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Coordinatore Prof. Giacomo Pietramellara

Greenhouse gasses emissions and crop performances through an energy and nitrogen mass balance approach

Settore Scientifico Disciplinare AGR 02

Dottorando / PhD student

Dott. Leonardo Verdi

Tutore / Supervisor

Prof. Simone Orlandini

Co-Tutore / Co-Supervisor

Dott.ssa Anna Dalla Marta

Co-Tutore / Co-Supervisor

Dr. Peter J. Kuikman

Coordinatore

Prof. Giacomo Pietramellara

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GREENHOUSE GASSES EMISSIONS AND CROP PERFORMANCES THROUGH AN ENERGY AND NITROGEN MASS BALANCE APPROACH

Abstract

In the last decades, human population growth and shifts in food preferences required an increase of crop productivity. This was mainly possible thanks to an intensification of agricultural activities based on the use of cheap and high performing fossil energy sources. However, the concurrence of many factors, among which the awareness of the non-renewability of fossil resources and the knowledge of their detrimental impacts on the environment, led to a rapid and continuous increase of prices.

Indeed, more and more attention has been focused on the development of innovative solutions for the production of “green” energy sources able to substitute fossil fuels, with the double effect of preserving natural resources and reducing the environmental impacts of productive activities.

In this context, the use of renewable energy in agriculture plays a key role for the abatement of greenhouse gas (GHGs) emissions. In fact, it is well known that beside the fuel used for machinery, the main energy-intense activity of agriculture is the use of synthetic fertilizers that account for about 10% of global GHGs emissions. This is due both to the high energy requirement involved in their production processes and to their mineral composition. In this research, different fertilization methods were evaluated through an energy and nitrogen mass balance approach for the assessment of their sustainability in terms of greenhouse gasses emissions and crop performances. In particular, the experiment was carried out on bare soil with different levels of organic matter, and on soil cultivated with maize for silage (*Zea mays L.*, var. Ronaldinio) and barley (*Hordeum vulgare L.*, var.

Meseta). In all cases the fertilization methods compared were liquid fraction of digestate from pig slurries, compost from organic fraction of municipal solid waste, and urea. Experiments were organized in tanks (one cubic meter of volume) that allow the control of all input and output factors of the system. GHGs emissions monitoring was performed through a system of closed static chambers and a portable gas analyzer for a direct measuring in field, while soil and crop sample analysis were used for the assessment of crop yields, nitrogen (N) mass balance and energy balance on the different systems. Results on bare soil demonstrated that soil organic matter positively affects GHGs emissions. Moreover, results suggested that compost represent an effective alternative for GHGs reduction to mineral fertilizers. In particular, carbon dioxide (CO_2) and ammonia (NH_3) emissions were lower on compost, meanwhile, methane (CH_4) and nitrous oxide (N_2O) emissions were similar between compost and urea. However, CH_4 emissions from digestate and compost showed a different trend compared to the other treatments and GHGs emissions were higher in correspondence of the lower soil organic matter content. The experiment on maize was carried on for evaluating N emissions losses from different fertilizers (digestate and urea). In this sense, digestate can be considered an alternative to mineral fertilizers as cumulative N emissions were 23.73% lower than those from urea. This was mainly due to the high NH_3 emissions reduction potential of digestate. In particular, digestate NH_3 emissions decreased of about 66.32% despite an increase of 22.63% of N_2O emissions, compared to urea. Similar yields and N uptake were measured in both treatments, which confirmed the role of digestate as replacing fertilizer. Finally, N mass and energy balances were assessed on maize for silage and barley treated with different fertilizers. N mass balance suggested that crop residues management plays a key role on N dynamics of the system. On barley, straw harvest cause a negative N surplus. Contrarily, straw incorporation into the soil provided positive N surplus and maintenance of soil fertility. N mass balance on maize highlights the inefficiency of both fertilization methods in providing a positive N surplus. This is due to the fact that silage maize

plant is completely harvested and a low amount of residues remains available for soil incorporation. However, energy balance and energy use efficiency evaluation showed that digestate can be an alternative to mineral fertilizers. In particular, digestate, as a biogas by-product, requires a lower amount of energy during production process than urea. Despite the higher energy consumption during transport and spreading, digestate still represent a valuable alternative to mineral fertilizers. Moreover, yields analysis on barley showed that digestate was able to induce higher crop production than urea, with a consequent higher energy production and higher energy use efficiency.

Keywords: carbon dioxide; methane; nitrous oxide; ammonia; digestate; compost; maize; barley; bare soil; static closed chambers; agriculture; sustainability

Author's address: Leonardo Verdi, Deparment of Agrifood Production and Environmental Sciences (DISPAA), Piazzale delle Cascine 18, 50144, Firenze, Italy

E-mail: leonardo.verdi@unifi.it

Riassunto

La crescita della popolazione mondiale e il mutamento delle preferenze alimentari degli ultimi anni hanno richiesto un rapido aumento della produttività agricola. Questo incremento produttivo è stato possibile grazie all'intensificazione dell'attività agricola basata sull'uso di fonti di energia fossili caratterizzate da bassi prezzi ed elevati rendimenti. Tuttavia, numerosi fattori, tra cui la cognizione della limitatezza ed il dannoso impatto sull'ambiente delle risorse fossili, ne hanno causato un rapido e continuo aumento dei prezzi. In questo senso, sempre maggiore attenzione è stata posta allo sviluppo di soluzioni innovative per la produzione di fonti energetiche rinnovabili capaci di sostituire i combustibili fossili, con il duplice effetto di preservare le risorse naturali e ridurre gli impatti ambientali dei vari processi produttivi. In questo senso, l'uso di fonti energetiche rinnovabili in agricoltura ricopre un ruolo fondamentale sulla riduzione delle emissioni di gas ad effetto serra (GHGs). È ampiamente accertato come, oltre ai consumi di carburante per i macchinari agricoli, il principale fattore di consumo energetico in agricoltura sia rappresentato dalla produzione e dall'utilizzo di fertilizzanti di sintesi che sono responsabili di circa il 10% delle emissioni globali antropiche di GHGs. Questo è principalmente dovuto agli elevati consumi energetici in fase di produzione dei fertilizzanti di sintesi, oltre che alla loro composizione minerale. In questa sperimentazione sono state valutate differenti strategie di fertilizzazione tramite l'analisi del bilancio di energia e di massa dell'azoto, al fine di definirne il livello di sostenibilità in termini di emissioni di GHGs e di rese colturali. In particolare, sono state svolte sperimentazioni su suolo nudo, a differenti livelli di sostanza organica, e su suolo coltivato con mais (*Zea mays L.*, var. Ronaldinio) ed orzo (*Hordeum vulgare L.*, var. Meseta). I fertilizzanti utilizzati nelle sperimentazioni sono stati: la frazione liquida del digestato da reflui suini, il compost da frazione organica di rifiuti solidi urbani ed urea. Le sperimentazioni sono state svolte in contenitori di un metro cubo di volume, che hanno permesso il controllo di tutti i fattori di input ed output del sistema. Il monitoraggio delle emissioni di GHGs è

stato svolto tramite l'utilizzo di un sistema di camere statiche chiuse e di un analizzatore di gas portatile che ha permesso la lettura diretta delle misure in campo. Inoltre, sono state svolte delle analisi sul suolo e sulle colture che hanno permesso la valutazione del bilancio di massa dell'azoto, del bilancio di energia e delle rese colturali dei vari sistemi. L'analisi dei risultati ha dimostrato come la sostanza organica influenzi positivamente le emissioni di GHGs da suolo nudo. Inoltre, i risultati mostrano come il compost rappresenti una valida alternativa all'utilizzo dei fertilizzanti minerali per l'abbattimento delle emissioni di GHGs. In particolare, è stato osservato come le emissioni di anidride carbonica (CO_2) e di ammoniaca (NH_3) erano inferiori nelle prove fertilizzate con il compost, mentre le emissioni di metano (CH_4) e protossido di azoto (N_2O) erano sostanzialmente simili fra compost ed urea. Tuttavia le emissioni di CH_4 da digestato e compost hanno mostrato un comportamento differente rispetto agli altri fertilizzanti dato che sono stati osservati valori di emissioni di GHGs superiori in corrispondenza del più basso livello di sostanza organica del suolo. La sperimentazione sul mais è stata svolta per valutare le perdite di N per volatilizzazione in seguito all'applicazione di differenti fertilizzanti (digestato ed urea). In questo senso, il digestato può essere considerato una valida alternativa ai fertilizzanti minerali in considerazione del fatto che ha determinato una riduzione delle emissioni totali di N pari al 23.73% rispetto all'urea. Questo è principalmente dovuto al fatto che il digestato ha determinato notevoli riduzioni di emissioni di NH_3. In particolare, le emissioni di NH_3 da digestato sono risultate inferiori del 66.32% a fronte di un incremento del 22.63% di quelle di N_2O, rispetto all'urea. Le analisi delle rese colturali e delle asportazioni di N non hanno fornito differenze sostanziali tra i due trattamenti, confermando il ruolo del digestato come fertilizzante. Infine, è stato svolto uno studio sul bilancio di massa dell'azoto e sul bilancio di energia su mais da insilato e orzo, concimati con differenti fertilizzanti. Il bilancio di massa di N ha dimostrato come la gestione dei residui colturali ricopre un ruolo fondamentale sulle dinamiche dell'N all'interno dei sistemi agricoli. L'asportazione della paglia in

seguito alla raccolta dell'orzo determina un surplus negativo di N all'interno del sistema. Al contrario, l'interramento della paglia fornisce surplus di N positivo contribuendo a preservare la fertilità del suolo. Il bilancio di N sul mais ha dimostrato l'inefficienza di entrambi i trattamenti a fornire surplus di N positivi. Questo è dovuto al fatto che la produzione di mais da insilato richiede l'asportazione dell'intera pianta riducendo notevolmente i quantitativi di residui colturali disponibili per l'interramento. Tuttavia, l'analisi del bilancio di energia e della sua efficienza d'uso ha dimostrato come il digestato rappresenti una valida alternativa ai fertilizzanti minerali. In particolare, il digestato, che è a tutti gli effetti un sottoprodotto del biogas, evidenzia limitate richieste energetiche in fase di produzione rispetto all'urea. Nonostante i maggiori consumi energetici in fase di trasporto e distribuzione, il digestato rappresenta comunque una valida alternativa ai fertilizzanti minerali. Inoltre, l'analisi delle rese colturali dell'orzo ha mostrato come il digestato è in grado di fornire produzioni maggiori rispetto all'urea, con una maggiore produzione di energia e maggiore efficienza d'uso energetico.

