high degree of temporal and spatial variability (Gangsheng and Shulin, 2012). In order to get results of greenhouse gas emissions for inventory purposes many countries use the IPCC default methodology for calculating N₂O emissions from agricultural soils for their national inventories (IPCC, 2007). This method assumes a fixed proportion (emission factor) of the applied nitrogen that is emitted as N₂O. Direct measurement of greenhouse gas emissions would require many measurements to be made over large areas and for long periods of time (Giltrap, 2010).

A more sophisticated option for the emissions estimation consists in the application of process-based models, which allow the simulation of agricultural greenhouse gas emissions at a range of scales up to national or global level, but also the exploration of potential mitigation strategies. Computer simulation models are effective and supplementary tools that extend quantitative calculations beyond limited observations in time and space (Gangsheng and Shulin, 2012).

In the last 40 years, a number of mathematical models of different level of complexity have been developed to describe biogeochemical processes in soils (Schaap et al., 2001). There are different categories of models: empirical or semi empirical model with simple dependencies derived from regressions between measured data on soil (ecosystem) properties and GHG emissions (Cai et al ., 2003), the so-called data-driven models (e.g., Smith et al., 1997a, 1998, 2000) and mechanistic models with an exact description of the basic processes common for all ecosystems combined with a detailed description of site-specific factors (process-oriented models, e.g., Li et al., 2000; Grant, 2001). Both categories need comprehensive data support but the second approach gives a deeper understanding of the emission dynamics.

Mechanistic models should, in general, describe reality better, as long as they can be parameterized successfully and the necessary driving data are available at the appropriate spatial and temporal scales (Blagodatsky, 2012).

Most soil models describe biological processes that determine how carbon and nitrogen are exchanged between soil and the atmosphere. Despite the model-specific structures, all the soil models describe the following key processes: external nitrogen (N) input (i.e. chemical fertilizer application, atmospheric deposition and the incorporation of organic materials); nitrification from ammonium to nitrate; mineralisation/immobilisation; nitrate leaching; denitrification and plant N uptake (Wu et al., 2007).

Emission of GHGs is one of the processes considered in models of carbon and nitrogen dynamics (Gangsheng and Shulin, 2012).

Models work in different ways: temperature as a driving/regulating factor can be found in most of the GHG emission models that implement the state equation for gases. The mechanistic approaches describe the processes controlling GHG emissions that are biochemical reactions, which lead to the production or consumption of greenhouse gases in soil, and physico-chemical processes, such as transport and exchange between gaseous and liquid phases. Such processes that produce greenhouse gas emissions from soil are complex and involve many feedback mechanisms.

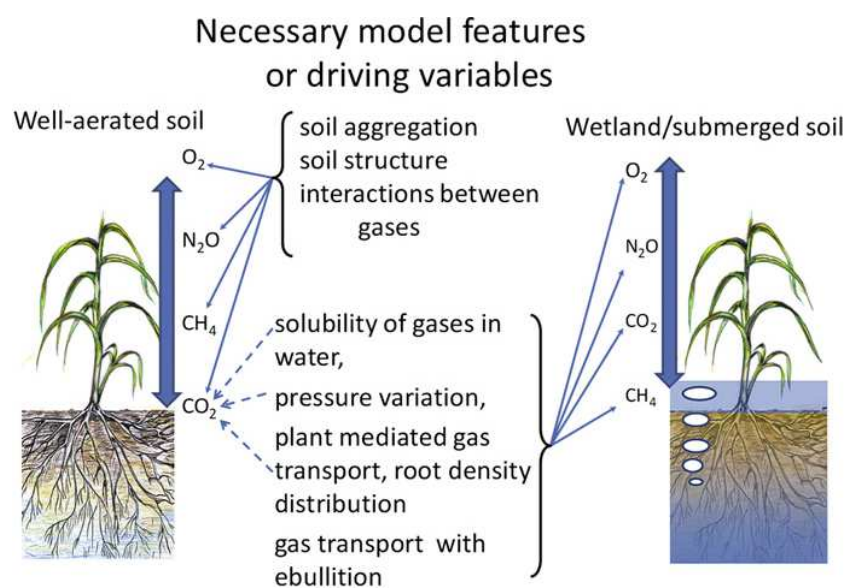


Fig 1: Physico-chemical conditions determining the transport and emission of greenhouse gases: CO₂, N₂O and CH₄, as well as O₂. Dashed lines show auxiliary dependencies. Source Blagodatsky et. al., 2012

Models should adequately consider soil properties (driving factors), in particular those involved in biochemical and gas transport processes (Figure 1): i) total and air-filled porosity (water saturation), ii) soil aggregation and soil structure, iii) the possible alternative transport mechanisms: diffusion in water, through plant tissues or ebullition, iv) the relative amount of modelled gas in soil air and its chemical properties (Blagodatsky et. al., 2012). Most models to date, however, have neglected the complex structure of plant root systems (Wu et al., 2007). Aggregate formation affects aeration and the gaseous composition in the intra-aggregate pore space. Depending on the type and intensity of soil aggregation, the intra

aggregate pores can be completely anoxic, while the inter aggregate pores can be completely aerated (Horn and Smucker, 2005).

Gaseous transport models are frequently based on Fick's Laws. When air permeability is not sufficiently high. So, the simple models based on one dimensional diffusion (which assumes equilibrium between gases in the gaseous and in the liquid phases of structured soils) are inappropriate for a detailed description of N₂O dynamics (Blagodatsky et. al., 2012). Complex transport models consider both diffusion and convective flow (using Darcy's Law) and account for Knudsen diffusion, i.e., diffusion of gas molecules due to collision with solid particles (Thorstenson and Pollock, 1989; Webb and Pruess, 2003).

Microbial growth and respiration as well as root respiration, dependent on oxygen availability, is modeled considering gaseous transport (diffusion) within a crop canopy and soil system (Blagodatsky et. al., 2012). Several reviews on models of carbon and nitrogen processes have been published (Chen et al., 2008; Ma and Shaffer, 2001; Smith et al., 1997b; Wu and McGechan, 1998, Blagodatsky et. al., 2012) and results show that no one model was better than the others for all datasets. This was probably a consequence of the capacity to apply the model under specific and local conditions and the utilization of site-specific calibration (Smith et al., 1997b). There is still a need to study the potential effect of local conditions (management, soil and climate) on total GHG emissions and, in order to implement strategies of mitigation, on the GHG contribution of each C and N source (Gangsheng and Shulin, 2012).

The DNDC model is a widely-used ecosystem biogeochemistry model (Abdalla, 2009) developed to assess N₂O, NO, N₂ and CO₂ emissions from agricultural soils (Li et al., 1992; 1994, Li, 2000). The model was used to estimate N₂O emissions from agricultural fields (Li et al., 2001; Gou et al., 1999) and dairy farms (Brown et al., 2001), CH₄ emissions from rice fields, and soil organic carbon dynamics (Li et al., 1997a). The DNDC model was compared with other similar models. Different authors (Frolking et al., 1998, Beheydt et al. 2007) compared N₂O flux simulations from DNDC against other models with field measurements, giving similar results for the general patterns of soil nitrogen dynamics through the agro-ecosystems, but simulated trace gas fluxes were different due to different processes embedded in the models.

SPACSYS is a multi-dimensional, field scale, weather-driven dynamic simulation model of C and N cycling between plants, soils and microbes, which operates with a daily time-step (Wu, 2010). It includes a plant growth and development sub-model with detailed representation of the root system, in addition to sub-models for C and N cycling in the soil with links to the plant, a soil-water component, and a heat transfer component.

Root systems are central to the acquisition of water and nutrients by plants (Fitter et al., 1991), but are also a major pathway for the inputs of carbon (C) and nutrients to soil (Persson, 1978; Ruess et al., 1996; Vogt, 1991).

The aim of this study was to compare the performance of a mechanistic farm-scale model (SPACSYS) and the widely-used ecosystem biogeochemistry model (DNDC) with lysimeters data.

3.2 Materials and methods

3.2.1 Experimental site

Eight lysimeters of polyethylene (HDPE) with a cross section area of 1 m² and a height of 0.5 m were placed in the Tadini experimental station located in Gariga di Podenzano (PC). Lysimeters were filled with a repacked silt-loam soil and four treatments (i.e. ammonium nitrate, digestate, compost, and control) were applied to distribute an equivalent of 100 Kg ha⁻¹ of N. Two lysimeters were not fertilised and they were considered as control.

Soil water content was measured throughout the course of the experiment (from April to May 2014) using soil moisture sensors (Spectrum technology SM100 Waterscout) connected to a weather station (WatchDog, Spectrum technology) and placed at 0.1 m of depth in the lysimeters. In addition one soil samples for each lysimeter was taken weekly at two depths (0-0.05 and 0.05-0.2). Samples were weighed fresh and then oven dried at 105°C until constant weight was reached. The dry and fresh weight were used to calculate volumetric water content by the following formula:

$$WC = \frac{W_w - W_d}{W_d} \times 100$$

Soil temperature was measured in one lysimeter. In case of heavy rains samples of leached water were collected from a drain outlet and analyzed for NO₃⁻-N and ammonium (NH₄⁺-N) content. Soil samples were collected at the start and at the end of the experiment to determine NH₄⁺-N and NO₃⁻-N concentrations. Total C and N contents were also determined on the same soil samples. In order to compare water status content between models and observed data water filled pore space (WFPS) was used as indicator of water content. WFPS was calculated as $WFPS = (\text{soil gravimetric water content} \times \text{bulk density}) / [1 - (\text{bulk density} \times \text{particle density})]$. (Linn and Doran, 1984).

3.2.2 CO₂ and N₂O flux measurements

CO₂ and N₂O measurements flux were carried out from 23th April to 23th May 2013, using static chambers (PVC ring 0.4 m diameter X 0.3 m height) and a cylindrical stainless steel frame (0.45 m diameter X 0.2 m height) positioned into the lysimeter. The outside of the chambers was coated with reflective paint. The frames were installed immediately after treatment application so that their base was inserted 10 cm deep in the soil. After closing each chamber, four gas samples were collected at six minutes intervals (0, 6, 12 and 18 min after chamber closure) by injecting a needle attached to a syringe in the vial. A small fan was installed under the lid to ensure adequate mixing of air within the chamber. Vials collected were therefore analyzed with a gas chromatography (TRACE GC ULTRA Thermo Electron Corporation gas chromatograph interfaced to a POLARIS Q mass-selective detector operating in the low-resolution selected-ion monitoring SIM and in tandem mass spectrometry MS/MS modes). The daily flux rates for each chamber were calculated using the HMR package of R software. The HMR function analyses the data series sequentially,

and starts each analysis by fitting the nonlinear function in term of flux over the time (C_t) (Hutchinson and Mosier, 1981):

$$C_t = \varphi + f_0 e^{-kt}$$

using a single-parameter (k) criterion (concentrated least squares; Seber and Wild, 1989). In this equation, f_0 denotes the initial flux, φ denotes the new chamber equilibrium concentration, and $K > 0$ is an adaption rate that depends on soil, gas, and chamber characteristics (the flux unit is expressed in $\mu\text{g m}^{-2} \text{h}^{-1}$). Flux data were checked for normal distribution and log transformed following the analysis applied by Abdalla et al (2010).

3.2.3 Models description

A common feature of DNDC and SPACSYS is their capability to simulate GHG emissions from the soil, though using different procedures for GHG emissions estimation. Both models have similar sub-models that are controlling soil gas diffusion by nutrient availability, water, and temperature. Nutrient supply is a function of soil organic matter (SOM) decomposition and external nutrient inputs. Daily maximum/minimum temperature and precipitation, timing and description of management events and soil texture data are needed as model inputs. Key sub-models include plant production, SOM decomposition, soil water and temperature by layer, nitrification and denitrification, and CH_4 oxidation.

Both models are able to track the fate of nitrogen, carbon and water in the rooting zone of the soil, simulating all relevant fluxes including, for the example in the case of nitrogen, uptake and export with the harvest, recycling through decomposition of crop residues, losses below the rooting zone and to the river system through leaching and run-off, and gaseous losses of NH_3 , NO_x , N_2O , and N_2 . The models are also driven by environmental (daily weather), ecological (nitrogen deposition) and management (land use, fertilizer application, field operations) factors and simulates the controlling processes on the basis of the characteristics of the soil profile, which must be initialized with information on soil organic carbon content, pH, bulk density and texture.

Biogeochemistry follows the production and consumption of NO , N_2O , and N_2 in the nitrification-denitrification chain (Li, 2000). Emissions of NO and N_2O from nitrification are calculated as a function of the predicted nitrification rate and temperature. Denitrification is simulated as a sequential reduction of nitrate to molecular nitrogen following the dynamic of the population of denitrifying bacteria, dissolved organic carbon and nitrogen oxides.

The next sections give an overview of the two applied models, and more specific of the GHG simulation procedures.

3.2.3.1 DNDC

The Denitrification Decomposition model (DNDC, Li et al., 1992) is a dynamic, process-oriented model to predict trace gas fluxes and nutrient turnover in agricultural soils (Li et al., 1992, 1994). DNDC was originally developed for USA conditions. It was applied at a regional scale in the United States (Li et al., 1996), China (Li et al., 2001), Canada (Smith et al., 2010), and Europe (Kesik et al., 2006).

As a process-based model, DNDC is capable of predicting the soil fluxes of all three terrestrial greenhouse gases: N₂O, carbon dioxide (CO₂), and methane (CH₄), as well as other important environmental and economic indicators such as crop production, ammonia (NH₃) volatilization and nitrate (NO₃) leaching.

DNDC consists of five interacting sub-models: thermal-hydraulic, aerobic decomposition, denitrification, fermentation (Li et al., 1992a), and plant growth (Li et al., 1992b). The last one contains sub-routines for handling management practices such as crop rotation, tilling, irrigation, and fertilizer and manure addition. In the DNDC model the nitrification/denitrification scheme was improved using the concept of an “anaerobic balloon” which swells or shrinks according to redox potential of the soil (Li et al., 2004). For each layer substrates, state variables such as DOC, NH₄⁺ and NO₃⁻ are allocated to the anaerobic or aerobic compartments based on oxygen availability. This enabled the nitrification and denitrification to occur simultaneously (Giltrap et al, 2010). Both soil temperature and pH play an important role in DNDC model for the simulation of the emission process, in addition to the biomass of denitrifiers, the carbon content, the availability of an appropriate N source and the gas diffusion rate, where the N gas fluxes depend on the rates of production, consumption, and escape (diffusion) from the reacting system (Beheydt et al., 2007; Li, 2000; Li et al., 2000).

N₂O emission was found to be sensitive to soil clay content, SOC and mean annual temperature; while CO₂ emission was significantly affected by SOC, clay fraction, mean annual temperature and annual precipitation (Li et al., 1992a, 1992b).

DNDC treats the soil as a series of discrete horizontal layers (down to a depth of 50 cm). Within each layer all the soil properties are assumed to be uniform (Giltrap et al, 2010).

The model was applied in different study to estimate N₂O emissions from agricultural fields (Li et al., 2001; Gou et al., 1999) and dairy farms (Brown et al., 2001), CH₄ emissions from rice fields, and soil organic carbon dynamics (Li et al., 1997).

3.2.3.2 Spacsys

SPACSYS is a multi-dimensional, field scale, weather-driven dynamic simulation model of C and N cycling between plants, soils and microbes, which operate with a daily time-step. Its novel feature is that it includes a plant growth and development sub-model with detailed representation of the root system, in addition to sub-models for C and N cycling in the soil with links to the plant, a soil-water component, and a heat transfer component. C and N are held in a number of aboveground and below-ground pools, and flows between pools are simulated. The representation of soil C and N processes is similar to that used in a number of existing models, which were reviewed by Wu and McGechan (1998a) and McGechan and Wu (2001), however more details in relation to nutrient cycling from decaying root material is implemented in SPACSYS. (Wu et al., 2007).

