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CICLO XXV

N balance and greenhouse gas emissions (CO_2, CH_4, N_2O) in soil with shallow groundwater

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Riassunto

Il lavoro qui presentato focalizza la sua attenzione sugli effetti che concimazioni, eseguite con refluo zootecnico, e differenti regimi idrici possono avere in una coltura di mais. Lo studio ha considerato le potenziali lisciviazioni di azoto verso la falda e l'emissione di gas serra ad effetto climalterante. Sono stati valutati due differenti regimi idrici, il primo ha previsto l'applicazione di quattro diversi livelli irrigui su suolo a drenaggio libero, il secondo ha comparato l'effetto di un suolo a drenaggio libero con quello di due suoli con falda superficiale controllata.

Lo studio è stato condotto presso l'azienda agraria sperimentale dell'Università di Padova. Un sito costituito da lisimetri interrati è stato coltivato con mais e fertilizzato con liquame ed urea secondo i limiti previsti dalla direttiva nitrati per zone vulnerabili e dalla recente deroga della direttiva, ottenuta dall'Italia. È stata determinata la produzione del mais, la lisciviazione di azoto e all'emissione di gas serra. I gas serra sono stati monitorati tramite misure in campo. La tesi si compone di cinque capitoli.

Capitolo 1, è un introduzione generale ai temi trattati.

Capitolo 2, intitolato "Interaction between irrigation and N fertilization in an area subject to the Nitrates Directive. Effects on N Balance" . Sono stati analizzati i dati provenienti da un quinquennio di mais in monosuccessione (2006-2010). Si è voluto verificare l'effetto dell'interazione tra quattro differenti regimi irrigui e quattro livelli di fertilizzazione azotata sul rendimento colturale, l'asportazione di azoto da parte della coltura e sulla lisciviazione dell'azoto. È stato poi elaborato un semplice metamodello capace di predire la lisciviazione dell'azoto.

Capitolo 3, intitolato "N balance and Nitrous Oxide emission in soil subject to derogation from the Nitrates Directive in free drainage and shallow groundwater conditions". Ha valutato l'effetto di tre diversi input azotati combinati con tre situazioni di falda, in due anni, nel 2011 e nel 2012. Il primo input azotato utilizzato è stato il limite della direttiva nitrati per zone vulnerabili, il secondo ed il terzo sono stati i nuovi limiti applicabili grazie alla deroga della direttiva nitrati. Si è considerato un suolo in drenaggio libero o soggetto a due falde superficiali. È stato analizzato il rendimento del mais, l'azoto

asportato dalla coltura, l'azoto lisciviato e l'emissione di N_2O del suolo. L'obiettivo è stato quello di valutare gli effetti dell'applicazione della deroga della direttiva nitrati.

Capitolo 4, intitolato "Carbon (CO_2 and CH_4) emissions from soil with shallow water table and approach to GHGs modeling". Sono stati considerati i flussi di CO_2 e di CH_4 dal sito sperimentale precedentemente descritto del capitolo 3. Infine un'ultima breve parte riguarda l'utilizzo di un modello di simulazione per verificare differenze o somiglianze con i dati reali ottenuti in capitolo 3 e 4.

Capitolo 5, riguarda le conclusioni generali sul lavoro svolto.

Summary

The work here presented deals with the effects that N, applied with manure, and the water regimes had in a cropping maize system. The study want to evaluate the N leaching trough groundwater and the potential greenhouse gas emission affecting global warming. Two different water regimes were studied: soil in free drainage conditions with different irrigation levels and two shallow water table conditions.

The study was conducted in the Experimental Farm of Padua University. Continuous maize was cropped in lysimeters fertilized with manure and urea according to the limit imposed by Nitrates Directive and the recent derogation of Directive obtained by Italy. Analysis of crop yield, N leaching and GHGs were done to compute a N balance. GHGs were obtained through direct measurements in the field. The thesis is composed by five chapter.

Chapter 1. is a general introduction to the topics discussed.

Chapter 2, entitled "Interaction between irrigation and N fertilization in an area subject to the Nitrates Directive. Effects on N Balance", analyzed data come from a five years study conducted in 2006-2010 and aimed to identify the effect of four different irrigation and four N input in N leaching, crop yield and N uptake by crop. In the chapter is processed a simple metamodel able to predict the leaching of nitrogen.

Chapter 3, entitled "N balance and Nitrous Oxide emission in soil subject to derogation from the Nitrates Directive in free drainage and shallow groundwater conditions". aimed to evaluate the effect of derogation of Nitrates Directive, quantifying the effect of three different N input combined with three water table conditions in two years, 2011 and 2012. The lower N input was the limit for nitrates vulnerable zones (NVZs) and the other two input were relative to the new limits that can be used due to the derogation of Nitrate Directive. We consider a free drainage and two shallow water table conditions. We performed analysis of maize yield, N uptake, N leaching and N_2O emissions. .

Chapter 4, entitled "Carbon (CO_2 and CH_4) emissions from soil with shallow water table and approach to GHGs modeling" we performed analysis of CO_2 and CH_4 fluxes for the experimental layout described in Chapter 2. The aim was to quantify the emissions as affected by free drainage or shallow water table conditions, considering the N limit

imposed in NVZs by Nitrates Directive and by the derogation. Finally a little part was dedicated at an approach in the use of a terrestrial ecosystem model for the simulation of data obtained in chapter 2 and 3.

Chapter 5, is a general conclusion of the work.

Chapter I

General Introduction

Replacement of natural ecosystems such as grassland and forest with agroecosystems and the transition from traditional agricultural to intensive agricultural has frequently increased the flux of soil carbon to the atmosphere, reducing levels of SOM and thereby decreasing soil fertility (Solomon et al., 2002). In Mediterranean soils the reduction of organic matter has led to an increase of erosion risk and fertility losses (Melero et al, 2006). This is a universally accepted issue (Smith et al., 1993) and the addition of organic amendments in soil is suggested as a way to improve organic carbon and nitrogen content (Madejón et al., 2001; Marschener et al., 2003). In areas with large livestock production this practice permits the disposal of the resulting manure. Manure represents an interesting option in terms of carbon sequestration in soil (Arrouays et al., 2002). Crops such as maize, which have a high N demand, urge the farmer towards the use of high N inputs to ensure production but, if all the nitrogen is not removed by the crop, N accumulation in soil can favor N leaching to groundwater. (Fox at al., 1989; Waskom et al., 1996).

A proper N management requires indicators of the N status of the soil-crop systems. Crops are considered a good indicator of the presence and availability of soil mineral N, and the crop growth depends on weather conditions and crop management (Schröder et al., 2000). However crop analyses are not useful to detect excess N in soil because plants reach a saturation limit for N use (Maghooff, 1991; Roth et al., 1992; Dwyer et al., 1995). Furthermore, N leaching is clearly related to mineral nitrogen present in soil, but is mediated by other variables such as irrigation and weather (Schröder et al., 2000). Soil analyses are also required to discriminate the quantity of N that is present, but reactions mediated by microorganisms are also responsible for the change of N content in soil (Whitmore, 1991). So the quest for a unique indicator to predict the release of organic N has been in vain (Jarvis et al., 1996; Powlson, 1997). A practical solution is to combine all indicators, creating a balance considering all N processes and all the parameters influencing these processes.

The “field balance”, as it is called by Öborn et al. (2003), requires detailed data input and its output data provides a measure of the net surplus or deficit caused by fluxes across the soil surface. It is connected with a defined soil profile and includes addition to or depletion of soil pools.

Nutrients and, in particular, N balance are a very useful tool to trim the management action program within the framework of the EU Nitrate Directive in Nitrate Vulnerable Zones (NVZS) (Grignani et al., 2007). Considering mass flows of N, it is possible to estimate deficits and surplus of N and, in the latter case, to quantify the possible losses from agroecosystems. These losses can have a potential impact on the environment through N leaching to groundwater or greenhouse gases emissions (GHGs). N rate and irrigation are the main factors influencing N leaching (Wang et al., 2010). In general an increase of soil water content enhances crop yield, in particular when high N rates are applied (Norwood, 2000). Pandey et al. (2001) reported a linear yield response to irrigation at all N levels, but, on the other hand, nitrate leaching can occur with high irrigation or rainwater (Fang et al., 2006).

Agriculture is usually considered a net source of GHGs but it can also act as a sink. The flux obtained at the soil/atmosphere interface is the result of dynamic production and consumption processes in the soil. Agriculture can be a global source of carbon dioxide (CO_2), methane (CH_4) (Chianese et al., 2009a; Castaldi and Fierro, 2005; Mosier et al., 2004) and nitrous oxide (N_2O) (Chianese et al., 2009b; Davidson, 1991; Del Grosso et al., 2000; Firestone and Davidson, 1989; Li et al., 1992; Parton et al., 1996; Xing et al., 2011). CO_2, with respect to CH_4 and N_2O, is cycled in the largest amount through agricultural cropping systems. Plants consume large amounts of CO_2 through photosynthesis, but the plant products emit CO_2 when they are consumed or decomposed. So the net emissions are low (Snyder et al., 2009). Several factors affect CO_2 emissions and the return of stored soil organic C to the atmosphere, such as soil temperature, soil water, type of vegetation, substrate quantity and quality, microbial biomass and activity, land use and management (Linn and Doran, 1984; Bowden et al., 2004; Fisk and Fahey, 2001).

N_2O is produced primarily from the microbial processes of nitrification and denitrification in soil. Nitrification is the oxidation of ammonia to nitrite and then nitrate. Denitrification is the microbial reduction of nitrate or nitrite to gaseous nitrogen, with NO and N_2O being produced as intermediate reduction compounds (Firestone, 1982; Firestone and Davidson, 1989; Robertson and Groffman, 2007). Denitrification is performed by heterotrophic bacteria that are facultative anaerobes. The general requirements for denitrification are: the presence of bacteria possessing the metabolic capacity, suitable electron donors such as organic C compounds, reduced S compounds or molecular hydrogen, anaerobic conditions or restricted oxygen availability, and N oxides as terminal electron acceptors (Firestone,1982, Mosier et al., 2004). N_2O “uptake” can also occur in soil. Consumption in this case is defined as “uptake”, so a negative flux, direct from atmosphere to soil: N_2O can disappear by reduction of N_2O to N_2 as well as the absorption of N_2O in soil water (Chapuis-Lardy et al., 2007).

Groundwater, by the reduction of nitrates, is a large accumulator of N_2O. Aquifers, and in particular shallow aquifers, can therefore be considered not only as passive subjects for N pollution but also depollutant agents. If this second function prevails, less restrictive limits on nitrogen fertilization can be conceivable. Methane is also subjected to an emissions and an uptake processes. Uptake is in general a relatively negligible process, while production is relevant in particular in flooded soil and paddy fields.

Emissions inventories have great uncertainty and this may have various origins (Rypdal and Winiwarter, 2001). Freibauer (2003) performed an inventory of GHGs from European agriculture. He developed a methodology to quantify emissions based on emissions factors and regional regressions equations derived from all available measurements in Europe. This methodology seems to be better than the IPCC methodology, reducing the uncertain by 50%. Freibauer affirms that nitrous oxide has rarely been measured in Mediterranean soils (Freibauer, 2003). Countries having ratified the United Nations Framework Convention on Climate Change (UNFCCC 1997) have committed themselves to report their emissions annually using the standard imposed by the IPCC methodology (IPCC, 2007). The default is the calculation of an emission factor that indicates the ratio between the cumulative flux of gas (e.g. N_2O or CH_4) with respect to the N input. This reduces the complex process of emission, transport and consumption to a simplified standard (Heyer, 1994; Chadwick et al., 1999). Furthermore this index is based on an assumption about the relationship between a given activity and emissions generated. The exact emission figures will always remain unknown. There is therefore a clear need for direct measurement of GHGs.

Global estimation of GHGs are usually made by multiplying averages of small chamber measurements for a given area (Potter et al., 1996). Chamber systems are the most common methods used to measure soil fluxes (Le Dantec et al., 1999; Livingston & Hutchinson, 1995; Pumpanen et al., 2004; Widen & Lindroth, 2003), due to short measurement times and small size (Lamouroux, 2008). Moreover, in a field comparison study, Freijer and Bouten)(1991) found them to be more accurate than other methods. Their main advantage is that the fluxes are measured directly from soil and associated with a particular emission site. Gas residence time in the chamber is minimal so the chemical transformations between emission and analysis can be minimized. However, it should be noted that the chamber system cannot completely simulate the ambient environment. The chamber measures over a small area, then requiring extrapolation which can become a problem when upscaling to large areas (Aneja et al., 2006). In this case the data obtained can be used to calibrate process-level models for estimating global fluxes and to evaluate potential effects on climate and land use (Potter et al., 1996). Since the chambers are site-specific, they offer the possibility of a rapid, exact and unambiguous answer based on the change of a specific parameter in a site.

As mentioned above, soil moisture is one of the main parameters that influences emissions. Soil water content, by influencing the availability of $O_{2,}$ can modify the soil environment, selecting a specific microflora and certain chemical and biological processes. A shallow groundwater can provide a great contribution to the amount of water stored in the root zone, but also to the vertical bidirectional movement of the water (up-flux and down-flux) (Logsdon et al., 2009).

Shallow water tables are a characteristic trait of ample areas of the Po Valley which are intensively cropped with high input levels. It is therefore important to assess the vulnerability as well as the potential for N removal of shallow water tables, evaluating the relationships between water table depth, GHG emissions and water pollution.

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Chapter II

Interaction between irrigation and N fertilization in an area subject to the Nitrates Directive. Effects on N Balance.

1.Introduction

The use of fertilisers, although required for obtaining high yields, is regulated by environmental and economic factors. Particularly in areas where intensive livestock rearing (and therefore manure production) and irrigated land coexist, there is growing concern about possible groundwater contamination by nitrates.

BMPs encourage a N balance for reducing N accumulation after crop harvest but it is also important to emphasize the role of irrigation management for reducing water percolation (Sacco and Bassanino, 2008; Morari et al., 2012). Irrigation management is even more important than fertilizer management for reducing leaching losses (Sexton et al., 1996). Many authors observed an increase in N leaching due to an increase of irrigation (Ferguson et al., 1991; Schepers et al., 1991; Burkart and James, 1999; Sogbedji et al., 2000; Gehl et al., 2005). Hu et al. (2005) reported that there is the potential to cut irrigation by 50% on the Northern China Plain without reducing yields. Other Authors (e.g. Pang et al., 2007) argue that higher water applications can reduce yields and are associated with higher N leaching for a given N application amount. However, on the other hand, irrigation increases water availability, promoting plant growth and enhancing nitrogen use efficiency.

The EU Nitrates Directive established a limit of 170 kg of organic N ha^{-1} + 60 kg N ha^{-1} from urea to limit N losses to groundwater in Nitrate Vulnerable Zones (NVZ). It is worth noting that this limit seems to reduce the usefulness of the nitrogen balance by imposing the same nitrogen input for every crop, soil and amount of irrigation. At the same time the Directive deals only with the concentration limit of NO_3-N in a water body, not considering total loads of NO_3-N directed to groundwater.

In Veneto Region (NE Italy), where a large part of the territory is classified as NVZs, livestock production is intensive and the resulting manure is mainly spread on maize, a crop with high N demand but frequently requiring consistent water supplies through irrigation. The objective of this study was to link crop production with groundwater protection. The effect was evaluated of four different irrigation levels and four N fertilization rates on maize production and N losses. The study was carried out in lysimeters as they provide an efficient controlled system of nitrates leached. Using the dataset obtained, a site-specific metamodel was developed that can predict the release of nitrogen according to N fertilization and irrigation amount.

2. Materials and Methods

The experiment was conducted in 2006-2010 at the University of Padova Experimental Farm in Veneto Region (northeast Italy, 45°19’ N, 11°31 E, 8 m a.s.l.). The local climate is sub-humid, with annual rainfall of about 850 mm and yearly average temperature of 12 °C. Reference evapotranspiration (ETo) is 945 mm with a peak in July (5 mm d^{-1}). Sixteen drainage lysimeters (1 x 1 m^2 width x 1.5 m depth) were cropped with maize (*Zea mays* L.).

The soil was a Fluvi-Calcaric Cambisol (CMcf) , with 35% sand, 48% silt, 17% clay and a pH of 8.1. Organic matter content was about 1.1 – 1.3% (tab. 2.1).

Soil properties	**Depth (cm)**	
	0-50 cm	**50-140 cm**
Sand (%)	31	35
Silt (%)	49	45
Clay (%)	20	20
pH	8.13	8.1
Total Nitrogen (%)	1.1	1.0
Organic carbon (%)	0.82	0.66
Organic matter (%)	1.41	1.14
C to N ratio	7.45	6.6
Total carbonate (%)	20.1	17.3
Soluble carbonate (%)	4.1	3.9
Salinity (mS cm^{-1})	0.28	0.26
Available P	1	9
Available K	135	128

Tab.2.1- Initial soil chemical and physical properties, April 2006.

The lysimeters were filled with a homogeneous profile of soil to a depth of 130 cm.

The drainage collection system was composed of an underground plastic pipe that connected the bottom of the lysimeter with a tower tank. In free drainage condition the tank was emptied to capture water from the lysimeter. By using the tank as a communicating vessels system it was possible to create a controlled water table inside the lysimeter.

In case of unfavorable weather conditions, an automatically-closing plastic roof allowed the lysimeter site to be covered.

Irrigation was provided by a drip micro-irrigation system that could integrate or replace rainfall.

2.1 Treatment and management

Sixteen treatments were studied: four water regimes with four levels of nitrogen input were compared in a randomized design. The experimental design has not provided the replications in order to maximize the number of combinations in the study. The water regimes (i.e. the sum of precipitation and irrigation (P+I)) were 800, 1100, 1400, 1700 mm y^{-1} with free drainage (FD) in 2006-2008. 800-1000 mm y^{-1} of rainfall is common in many area of Veneto Region.

In 2009-2010, 1700 mm y^{-1} of water was changed to 1100 mm y^{-1} with a controlled 1-m depth water table (WT) and the overall situation was 800, 1100, 1400 mm y^{-1} (FD) and 1100 mm y^{-1} (WT). During the winter period the automatic roof was blocked in open position so the bare soil received the rainfall. In summer water supply was provided by irrigation, integrating the observed rainfall to reach the scheduled amounts of water.

Soil tillage was a spring spading at 25 cm followed by nitrogen fertilization and crop sowing (mid-April every year). Lysimeters were manually sown with maize at a density of 8 plants m^{-2}, in two rows with a distance of 70 cm and 20 cm between plants. An edge (2 rows) was provided at the sides of lysimeter, to reproduce a field situation as much as possible.

Maize received a mix of beef cattle manure and poultry litter (M) at 85, 170, 255, 340 kg N ha^{-1} y^{-1} at sowing. We tested the limits of 170 and 340 kg N ha^{-1} y^{-1} that are the limits for vulnerable and not vulnerable zones respectively (EEC, 1991). The fertilizer composition was as follows: total nitrogen 2.8%, P_2O_5 3%, K_2O 2% and organic matter 65%. A supplementary N input (60 kg N ha^{-1}) was applied using urea split in two doses, the first 40% at sowing and the remaining 60% after maize emergence (mid-May). Crop aboveground biomass was harvested in the first week of September every year. No cover crop was used so during the winter the soil was bare until the next spring sowing.

Volumes of water input (rain and irrigation) and output (drainage water) were recorded and samples analysed for the main chemical-environmental parameters.

2.2 Maize analysis

Grain and the residual aboveground biomass were dried in a forced draft oven at 65 °C and then analysed for total Kjeldahl nitrogen (TKN) and residual moisture content (from 65 to 105 °C). Total Kjeldahl nitrogen was determined by digesting 3 g of tissues with H_2SO_4 and $CuSO_4$. After chemical decomposition, samples were processed with NaOH and the amount of ammonia produced was determined by back titration with HCl. The amount of N (% w/w) was corrected for the residual moisture of the tissue samples.

2.3 Soil collection and analysis

The soil profile was sampled every year in mid-March and at the beginning of October.

Soil samples were taken at six depths (0-5, 5-30, 30-55, 55-75, 75-95, 95-120 cm) with randomized repetitions in each lysimeter. A portion of soil was dried in a forced draft oven at 105 °C for determining the gravimetric humidity. Another set of samples was stored frozen prior to analyses for NO_3^-- N; nitrates were determined colorimetrically after extraction in 0.5 M K_2SO_4 (Cataldo et al., 1975). The remaining soil was air-dried and then assayed for TKN analysis.

2.4 Water analysis and water balance

Water input (irrigation, rainfall and simulated groundwater) and output (drainage water) were stored frozen and later analysed for NO_3^--N and TKN. Samples of water were filtered before analysis performed by the colorimetric method (Cataldo et al., 1975) and total Kjeldahl method respectively.

Volumes of water input and output were used to determine the annual effective evapotranspiration (ET_e in mm y^{-1}) through the following water balance:

[1] $ET_e = ((Ui\text{-}Uf) + (P+I) - D)$

where Ui and Uf are the initial and the final moisture of soil every year, P is the volume of precipitation and I the volume of irrigation. D is the total drainage water.

2.5 Nitrogen Balance

Cropping systems are dynamic, with dramatic disparity in both timing and extent of crop status (soil cover, root depth, N uptake pattern) and management events (tillage, irrigation and fertilization) over the year. The timing of fertilizer and irrigation applications in relation to plant demand has an important influence on the nutrient balance of cropping systems (Cichota et all., 2010). An annual balance can capture the difference between years and provide information on depletion or accumulation of N in the soil.

An annual N balance was applied according to the following equation:

[2] $$N\ residual = N_{input} - N_{biomass}$$

$$N\ input = N_{manure} + N_{urea} + N_{irrigation} + N_{rain}$$

where $N_{residual}$ (kg N ha^{-1}) is a term comprehensive of N leaching and the change in N content of the soil profile between the beginning and end of the year. N_{manure}, N_{urea}, $N_{irrigation}$ and N_{rain} (kg N ha^{-1}) are the N inputs as fertilizer, rainfall and irrigation. $N_{biomass}$ (kg N ha^{-1}) is the N exported by maize biomass. $N_{biomass}$ is the sum of $N_{grain} + N_{stalks}$. $N_{leached}$ is the product of NO_3^--N concentration and water loss:

[3] $$N_{leaching} = \sum_i P_i\ C_i$$

where P_i is the percolation (l) for a single event "i", and C_i is the respective N concentration in water (mg N l^{-1}).

2.6 Development of a metamodel for nitrogen release

In order to improve the water and groundwater quality we developed an algorithm able to simulate the N leached in agricultural systems (Fig. 2.6.1). The results from our five-year experiment were used for the identification of a set of empirical functions. Basic water and nitrogen balances were calculated to obtain the drivers of the model. The model works with an annual time–step, focusing on good-reproduction of long-term and large-scale behaviour.

The general function of the model can be simplified as follows:

$y = f(x)$

The output $\boldsymbol{y}$ is a scalar ($N_{leached}$) whereas $\boldsymbol{x}$ can have a large number of components, in our case $\boldsymbol{x}$ is the percolation water (*Perc*) obtained from water balance.

The driving variables (input) and output are simplified as shown in fig. 1.

The building of the model follows four steps:

- the definition of dataset, input (x) and output variables (y);
- the definition of the form of the model (calibration), that is the mathematical equation:

$$y = A' \quad \frac{x}{1+x}$$

- the use of real input (called training data) to obtain the estimated-output;
- the validation of the model where estimated-output is compared with real-output.

$N_{leached}$ in function of percolation water (Perc) is approximated by an equilateral hyperbolic function:

$$[4] \qquad N_{leached} = (a \cdot N_{res} + b) \cdot \frac{i \cdot (kw \cdot Perc)}{1 + i \cdot (kw \cdot Perc)}$$

When Perc is zero N leached is zero. The horizontal asymptote is $a \cdot Nres + b$ and is equal to 1. N_{res} is the residual N at the end of the year shown in equation [2] while a and b are respectively the slope and intercept of the linear regression performed between $N_{leached}$ and N_{res} data; $N_{leached\text{-}REAL}$ is strongly influenced by N_{res} that is a pool of N not used by plants and therefore potentially leachable. Moreover *i* is the curve slope, *kw* a coefficient of water availability and *Perc* the percolation water per year.

$N_{leached}$ is the annual N loss in the site.

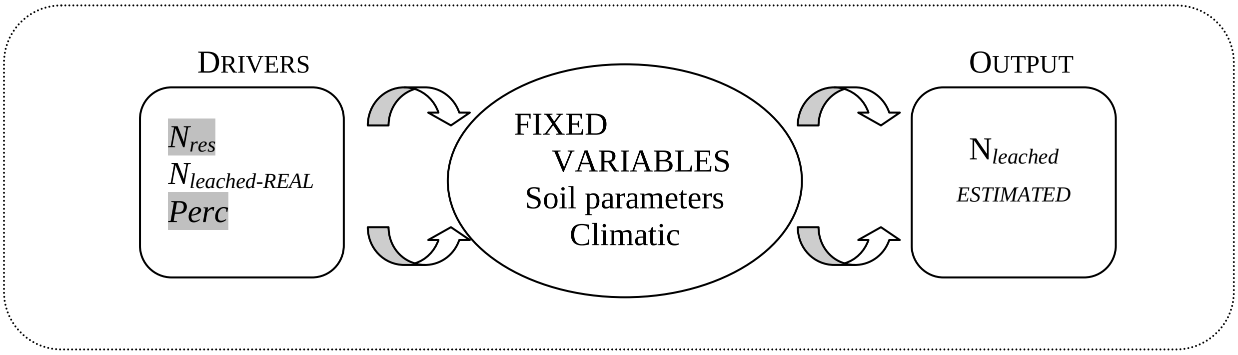

Fig. 2.6.1- Operation of the metamodel.

The input data set were randomly divided in two groups, 60% of data were used for training (for defining a, b, N_{res}, i and kw) and the remaining 40% were used for the validation of the metamodel. Both groups contained data coming from each of the five years. The behaviour of the metamodel was evaluated calculating the R^2 coefficient between the estimated ($N_{leached\text{-}ESTIMATED}$) and real output ($N_{leached\text{-}REAL}$) to achieve the good approximation of the model.

The availability of a large number of training data plays an important role in the choice and soundness of the model. The metamodel we performed had a site-specific calibration, so intrinsically considering the local characteristics of the area (climate, soil physical characteristics) and can be extended to field and territorial scale.

2.7 Statistical analysis

A multiple linear regression analysis (MR) was applied to establish the different effects and a possible interaction of N rates and water regimes on total biomass and grain yield of maize, on N uptake by plants and N concentration in crop tissues.

MR is a highly flexible system for examining the relationship of a collection of independent variables (or predictors) to a single dependent variable (or criterion) (Aiken et al., 2003).

Using the same approach as simple regression, the model could calculate the best single predictor, and then keep adding the next best predictor to make the estimates more accurate, until either we run out of possible predictors or the model cannot improve its R^2 any further with the available predictors (Arthur et al., 2012).

Analysis were performed using SAS (Statistical Analysis System) p = 0.05. A multiple non-linear regression was used instead for N leached. The Kruskall-Wallis multicomparison test (performed with R) was used to obtain differences in NO_3^--N concentration in leaching water (p=0.05)

3. Results

The same experiment management applied in five successive years was affected by different weather conditions. During summer 2006 and 2007 median temperatures were hotter than the climatological standard normal for the site and maize water demand was high.

Maize yields are very sensitive to water stress, especially at flowering and pollination stages. For instance, NeSmith and Ritchie (1992) reported that the reduction in maize yield exceeded 90% due to water deficit during flowering and pollination stages; so to prevent excessive water stress the fixed water regimes (800, 1100, 1400, 1700 mm y^{-1}) were increased as needed during the summer period by an amount of water ranging between 50 and 300 mm, while maintaining the proportion between the different regimes. Annual water regime and evapotranspiration are shown in fig. 3.1. The years 2009-2010 are plotted separately because in 2009 the regime 1700FD was changed to 1100WT; for this reason the discussion breaks down the first three years of data from the latter two.