Parole chiave: anidride carbonica; metano; protossido di azoto; ammoniaca; digestato; compost; mais; orzo; suolo nudo; camere statiche chiuse; agricultura; sostenibilità

Recapiti autore: Leonardo Verdi, Dipartimento di Science delle Produzioni Agroalimentari e dell'Ambiente (DISPAA), Piazzale delle Cascine 18, 50144, Firenze, Italia
E-mail: leonardo.verdi@unifi.it

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Chapter 1. General Introduction

Agricultural productivity was intensely increased during the last decades as effect of world human population growth and especially the food demand. Since 1960 to 2005 world's human population increased by 111% meanwhile, crop production by 162%. This increase was due to expanding agricultural area (extensification) and by improving of crop yields (intensification). However, croplands grew around 27% but crop yields increased by 135% (Burney et al. 2010; Tilman et al. 2011). The increase of agricultural activities requires more and more energy at relative low cost to satisfy the growing food demand. Due to the easy availability of fossil energy source, their high net energy potential and the relative cheap prices, a great increase in their use occurred during the last century. Agriculture, in this regard, mainly took advantage from fossil energy source from chemical (fertilizers, herbicides/pesticides) and mechanical (machinery) inputs. However, fossil energy sources intensive use had led to a fast reduction of them coupled to an increase of environmental impacts from modern agriculture mainly related to greenhouse gasses (GHGs) emissions (Zegada-Lizarazu, 2010). The direct impact of exponential increase of GHGs as carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4) emissions is essentially related to their contribution on the Global Warming of Earth's surface that improved global surface temperature by 0.85°C in the last 130 years (IPCC, 2014). Global Warming Potential (GWP) is a factor that express the impact that each gas have on the absorption of energy into the atmosphere, the slowing on the rate of energy that escape from Earth to the space and their permanence into the atmosphere. The first two factor are also known as "radiative efficiency" and the last as "lifetime", both contribute on the definition of GWP of each gas. GWP was developed to make a comparison between different gasses. It measure how much energy is absorbed by 1 ton of gas, over a given period (usually 100 years), compared to 1 ton of CO_2. The larger the GWP, the more that a given gas warms the Earth compared to CO_2 over that time period (EPA, 2017). In this regard, on a lifetime of 100 years CH_4 show a GWP of 25 and N_2O show a greater GWP reaching 298 value compared to CO_2. Nowadays, following the directives of Paris Agreement (2015) the reduction of GHGs emissions and mitigation of Global Warming are fundamental issues at global level adopted by several countries. Agriculture, in this way, may contribute on the reduction of human activities impacts on the environment adopting more sustainable management strategies to minimize inputs and preserve fertility of soils. In this regard, agriculture potential on Global Warming mitigation is represented by GHGs reduction. More than GHGs, ammonia (NH_3) represent one of the main emitted gas by agriculture contributing of 50% of global emissions and 90% of European emissions (Carozzi et al., 2013) with indirect impacts on the environment. NH_3 is one of the main responsible factors of acidifying and eutrophying because the deposition of NH_3-derived compounds causes acidification of soil (Asman et al., 1998) and natural water resources (Sutton and Fowler, 2002). Moreover, NH_3 is considered an indirect GHGs because is a precursor of N_2O

(Moiser, 2001). Data observed by Eurostat (2015) reports a reduction of 147.3 million tons of CO_2 equivalent from agriculture in EU 28 between 1990 and 2012. This is the result of more efficient farming practices, the reduced application of nitrogen-based fertilizers (Nitrates Directive), as well as better forms of manure management during last decades. However, in 2012 agricultural GHGs emissions from EU 28 were still at significant level with 470.6 million tons of CO_2 equivalent that represent roughly 10% of global GHGs emissions.

GHGs emissions from EU 28 agriculture mainly came from three sources as soils, enteric fermentation and manure management; the other two sources that affect global GHGs agricultural emission, as burning of agricultural residues and rice cultivation, have only minor contribute in Europe (Eurostat, 2015). Several strategies are proposed and adopted for the reduction of agricultural impacts and, due to its high weight on the environment, fertilizer sector is one of the main studied. An alternative of mineral fertilizers that require high-energy input during the production process (Zegada-Lizarazu, 2010) is the re-use of organic by-product both from rural and urban systems. In this regard, the combination of renewable energy production and the reuse of by-product represent an effective strategy to reduce impact related to energy production and the maintaining of soil fertility. Alternative energy sources are widely proposed to replace fossil one. However, little attention is given on their low net energy potential (Zegada-Lizarazu, 2010). In this regard, a holistic point of view is fundamental to provide a complete overview of the situation considering further factors other the energy production. In particular, the raw material involved on energy production, impact of gross energy production and the opportunity to re-use by-product in agricultural systems have to be considered. Biogas production, as other renewable energy sources, is a strategy that satisfy the most part of previous assumptions. Technological innovation, propose progressively options to produce biogas with agricultural waste or with no-food crops that are not competitive to food-crops (Schievano et al., 2009). Moreover, the use of biogas by-product, digestate, as fertilizer is an interesting strategy to maintain soil fertility and reduce of emissions related to mineral fertilizers production (Clemens et al., 2006; Möller and Stinner, 2009; Walsh et al., 2012; Comparetti et al., 2013).

Digestate is liquid-solid by-product from anaerobic fermentation of organic wastes by a wide range of microorganisms. Generally, at the end of anaerobic digestion phase, digestate is separated in a solid and liquid fraction. The first is characterized by a low water (< 75%) and high dry matter (>20%) content, and accounts for the main part of organic matter remained after fraction separation. Liquid fraction is the main part of digestate (about 85-90% of total volume) with a small dry matter content (1.5-8%) and a high concentration of available elements for plants, such as ammonium (NH_4^+) that can reach 70-90% of total nitrogen (N). It contains considerable amounts of nutrients as N mainly represented by NH_4^+, phosphorus (P), and potassium (K). Due to the rapidity of absorption by plants, it is similar to mineral fertilizers since N, P and K are easily available for plants. Digestate also contains organic matter, which has a positive effect on physic-chemical properties of soils. Several authors (Chiew et al., 2015; Alburquerque et al., 2012) affirm that digestate use as replacing fertilizer increases macro- and microelements content in soil and plants. Nevertheless, a mismanagement of digestate can lead to an increase of emissions of NH_3 and N_2O, as well as of the others GHGs such as carbon dioxide (CO_2) and methane (CH_4). In particular, the amount, spreading method and climate (temperatures and rainfall) are the main factors that affect digestate efficiency use from the plants and its impact on the environment. According to Pezzolla et al. (2012), an overabundance application of digestate to agricultural soils without considering strategies that minimize emission losses can represent a point of weakness of the system. Hence, the definition of correct management strategies represents one of the best opportunities for GHGs mitigation. Several authors observed as the reduction of air contact to digestate with injection or incorporation represent an efficient strategy to minimize GHGs and NH_3 emissions (Sommer & Hutchings, 2001; Wulf et al., 2002; Walsh et al., 2012; Severin et al., 2015). Hence, anaerobic digestion, more than renewable energy source, represent a strategy for a sustainable re-use of organic wastes from different systems. Moreover, in accordance to Riva et al. (2016) and Orzi et al. (2016) anaerobic fermentation contribute to the abatement of odors and the reduction of pathogens content in slurries from the stables.

As previous affirmed, one of the point of weakness of the use of digestate as replacing fertilizer is represented by GHGs and NH_3 emissions related to its use. Nowadays the monitoring of emissions produced by the spreading of digestate into the soil is performed through a wide range of technologies (Oertel et al., 2016): (i) chamber systems. This method is widely applicable in field and require a box cylinder that have to be placed into the soil. Chambers have to be coupled with an emission measuring system with different sensors (NDIR, FID) for different gas and cumulative fluxes are calculated considering gas concentration, environmental factors (temperature, wind speed, rainfall, soil moisture) and dimensions of chamber. Particular attention have to be referred on dimensioning of the chamber, due to different molecular weight and inhomogeneous distribution of gas into the chamber, a too high chamber might promote errors during monitoring of gas fluxes. Chambers system can be divided in open and closed chambers, with closed chambers being subdivided into static and dynamic ones. Open chambers allow to measure dynamic flux of gas that pass through two draw, is analysed and return to atmosphere. Closed static chambers are the cheapest and easiest ones. They need an operator that close the chamber, make the measurement and remove the chamber at the end of measuring time. Dynamics chambers perform automatically the measurements analysing the gas accumulated into the chamber and pumped back outside after measuring. All of methodologies require a collar system, generally in PVC in order to prevent gas losses from the chamber to the atmosphere. To minimize collar influence on soil structure and root system it should be embedded into the soil at a few centimeters and immediately after sowing. The use of opaque materials for chamber construction is suggestable to insulate chamber to temperature and solar radiation. The use of reflective materials in the external part of the chamber is recommended for a better insulation; (ii) micrometeorological methods. Eddy covariance and 3-D ultrasonic anemometer coupled to a gas analyser attached to a tower of at least a 2-m height are the most common adopted techniques in this way. Measurements can run continuously but the limited accuracy, especially when turbulent mix occur near grown, significantly reduce their application; (iii) laboratory experiments. These methods are helpful when the influence of single parameters on soil emissions have to be assessed and is possible to obtain a complete overview of the system. However, undisturbed soil samples are needed for this methods and this factor is a point of weakness of the system. Lysimeters are an additional option to study soil emissions under controlled conditions in the field. Emissions can be analysed jointly with the analysis of nutrient leaching (Velty et al., 2007; Zhou et al., 2013); (iv) spaceborne measurements. Remote sensing from satellite may provide information about GHGs emissions. However, at the moment uncertainties are still present related to technical limitations of the sensors and to derived data products. However, independently to the measuring strategy, emission monitoring is fundamental for the evaluation of the sustainability of an agricultural system and to define the point of weakness of the system.

A more in depth approach for the evaluation of the sustainability of the agricultural systems is represented by the application of specific indicator that allow to comprehend the entire dynamics of the systems. Nutrient budgets consider all the input / output factors of a specific system in a defined limited time. In this way, it is possible to evaluate the entire cycle of the studied nutrient. Nevertheless, N cycle evaluation is extremely challenging and the obtaining of a complete N mass balance require to consider a great number of factors. This also considering the great complexity of N cycle and the difficulties in directly measuring of various factors as denitrification (Davidson and Seitzinger, 2006). Thus, generally a simple input/output field budget is used for the evaluation of nutrient management in the agricultural systems (Oenema et al., 2003). However, the weight of each input factors varies according to the considered agricultural system. N input factor list is commonly composed by: (i) N provided by fertilizers and manures. Generally it represent the main factor due to the great amount of N spread to increase yields; (ii) N content of soil that is strictly related to the rotation and the previous crop; (iii) N fixation by leguminous crops. As previous is strictly related to crop rotation; (iv) N from wet and dry deposition. Deposition is related to the latitude and longitude of the examined area, more than the surrounding environment. N deposition is commonly estimated by models (e.g. EMEP/MSC-W). Regarding to the output factor, it is possible to summarize them in: (i) N uptake by marketable part of the crop. This factor have to be divided to the residual part of plants if them come back to the field through mechanical incorporation (e.g. straw or roots); (ii) N leaching. This is one of the main pollution factor related to N that dissolve in groundwater and reach the aquifer with high risk of acidification and eutrophication; (iii) N volatilization. As previous, N_2O and NH_3 represent the main volatile N compound from agricultural systems;(iv) N biological fixation; (v) N soil erosion and surface runoff. This factor is dependant to a wide range of aspects (soil texture, rainfall, the slope of fields etc.) and it cause soil and organic matter losses, loss of inherent fertility, and water contamination (Napoli et al., 2017). In conclusion, nutrient mass balance represent a useful tools to improve the quantitative understanding of nutrient cycle and to define the point of strength and weakness of the systems. Moreover, this indicators may be applied to provide information about nutrients dynamics and environmental policies managements (Oenema et al., 2003).