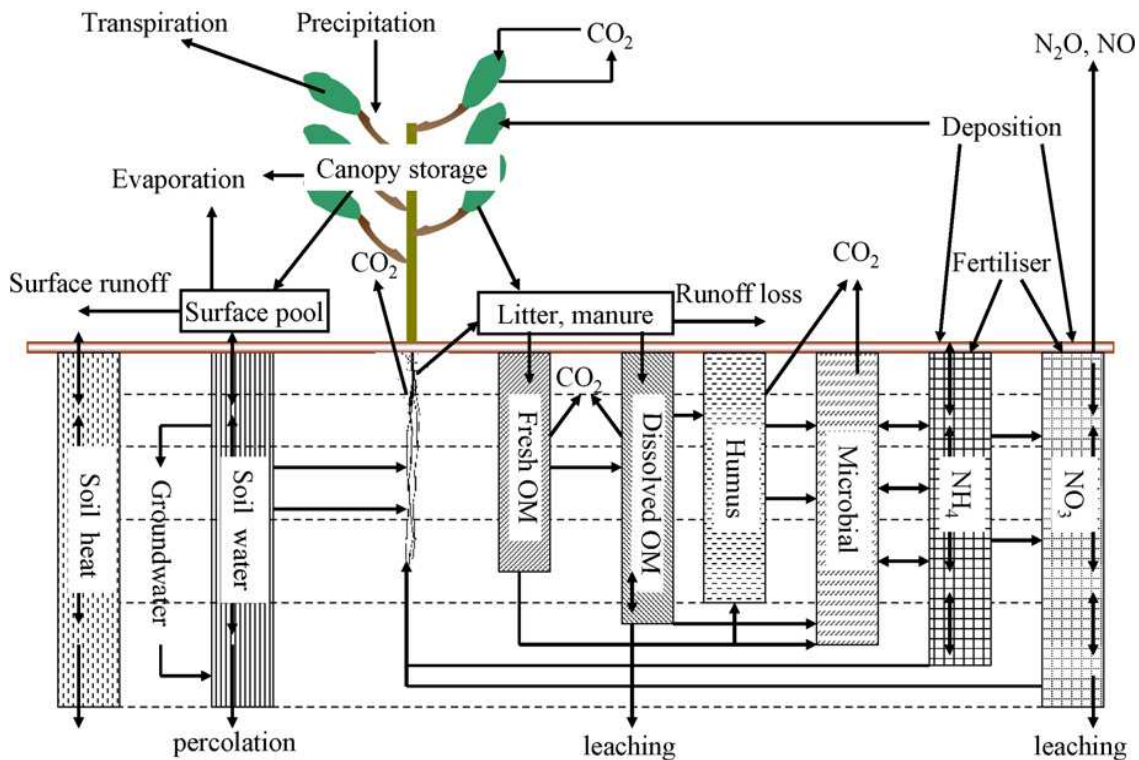


Figure 2 – Framework of Spacsys model components (Wu et al. 2007).

The water, heat and soil N components are considered as two-dimensional sub-models because the water component includes a horizontal water flow that drives heat and nitrate moving. The soil C cycling is a one-dimensional component. The values of state variables in a soil layer that need to be derived from the root systems are set by taking into account each root segment value within the soil layer. The model is presented schematically in Figure 2.

Estimated nitrogen dynamics adopted by Wu and McGechan (1999) in the SPACSYS model are based on the assumption that inorganic N concentration in soil, soil temperature, soil water and the size of root nodules are the main factors controlling the N₂ fixation process.

In the SPACSYS model, the soil organic C and N pools are divided into four sub-pools, fresh OM, humus, DOM and microbial biomass. The model also considers manure or slurry to contain a soluble organic component, and this is added to the DOM pool in the uppermost soil layer when manure or slurry are applied. Fluxes between pools occur in a particular way according to physical and biological conditions in the source and destination pools. User settable parameters that influences C and N paths include the assimilation factor (synthesis efficiency constant, f_{se}), the humification fraction (f_h), and the dissolved fraction (f_d). The nitrification rate is estimated on the basis of a specific nitrification rate (k_{nitri}), modified according to the soil ammonium and nitrate contents measured at the beginning of the experiment, temperature, water content and acidity (Wu et al., 2007). SPACSYS, as most published models (Johnsson et al., 1987; Knisel, 1993), use first-order kinetics to describe the denitrification rate.

Other models (e.g SOIL-SOILN, DAISY and DNDC) have defined fast cycling, slow cycling and passive organic matter pools with various names to simulate decomposition and transformation between pools. Additional pools, DOC and DON pools are defined in the SPACSYS model to reflect the contribution of DOM to N and C cycling (Wu et al., 2007), this because DOM is considered to have an important role in N cycling in ecosystems (Murphy et al., 2000; Jones et al., 2004; Cookson et al., 2005).

Observed data of weather, soil property, initial water, C, and N content, and fertilizers were used in the models as input (Table 1). No calibration was carried out for the DNDC model, that was applied to provide a simulation without any parameter optimization, using the default values for all the parameters. For the simulation of soil water dynamics, the characteristics were calculated by the model using the implemented pedotransfer function that run on the soil data reported in Table 1. The temperature and water effect on the C and N related process, the mineralization rates of dissolved litter and humus fraction, and the coefficients involved in the nitrous oxide production operated by the microbial biomass were calibrated for Spacsys model. Maximization of the EF of the agreement between observed (O) and simulated (S) data of soil water content and soil temperature was pursued as the objective function; subsequently, the same was done for data of N₂O and CO₂ emissions.

Parameters	SPACSYS	DNDC
Weather data	X	X
Soil property		
Clay, sand and silt content	X	X
pH value	X	X
SOM EACH LAYERS		(0-5 CM)
tortuosity	X	-
Dry soil bulk density	(g cm ⁻³)	(g cm ⁻³)
Residue water content (vol %)	X	-
Saturated water content (vol %)	X	-
Field capacity	(vol %)	% WFPS
Water content at the wilting point	(vol %)	% WFPS
Saturated conductivity (mm/day)	X	-
Pore distribution index	X	X
Initial water (mm/vol) and temperature status		
Water soil content	X	-
soil temp	X	-
Initial Carbon soil pool:		
Carbon content in humus	(gC m ⁻²)	-
Carbon in DOM	(gC m ⁻²)	fraction
Carbon content in fresh litter derived from plant grown in the field	(gC m ⁻²)	-
Initial Nitrogen soil pool:		
NO ₃ ⁻ content	(gC m ⁻²)	(mg N Kg ⁻¹)
NH ₄ ⁺ content	(gC m ⁻²)	(mg N Kg ⁻¹)
Nitrogen in humus	(gC m ⁻²)	-
Nitrogen in DOM	(gC m ⁻²)	(C/N)
Nitrogen content in fresh litter from plant grown in the field	(gC m ⁻²)	-
Fertilizer property		
amount	Kg	Kg C
Fraction of DOM form from applied nitrogen	X	-
C/N ratio in an organic pool	X	-
C/N ratio in an fresh pool	X	(just for manure)
NO ₃ content	fraction	-
NH ₄ content	fraction	-

Table 1. Summary of input data for the Spacsys and DNDC models application.

3.2.4 Evaluation of the models performance

The match between observed and simulated values of WFPS, CO₂ and N₂O emissions was expressed by the following indexes: the relative root mean squared error (RRMSE), the coefficient of residual mass (CRM), the Pearson correlation (r), and modelling efficiency (EF). RRMSE (Loague and Green, 1991) has a minimum and optimum value at 0. It is a difference-based measure of the model performance in a quadratic form divided by observed mean, being a relative measure of the fitting [1].

$$RRMSE = \sqrt{\frac{\sum_{i=1}^n (S_i - O_i)^2}{n}} \times 100 \quad [1]$$

Positive values of CRM indicate an underestimation of the model outcome, while values close to zero indicate the absence of trends [2].

$$CRM = \frac{\sum_{i=1}^n O_i - \sum_{i=1}^n S_i}{\sum_{i=1}^n O_i} \quad [2]$$

The coefficient of correlation r (Addiscott and Whitmore, 1987) has its optimum value to maximum (+1) values; zero means no correlation [3].

$$r = \frac{\sum_{i=1}^n (O_i - \bar{O})(S_i - \bar{S})}{\sqrt{\sum_{i=1}^n (O_i - \bar{O})^2} \sqrt{\sum_{i=1}^n (S_i - \bar{S})^2}} \quad [3]$$

The slope is an index quantifying the steepness of the linear regression [4].

$$slope = \frac{\sum_{i=1}^n (O_i - \bar{O})(S_i - \bar{S})}{\sum_{i=1}^n (O_i - \bar{O})^2} \quad [4]$$

The EF index (Nash and Sutcliffe, 1970) assumes a maximum and optimum value equal to 1 and it can get either positive or negative values. EF values lower than 0 result from a worse fit than the average of measurements [5].

$$EF = 1 - \frac{\sum_{i=1}^n (S_i - O_i)^2}{\sum_{i=1}^n (O_i - \bar{O})^2} \quad [5]$$

For all the indexes O_i is the i^{th} observed value, S_i is the estimated i^{th} value and n is the number of data pairs. \bar{O} and \bar{S} are the mean of observed and simulated soil water content, respectively.

Moreover the relative deviation (RD) has been evaluated, in order to measures the amount of variability in the model output, and is similar to a coefficient of variation [6].

$$RD = \left(\frac{\sum_{i=1}^n S_i - \sum_{i=1}^n O_i}{\sum_{i=1}^n O_i} \right) \times 100 \quad [6]$$

3.3 Results

The physical and chemical properties of the soil were measured on soil cores taken at different depth of the soil in the lysimeter (Table 2).

During the sampling period the air temperature range was between 6,2 and 25,8 °C (26th Mat 5 2013 at 5 AM and 9th May 2013 at 4 PM respectively), corresponding to the seasonal average temperature with a total amount of 29.49 mm of rain (most rainy day was 29th April 2013; Figure).

We evaluated the results obtained from observed data in order to study the soil CO₂ and N₂O fluxes from lysimeter (Table 3). Both fluxes increased after fertilization event and after rainfalls following different dynamics for different treatments (Figure 3a and 3b).

Concerning the models performance, temporal patterns of observed and DNDC simulated CO₂ fluxes from different fertilization did not match for all of the treatments (Figure 4). DNDC overestimated CO₂ peaks, in particular for compost and ammonium nitrate simulations (CRM= -0.25 and -0.29 respectively; Table4). After fertilization and tillage the simulated patterns showed an increase in carbon decomposition and soil respiration. Due to these peaks DNDC estimation was significantly different from observed data showing RD fitting values from 1.45% (control) to 30.09% (compost). During the following days of sampling after fertilization data obtained with DNDC showed a slight decrease in term of CO₂ emission but no response to rainfall events was simulated by DNDC. DNDC simulations resulted in higher CO₂ fluxes compared with measured ones (Figure 4), in particular for ammonium nitrate and compost simulations, which correspond to a relative deviation of 25.21 and 30.09% respectively from measured flux. In Figure 7 and Figure 8 is illustrated a linear regression between observed and modeled data, showing a low correlation of data (R²) of 0.29 for ammonium nitrate simulation (RMSE= 0.29;) and 0.30 for compost (RMSE= 0.38). Simulations for digestate and for control plot better agreed with measured data. In these cases peaks observed after fertilization were in agreement with measured data, (CRM= -0.1 and 0.01 respectively), but positive CRM values of control simulation indicates under-estimation against measured values. In the control pattern, after a first peak due to tillage, a second peak was measured after rainfall that DNDC did not simulate (Figure. 4).

BD	Clay	Silt	Sand	pH	SOC	SOM	N	NO ₃ ⁻	DOC	DON
(g/cm ³)	(%)	(%)	(%)		(g/Kg)	(%)	(g/Kg)	(mg/l)	(g/Kg)	(g/Kg)
1,02 ±	27,85	57,5	14,65	7,8	26,11 ±	4,5 ±	2,54 ±	13,84 ±	0,12 ±	0,02 ±
0,11					1,57	0,27	0,16	1,52	0,06	0,001

Table 2: Soil physical and chemical properties used for models input (0-30 depth.)

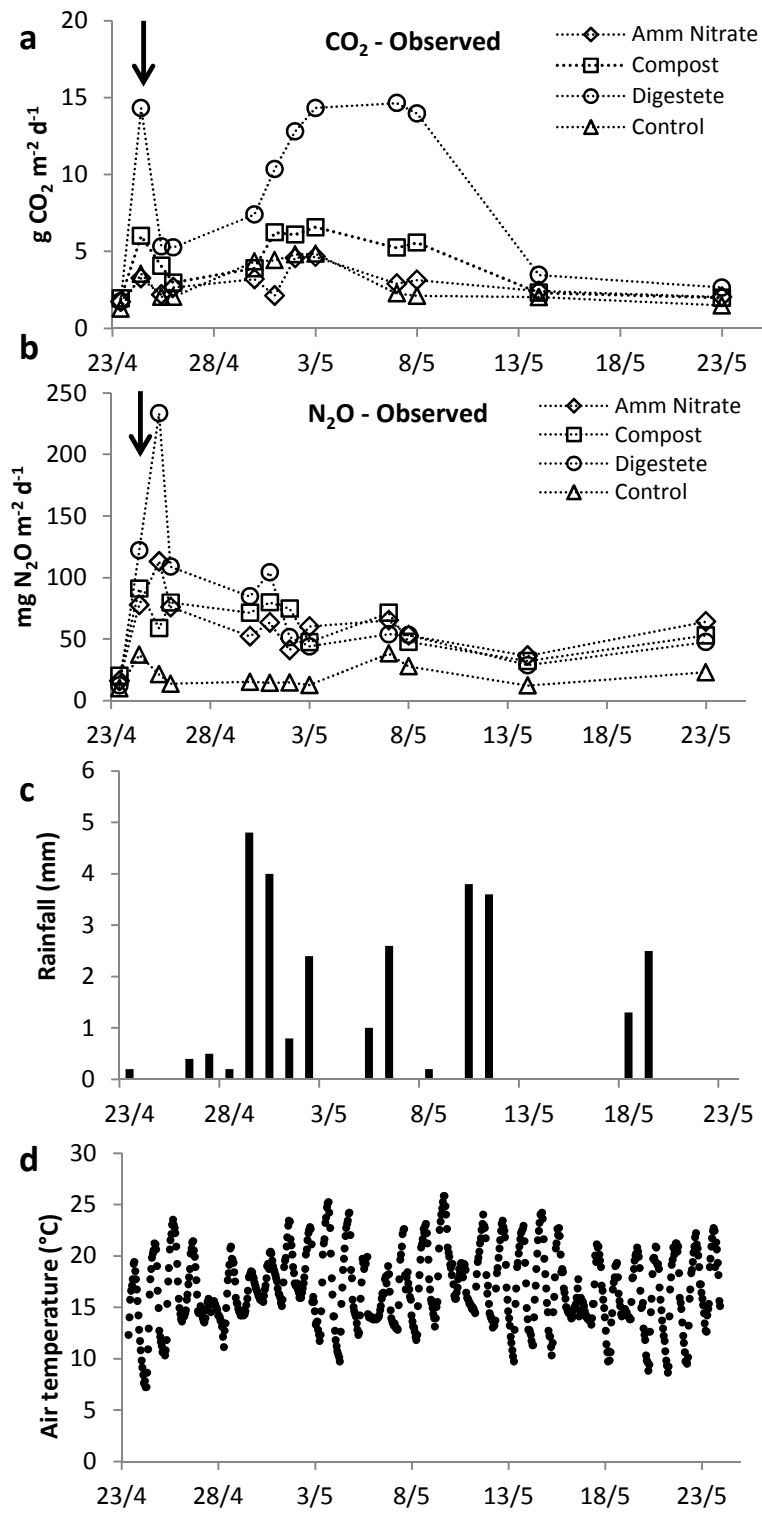


Figure 3: Observed carbon dioxide and nitrous oxide fluxes (a and b), measured precipitation (c) and hourly temperature measured from different lysimeter.