The effect of N rates and water regime on maize biomass production and N uptake is analyzed first, then the N leaching towards the groundwater due to different N doses and irrigation+rain is considered. With our dataset we tried to propose an equation able to provide the N release related with dose and water regime. This is useful to understand what effects the limit imposed in Nitrate Vulnerable Zones (NVZs) has. The equation is site-specific but easy to transfer to different areas.

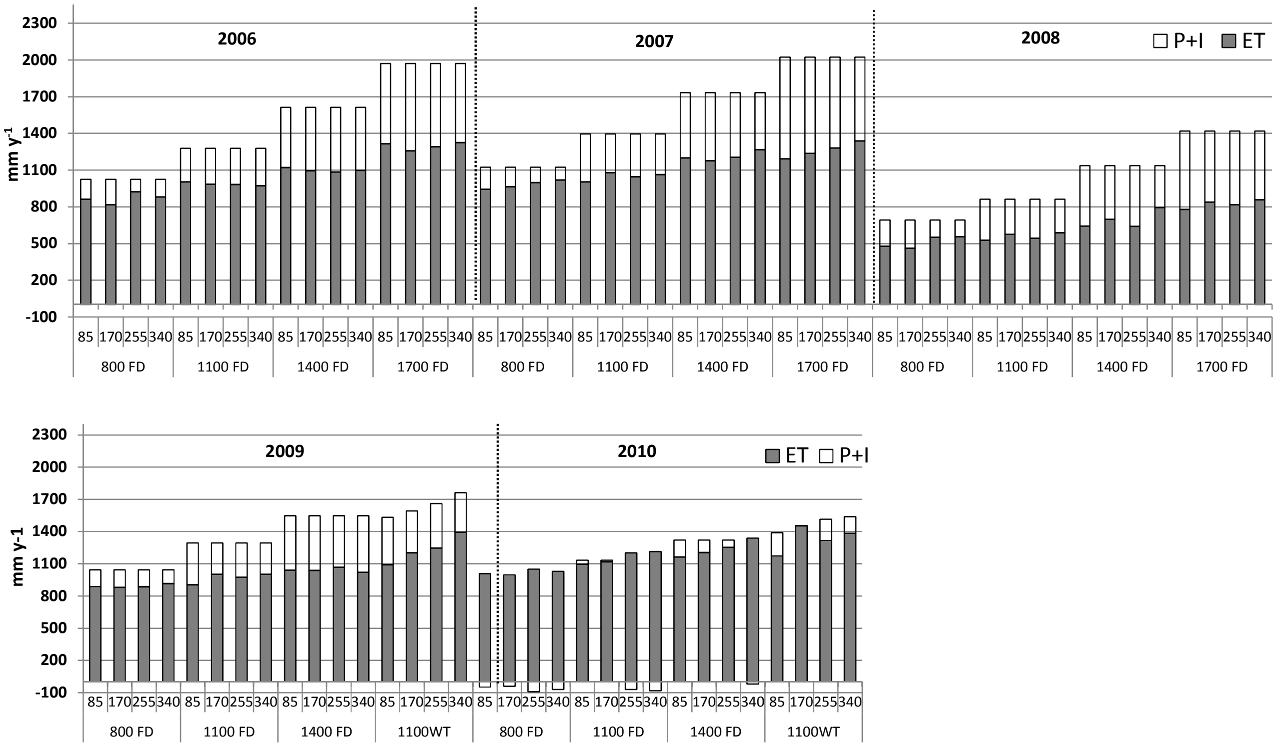

Fig.3.1 – Water regime and effective evapotranspiration (ET_e) per year (April to April). The four N rates and different water regimes are on the x axis.

3.1 Biomass and yield

N rate significantly increased the total aboveground biomass and grain yield in the first three years (fig. 3.1.1). Total aboveground biomass ranged between a 3-year average of 27 t ha^{-1} with the lowest fertilization (85_M) to 33 t ha^{-1} with the highest (340_M). Averages were 12 and 16 t ha^{-1} for grain yield respectively. In the second two years the differences were also significant, but the grain yield was higher with 170_M than in the previous years and without significant increases until 340_M. Biomass yield instead rose with N rates. Stalks production (stem, leaves and cob) had significant differences in both periods (2006-2008 and 2009-2010).

Likewise, water regime affected the production of maize with a positive effect for every rate of N. In 2006-2008 the water effect on maize production was very significant. Water regime and N rates influenced production and N uptake separately, in fact the statistical analysis didn't underline any interaction between the two studied parameters (Tab.3.2.1).

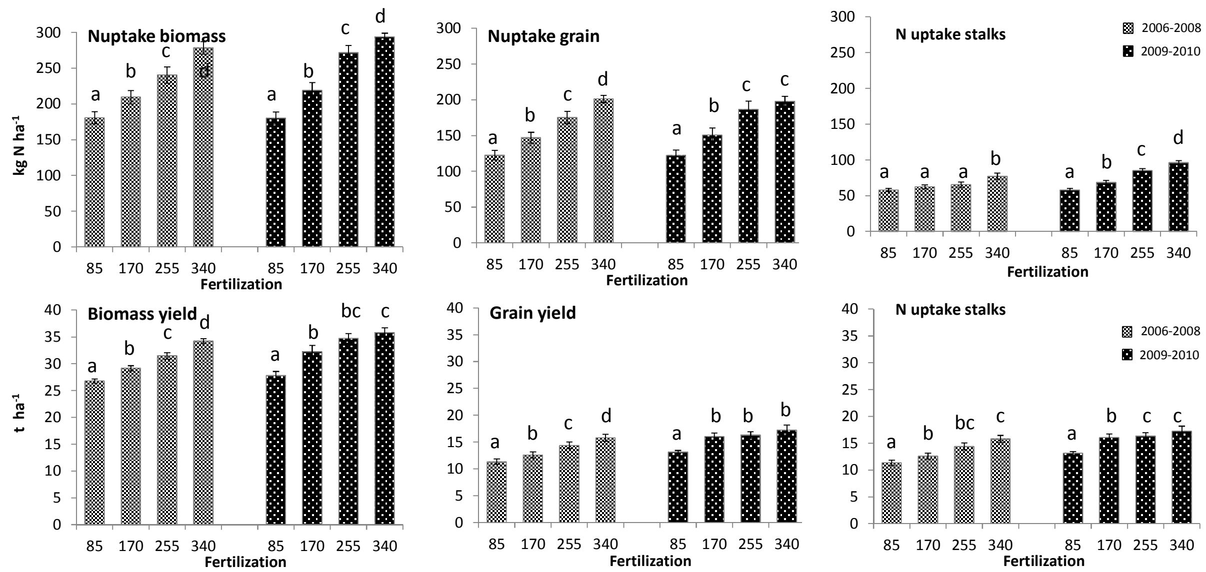

Fig. 3.1.1 – Averages of maize production and N uptake in 2006-2008 and 2009-2010.

3.2 N uptake

In both periods (2006-2008 and 2009-2010) N rates significantly affected N uptake in total biomass, grain and stalks (Fig.3.1.1). Statistical analysis only underlined the same level of N uptake in grain for 255_M and 340_M during the 2009-2010 period.

Maize also responded positively to water regime; in 2006-2008 only the interaction between P+I and N_{grain} was not significant (Tab.3.2.1). In this case it seems that the N in maize didn't respond to an increase in irrigation. This situation was created by the different volume of water received in the years. In 2006 and 2007 the water regime was about 20-25% higher than the fixed regime; in particular at 1400FD and 1700FD it could be excessive with respect to the crop water demand, encouraging nitrogen leaching.

Furthermore, at the lower rate of N (85_M), even a small part of the nitrogen loss involves a strong reduction of nitrogen available to the crop. In 2009-2010 only $N_{residual}$ is not influenced by water regime. Moving from 85_M to 340_M, a change of about 80-100 kg in N biomass uptake was observed. The increase in water supply caused smaller effects on N uptake (6-38 kg). N uptake in grain ranged from 157 to 254 kg N ha^{-1} in 2006-2008 and from 164 to 314 in 2009-2010.

The N_{grain} and $N_{biomass}$ rate was about the 70%. Less than 30% of total N was stored in residues (in both periods).

A significant increase of N concentration (g N kg^{-1}) in crop tissues was associated with increasing rates of N fertilizer; but instead a negative effect on N concentration was due to an increasing of water regime (in both periods). In this case the highest biomass production (and grain yield in particular) was connected with the lowest N concentration; there is a sort of dilution effect of N concentration in crop tissues. As mentioned by Al-Kaisi and Yin (2003), N uptake seemed to be more related to an increase in dry matter production than to an increase in N concentration in plants.

In the 2009-2010 period the effect of the shallow water table (WT) on maize yield and N uptake was also tested. WT positively affected total biomass and stalks production. Water from the WT increased the water availability provided by irrigation+rain, so maize production rose to the detriment of nitrogen concentration in crop tissue ($[N]_{biomass}$ and $[N]_{grain}$ $p<0.05$).

		Total biomass (t ha^{-1})		Grain yield (t ha^{-1})		Stalks (t ha^{-1})		$N_{biomass}$ (kg N ha^{-1})		N_{grain} (kg N ha^{-1})		N_{stalks} (kg N ha^{-1})		$[N]_{biomass}$ (g kg^{-1})		$[N]_{grain}$ (g kg^{-1})		$[N]_{stalks}$ (g kg^{-1})	
		estimate	se	estimate	se	estimate	se	estimate	se	estimate	se	estimate	se	estimate	se	estimate	se	estimate	se
2006-2008	Precipitation and Irrigation(P+I) ǂ	0.0133	0.0018	0.0053	0.0010	0.0078	0.0010	0.0260	0.0131	0.0087	0.0103	0.0172	0.0055	-0.0026	0.0004	-0.0045	0.0007	-0.0008	0.0003
	P (0.05)	*< 0.0001*		*< 0.0001*		*< 0.0001*		*0.0529*		*0.4035*		*0.034*		*< 0.0001*		*< 0.0001*		*0.0174*	
2009-2010	Precipitation and Irrigation(P+I) ǂ	0.0127	0.0026	0.0058	0.0016	0.0050	0.0020	0.0392	0.0177	0.0367	0.0162	-0.0269	0.0085	-0.0014	0.0006	-0.0013	0.0008	-0.0013	0.0005
	P (0.05)	< 0.0001		0.001		0.0209		0.036		0.0325		0.7551		0.0292		0.1057		0.0265	
	Water table(WT)	-2.1338	1.2106	-0.0612	0.6122	-1.9853	0.8080	7.3243	6.9505	10.0172	6.3595	-2.4490	4.0082	0.6858	0.2402	0.7427	0.3555	0.3562	0.2191
	P (0.05)	*0.0902*		*0.9212*		*0.0213*		*0.3021*		*0.1278*		*0.5467*		*0.0085*		*0.047*		*0.1165*	

Tab. 3.2.1 – Comparison of two different treatments (fertilization and irrigation+rain) on yield components. Results of multiple regression.

ǂ Precipitation and irrigation are relative to the period sowing-harvesting.

3.3 N balance

Table 3.3.1 shows the average inputs and outputs (i/o) on nitrogen balance. Water regime changed from 1700FD to 1100WT in 2009 and 2010 so in this case we split the data (i/o) in two groups, the first relative to the years 2006-2008 and the second to 2009-2010 (when the simulated water table was applied). There was a significant effect of both N rate and P+I and a significant interaction. (Tab.3.3.2).

Years 2006-2008		N_{input}			N_{output}		$N_{residual}$	$N_{efficiency}$
abbreviation		Manure	Urea	$N_{irrig+rain}$	N_{uptake}	$N_{leached}$		
		kg N ha^{-1}	kg N ha^{-1}	kg N ha^{-1}	kg N ha^{-1}	kg N ha^{-1}	kg N ha^{-1}	(%)
800FD	85M	85	60	18.9	169.8	38.0	**-5.9**	103.6
	170M	170	60	18.9	175.8	35.0	**73.1**	70.6
	255M	255	60	18.9	206.8	41.4	**127.2**	61.9
	340M	340	60	18.9	240.6	46.4	**178.3**	57.4
1100FD	85M	85	60	23.6	157.8	29.9	**10.8**	93.6
	170M	170	60	23.6	184.1	29.7	**69.5**	72.6
	255M	255	60	23.6	211.7	39.4	**126.9**	62.5
	340M	340	60	23.6	238.8	52.7	**184.8**	56.4
1400FD	85M	85	60	29.9	162.9	40.4	**12.0**	93.1
	170M	170	60	29.9	202.2	28.7	**57.7**	77.8
	255M	255	60	29.9	221.6	34.1	**123.3**	64.2
	340M	340	60	29.9	264.2	56.9	**165.7**	61.5
1700 FD	85M	85	60	36.1	153.3	26.9	**27.8**	84.6
	170M	170	60	36.1	187.9	31.2	**78.2**	70.6
	255M	255	60	36.1	223.0	39.8	**128.1**	63.5
	340M	340	60	36.1	254.6	55.6	**181.5**	58.4

Years 2009-2010		N_{input}			N_{output}		$N_{residual}$	$N_{efficiency}$
abbreviation		Manure	Urea	$N_{irrig+rain}$	N_{uptake}	$N_{leached}$		
		kg N ha^{-1}	kg N ha^{-1}	kg N ha^{-1}	kg N ha^{-1}	kg N ha^{-1}	kg N ha^{-1}	(%)
800FD	85M	85	60	20.0	164.3	17.2	**0.7**	99.6
	170M	170	60	20.0	205.4	15.9	**44.6**	82.1
	255M	255	60	20.0	255.7	15.6	**79.3**	76.3
	340M	340	60	20.0	284.3	25.5	**135.8**	67.7
1100FD	85M	85	60	24.3	190.9	17.6	**-21.6**	112.8
	170M	170	60	24.3	240.3	17.7	**14.0**	94.5
	255M	255	60	24.3	281.4	20.1	**57.8**	83.0
	340M	340	60	24.3	314.4	28.0	**109.9**	74.1
1400FD	85M	85	60	28.7	188.0	15.5	**-14.3**	108.2
	170M	170	60	28.7	239.6	18.2	**19.0**	92.6
	255M	255	60	28.7	272.6	20.9	**71.1**	79.3
	340M	340	60	28.7	301.6	32.5	**127.1**	70.4
1100WT	85M	85	60	29.2	168.9	1.4	**5.4**	96.9
	170M	170	60	30.5	201.2	1.9	**59.3**	77.2
	255M	255	60	31.8	256.5	3.3	**90.3**	74.0
	340M	340	60	33.0	295.6	3.6	**137.5**	68.3

Tab.3.3.1- Average of N input and output in N balance (periods 2006-2008 and 2009-2010).

N uptake by maize was a bit higher in the second period than in the first, so more N could be lost in the first period than in the second. $N_{leached}$ in 2006-2008 was higher in 85_M than in 170_M. In 85_M maize was probably stressed by the low input and adsorbed nitrogen was low.

		$N_{leached}$ (kg N ha^{-1})	N_{res} (kg N ha^{-1})	$N_{Efficiency}$ (%)
		P (0.05)	*P (0.05)*	*P (0.05)*
2006-2008	N rate	*0.0052*	*< 0.0001*	*< 0.0001*
	Precipitation and	*0.0039*	*0.1669*	*0.2931*
	$N_{biomass}$	*0.0737*	-	-
	$N_{biomass}$*N rate	*0.0146*	-	-
	P+I* N rate	*0.0029*	-	-
	P+I* N rate* N_{biom}	*0.0034*	-	-
2009-2010	N rate	*0.0236*	*< 0.0001*	*< 0.0001*
	Precipitation and	*0.0838*	*0.0975*	*0.0722*
	Water table (WT)	*< 0.0001*	*0.0014*	*0.0035*
	N rate * WT	*0.048*	-	-

Tab.3.3.2 – Results of multiple regression for $N_{leached,}$ $N_{res\ and}$ $N_{efficiency}$.

ł Precipitation and irrigation are relative to one year (April to April).

The timing was not propitious for nitrogen uptake by maize, and N leached more than in $170_{M.}$ In 1700FD, $N_{leached}$ was similar to 1400FD; we supposed that the high level of water could create some temporary anaerobic condition, able to stimulate a weak denitrification process.

The comparison between the water table condition and free drainage condition was very interesting. $N_{leached}$ in 2009-2010 was equal to an average of 1.4, 1.9, 3.3 and 3.6 kg N ha^{-1} (for 85, 170, 255, 340_M) compared with values in 1700FD of between 26.9 and 55.6 in the first three years. Also in 1100FD, where the lysimeter received the same P+I as in 1100WT, average N loss ranged between 35 and 65 kg N ha^{-1} y^{-1} in 2006-2008 and 18-28 kg N ha^{-1} y^{-1} in 2009-2010. Water table therefore seems to significantly reduce N leached, with any N rate.

$N_{residual}$ calculated as in equation [2] presented some negative values for 85_M in both periods and this means that the plants depleted the soil N pool and the N efficiency was over 100%. Over 85_M the nitrogen balances are positive, and its are more positive increasing fertilization. $N_{residual}$ showed a significant relationship with N rates. Statistical analysis indicates that also water regime affected $N_{residual}$. An increase of water regime decreased $N_{residual}$ until 1400FD. In 1700FD and 1100WT $N_{residual}$ started to increase again. The gap between N i/o in 2006-2008 was particularly evident over 170_M, for 255_M $N_{residual}$

ranged between 123 and 128 kg N ha^{-1} and for 340_M between 165 and 184. In this last case the N efficiency goes down, reaching 56-62%.

In 2009-2010 $N_{residual}$ was particular high in 1100WT. N uptake was lower than in 1400FD, the water table, on the one hand, limited the depth of the maize roots but, on the other, stimulated an anaerobic condition and probably a denitrification process, leading to N reduction in groundwater and successive N loss.

3.4 N concentration in percolation water

The Nitrates Directive gives more emphasis to nitrogen concentration in groundwater as a potential source of pollution than to the total loss towards groundwater. A graph of NO_3^--N medians in percolation water is presented in Fig. 3.4.1. Volume of percolation water and nitrates concentration is lowest in the summer and highest values are detected in late autumn and spring. N concentration in irrigation water and rain in general didn't exceed 2 mg NO_3-N l^{-1}. In 2006-2008 concentrations were significantly affected by N rate and water regime.

Medians for 800FD (for every N rate) and for 340_M (with 800FD and 1100FD) exceeded the drinking water limit of 11 mg NO_3-N l^{-1} established by the Nitrates Directive. The rate of 340 kg N ha^{-1} y^{-1}(340_M) seems to be too high in free drainage conditions while the presence of a shallow water table substantially reduces NO_3^--N concentration independently of N rate applied. Lower variability and lower medians characterized 1400FD. 1400FD promotes the biomass development and also the N uptake. With 1700FD medians were about 4-5 mg NO_3-N l^{-1}; median was only close to the limit in 1700FD-340_M.

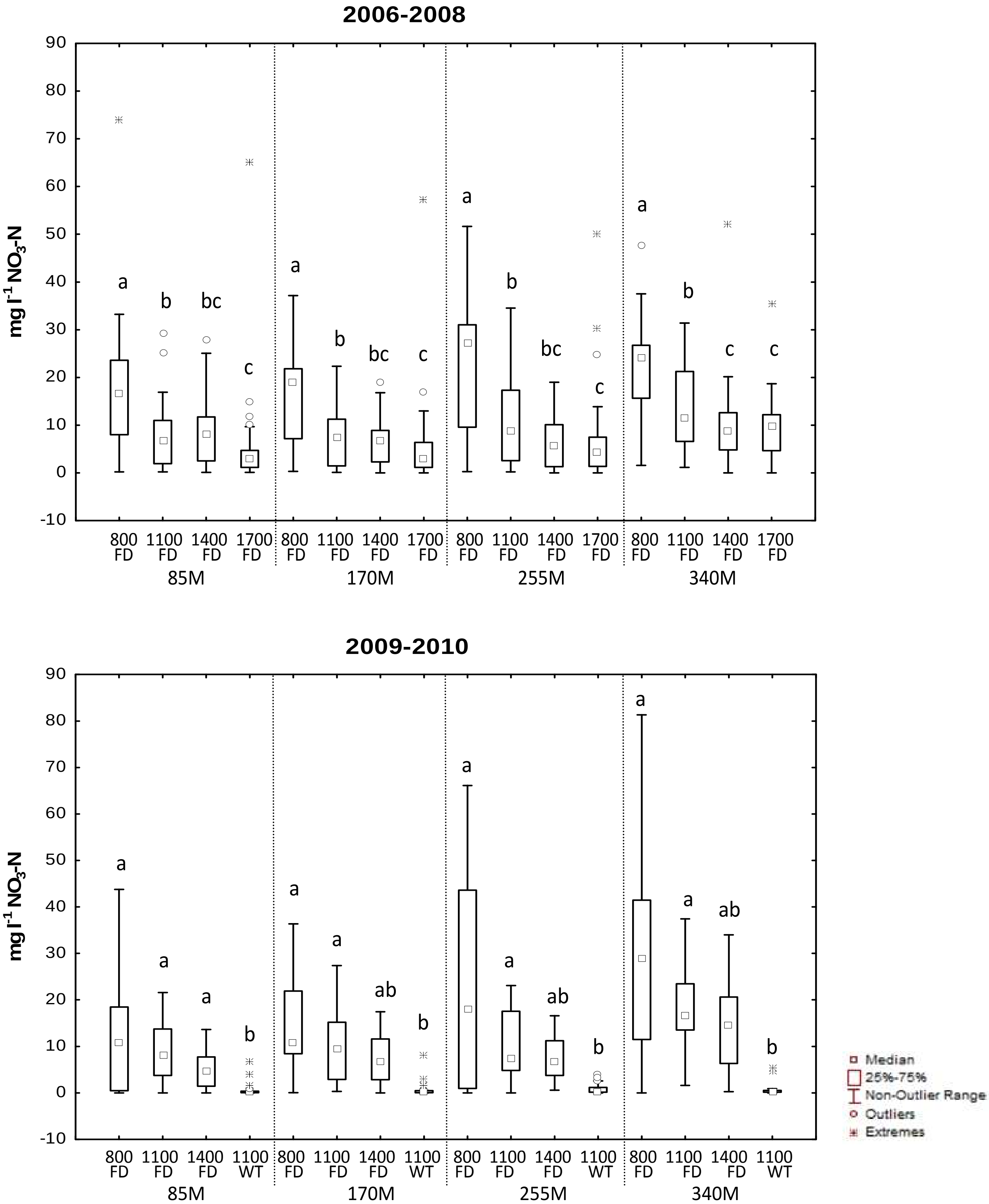

Fig.3.4.1 – NO_3^--N concentration in leaching water during the 2006-2008 and 2009-2010 periods. Significance tested with Kruskal -Wallis multicomparison (p = 0.05).

In 2009-2010 the concentrations were higher than the previous years in particular in 85_M, but the volume of percolation water was lower than in 2006-2008. The concentrations in 1100WT were very low, in general between 1 and 1.5 mg NO_3-N l^{-1}.

The difference in N concentration between 1100FD and 1100WT reflects the difference observed in $N_{leached}$. The decrease of concentrations in 1100WT is not linked to a simple effect of dilution caused by the volume of water in simulated groundwater. As a matter of fact, cumulated $N_{leached}$ is very low, for example with respect to the same water regime but with free drainage (1100FD).

3.5 Metamodel - Calibration and Validation

The precipitation and irrigation surplus that resulted in percolation water beneath the root zone ranged, depending on the water regime, from 100 to 600 mm y^{-1} in 2006-2008 and from 50 to 150 mm y^{-1} in 2009-2010. So we could test a large variability of percolation volume and relative N loss, placed in the central part of the curve and towards the horizontal asymptote.

For the calibration of the model we excluded the data from 1100WT, because there were too few to depict the behavior of N losses with a shallow water table. The analysis was therefore restricted to free-drainage situations. Fig. 3.5.1 shows the calibration and validation of the metamodel. 60% of the five-years data were used for calibration of the model while the remaining 40% were used for the validation.

The model hypothesizes no leaching if there is no water moving through the soil profile and then a hyperbolic increase in Perc towards an asymptote depending on the amount of residual N present in the profile. This hypothesis can fit the case of free drainage condition, while the model should be more complex in the presence of a shallow water table to account for possible upward movements of both water and dissolved N and for dilution effects of percolated water in the water table.

In the calibration phase the metamodel gave good results for a wide range of $N_{leached}$ values even if there was a tendency to underestimate the higher N losses. In the validation phase the model gave very good results except for 2006, when N losses were markedly underestimated. It is worth noting that 2006 was the first year of experimentation and, despite the attempt to fill the lysimeters in a homogeneous way, some preferential pattern allowing rapid deep percolation was still possible before the final soil settlement.

On this basis we tried to recalibrate and validate the model without data from 2006. Fig. 3.5.1 presents both sets of calibration/validation. The validation without 2006 presents a far lower RSME than that with 2006 (23.6 against 41.2) and a CRM very close to the optimum value of 0. The simple metamodel therefore seems able to give reliable estimates of N leaching over a wide range of both $N_{residual}$ and Perc values in free drainage conditions. Given the above, the second validation has been chosen for the representation of N leaching.

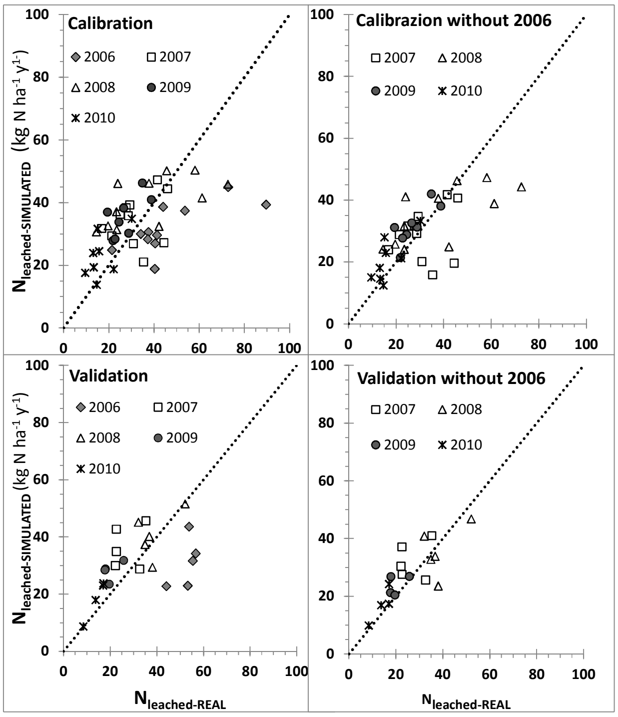

Fig. 3.5.1 – Calibration and validation of the metamodel.

4. Conclusion

Nitrogen turnover is a very complex process, characterized by a high spatial variability and a strong dependence on environmental factors such as meteorological conditions and soils (Shaffer and Ma, 2001; Zhang et al., 2002). Climate influenced maize yield and water supply, this has created some variability in annual production, N uptake and N leaching. Anyway we understood that N rate and water regime positively increase maize yield and maize uptake.

The effect of the interaction between N rates and irrigation on maize production was investigated by different authors (Martinet et al., 1982; Eck, 1984; Sexton et al., 1996; Burman et al., 1962). Burman, in particular, highlights that an increase in soil moisture enhances maize yield response to N fertilization, especially when high N rates are applied. In our study the highest fertilization combined with higher water regime (1400FD and 1700FD) enhanced the production. However manure, applied at rates higher than those required by the crop, caused an increase of N in the root zone. Our data showed that only a small part of N stored in soil was lost to the groundwater; most of it could be retained in the soil as organic N, potentially not immediately leachable, but available as fertilizer for the next crop.