Nevertheless, N management is not the only one aspect that affect agricultural impacts on the environment. Indeed, the entire agricultural management strategy, from the used raw materials to the marketable products, play a key role on environmental pressure of agriculture. Several indicators are proposed to evaluate the environmental pressure of agriculture, however, energy balance represent a tool for an holistic point of view of agricultural system that consider all the factors involved. Zegada-Lizarazu et al. (2010), affirm that energy balance is a commonly methodology for the assessment and comparison of agricultural systems performances. Taking into account the energy flows (input and output) and giving the energy value of each factors is possible to evaluate the energy consumed and produced, hence to understand how the system works and how each factor affect the system. Comparing different energy sources it’s possible to obtain information about GHGs impact of different agricultural systems. During the second half of the last century agriculture activity was characterized by a great use of fossil energy sources as chemical (fertilizers, pesticides, herbicides) and mechanical (machinery) inputs (Zegada-Lizarazuet al., 2010). Hence, new agricultural policies that include more sustainable strategies as the use of renewable energy sources or low-impact fertilizers have been adopted and encouraged. Nowadays, is important to consider there is an absence of universally accepted method for energy balance assessment and also the value of each factors are matter of debate (Zegada-Lizarazu et al., 2010). However, the input/output ratio assessment is generally accepted and applied as general method for energy balance evaluation. The main input factors on the energy balance budget are represent by: (i) energy to produce applied input. This factor consider the energy consumed during the production process of materials as seeds, fertilizers, pesticides, herbicides etc.; (ii) energy for machinery manufacture. The energy consumed during the construction of machinery, included the obtaining and processing of raw materials, is included inside this factor as the lifetime of each machinery; (iii) fuel energy. Fuels consumption for the processing of agricultural works, fuel efficiency of each machinery and the type of fuels are considered for the calculation of this factor. Based on the type of agricultural system, more factors can play a relevant role on the energy balance evaluation. In particular, in dry or semi-dry climate area energy consumed for the irrigation represent a relevant factor able to strongly affect the entire energy balance. In developing countries, indeed, the energy consumed by human labor may be an important cost. However, in general in the highly mechanized countries these two factors may represent negligible factors that is not able to affect in a significant way the total energy balance. Output factors are represented by the quantitative and qualitative evaluation of marketable part of crops that are sold on market. In accordance to Hülsbergen et al. 2000; Romanelli & Milan, 2005; Brehmer et al., 2008; Zegada-Lizarazu et al., 2010 the more detailed way for output factors estimation into the energy balance is the elemental characterization of yields (crude protein, crude fiber, ether extract, N-free extract and ash). The energy produced by an agricultural system is strictly connected to the type of crop and its quality. Through the analysis of elemental characterization of yields and the energy content of each component is possible to obtain the gross energy production. There are several available database for the calculation of energy production for different crops without analyse yields. However, due to the wide variability of agricultural systems, the adoption of measured data are suggestable. Literature review (Zegada-Lizarazu et al., 2010) affirm that comparing energy balance assessed using measured data and data-base data, results from each methodology are not too different. However, the use of literature data is adoptable for a general overview but, for a better understanding of each specific system, the use of data from laboratory analysis is suggested. Results from an energy balance evaluation provide information about the energy fluxes and the energy use efficiency of the system. However, it’s possible to achieve data also about the impact that different agricultural systems have from an environmental point of view. In particular, the consumption of energy require a certain amount of GHGs emissions that increase using fossil energy sources and low efficiency agricultural management strategies. The critical adoption of low GHGs emission energy source and management strategies that allow to reduce input (e.g. reuse of by-product) and maintain soil fertility are suggestable for a sustainable management of agricultural systems.

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Chapter 2. Objectives

The aim of this work was the assessment of different agricultural strategies and their role on the reduction of environmental impacts from agriculture. In particular, specific attention was related to greenhouse gasses emissions from fertilization and the opportunity to reduce them through the application of sustainable management strategies. The evaluation of the role of digestate as replacing mineral fertilizer has been identified as one of the strategies that can allow a reducing of agricultural impact on the environment. In this work the emissions from digestate spreading on bare soil and cultivated soil, with a summer crop (*Zea mays L.*) and a winter crop (*Hordeum vulgare L.*), were evaluated. For cultivated soils, an evaluation of the potential in yield production was evaluated to define the potential of digestate as replacing fertilizers. Finally, a N mass balance and energy balance were assessed for the understanding of digestate use performances from an environmental point of view and its role on the mitigation of agriculture impacts.

Chapter 3. List of papers

Following papers are produced from experimental field of Department of Agrifood Production and Environmental Sciences (DISPAA), University of Florence.

Experimentations were assessed in the period between October 2014 and September 2017, also in collaboration with Wageningen University and Research (WUR).

First Paper:

Greenhouse gas and ammonia emissions from soil: the effect of organic matter and fertilization method. *L. Verdi, M. Mancini, M. Ljubojevic, S. Orlandini, A. Dalla Marta*. Under submission to Italian Journal of Agronomy

Second Paper:

Does the use of digestate to replace mineral fertilizers have less emissions of N_2O and NH_3? *L. Verdi, P. J. Kuikman, S. Orlandini, M. Mancini, M. Napoli, A. Dalla Marta*. Under submission to Agricultural and Forest Meteorology

Third Paper:

Impacts of different fertilization strategies on energy and nitrogen use efficiencies of maize and barley cultivation *L. Verdi, W. de Vries, M. Mancini, S. Orlandini, A. Dalla Marta*

Chapter 3.1 First paper

Greenhouse gas and ammonia emissions from soil: the effect of organic matter and fertilization method

L. Verdi[a*], M. Mancini[a], M. Ljubojevic[b], S. Orlandini[a], A. Dalla Marta[a]

[a]Department of Agrifood Production and Environmental Sciences (DISPAA), University of Florence, Piazzale delle Cascine 18 – 50144 Firenze, Italy
[b]Department for Fruit Growing, Viticulture, Horticulture and Landscape Architecture, Faculty of Agriculture, Trg Dositeja Obradovića 8, Novi Sad, Serbia

*Corresponding author: leonardo.verdi@unifi.it
+39.055.275.5741
+39.3477656423

Abstract

Gasses emission into the atmosphere derived from the use of fertilizers is a serious issue for the sustainability of agricultural systems, also considering that the growing global demand for food requires an increasingly productive agriculture. Emissions dynamics are very variable and are determined by many factors and their reciprocal interactions. Among driving factors, soil type (mineral, organic and microbiological composition), fertilization method, climate, and the cropping system. In the present experiment, the combined effect of soil organic matter and fertilization method on the emissions of greenhouse gasses and ammonia was investigated. In particular, liquid fraction of digestate from pig slurries, compost from organic fraction of municipal solid wastes, and urea were applied on bare soil with two levels of organic matter (1,3% and 4,3%). Emissions were directly monitored through the use of a static chamber system and a portable gas analyser. Results show that soil organic matter as well as the composition of the fertilizers affect greenhouse gasses emissions. Emissions of methane produced by digestate and compost were higher in correspondence of lower organic matter content (15.07 - 12.65 kg CH_4 C/ha/26 days and 9.62 – 8.38 kg CH_4 C/ha/26 days for digestate and compost respectively), contrary to what was observed for urea. For all fertilizers, carbon dioxide and nitrous oxide emissions were higher in correspondence of high organic matter level. The obtained results show that the content of organic matter in soils plays a key role on the emissions of GHGs, generally enhancing the levels of gas emissions.

Keywords: agriculture, carbon, compost, digestate nitrogen, static chamber

1. Introduction

Several strategies were developed and proposed in the last decades to reduce the environmental impacts from agriculture. In particular, fertilization is one of the most studied practices due to its detrimental effects on the environment, such as groundwater pollution, eutrophication and greenhouse gasses (GHGs) emissions. An alternative to chemical fertilizers is the use of recycled organic waste materials, as slurries and manure, characterized by low environmental impact and satisfactory crop yields (Alburquerque et a., 2012; Walsh et al., 2012).

In addition to slurry, organic wastes from household and food processing industries are increasingly used as fertilizers in agricultural systems. Of increasing relevance in this context is the combined anaerobic fermentation of organic wastes with slurry in biogas (Wulf et al., 2002) and compost plants. On the other hand, the inputs of organic matter (OM) into the soil play a key role in the productivity of arable land by providing nutrients, through decomposition, and by maintaining soil fertility through OM turnover (Palm et al., 2001). Researchers (Miller and Wali, 1995) have increasingly emphasized the benefits of a balanced fertilization, by using organic amendment (e.g., crop residues, manure, compost) for enhancing or maintaining soil OM level in soils. However, the efficient and appropriate use of organic fertilizers coming from organic wastes requires more in-depth knowledge both in terms of quality and fertilizer value (Rowell et al., 2001) aiming to support crop production and protect the environment while saving the soil resource (Mamo et al., 1999). Moreover, a deep knowledge is also required for managing organic fertilizers.

Digestate management plays an important role on the real GHGs impact reduction. Due to its composition, rich in easily available nitrogen for plants and organic carbon, digestate can increase emissions of GHG such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and ammonia (NH_3). An excessive application of digestate to agricultural soil without taking into account strategy to minimize losses through emissions can represent a point of weakness of the system.

Within this context, the definition of appropriate management techniques represents one of the best opportunities for GHG mitigation (Pezzolla et al., 2012). Bouwman et al. (2010) suggested that the recycling of N in animal manure, human excreta and compost to reduce inorganic fertilizer decreased N_2O emissions from agricultural ecosystems. In a Spanish typic xerofluent with a sandy loam texture, Lopez-Fernandez et al. (2007) demonstrated that organic fertilizers reduced N_2O emissions by 74% (compost) to 27% (pig slurry) in comparison with urea. This reduction was due to the consumption of N_2O by denitrifying bacteria during the irrigation period, which was driven by the addition of labile organic C (Vallejo et al., 2006). In contrast, Hayakawa et al. (2009) observed that adding poultry manure and especially pelleted poultry manure to an andisol increased N_2O emissions by approximately 2 and 7 times, respectively, but reduced NO emissions by 49% and 56%, respectively, compared with inorganic fertilizer. These inconsistent results and reports in the literature may reflect differences in manure composition, C:N ratios, incorporation method and depth into the soil, and the effect of their interaction with soil properties, such as soil organic carbon (SOC) and texture, on N_2O production under different environmental, soil moisture and temperature conditions (Huang et al., 2004; Van Groenigen et al., 2004; Stehfest & Bouwman, 2006).

For a better understanding of the emission dynamics from agricultural lands, particular attention has to be addressed to the system in absence of crops, which of course affect N and C cycles through uptake and assimilation processes. As affirmed by several authors, nowadays available data are scarce and referred only to specific areas and crops (Le Mer & Roger 2001; Oertel et al. 2016). Authors affirm there is an inadequate data availability in Mediterranean area, and bare soil in general, with a strong bias towards temperate climate regions. Le Mer & Roger (2001) observed that available data on CH_4 emissions are mainly focused on wetlands that represent the main source of CH_4 from soils. In this way, upland CH_4 emission dynamics are unexplored. Despite the fact that N_2O emissions are widely explored, contradictory results are observed regarding the effect of soil organic matter on N_2O emissions. Velthof et al. (2003) observed that an addiction of organic carbon on arable soils encourage N_2O emissions through denitrification. However, authors recommend further investigation on the interaction between manure/fertilizer composition and soil characteristic and utilization. Instead, Oertel et al. (2016) reported a different behavior and described how the addiction of OM into the arable soils decrease N_2O emissions. Considering the often discordant results, but also the great variability of soil and fertilizer compositions, and the influence of local climate factors (temperature, rainfall, wind, etc.), GHGs emissions dynamics need more in-depth specific investigations. Moreover, as affirmed by Minoli et al. (2016), also NH_3 emission dynamics need a deep-in-knowledge assessment mainly due, especially for Italy, to inconsistencies in the measurement methods.

The aim of this research is to study the emissions (GHGs and NH_3) of liquid fraction of digestate and compost after incorporation into bare soil, and to investigate the effect of organic matter in emission dynamics.

2. Materials and methods

Experimental filed was located at the ITAGR (Istituto Tecnico Agrario Statale) via delle Cascine, Firenze (43°47’02.3”N 11°13’13.4”E), Italy. The experiment was conducted on 9.5 litres pots, placed in the open field and exposed to the environmental conditions. Each pot was filled with 8 kg of a silty-clay soil (24% clay, 31% silt and 45% sand) from experimental fields of CREA-ABP located in Scarperia, Firenze (43°58’56” N, 11°20’53” E). The experiment was set on bare soil in order to investigate the effect of the different fertilizers excluding any possible interference of the crop.