Results of SPACSYS CO₂ simulation showed an overestimation in two cases, compost (CRM= -0.08) and digestate (CRM = -0.46), while for ammonium nitrate and control the trend appeared to be opposite with values of CRM index very close to 0 (CRM = 0.16 and 0.11 respectively) (Table4).

Treatment	CO ₂		N ₂ O	
	Average flux	Standard deviation	Average flux	Standard deviation
	(g CO ₂ m ⁻² d ⁻¹)		(mg N ₂ O m ⁻² d ⁻¹)	
Ammonium nitrate	2.76 ^a	0.90	61.60 ^{ab}	53.49
Compost	4.25 ^{ab}	1.78	59.24 ^a	24.78
Controll	5.63 ^b	4.85	50.87 ^a	30.05
Digestate	8.50 ^c	5.40	81.19 ^b	61.53

Table 3: Soil CO₂ and N₂O fluxes from different treatments. Values with different letters for the same column are significantly different from each other (P <0.05).

	CO ₂							
	DNDC				SPACSYS			
	Amm Nitrate	Compost	Control	Digestate	Amm Nitrate	Compost	Control	Digestate
RRMSE	32.77	36.83	18.58	21.71	24.84	30.05	25.36	115.89
RD (%)	25.21	30.09	1.45	11.62	-0.11	8.92	-5.78	19.84
r	0.53	0.54	0.6	0.67	0.66	0.66	0.82	0.84
EF	-4.09	-2.95	0.34	0.17	0.12	0.39	0.58	0.43
CRM	-0.25	-0.29	0.01	-0.10	0.16	-0.08	0.11	-0.46

Table 4. Model accuracy indices for DNDC and SPACSYS simulation against observed data for fluxes of CO₂.

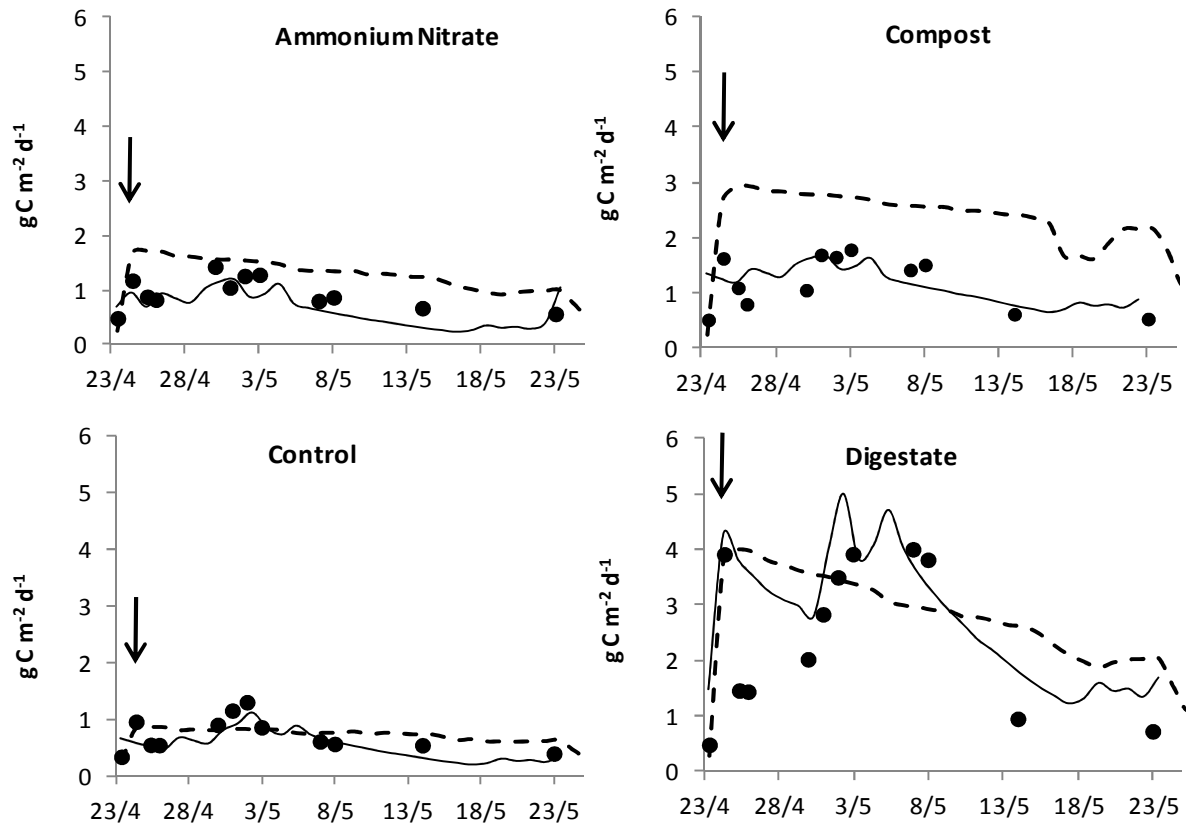


Figure 4: Comparison of DNDC (dashed curve), SPACSYS (solid curve) and measured (black point) CO₂ fluxes from different treatments and control. Arrow show time of fertilizer application and tillage.

N₂O fluxes simulated by DNDC (Figure 5) were significantly lower than observed data, and CRM values confirmed how DNDC model also underestimated the emission from soil (Table 5). The regression between observed and modelled fluxes accounted for 38, 40, 5 and 59% of the variation in the data (RRMSE= 43.92, 36.48, 59.47 and 35.24 respectively; Table) respectively for ammonium nitrate, compost, control and digestate (Figure 9, Figure 10). DNDC predicted a N₂O peak on the second day (after fertilization) with higher values compared with the observed data for ammonium nitrate and digestate plot, while compost and control show lower values of emission. In fact the model performed poorly for all simulation with a RD index of (-34.66%, 34.07%, -51.67% and -30.30% respectively for ammonium nitrate, compost, control and digestate. SPACSYS N₂O simulations agreed well with the measurements data (Figure 5; Table 5), showing the lowest value for the control plot (CRM= 0.19), and the highest for the digestate thesis (CRM= 0.47) (Table 5). SPACSYS predicted significantly higher peaks after fertilization for all the simulations in accordance with observed data, and predicted accurately the trend of the following days. EF index showed positive values for all simulations done with minimum for ammonium nitrate (0.12) and maximum for the control plot (0.58), indicating a good performance of the model.

N₂O

	DNDC				SPACSYS			
	Amm Nitrate	Compost	Control	Digestate	Amm Nitrate	Compost	Control	Digestate
RRMSE	43.92	36.48	59.47	35.24	47.84	65.86	95.72	152.87
RD (%)	-34.66	-34.07	-51.67	-30.30	1.21	4.27	3.49	-8.92
r	0.62	0.63	0.22	0.77	0.82	0.55	0.58	0.71
EF	-22.59	-19.56	-31.25	-5.49	0.73	0.70	0.57	0.55
CRM	0.33	0.34	0.52	0.29	0.28	0.20	0.19	0.47

Table 5: Indices model accuracy for DNDC and SPACSYS simulation against observed data for fluxes of N₂O.

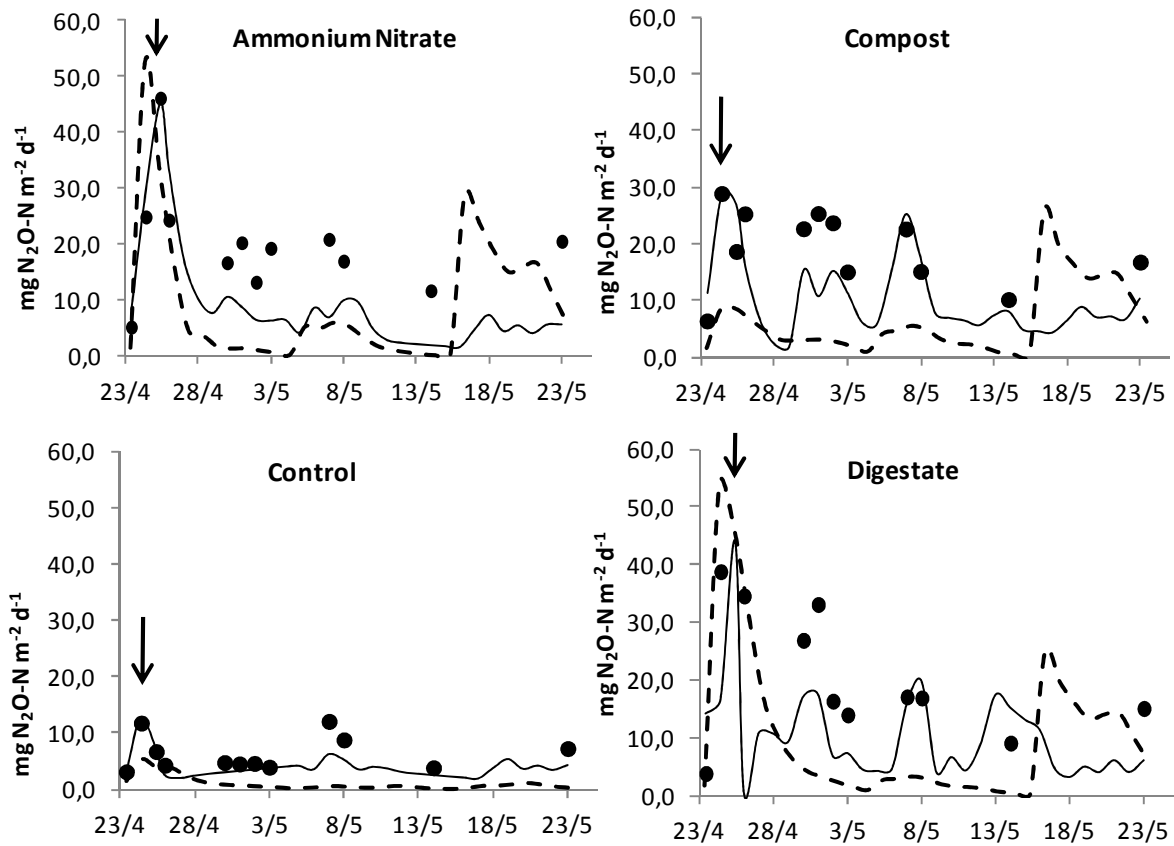


Figure 5: Comparison of DNDC (dashed curve), SPACSYS (solid curve) and measured (black point) N₂O fluxes from different treatments and control. Arrow show time of fertilizer application and tillage.

The WFPS is a controlling variable and its prediction is crucial for a reliable simulation of gas emission flux from soil in particular for N₂O. Increasing this parameter may reduce the contribution of nitrification and increase denitrification (Dobbie and Smith, 2001). DNDC model overestimated WFPS by 27%, while SPACSYS predicted more accurately this parameter showing fitting index values very close to the optimum value (Figure 6 and Table 6).

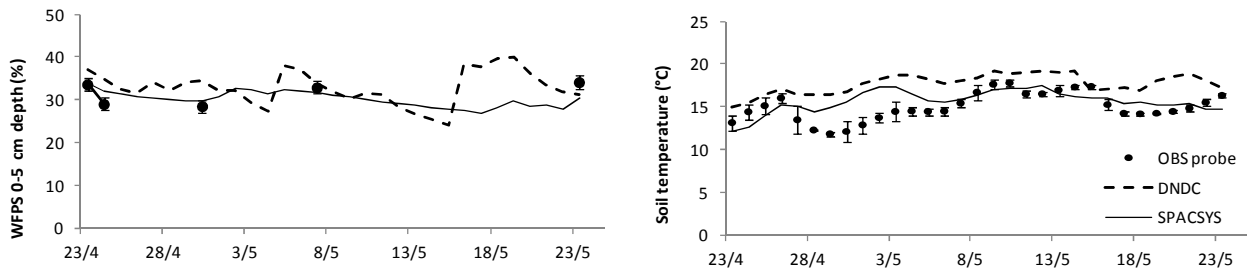


Figure 6: Comparison between the simulated WFPS and soil temperature by DNDC (dashed curve), SPACSYS (solid curve) and measured (black point). Error bars for measured values are \pm standard error.

	Soil temperature		WFPS	
	DNDC	SPACSYS	DNDC	SPACSYS
RRMSE	5,82	3,30	1,53	0,83
RD (%)	153,61	10,35	11.82	3.01
R	0,65	0,59	0,22	0,4
EF	-0,84	0,33	1.00	1.00
CRM	-0,04	0,00	-0,01	0.00

Table 6: Model accuracy indices for DNDC and SPACSYS simulation against observed data for soil temperature and WFPS.

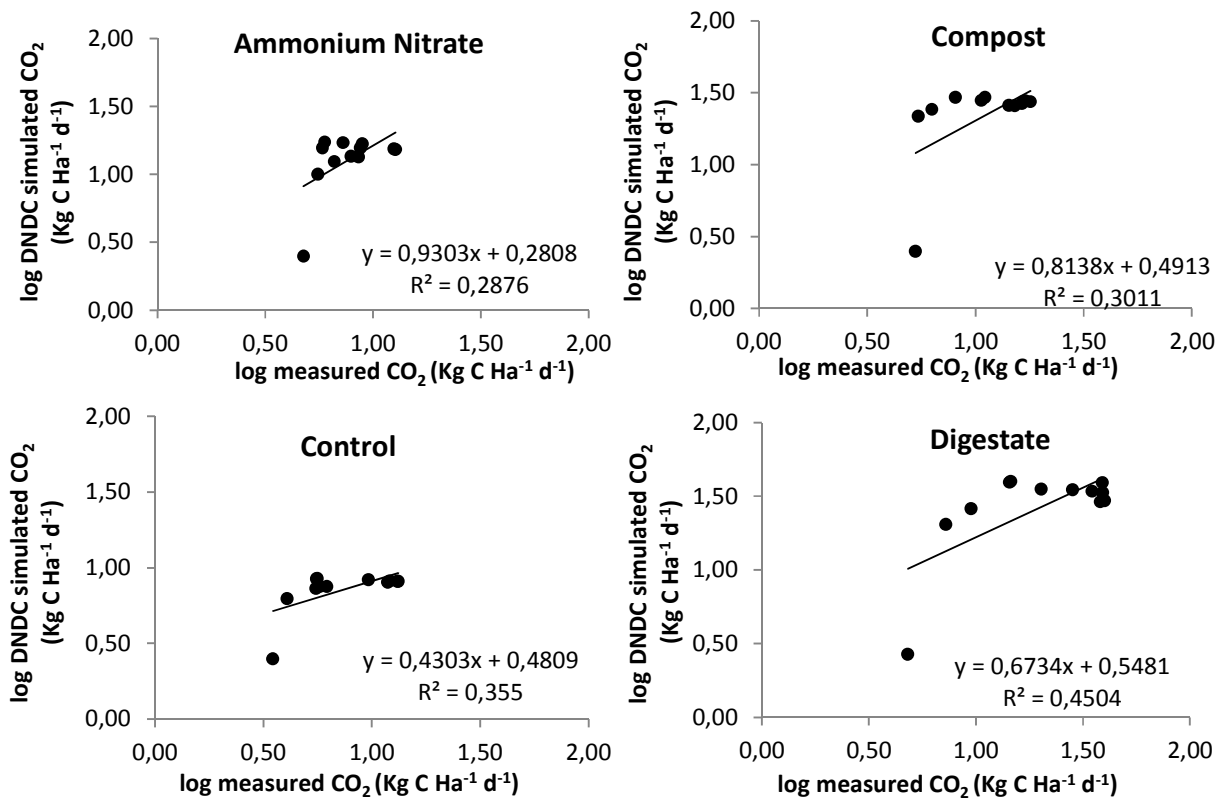


Figure 7: Correlation between the DNDC model simulated and measured CO₂ fluxes from lysimeter.