Water regime can stimulate biomass production and N uptake but without increasing N concentration in grain. On the contrary an increase in production involves a reduction in N concentration in crop tissues. Maize productions and consequently N uptake are not very high with 85_M and 170_M. Uptake of N over 200 kg N $ha^{-1}y^{-1}$ occurred with an N rate of 255 kg N $ha^{-1}y^{-1}$ +60 kg N $ha^{-1}y^{-1}$ urea (255_M). In this case N leached ranged from 34 to 41 kg N $ha^{-1}y^{-1}$ in 2006-2008 and 15 to 20 kg N $ha^{-1}y^{-1}$ in 2009-2010 depending on water regimes. So if the water regime is controlled and there is little surplus water that can percolate (similar to the situation in 2009-2010), 1100FD and 1400FD seem to be a good solution for reducing N leaching and maintaining high production. These levels of water supply seem to be appropriate even for NVZ, also in the case of N supply of 255 kg N $ha^{-1}y^{-1}$+ 60 kg N $ha^{-1}y^{-1}$ from urea.

Water regimes over 1400FD are not recommended, because there is a possible decline in production. Areas with shallow water table don't seem as potentially endangered regarding pollution by nitrates, thanks to a positive effect of the water table on the denitrification process. It still remains to be studied whether the denitrification process leads to the dangerous N_2 or to the very relevant greenhouse gases NO and N_2O. Median concentrations in leaching water showed that the N rates of 170 and 255_M and water regime over 800FD in general didn't exceed the limit of 11mg l^{-1}. 85_M reduced crop growth; instead 340_M created an excess of N input, leading to consistent N losses.

Summarizing, N leaching is connected with the N rate and in particular with the residual nitrogen (N_{res}) in soil after the harvest, and with percolation water (Perc). The metamodel developed is based on a very limited set of input data. The dependence on site-specific factors is mediated by the percolation rate, thus allowing a very straightforward extension of the model to different areas if a basic water balance model is available. The equation seems to be quite robust, allowing the representation of N losses over a wide range of N supplies and water regimes.

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Chapter III

N balance and Nitrous Oxide emission in soil subject to derogation from the Nitrates Directive in free drainage and shallow groundwater conditions.

1. Introduction

The use of manure as a N fertilizer in cropping systems can cause N leaching and interact with the SOC cycle, leading, depending on specific environmental conditions, to C sequestration or to greenhouse gas emissions (GHGs). The Nitrates Directive operates in support of water protection, by imposing limits for the distribution of organic fertilizers. The European Council has recently granted a derogation of the Directive in Italy, with the possibility in Nitrate Vulnerable Zones (NVZs) to spread 250 kg instead of 170 kg of organic N ha^{-1} y^{-1}.

Anyway, at present, atmospheric pollution by greenhouse gas emissions from agricultural sources is not considered by EU regulations. N gaseous losses in cropping systems, as a result of N fertilization, seem to contribute 35% of the total N_2O emissions (FAO and IFA, 2001). But there are gaps in the understanding of N gaseous emissions because of the large number of reactions that N has in soil.

The bacterial processes of denitrification are the dominant source of N_2O and NO. Denitrifying bacteria are ubiquitous in agricultural soil (Payne 1981) and they tend to concentrate around microsites in the soil matrix; these sites should be characterized by high availability of oxidizable organic matter and/or by conditions limiting oxygen diffusion. Furthermore not-limiting nitrates concentrations are required. The processes occur when NO_3^- is reduced to dinitrogen (N_2) gas following the pathway $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$. The conversion of NO_3^- to N_2 can be complete, but a small and variable portion of N is often lost as N_2O gas (Firestone, 1982; Firestone and Davison, 1989; Robertson and Groffman, 2007).

There is no solid evidence about the partitions in N_2 and N_2O emissions. In contrast to N_2, which is a natural atmospheric component, N_2O is a strong greenhouse gas: for a 100-year timeframe, a unit mass of N_2O is considered to have 296 times the Global Warming Potential (GWP) than a unit of CO_2 (IPCC, 2001). IPCC (2007) estimated the emission of N_2O as 1% of the N input. Other authors (Bouwan 1996; Mosier et al. 1996) indicate that total N losses range from 1 to 2% of the applied fertilizer.

Many authors have considered the possible effects of denitrification on nitrate pollution in groundwater (Knowles, 1982; Paul and Zebarth, 1997).

Significant N gaseous losses may represent either a loss of plant-available-N during the growing season, or a desirable process, reducing the amount of NO_3^- in the drainage water (Paul and Zebarth, 1997).

The optimum conditions for denitrification are generally found where oxygen supply is limited by restricted gas diffusion caused, for example, by high soil-water content, impeded drainage, shallow groundwater, or soil compaction. Under such conditions the probability of N_2O and NO being reconsumed by denitrifiers is greatly enhanced leading to low N_2O and NO emissions (Davidson, 1991; Skiba et al., 1997).

The presence of a shallow water table, providing an anaerobic environment, has been recognized as a potential factor for controlling N_2O losses from organic soils (Flessa et al., 1998; von Arnold et al., 2005). N_2O in shallow groundwater may remain for quite a while after production, due to high solubility and slow diffusion. This is a cause of temporal retardation and spatial separation of N_2O production and N_2O emission. (Bowden and Bormann, 1986; Rice and Rogers, 1993; Rolston and Marino, 1976; Tindall et al., 1995).

Apart from limiting oxygen conditions, denitrification in soil is also favored by NO_3^- concentration in soil and by the amount of available energy sources (organic carbon) for the denitrifying bacteria: NO_3^- is present in both mineral and organic fertilizer, while C is made available by organic fertilizer applications and soil organic matter decomposition. The composition of fertilizers applied to soils has a great influence on NO and N_2O emissions. The addition of organic fertilizers temporarily modifies dissolved organic carbon (DOC) and mineral N in soil, which affects denitrification and nitrification rates. Under wet conditions, the application of organic fertilizers produces a reduction in NO and N_2O in comparison with emissions from urea, at the same available N rate, in soils with a low organic C content (Meijide et al., 2007).

The combination of a shallow water table with manure fertilization can create the conditions enhancing denitrification because the shallow groundwater allows more rapid organic C transport to the saturated zone near the water table (Starr and Gilham, 1993). At the same time the availability of NO_3^- from manure ensures higher denitrification rates immediately above and below the water table (Trudell et al., 1986) reducing nitrates pollution.

As reported by Morari et al. (2012) in a recently study performed in NE Italy, the areas with shallow groundwater seem less vulnerable to nitrogen pollution with respect to the prediction of the regional methodology of NVZ assignment. The authors found low nitrogen concentration in soils fertilized with manure, where a shallow water table was present. In this case the agricultural impact on water quality did not appear to be very high in many areas as evidenced by N leaching and N balance. The water table level influenced the return of N leached in the root zone, by upward water movement, as well as N gaseous losses. This situation promoted a reduction in N losses to water bodies.

In the European Union the Nitrate Vulnerable Zones (NVZs) cover large areas of land with water tables exceeding or being at risk of exceeding 50 mg NO_3^- l^{-1} in the groundwater. Shallow groundwater is generally considered as being greatly at risk of contamination by pollutants, because of the narrow distance between surface and water table (Nolan et al., 2002). Considering all these aspects, our main questions are if areas with a shallow water table are effectively at risk of pollution or if the denitrification process can mediate this, and whether the fertilization derogation, acquired for NVZs in Italy, is a potential factor of N pollution or is a good way to ensure a high N supply to crops without affecting water bodies.

The aim of our work was therefore to quantify the N fluxes in agricultural ecosystems cropped with maize and fertilized with manure and urea, following the limit imposed in NVZs by the Nitrates Directive and the recent derogation and considering different water table depths.

2. Materials & Methods

The experiment was conducted in 2011-2012, at the Experimental Farm of Padua University in Veneto Region (northeast Italy, 45°19’ N, 11°31 E, 8 m a.s.l.). The local climate is sub-humid, with annual rainfall of about 850 mm and yearly average temperature of 12 °C. Reference evapotranspiration (ETo) is 945 mm with a peak in July (5 mm d-1). Eighteen lysimeters (1 x 1 m^2 width x 1.5 m depth) were cropped with maize (*Zea mays* L.). The soil that filled the lysimeters was a Fluvi-Calcaric Cambisol (CMcf) according to the FAO-UNESCO classification, characterized by 35% sand, 48% silt and 17% clay and a pH of 8.1. Organic matter content was about 1.1 – 1.3% (tab. 2).

The soil profile was homogeneous to a depth of 130 cm. The collection of drainage water was via an underground plastic tube connecting the bottom of the lysimeters with an external tank. The tank permitted the water table level to be controlled inside the lysimeters. With this system it was possible to maintain a water table approximately constant throughout the year. Instead, in free drainage condition the tank was emptied to capture water from the lysimeters (Fig. 2.1).

Soil properties	**Depth (cm)**	
	0-50 cm	**50-140 cm**
Sand (%)	31	35
Silt (%)	49	45
Clay (%)	20	20
pH	8.13	8.1
Total Nitrogen (%)	1.1	1.0
Organic carbon (%)	0.82	0.66
Organic matter (%)	1.41	1.14
C to N ratio	7.45	6.6
Total carbonate (%)	20.1	17.3
Soluble carbonate (%)	4.1	3.9
Salinity (mS cm^{-1})	0.28	0.26
Available P	1	9
Available K	135	128

Tab.2 - Initial soil chemical and physical properties.

An automatically-closing plastic roof allowed the lysimeters to be covered in case of rainfall. In this way the total volumes of water (irrigation+rain) received in the lysimeters could be managed. The roof also permitted the crop to be protected from extreme weather events (hailstorms in particular) during the growing season.

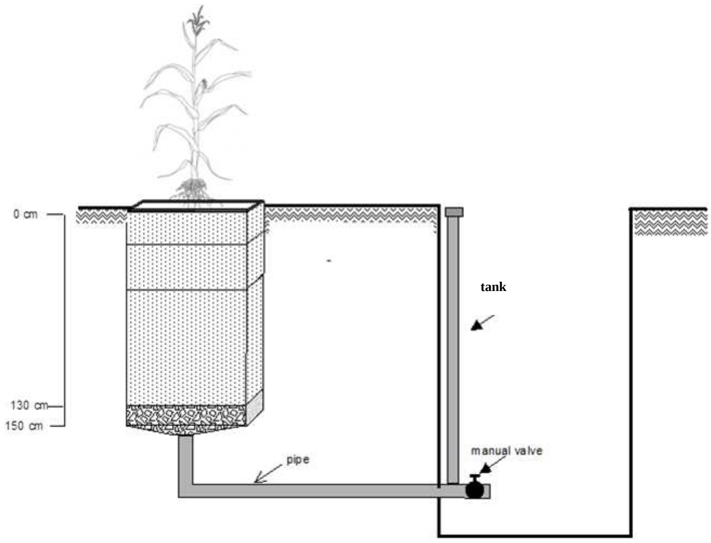


Fig.2 - Structure of the lysimeters.

2.1 Treatments and managements

Three N inputs combined with three water table conditions were tested. The experimental layout was a completely randomized design with two replications, using eighteen lysimeters. The water table levels were: a) absence of groundwater (lysimeter in free drainage condition - FD), b) water table at 60 cm depth (WT60) or c) water table at 120 cm depth (WT120).

A spading at 25 cm was done in spring followed by fertilization and crop sowing. Tillage and fertilization were carried out in three days (mid-June in 2011 and beginning of May in 2012). Lysimeters were manually sown with maize at a density of 8 plants m^2, in two rows with a distance of 70 cm and 20 cm between plants. An edge (2 rows) was provided at the sides of lysimeter, to reproduce a field situation as much as possible.

Manure (M) was applied at maize sowing. The fertilizer composition was as follows : total nitrogen 2.8% , P_2O_5 3% , K_2O 2% and organic matter 65%. A supplementary N input was applied using urea (U).

The studied N rates, according to Nitrates Directive, were: $170_{(M)}+80_{(U)}$, $170_{(M)}+195_{(U)}$ and $250_{(M)}+118_{(U)}$ kg N ha^{-1} y^{-1}. Urea was split in two applications in 2011 and three in 2012; the first dose (40% of N) was applied with manure at sowing and the subsequent doses with an interval of one month between them. Crop aboveground biomass was harvested in mid-October in 2011 and at the beginning of September in 2012. During the winter 2011-2012 no cover crop was used and the soil was bare.

The regulation of water table levels was made every day in summer and every three days in autumn, winter and spring, in this way maximum fluctuations of water table, respect to the scheduled level, not exceeded ± 10 cm. Volume of irrigation and upflux water (water input) and drainage water (water output) were recorded and samples analyzed for the main anions and cations.

2.2 Derogation of Nitrates Directive in Nitrate Vulnerable Zones (NVZs)

In November 2011 the European Commission promulgated a derogation (Decision 2011/721/EU) for the application of the Nitrates Directive in the North of Italy.

As requested by Italy, for Emilia Romagna, Lombardy, Piedmont and Veneto Regions, the EU established that the amount of cattle manure, both treated and by the animals themselves, applied to the land each year on farms benefiting from a derogation, must determine a total N input lower than 250 kg N ha^{-1}, subject to the conditions laid down in paragraphs 2 to 12 of L287/36 (Decision 2011/721/EU). The total nitrogen inputs must not exceed the foreseeable nutrient demand of the crop grown. Inputs take into account the supply from the soil and the increased nitrogen availability due to manure treatment. The N applied doesn’t exceed maximum application standards, as established in the action programs applicable to the farm. This Decision must be applied on an individual basis to farms where 70% or more of the farm acreage is cultivated with crops with high nitrogen demand and long growing season.

2.3 Maize analysis

Grain and residues were oven-dried at 65 °C and dried tissues were analyzed both for total Kjeldhal nitrogen (TKN) and residual moisture content (105 °C). TKN was determined by digesting 3 g of tissues with H_2SO_4 and $CuSO_4$. After chemical decomposition, samples were processed with NaOH and the amount of ammonia produced was determined by back titration with HCl. The amount of N (% w/w) was corrected for the residual moisture of the tissue samples.

2.4 Soil samples and water samples

Soil samples, taken at six depths (0-5, 5-30, 30-55 , 55-75, 75-95, 95-120 cm) in mid-October 2011 and 2012 , were dried at 105 °C to establish the gravimetric humidity.

Volumes of irrigation, rainfall and upflux water (input) and drainage water (output) were recorded and samples analyzed for TKN and the main anions and cations: NO_2^--N, NO_3^--N, $NH4^+$-N, $SO4^{2-}$, PO_4^{3-}, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+} (analysis performed using an ion chromatograph (Dionex ICS-900, column Ion Pac CS12A).The same analysis were performed in water samples coming from the simulated groundwater. A phreatimeter positioned in the center of the lysimeters permitted water samples to be taken every two weeks.

2.5 Water-filled pore space

Water content was measured using a Moisture Point MP-917 (ESI Environmental Sensors Inc. Sidney BC - Canada) connected with 18 time domain reflectrometry (TDR) probes (PRB-F). The probes were a long rod with a rectangular cross section and a length of 90 cm determined by five segments. The probes were installed permanently in the soil. MP-917 interrogated the probes and reduced the segments data to a numerical dataset for display, expressed in volumetric humidity for the profile 0-15, 15-30, 30-45, 45-60, 60-90 cm. Volumetric water content was measured every five days.

A practical index of soil water content is the water filled pore space (WFPS), that is the percentage of soil porosity filled by water. This index required only the volumetric water content of soil and the bulk density (assuming the particle density of mineral soils=2.65 Mg m^{-3}). WFPS is independent of soil type and is the main index used to explain microbial denitrification activity (Stanford and Epstein, 1974; Linn and Doran, 1984; Doran et al., 1988,1990):

$$WFPS = \frac{VWC}{1 - \frac{BD}{2.65}}$$

where VWC is the volumetric water content; BD is the bulk density

2.6 Soil Temperature

Soil surface temperature (top 7 cm of soil) was taken every 30 minutes every day, using 12 thermocouples connected to a datalogger (CR-1000 Campbell Sci. Inc. Lincoln Nebraska – USA).

2.7 Measurement technique of GHGs

An automatic chamber system (Delle Vedove et al., 2007) was used to monitor GHGs emission. The system can be classified as a closed dynamic system according to Livingston and Hutchinson (1995). Each chamber consisted of a steel collar (16 cm in diameter and 8 cm height) and a motor closing steel lid. The chamber must be supported on another collar inserted in the soil to prevent air leaks between soil and chamber. The steel lid was in a vertical position when the chamber was open and on north side of the soil collar to avoid shadowing.

CO_2 and N_2O move from the sites of production to the atmosphere primarily by diffusion through air-filled pores and cracks, but can also driven by local changes in pressure due to wind or volumetric displacement by rain (Li-Cor, 2010). Moreover, for a valid estimation of the flux , conditions inside and outside the chamber must be similar: these conditions include barometric pressure, temperature and moisture of soil. To avoid air pressure difference between inside and outside the chambers, each one was equipped with a pressure vent. This vent was designed to remain insensitive to wind direction. In fact, as reported by Conen and Smith (1998), wind movement around the vent of a closed chamber creates a "Venturi effect" leading to overestimated soil gas efflux. Conen and Smith proposed that wind de-pressurized the chamber by pulling air out of the chamber headspace, leading to the mass flow of soil gases from the permeable soil column into the chamber interior.

The air was sampled from the center of the lid and was returned by a manifold inside the collar. A connection between the chamber and the auto-sampler that contains evacuated tubes (crimp vials) was realized with high density PVC tubing. N_2O emissions were measured, chamber closed, on a daily basis in the first week after fertilization and subsequently every two weeks.

Twenty milliliters of air chamber were injected into 20-ml of evacuated tubes using an auto-sampler and transported to the laboratory for analysis by gas chromatography. The gas chromatograph (Agilent 7890A, mod. G3440A) was equipped with an electron capture detector (μECD) to quantify N_2O. Three samples were taken for every chamber at time zero (at closure) at 25 min and 50 min after chamber closure. A linear regression was applied to [N_2O] concentration and time. Soil N_2O efflux was expressed as:

$$F_{N2O} = \frac{dC}{dt} MC \cdot \frac{V}{S} \qquad [\ kg\ N\ ha^{-1}\ d^{-1}\ ]$$

where MC is the mass coefficient (g N_2O m^{-3} N_2O) and V and S the volume of the system (cm^3, chamber and tubes) and chamber basal area (cm^2) respectively.

2.8 N_2O analysis in groundwater

A 50 ml sample of water was collected from the groundwater, with a pump, inside an evacuated serum bottle (118 ml). The samples were transported to the laboratory and immediately shaken vigorously for 2 h to equilibrate the dissolved and headspace gas phases. A 40-ml aliquot of gas from the headspace was transferred into a double – syringe system as reported by von der Heide et al. (2008). The gas was injected into a fully evacuated vial (20ml). N_2O was measured using a gas chromatograph (Agilent 7890A, mod. G3440A) equipped with an electron capture detector (µECD).

Gas concentrations of the sample solution were calculated according to following equation (Davidson and Firestone, 1988):

$$M = C_g \cdot (V_g + (V_l \cdot \alpha)$$

where C_g is the headspace gas concentration (µL L^{-1}), V_g is the volume (L) of gas, V_l. is the volume (L) of liquid, and α is the Bunsen absorption coefficient. The concentration of N_2O in the flask solution was then calculated from the equation:

$$(N_2O)_{liquid} = M / V_l$$

where M and V_l are defined as above.

2.9 Global Warming Potential

Global Warming Potential (GWP) is a type of simplified index based on radioactive properties that can be used to estimate the potential future impacts of emissions of different gases on the climate system in a relative sense.

The impact of greenhouse gas emissions on the atmosphere is related not only to radioactive properties, but also to the time-scale characterizing the removal of the substance from the atmosphere. Radioactive properties control the absorption of radiation per kilogram of gas present at any instant, but the lifetime controls how long an emitted kilogram is retained in the atmosphere and hence is able to influence the thermal budget (IPCC, 2001).

$$kg\ CO2\ eq = kg\ molecule * GWP$$ (GWP for given time horizon)

GWP is therefore a relative measure of how much heat a greenhouse gas traps in the atmosphere. It compares the amount of heat trapped by a certain mass of the gas in question to the amount of heat trapped by a similar mass of carbon dioxide. A GWP is calculated over a specific time interval, commonly 20, 100 or 500 years. GWP is expressed as a factor of carbon dioxide (whose GWP is standardized to 1) (Tab 2.9.1).

For example, the 20 year GWP of nitrous oxide is 289, which means that if the same mass of nitrous oxide and carbon dioxide were introduced into the atmosphere, the nitrous oxide would trap 289 times more heat than the carbon dioxide over the next 20 years.

Industrial Designation or Common Name	**Chemical Formula**	**Lifetime (years)**	**Radiactive Efficiency ($W\ m^{-2}\ ppb^{-1}$)**	**Global Warming Potential for Given Time Horizon**		
				20-yr	**100-yr**	**500-yr**
Methane	CH_4	12	3.7×10^{-4}	72	25	7.6
Nitrous oxide	N_2O	114	3.03×10^{-3}	289	298	153

Tab.2.9.1 – GWP for methane and nitrous oxide.

2.10 Statistical analysis

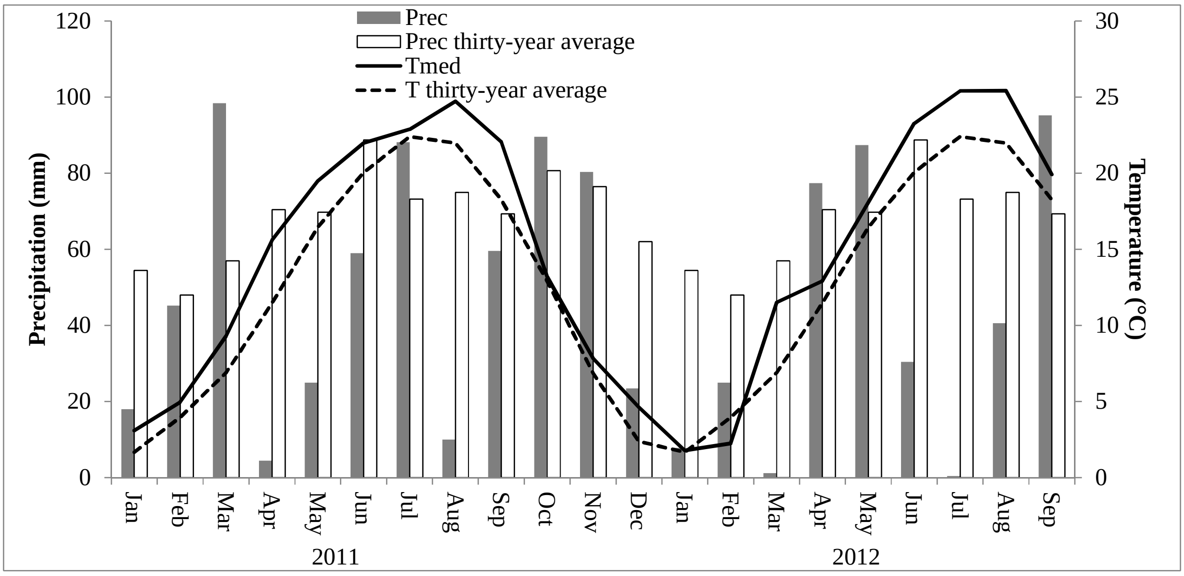
Analysis of Variance (ANOVA) was performed using the Mixed Model of SAS (SAS Institute, Inc., Cary, NC, Version 8). Fixed variables were fertilization, year and groundwater level. Comparisons of model least square means were adjusted using Tukey’s procedure. Treatment effects were considered statistically significant at $P < 0.05$.

3. Results

3.1 Weather conditions and evapotranspiration

Maize yield, evapotranspiration and N leaching were affected by weather conditions. In 2011 the late sowing of maize (end of June) led to both growth and evapotranspiration maximum at the end of July, the hottest period of the year in northeast Italy; the heat stress damaged yield (Fig. 3.1.1). In 2012 a very rainy spring was followed by a summer when temperatures were very high from July throughout August; at the same time no rain fell in July making the 2012 season one of the most critical for crop growth. Water irrigation between sowing and harvest was very similar in both years (460 mm in 2011 and 425 mm in 2012).

Reference evapotranspiration (ET_0) during the same period was about 730 mm in 2011 and 762 mm in 2012, but actual evapotranspiration (ET_a), calculated in our lysimeters, was lower in free drainage condition and higher in water table condition (Tab.3.1.1 and 3.1.2). ET_a is sensitive to climate change and is an important parameter for crop development. In FD, ET_a was 500 mm in 2011 and only 300 mm in 2012 due to problems in water supply caused by the high temperatures. Instead in WT condition the availability of water was never a limiting factor and the increase of temperatures in 2012 led to a corresponding increase of ET_a. Maize gained advantage with shallow groundwater and responded to high temperature with a high evapotranspiration and biomass production. For this reason groundwater recharge in 2012 required about 40-50% more of up-flux water than in 2011.



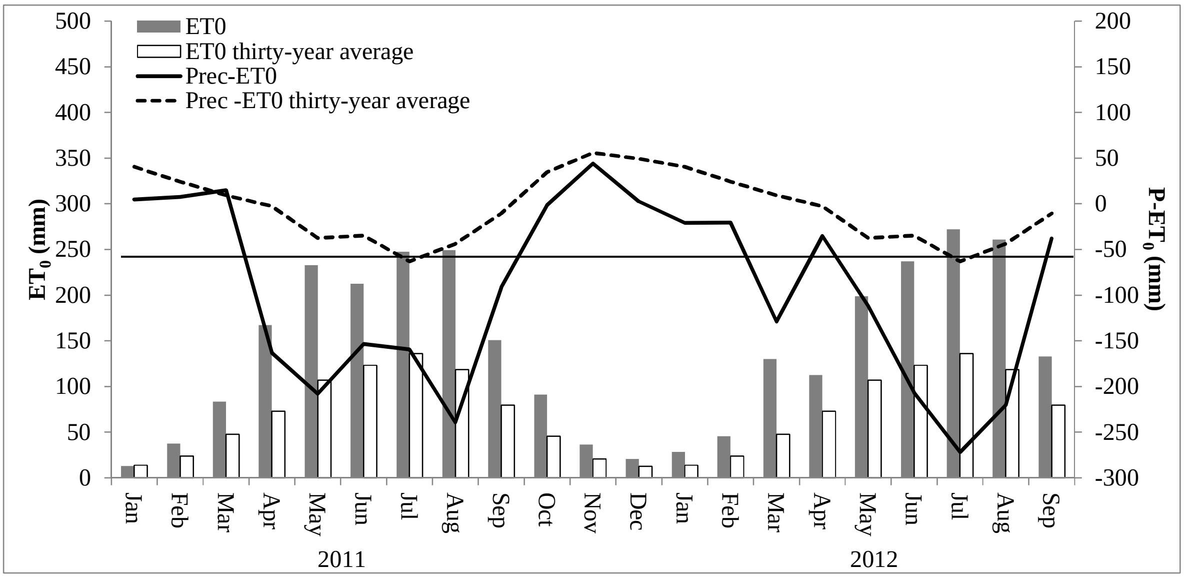


Fig.3.1.1 – Comparison between annual and thirty-year average in reference and actual evapotranspiration (ET_0 and ET_a), temperature and precipitation.