A layer of 30 cm of soil was taken from the experimental site including top and sub soil layer, and mixed before filling the pots in order to homogenise it. Soil sample was analysed in laboratory for elemental characterization (Tab. 1). Experimental design consisted of two contrasting levels of soil organic matter - OM1 1,3% (that was the original OM content in the soil) and OM2 4,3% - with four treatments. Enrichment of OM into the soil was performed by adding 320 gr of commercial manure (GoldenAgro Ecolife). Treatments included two types of organic fertilizers (liquid fraction of digestate from pig slurries and compost from organic fraction of municipal solid waste) as well as one organo - mineral fertilizer (urea), with the non-fertilized pots as control treatment. The digestate was produced by 'Fattoria di Corte Marchesi De' Frescobaldi' farm (Florence, Italy, 43°58'29" N, 11°23'21" E), while the compost derived from composting plant of 'Alia Servizi Ambientali Spa' (Florence, Italy, 43°55'580.95'' N, 11°21'00.09'' E). The amount of each fertiliser varied according to its N content (Tab. 2) and was calculated on the base of a pre-defined quantity of 150 kg N/ha. Fertilizers were incorporated into the soil by manually replacing injection, for digestate and mechanical incorporation for compost and urea. Immediately after fertilization the anchors were placed into the soil and the chambers were connected. Emission measurements were conducted three times in the first week after fertilization (0h, 48h and 96h) and once a week in the following three weeks in order to investigate the emission trend (26 days of measuring period). Experimental pots remained opened between successive measurements to enable volatilization, as these conditions would be the closest to the ones occurring naturally. CO_2, CH_4, N_2O and NH_3 emission rates were measured by means of a static chambers system (Parkin and Ventera, 2010), equipped by two thermocouples per chamber, and a portable gas analyser XCGM 400 (Madur) that use nondispersive infrared sensors (NDIR) technology for CO_2, CH_4 and N_2O analysis and electrochemical technology for NH_3. Samplings were performed by holding the sensor inside the chamber for 1 minute recording gas accumulation at time 0 (immediately after chamber closing) and at time 1 (after 1 hour).

Gas fluxes were calculated starting from the gas concentration into the chamber, chamber dimensions (area and volume), closing time and molecular weight of each gas. As temperature had a similar trend inside each chamber (data not shown), the whole experiment was assumed to be at standard temperature and pressure (STP) conditions and the molar volume of the air is assumed as 22,4 liters.

An automatic meteorological station placed 20 meters far from the experimental field continuously monitored air temperature, atmospheric pressure and precipitations (Fig. 1). However, during the experiment any precipitation were observed. In the second and the third day after fertilization, two hours prior to the gas measurements 10 mm of water were added to each pot for accelerating the beginning of the emissions process.

The observed data were statistically processed using STATISTICA 13.0 (StatSoft, DELL, USA). In order to test the differences of measured (calculated) parameters between the samples Duncan's multiple range tests with the confidence of $p \leq 0.05$ was performed.

Table 1 – Soil characterization

		Unit	Soil
Texture	silt	%	31
	clay	%	24
	sand	%	45
N total		%	0.14
P total		%	0.07
K total		%	0.23
pH			8.06

Table 2 – Elemental characterization of tested fertilizers

	Urea	Digestate	Compost
N content Total %	46	0.319	2.27
$N\text{-}NH_4^+$ %	-	0.284	0.15

N-NO_3^- %	-	0.035	0.0013
P content Total %	-	1.84	0.34
K content Total %	-	6.94	0.97

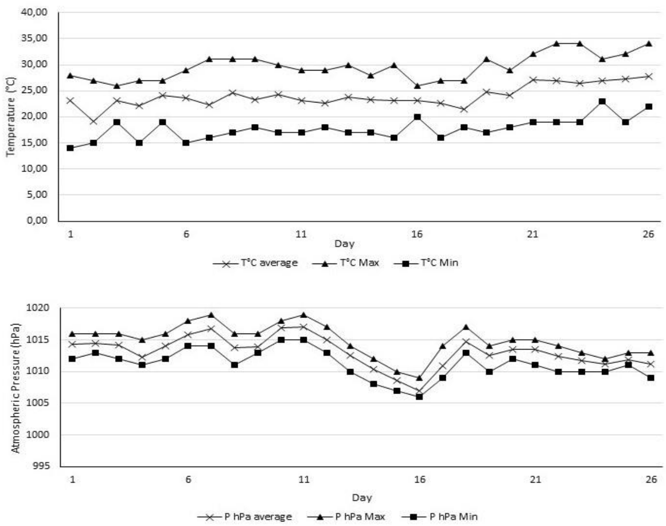

Figure 1 – Temperature (°C) and Atmospheric Pressure trend (hPa)

3. Results

Table 3 - Cumulative emission fluxes on 26-days measuring period for each fertilizer and OM rate

	kg CO_2-C ha^{-1}		kg CH_4-C ha^{-1}		kg N_2O-N ha^{-1}		kg NH_3-N ha^{-1}	
	OM1	**OM2**	**OM1**	**OM2**	**OM1**	**OM2**	**OM1**	**OM2**
No-fertilizer	$38,50^{g}$	$129,19^{e}$	8.06^{d}	8.06^{d}	0.04^{c}	0.31^{bc}	0.00^{e}	0.06^{de}
Digestate	$604,12^{b}$	$679,75^{a}$	15.07^{a}	12.65^{b}	0.96^{b}	7.65^{a}	0.61^{b}	0.59^{b}

Urea	$67,04^{f}$	$206,67^{c}$	8.95^{d}	11.17^{bc}	0.09^{c}	0.29^{bc}	0.09^{de}	1.15^{a}
Compost	$29,22^{h}$	$169,35^{d}$	9.62^{cd}	8.38^{d}	0.03^{c}	0.38^{bc}	0.26^{cde}	0.54^{bc}

* - values marked with the same letter do not differ significantly according to Duncan's multiple range tests

3.1 Carbon Dioxide

Carbon dioxide is produced in soil as result of decomposition of organic material by microorganisms and root respiration. Observed data from 26-measurement days show that CO_2 was the most emitted gas from all fertilizers, although a high variability in the amount of emissions was observed (Tab. 3).

The highest rate of CO_2 emissions was produced by digestate. In particular, emissions were more than ten times higher than the other treatments in OM1 (604.12 Kg CO_2-C/ha/26 days), and more than three-to-four times than other treatments in OM2 (679.75 Kg CO_2-C/ha/26 days). As for digestate, emissions from other fertilizers were positively affected by the increase of OM into the soil. In all treatments, emissions were higher compared to control with the exception of compost in OM1 that produced less CO_2 than control. Emissions trend show the high variability in all treatments (Fig. 2). Urea and compost (and control) emit 16 – 30 Kg CO_2-C/ha/day and, except for urea in OM2, emissions increased until the third – fourth day and then decreased following a similar trend. In OM2, urea produced the highest amount of emissions in the first days and then emissions decrease regularly. Digestate showed the highest daily emission of 327 (OM2) and 259 (OM1) of Kg CO_2-C/ha/day, however, as observed by Maucieri et al. 2016, it immediately decreased after fertilizer spreading in both OM levels. At the end of the measurement period, CO_2 emissions were still observed. However, it is widely known that CO_2 emissions occur all year long with fluctuating trend.

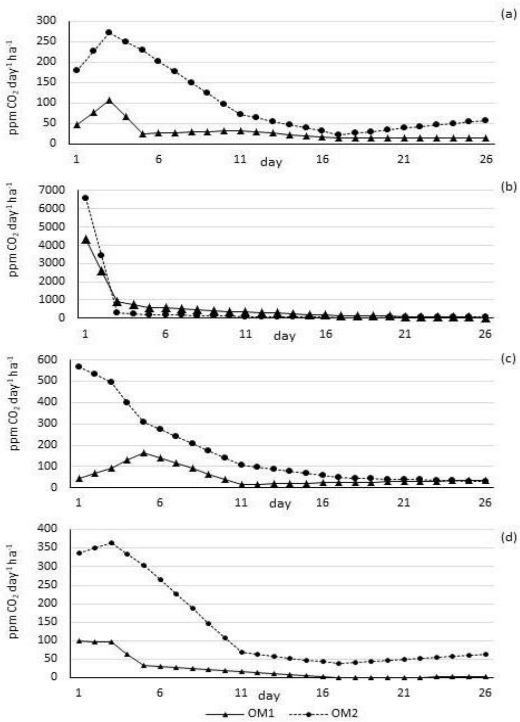

Figure 2 – CO_2 emission trend (parts per million) on 26-day measuring period for control (a), digestate (b), urea (c) and compost (d) at OM1 (▲) and OM2 (●)

3.2 Methane

In contrast with previous results, digestate and compost produced more CH_4 emissions in correspondence of the lower OM content of soil. If for digestate differences are significant in compost they are negligible (Tab. 3). CH_4 emissions from urea were still higher in OM2 than in OM1. For all fertilizers, emissions decreased immediately after spreading; at day 5, an increase in the emissions from urea in OM2 and from digestate, and compost, in OM1 were observed (Fig. 3). As for CO_2, at the end of measurement period CH_4 emissions were still occurring (Flessa et al., 1998).

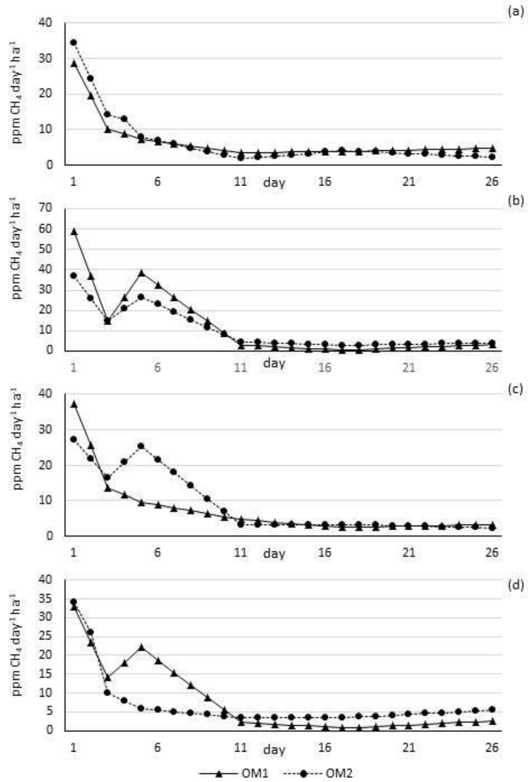

Figure 3 – CH_4 emission trend (parts per million) on 26-day measuring period for control (a), digestate (b), urea (c) and compost (d) at OM1 (▲) and OM2 (●)

3.3 Nitrous oxide

In accordance to CO_2 fluxes, N_2O emissions were positively correlated to OM content of soil. However, significant differences were observed only for digestate that produced roughly seven times more N_2O in OM2 than in OM1 (Tab. 3). As confirmed by Wulf et al. (2002), N_2O was produced a few days after fertilizers spreading in correspondence of irrigation. In all treatments, a peak of emissions in the third day was observed; then emissions decreased regularly until complete depletion in the first week, for urea, and in the second week for digestate and compost (Fig. 4).