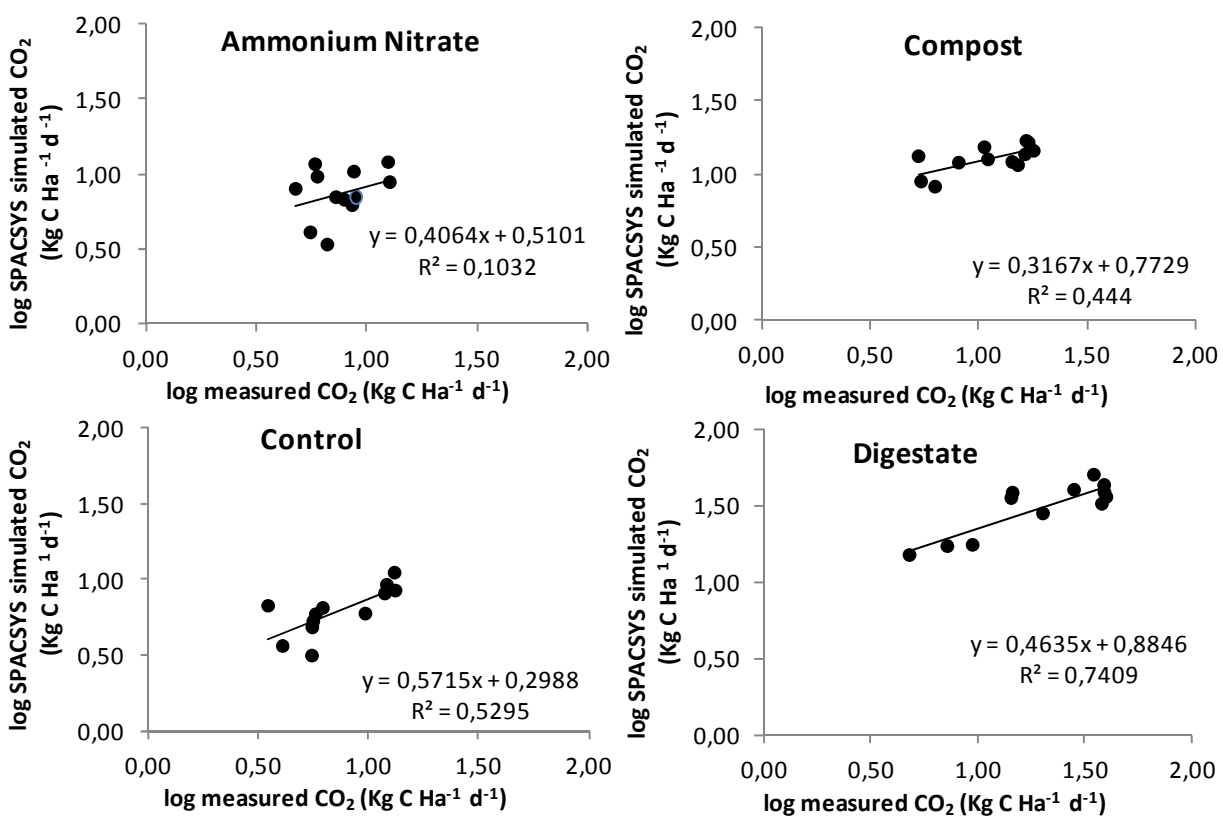


Figure 8: Correlation between the SPACSYS model simulated and measured CO₂ fluxes from lysimeter

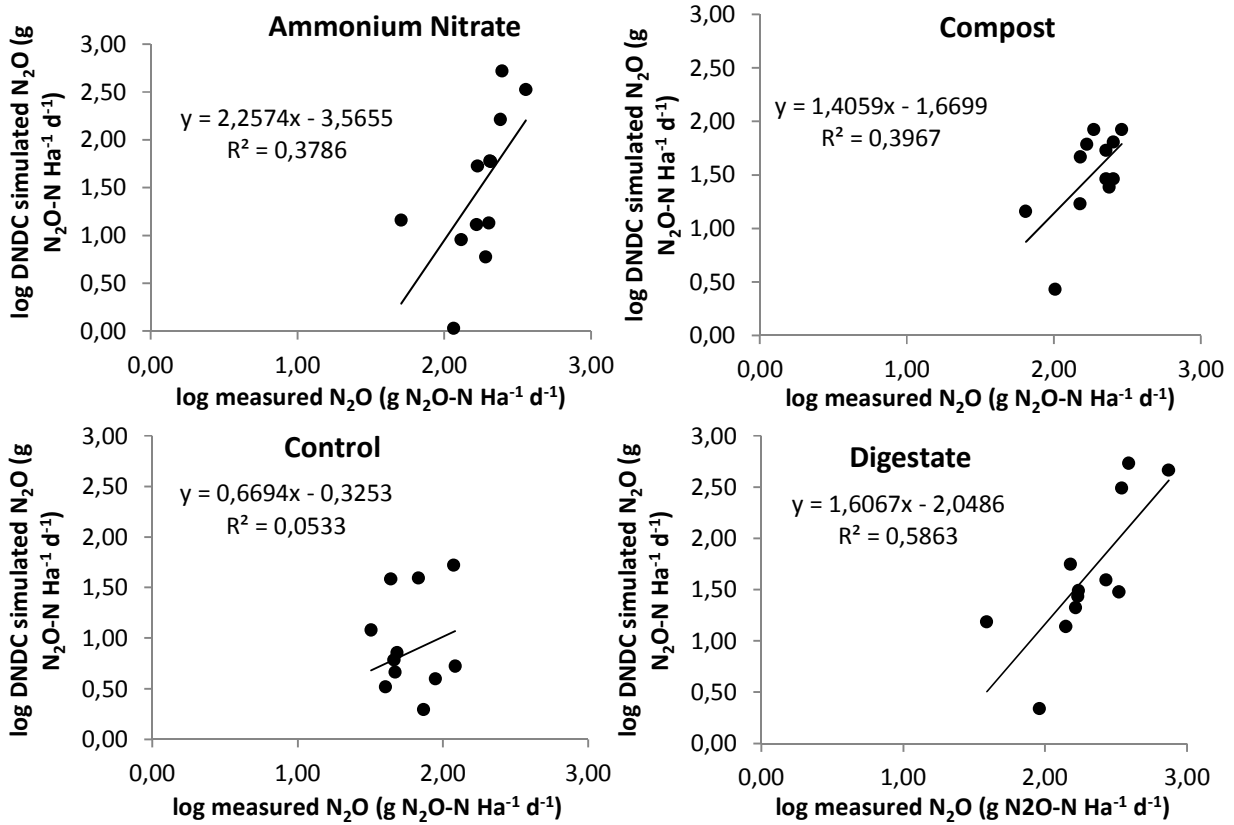


Figure 9: Correlation between the DNDC model simulated and measured N₂O fluxes from lysimeter

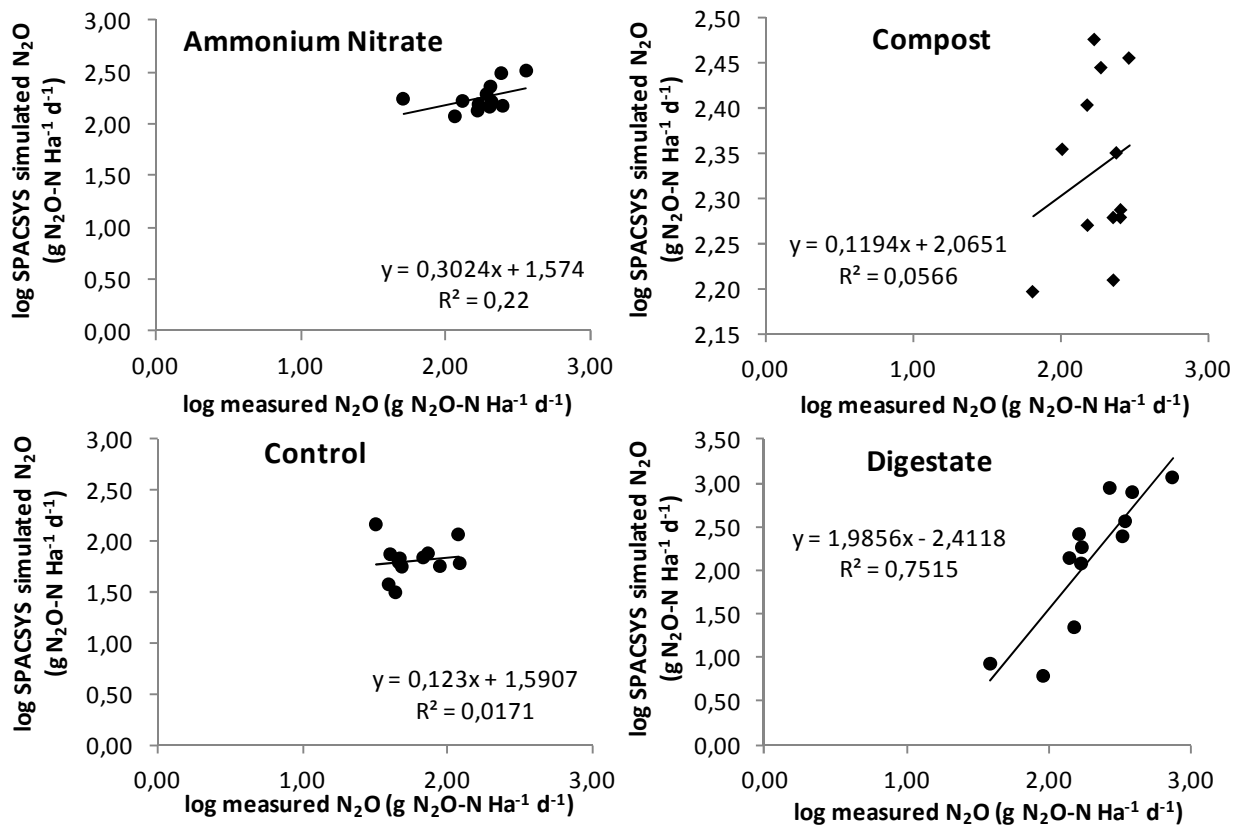


Figure 10: Correlation between the SPACSYS model simulated and measured N₂O fluxes from lysimeter

3.4 Discussion

Over the 1-month monitoring period, temporal patterns of CO₂ and N₂O flux (

Treatment	CO ₂		N ₂ O	
	Average flux	Standard deviation	Average flux	Standard deviation
	(g CO ₂ m ⁻² d ⁻¹)		(mg N ₂ O m ⁻² d ⁻¹)	
Ammonium nitrate	2.76a	0.90	61.60ab	53.49
Compost	4.25ab	1.78	59.24a	24.78
Controll	5.63b	4.85	50.87a	30.05
Digestate	8.50c	5.40	81.19b	61.53

Table3 showed significant differences ($P < 0.001$) between the three treatments and the control, with the digestate treatment producing higher fluxes of CO₂ and N₂O; this could be attributed to the rapid depletion of easily mineralizable carbon and to the release of CO₂ dissolved in the digestate (Fangueiro et al., 2010; Bol et al., 2010). As reported by Chadwick et al. (2000) the application of liquid manure to the soil enhances soil conditions providing a source of nitrogen, adding easy degradable C and water, factors that have a role on stimulating N₂O emission from soil. Concerning the CO₂ emissions, the DNDC model fitting indexes were not similar for the most of the scenarios of fertilization, and that was likely due to the overestimation of CO₂ peaks, in particular for compost and ammonium nitrate simulations after the fertilization event. The simulated CO₂ emissions were higher than observed data, overestimating the fluxes in three scenarios (ammonium nitrate, digestate and compost). Similar overestimates of the effects of CO₂ emission by DNDC were also reported by Li et al. (1992), Brown et al. (2002) and Hsieh et al. (2005). Rainfall occurring after distribution of fertilizer caused an increase of N₂O fluxes but DNDC poorly simulated such gas peaks (Figure 5). The discrepancies observed in DNDC simulation could be related to insufficient of input data and caused by default parameter. In particular, for compost and digestate simulations it was possible to use as input only the total amount of manure, the C:N ratio and the amount of N (Kg h⁻¹). It is well know that the characteristics of some fertilization vary in particular in term of different N fractions (Bertora et al., 2008;), which could contribute to the discrepancies between observed and modeled gas emissions. These differences has been reported in other studies where observed and DNDC simulated data has been compared (Cai et al, 2003). DNDC model overestimated the measured WFPS that may result in significant flux discrepancies between the measured and modelled data, since WFPS is one of the main controlling variables on N₂O emissions (Keller and Reiners, 1994; Dobbie and Smith, 2001, Abdalla et al, 2009). Ludwig et al. (2011) reported the results of DNDC applications to predict N₂O emissions from sandy soil, whereby they employed the same approach adopted in the present study and they found out that the WFPS prediction was poor, obtaining a mean value of 12% when the observed mean was 32% (mean

overestimation=63%). In our application, the discrepancies on WFPS were smaller (simulated=55% vs observed=40%; mean overestimation=27%).

Temporal CO₂ emission were well simulated by SPACSYS model in all the scenarios, showing patterns nearest to field measured fluxes. The model seems to underestimate the flux on the day of fertilization despite the similar pattern of fluxes. This could be attributed at the high degree of precision which is required on the model input data, in term of soil (C and N pool), fertilizer properties (Table 1). A very small variation of the data (soil organic content, microbial biomass, water content) could determine a different effect in term of gas emission.

SPACSYS predicted better than DNDC the daily variations of fluxes during the whole period, considering also the CO₂ and N₂O peaks due to rainfall events. Considering all the examined aspects, SPACSYS well simulated trace gas emission (CO₂ and N₂O) and soil condition (temperature and WFPS). This could be due to an accurate parameterization that was carried out in particular for the hydraulic characteristics.

The short-term simulations carried out in this experiment demonstrated how different model structures and accurate parameters setting may be needful in order to reproducing the observed soil flux behavior.

In our analysis DNDC model performance was poor and it did not lead to a clear understanding of carbon and nitrogen emission from soil, despite its user-friendly feature.

The mechanistic model SPACSYS allowed for a parametrization that can be carried out on the basis of the field observation and literature review parameters. Therefore, although SPACSYS model needs to be parameterized for application in different soil types, the model application resulted in a well agreement pattern of emissions match with measured data.

3.5 Conclusion

Even though it is difficult to develop simple empirical models that can adequately predict greenhouse gas emissions over a range of different soil conditions and management practices, the present work confirmed that only a good parameterization of a process-based models allows for a reliable prediction of fluxes. Theoretically process-based model should be able to well simulate seasonal variation pattern better than that daily step, but in our case DNDC could not satisfactorily simulated patterns in a short time period and more adjustment are required to obtain accurately predict emissions.