2011

Manure	Urea	Water table (WT) depth (cm) or free drainage (FD)	Ui (mm)	Irrigation	$Water_{upflux}$	Percolation	Uf (mm)	Eta
170	80	FD	112.2	459.8	0	0	177.6	525.2
170	80	WT120	222.9	459.8	297.5	35.6	289.0	787.7
170	80	WT60	260.0	459.8	351	12.8	310.1	848.1
170	195	FD	114.4	459.8	0	1.5	137.0	480.9
170	195	WT120	144.9	459.8	372.5	21.1	177.9	844.1
170	195	WT60	266.5	459.8	310.8	20.6	294.2	777.5
250	118	FD	123.8	459.8	0	0	158.6	494.6
250	118	WT120	160.4	459.8	425	18.0	239.0	945.4
250	118	WT60	266.3	459.8	424	20.8	284.7	881.4

Tab.3.1.1 – Water balance in 2011 (June - October 2011).

Ui= initial soil moisture (in spring), Uf= final moisture (in autumn).

2012

Manure	Urea	Water table (WT) depth (cm) or free drainage (FD)	Ui (mm)	Irrigation	$Water_{upflux}$	Percolation	Uf (mm)	Eta
170	80	FD	178.4	424.8	0	0	71.3	317.6
170	80	WT120	284.6	424.8	560.0	7.7	282.8	975.4
170	80	WT60	321.9	424.8	644.5	0.0	319.8	1067.2
170	195	FD	198.8	424.8	0	0	103.5	329.5
170	195	WT120	255.5	424.8	656.5	3.2	220.5	1043.0
170	195	WT60	311.3	424.8	781.8	0.0	192.5	1087.8
250	118	FD	210.9	424.8	0	0	100.8	314.7
250	118	WT120	241.7	424.8	717.0	5.6	254.0	1148.5
250	118	WT60	325.8	424.8	661.0	0.0	308.5	1068.5

Tab.3.1.2 – Water balance in 2012 (May – September 2012).

Ui= initial soil moisture (in spring), Uf= final moisture (in autumn).

No percolation occurred in either year in FD condition. Likewise percolations in WT were limited, particularly in 2012.

3.2 WFPS

The percentage of soil pore space filled with water (% WFPS) had a wide range of variability (Fig. 3.2.1-3.2.3). The top 15-cm of soil was strongly influenced by both season and plant growth but less by groundwater. During summer the high temperature stimulated the evaporation process; irrigation increased WFPS by 5% with an irrigation of 10mm and by 20% with an irrigation of 60mm. At the end of the growing season the soil was strongly water depleted (WFPS 9-10%). Precipitation increased the water content during winter, and for several weeks in February the soil was frozen during the night and in the morning.

Going deeper through the profile, water content increased but a clear difference appeared in response to water table level. In FD differentiation between water content in the top 15-cm and in the rest of the profile was evident only between December 2011 and May 2012. In this period, water percolation due to irrigation caused an increase in WFPS in deeper horizons of the lysimeters (Fig. 3.2.1). In WT separation between 0-15 cm and the other horizons of the soil profile was pronounced. WT120, in the 30-45cm profile, reached a steady WFPS of 60% between December 2011 and May 2012 and a WFPS of about 80-85% in the 60-90cm profile (Fig. 3.2.2).

WT60 showed values of 80% in the 30-45cm profile (Fig 3.2.3). A sharp decline of WFPS occurred in July 2012 in the 30-45cm profile (for both WT60 and WT120) when the development of maize and the high temperature made it impossible to maintain the scheduled water level for about a week (Fig. 3.2.2 and 3.2.3). No differences occurred in WFPS between the two N inputs (170_M+80_U and 250_M+118_U).

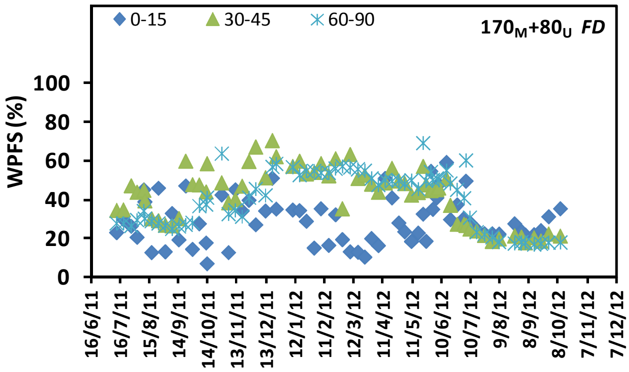


Fig. 3.2.1- % WFPS in free drainage conditions for the two $N_{input.}$

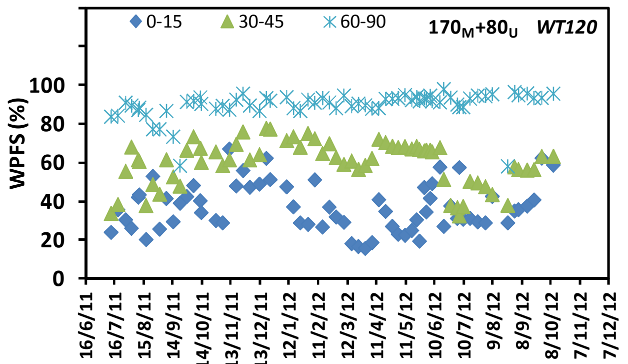


Fig. 3.2.2- % WFPS in 170_M+80_U with water table 120 cm or 60 cm deep.

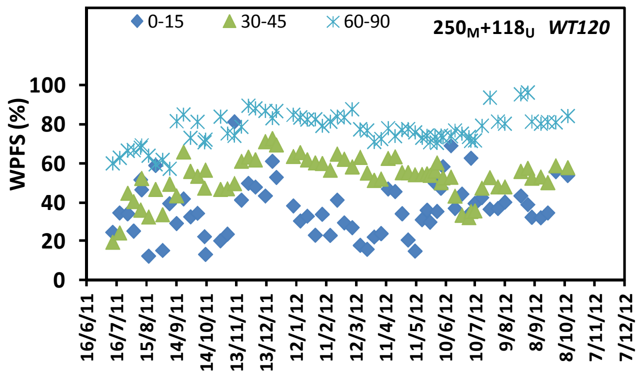


Fig. 3.2.3- % WFPS in 250_M+118_U with water table 120 cm or 60 cm deep.

The average of WFPS through the soil profile again evidenced the differences between a free drainage condition and shallow groundwater conditions (Fig.3.2.4).

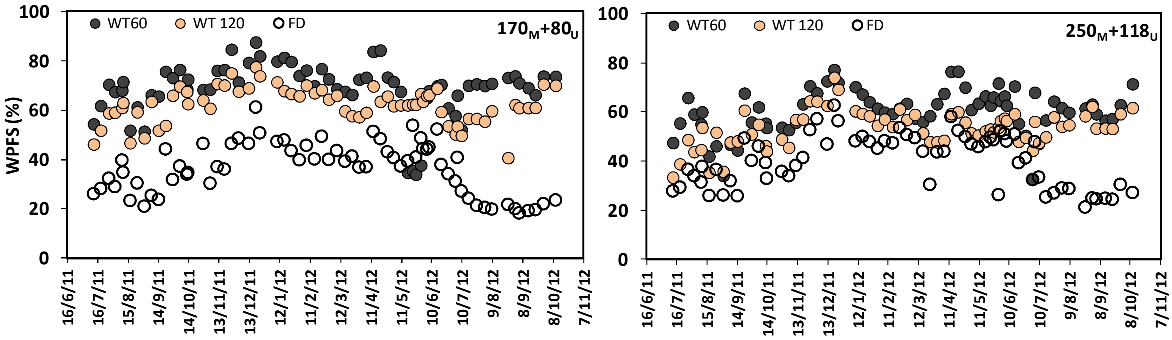


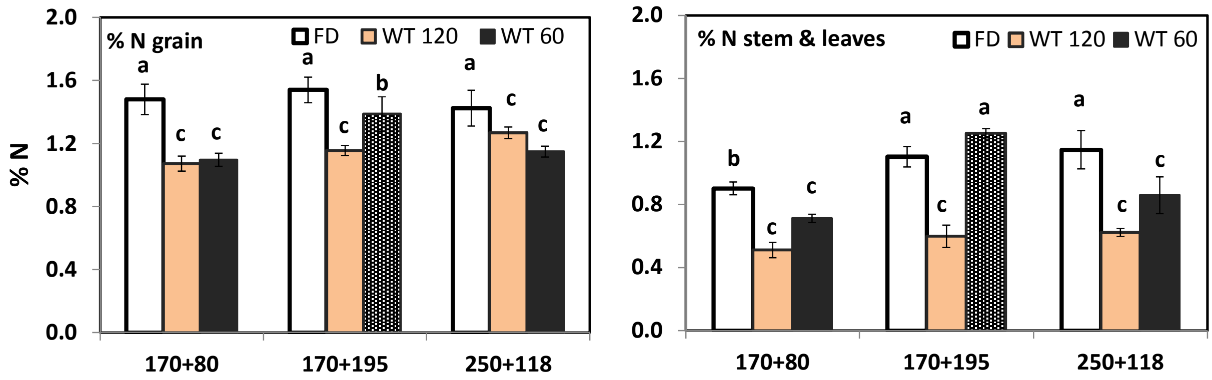
Fig. 3.2.4 - Average WFPS through the soil profile for the three water table conditions and two $N_{input.}$

N_2O and NO production depend heavily on soil moisture, which controls the degree of soil aeration and its O_2 content and determines whether nitrification or denitrification prevails (Smith et al., 2003; Linn and Doran, 1984). During nitrification, nitric oxide emissions are generally considered to peak at a low WFPS of around 25% (Yang and Meixner, 1997) while nitrous oxide production is observed to peak at medium WFPS between 50% and 60% (Davidson et al., 1991). Nitrous oxide emission peaks from denitrification are expected for WFPS higher than 60% (Grundmann and Rolston, 1987).

3.3 Crop yield

The lysimeters subjected to fertilization 170+195 and WT60 had unexpected growth; in the previous years they had been used in other experiments and the soil had been fertilized at higher rates that reached even 340 kg N $ha^{-1}y^{-1}$, a quota of this N may have been used in 2011-2012. For this reason, data from these lysimeters should be considered with care.

Nitrogen concentrations in grain, stem and leaves were higher in FD than in WT for every fertilization at a percentage of 1.5 (Fig. 3.3.1). In WT no differences occurred between the two water table levels with values ranging between 1.1 and 1.3%.



Lysimeter coming from a previous experimental-test, with high N residual in soil.

Fig. 3.3.1 – N concentration in maize grain, stem and leaves, average of 2011 and 2012.

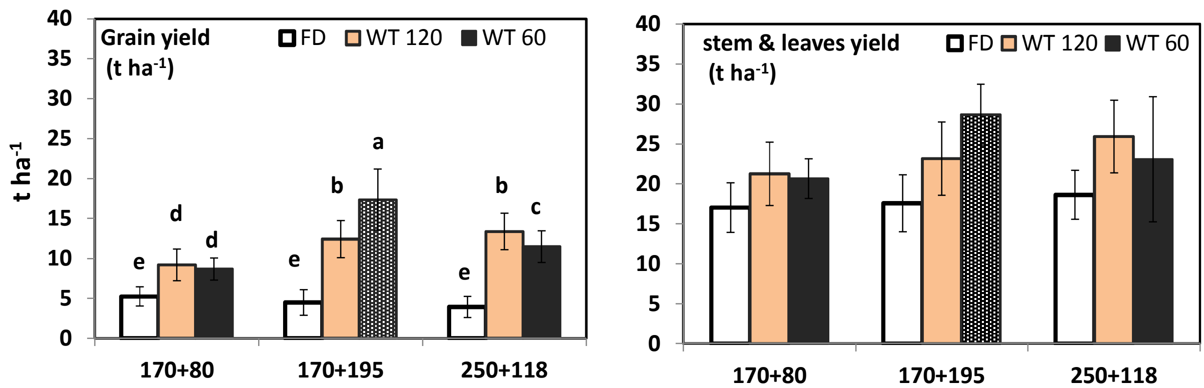


Fig. 3.3.2 – Grain yield and yield in residues, average of 2011 and 2012.

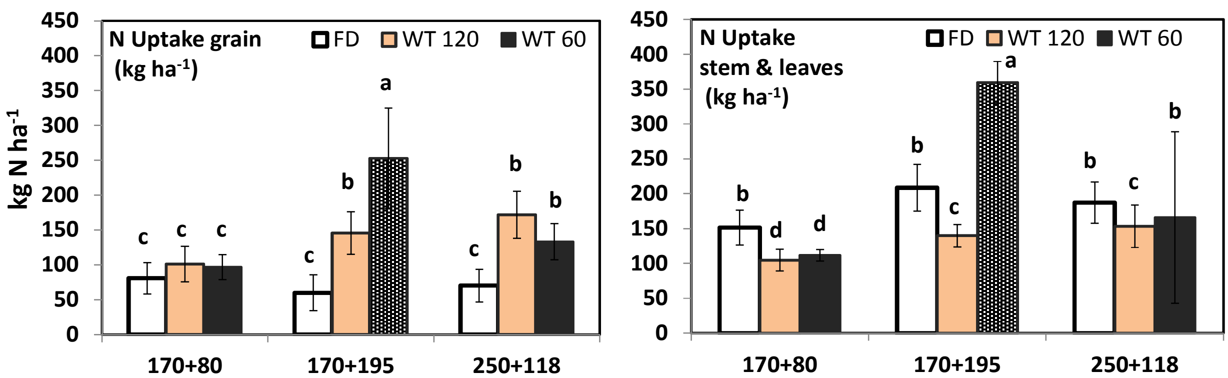


Fig. 3.3.3 – N uptake in grain, stem and leaves, average of 2011 and 2012.

Maize grain yield was higher in WT condition, maximum production (13 t ha^{-1} dry matter) was obtained with the water table at 120 cm depth (Fig. 3.3.2). Yield didn't exceed 5 t ha^{-1} in free drainage conditions (FD). The same behavior occurred for stem and leaves. In WT, grain and residues biomass increased with the fertilization rates, but in FD the yield declined with increasing N doses.

N uptake by grain was significantly lower in FD than in WT, due to the low grain yield (Fig. 3.3.3).. Nitrogen was accumulated in the residues due to a partial water stress limiting N translocation into the grain. Although no statistical differences occurred between WT60 and WT120, WT120 had the maximum uptake of nitrogen in grain and minimum in residues. The water table 120 cm depth seemed to stimulate the nutrient uptake through a larger root development. We supposed instead, that water table 60 cm depth, by imposing anaerobic soil conditions, limited roots deepening , reducing nutrient uptake.

In 170_M+195_U and WT60 the high residual N in the soil allowed a very high production and N uptake (over 600 kg N ha^{-1} considering grain+residues). This situation gives important information about the use of N: when the water supply is not a limiting condition (e.g. with shallow groundwater) the high growth of maize stimulates high N uptake.

3.4 N_2O fluxes

Analyses were performed initially on a daily basis, for a week after organic fertilization and successively during the irrigation and with top-dressed urea application. During the rest of the crop cycle, at least one sampling was performed every two weeks. The N_2O emissions are reported in Fig 3.4.1- 3.4.6. Daily fluxes were different throughout the years; in 2012 fluxes reached, during the emission peaks, values 4 times higher than in 2011.

In 2011 emissions appeared the day after fertilization with the maximum peak at 45-50 g N_2O-N ha^{-1} d^{-1}achieved the third day (Fig. 3.4.1-3.4.2) Fluxes reverted to zero in two days. Maximum fluxes were in FD for 170_M+80_U (Fig. 3.4.3) and in WT60 for 250_M+118_U. (Fig 3.4.4) A second peak on July 8th was related to an irrigation of 55mm. Perhaps temporary anaerobic conditions of the soil surface, generated by irrigation, encouraged denitrification. A minor peak on August 11th followed the application of top-dressed urea (on August 8th). The fluxes with lower fertilization (170_M+80_U) were comparable with those at higher fertilization (Fig. 3.4.3 and 3.4.4). Anyway, in

170_M+80_U fluxes were higher in FD than in WT, while in 250_M+118_U the reverse situation occurred. After maize harvest no emission occurred.

Also in 2012 the highest emissions were related to fertilization, maximum fluxes were in WT120 reaching 390 and 420 g of g N_2O-N ha^{-1} d^{-1} for the lowest and highest fertilization respectively (Fig. 3.4.5 and 3.4.6). Two peaks on May 30th and June 19th, of a magnitude ten times lower than that at sowing, corresponded to top-dressed urea application. In the second year irrigation events didn't stimulate N_2O emissions.

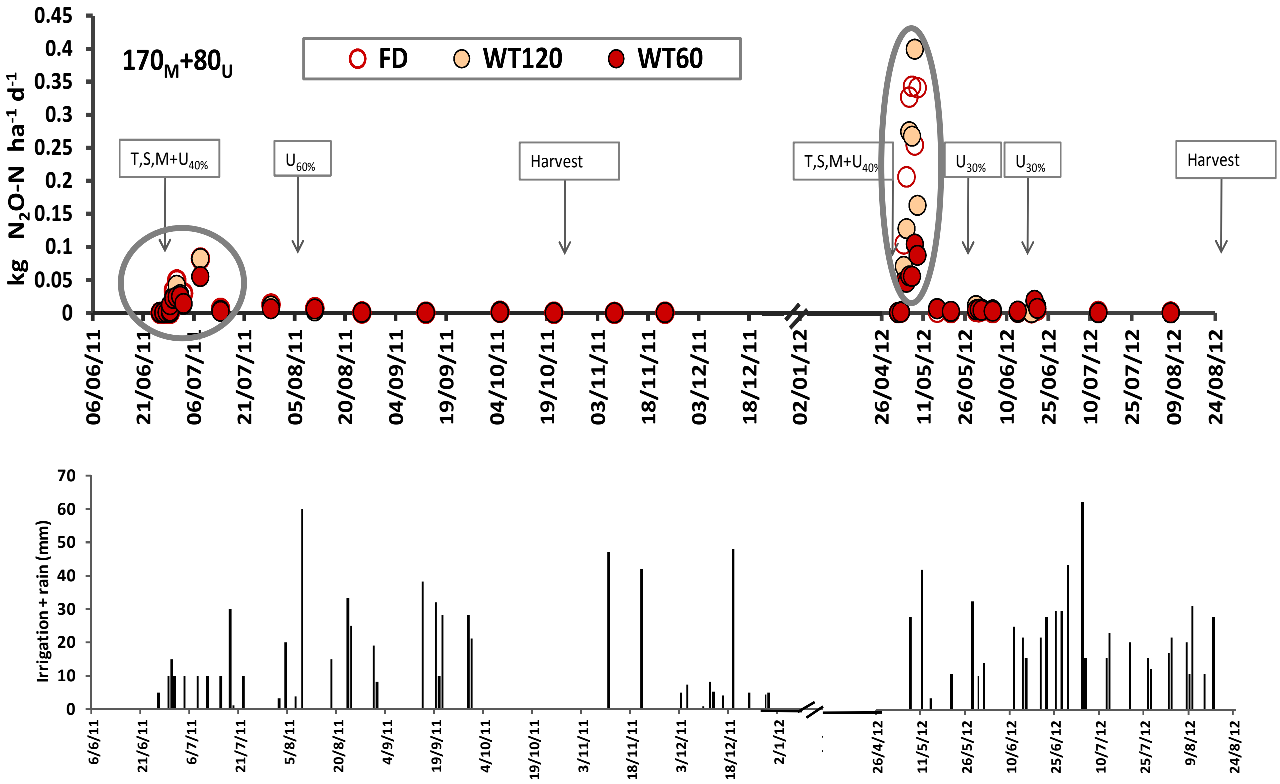


Fig. 3.4.1- Irrigation +rain and fluxes of N_2O –N with fertilization at 170+80 kg N ha^{-1} y^{-1} in 2011 and 2012. T=tillage, S=sowing, M=manure, U= urea

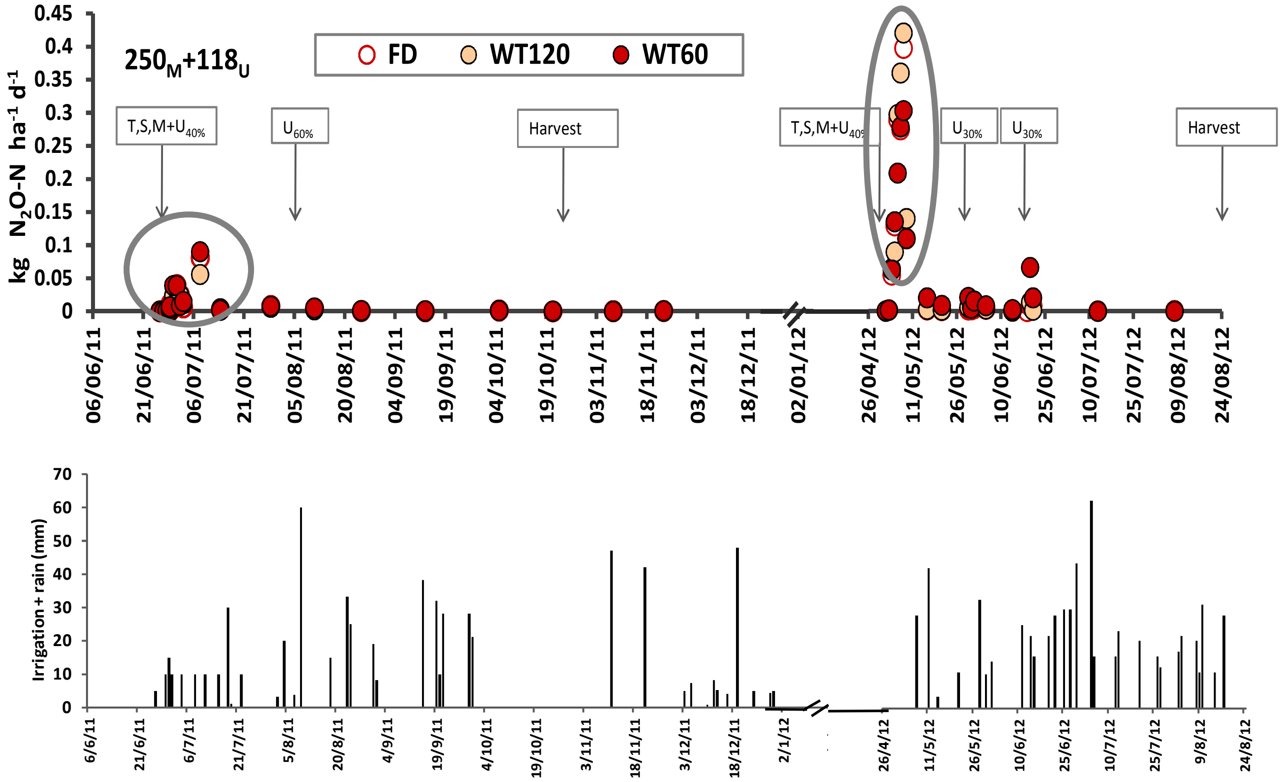


Fig. 3.4.2 – Irrigation+rain and fluxes of N_2O –N with fertilization at 250+118 kg N ha^{-1} y^{-1} in 2011 and 2012. T=tillage, S=sowing, M=manure, U= urea

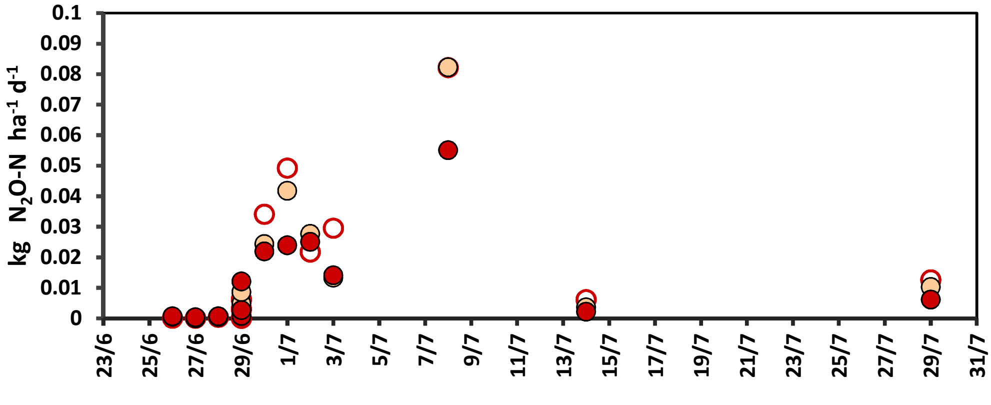


Fig.3.4.3 – First peak of N_2O-N emissions at 170+80 kg N ha^{-1} y^{-1} in 2011.

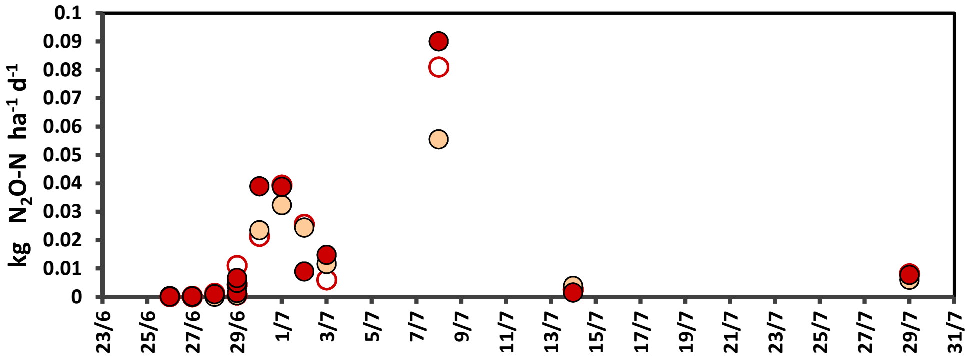


Fig.3.4.4 – First peak of N_2O-N emissions at 250+118 kg N ha^{-1} y^{-1} in 2011.

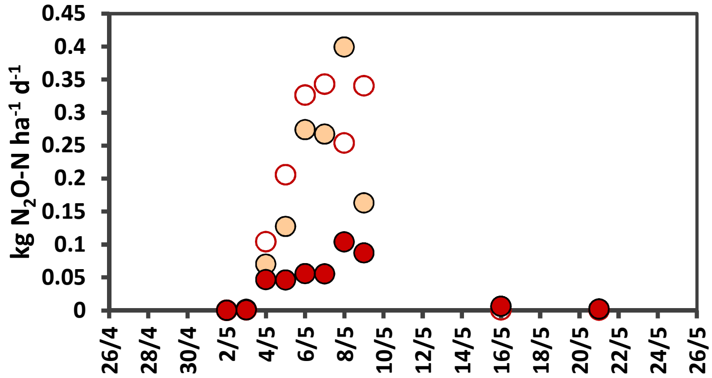


Fig.3.4.5 - First peak of N_2O-N emissions at 170+80 kg N ha^{-1} y^{-1} in 2012.

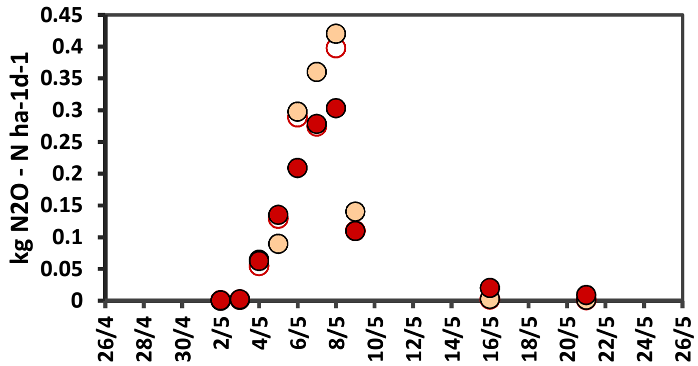


Fig.3.4.6 - First peak of N_2O-N emissions at 250+118 kg N ha^{-1} y^{-1} in 2012.

N fluxes were not correlated with WFPS in all the WT conditions, even if the reduced number of data points doesn't permit reliable conclusions to be drawn on this aspect. In addition the steady moisture content at the level of water table linked the fluxes primarily to the fertilization event. Emission probably reflected the availability of NO_3^- in soil.