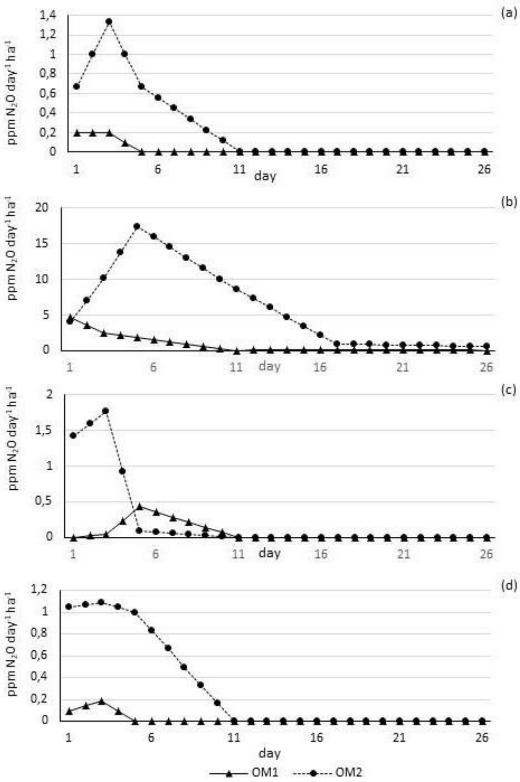

Figure 4 – N_2O emission trend (parts per million) on 26-day measuring period for control (a), digestate (b), urea (c) and compost (d) at OM1 (▲) and OM2 (●)

3.4 Ammonia

Any influence of OM on NH_3 emissions from bare soil was observed (Tab. 3). All fertilizers produced a similar amount of NH_3 emissions. The only exception was represented by urea in OM2 that showed a higher production of NH_3. However, the main part of the emissions were produced by urea in OM2 during the first day after fertilization. For all fertilizers emissions occurred only during the first week, with complete emission depletion on the fifth day. Urea in OM2 and compost in both OM levels had the highest emission rate on the first day and a regular decrease in the following days. Urea on OM2 and digestate in both OM levels had a peak of emissions on the third day with a consequentially complete depletion on the fifth day, as other treatments. (Fig. 5)

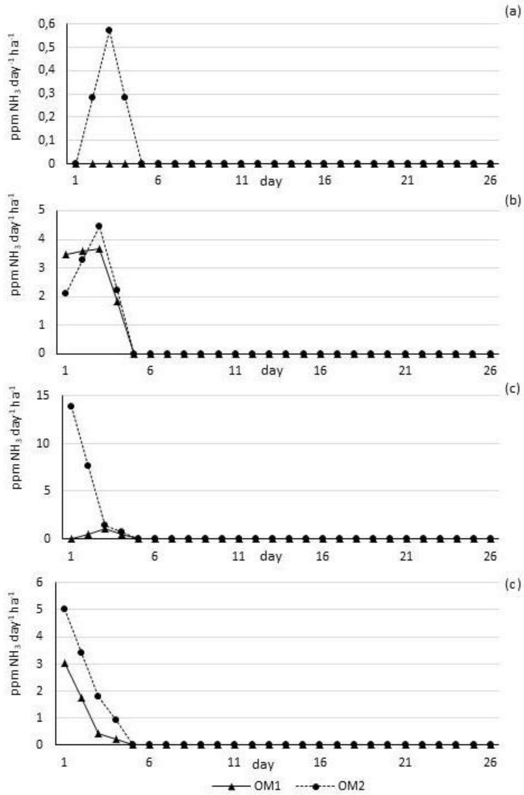

Figure 5 – NH_3 emission trend (parts per million) on 26-day measuring period for control (a), digestate (b), urea (c) and compost (d) at OM1 (▲) and OM2 (●)

4. Discussion

In this experiment, GHGs and NH_3 emissions were measured in absence of crop, so that no C and N removal from plant uptake occured and soil nutrients content was assumed constant during the measurement period. This may have caused higher emission compared to open field conditions. However, especially for compost, fertilizers are often applied several weeks before crop sowing. In this period, between soil fertilization and the presence of the crop in the field, C and N mineralization and nitrification, with consequent emissions, may occur. In this context, a careful evaluation of most appropriate agronomic strategies to mitigate the risk of emissions is needed.

4.1 Carbon Dioxide emissions

Results show that an enrichment in soil OM content positively affects CO_2 emissions. As affirmed by several authors, CO_2 emissions dynamics from agricultural soil are affected by a wide range of factors (Six et al., 1999; La Scala et al., 2000; Paustian et al., 2000). In this respect, OM represents one of the main ones due to its influence on soil respiration. A higher soil OM is able to increased soil respiration and consequently CO_2 emissions, as observed in the experiment. Digestate produced higher emissions compared to urea. In particular, this is due to digestate composition, rich in water, which allows the infiltration into the soil. An enrichment of water content of soil combined to the mild air temperatures occurred probably encouraged the proliferation of soil microorganisms and consequentially soil respiration. However, differences in digestate emissions behavior between OM1 and OM2 were not statistically significant.

Urea produced a higher level of CO_2 compared to compost, and the role of OM was evident. In fact, cumulative CO_2 emissions in OM2 were more than 3 times higher than in OM1. This effect was also enhanced by irrigation that ensured hydrolysis of urea with a consequent production of CO_2.

4.2 Methane emissions

Results obtained from manures (digestate and compost) showed that CH_4 had an opposite trend compared the other gasses monitored. In particular, digestate and compost produced more emissions in OM1 than in OM2. As described by Le Mer and Roger (2001) CH_4 emissions from soil are again affected by many factors and a negative correlation between CH_4 emissions and C/N ratio was reported. An enrichment of available C stimulates the population soil microorganisms that use a great part of C for their metabolism with a reduction of available C for methane production (Bernet et al., 2000; Norberg et al., 2016). In this respect, the composition of manure used to obtain the two levels of OM, which represent the 25% of total organic C, partially explain the behavior of CH_4 emissions from organic fertilizers. In addition, the composition of organic fertilizers, rich in total organic C (34.5% and 25.6% for digestate and compost, respectively), may have reduced CH_4 emissions. Moreover, an addiction of liquid (digestate) and fine milled (compost) fertilizers to the soil may had created compaction and so anaerobic conditions that modified the balance between denitrifying and methanogenic bacteria, in favor of the first ones (Saggar et al., 2004; Bunemann et al., 2006). In the case of urea, that does not contain organic C, the positive correlation between OM level and CH_4 emissions was confirmed.

4.3 Nitrous Oxide emissions

Results obtained demonstrated that N_2O emissions are positively affected by the OM content of soil. For all tested fertilizers N_2O emissions in OM2 were higher than in OM1. In particular, digestate produced the highest emissions and this was due to its high water content that determines anaerobic conditions with consequent higher N_2O losses compared to the other fertilizers (Wulf et al., 2002). Moreover, the higher amount of organic C available into the soil in OM2 probably encouraged denitrification activity and N degradation (Velthof et al. 2003). The high rate of readily available N compounds of digestate and the mild temperature occurred during the experiment (average of 28.4°) enhanced N losses in the first two weeks after fertilization. On the other hand, compost emitted a N_2O rate comparable with the control, probably due to its low water content. This result, in fact, is in accordance with the findings of Dalal et al. (2010), confirming that the application of compost can be considered an efficient strategy to reduce N_2O emissions. Moreover, differences on emissions between the two fertilizers are in accordance to Aguilera et al. (2013) that found more N_2O emissions from liquid than solid organic fertilizers. Finally, concerning urea, its low water content reduces the risk of anaerobic conditions at soil level and the consequent N_2O emissions that are comparable with those of compost. Further, during hydrolysis the majority of N contained in urea is transformed into ammonia with a reduction of N available for denitrification.

4.4 Ammonia emissions

NH_3 emissions were nearly five times higher in OM2 than OM1 treated with urea. Again, this confirms that higher organic C content into the soil modifies the C/N ratio and encourages bacteria activity with greater degradation of N and NH_3 losses. Moreover, the irrigation may have encouraged the hydrolysis process on urea with great NH_3 losses.

Digestate and compost are an exception: digestate showed the highest rate of NH_3 emissions. However, no differences between emissions in the two OM levels were observed. As on digestate, also on compost no significant differences were observed between the OM levels. This suggests that OM content of soil does not affect NH_3 volatilization dynamics.

5. Conclusion

This experiment was performed to evaluate the effect of soil organic matter on gas emissions that occur from soil after fertilization with different fertilizers. The study focused on bare soil, allowing to investigate the emissions dynamics without the influence of the plants. A wide range of factors affects emission dynamics into the soil, however, organic matter is one of them and plays a key role, generally enhancing the levels of gas emissions. Nevertheless, results about CH_4 emissions of digestate and compost, which were higher in OM1 than in OM2, require further investigation with particular attention to the role of microorganisms population.

A comparison between urea and compost emissions highlighted a mitigation potential for CO_2 and NH_3 from the use of compost. At the same time, the use of compost produced the same amount of N_2O and CH_4 than urea. From these observations, it is possible to affirm that the use of compost on bare soil is an alternative to mineral fertilizers for mitigating GHGs emissions. However, further experiments are needed to exclude the influence of pot and investigate the effect of OM on GHGs and NH_3 emissions in open field.

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Chapter 3.2 Second paper

Does the use of digestate to replace mineral fertilizers have less emissions of N_2O and NH_3?

L. Verdi[a*], P. J. Kuikman[b], S. Orlandini[a], M. Mancini[a], M. Napoli[a], A. Dalla Marta[a]

[a]Department of Agrifood Production and Environmental Sciences (DISPAA), University of Florence, Piazzale delle Cascine 18 – 50144 Firenze, Italy
[b]Alterra, Wageningen University and Research Centre, P.O. Box 47, 6700 AA Wageningen, The Netherlands

*Corresponding author: leonardo.verdi@unifi.it
+39.055.275.5741
+39.3477656423

Abstract

Digestate is considered a sustainable opportunity to reduce environmental impact from fertilization, due to high content of nitrogen easily available for plants and for the low impact of its production. We tested liquid fraction of digestate from anaerobic digestion of pig slurries and urea, to assess the emissions of nitrous oxide and ammonia from soil on silage maize (*Zea mays L.)*. Nitrogen rate was the same for both treatments (150 kg/ha) spread replacing common methods. Emissions measurements were performed immediately after fertilization using static chamber method and a portable gas analyser. Measurements were performed daily during the first week, and twice per week until no emissions from the soil were observed. Cumulative nitrogen emissions show that digestate can be an efficient method to reduce total nitrogen losses (2.867 kg N/ha/25 days and 3.759 kg N/ha/25 days for digestate and urea respectively). However, the two fertilizers emitted different kind of gases: compared to urea, digestate emitted the 22,63% of nitrous oxide more, on the other hand urea emitted 66,32% of ammonia more than digestate. Crop yield obtained under the two fertilization methods did not significantly differ (13.63 t DM/ha and 13.24 t DM/ha for digestate and urea, respectively) ($\alpha > 0.5$).

Keywords

Maize, biogas, nitrogen, greenhouse gasses, static chambers

1. Introduction

Intensification of the human activities requires an ever increasing energy demand. Until a few years ago this request was fulfilled by fossil fuel sources with consequentially harmful impacts on the environment. Approximately 88% of world energy is at present produced by non-renewable primary sources (mainly reserves of fossil sources as oil, coal and natural gas), destined to run out in the next years (IEA 2015). As a result, anthropogenic greenhouse gases (GHG) emissions and human-induced global warming are fundamentally linked to future energy production. Projections of how the global energy system will develop over the next century are cornerstones in the assessment of future climate change caused by mankind (Hook and Tang, 2013). For the above reasons, after the Kyoto Protocol in 1997, the Parliament and European Council issued Directive 2009/28/EC on the promotion of energy from renewable sources, with the intention of ensuring an average of 20% of final energy consumption from renewable sources by 2020; a target recently raised to 27% for 2030 (European Commission 2014). Nowadays, European renewable energy sector is growing, pushed by the above ground legislation, and Italy is faithfully following European trend. In this regard, one of the most widespread renewable energy source in Italy is biogas from anaerobic digestion of livestock slurries. This is strictly connected to the great number of livestock farms: about 138000 cattle farms (6 million cattle) and about 145000 pigs farms (8.7 million pigs) (Ministero della Salute Italiano 2014). That, combined with anaerobic digestion technology, represents the opportunity to produce energy from renewable sources, while obtaining additional income for farmers. As a result, Italy is experiencing a proliferation of biogas energy plants. In a few years, the number of plants has grown from 10 to nearly 900 (Fabbri et al. 2013), and many more plants are under construction (Carrosio 2013). According to a recent census (Fabbri et al. 2013), at present there are 1054 biogas plants operating in Italy (Carrosio 2013) making Italy the second producer in Europe after Germany.

On the other hands, Italian agriculture accounts for 68% of total nitrous oxide (N_2O) and 94% of total ammonia (NH_3) emissions (ISPRA 2008) mainly due to nitrogen (N) fertilization practices, and intense livestock systems (Ranucci et al. 2011; Schils et al. 2008; van Groenigen et al. 2004; Del Grosso et al. 2006; Moisier et al. 1986).