SPACSYS predicted both CO₂ and N₂O fluxes, soil temperature and WFPS with better agreement with observed data for all the examined treatments. The parameterization of the fertilizer related parameters leads to a better prediction of the fertilizer C and N pathways in the soil.

Although further improvements are possible, the SPACSYS model effectively estimated CO₂ and N₂O fluxes and its performance was better than DNDC model. These results suggest that expert users may obtain reliable results predicting GHG emission by improving the parameterization of model through observed data and deep knowledge of the implemented algorithms.

3.6 References

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4. Field evaluation combined to modelling analysis to study fertilizer and tillage as factors affecting N₂O and CO₂ emissions: a case study in Po valley (Northern Italy)

4.1 Introduction

Arable soils are the main anthropogenic source of nitrous oxide (N₂O), that is one of the major greenhouse gas that has a Global Warming Potential (GWP) that is about 296 times larger than that of CO₂ (IPCC, 2007). The magnitude of soil gas emissions is strictly related to mineral fertilizer-N and manure distribution (Fowler et al., 2014), with soil N₂O emissions that are particularly relevant in over-fertilized systems (Shcherbak et al., 2014).

The Po valley (Northern Italy) is characterized by intensive cropping systems where high N inputs often result in nutrient surplus (Acutis et al., 2014); recent studies providing estimates of N surplus at European scale highlighted that Po valley is one of the highest exceeding N areas (>30 kg N ha⁻¹, EEA 2010) along with The Netherlands, North Western France, Western United kingdom and Ireland. The intensive systems of the Po valley offer an ideal case study to estimate the actual magnitude of the N₂O fluxes from soil fertilizer application. According to farmers practices, mineral and manure N fertilizers are both commonly used for winter and summer crops at a high rate (200-500 kg N ha⁻¹y⁻¹; Perego et al., 2013). The emissions of N₂O derived from mineral and organic fertilization were studied by several authors worldwide (Carter et al., 2012; Pelster et al., 2011; Rees et al., 2013; Nyamadzawo et al., 2014; Yonemura et al., 2014; Snyder et al., 2014; Bayer et al., 2015). The effect of tillage on N₂O emissions was also investigated: reduced tillage has been recognized as a practice that enhances the N₂O emissions because of higher soil compaction and larger soil water content and in turn lower O₂ diffusion and anaerobic processes which lead to N gas emissions (Rochette et al., 2008; Regina and Alakukku et al., 2010), especially in the short term period (Six et al., 2004).

Available works, however, do not provide data on N₂O emissions from comparable pedoclimatic conditions and management practices to those of Po Valley. The aim of the present work was to compare the actual field N₂O emissions from manures frequently used in the Po valley (i.e. cattle slurry and digestate from biogas production), compost, and mineral N fertilizer (i.e. ammonium nitrate) in conventional tillage (CT) and minimum tillage (MT) under a crop rotation with winter and summer biomass crops. Data were measured during four field monitoring over a 2-year experiment.

Together with N₂O emissions, carbon dioxide (CO₂) fluxes were also measured to test the effectiveness of minimum tillage to reduce carbon (C) emissions, as reported by several authors (Freibauer et al., 2004; Lal, 2004; Oorts et al., 2007; Ogle et al., 2012). This practice has been considered as an effective way for C sequestration and it has been recently promoted by policymakers in Europe (Regulations 74/2009/CE) and in various Italian regions among which Emilia-Romagna (Rural Development Programme, 2015), where our

experiment was set up. Farmers of this region have been approaching to conservation agriculture and evidences of its impact on gas emissions in our pedoclimatic conditions are needed. The aims of this work is have higher knowledge about soil CO₂ and N₂O emissions from different combination of organic and mineral fertilizers and tillage in a dairy farm applying all the knowledge acquired from experimental trials on a field case study (Gas-Off LIFE+ Project).

4.2 Material and methods

4.2.1 Case study

The field trial was carried out from May 2011 to September 2013 at Vittorio Tadini Experimental Station (44° 58' N 9° 41' E; 118 m a.s.l.) in Gariga di Podenzano (Piacenza), located in Po valley. The rainfall recorded by the meteorological station placed at the experiment site was 439, 590, and 354 mm, respectively in 2011 from May to December, in 2012, and in 2013 from January to September; the mean annual temperature was 14.9°C (Figure 1). The soil is a Chromic Luvisol, with a silt loamy texture (sand 12%, silt 64%, and clay 24%) in the upper layer (0-30 cm), according to soil taxonomy (FAO, 2006). The soil has a low percentage of carbonates, a subacid to neutral pH (6.9) and the CEC is 14.9 meq/100 g.

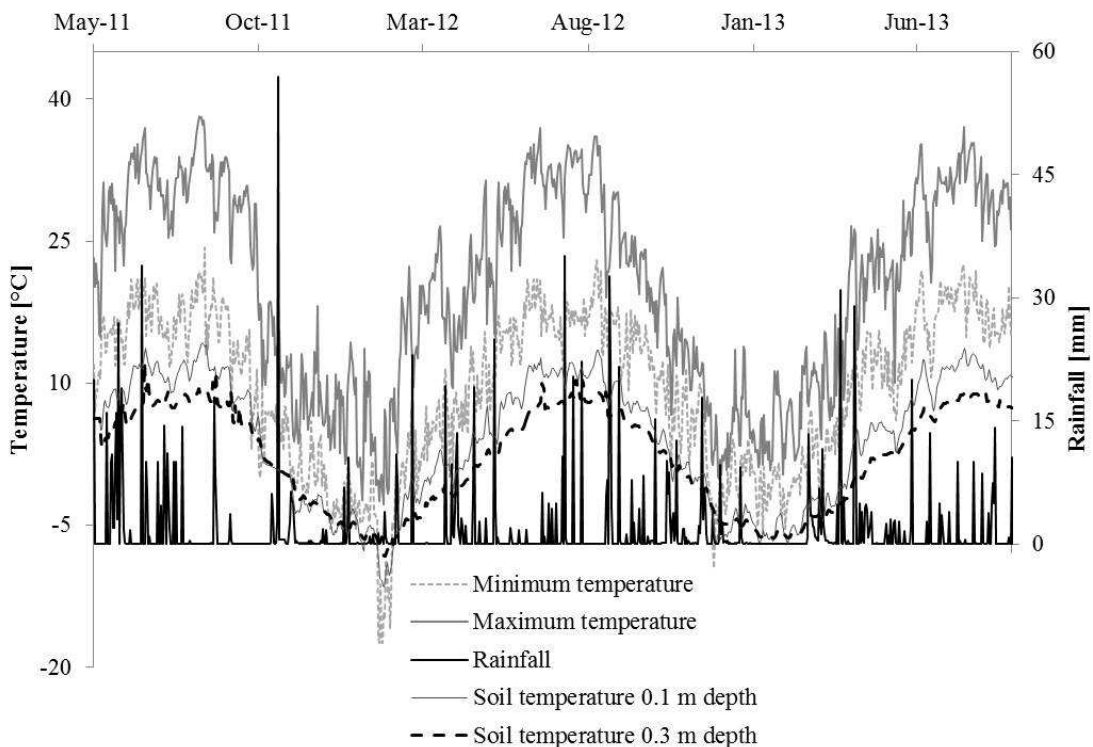


Figure 1: Air and soil Temperature (left axis) and rainfall (right axis)

4.2.2 Experimental design

The field experiment was conducted in a crop rotation comprising both summer and winter crops: fiber sorghum (*Sorghum bicolor* L. Moench), Italian ryegrass (*Lolium multiflorum* Lam.), maize for silage (*Zea mays* L.), barley (*Hordeum vulgare* L.), and sweet sorghum. Plant biomass was mainly used to feed the biogas plant.

The trial was set up in 1 ha field that was split into five 2000 m² plots, on which four fertilizers were applied (compost, digestate, liquid slurry, and ammonium nitrate) and one was left unfertilized as a control. The N rate was defined according to the crops demand and it was equal for all the fertilizers (Table 1). Overall, the contribution of N as ammonium (NH₄-N) on the total applied N was 47%, 39 %, 18 %, and 50 %, respectively in slurry, compost, digestate, and ammonium nitrate. For the winter crops, organic fertilization was applied immediately before soil tillage (early October) at a rate that depended on fertilizer type: the entire amount for compost and half dose for liquid manure and digestate, while no mineral fertilization was carried out. The total amount of mineral fertilizer was applied at the winter end when the remaining dose of digestate and liquid manure was spread. For the summer crops, the entire amount of organic fertilizer was spread prior to soil tillage along with 50% of mineral fertilizer (generally in May). The additional 50% was applied as sidedress when crops were at V6 stage.

Each plot was further split into two subplots where conventional tillage (CT) and minimum tillage (MT) were respectively carried out. Soil tillage was performed in spring and in autumn. In the CT thesis, soil was ploughed at 35 cm depth, and it was subsequently tilled with a harrow for seedbed preparation, while for the MT thesis seedbed was prepared with a single passage of a combined ripper and rotating hoe machine that tilled only the upper 10 cm of soil.

Harvesting and sowing dates were influenced by weather condition, generally winter crops were sown in September or October and harvested in May, while spring-summer crops were seeded in May and harvested in September or October (Table 1). Four to nine events of sprinkler irrigation occurred in summer to avoid water stress; in each event irrigation water ranged between 15 to 40 mm (Table 1).

Soil water content was measured throughout the course of the experiment using soil moisture sensors (Spectrum technology SM100 Waterscout) connected to a weather station (WatchDog, Spectrum technology) and placed at 0.1 m (CT) and 1.15 m(MT) of depth in the soil.

4.2.3 Sampling and analysis of gases

The N₂O and CO₂ emission was measured was measured with SASSFlux (Static Automatic Sampler for Soil FLUX measurement developed by Ecometrics, a spin-off of Università Cattolica del Sacro Cuore of Brescia) using automatic chambers (base-lid type of 20 l volume) that are automatically (by motors controlled by a computer) closed over a metal collar (35x35 cm basal area and 7 cm height) that bounds the soil surface (inserted into the soil to a depth of 5 cm), which were placed in each of the subplots, between the soil spaces of two lines of plants (summer crop) or removing them (winter crop), where the combined effect of

different fertilizer and tillage was evaluated. A small fan was installed under the lid to ensure adequate mixing of air within the chamber. When the chamber is closed (about 180 seconds) a 3 l min⁻¹ membrane pump takes an air sample and directs it (through a Teflon tube) to the control unit that contains an Infrared Gas Analyzer (IRGA Carbocap 343, Vaisala, SF) which is used to measure CO₂ concentration, while a rotative gas-filter photometer (IRGA T320U, Teledyne, CA) measures N₂O concentration. A dedicated software manages data acquisition, the control of chambers' opening and closure, air sampling time, and chambers' "washing out" (settling time) time to allow gas concentration to return to environmental values before each new sampling.

Soil CO₂ and N₂O flux were calculated as the quantity of gas that pass through a unit of volume per unit time and it can be represented as the scalar variation on time (dCO₂/dt) related to chamber volume (V) and area of soil surface (A) as described in the following formula

$$F_{\chi} = \frac{d\chi}{dt} \frac{P V}{R T A} \quad [1]$$

where P is the atmospheric pressure, T is the temperature and R is the universal gas constant. For the previously explained reasons, the zero-time (dCO₂/dt) value is needed.

Flux calculation has been carried out using a tool developed by Ecometrics for the treatment of the SASSFLUX data. This software calculates the fluxes using a linear regression on the data collected in the first 70 seconds after the lid closure (one datum per second), taking into account chamber temperature and air pressure. This approach has been demonstrated to be efficient and well correlated with the HMR approach (R²=0.91, Flux70s=1.12*FluxHMR +0.027, paper in preparation). A rotation of the chambers, more frequently after fertilization (every 3 hours) reducing the frequency over the days (till once a week after 4 week), allowed us to collect data from all thesis available. This could be possible installing one collar for each plot in order to avoid any soil disturbance, moving only the lid and its automation.

4.2.4 Lysimeter trial

In order to test the reliability of the approach that was adopted in the field experiment, a lysimeter trial was set up in which N₂O and CO₂ fluxes were measured with SASSFlux (Static Automatic Sampler for Soil FLUX measurement) from 23th April to 23th May 2013, after the four fertilizers (compost, digestate, liquid slurry, and ammonium nitrate) application. For this purpose, eight lysimeters of polyethylene (HDPE) with a cross section area of 1 m² and a height of 0.5 m were placed at the experimental site; they were loaded with a repacked silt-loam soil and the four fertilizers were applied at a rate of 100 kg N ha⁻¹. One lysimeter was not fertilised and it was used as a control. Soil water content was measured sampling 0.1 m depth soil cores five times over the trial period. Soil temperature was measured in one lysimeter. The gas emissions were measured using conventional static chambers (PVC ring 0.4 m diameter X 0.3 m height) and a

cylindrical stainless steel frame (0.45 m diameter X 0.2 m height) placed into the lysimeter. All of the measurements were executed following the procedure employed in the field experiment. For calculating GHG flux, in that case; the concentration data were analyzed by using the HMR package of R software. The HMR function analyses the data series sequentially, and starts each analysis by fitting the nonlinear function (Hutchinson and Mosier, 1981):

$$C_t = \varphi + f_0 e^{-kt} \quad [2]$$

using a single-parameter (k) criterion (concentrated least squares; Seber and Wild, 1989). In this equation, f_0 denotes the initial flux, φ denotes the new chamber equilibrium concentration, and $K > 0$ is an adaption rate that depends on soil, gas, and chamber characteristics.

Table 1: Data on field management. Conventional tillage (CT) consisted in ploughing at 0.35 depth and harrowing, while minimum tillage (MT) was executed by a ripper and rotating how machine at 0.15 cm depth. In brackets, the C%, N%, C:N, and ammonium-N:total N of the manure (% fresh matter weight); the N% in ammonium nitrate is 27%. In ammonium nitrate, NO₃-N contributed to the remaining 50% of the total N content. ± mean standard error. * In 2013, sorghum biomass was significantly higher in CT than in MT, while no differences were observed for the other crops.