Temperature influenced the different fluxes that occurred in 2011 and 2012 with a significant "year" effect. However no relationship was found between emissions peaks and temperature, within a specific year. Table 3.4.1 shows the mean and median of N_2O-N emission for the different treatments.

Due to the very skewed distribution of data, average fluxes were influenced by the maximum peak of emission, while the median, indicating the middle value of the distribution, gives emphasis to the general trend of the dataset. In 2011 the mean was higher for FD, followed by WT60. Instead medians were similar in FD and WT60. The same behavior was evident in 2012 for the lower fertilization. This indicates that FD quickly reached the peak emissions and then reduced just as quickly, while WT60 had generally lower emissions but also a slower return to zero emissions. A difference occurred in 2012 for the highest fertilization; both mean and median were higher in WT60.

Fertilization	Free Drainage or Water table	Mean 2011 (Kg N ha-1 d^{-1})	Mean 2012 (Kg N ha-1 d^{-1})	Median 2011 (Kg N ha-1 d^{-1})	Median 2012 (Kg N ha-1 d^{-1})
$170_M + 80_U$	FD	0.051	0.148	0.014	0.023
$170_M + 80_U$	WT120	0.031	0.110	0.009	0.034
$170_M + 80_U$	WT60	0.032	0.048	0.012	0.026
$250_M + 118_U$	FD	0.049	0.096	0.010	0.017
$250_M + 118_U$	WT120	0.023	0.101	0.011	0.019
$250_M + 118_U$	WT60	0.042	0.114	0.009	0.070

Tab.3.4.1 - Mean and median of annual fluxes of N_2O-N.

Cumulative annual N_2O-N (Fig. 3.4.7) emissions ranged between 0.58 and 1 kg N ha^{-1}. No statistical differences were observed in 2011. In 2012, values were different with the lower fertilization: FD reached 2.91 kg of N_2O-N ha^{-1} followed by 2.16 and 0.94 kg of N_2O-N ha^{-1} respectively in WT120 and WT60. With the highest fertilization cumulative emissions ranged from 1.84 and 2.20 kg of N_2O-N ha^{-1} without statistical differences.

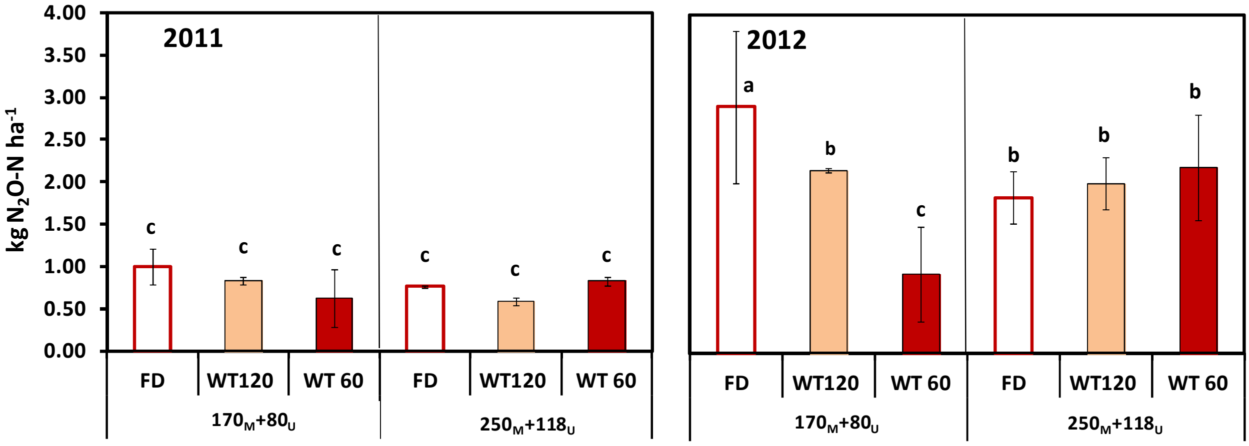


Fig.3.4.7 – Average of cumulative N_2O-N emissions in 2011 (June – November) and 2012 (May – August) ($p = 0.05$) .

In 2012, moving from lower to higher fertilization, emissions had a reduction in FD and an increase in WT60. WT120 maintained the same emissions. In conclusion, the effects of water table and N input were evident in 2012 but not in 2011. The differences in fluxes between 2011 and 2012 were related to air and soil temperatures, which were higher in 2012. However temperature wasn't the only factor that stimulated the difference in fluxes magnitude.

In 2011 the system probably lacked equilibrium: most likely there weren't a suitable number of optional anaerobic microorganisms, which are able to denitrify nitrates. It is worth noting that the necessary condition for denitrification, such as WFPS over 60%, an availability of NO_3^- and dissolved organic carbon, weren't present in the site at the beginning of the test. In fact the groundwater inside the lysimeters was raised for the first time in May 2011, i.e. one month before the start of the test. So at the beginning of flux measurements, the horizons within the water table had probably not reached total saturation. Nitrogen and carbon were also probably limiting, given that the fertilization was applied in June.

N_{input} kg N ha^{-1} y^{-1}	Free Drainage or Water table	Cumulate Fluxes 2011 kg N ha^{-1} y^{-1}	Cumulate Fluxes 2012 kg N ha^{-1} y^{-1}	$\frac{N_2O\text{-}N}{N_{input}}$ (%) 2011	$\frac{N_2O\text{-}N}{N_{input}}$ (%) 2012
170_M+80_U	FD	1.061	2.910	0.42	1.16
170_M+80_U	WT120	0.649	2.161	0.26	0.86
170_M+80_U	WT60	0.669	0.930	0.27	0.37
250_M+118_U	FD	1.035	1.840	0.28	0.50
250_M+118_U	WT120	0.487	2.006	0.13	0.55
250_M+118_U	WT60	0.886	2.190	0.24	0.60

Tab.3.4.2- Ratio between N_2O-N emissions and N input.

Annual N_2O-N emissions as percentage of total N inputs didn't exceed 1.2% (Tab. 3.4.2), being generally lower than the IPCC standard of 1%.

The emissions were in general smaller in WT than in FD (Fig.3.4.8).

The increase in emission rate was only partly proportional to the increase in groundwater depth (Fig. 3.4.8).

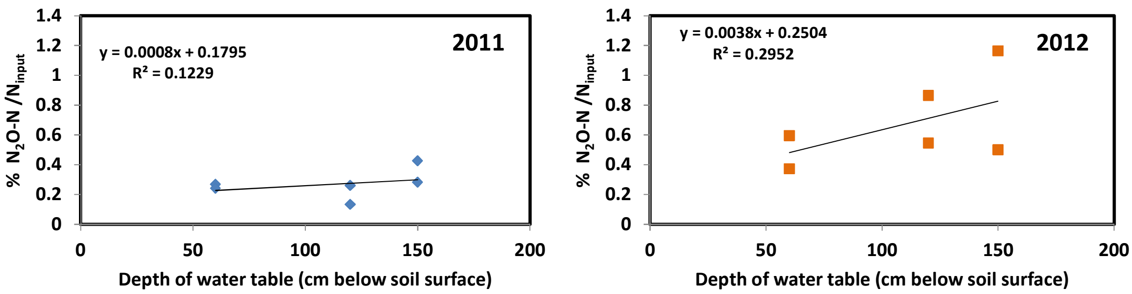


Fig. 3.4.8 - Linear regression between groundwater depth and % N2O-N emission/N input.

3.5 N balance

An N balance was applied following the equation [2] section 2.5 chapter I (Tab. 3.5.1). Values were the average of the two years and the replications. N from irrigation and groundwater up-flux was about 6.5% of total input in 170_M+80_U, and 5% of total input in 250_M+118_U and 170_M+195_U. With the lower fertilization, the maximum uptake was in FD. Instead in WT, N uptake was lowered by the anaerobic soil conditions, limiting roots deepening and therefore reducing nutrient uptake. A quota of N in the soil solution could probably have been lost via denitrification.

Increasing N input, the shallow water table enhanced production by an adequate water supply. Due to high temperature, particularly in 2012, water demand by crops was high and water percolation was very small. In FD no percolation occurred: maize water demand was too high and depleted the soil-water content. N efficiency followed the trend of N uptake and was maximum in 170_M+80_U FD. In 250_M+118_U and 170_M+195_U N efficiency was higher in WT. High N uptake in 170_M+195_M -WT60 was linked with the high level of nitrates present in the soil, as discussed previously. In this treatment maize presented an N uptake higher than the N applied, thus leading to a negative N residual and, then, to a depletion of organic N in the soil.

Average year				N_{input}			N_{output}		$N_{residual}$	$N_{efficiency}$
abbreviation	Free drainage or water table	Manure kg N ha^{-1}	Urea kg N ha^{-1}	Total Fertilizer kg N ha^{-1}	N_{irrig} kg N ha^{-1}	$N_{up\text{-}flux}$ kg N ha^{-1}	N_{uptake} kg N ha^{-1}	$N_{leached}$ kg N ha^{-1}	kg N ha^{-1}	(%)
170_M+80_U	FD	170	80	250	10.22	0	232.0 **b**	0	28.2	89.15
170_M+80_U	WT120	170	80	250	10.22	6.69	206.0 **c**	0.15	60.9	77.18
170_M+80_U	WT60	170	80	250	10.22	7.97	208.4 **c**	0.26	59.8	77.71
250_M+118_U	FD	250	118	368	10.22	0	268.5 **b**	0	109.8	70.98
250_M+118_U	WT120	250	118	368	10.22	8.84	324.9 **b**	0.23	62.1	83.95
250_M+118_U	WT60	250	118	368	10.22	8.68	299.0 **b**	0.17	87.9	77.29
170_M+195_U	FD	170	195	365	10.22	0	257.4 **b**	0	117.8	68.61
170_M+195_U	WT120	170	195	365	10.22	7.96	285.3 **b**	0.15	97.8	74.47
170_M+195_U	WT60	170	195	365	10.22	9.05	612.4 **a**	12.42	-228.2	159.38

Tab.3.5.1 – Average N balance.

3.6 N concentration in groundwater

Anions and cations

Analyses of soluble N in groundwater were carried out using the phreatimeter positioned inside the lysimeter. Principal anions and cations evaluated were: NO_3^--N NO_2^- -N and NH_4^+-N.

Medians of NH_4^+-N (Fig. 3.6.1) were close to zero, with a 75^{perc} that didn't exceed 0.73 mg l^{-1}. The same situation was evident for NO_3^--N concentration, that was lower than the limit of 11 mg l^{-1} established by the Nitrates Directive. NO_2^- -N was not present in water samples.

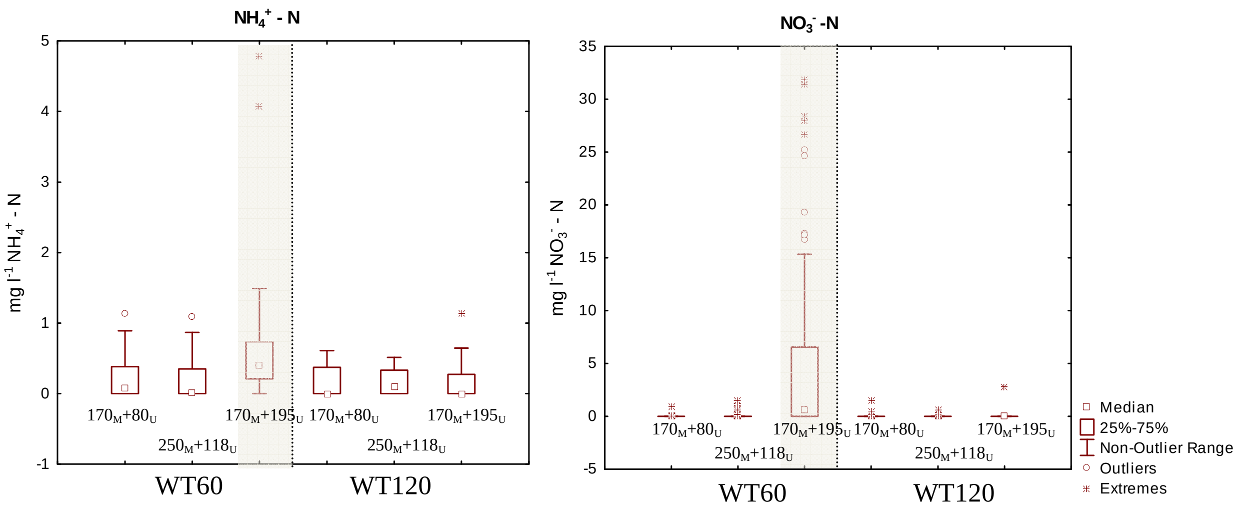


Fig.3.6.1- NO_3^--N and NH_4^+-N concentration in groundwater.

No differences of N concentration were observed for the three different fertilizations. Low nitrates concentration in groundwater associated to low N leaching for every level of fertilization seemed to indicate an adequate N uptake by maize and a possible depletion of nitrates via denitrification. Maximum concentrations were present in 170_M+195_U with WT60 (highlighted in gray in the box – Fig. 3.6.1). As mentioned above, that situation was particular because high fertilization, applied in a previous experiment, had increased nitrate concentrations in soil, favoring a higher N concentration in groundwater compared to the other treatments.

N$_2$O concentration in groundwater

As mentioned by Heincke and Kaupenjohann (1999), N_2O is highly soluble in water and a large amount may remain dissolved in waters after having arisen from nitrification and denitrification. Our data show a continuous increase over time of N_2O dissolved in water (Fig. 3.6.2). Data were very similar for the higher and lower fertilization rates. Instead the groundwater level didn't modify concentration, which ranged from 0.6 to 1.8 μg N_2O l^{-1} of H_2O.

Soil air can contain N_2O at concentrations several orders of magnitude higher than ambient air. At a temperature of 20 °C, distilled water equilibrated with 1 atm of N_2O presents a concentration of 0.79 g N_2O –N l^{-1} (Chemical Society of Japan, 1984). At the same temperature, distilled water equilibrated with ambient air contains dissolved N_2O at concentrations of 0.25 μg N_2O l^{-1} of H_2O (Sawamoto et al., 2002). Very few data of dissolved N_2O in groundwater, drainage water and stream water are present in the literature (Tab. 3.6.1) and contrasting values are reported.

Our data seem to be lower than those of Linn and Doran (1984), but climate and type of fertilization were different. In particular mineral fertilizer can release N more quickly than an organic fertilizer. But, considering the positive trend in the two years, an N_2O accumulation in water can be expected for the coming years.

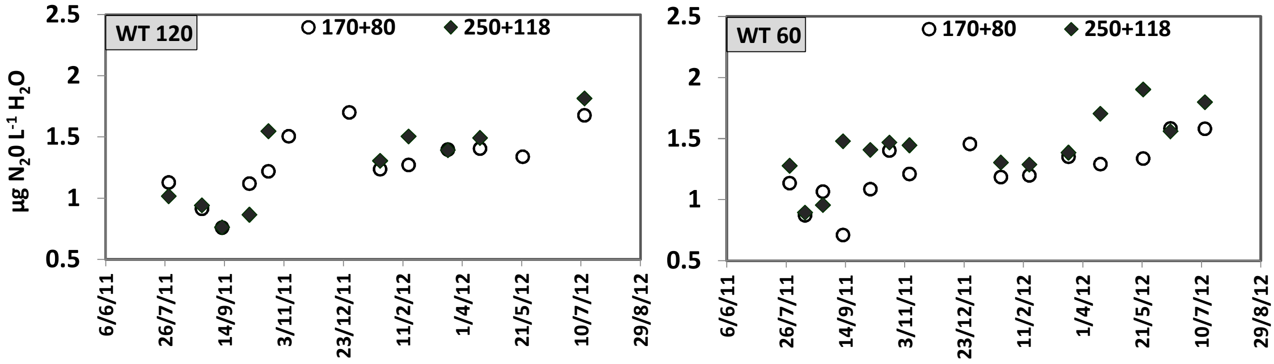


Fig. 3.6.2 - Dissolved N_2O in groundwater.

Ecosystem	Location	Average concentration dissolved N_2O µg N_2O l^{-1}	Reference
silt loam, corn, plowed mineral N-fertilization	Illinois, USA	12	Linn and Doran, 1984
silt loam, corn, plowed mineral N-fertilization	Kentucky, USA	234	Linn and Doran, 1984
silty clay loam, corn, plowed mineral N-fertilization	Nebraska, USA	39	Linn and Doran, 1984
clay loam, corn, plowed mineral N-fertilization	Minnesota, USA	50	Linn and Doran, 1984

Tab.3.6.1- Dissolved N_2O in water in different experiments conducted with maize.

As reported by many authors (Bowden and Bormann, 1986; Rice and Rogers, 1993; Rolston and Marino, 1976; Tindall et al., 1995), N_2O may remain in shallow groundwater for quite a while after production, due to high solubility and slow diffusion. This is a cause of temporal retardation and spatial separation of N_2O production and emission.

4.Conclusion

A shallow groundwater influenced both maize yield and N_2O emissions. The simulated 120 cm depth water table didn't limit root development and at the same time allowed an optimum water supply the for crop as well as optimal conditions for root growth. Weather conditions affected the variability of maize yield in the two years. The summer in 2012 was very hot, enhancing the crop water demand. In these conditions shallow groundwater was necessary to ensure crop growth. In fact, yield in free drainage condition was very penalized especially at higher fertilization. Actual evapotranspiration (ET_a) was a sensitive parameter to define crop growth and water supply. In WT conditions ET_a, between sowing and harvest, reached 881 mm in 2011 and 1080 mm in 2012, while, in FD, ETa in the two years was 350 and 750 mm lower respectively. The high ETa in WT lowered the amount of water and N leaching in both years. N concentration in groundwater, as NO_3^--N and NH_4^+-N, didn't in exceed general 1 mg l^{-1}. No percolation occurred in FD conditions; irrigation and precipitation restricted to 900 mm y^{-1}, combined with hot summer conditions, prevented the percolation of water and with it, the loss of nitrogen. This situation led to high N concentration in crop tissues, but because of a low biomass production, to a lower total N uptake than in WT conditions.

N_2O emissions were affected by N fertilization at sowing. Peaks of emissions were usually evident three days after fertilization. WT60 presented a lower concentration, which means lower peaks with respect to WT120 and FD, but emissions were in general extended in terms of duration. The period of higher emissions followed manure and urea application, while the absence of fluxes later the growing season despite high WFPS level, indicated that N input was the main parameter driving denitrification. Top-dressed urea had a far lower effect on N_2O emissions, perhaps due to the low doses and absence of a C supply as that given by manure. The absence of fluxes far from fertilization can be related to N-limiting conditions, as mentioned by Smith and Tiedje (1979) and Ryden (1983), due to the growing roots competing with denitrifiers for available NO_3^- and thus depressing denitrification. WT60 generally had lower emissions but also a slower return to zero emissions.

N_2O emission in FD can either be related to a nitrification process, rather than a denitrification process limited by N availability and well-aerated soil, or to a denitrification process stimulated by anaerobic microsites. In effect the soil texture, rich in silt and clay, could stimulate temporary anaerobic situations. Paul and Beauchamp (1989) showed that denitrification of soil NO_3^- occurred within hours of manure application due to oxidation of short-chain fatty acids present in the manure which provides electron donors for the denitrifying bacteria and increases the oxygen demand in the soil. The estimate of cumulative denitrification using periodic measurements could have been subject to error, because we used integration of the emissions for the missing data. The problem is difficult to solve because is not practical and very expensive to measure emissions every day. Anyway the trend of data demonstrates that emissions in general are related primarily with the fertilization events.

Sampling performed after consistent irrigations showed no N_2O emissions. Only in 2011 a peak was generated after an irrigation that was, however, close to the period of fertilization. Far from fertilization, irrigation did not promote N_2O emissions, at least on the days sampled, which were usually the day of irrigation and the day after. Even the temperature didn't have effect on emissions within each year. But to understand the effect of temperature more than one sampling would probably be necessary every day. Sampling N_2O once a day, it was not possible to quantify the effect of soil temperature on emissions; however, the effect of temperature seems evident comparing the two years, which had very different average soil temperatures. Cumulative emissions in 2012 were in fact 4 times higher than the emissions in 2011. It is anyway worth noting that 2011 was the first year of experimentation and, although the experimental setup was the same, the systems maybe required time to reach a steady state, in particular in terms of moisture content and saturation of the soil and microbial settlement, thus affecting the emissions.

In 2011 there were no differences in cumulative emissions regarding fertilization and WT/FD conditions, while in the following year differences occurred for the lower fertilization (170_M + 80_U kg N ha^{-1} y^{-1}). FD reached the higher cumulative emissions (2.91 kg N_2O-N ha^{-1}) while WT60 had the lowest value (0.94 kg N_2O-N ha^{-1}). With the highest fertilization cumulative emissions ranged from 1.84 (FD) to 2.20 kg of N_2O-N ha^{-1} (WT60) without statistical differences. WT120 seemed to maximize crop yield with the same emissions as in WT60 and FD.

Our data agree with the study of Laville et al. (2011) who found a cumulative emission of 2.9 kg N ha^{-1} during the maize growing season, in soil in free-drainage conditions, fertilized with manure at rate of 150 kg N ha^{-1} y^{-1}. Liu et al. (2005) found, in a 2-year study in an irrigated corn field, cumulative emissions of 2.44 and 3.38 kg N_2O-N ha^{-1} for mineral fertilization of 134 and 225 kg N ha^{-1} respectively in 2003. In 2004 emissions were 0.75 and 1.28 kg N_2O-N ha^{-1} respectively. Continuous corn in this case seemed to contribute to a reduction of N_2O emissions contrary to our situation.

Rochette et al. (2008) found emissions of 2.12 and 3.28 kg N_2O-N ha^{-1} in 2002 using 150 kg N ha^{-1} y^{-1} of liquid and solid cattle slurry respectively on maize growing in a loam soil. In 2003 emissions were 1.09 and 1.38 kg N_2O-N ha^{-1}. Emissions with liquid pig slurry in 2003 are similar to our emission in FD 2012 in similar soil. Emissions of 0.19, 0.92 and 0.85 kg N_2O-N ha^{-1} were described by Ellert and Janzen (2008) in maize in a rotation using manure (425 kg N ha^{-1}), NH_4NO_3 (150 kg N ha^{-1}) and manure+ NH_4NO_3 respectively.

Gregorich et al. (2008) recorded an emission of 4.12 kg N_2O-N ha^{-1} in the same situation (corn fertilized with 150 kg N ha^{-1} - NH_4NO_3+urea). Emission of about 2-4 kg of N_2O-N ha^{-1}, similar to ours, was also reported by Dambreville et al. (2008) in maize fertilized with 110 kg N of NH_4NO_3. Halvorson et al. 2010, found an emission of 2.3 kg N_2O-N ha^{-1} y^{-1} in corn–dry bean rotation with conventional-tillage using urea and polymer-coated urea. Emission lowered to 0.2 kg N_2O-N ha^{-1} y^{-1} in the control without urea. Alluvione et al. (2010) recorded daily peaks of emission of 0.8 and 0.2 kg N_2O-N ha^{-1} d^{-1}respectively for urea and compost utilization in maize crop. Our peak reached 0.45 kg N_2O-N ha^{-1} d^{-1} with manure mixed with urea.

All the studies cited above considered soil in free drainage condition. Very few studies tested the effects of shallow groundwater on N gaseous losses. In The Netherlands, van Beek et al. (2010) recorded the emissions in relation to groundwater level. With a water table 55 cm below the soil surface, emissions were equal to 29.5 kg N_2O-N ha^{-1} y^{-1} and with a water table 40 cm below the soil surface, emissions were 11.6 kg N_2O-N ha^{-1} y^{-1}. These results are very different from ours, but soil and climate conditions were different.

In particular, soil with high organic content as those in The Netherlands can stimulate denitrification. Velthof and Oenema (1995) reported an average N_2O emission of 2 kg N_2O ha^{-1} y^{-1} in “wet” condition and 8.6 kg N_2O ha^{-1} y^{-1} in “dry” conditions.

In British Columbia Paul and Zebarth (1997) found emissions of 48 and 17 Kg N_2O-N ha^{-1} during corn growth in 1991 and 1992 respectively with a 1 m depth water table. In this case manure fertilization was very high (600 kg N ha^{-1} y^{-1}). In our study emissions from the water table are significantly lower than those found by van Beek or Paul and Zebarth. Emissions are similar to the IPCC standard that indicates an emission equal to 1% of N input. Our input of 170+80 (manure +urea) and 250+118 kg N ha^{-1} y^{-1} indicates an emission of about 2.5 and 3.7 kg N_2O-N ha^{-1}y^{-1}. The emissions we recorded are similar and never more than 3 kg N_2O-N ha^{-1}y^{-1}. The increasing rate of N input didn’t stimulate an increase in emission but a reduction; the increasing N input only stimulated emission in WT60.

Annual N_2O-N emission as percentage of N input was maximum in FD 170_M+80_U and equal to 1.2%. The other emissions ranged between 0.8 and 0.13%. Alluvione et al. (2010) found in corn emissions of 0.11% of N supplied in compost and 3.4% of applied N using urea. The proportion of fertilizer-N released as N_2O was 1.3% for the corn system in Ellert and Janzen (2008). A ratio of 1.9% was found in maize by Laville et al. (2011). van Beek et al. (2010) found a ratio of 3.1% with a 40 cm depth water table and a ratio of 7.6% with a water table 55cm below the soil surface.

Fluxes of N_2O are characterized by high levels of spatial and temporal variability (Ambus and Christensen,1994; Corre et al., 1996). Fluxes are in general site-specific and with a variability due to the climate and type of soil. An accumulation of dissolved N_2O occurred in groundwater, without statistical differences related to N doses and water table level. N_2O may remain for quite a while after production due to high solubility and slow diffusion. This is a cause of temporal retardation and spatial separation of N_2O production and N_2O emission as reported by Bowden and Bormann (1986), Rice and Rogers (1993), Rolston and Marino (1976) and Tindall et al. (1995).

We assume that the fertilization of 250+118 and 195+118 , combined with WT120, are close to the optimal fertilization. The 120 cm depth water table ensured an adequate water supply to the crop in respect to FD, leading to high maize yield and low N_2O

emission. N leaching was negligible, losses were equal to or lower than 0.26 kg N ha^{-1} y^{-1}. The use of about 400 mm of irrigation water during the crop season is however insufficient to ensure an adequate growth of maize in FD. In conclusion, the limit imposed by the derogation of the Nitrates Directive in NVZs seems be fully applicable to the conditions of northern Italy if a good water supply is assured to maximize maize yield and subsequently N uptake. Optimum water management can be ensured by the presence of a shallow water table or by irrigation, calibrated on the needs of the crops, leading to very limited N losses (leaching + gaseous fluxes).

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Chapter IV

Carbon (CO_2 and CH_4) emissions from soil with shallow water table and approach to GHGs modeling

1. Introduction

The use of organic fertilizers in soil, although permitting an increase in soil C, require greenhouse gas accounting. (Del Grosso et al., 2001a). N available from fertilizers needs energy consumption resulting in CO_2 emissions, and contributes to nitrate leaching and N_2O emissions (Granli and Bockman, 1994) .

Efflux of CO_2 indicated as *Soil Respiration (RS)* (Fig.1.1) is a combination of the activity of autotrophic roots and associated rhizosphere organisms *(Autotrophic Respiration (Ra))* and the heterotrophic bacteria and fungi active in the organic and mineral soil horizons, and soil faunal activity *(Heterotrophic Respiration (Re))* (Edwards et al., 1970). Whereas the activity of soil heterotrophic organisms is proportional to soil C decomposition, CO_2 lost from root and rhizosphere activity is tied to the consumption of organic compounds supplied by aboveground organs of plants (Horwath et al., 1994).