Indeed Bowman et al. (1997) and van Groenigen et al. (2005) affirm that N_2O emissions from animal production systems are likely to rise further in the future. Approximately 60% of the global N_2O emissions and N excretions from animal production systems originates from cattle. Also manure and fertilizers affect N_2O

emissions in several ways. The type of N (NO_3^-, NH_4^+, and organic N) affects N_2O production during nitrification and denitrification; the presence of easily available C, stimulates denitrification activity and O_2 consumption in the soil; and fertilizers and manure affect biological, chemical and physical soil processes because of changes in pH and the addition of other compounds (salt, water) (Velthof et al. 2003). Furthermore, temperature and water content can strongly affect emission from the soil. In livestock systems, the main source of N emissions is the urine and dung excreted by the animals, either in pastures or in confinements (stables, barns, sheds, corrals) (Oenema 2005). Moreover, volatilization of NH_3 from animal wastes can occur in stables and after application to soil from the microbial breakdown on N-organic compounds to ammonium (NH_4^+) (Minoli et al. 2015). NH_3 can cause eutrophication of N limited aquatic and terrestrial ecosystems, contributing to the increased acidification of sensitive ecosystems (Schulze et al. 1989) and indirectly to N_2O emissions by increasing the N-cycling in natural ecosystems. Manure and N-fertilizers cover the major part (approximately 56%) of the global emissions from the planetary surface, estimated to be 65.4 Tg N yr^{-1} for 2008 (Sutton et al. 2013).

Biogas production is an excellent way of using organic waste for energy generation, followed by the recycling of the digested substratum (digestate) as fertiliser (Comparetti et al. 2013) with lowest emissions than urine or dung. Digestate can be defined as liquid-solid from anaerobic decomposition of animal and plant waste by microorganisms. It contains considerable amounts of nutrients as nitrogen, phosphorus, and potassium. In terms of rapidity of action (absorption by plants) it is similar to mineral fertilizers since N, P and K are easily available for plants. Digestate also contains organic matter, which has a positive effect on physicochemical properties of soils. Chiew et al. (2015) and Alburquerque et al. (2012) say that the use of digestate as a fertilizer increases the content of macro- and microelements in the soil and plants. Nevertheless, a mismanagement of digestate can lead to an increase of emissions of NH_3 and N_2O, as well as of the others GHGs such as carbon dioxide (CO_2) and methane (CH_4).

The main aim of this research was to investigate the potential of digestate as fertilizer and to assess its mitigation potential on N_2O and NH_3 emissions from an irrigated silage maize system, compared to conventional mineral fertilization.

2. Materials and methods

2.1 Site description and experimental setup

The experimental field is located at the ITAGR (Istituto Tecnico Agrario Statale), Firenze (43° 47’ 07”N 11° 13’ 11” E), Central Italy. Twelve tanks (volume 1 m^3 each) creating a controlled environment by preventing any interactions with surroundings conditions were utilized. Tanks were positioned into 2 rows on a supporting structure built with reinforced concrete and soil. Under tanks, a plastic mulching film was positioned to stop weeds growth and to facilitate field operations (sampling, crop management, maintenance of trials, etc.). Tanks were filled with soil from experimental fields of CREA-ABP located in Scarperia, Firenze (43°58’56” N, 11°20’53” E). A silty-clay soil was used and soil layers (90-60; 60-30; 30-0 cm of depth) were kept divided to reproduce soil profile into the tanks. Water supply was provided by a drip irrigation system (Fig. 1).

13 seeds of silage maize (Var. Ronaldinho) were sowed on (17th June 2016) to reproduce a field plant density of 12.000 plant/ha. Three fertilization treatments were tested: liquid fraction of digestate from pig slurries, urea and no fertilization (control). For each treatment, four replicates (tanks) were carried out in a randomized block design. In particular, digestate was provided by the plant of “Marchesi de’ Frescobaldi, Tenuta di Corte” farm (43°58’29” N, 11°23’21” E). Anaerobic digester treats a mixture of pig slurry and agricultural by-product as straw, olive cake and small part of sorghum silage. Digestion temperature is 35 °C with a hydraulic residence time of almost 30 days. For the experiment, only the

liquid fraction was used and the separation was manually done replacing the industrial process.

The dose of each fertilizer was determined in order to supply 150 kg/ha of N. To this aim, nutrient content (N, P, K) and N type (NH_4^+ and NO_3^-) of digestate were laboratory determined (Tab.1). Total N was obtained by Kjeldahl analysis, while the method described in “Regione Piemonte Metodi di analisi del Compost Met. C.7.3 and EPA 9056A 2007” was used for NH_4^+ and NO_3^- determination. Finally, P and K amounts were measured with ICP Iris Intrepid II XSP analyzer.

Table 1 Elementary composition of digestate

	Unit	Liquid fraction of
N (Kj)	g/Kg	3.14
NH_4^+	g/Kg	2.81
NO_3^-	g/kg	0.081
P	g/Kg	18.44
K	g/Kg	69.46

According to Vallejo at al. 2005, digestate was manually applied by replacing slurry injection method, while urea was conventionally spread. In both treatments, fertilization was split into two doses: 18 days (F1) and 36 (F2) days after sowing.

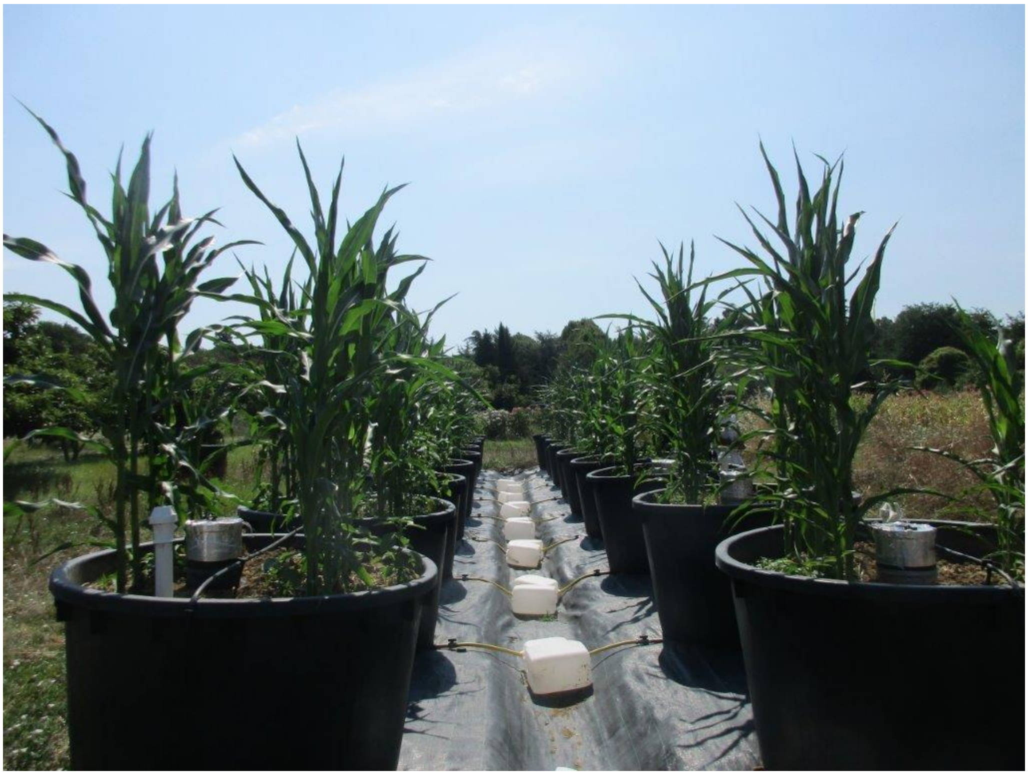

Fig. 1 Maize experimental field with static chamber placed into the soil for emission monitoring

2.2 Emissions measurement and flux calculation

For the monitoring gas emissions twelve static chambers (one per tank) were constructed as described by Parkin and Venterea (2010). Chambers are composed of two parts: the lid of the chamber and the anchor system to be inserted into the soil as support.

The anchor system is made by a PVC cylinder 15 cm high and with a diameter of 20 cm. Two thirds of the cylinder was inserted in the soil so that 5 cm remained above the surface. To reduce roots disturbance, it was positioned between plant rows immediately after sowing.

Another PVC cylinder with the same diameter (20 cm) and 25 cm high, and a PVC stopper sealed with silicon glue, were used for the lid of the chamber. A reflective Mylar tape was placed on the side and on the top of the chamber to shield solar radiation. A hole (13.2 mm of diameter) was drilled on the top of the chamber approximately halfway between the center of the circle and the outside edge. A butyl rubber septum of 20 mm of diameter was fixed inside the hole for allowing sampling operations.

A 7 cm wide strip of tire tube was used for ensuring a hermetic connection between the lid and the anchor system. The strip was putted around the bottom of the lid and fixed with tape and silicone glue. The part exceeding from the chamber (about a half of the strip height) was kept folded back onto the PVC ring and then folded down to connect the lid to the anchor during sampling.

Gas samplings were performed by means of a portable gas analyzer Madur Sensonic X-CGGM 400. The gas analyzer uses Nondispersive Infrared technology (NDIR) for NH_3 detection and electrochemical technology for N_2O. Samplings were performed once a day during the first week after fertilization and twice a week during the second by holding the sensor inside the chamber for 1 minute immediately after chamber closing and then repeated at 1 hour intervals.

Gas fluxes were calculated starting from the gas concentration into the chamber, chamber dimensions (area and volume), closing time and molecular weight of each gas. As temperature had a similar trend inside each chamber (data not shown), the whole experiment was assumed to be at standard temperature and pressure (STP) conditions and the molar volume of the air is assumed as 22,4 liters.

2. 3 Crop and soil analysis

The assessment of the fertilization potential of each fertilization treatment was determined through the analysis of crop performances. In particular, at harvest the number of plants per tank, biomass fresh and dry weight, dry matter content, and crop N uptake were determined.

Fresh weight was measured on the total biomass harvested from each tank, for which also dry weight was measured after drying in hoven for 48 hours at 80 °C. Dry matter analysis was carried on in accordance with AOAC 2010 procedure. Nitrogen content was determined using a CHN analyzer (Flash EA 1112-

ThermoFisher). In order to better determine the crop N uptake process, N content of soil was also determined for each tank before sowing and after harvest.

2.2.4 Statistical analysis

The statistical analysis was performed using IBM SPSS Statistics 20. Dependence of N_2O and NH_3 emission fluxes on fertilizer treatment was investigated by means of the Analysis of Variance (ANOVA) model and Kruskal – Wallis test, when it wasn't possible to satisfy all of the assumption of ANOVA analysis. ANOVA was used for all the results analysis except for the N_2O – N emissions, for which the K –W test was used.

3. Results

3.1 Emissions

The first fertilization produced lower N_2O emissions (11.96 ppm/11 days and 1.93 ppm/11 day for digestate and urea respectively) compared to the second (32.39 ppm/11 days and 32.37 ppm/11 days for digestate and urea respectively). This difference was probably due to rainfall, that was absent between F1 and F2, while a 7,4 mm event happened seven days after F2.

Further, in F1 emissions from the two fertilizers had a different trend, while the trends were similar in F2 with two peaks measured during the first week (Fig. 2A, 2B, 3A, 3B). On the other hand, in F1 N_2O emissions were higher from digestate.

Concerning cumulative data, they are referred to a 25-days period as we consider 11 days of measurements after each fertilization (22 days in total) plus the period left between the end of F1 measurements and the second fertilization (3 days) (experiment started in 4th of July 2016 and finished on 28th of July 2016).