Crop	Operation	Date	Fertilizers kg N ha ⁻¹				Irrigation mm	Aboveground Biomass Mg DM ha ⁻¹	
			Compost	Digestate	Slurry	Amm. Nitrate*		CT	MT
Sorghum	Fertilization, Tillage	30/05/2011	340 (5.7,1.5,4,2)	100 (1.3,0.2,7,44)	100 (1.7,0.2,5,54)	50			
	Sowing	31/05/2011							
	Spraying	17/06/2011							
	Irrigation	27/06/2011					18		
	Fertilization, Row weedir	29/06/2011				50			
	Irrigation	02/08/2011					35		
	Irrigation	10/08/2011					35		
	Irrigation	02/09/2011					40		
	Harvesting	20/09/2011					10.2±1.4	12.5±1.9	
It. Ryegrass	Fertilization, Tillage	18/10/2011	170 (8,1.6,5,1)	50 (0.8,0.2,4,49)	50 (0.6,0.3,2,47)				
	Sowing	21/10/2011							
	Fertilization	21/03/2012		50 (1.0,2,5,45)	50 (1.6,0.3,6,47)	100			
	Harvesting	10/05/2012					7.8±0.7	7.5±0.6	
Maize	Fertilization, Tillage	24/05/2012	340 (10,1.4,7,1)	150 (1.2,0.3,4,56)	150 (3.3, 0.3,10,41)	60			
	Sowing	28/05/2012							
	Irrigation	31/05/2012					30		
	Irrigation	11/06/2012					15		
	Irrigation	18/06/2012					20		
	Spraying	22/06/2012							
	Fertilization, Row weedir	26/06/2012				90			
	Irrigation	03/07/2012					35		
	Irrigation	13/07/2012					40		
	Irrigation	24/07/2012					35		
	Irrigation	01/08/2012					30		
Irrigation	08/08/2012					30			
Irrigation	17/08/2012					40			
	Harvesting	28/08/2012					11.0±0.6	9.9±1.1	
Barley	Fertilization	22/10/2012	170 (7,1.6,4,4)	25 (0.4,0.2,2,34)	30 (0.7,0.3,2,85)				
	Tillage, Sowing	23/10/2012							
	Fertilization	17/04/2013		75 (1.0,2,4,37)	70 (1.5,0.3,6,53)	100			
	Harvesting	05/06/2013					1.9±1.1	11.8±0.8	
Sorghum	Fertilization, Tillage	11/06/2013	340 (8,1.6,5,2)	100 (1.3,0.3,5,48)	100 (2.5,0.3,8,44)				
	Sowing	20/06/2013							
	Irrigation	22/06/2013					22		
	Irrigation	27/06/2013				10	20		
	Irrigation	02/07/2013					22		
	Spraying	02/07/2013							
	Irrigation	15/07/2013					22		
	Fertilization, Row weedir	18/07/2013							
	Irrigation	21/07/2013					30		
	Irrigation	08/08/2013					30		
	Irrigation	14/08/2013					30		
	Harvesting	18/09/2013					15.4 ±1.2*	11.9± 1.2*	

4.2.5 Model description

The Spacsys simulation model was run to predict the cumulative flux of N₂O and CO₂ for the whole experimental period under the different organic fertilizers and ammonium nitrate application. The model validation was performed using the measured data during the field monitoring, while the calibration was run over the data set gathered in the lysimeter trial.

Spacsys is a multi-dimensional, field scale, weather-driven dynamic simulation model of C and N cycling between plants, soils and microbes, which operate with a daily time-step. It includes a plant growth and development sub-model with detailed representation of the root system, in addition to sub-models for C and N cycling in the soil with links to the plant, a soil-water component, and a heat transfer component. C and N are held in a number of aboveground and below-ground pools, and flows between pools are simulated. The representation of soil C and N processes is similar to that in a number of existing models, which were reviewed by Wu and McGechan (1998a) and McGechan and Wu (2001), but there is more detail in relation to nutrient cycling from decaying root material (Wu et al., 2007). Within Spacsys simulation, N₂O is emitted during nitrification and denitrification. The latter is simulated alternatively through a simplified estimation of denitrification rate and an approach based on microbial activity. According to the microbiological processes, which is the one that was used in the present analysis, denitrifying activity of microbial biomass is highly correlated with water-extractable organic C. The reactions of the denitrification process are defined by competitive Michaelis-Menten type kinetics. Each reduction involved in the denitrification process is quantitatively described as a function of microbial denitrifiers growth that is in turn calculated on the basis of the response function to dissolved organic C content, acidity, temperature, water-filled pore space content (Davidson, 1991; Reth et al., 2005), and concentrations of nitrous oxides (i.e. NO⁻³, NO⁻², NO, and N₂O) (Wu et al., 2007).

Nitrification rate is estimated based on ammonium and nitrate contents in the soil, soil temperature and moisture, and soil acidity. Nitrification-induced N₂O is a fraction of nitrification rate. Following the DNDC model (Li, 2000), N₂O production is estimated with temperature and nitrification rate. Gas emission rates are proportional to NO, N₂O and N₂ contents near the soil surface and adjusted by a reduction function which depends on soil gas diffusion rate, that in turn depends on air-filled porosity, soil temperature and soil texture.

CO₂ emissions from soil are simulated as response of both microbial respiration of soil organic matter and roots. The C release from microbial pool because of microbe respiration is linked with the pool size of microbial biomass, microbial maintenance respiration rate and response function to temperature and soil moisture. Root respiration, as well as that of the whole plant, is divided into two parts: growth respiration and maintenance respiration. The first part is taken account when daily net photosynthesis is estimated. The latter is estimated with Q₁₀ expression, being a function of air temperature. The calibration of the model parameters was carried out in two steps for water and then nitrogen fluxes; according to a trial-and-

error approach the soil water retention and conductivity functions were calibrated for the van Genuchten–Mualem parameters θ_s , n , α and for K_s in the two layers at 0.1 and 0.2 m depth, for which the data of soil water content were measured. Then the temperature and water effect on the C and N related process were calibrated. The mineralization rates of dissolved litter and humus fraction as well as the coefficients involved in the nitrous oxide production operated by the microbial biomass were set according to the range suggested by Spacsys developers (personal communication). Maximization of the EF of the agreement between observed and simulated data of soil water content and soil temperature was pursued as the objective function; subsequently, the same was done for data of N_2O and CO_2 emissions.

4.2.6 Statistical analysis and evaluation of the model performance

The fertilizer and tillage effects on the N_2O and CO_2 emissions that were measured during the field monitoring in a randomized complete-block design were tested by a linear mixed model with repeated measures with heterogeneous compound symmetry covariance matrix, using IBM – SPSS 21 (IBM Corporation, Armonk, New York, US), after the arcsine transformation of data to satisfy the assumption of normality of the distribution (Shapiro and Wilks test; Shapiro and Wilk, 1965). Means were then separated by the Sidak post-hoc test.

The match between observed and simulated values of N_2O and CO_2 emissions ($g\ m^{-2}\ d^{-1}$) was expressed by the following indexes: the coefficient of residual mass (CRM), the Pearson correlation (r), and modelling efficiency (EF).

Positive values of CRM indicate an underestimation of the simulated values, whereas values close to zero denote the absence of trends [2].

$$CRM = \frac{\sum_{i=1}^n O_i - \sum_{i=1}^n S_i}{\sum_{i=1}^n O_i} \quad [2]$$

The Pearson coefficient of correlation r has its optimum value to maximum (+1) values; zero means no correlation [3].

$$r = \frac{\sum_{i=1}^n (O_i - \bar{O})(S_i - \bar{S})}{\sqrt{\sum_{i=1}^n (O_i - \bar{O})^2} \sqrt{\sum_{i=1}^n (S_i - \bar{S})^2}} \quad [3]$$

The slope is an index quantifying the steepness of the linear regression [4].

$$slope = \frac{\sum_{i=1}^n (O_i - \bar{O})(S_i - \bar{S})}{\sum_{i=1}^n (O_i - \bar{O})^2} \quad [4]$$

The EF index (Nash and Sutcliffe, 1970) assumes a maximum and optimum value equal to 1 and it can get either positive or negative values. EF values lower than 0 result from a worse fit than the average of measurements [5].

$$EF = 1 - \frac{\sum_{i=1}^n (S_i - O_i)^2}{\sum_{i=1}^n (O_i - \bar{O})^2} \quad [5]$$

For all the indexes O_i is the i th observed value, S_i is the estimated i th value and n is the number of data pairs. \bar{O} and \bar{S} are the mean of observed and simulated soil water content, respectively.

4.3 Results

4.3.1 The field measurement of N₂O and CO₂

The interaction between fertilizer and tillage resulted in significant differences of N₂O emissions ($P < 0.05$), which decreased from 13.8 mg to 9.8 mg N₂O-N m⁻² d⁻¹ respectively under conventional tillage (CT) and minimum tillage (MT). Within the CT treatment, ammonium nitrate and slurry showed the largest fluxes and compost and digestate treatments caused significantly higher emissions than the control thesis (Figure 2a). In MT all the fertilizer treatments and the control thesis resulted in similar emissions ($P > 0.05$).

The highest emission peaks were measured for all fertilized treatments during the summer seasons due to the high soil water content maintained by irrigation and to high soil temperature (Figure 1). The soil temperatures were simulated by the Spacsys model after calibrating with observed data collected during the field monitoring ($EF = 0.86$, $r = 0.91$). When each field campaign was considered independently, the mean N₂O emission was higher in the summer season of 2012 (13 mg N₂O-N m⁻² d⁻¹); it was 11% and 8% higher than the mean flux observed respectively in autumn 2012 and summer 2013. The mean N₂O emissions in May 2011 after fertilizers application was significantly lower (6 mg N₂O-N m⁻² d⁻¹) than the average fluxes observed during summer and autumn periods; the mean soil temperature (16.1 °C) in May 2011 resulted in lower N₂O emissions than those observed in summer 2012, autumn 2012, and summer 2013, when the mean soil temperature was 20.2 °C, 16.6 °C, and 19.4°C respectively.

In the first fertilization event (at the end of May 2011), N₂O emissions increased one day after fertilizer distribution, with the exception of the slurry spreading that produced the highest peaks of emissions on the same day of soil application (Figure 3). During the second and the fourth monitoring campaign (summer 2012 and 2013), the highest emissions values were recorded one day after the irrigation events and after maize harvest, especially under the compost treatment in MT. The mean N₂O emissions which were recorded during the third monitoring period (autumn 2012) showed higher values under ammonium nitrate and slurry treatments in CT ($P < 0.001$), on average 18.5 ± 0.7 mg N₂O-N m⁻² d⁻¹ and 17.8 ± 0.66 mg N₂O-N m⁻² d⁻¹, respectively. In the same period, N₂O emissions were 6.8 mg N₂O-N m⁻² d⁻¹ and 4 mg N₂O-N m⁻² d⁻¹, respectively ammonium nitrate and slurry treatments in MT, while the emissions from digestate treatments under CT and MT were 5.1 mg N₂O-N m⁻² d⁻¹ and 4 mg N₂O-N m⁻² d⁻¹.

Tillage and fertilizer had significant main effects ($P < 0.001$) on CO₂ emissions. MT determined lower emissions than those from CT (0.1 and 0.13 g CO₂-C m⁻² d⁻¹, respectively). Considering the effect of the fertilizer treatments, the highest CO₂ emissions were measured under slurry treatment (on average 0.12 g CO₂-C m⁻² d⁻¹), while the lowest emissions were emitted from ammonium nitrate application and the control plot, respectively 0.09 and 0.087 (Figure 2b). Emissions from digestate and compost (on average 0.11 and 0.14 g CO₂-C m⁻² d⁻¹, respectively) were homogenous to those from both control plot and slurry application.

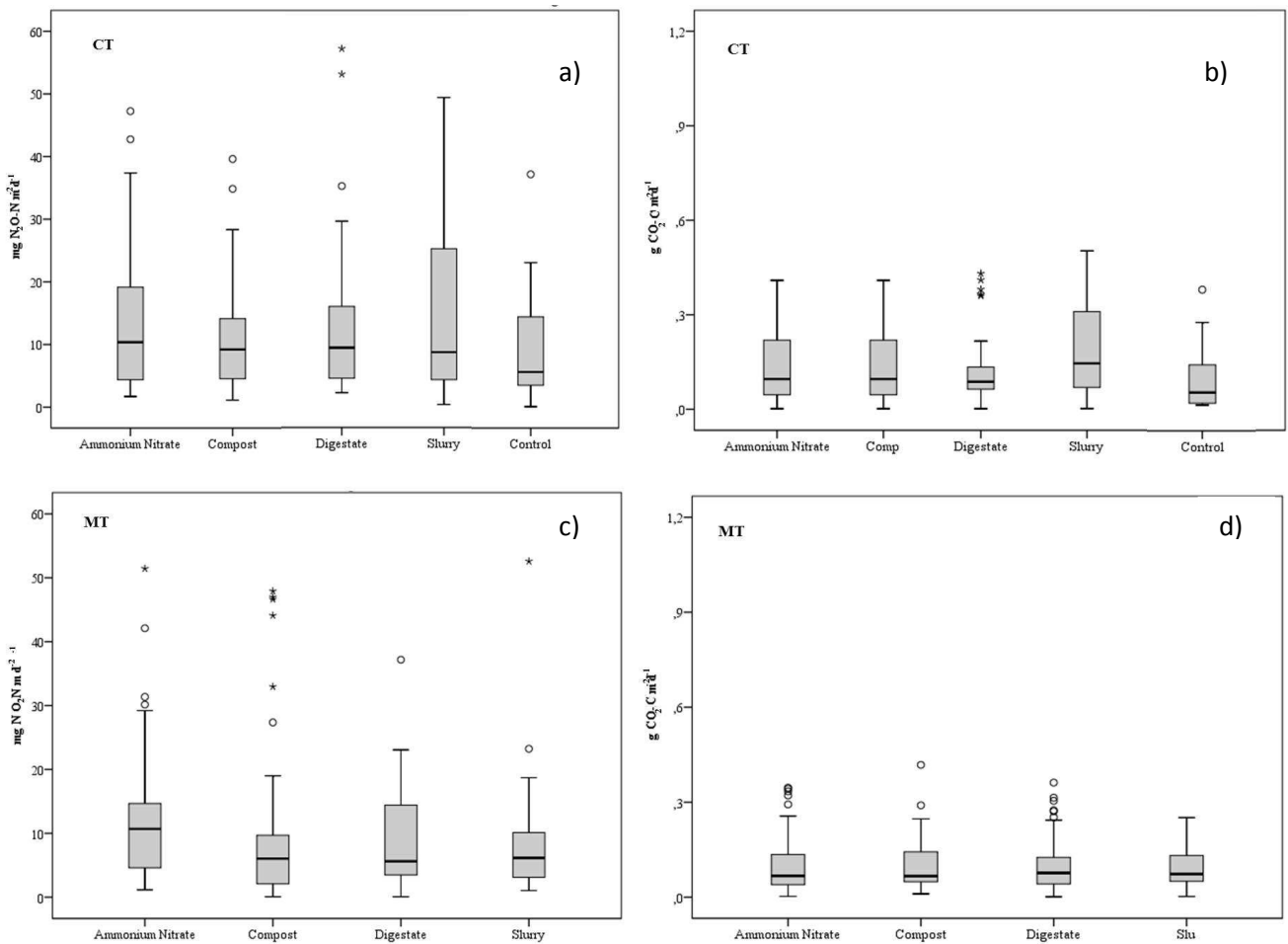


Figure 2: CT(a and b), MT(c and d), and fertilizer effect on N₂O (left) and CO₂ (right) emission (P<0.001).

4.3.2 N₂O measured and modeled emissions in the lysimeter trial

The mean of the N₂O emissions from the three fertilizers was statistically higher than the control thesis (P<0.01). For the two organic fertilizers, the highest peak was observed the day after fertilizers' application for digestate and ammonium nitrate, while it occurred one day earlier in the compost and control plots (Figure 3); peaks were 28.9 mg N₂O-N m⁻² d⁻¹, 74.4 mg N₂O-N m⁻² d⁻¹, and 46 mg N₂O-N m⁻² d⁻¹, respectively for the compost, digestate, and ammonium nitrate treatments. Other two peaks of N₂O emissions occurred during the experiment and they were likely due to the rainfall on the 29th and 30th May (2 mm), and the 4th and 6th May (9 mm).

Regarding CO₂ emission digestate showed the highest peak after the application (15.8 gCO₂ m⁻² d⁻¹), while compost and chemical fertilizers resulted with lower emission (7.56 gCO₂ m⁻² d⁻¹ and 4.8 gCO₂ m⁻² d⁻¹ respectively).

The results from the Spacsys model application were in agreement with the observed data (see Chapter 3, Figure 3 and Table 3). The Spacsys model predicted well the soil water content despite the small number of observed data that were available (n=5). One shortcoming was the underestimation of the two peaks of

N₂O emissions under the digestate treatment; in this case the Pearson's coefficient *r* was lower than the one for the other treatments.