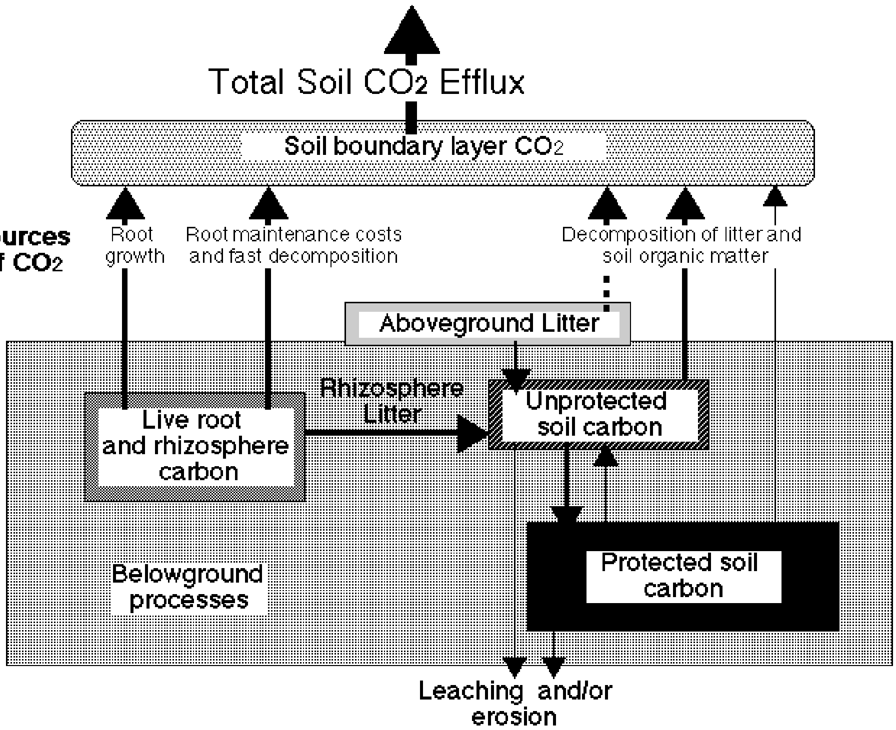


Fig.1.1- CO_2 soil efflux *(Soil Respiration (SR))*. From Hanson et al. (2000).

Critical factors reported to influence rates of soil respiration include (1) temperature (Singh and Gupta, 1977; Peterjohn et al., 1993, 1994; Kirschbaum, 1996; Winkler et al., 1996;

Rustad and Fernandez, 1998), (2) soil moisture (Schlenter and Van Cleve, 1985; Davidson et al., 1998), (3) vegetation and substrate quality (Tewary et al., 1982), (4) net ecosystem productivity (Schlesinger, 1977; Raich and Potter, 1995), (5) the relative allocation of NPP above- and belowground (Boone et al., 1998), (6) population and community dynamics of the aboveground vegetation and belowground flora and fauna (Raich and Schlesinger, 1992), and (7) land-use. Water table variations also had major effects upon CO_2 flux (Billings et al., 1982, 1983).

The rates at which CO_2 moves from soil to the atmosphere is controlled by the rate of CO_2 production in the soil, the strength of the CO_2 concentration gradient between the soil and the atmosphere, and properties such as soil pore size and wind speed, which influence the movement of CO_2 through and out of the soil (Raich and Schlesinger, 1992). The C-flux in soil respiration defines the rate of C-cycling through soils, but the global magnitude and distribution of the process is poorly quantified (Raich and Schlesinger, 1992).

The net flux (emission or consumption) of CH_4 will vary depending on the nature of the agricultural system and the management practices adopted (Fig. 1.2). Measurements made at various locations in the world show that there are large temporal variations of CH_4 flux which differ with soil type, application of organic matter and mineral fertilizer, and soil water regime. Methane production occurs only under highly anaerobic conditions such as those typically occurring in natural wetlands and lowland rice fields. Flooding decreases O_2 concentration and selects a microbial flora in soils able to ferment organic matter. The main products are ethanol, acetate, lactate, propionate, butyrate, H_2,N_2,CH_4 and CO_2. The latter three gases usually constitute the largest portion of the gas phase of flooded soils. So saturated soil releases methane to the atmosphere:

$$\mathbf{C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4}$$

CH_4 oxidation in non-saturated soil acts as a sink for atmospheric CH_4 (Mosier et al., 2004), but N fertilization and tillage tend to decrease CH_4 uptake in soil because the enzyme that oxidizes CH_4 also has affinity for ammonium (Bronson and Mosier, 1994). Knowles (1993) described in detail microbial pathways of CH_4 oxidation in soil by methanotrophic organisms. He noted that all isolated methanotrophs were obligate aerobes. This seems reasonable since the enzyme responsible for the initial step in CH_4 oxidation is a monooxygenase enzyme (MMO) that requires molecular O_2. The first product is methanol followed by formaldehyde and finally there is the possibility to convert formaldehyde in different organic products used as biomass by microorganisms or for ATP production with the release of CO_2 and H_2O:

First reaction: $\mathbf{CH_4 + O_2 \rightarrow CH_3OH + H_2O}$

Other reaction: $\mathbf{CH_3OH \text{ ----> } CH_2O \text{ ---> } HCOO^- \text{ ---> } CO_2}$

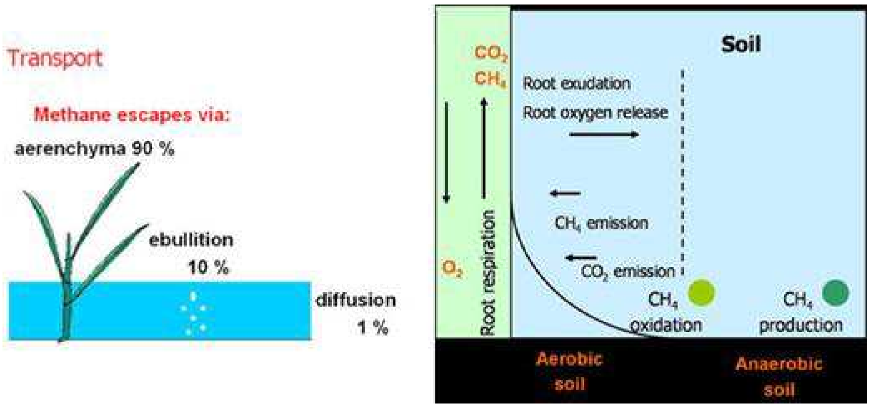


Fig.1.2- Flux of methane, sink and sources. From Radbourd University Nijmegen (The Netherlands) web site.

Del Grosso et al. (2000) observed that oxidation of CH_4 in the soil is clearly dependent on soil water-filled pore space (WFPS). The optimum soil WFPS was dependent on soil texture, with optima of about 7.5% for coarse textured and 13% for fine textured soils. Much research has been developed to improve estimates of soil GHGs fluxes and find ways to reduce N_2O emissions and enhance C storage in soils (Del Grosso et al., 2008). Because it is not simple to measure N_2O emissions and changes in soil C levels on a large scale, process-based models have been developed to estimate regional and national soil GHG fluxes.

Different types of model exist for the estimation of GHGs, ranging from very simple models to extreme complex ones. Highly mechanistic models require detailed parameterization and intensive computation with more input and, in general, are difficult to run. The use of these models has therefore been questioned (Nuttle, 2000). On the other hand, simple models overly generalize the process and cannot represent the heterogeneity of most real system conditions.

DAYCENT (Kelly et al., 2000; Parton et al., 1998) is a terrestrial ecosystem model used to simulate exchanges of C, N and trace gases among the atmosphere, soils and vegetation. DAYCENT is of intermediate complexity; important processes are represented mechanistically but the model makes use of empirically derived equations, and the required input parameters are relatively easy to acquire.

The ability of DAYCENT to simulate plant growth, SOC, N_2O emissions, NO_3^- leaching and CH_4 oxidation has been tested with data from various natural and agricultural systems (Del Grosso et al., 2000a, 2001b, 2002, 2005). The use of this model gives a greater degree of knowledge with respect to the accounted N_2O emissions obtained through IPCC (1997) guidelines. The IPCC (1997) methodology has a large number of limitations for estimation: the guidelines consider all agricultural systems and don't take into account different crops, soils, climate and management (Monsier et al., 1998). The guidelines also do not consider the interaction between weather patterns from year to year (Dobbie et al., 1999).

The aim of this work was to quantify the CO_2 and CH_4 fluxes in lysimeters cropped with maize and subject to irrigation, manure fertilization, free-drainage or shallow water table condition. After determining emissions we tested the ability of DAYCENT to simulate the N and C fluxes in maize cropping. In particular the performance of DAYCENT was evaluated in simulations of CO_2, CH_4, N_2O emissions, crop yields, soil water content and N leaching.

2. Material & Methods

2.1 Field test: CO_2 and CH_4 emissions

The site and treatments used have been described in chapter 3 section 2. Chapter 3 evaluated the N balance and N emissions in an irrigated maize crop. This chapter discusses the fluxes of CH_4 and CO_2 during the same period (June 2011 – October 2012). The same automatic chamber system described for N_2O emission was used for monitoring the emissions. The chambers closed six times a day to monitor CO_2 fluxes, air was taken to an infrared gas analyzer (IRGA). A datalogger (CR-1000 Campbell Sci. Inc. Lincoln Nebraska – USA) controlled the closure of every chamber and recorded the data from the IRGA. The system used the CO_2 rate of increase inside the chamber to estimate the rate at which CO_2 diffused into the free air outside the chamber (Fig. 2.1.1).

Ten measurements of CO_2 were taken during lid closure, the average of these measurements was used as C_0, that was the CO_2 at lid closure. About 30 s were necessary inside the chamber so that a steady mixing was established. Only after this was it possible to apply a non-linear regression between CO_2 and time as follows:

$$C_{(t)} = C_x - (C_x - C_0)\, e^{-a\,(t-t_0)} \qquad [\,\mu\text{mol } CO_2 \text{ mol}^{-1} \text{ of dry air}]$$

For every measurement of CO_2 the system recorded water vapor mole fraction (W, mmol mol^{-1}), air temperature (T, °C) and pressure (P, kPa). $C_{(t)}$,the CO_2 concentration at time *t*, was corrected by the water vapor mole fraction, air pressure and temperature. T_0 represents the time when C_x is equal to C_0. C_0 is the initial concentration at chamber closure. C_x and a are the regression parameters.

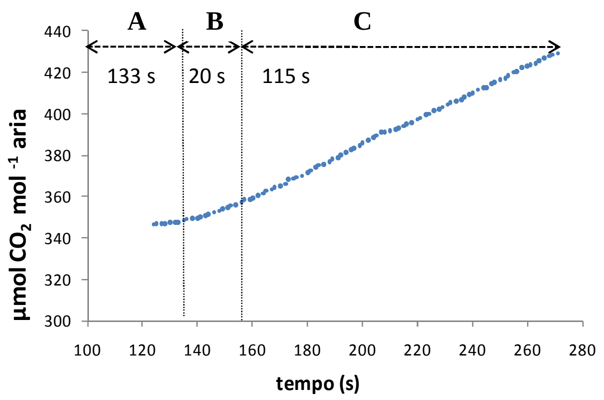


Fig. 2.1.1 – (A) Last ten measurements before chamber closure [CO_2], **(B)** mixing for 20 s, **(C)** non-linear regression computation for 115 s (Delle Vedove et al., 2007).

The exchange of CO_2 between soil and atmosphere was computed using the equation below:

$$\frac{dC}{dt} = a\,(C_x - C_0\,)e^{-a\,(t-t_0)}$$

Soil CO_2 efflux (*SR*, soil respiration) was expressed as:

$$SR = \frac{V}{S} \cdot \frac{dC}{dt} \cdot \frac{P_0}{R \cdot (T_0 + 273.5)} \qquad [\mu mol\ CO_2\ m^{-2}\ s^{-1}]$$

where P_0 and T_0 are the pressure and temperature at t_o. R is the universal gas constant (8.31 J mol^{-1} K^{-1}) and V and S the volume of the system (cm^3, chamber and tubes) and the chamber basal area (cm^2) respectively. Another commonly used method is to fit a linear function between CO_2 and time in the period that is sometimes referred to as the "linear portion" of the curve. The non-linear regression in general effected about 5 iterations to improve the values of C_x and a. If the number of iterations exceeded 10, the system compared the residual sum of squares (RSS) of the non-linear model with the results of a linear model, selecting the model with the lowest residual.

For measuring CH_4 emissions, the chambers closed on a daily basis in the first week after fertilization and subsequently every two weeks. The method used was the same as that adopted for N_2O.

Twenty ml of chamber air were injected into 20-ml evacuated tubes using an auto-sampler and transported to the laboratory for analysis by gas chromatography. The gas chromatograph (Agilent 7890A, mod. G3440A) was equipped with a Flame Ionization Detector (FID) to quantify CH_4. Three samples were taken for every chamber at time zero (at closure), at 25min and 50 min after chamber closure. A linear regression was applied to CH_4 concentration and time. In this way *dC/dt* was the slope of the linear regression and soil CH_4 efflux was expressed as:

$$F_{CH4} = \frac{dC}{dt} MC \cdot \frac{V}{S} \qquad [\text{kg C ha}^{-1} \text{ d}^{-1}]$$

where *MC* is the mass coefficient (g CH_4 m^{-3} CH_4), and *V* and *S* the volume of the system (cm^3, chamber and tubes) and the chamber basal area (cm^2) respectively.

2.2 DAYCENT model overview

In DAYCENT, flows of C and N between the different pools are controlled by the size of the pools, C/N ratio and lignin content of material and by water and temperature as abiotic factor (Parton et al., 1994). Soil water content and temperature are simulated for each horizon throughout the defined soil profile. Water flow (Fig. 2.2.1) is simulated through the plant, litter and soil layer. Rainfall is intercepted first by the canopy, then by the surface litter and evaporated from these surfaces following the potential evapotranspiration (ET_p) computed using the Penman (1948) equation. If water input intensity is greater than the rate at which water could enter the soil, the water difference is added as runoff. Infiltration and saturated flow of water has a unidirectional downward flow. Only when a soil layer is filled with water, the water can percolate to the next layer. Saturated flow is represented by a bidirectional vertical flow. In base of the hydraulic potential and hydraulic conductivity the water moves downwards from layer *i-1* to *i* or upwards from layer *i* to *i-1*. (Parton, 1978).

Plant production is a function of genetic potential, phenology, nutrient availability, water/temperature stress, and solar radiation (Del Grosso et al., 2008).

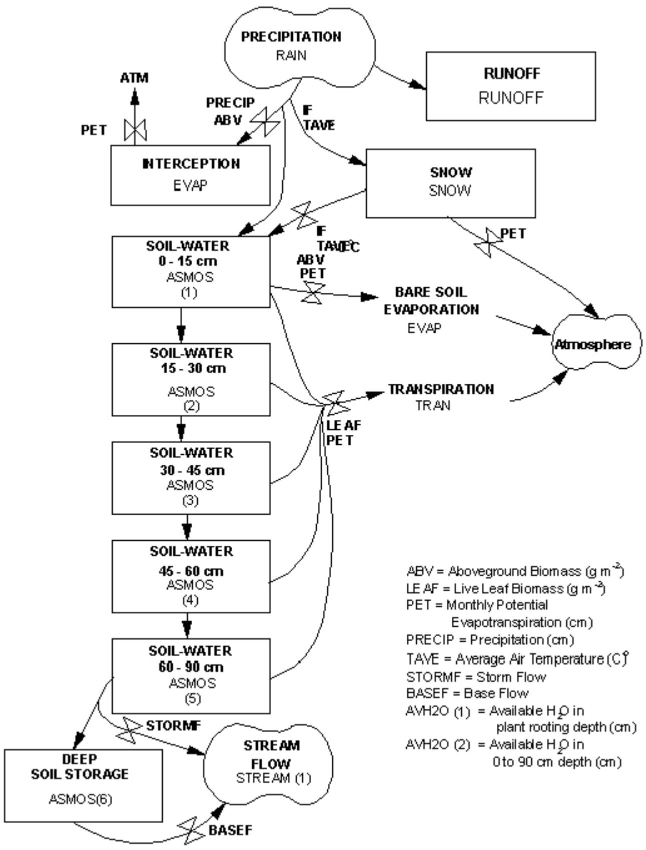


Fig. 2.2.1 – Flow diagram for the water sub-model. The figure considers 5 layers in the soil profile.

The organic matter sub-model (Fig. 2.2.2) includes three soil organic matter pools (active, slow and passive), with different potential decomposition rates, that receive material from aboveground and belowground plant residues (shoot and root plant biomass) and from the microbial community. Each pool is portioned in a metabolic part and structural part, the structural part contains plant lignin. The decomposition of both plant residues and SOM are assumed to be mediated microbially with an associated loss of CO_2. The active pool represents soil microbes and microbial products and has a turnover time of months to a few years. The slow pool includes resistant plant material and soil-stabilized microbial products derived from the active pool. C and N are physically protected and/or in chemical forms with more biological resistance to decomposition. It has a turnover time of 20 to 50 years. The passive pool is very resistant to decomposition and includes physically and chemically stabilized SOM and has a turnover time of 400 to 2000 years.

The model also assumes that the decay rate of structural material is a function of its lignin content and that the lignin is incorporated into the soil slow pool (Parton et al., 1987). The flow of lignin into the different pool is based on laboratory data. The model assumes that lignin is distributed fairly uniformly through the structural material and is released through the activities of microbes which decompose the more labile components of the structural material (e.g. hemicelluloses and cellulose). The model assumes that 55% of C decomposition comes from non-lignin structural C, metabolic C and slow and passive SOM is lost as microbial respiration. Non-lignin components of litter have a low respiration (45%) by fungi. Stabilized lignin has a respiration loss of only 30% (Stott et al., 1983).

The split of plant residues into metabolic and structural components is based on a function of the L/N (lignin/nitrogen) ratio of the residues (Melillo et al., 1984). The decomposition rates for structural materials are calculated in relation to the same constants obtained in laboratory incubations. Temperature and soil texture influence the decomposition process of SOM. The proportion of product which enters the passive pool from the active and slow pools increases with increasing soil clay content (Parton et al., 1987). Anaerobic conditions (e.g. high soil water content) cause the decrease of decomposition.

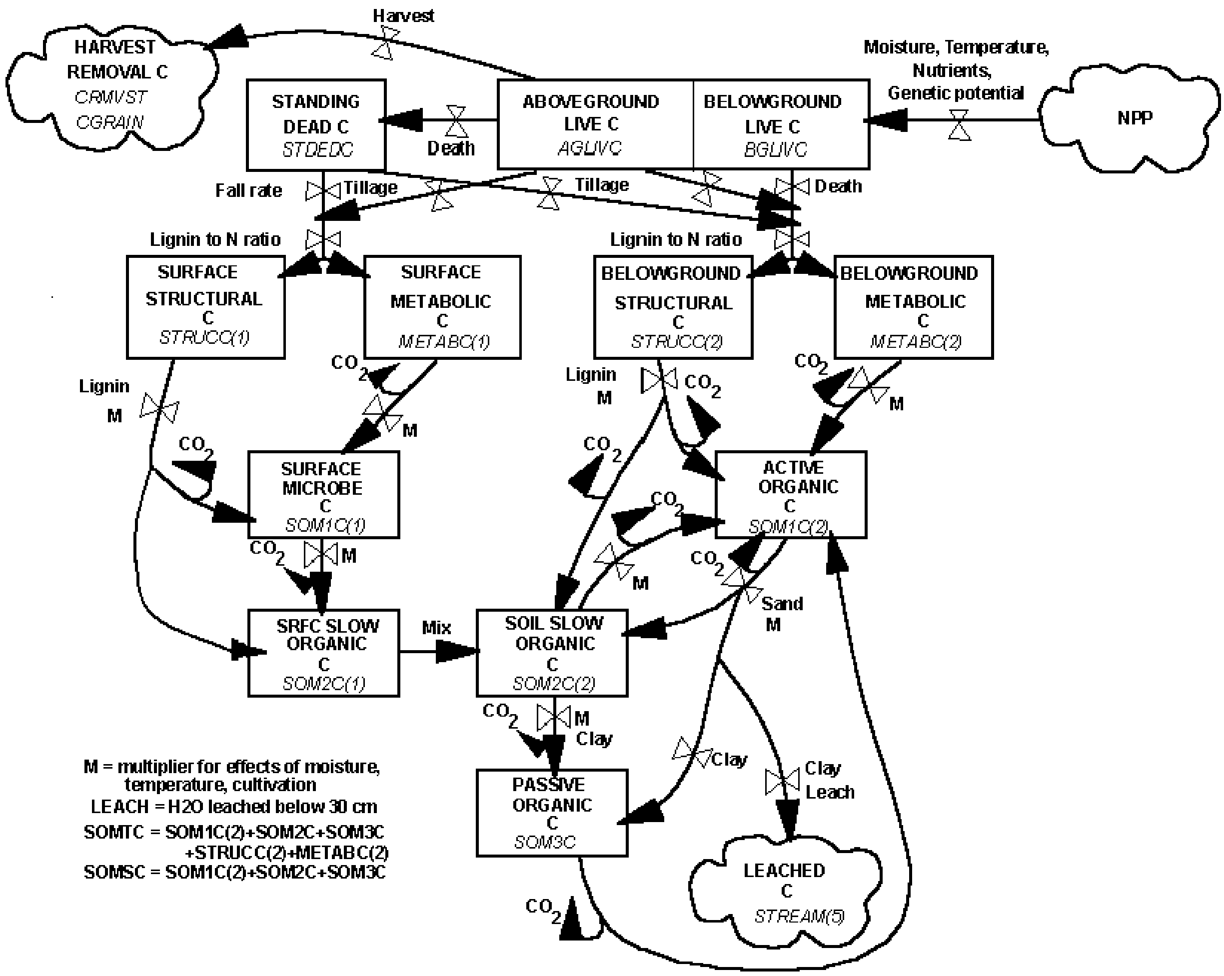


Fig. 2.2.2 - The pools and flows of carbon in DAYCENT model.

The N sub-model (Fig. 2.2.3) has the same structure as the soil C model. The N flow follows the C flow and this reflects the concept that N is stabilized in direct association with C. C to N ratios are constrained within a narrow ranges of values. The C:N ratio of the structural pool (150), active (8), slow (11) and passive (11) fractions remains fixed. The C:N ratio for the active SOM is based on a typical C:N ratio for microbes and microbial products. The N content in the metabolic pool is allowed to vary as a function of the N content of the incoming plant material. The N flow is stechiometrically related to C flow. Either mineralization or immobilization of N can result from C flow, depending on the initial C:N ratio of the materials, C:N ratio of the pools receiving the materials, and the fraction of C flow lost as CO_2 respiration. The N associated with C lost in respiration is assumed to be mineralized. The model assumes the input to atmospheric deposition and eventually N_2 fixation.

N losses due to leaching of mineral N are computed as a function of the stream water. Loss of organic N occurs with the leaching of organic matter. The model also calculates the gaseous losses from soil. N emissions are considered first. The nitrification sub-model simulates N_2O, NO and N_2 emissions from soil as a function of soil NH_4^+, water content, temperature, pH and texture (Parton et al., 2001). Nitrification is limited by moisture stress when soil water-filled pore space (WFPS) is too low and by O_2 availability when WFPS is too high. The denitrification sub-model simulates N_2O, N_2 and NO emissions as a function of soil NO_3^-, water content, labile C availability (because more denitrifiers are heterotrophs), and texture, which influence gas transport (Del Grosso et al., 2000b). Denitrification occurs over a WFPS of 60% and increases esponentially with moisture. NO emissions are calculated using total emission of N_2O according to gas diffusivity. When gas diffusivity decreases the reducing environment makes NO very reactive and a smaller portion of NO is emitted.

The effects of WFPS on N gas flux from denitrification was found to interact significantly with CO_2 emissions. The ratio of NO_3^- to CO_2 emissions is a reliable predictor of the N_2/N_2O ratio (Del Grosso et al., 2000b). C emissions are referred to CO_2 and CH_4 production. CH_4 emission and uptake is controlled by soil gas diffusivity, water content and temperature (Del Grosso et al., 2000a). The CH_4 oxidation in soil is assumed to be limited by high moisture that limits the gas diffusivity but conversely low moisture creates stress for biological activity. CO_2 emissions are related with activity of heterotrophic microorganisms in the soil.

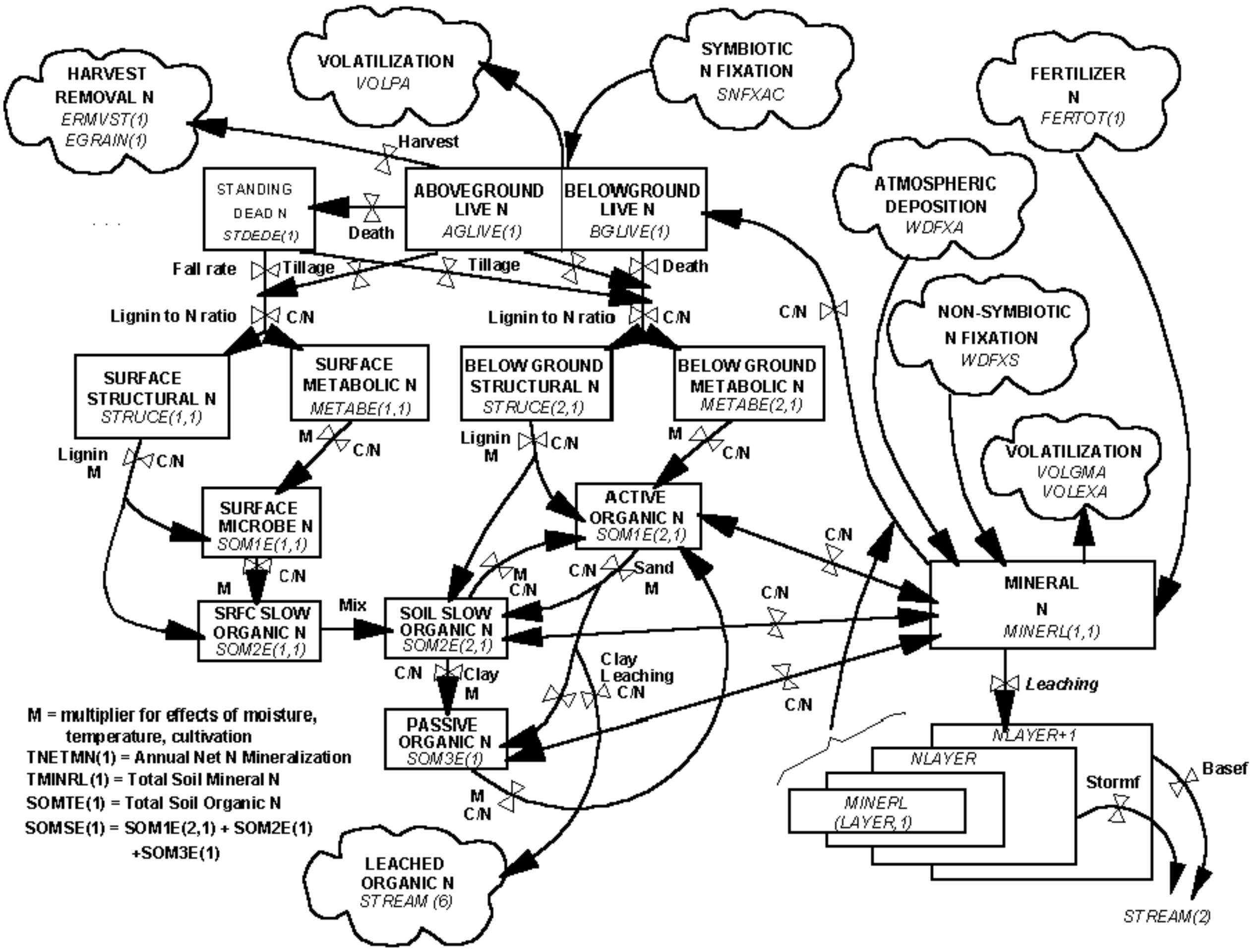


Fig. 2.2.3 - The pools and flows of nitrogen in DAYCENT model.