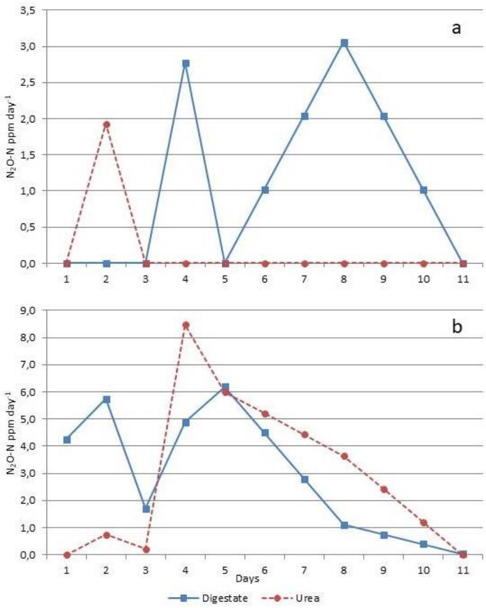

Fig. 2 Trend of N_2O-N emissions following first (a) and second (b) fertilization

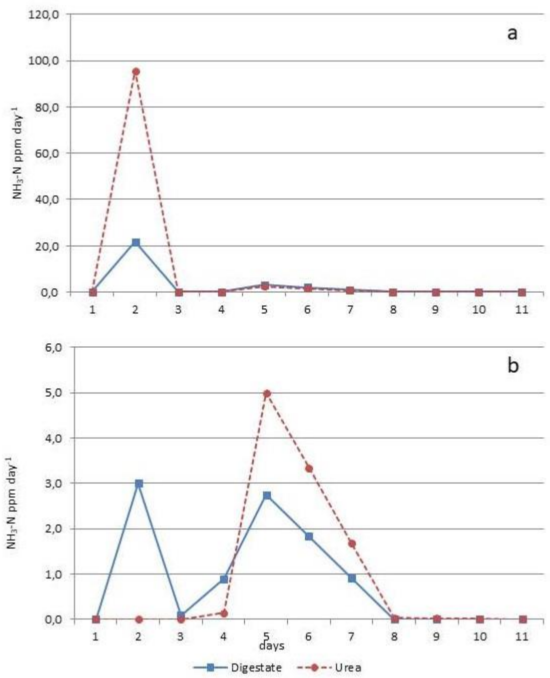

Fig. 3 Trend of NH_3-N emissions following first (a) and second (b) fertilization

Considering the cumulative values, we found that in F1 digestate produced more emissions than urea (44.35 ppm/25 days and 34.30 ppm/25 days respectively), while no significant differences were observed between the two fertilizers in F2 (Table 2).

Although emissions of NH_3 had similar trends for both fertilizations (F1 and F2) and both fertilizers (Fig. 3A, 3B), in F1 they were higher from urea.

More in general, the highest levels of emissions were observed in F1 (27.75 ppm/11 days and 100.27 ppm/11 days for digestate and urea respectively) than in F2 (9.488 ppm/11 days and 10.25 ppm/11 days for digestate and urea respectively). Results showed that, in total, urea lost more N than digestate (81.59 ppm/25 days and 144.82 ppm/25 days for digestate and ammonia, respectively) due to NH_3 emissions. This is probably due to the spreading method as, differently from digestate, urea is not incorporated into the soil so volatilization is higher.

Table 2 Nitrous oxide and ammonia emission data (ppm) for each fertilization and cumulative for digestate and urea

		Digestate (ppm)	Urea (ppm)	Control	ANOVA
N-N_2O	1 fert	11.96a	1.93b	1.54b	**
	2 fert	32.39a	32.37a	6.96b	NS
	Total	44.35a	34.30b	8.50c	**
N-NH_3	1 fert	27.75a	100.27b	8.09c	**
	2 fert	9.488a	10.25a	7.97a	NS
	Total	37.24a	110.51b	16.05c	**
Total		81.59a	144.82b	24.56c	**

NS: not significant

* Significant at probability level P<0.05

** Significant at probability level P<0.01

3.2 Fluxes

Starting from emissions, fluxes of NH_3 and N_2O were also calculated as kg of N losses in F1 and F2 and as cumulative data (Tab. 3). Those data are useful to understand the N losses from the system regardless the kind of gas.

Table 3 Flux calculation results

	First fertilization kg N/11 days		Second fertilization kg N/11 days		Cumulative losses kg N/25 days		
Treatment	N_2O-N	NH_3-N	N_2O-N	NH_3-N	N_2O-N	NH_3-N	N
Digestate	0.584	0.523	1.581	0.179	2.165	0.702	2.867
Urea	0.094	1.891	1.580	0.193	1.675	2.084	3.759
Control	0.075	0.153	0.340	0.165	0.415	0.318	0.733

Through the ratio between the emissions from digestate and urea (%) it's possible to assess the relative reduction of N emissions obtainable from the use of each fertilizer, and used by farmers to quantify the impact reduction due to the adoption of best fertilization practices.

Based on our results, the net reduction of total N emissions produced by the use of digestate compared to urea is 23.73%. More specifically, the digestate allowed to reduce $N–NH_3$ emissions by 66.32% while increasing $N–N_2O$ emissions by 22.63%, showing that the main factor affecting the impacts of tested fertilizers is volatilization of NH_3.

3.4 Crop performances and soil N

The analysis of yields showed that there is not significant difference between the two treatments ($\alpha = 0.05$), confirming the fertilization effect of digestate compare to conventional fertilizers (Tab.6). This is also confirmed by N uptake of plants that was not significantly different between the two treatments at a significance level α is = 0.05 (Table 5).

Table 4 Yield production of maize

	Fresh weight (kg/tank)	DM (%)	DM (kg/tank)	Yield DM (kg/ha)	Yield DM (t/ha)
Digestate	2.18	64.56	1.36	13627.40	13.63 (5.387)
Urea	2.16	60.37	1.32	13244.05	13.24 (5.525)
Control	1.85	49.46	0.91	9115.33	9.11 (1.915)

Standard Deviations of data are in brackets

Table 5 Average N uptake for each treatments

	N uptake %	N uptake kg/ha	Yield DM kg/ha
Digestate	1.44	129.79 (0.066)	13627.40
Urea	1.53	131.30 (0.076)	13244.05
Control	1.41	128.52 (0.056)	9115.33

Standard Deviations of data are in brackets

Results on soil analysis showed that tanks fertilized with digestate had a lower content of N than those treated with urea (Table 6). Therefore, we can assume that N emissions from digestate last longer than expected. This is probably due to denitrification losses, which occurred between measuring period and harvest. Finally, based on the analysis on water, N was not lost through leaching.

Table 6 Total N content of the soil before and after maize cultivation

Sample	N %
Soil Beginning	0.157
Soil + digestate	0.125
Soil + urea	0.167
Soil + control	0.161

4. Discussion

In the present study we hypothesized that the use of digestate to replace mineral fertilizers in crop production could serve as an effective strategy to mitigate N_2O and NH_3 emissions from agricultural soils while maintaining satisfactory crop yields. We observed that emissions of N_2O were higher in digestate than in urea treatment. According to Pezzolla et al. (2012) and van Groenigen et al. (2004), we hypothesized that this trend is likely due to the higher content of organic carbon (C) in digestate (Moller and Muller 2012).

These authors affirm that the presence of organic C increases the soil denitrification effect with greater potential for the production of N_2O as well. It is not likely that digestate after processing would contain high concentrations of decomposable organic C yet the microbial biomass resulting from transformation in the digester might very well be the source of energy for denitrification with N_2O emissions following application of the digestate to the soils.

In order to decrease this effect the use of specific inhibitors can be considered. As observed by Wolf et al. (2014), the use of nitrification inhibitors directly mixed with digestate before spreading can be an effective strategy to reduce those kind of emissions. Authors affirmed that the mixing those inhibitors with digestate results in a reduction of N_2O emissions by 37 to 62% dependently of the length of the examined period.

Moreover, Pezzolla et al. (2012) and Vallejo et al. (2005) suggest that N_2O emissions are also affected by soil moisture. This seems to be confirmed by our observations, as the absence of rainfall in F1 in addition to higher temperature, hampered N_2O emissions from urea, which is a solid fertilizer. On the other hand, this was not true for digestate, for which N_2O emissions were anyway produced because of its own water content. So that, the physical state of the two fertilizers (solid for urea and liquid for digestate) determined a difference in the level of N_2O emissions. At the same time, the absence of rainfall in F1 lead to higher NH_3 volatilization from urea, which is left on soil surface after spreading.

On the other hand, the cumulated rainfall in F2 reduced the wetting effect of digestate on the soil and N_2O emissions were similar between treatments. Moreover, precipitation enhanced the dissolution of urea that moved into the soil with a consequent decrease of NH_3 emissions.

In addition, as confirmed by Bouwman (1996), we found that the fertilizer distribution method plays a key role in gas emissions. Urea is distributed on the soil surface where the water from irrigation and rain quickly evaporates and the interaction between water and fertilizers is negligible. On the contrary, digestate is incorporated into the top layer of soil where moisture is higher and retained for longer. Such results showed that the more the fertiliser is incorporated into the soil, the less NH_3 is lost through volatilization, in agreement with observations and with Riva et al. (2016). So that, the relation between the depth of fertilizer spreading and the amount of NH_3 emission found by Wulf et al. (2002) seems to be confirmed.

Then, we can finally affirm that the higher N_2O emissions observed from soil treated with digestate are due to the combined effect of its organic C content, soil moisture and distribution method.

By the way, we anticipate that N losses from urea are mainly due to the volatilization of NH_3. Tanks fertilized with urea, in fact, emitted about three times more NH_3 compared to those fertilized with digestate.

However, soil analysis showed that tanks treated with digestate contained less N than those treated with urea, probably due to a higher denitrification activity.

Regarding the fertilization potential, no significant differences in crop N uptake and in crop yield were observed at harvest under the two treatments. These results lead us to conclude that injected digestate from pig slurries can be an efficient strategy to maintain crop productivity at a standard level thus confirming our hypothesis that digestate can be an effective and sustainable substitute of mineral fertilizers.

However, it is important to consider that the nutrient content of anaerobic digestate mainly depends on the nature of the feedstock and the efficiency of the digestion process (Alburquerque 2012).

5. Conclusions

The major conclusion drawn on the basis of the present study is that the use of digestate from anaerobic digestion of pig slurries as fertilizer in crop production is an effective method to lower total emissions of N (2.867 kg N/ha/25 days and 3.759 kg N/ha/25days for digestate and urea, respectively). In particular, application of digestate instead of mineral fertilizer led to a reduction of NH_3 emission from soil. Nevertheless, N_2O emissions are higher and we hypothesize that this is due to the higher organic C content of the digestate.

In this sense further studies on the effect of nitrification inhibitors might provide useful information for reducing N_2O emissions from the use of the use of digestate as fertilizer.

Together with a better environmental performance, the measurements on crop production showed that the digestate provide yields comparable to those obtainable with urea.

However, N content in digestate is extremely low so that a large amount of product is required to satisfy the nutrient demand of silage maize. It means that several passes on the field are needed with consequent effects on GHG emissions from tractors, soil compaction and total economic cost. On the other hand, urea is a product of an industrial process that also has significant impacts in terms of gas emissions and economic costs. So that, a complete cost-benefit analysis of the entire process may be necessary to support farmers decisions.

The evaluation of total N content into the soil before sowing and after maize harvest provided information about the N losses due to denitrification. The lower total N content of tanks treated with digestate than those with urea, in fact, can be considered as N losses through denitrification. However, the lack of direct measurement could led to an underestimation of N losses from tested fertilizers.

We suggest that future experiments would focus on control on the nature of N losses i.e. the (environmental) factors that control N_2O emissions from the soil after digestate application (DM, organic C content, soil moisture, spreading methods and nitrification inhibitors), and issues connected with digestate spreading and urea production chain emissions is required to achieve the maximum level of sustainability in the digestate use.