4.3.3 Model application to the field experiment

Statistical evaluations showed that the simulated daily N₂O fluxes were consistent with measured values over the experimental period (Table 3). The model tends to underestimate the peaks of emissions after irrigation events although the modelled distribution was consistent with the observed one, as shown by EF values. Such an underestimation occurred mostly under the compost treatment both in CT and MT; this shortcoming was likely due to the low rate of manure decomposition that was set for compost.

A significant influence of tillage on N₂O emissions was observed and accordingly it was predicted by the model, showing lower annual cumulative fluxes under MT for all the fertilizers' treatment. Across the fertilizer treatments, the annual cumulative N₂O emissions was 16 mg N₂O-N m⁻² y⁻¹ in CT and 14.2 mg N₂O-N m⁻² y⁻¹ in MT. On average, the annual cumulative fluxes from ammonium nitrate application were 20% and 33% higher than the emissions from organic fertilizer treatments in CT and in MT, respectively.

The larger simulated emissions occurred in summer and autumn; particularly, the simulated N₂O emissions were in agreement with the amount observed following the harvest of maize in 2012, with the exception of the slurry treatment in CT whereby the model underestimated the peak of emissions.

The pattern of N₂O emissions was determined by the combination of weather and soil factors. In Figure 5, the mean simulated N₂O emissions in CT and MT are plotted with the soil nitrate content (g NO₃-N m⁻² d⁻¹) and water-filled pore space (WFPS, %), that is calculated as a function of soil water content and bulk density. The WFPS values were predicted by the model that was validated with data of soil water content measured in April and May 2013 at 0.1 m, 0.2 m and 0.3 m depth (EF=0.31; *r*=0.71). WFPS did not differ from CT to MT (*P*>0.05). Higher values of WFPS generally implies a reduction of the nitrification rate and at the same time an increase of the gas emitted through the denitrification process, and both of these processes involve N₂O emissions. A higher soil NO₃-N content was simulated in CT that was characterized by higher emissions of N₂O. The rank correlation test (Spearman coefficient, *ρ*) showed that N₂O emissions resulted in a significant correlation with WFPS (*ρ*=0.51 and 0.47 in CT and MT), nitrate soil content (*ρ*=0.35 and 0.42 in CT and MT), soil temperature (*ρ*=0.3 in CT and MT), microbial-N (*ρ*=0.4 and 0.33 in CT and MT), undissolved fraction of N fertilizer (*ρ*=0.29 and 0.32 in CT and MT), and humus-N (*ρ*=0.17 and 0.27 in CT and MT); N₂O emissions resulted in significant correlation with dissolved organic C in CT (*ρ*=0.12) but not in MT (*ρ* =0.06). A stepwise multiple regression analysis was performed to quantify the contribution of the aforementioned variables to N₂O emissions from CT and MT. The CT and MT regression models were significant but they had low R² values (0.232 and 0.223 for CT and MT); in the first case significant variables were WFPS, undissolved fertilizer-N, and dissolved organic matter and C. The regression model for MT emissions encompassed the same driving variables for Ct emissions and in addition humus-N, NO₃-N, and root litter-N.

The simulation results of CO₂ emissions were consistent with the observed distribution for all the combination of tillage and fertilizer treatments (Table 3). The highest annual cumulative CO₂ emissions was estimated from compost application under CT. The relative difference between gas fluxes from compost and the slurry treatment was more relevant in MT rather than in CT (26% and 10%, respectively), while the differences with digestate and ammonium nitrate were similar under CT and MT (33%).

The highest peaks of CO₂ emissions were simulated in the summer periods and that was likely due to the concurrence of high soil temperature and higher WFPS because of the irrigation events. Considerable fluxes were also simulated in response of root respiration, especially in May at the end of the growth period of winter crops and it was probably due to the increasing temperature.

In order to investigate the factors controlling the CO₂ emissions under the compost treatment in CT, that involved the highest annual cumulative fluxes, a stepwise multiple regression analysis was executed accounting for all the C related variables. The model was significant ($P < 0.01$; $R^2 = 0.75$) and included mainly the microbial-C, and, to a minor extent, soil temperature, dissolved organic C, C that was mineralized from litter, humus-C, immobilization rate, and fresh litter.

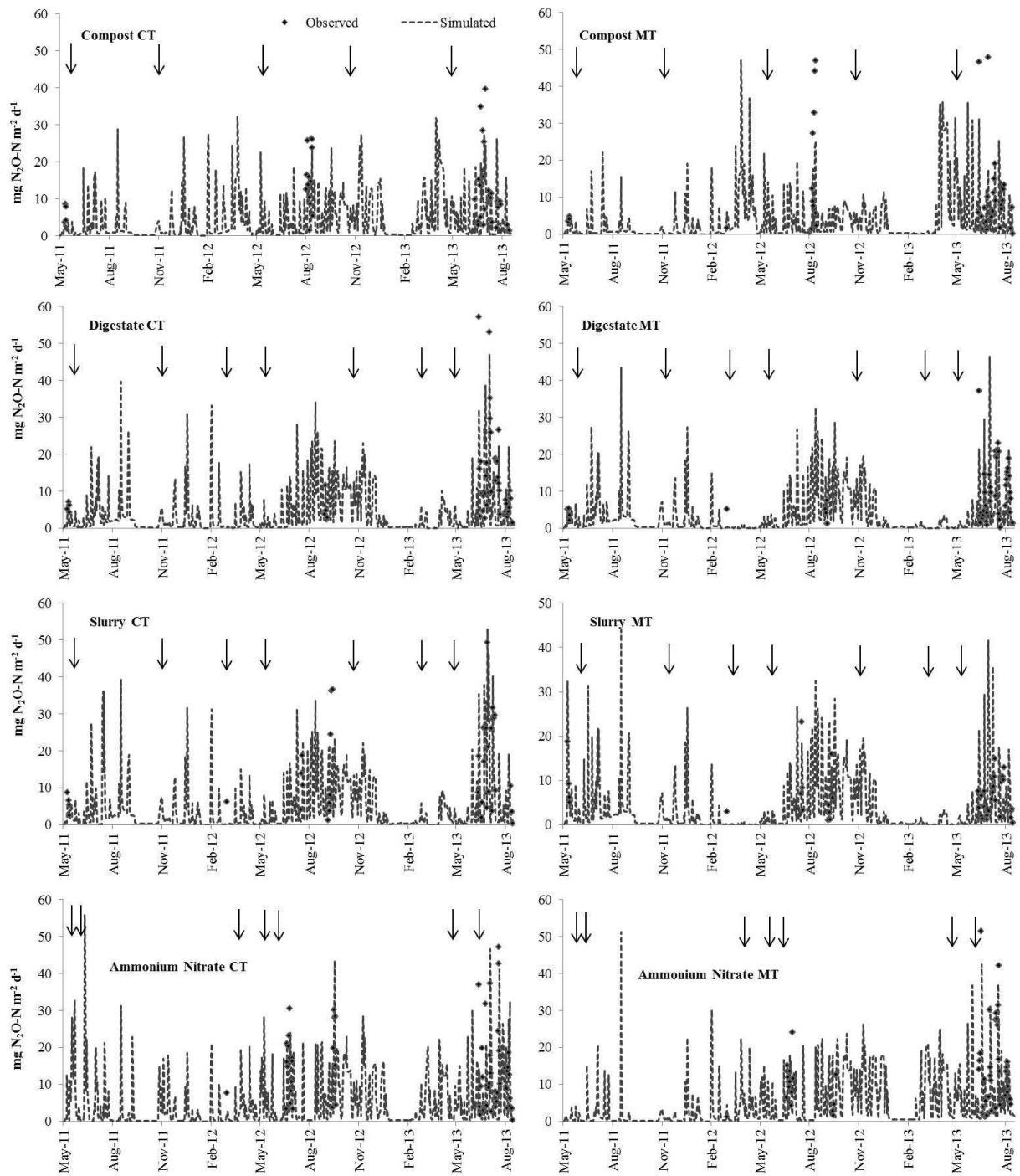


Figure 3: Observed (point) and simulated (dotted line) N_2O fluxes for different fertilization in conventional (left) and minimum tillage (right). Arrows indicate fertilization application.

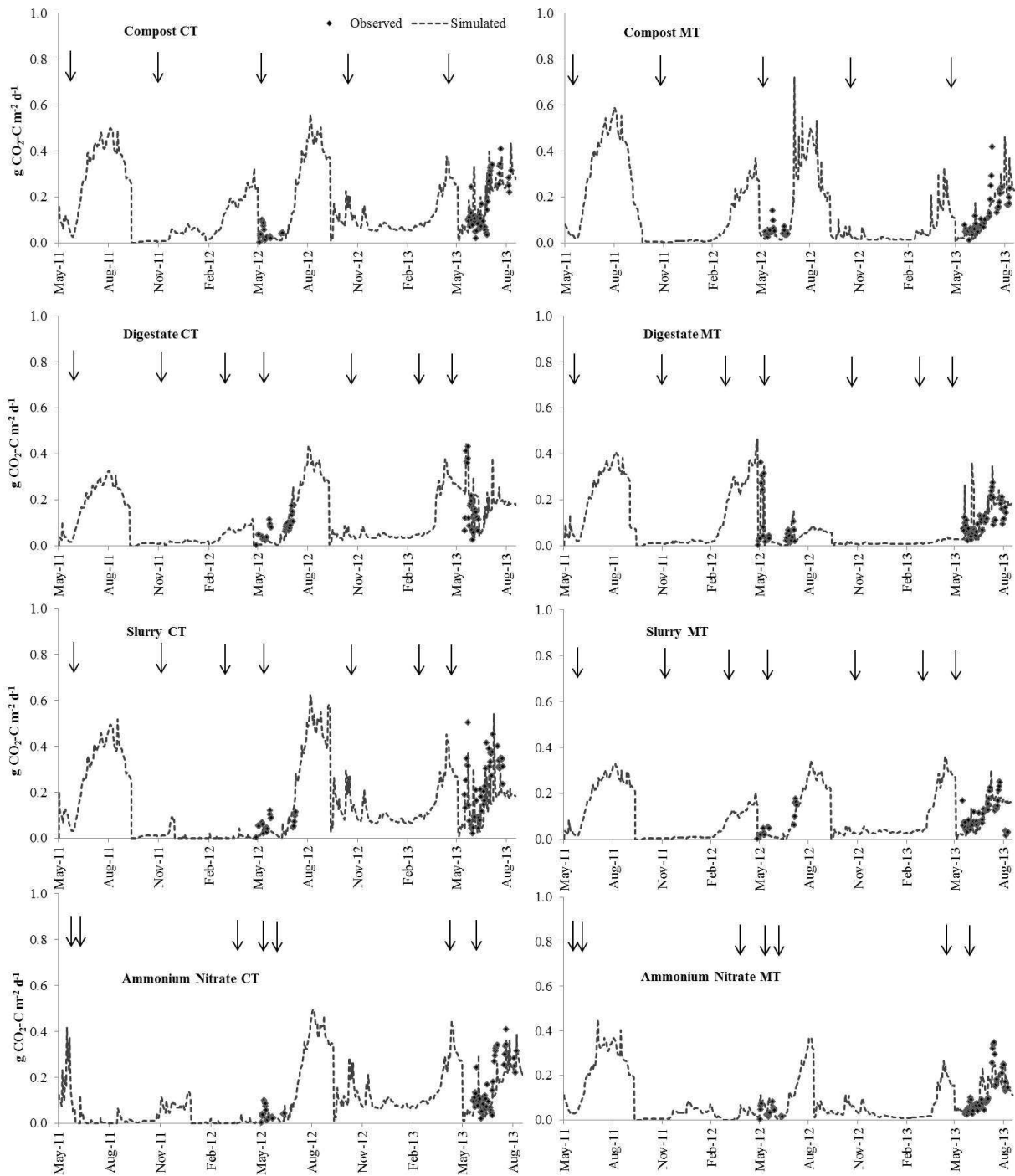


Figure 4: Observed (point) and simulated (dotted line) CO₂ fluxes for different fertilization in conventional (left) and minimum tillage (right). Arrows indicate fertilization application.

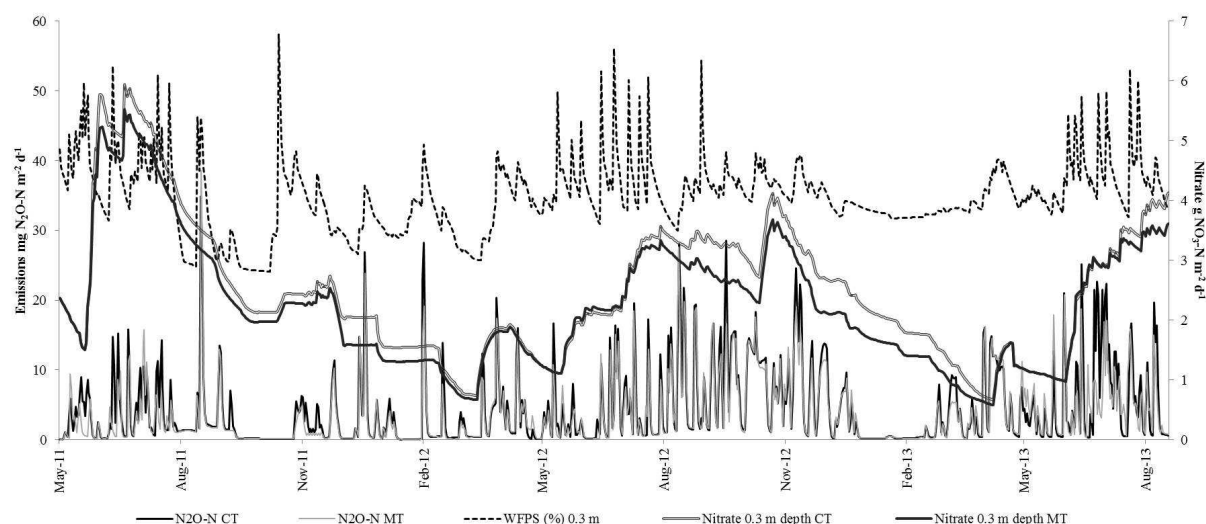


Figure 5: Pattern of the N₂O emissions over the simulated period (from May 2011 to September 2013) for different tillage (CT vs MT); WFPS and nitrate leaching simulated by Spacsys

Table 2: Fitting indexes between observed and simulated data of N₂O and CO₂ emissions under the four fertilizer treatments in conventional (CT) and minimum tillage (MT) during the field experiment (from May 2011 to September 2013). CRM=coefficient of residual mass; r=the Pearson's coefficient of correlation; EF=modelling efficiency.

Tillage	Fertilizer	Fitting Indexes				Cumulative N ₂ O emissions (kg N ₂ O-N ha ⁻¹ y ⁻¹)
		CRM	r	Slope	EF	
CT	Compost	-7.11	0.59	0.41	0.94	15.26
	Digestate	-3.73	0.44	0.78	0.84	14.54
	Slurry	-6.54	0.53	0.62	0.88	15.99
	Ammoniu	-1.56	0.63	0.68	0.92	18.27
	Control	-3.53	0.44	0.78	0.79	11.20
MT	Compost	-7.32	0.78	0.47	0.91	13.71
	Digestate	-76.95	0.48	0.57	0.99	12.66
	Slurry	-19.74	0.48	0.64	0.96	12.89
	Ammoniu	-18.01	0.55	0.49	0.84	17.39

Table 2: Fitting indexes between observed and simulated data of CO₂ emissions under the four fertilizer treatments in conventional (CT) and minimum tillage (MT) during the field experiment (from May 2011 to September 2013). CRM=coefficient of residual mass; r=the Pearson's coefficient of correlation; EF=modelling efficiency.