2.3 DAYCENT inputs

The simulation process can be divided in 4 steps: (1) acquisition and formatting of the model input data required to run DAYCENT; (2) simulation of the native soil and crops; (3) conducting simulation of modern cropping and GHG mitigation options (4) post processing and compilation of model output. The model requires a stabilization of soil parameters (organic matter, soil structure and mineral N) prior to the simulation of real data, so we first simulated a 40-year period. Values for the state variables from the historical period were saved and used as initial condition for the simulation of the actual cropping system (Del Grosso et al., 2009). The model obtains input values through twelve data files. Each file contains a certain subset of variables. Within each file there may be multiple options in which the variables are defined for multiple variations of the event.

Each data input file is named with a ".100" extension, as follows:
crop.100 - crop options file;
cult.100 - cultivation options file;
fix.100 – soil properties;
fert.100 - fertilization options file;
fire.100 - fire options file;
graz.100 - grazing options file;
harv.100 - harvest options file;
irri.100 - irrigation options file;
omad.100 - organic matter addition options file;
tree.100 - tree options file;
trem.100 - tree removal options;
weather.100 – weather file.

These files can be updated and new options created through the FILE100 program (Fig. 2.3.1). For example, within the cult.100 file, there may be several cultivation options defined such as plowing or rod-weeder. For each option, the variables are defined to simulate that particular option. A description follows of the detailed input file we used. Daily maximum/ minimum temperature and precipitation (weather.100) were acquired from a weather station of the Regional Agency for Environmental Protection (ARPAV) located 10 m from our site. The weather data from 1970 to 2010 was used for the historical period.

Specific values of soil properties (fix.100), such as texture, organic matter content, bulk density, field capacity, wilting point and hydraulic conductivity are required for each layer of the profile. The number of soil layers (NLAYER) is an input variable in the model. Fifteen cm increments were used for each layer up to the 60 cm soil depth and 30 cm increments below the 60 cm depth (NLAYER = 7: 0-15, 15-30, 30-45, 45-60, 60-90, 90-120, 120-150 cm). For each layer it is necessary to specify the properties mentioned above.

The model requires two separate files, one relative to information for mineral fertilizer and one for organic fertilizer. In fert.100 it was necessary to indicate the total amount of N in g N m^{-2} and share the quota coming from NO_3^- or NH_4^+. We applied urea at level of 80 and 118 kg of N ha^{-1}. For organic nitrogen (omad.100), manure in our case, the model requires total C applied (g m^{-2}), C/N ratio and lignin content. The doses applied were 170 and 250 kg N ha^{-1}, with a C:N ratio = 13, so the amounts of C applied were 221 g C m^{-2} and 325 g C m^{-2} respectively. The main information required about the crop (crop.100) are the type, potential aboveground monthly production (g C m^{-2}), allocation of C in roots and the water stress factor (0 no water stress, 1 water stress). Irrigation (irri.100) amounts can either be fixed amounts or automatically set according to the soil moisture status. Cultivation (cult.100), was a spading at 20 cm. Cultivation options allow for the transfer of defined fractions of shoots, roots, standing dead and surface litter into standing dead, surface and soil litter pools as appropriate. Thus the model can simulate a variety of conventional cultivation methods. Finally, to simulate the water table levels, another file was compiled. In this case we fixed a steady level of water table for the whole year. Saturation of the soil was expected in this case and it was necessary to specify the saturated hydraulic conductivity of soil. Tab. 2.3.1 reports the main parameters used for the simulations.

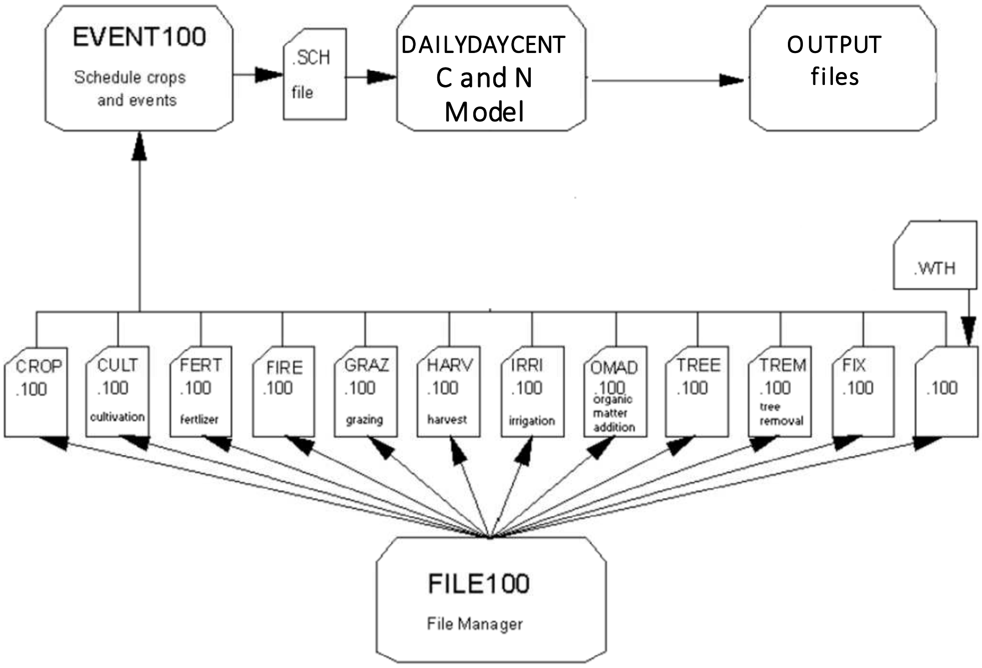
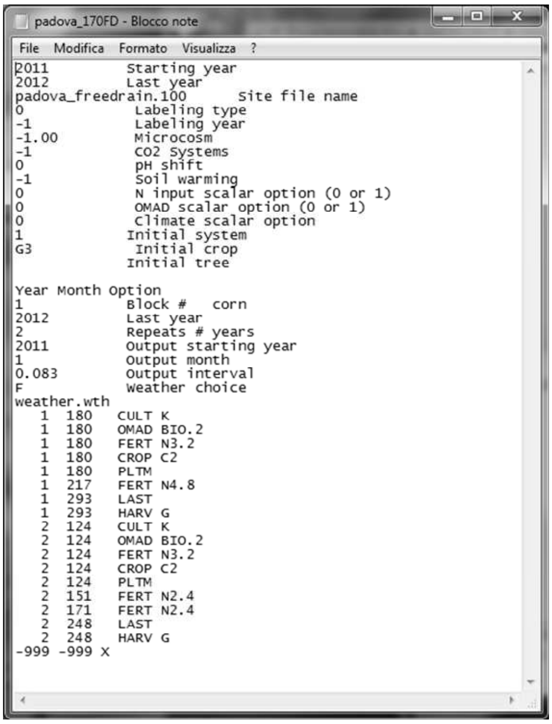


Fig. 2.3.1 – File structure of DAYCENT.

File	**Parameters**		
crop.100 - crop options file	potential aboveground monthly	low- yield	1.5
	production for crops (g C m^{-2})	medium- yield	2
cult.100 - cultivation options file	fraction of the aboveground N	low- yield	0.5
	which goes to grain (g N m^{-2})	medium- yield	0.65
fix.100 – soil properties	bulk density (g cm^{-3})		1.44
	sand		36%
	clay		15%
	pH		8
	FC, Field Capacity		30%
	WP, Wilting Point		10%
fert.100 - fertilization options file	urea (g N m^{-2})	80 kg Nha^{-1}	8
		170 kg Nha^{-1}	11.8
omad.100 - organic matter addition	manure (g C m^{-2})	170 kg Nha^{-1}	221
		250 kg Nha^{-1}	325
	C/N		13
	lignin fraction content of organic matter		0.13

Tab. 2.3.1 - Main parameters used to calibrate the model.

The simulation is driven through a schedule file, created with EVENT100 or manually, containing all instructions relative to the years to be simulated. Every event, such as cultivation, sowing, fertilization is indicated in Julian days (Fig. 2.3.2).



```
padova_170FD - Blocco note
File  Modifica  Formato  Visualizza  ?
2011          Starting year
2012          Last year
padova_freedrain.100      Site file name
0              Labeling type
-1             Labeling year
-1.00          Microcosm
-1             CO2 Systems
0              pH shift
-1             Soil warming
0              N input scalar option (0 or 1)
0              OMAD scalar option (0 or 1)
0              Climate scalar option
1             Initial system
G3             Initial crop
              Initial tree

Year Month Option
1             Block #   corn
2012          Last year
2             Repeats # years
2011          Output starting year
1             Output month
0.083         Output interval
F             Weather choice
weather.wth
   1  180   CULT K
   1  180   OMAD BIO.2
   1  180   FERT N3.2
   1  180   CROP C2
   1  180   PLTM
   1  217   FERT N4.8
   1  293   LAST
   1  293   HARV G
   2  124   CULT K
   2  124   OMAD BIO.2
   2  124   FERT N3.2
   2  124   CROP C2
   2  124   PLTM
   2  151   FERT N2.4
   2  171   FERT N2.4
   2  248   LAST
   2  248   HARV G
-999 -999 X
```

Fig. 2.3.2 – Example of schedule file of DAYCENT.

3. Results

3.1 CO_2 emission

Soil respiration, recorded using the automatic chamber system, is the sum of heterotrophic (R_E) and autotrophic respiration (R_A). Six measurements were obtained every day. The average of daily measurements was utilized to estimate cumulative emissions between sowing and harvest in 2011 and 2012. Emissions were lower in 2011 than in 2012 with an evident "year effect" (Fig. 3.1.1). Fertilization also significantly affected total CO_2 emission: with WT, emission increased going from 170_M+80_U to 250_M+118_U.

The presence of a shallow water table affected CO_2 emissions that were higher than in free-drainage condition. A potential increase in R_A (CO_2 emitted by plant) can be offset by the reuse of CO_2 through photosynthesis (CO_2 uptake by plant) while an increase of R_E represent a direct flux of CO_2 in the atmosphere. In our experiment, due to the small size of the lysimeters, we couldn't apply a system such as a root exclusion to separate R_A and R_E, so we decided to use a modeling approach that will be discussed in section 3.4.

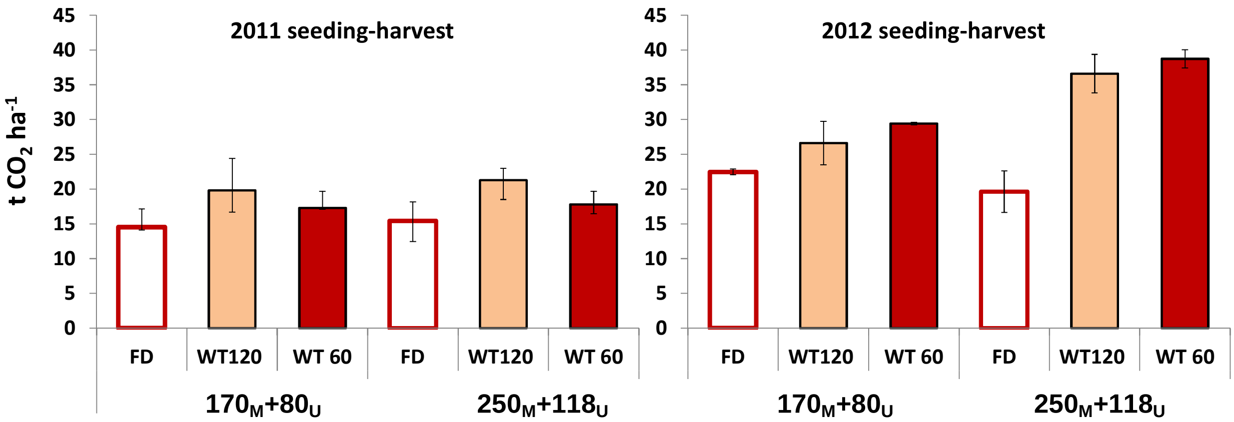


Fig. 3.1.1 – Cumulative CO_2 emissions in 2011 and 2012.

	average		es
2011	17.68	**b**	1.80
2012	28.91	**a**	5.37
FD	18.01	**b**	2.62
WT	25.94	**a**	5.92
170_M+80_U	21.69	**b**	3.99
250_M+118_U	24.91	**a**	7.17

Tab.3.1.1 – Differences in year, water table conditions and fertilization (p=0.05)

3.2 CH_4 emissions

A net negative, but relatively small, flux of CH_4 appeared in our site. CH_4 concentration decreased linearly with increasing the time of chamber closing (Fig. 3.2.1). This indicates a soil uptake of atmospheric CH_4. Similar results have been obtained by Knowles (1993) and Mosier et al. (2004), and this process is mediated by methanotrophic organisms which cause CH_4 oxidation in soil. Only in 23% of cases net fluxes are positive and soil produces CH_4 (Fig. 3.2.2).

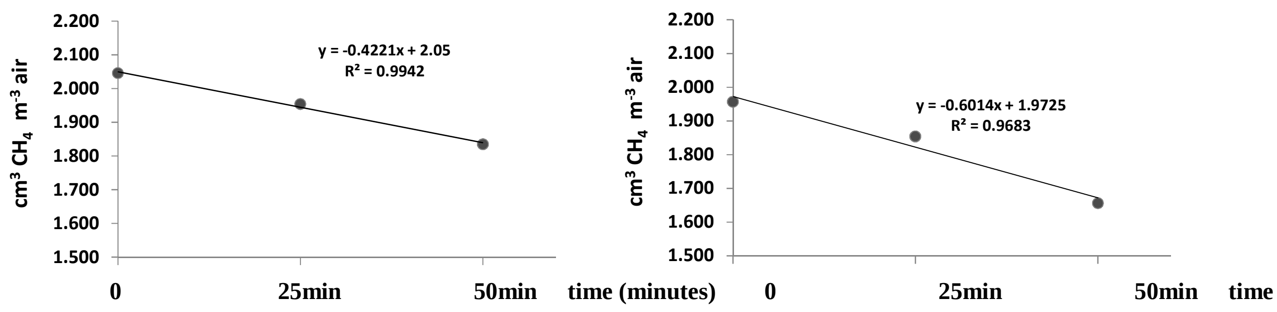


Fig. 3.2.1 – Two examples of CH_4 depletion inside the chamber during the monitoring time (at closure, at 25 and 50 minutes after closure).

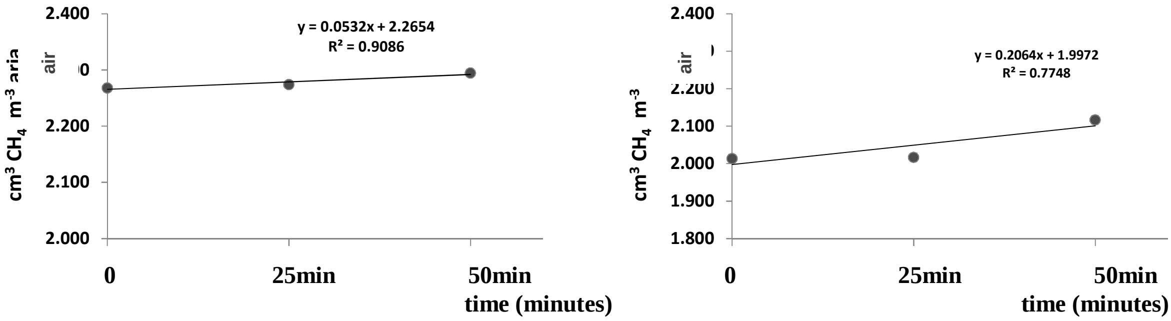


Fig. 3.2.2 – Two examples of CH_4 accumulation inside the chamber during the monitoring time (at closure, at 25 and 50 minutes after closure).

Fluxes reached a peak of 25 g ha^{-1} in mid-May 2012 for both fertilization levels. But in general fluxes were negative and ranged between -12 and -2 g ha^{-1}. The few cases of positive emission were about 4-5 g ha^{-1} (Fig. 3.2.3 and Fig. 3.2.4). No relationship was found between CH_4 daily fluxes and precipitation, soil moisture and temperature, in accordance with the observations of Dobbie and Smith (1996) found a relationship between CH_4 fluxes and moisture content, soil temperature and soil ammonium concentration in woodland, but none in arable soil.

However, many authors reported the influence of soil moisture on CH_4 uptake in WT condition; soil moisture increased and air-filled porosity decreased, resulting in a reduction of methane diffusion into the soil (Potter et al., 1996). Instead a low moisture content permits a rapid gaseous diffusion. Dry and warm ecosystems could thus be expected to give a primary contribution to CH_4 uptake, with subsequent CH_4 oxidation (Castaldi et al., 2005; Potter et al., 1996). Otter and Scholes (2000) observed high CH_4 uptake in Savanna at WFPS ranging between 20% and 5%. However, at lower WFPS (<5%) the oxidation capacity was lower. Methanotrophic organisms may be less adapted to water stress than other microflora (Castaldi et al., 2005). In arable soil the water content strongly decreases during summer and evaporation makes the top few centimeters of soil very dry.

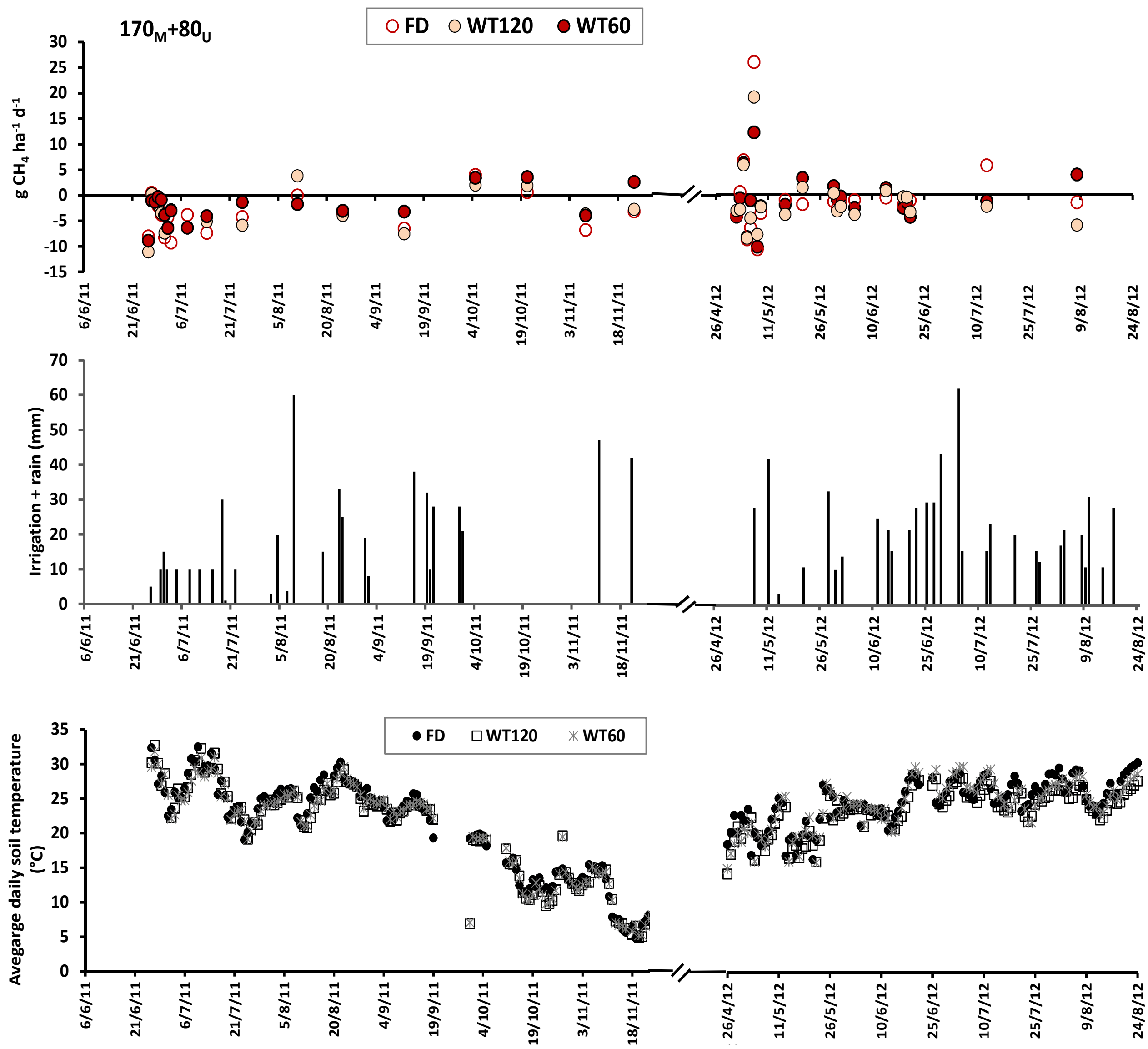


Fig. 3.2.3 – Daily fluxes of CH_4, irrigation+rain and soil temperature in 170_M+80_M.

This situation associated with the high transpiration of maize can make the most superficial layers of the soil very inhospitable for methanotrophic organisms with an inhibition of CH_4 oxidation as reported by Striegl et al., (1992). Temperatures in 2012 were higher than in 2011 and this probably further affected CH_4 uptake. In our experiment N rates didn't affect daily and cumulative fluxes, while other Authors found that fertilization can modify the net exchange of CH_4. In particular the increase of NH_4^+ in soil seems to negatively affect oxidation processes (Bronson and Mosier, 1994).

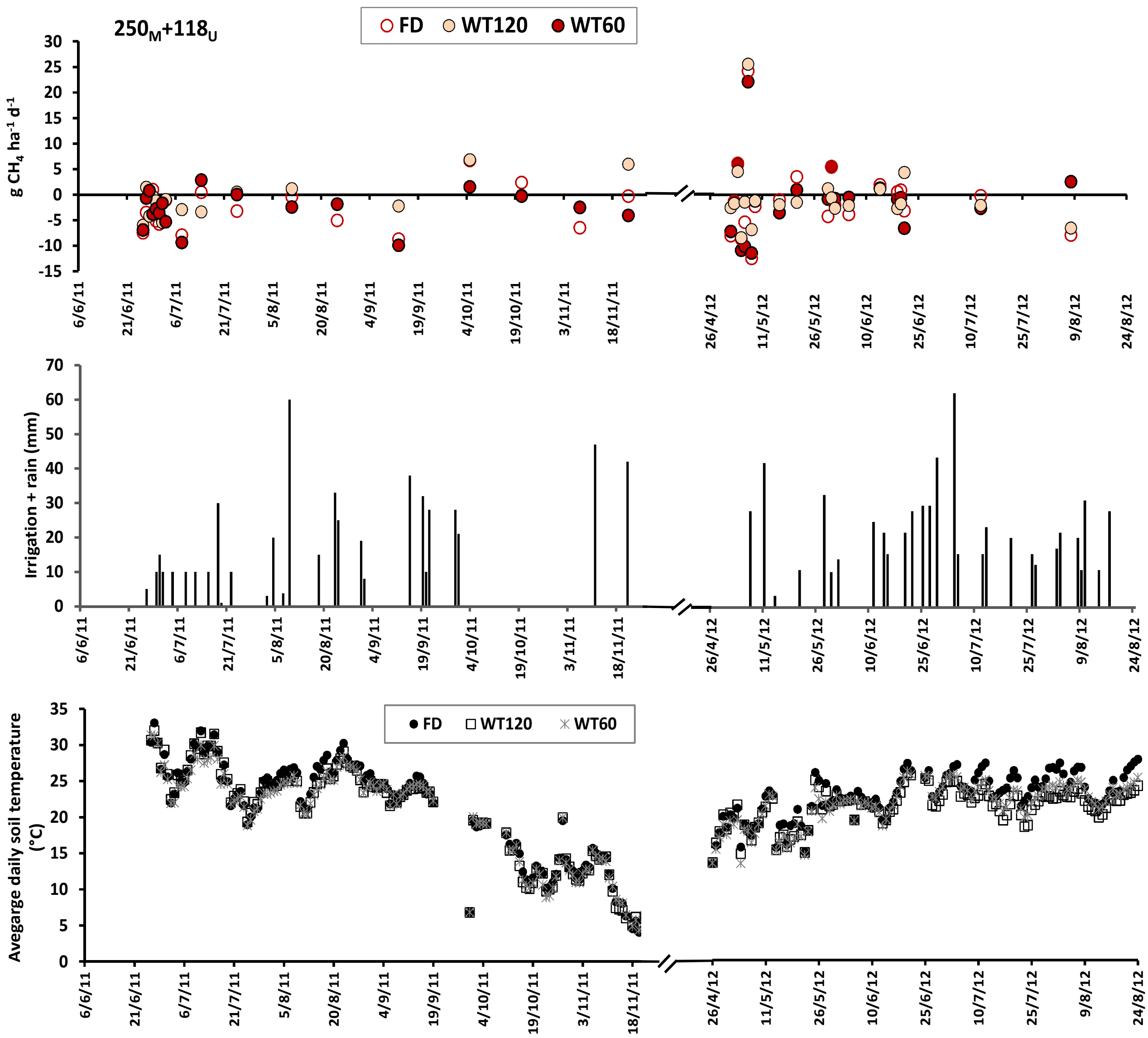
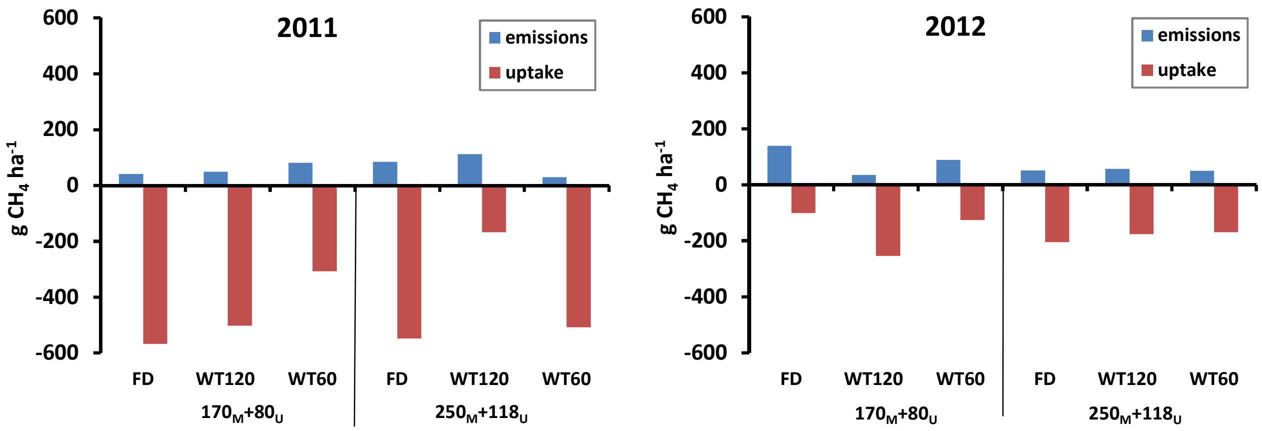


Fig. 3.2.4 – Daily fluxes of CH_4, irrigation+rain and soil temperature in 250_M+118_M.

The lack of a fertilization effect in our experiment is probably due to soil conditions not favorable for CH_4 production, leading to almost insignificant CH_4 emissions, particularly in respect to those coming from anthropogenic activities. At the same time, CH_4 uptake was relatively low and reached at maximum 0.55 kg of CH_4 ha^{-1} y^{-1} (Fig. 3.2.5).



2011 ≠ 2012
FD ≠ WT
$p = 0.05$

Fig. 3.2.5 – Source and uptake of CH_4.