Tillage	Fertilizer	Fitting Indexes				Cumulative CO ₂ emissions (kg CO ₂ -C ha ⁻¹ y ⁻¹)
		CRM	r	Slope	EF	
CT	Compost	-7.40	0.73	0.73	0.51	574.72
	Digestate	-7.10	0.84	1.10	0.38	408.01
	Slurry	-4.55	0.65	0.46	0.47	517.27
	Ammoniu	-7.09	0.77	0.6	0.61	365.63
	Control	-0.11	0.85	0.83	0.70	258.02
MT	Compost	-5.39	0.81	0.97	0.62	478.33
	Digestate	-1.35	0.79	0.98	0.50	317.27
	Slurry	-10.90	0.86	0.98	0.98	353.84
	Ammoniu	-4.26	0.86	0.70	0.94	319.71

Table 3: Data of N application rate and N₂O emissions. The emission factor (EF) is calculated as the percentage of fertilizer rate that was lost as N₂O emissions. The annual EF is based on the whole annual of applied N, comprising the additional amount applied to winter crops in March 2011 and in October 2013.

Fertilizer	Year	Fertilizer amount (kg FM ha ⁻¹)	N (% FM)	N rate* (kg N ha ⁻¹)	Annual N rate (kg N ha ⁻¹)	Tillage	EF ** (%)	Annual EF** (%)
Compost	2011	32588	1.6	510	510	CT	0.8%	0.8%
						MT	0.5%	0.5%
	2012	33650	1.5	510	510	CT	0.8%	0.8%
						MT	0.5%	0.5%
	2013	21250	1.6	340	340	CT	1.2%	1.2%
						MT	0.7%	0.7%
Digestate	2011	80197	0.2	150	200	CT	2.2%	1.7%
						MT	1.0%	0.7%
	2012	107143	0.2	225	225	CT	1.5%	1.5%
						MT	0.7%	0.7%
	2013	69497	0.3	175	225	CT	1.9%	1.5%
						MT	0.8%	0.7%
Slurry	2011	49342	0.3	150	200	CT	3.2%	2.4%
						MT	1.1%	0.8%
	2012	72964	0.3	230	230	CT	2.1%	2.1%
						MT	0.7%	0.7%
	2013	58154	0.3	170	220	CT	2.8%	2.2%
						MT	1.0%	0.8%
Amm. Nitrate	2011	370	27.0	100	150	CT	7.1%	4.7%
						MT	6.2%	4.1%
	2012	926	27.0	250	250	CT	2.8%	2.8%
						MT	2.5%	2.5%
	2013	741	27.0	200	200	CT	3.5%	3.5%
						MT	3.1%	3.1%

*This rate accounts only for the N rate that was applied during the field experiment (from May 2011 to September 2013)

**The N₂O-N emissions in the ratio were calculated subtracting the cumulative annual value by the one that was estimated in the control

4.4 Discussion

Evident effects of fertilization and soil tillage on gas emissions were observed in the present study. Differences in gas emissions were triggered by several factors; fertilizer type and soil conditions that were determined by the combination of tillage and water inward from both rainfall and irrigation. Results on seasonal and annual emissions are discussed based on the abovementioned controlling factors.

4.4.1 N₂O emissions from mineral and manure N fertilizers

Under conventional tillage (CT) the N₂O emissions from the soil subjected to mineral and slurry fertilization exceeded the emissions from compost and digestate. The same occurred in MT, with the exception of the

slurry treatment. This can be probably explained by the higher supply of available forms of N in the ammonium nitrate and slurry treatment compared to that in compost and digestate (Table 1). Comparing the mineral and slurry fertilization to the other manure treatments, the model predicted an increase of the nitrate-N content (33%, $P < 0.001$) and a subsequent increase of the denitrification rate (21%, $P < 0.01$) and in turn higher N_2O emissions. Digestate and compost low emissions were due to their chemical composition that resulted from slurry treatment, respectively anaerobic digestion and composting with maize stover. Anaerobic digestion is a treatment that changes the composition of slurry, reducing the organic C and easily degradable C and enhancing the relative content of recalcitrant form of C (Field et al., 1984; Chantigny et al., 2004; Clemens et al., 2006). Therefore, the rate of soil microbial degradation and oxygen consumption is likely reduced under digestate distribution in comparison with untreated slurry spreading (Clemens and Huschka, 2001). The resulting higher content of oxygen may induce lower denitrification rate and then reduced N_2O emissions (Moller and Stiller, 2009; Arthurson, 2009). In our experiment, the mean slurry and digestate C fraction and C:N were respectively 1.7% and 1%, and 6% and 5% (Table 1), and N_2O emissions decreased by 6%. In addition, digestate lower emissions than slurry were also due to the lower fraction of ammonium-N on total N content (-15%) (Table 1). Conversely a ratio is usually enhanced by the anaerobic treatment and increase of N_2O emissions are expected passing from untreated slurry to digestate (Sommer et al. 2000). Bertora et al. (2008) reported that anaerobically digested liquid fraction resulted in significantly lower N_2O emissions with respect to the original slurry, respectively 5.8 and 18.7 g N_2O -N soil over a period of 58 days. A similar pattern was reported by Meijide et al. (2007) who showed results on N_2O emissions from mineral fertilizer (i.e. urea, 8.6 kg N_2O -N ha^{-1}), untreated pig slurry (8.3 kg N_2O -N ha^{-1}) and anaerobically digested thin pig slurry fraction (7.7 kg N_2O -N ha^{-1}) during a maize growing season (142 days) under Mediterranean climate conditions on an irrigated sandy loam soil. In our study, during the maize season (from May 24th to August 28th 2012, 97 days), mineral fertilizer and slurry resulted in significantly higher N_2O emissions (on average 4.5 kg N_2O -N ha^{-1}) compared to digestate and compost (on average 3.5 kg N_2O -N ha^{-1}) in CT, while no significant differences were detected in MT between fertilizer treatments (on average 3.6 kg N_2O -N ha^{-1}). Among slurry treatments, composting ensures an increase of C recalcitrant fraction (Lynch et al., 2006) along with a strong decrease of ammonium-N:total (Ko et al., 2008) in comparison with untreated slurry. In our study, compost and slurry values of C fraction (the recalcitrant fraction was not measured) and ammonium-N:total were respectively 2% and 53%, and 7.7% and 1.7%, and that was likely why compost application resulted in a significant 5% decrease of N_2O emissions in comparison with the untreated slurry under CT, even though the total N input from compost was two to three-fold higher than slurry-N (Table 1).

4.4.2 Tillage effects on N_2O emissions

Emissions of N_2O were on average 17% lower under minimum tillage (MT) compared to conventional tillage (CT). A similar result was reported by Choudhary et al. (2002) in New Zealand, comparing N_2O emission from

CT ($9.2 \text{ kg N}_2\text{O-N ha}^{-1} \text{ y}^{-1}$) and no tillage ($12 \text{ kg N}_2\text{O-N ha}^{-1} \text{ y}^{-1}$) in a trial with a rate of mineral fertilization equal to $120 \text{ kg ha}^{-1} \text{ y}^{-1}$. Fuß et al. (2011) reported no significant differences in the total amount of N_2O emissions from CT to MT, while Chatskikh and Olesen (2007) showed that N_2O emissions from loamy sand soil under spring barley were significantly higher for CT compared with MT, before tillage and to a major extent after tillage.

WFPS is recognized to play a key role in affecting N_2O emissions, in fact WFPS values higher than 60% generally promote the denitrification process (Ruser et al., 2006). When reduced tillage techniques are applied the soil tends to have a lower macro porosity and in turn a larger proportion of pore space filled by water ($>\text{WFPS}\%$), this however depends on soil characteristics: increases of N_2O emissions after no-tillage adoption mainly occurred in clayey (Mutegi et al., 2010) and poorly-drained soils (Rochette, 2008); conversely, reduced tillage in well aerated soils can decrease N_2O emissions (Soane et al., 2012). Conversely, Pelster et al. (2011) reported no significant differences in N_2O emissions in a 2-year experiment under a maize–soybean rotation despite the clay loam soil. In our experiment, the silt loamy soil was seldom saturated and WFPS was on average 33% both in CT and MT (Figure 5) and this aspect may explain the lower emissions that were observed under reduce tillage.

4.4.3 Irrigation effects on N_2O emissions

The pattern of the N_2O emissions over the simulated period (from May 2011 to September 2013) appeared to be driven by the combined effect of soil water content and N availability (Figure 5). The cumulative N_2O emissions estimated by the model during the summer were significantly higher (+21%, $P<0.01$) than the average value predicted in the other seasons, respectively 5.6 and 4.4 $\text{kg N}_2\text{O-N ha}^{-1}$. This was the consequence of the high peaks of the emissions that were observed and simulated soon after the irrigation events. As a consequence, the N fertilization induced peaks of N_2O emissions only when the soil water content reached a critical value of $0.29 \text{ m}^3 \text{ m}^{-3}$ that corresponded to a WFPS of 40%. This is in agreement with previous research carried out to study the effect of WFPS on N_2O fluxes (Dobbie and Smith, 2003), and to study the response of N_2O emissions to incremental fertilizer rate in a 3-year experiment in Michigan (US) (McSwiney and Robertson, 2005).

4.4.4 Emissions factor estimation

The N_2O emissions factor (EF) is the percentage of fertilizer N applied that is transformed into fertilizer-induced emissions and it is calculated as the difference in N_2O emission between fertilized and unfertilized soil under identical conditions (Shcherbak et al., 2014). Measured and estimated N_2O EF reported in Table 3 exceeded the current global mean value of 1% that is indicated as standard for the emissions estimation by the Intergovernmental Panel on Climate Change (de Klein et al., 2006). The overall calculated mean was 2% accounting for the N applied during the experiment from May 2011 to September 2013; this value decreases to 1.7 % when the whole annual N rate is accounted for, comprising the additional amount

applied to winter crops in March 2011 and in October 2013. The results of the two-way ANOVA, which was carried out to test the significance of differences of EF between fertilizers and tillage, indicated that annual EF was significantly higher in CT than in MT ($P < 0.001$, 2.1% and 1.3%). Ammonium nitrate induced the highest annual EF (3.5%) and differed statistically from the others fertilizers; digestate and compost resulted homogeneous (1.1% and 0.8%) and slurry had a medium value of EF (1.6%). This pattern is consistent with the N_2O distribution across the fertilizer and tillage treatments. Van Groeningen et al. (2010) and Scherbak et al. (2014) carried out two meta-analysis that encompass more than one hundred observations and reported higher EF than the IPCC default value of 1%, in particular when N applied is higher than 150 kg N ha^{-1} . These studies, as well as the one here presented, highlight that N_2O emissions have a higher impact than the one assumed by the Intergovernmental Panel on Climate Change.

4.4.5 Fertilizer and tillage effects on CO_2 emissions

The CO_2 emissions showed different trend within the different treatments and tillage. The application of organic materials to agricultural land has been considered good practice to improve soil organic matter content, within application of appropriate amount (Loubet et al., 2011). However the application of liquid manure or fresh slurry increases CO_2 emissions compared with the unfertilized soils (Chadwick et al., 2000), as confirmed also in our results. In particular under CT and MT, the CO_2 emissions from the soil subjected to organic fertilization exceeded the emissions from ammonium nitrate. This could be attributed to the rapid depletion of easily mineralizable carbon by respiring microorganisms as well as to the release of CO_2 dissolved in digestate (Möller et al., 2009), slurry and compost (Rochette et al., 2000), depending on soil WFPS and temperature, as reported by Pezzolla et al. (2012).

The CO_2 emitted by the soil after ploughing in CT was 16 to 31% higher (in compost and ammonium nitrate treatments, respectively) than MT; this result was also reported by Rochette and Angers (1999). Such higher emissions in CT were due to the tillage operations, which enhanced soil permeability that increased the air transport coefficient from soil profile (Reikosky et al., 1997). Results from control plots in CT and MT indicated that the higher soil disturbance led to a higher gas release. In other studies (Rochette and Angers 2007) has been reported an increase of soil CO_2 emission from soil up to 3.8 to 10.3 times larger than no tilled soils due to tillage management (different plowing depth). CT generally exposes new part of soil to wet-dry and freeze-thaw conditions at the surface (Beare et al, 1994), thereby reducing the stability of soil aggregate (Six et al., 1999).

4.5 Conclusion

Our results suggested that the portion of N applied to N_2O emissions exceeded the standard value of 1% in our climatic conditions despite the balanced N supply. Digestate and compost use represents a viable way to reduce the emissions factor, especially under conventional tillage. The outcome of the present study showed that reduced tillage induces decrease of N_2O and CO_2 emissions under the examined pedoclimatic

and management conditions, and it represents an effective way to reduce gas emissions from crop land. Together with the options of fertilization and tillage, the supply of lower amounts of irrigation water is likely to reduce the N₂O and CO₂ emissions peaks. A site and crop specific computation of the irrigation water is needed to define a trade-off between reducing the temporal water saturation of soil pore spaces and meeting the actual evapotranspiration of cultivated plants.

The study confirmed that specific pedoclimatic conditions and management practices determined a wide range of N₂O emissions, and it suggests that investigation needs to be carried out at local scale.

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5. General conclusion.

Based on the results obtained in this thesis, it can be concluded that:

- a large variability in GHG emission values was experienced when using different measuring systems. The two widely used measuring systems, based on the coupling of static chambers with GC and B&K (Nay, 1994), showed similar temporal sampling resolution, and gas concentration data over time. These techniques are complex, expensive and time consuming for the management of the static chambers. The SASSFlux system provided more stable results being less influenced by external conditions such as soil type and soil treatments. Main quality of the SASSFlux system is the continuous data collection (during day and the night) thanks to its automatic chambers sampling system. Further improvements are needed on the SASSFlux system, in particular to establish a correct flux calculation methodology.
- The choice of the most suitable measuring system should be made in consideration of the specific characteristics of the sampling place and should be evaluated considering the whole chain of activities required (sampling unit, detector and data treatment), as confirmed by Neftel et al (2006).
- Simulation models can adequately predict GHG emissions over a range of different soil conditions and management practices. The present work confirmed that a reliable prediction of GHG fluxes is only possible with an adequately parametrized process-based model. The two models used in this thesis, DNDC (partially empirically process-based) and Spacsys (mechanistic process-based) showed that satisfactory simulation of GHG emission could be obtained over a range of different soil conditions and management practices, however a deeper understanding of the model process is needed and conspicuous adjustments (Ludwig et al., 2011) are required to accurately predict fluxes emissions and define GHG mitigation strategies.
- The combination of innovative detection methods (direct measurements) and the use of simulation models can provide a valuable approach to study the effect of different agronomic management systems. Our results suggest that the use of digestate and compost represents a viable solution to reduce soil emissions, compared with conventional practices largely used (chemical fertilization), as confirmed by Pezzolla et al. (2012). Moreover reduced tillage can represent another mitigation option (Curtin et al., 2000). Under the experimental conditions of the field trial described in this thesis, reduced tillage induced a decrease of N₂O and CO₂ emissions. The study confirmed that specific pedoclimatic conditions and management practices determined a wide range of GHG

emissions, this suggests that investigation on GHG emissions needs to be carried out at local scale, and the use of average values (i.e. N₂O emission factor proposed by IPCC) can be misleading when assessing GHG emission at field scale.

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