3.3 DAYCENT: Production and maize yield

Simulations were run for the period April 2011 – October 2012, assuming a constant soil texture through the profile. Six different situations were simulated, coming from the factorial combination of three water table conditions and two levels of organic fertilization. Free drainage (FD), water table at 60 cm depth (WT60) and water table 120 cm depth (WT120) from the soil surface were compared at two levels of N input, 170+80 and 250+118 kg N ha^{-1} y^{-1} (N from manure + N from urea).

A maize with medium-low production was considered for the first year because the sowing was very late (end of June) compared to the traditional climate period required by the area (in general April) and to cope with the observed phenology of the crop. A maize with high production was chosen for 2012 when sowing was in April. DAYCENT gives yield estimates in g C ha^{-1}, the conversion into biomass was done assuming a grain C content of 42% of d.m. (Follett et al., 2009). DAYCENT satisfactorily (R^2= 0.81) simulated average grain yield (Fig. 3.3.1). Also C in total biomass fitted well (R^2= 0.87) (Fig. 3.3.2).

N content of grain (Fig. 3.3.3) presented a good agreement with the observed data, with R^2 =0.93.

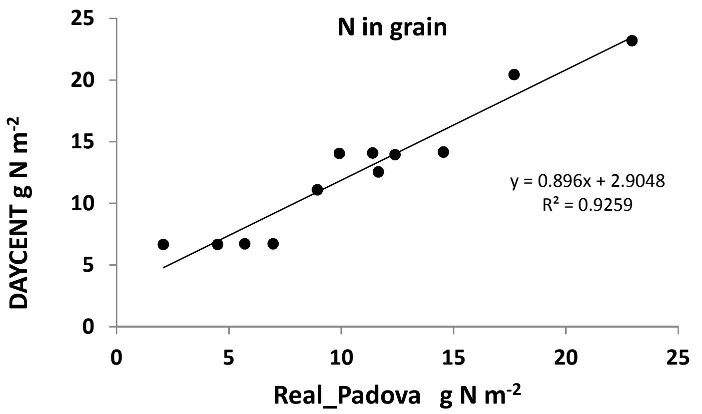


Fig. 3.3.1 - Relationship of real and DAYCENT-simulated grain yield.

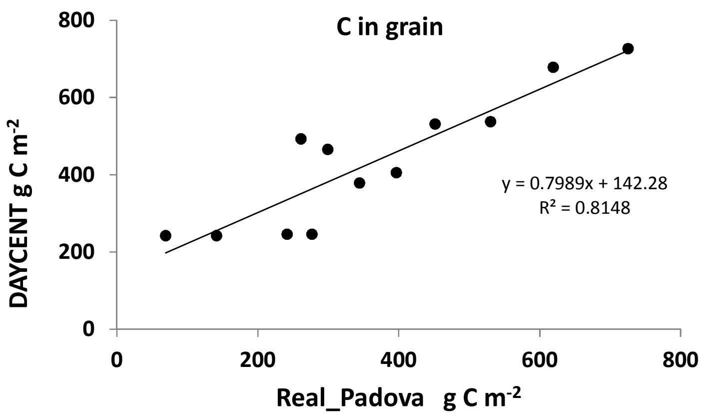


Fig. 3.3.2 - Relationship of real and DAYCENT-simulated total biomass.

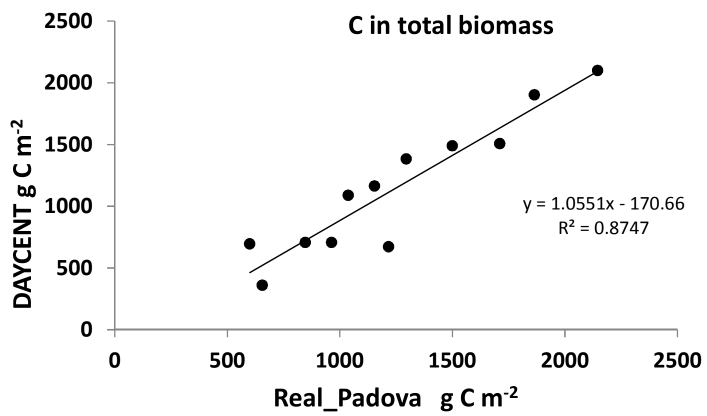


Fig. 3.3.3 - Relationship of real and DAYCENT-simulated N in grain.

Differences in N leaching were evident in simulation versus real data. In WT condition leaching per year was negligible for real data and in DAYCENT, but in free drainage condition DAYCENT simulated about 70 kg of NO_3^--N losses with percolation water below the deepest soil layer, i.e. 120-150 cm. In our data no percolation of water occurred in free drainage condition and consequently no N leaching. Average ET is similar in FD condition but is underestimated in groundwater conditions (Fig. 3.3.4). It is worth noting that in the lysimeters water table greatly contributed to the crop water supply, while DAYCENT, using a cascade approach for water movement, underestimates upward flux. The model stops the growth of the roots at the groundwater level, greatly reducing available water and, thus, limiting ET in respect to observed data.

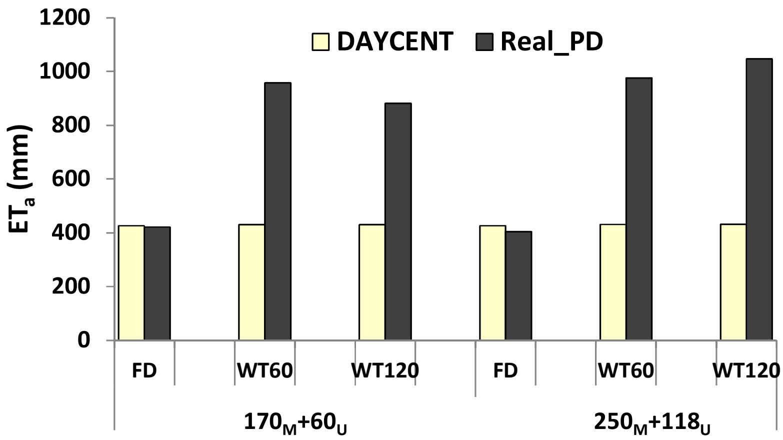


Fig. 3.3.4 – Comparison of the average evapotranspiration (2011-2012).

3.4 DAYCENT: Greenhouse gas production

<u>N_2O production</u>

DAYCENT gives daily fluxes of N_2O (Fig. 3.4.1). In 2011, fluxes in 170_M+80_U appeared the day after fertilization with peaks of 0.08-0.09 kg N_2O-N ha^{-1} d^{-1}. Fluxes had peaks of magnitude similar to real data (Chapter 3, sect. 3.4), but the temporal dynamic was different. Real fluxes reached the peak and returned to zero in about 7 days, while simulated fluxes have a slower temporal dynamic, leading to a superposition of peaks due to different fertilizations. Simulated fluxes only decreased approaching zero at the end of the season. Irrigation influenced emissions, a peak followed every irrigation event in WT while in FD fluxes seem to be independent of irrigations. 250_M+118_U had a different behavior, the first peak was higher, and reached 0.15 kg N_2O-N ha^{-1} d^{-1}. Only WT120 seems to be strongly influenced by irrigation.

In 2012 peaks reached approximately the same peaks as 2011, unlike the real data arrived at 0.45 kg N_2O-N ha^{-1} d^{-1} that is a daily emission 4 time higher. In 170_M+80_U WT and FD initially had different fluxes. After the second dose of urea fluxes were very similar. In 250_M+118_U soil in FD maintained very high values.

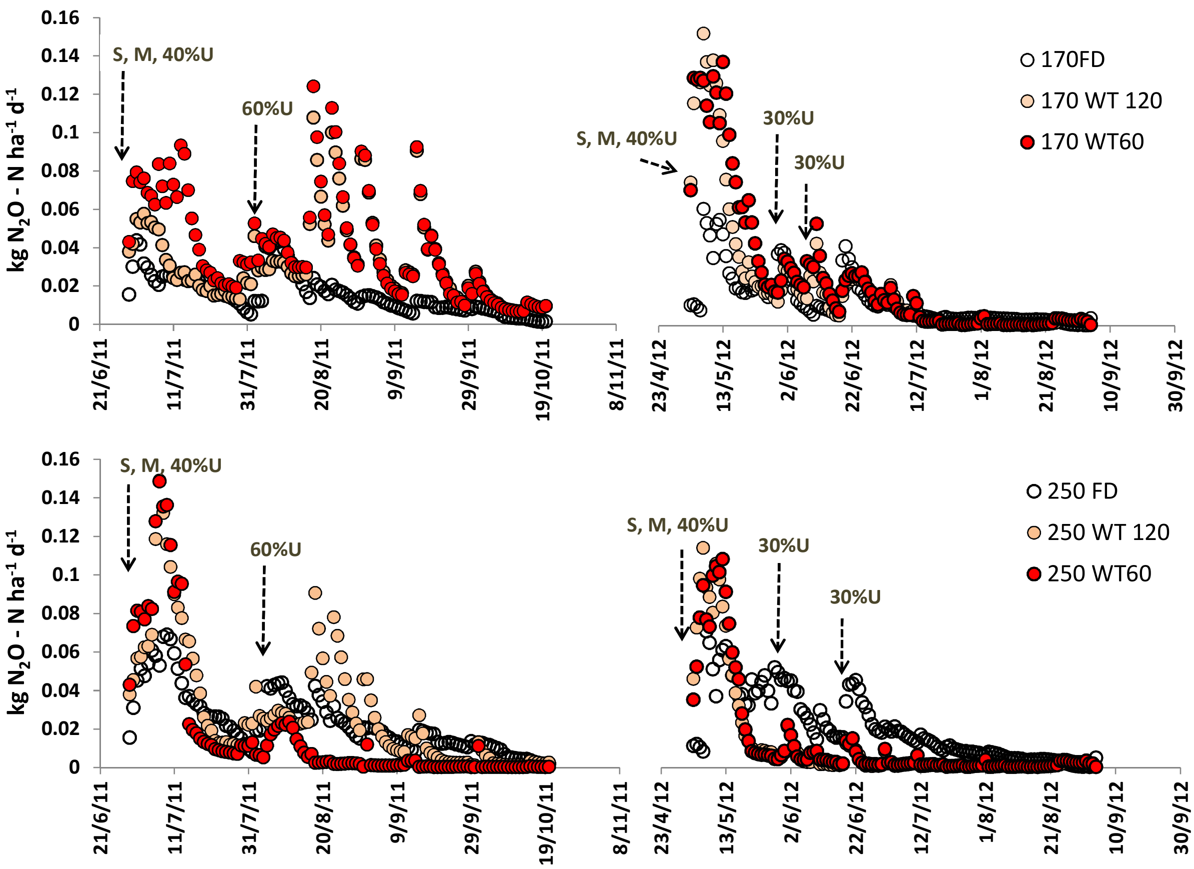


Fig. 3.4.1- DAYCENT N_2O fluxes in 2011 and 2012.

In DAYCENT N_2O cumulative emission between sowing and harvest are the sum of daily values. Instead for real data, because the sampling was not done daily, fluxes were integrated for the missing data to obtain cumulative emissions. The cumulative annual emission between sowing and harvesting shows that DAYCENT fluxes decrease passing from WT60 to FD. Real data show the opposite behavior (Fig. 3.4.2).

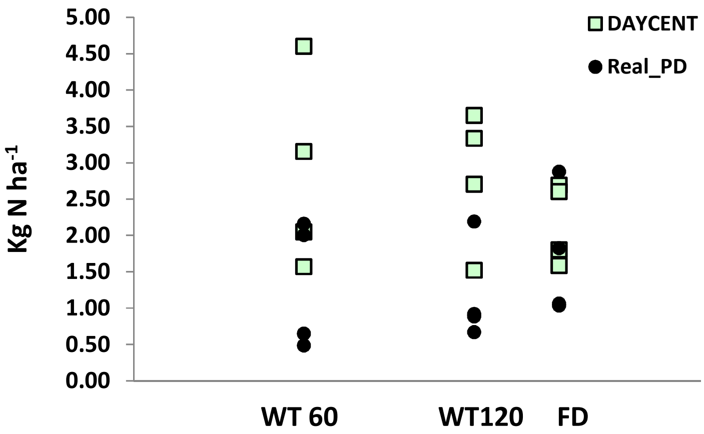


Fig. 3.4.2- N_2O cumulative fluxes, sowing-harvest in the two years.

Cumulative emissions in 2011-2012 are generally higher in DAYCENT than in real data (Fig. 3.4.3).

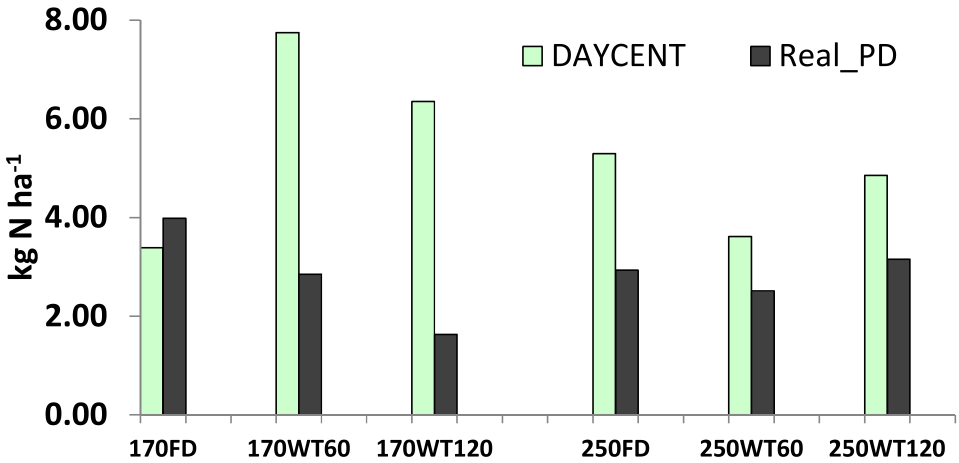


Fig. 3.4.3- Cumulative fluxes of two years.

In DAYCENT, with the higher fertilization, it seems that WT condition stimulates a reduction of N_2O losses with respect to FD. Most probably the differences in N loss, between real data and DAYCENT, are related to N residual in the soil. We can suppose that more N is retained in soil in real condition with respect to the simulation. The C:N ratio drives the emission in the model, but real decomposition of organic fertilizer in soil can determine a different situation with respect to the ratio predicted by the model.

CO_2 production

To share the quota of autotrophic and heterotrophic respiration we compared our data (SR) with the data of DAYCENT. In fact the model gives only the quota of heterotrophic respiration, which has been assumed as an estimation of R_E. Fig. 3.4.5 shows the overlap between SR and R_H. Both SR and R_E increased at sowing (i.e. with fertilizer application). SR then reached a peak related most probably to R_A. At harvest both components SR and R_E increased. The dead maize roots probably stimulated the respiration by microorganisms. During the growth phase, SR is mainly related to autotrophic respiration and heterotrophic respiration seems fairly constant over time. The ratio between $R_{E:}$SR (Fig. 3.4.6) indicates that in FD condition R_E was about 30-31% of RS. In WT R_E ranged between 21 and 24% of SR.

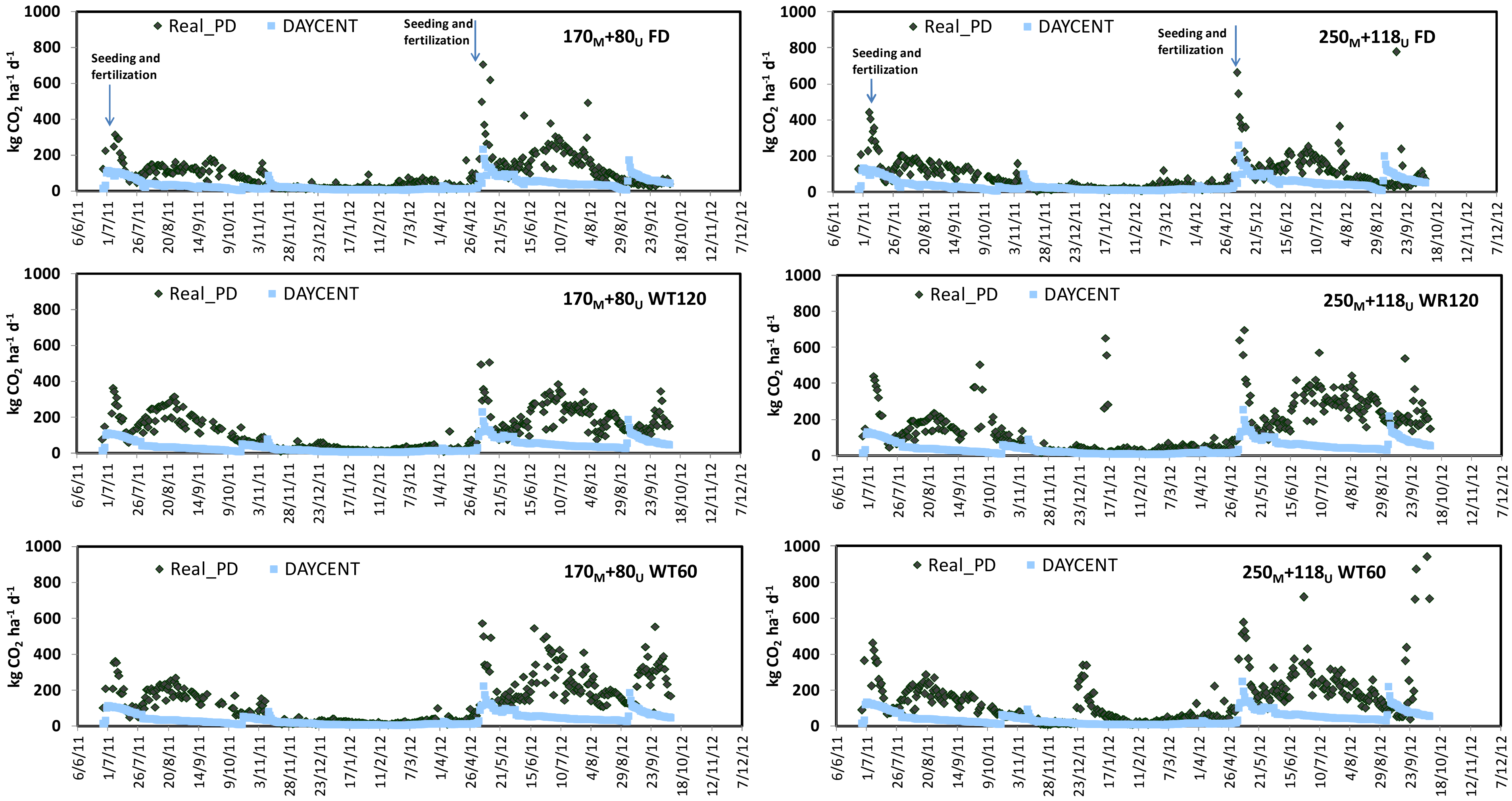


Fig. 3.4.5- Total respiration measurements using the chamber and heterotrophic respiration simulated with DAYCENT.

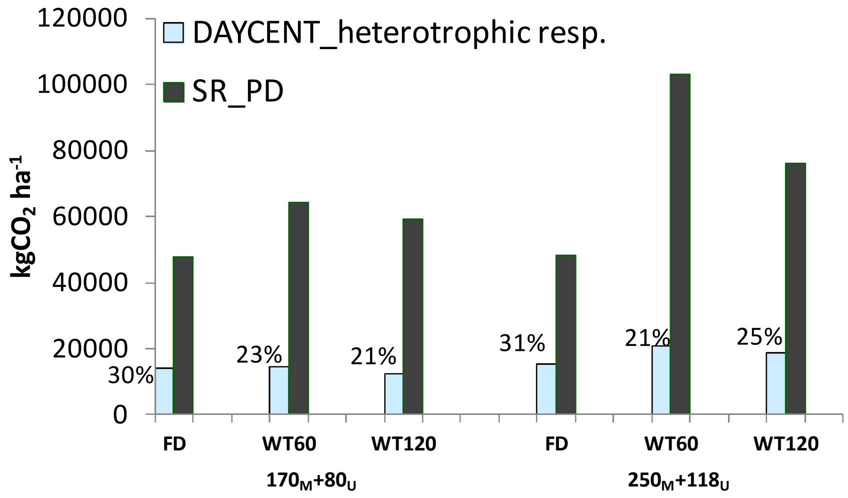


Fig. 3.4.6 – Total respiration (real data) and heterotrophic respiration (simulated with DAYCENT).

<u>CH_4production</u>

DAYCENT simulated a similar cumulative flux of methane in 2011 and 2012. Simulated fluxes were higher in FD than in WT condition. In WT fluxes were equal to about 0.17 kg CH_4 ha^{-1} in 2011 and also 2012 for both N input and so of the same order of magnitude as observed data. In FD conditions fluxes were 0.49 and 0.55 kg CH_4 ha^{-1} in 2011 and 2012 without differences given by the level of N input.

4. Conclusions

CO_2 is released into atmosphere mainly by autotrophic respiration and responds to nitrogen fertilization, tillage and crop development. Heterotrophic respiration also reflects the agrotechnique, such as tillage and fertilization, but the magnitude of emission is clearly lower. An increase of heterotrophic respiration also occurred at maize harvest. Cumulative CO_2 was strongly affected by climate conditions. 2012 was characterized by high and steady temperature that favored emission. The emissions increased in 2012, passing from the lower to higher fertilization. CO_2 also responded positively to an increase of soil moisture due to WT conditions, in this case in both years.

Cumulative CO_2 emissions in free drainage conditions ranged between 14.5 and 21.1 t CO_2 ha^{-1} (from sowing to harvest). This result seems in line with the results obtained by Drury et al. (2008) who found, in continuous corn fertilized with mineral nitrogen at 170 kg N ha^{-1} y^{-1}, emissions of 14.3, 10.1 and 18.75 t CO_2 ha^{-1} in 2003, 2004 and 2005 respectively. Instead our result is higher than those found by Alluvione et al. (2010) . Corn fertilized with green compost or urea during a two-year study, reached average values of 6.67 and 5.94 t CO_2 ha^{-1}. However fertilizer rate was inferior to ours and equal to 130 kg of N ha^{-1} y^{-1} in both urea and compost. Emission reached a peak of 470 for compost and 330 kg of CO_2 ha^{-1} d^{-1} for urea treatment in spring as a result of fertilizer application. Our peak reached about 400 and 600 kg of CO_2 ha^{-1} for 170_M+80_U and 250_M+118_U respectively. Emission peak generated by fertilization seems comparable. No study was found relative to CO_2 emission in shallow groundwater condition.

Our data shows a tendency of the soil to consume methane by the oxidation process. The soil can be defined as a sink for atmospheric CH_4. But anyway the uptake and emissions fluxes are relatively small in the global budget of atmospheric methane, as mentioned by Potter et al. (1996). Denitrification requires undecomposed organic matter, as electron donor, to obtain energy for microorganisms, with consequent CO_2 emission. This could explain the increase of CO_2 emission in WT condition. However, no relationship was found between N_2O and CO_2 emissions. Results on denitrification process given by DAYCENT tend to overestimate the N_2O fluxes. The model works simulating N emissions based primarily on moisture and nitrates concentrations in soil. The model is not very sensitive to water table condition: the soil moisture simulated in WT conditions was much lower than in the real data and this probably results in an incomplete denitrification with N_2O production instead of N_2. At the same time the model doesn't allow the accumulation of N, coming from fertilizer, in the soil.

The higher emission of N_2O suggests, as reported by Bakken and Bleken (1998) and Del Grosso et al. (2005), that N_2O emission factors should be based on multiple years and not on the assumption that the N that is applied to a system in one year is entirely cycled during that year. Similar to N gaseous losses, CH_4 emissions were higher in DAYCENT. The model's ability to predict crop production seems quite good. Both biomass production and N uptake by plants had a good fitting with the real data.

In conclusion it is noteworthy that DAYCENT has been developed mainly for long-period simulation while our experiment considered only two years. On the other hand we worked with small plots limiting the variability in respect to the open field, but with the risk of overestimating parameters such as production and evapotranspiration.

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Chapter V

General Conclusion

Conclusion

The thesis deals with the independent and interactive effects of N input and water regime on N losses via leaching and on greenhouse gas production. Water regime and the resulting soil water dynamics strongly regulate N cycling, influencing plant growth, N uptake, N leaching, and also involving soil microbial N transformation. N losses in soil were a sporadic process: nitrogen leaching usually occurred after maize harvesting and followed irrigation or heavy rains; gaseous N emission had a short temporal extension after fertilization events, but with different magnitude due to soil water content (free-drainage or water table conditions).

Specifically, the first chapter evidenced that high fertilization (i.e. 250 and 340 kg N ha^{-1} by manure + 60 kg N ha^{-1} by urea) combined with water regime of 1100 versus 1400 mm y^{-1} enhanced production and consequently N uptake. However N concentration in maize grain remained the same for each level of fertilization. Free drainage conditions ensured production only if combined with a suitable water regime. 800 mm y^{-1} seemed not sufficient to ensure production and cause an increase of N residual in soil. At the same time too high water regime, such as 1700 mm y^{-1}, resulted in substantial N leaching and a smaller crop production due to the loss of N with percolation water. The dependence of N leaching on the N rate, N residual in soil and percolation water seems quite robust, giving the possibility to build a simple but specific prediction model of N losses.

The approach used with our metamodel is quite different from that used by the DAYCENT model in chapter 4. With DAYCENT we simulated many outputs such as maize yield, water balance and evapotranspiration, GHGs and also N leaching. The choice between a simple metamodel or a mechanistic model should be made depending on the needs and available data. The results we obtained indicated that the use of a multi-output model gives a lower resolution and is better adapted to long-term evaluations.

The metamodel is instead very sensitive to minor changes during the experimental period but requires more specific input for the site and gives only one output but, in our case, with a greater reliability. It is worth noting that simulation of GHGs is possible only with the use of the mechanistic model because of the large number of parameters affecting gaseous emissions and in particular, a very detailed simulation is required on a daily basis or, even better, on an hourly basis, of the changes in soil water content through the soil profile.

Chapter 3 describes how we found that emission peaks of N_2O generally occurred after the application of fertilizer and soil tillage and lasting up to 6 days. After that time the emission rate fell and fluctuated close to 0. The major emission occurred in free drainage conditions after fertilization, ranging from 80 to 95% of total emissions. In water table conditions, emission just after the fertilization ranged in general from 74 to 84% of the total. As a consequence, in water table conditions small fluxes also occurred during the growth of maize following the application of top-dressed urea. Annual N_2O-N emissions as percentage of N input ranged between 0.8 to 0.13% . The value only reached 1.2% in free drainage condition in 2011. Our values, in particular for WT conditions, are lower than the IPCC standard of 1%. Groundwater stimulated plant growth and an accumulation of N_2O in water with a residence time that cannot be defined.

CO_2 emissions were higher in WT condition than in FD, and this is probably due to a bacterial denitrification process that used organic matter as energy source. Anyway heterotrophic respiration simulated using the DAYCENT model seems not very different between FD and WT conditions. So the greater CO_2 emission in WT can also be in part connected with higher root respiration due to major biomass production. Soil appears to be a weak sink of atmospheric methane in both FD and WT conditions. The interaction between chemical, physical and biological factors in soil generated a very complex set of reactions, with fluxes varying in space and time.

The analysis of N_2O fluxes is an interesting way to closely approximate the N cycle in agroecosystems and to implement the action program laid down by the European Nitrates Directive. Considering the derogation of fertilization for NVZs in Italy, the limit of 250+118 kg N ha^{-1} y^{-1} seems applicable, provided that an optimal water supply is used, to maximize maize yield. The optimum water management can be ensured by the presence of shallow groundwater or by a calibrated irrigation. Groundwater can mitigate nitrates pollution because it influences the return of N leached in the root zone, by upward water movement. At the same time greenhouse gas emissions and potential global warming effects seem to be negligible.

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