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Chapter 3.3 Third paper

Impacts of different fertilization strategies on energy and nitrogen use efficiencies of maize and barley cultivation

L. Verdi[a*], W. de Vries[b], M. Mancini[a], S. Orlandini[a], A. Dalla Marta[a]

[a]Department of Agrifood Production and Environmental Sciences (DISPAA), University of Florence, Piazzale delle Cascine 18 – 50144 Firenze, Italy

[b]Alterra, Wageningen University and Research Centre, P.O. Box 47, 6700 AA Wageningen, The Netherlands

*Corresponding author: leonardo.verdi@unifi.it

+39.055.275.5741

+39.3477656423

Abstract

The rational use of primary energy sources and the reduction of energy consumption are fundamental for the mitigation of current trend of GHGs emissions in agriculture. In this context, crop fertilization represents one of the main impactful activities. In this work, energy and nitrogen (N) mass balances were computed for a quantitative assessment of crop input utilization and the agricultural performances of two different fertilization strategies. A comparison between liquid fraction of digestate and urea on silage maize (*Zea mays*) or ammonium nitrate on barley (*Hordeum vulgare*) was performed. Results highlights that the management of crop residues strongly affects the N dynamics. On maize for silage, where the entire plant is harvested, a N deficit; on barley two different scenarios, with and without straw incorporation into the soil after harvesting, were hypothesized and only straw incorporation provided a N surplus.

The use of digestate as fertilizer provided a higher energy utilization efficiency. This was mainly due to the low energy costs of production of the fertilizer and to the higher crop yields obtained.

Keywords: Maize; barley; nitrous oxide; ammonia; digestate; fertilizers; energy input; energy output; energy use efficiency; net energy.

1. Introduction

Since the last few decades of the twentieth century, agricultural productivity has intensely increased in response to the growth of world human population and food demand. Between 1960 and 2005 population increased by 111%, meanwhile, crop production by 162%. This increase was due to an expansion of agricultural area and to an improvement of crop yields (intensification). However, while croplands grew around 27% crop yields increased by 135% (Burney et al. 2010; Tilman et al. 2011). The increase of agricultural production was possible thanks to a growing use of cheap fossil-source inputs as fuels, chemical fertilizers, pesticides and intensive machinery (Lizarazu et al. 2010) that substitute human labor and maximize capture and conversion of solar radiation into crop biomass (Grassini & Cassman, 2012). As a result, the global economy has become progressively dependent on fossil fuels. However, nowadays the rapid depletion of fossil energy sources and their dramatic contribution on greenhouse gasses (GHGs) emissions are imposing the adoption of new strategies for agricultural management for ensuring the reduction of environmental burden. In fact, agriculture has major global environmental impacts: about one-quarter of global GHGs emissions resulting from land clearing, crop production, and fertilization, negatively affect atmosphere, freshwater, and terrestrial ecosystems (Vitousek et al. 1997; Burney et al. 2010). The rational use of primary energy sources, reduction of energy consumption and the intensive exploitation of renewable energy source are fundamental for the mitigation of current trend of GHGs emissions.

In conventional agricultural systems, N represents the main input to maximize yields. However, the uncontrolled use of N-based fertilizers and the low efficiency of application methods have led to considerable N losses through volatilization, leaching and soil erosion with consequentially detrimental ecological effects (eutrophication and decrease in biodiversity of natural lands, atmosphere, surface waters and groundwater). In this context, input/output N budget calculation is a useful tool for a quantitative understanding of N dynamics, for assessing its overall availability to the target crop species, and for determining the efficiency of utilization (Gentry et al. 2009). However, due to the wide range of factors affecting N dynamics, a complete assessment of its mass balance is extremely challenging (Davidson and Seitzinger, 2006). For this reason, a simple field budged is commonly used as a performance indicator of N management (Oenema et al., 2003). Specific measures have been taken at the European level to encourage a more sustainable agricultural production that maximize yields while minimizing environmental impacts (Gerin et al., 2008). In addition to N dynamics, the evaluation of the energy required and consumed by the systems is fundamental. The source of energy (fuels, fertilizers, pesticides, herbicides etc.) and the energy consumption of the systems determine its environmental impact. In this context, innovative strategies, such as the use of renewable energy sources and low impact fertilization techniques, provide a higher energy use efficiency and lower environmental impact than conventional fossil fuels based agriculture. In this sense, the use of N-based by-product with a low energy cost of production and high

N content represents an effective strategy to reduce impacts while maintaining high yields. Several solutions are proposed for this goal and replacing mineral fertilizers with biogas by-product, digestate, is one of the most promising (Pezzolla et al., 2012). Digestate is a liquid-solid substrate that is produced at the end of anaerobic digestion phase and is generally separated in a solid and a liquid fraction. The first is characterized by low water (< 75%) and high dry matter (>20%) content, and accounts for the main part of organic matter remained after separation. Liquid fraction is the main part of digestate (about 85-90% of total volume) with a low dry matter content (1.5-8%) and a high concentration of available elements for plants, such as ammonium (NH_4^+) that can reach 70-90% of total nitrogen (N). Moreover, digestate contains a considerable amount of micronutrients easily available for the crops (Chiew et al., 2015; Alburquerque et al., 2012) that make digestate an alternative to mineral fertilizers. Differently to mineral fertilizers, digestate, as biogas by-product, is assumed to require no energy during the production process. Understanding the future environmental impacts of crop production, and how to achieve higher yields with lower impacts, requires a quantitative assessment of crop input utilization and of how different production practices affect the environment. In this regard, energy and mass balances are useful tools for the performance evaluation of different agricultural strategies. Nonetheless, the maintenance of high-level yields should be considered while assessing the efficiency of such strategies.

In order to evaluate the opportunity to reduce crop input and improve cultivation methods, a study on energy and N mass balance of a summer crop (*Zea mays L.*) and a winter crop (*Hordeum vulgare L.*) with different fertilization strategy was carried out. In particular, the evaluation of nitrogen use efficiency (NUE) and the energy use efficiency (EUE) of crops from the digestate and mineral fertilizers application were carried on. Moreover, this work aims also to propose a methodology for energy balance assessment, also in consideration of the absence of a universally accepted standard methodology for energy balancing (Romanelli & Milan, 2005; Zegada-Lizarazu et al., 2010).

2. Materials and Methods

2.1 Experimental Approach

The experimental field was located at ITAGR (Istituto Tecnico Agrario Statale) in Firenze (43° 47' 07"N 11° 13' 11" E), Central Italy. Twelve tanks, of 1 m^3 volume each, were positioned along 2 rows on a supporting structure built with reinforced concrete and soil. On the bottom of each tank a pipe system was arranged, in correspondence of a drainage structure (non-woven agricultural fabric, supported by metal grid, and sand) for the collection of leachate. Leachate was collected after each rainy event in PVC cisterns, one per each tank, located in a ditch excavated between the two rows. Under tanks, a plastic mulching film was positioned to prevent weeds growth and to facilitate field operations (sampling, crop management, maintenance of trials, etc.). Tanks were filled with silty-clay soil from experimental fields of CREA-ABP located in Scarperia, Firenze (43°58’56” N, 11°20’53” E). Soil layers (0-30; 30-60; 60-90 cm of depth) were kept divided to reproduce the original soil profile into the tanks. Water supply, for maize, was provided by a drip irrigation system. Thirteen seeds of silage maize (Var. Ronaldinio) were sowed on 17/06/2016 to reproduce a field plant density of 12.000 plants/ha. Maize was harvested on 30/08/2016 after a growing period of 71 days. Barley (Var. Meseta) was sown on 02/11/2016 with 26 gr/tank (200 Kg/ha) of seeds to reach a plant density of 400/500 plants/m^2. Due the wet season (364 mm of rain) occurred during barley’s cultivation season (November 2016 to June 2017) no irrigation was organized. Barley was harvested on 07/06/2017 after a growing period of 217 days. Two fertilization treatments were tested: liquid fraction of digestate from pig slurries and mineral fertilizer (urea for maize and ammonium nitrate for barley); no fertilization was used as control. Urea-N require nitrification transformation to be available for crops, for this reason is commonly spread on summer crops, as maize, when temperatures are warm. Moreover, urea has a high dissolution potential in water and the application on wet season is commonly discouraged. Instead, ammonium nitrate represent the main mineral fertilizer spread on winter crops in Italy (Ceccon et al., 2017). For each treatment, four replicates (tanks) were carried out in a randomized block design. Digestate was provided by the plant of “Marchesi de’ Frescobaldi, Tenuta di Corte” farm (43°58’29” N, 11°23’21” E), where a mixture of pig slurry and agricultural by-product as straw, olive cake and small part of sorghum silage is treated in an anaerobic digester. Digestion temperature is 35 °C with a hydraulic residence time of almost 30 days. For the experiment, only the liquid fraction was used and the separation was manually done. 150 Kg ha^{-1} of N were used and fertilizers were incorporated into the soil by manually replacing injection for digestate, and mechanical incorporation for urea and ammonium nitrate. Fertilization occurred on 04/07/2016 and on 18/07/2016 for maize and on 13/03/2017 and on 10/04/2017, in correspondence of the maximum crop requirement.

2.2 Measurement devices and sampling methods

For N mass balance assessment purpose, all input and output factors were quantified and reported as following:

N_{fert}: Represent the N amount spread with fertilization. Nutrient content (N, P, K) and N type (NH_4^+ and NO_3^-) of digestate were determined (Tab. 1). Total N was obtained by Kjeldahl analysis, while the method described in "Regione Piemonte Metodi di analisi del Compost Met. C.7.3 and EPA 9056A 2007" was used for NH_4^+ and NO_3^- determination. Finally, P and K amounts were measured by ICP Iris Intrepid II XSP analyzer to obtain a complete overview of digestate characteristics.

N_{dep}: N deposition was estimated with the EMEP N deposition model for the year 2013, including both wet and dry N deposition (Tab. 2).

N_{soil}: Soil sampling was performed before sowing and after harvesting to assess the change in soil N content. N soil content was not an input factor but it was considered as such for a purpose of complete N mass balance evaluation. Samples were analyzed using a CHN elemental analyzer (Flash EA 1112-ThermoFisher).

N_{harv}: After harvesting, crop samples were dried in a forced air oven at 60°C to constant weight, for each tank including control, then they were ground through a mill (Brabender Ohg, Duisburg) to pass 1 mm screen. Total N content of marketable part of crops (entire plant for maize, grains and straw for barley) were determined through a CHN analyzer (Flash EA 1112-ThermoFisher).

$N_{volatil}$: For the monitoring of gas emissions twelve static chambers (one per tank) were constructed as described by Parkin and Venterea (2010). Chambers were composed of two parts: the lid of the

chamber and the anchor system to be inserted into the soil as support. The anchor system was made by a PVC cylinder 15 cm long and with a diameter of 20 cm. The cylinder was inserted in the soil for two thirds of its length so that 5 cm remained above the surface. To reduce roots disturbance, anchor was positioned into the soil immediately after sowing. Another PVC cylinder with the same diameter (20 cm) and 25 cm long, and a PVC stopper sealed with silicon glue, were used for the lid of the chamber. A reflective Mylar tape was placed on the side and on the top of the chamber to shield solar radiation. A hole (13.2 mm of diameter) was drilled on the top of the chamber approximately halfway between the center of the circle and the outside edge. A butyl rubber septum of 20 mm of diameter was fixed inside the hole for allowing sampling operations.

A 7-cm wide strip of tire tube was used for ensuring a hermetic connection between the lid and the

anchor system. The strip was putted around the bottom of the lid and fixed with tape and silicone glue. The part exceeding from the chamber (about a half 150 of the strip height) was kept folded back onto the PVC ring and then folded down to connect the lid to the anchor during sampling.

Gas samplings were performed by means of the portable gas analyzer Madur Sensonic X-CGGM 400. The gas analyzer uses Nondispersive Infrared technology (NDIR) for NH_3 detection and

electrochemical technology for N_2O. Samplings were performed until no N emissions occurred from the soil, in particular measurements periods were 25 and 47 days for maize and barley, respectively. Measurements occurred once a day during the first week after fertilization and twice a week during the following weeks by holding the sensor inside the chamber for 1 minute immediately after chamber closing and then repeated at 1 hour intervals. Chambers were equipped by two thermocouples for temperature monitoring inside the chamber. For air temperature and atmospheric pressure monitoring, an automatic meteorological station located 20 meters from experimental field, was used. Gas fluxes were calculated starting from the gas concentration into the chamber, chamber dimensions (area and volume), closing time and molecular weight of each gas. As temperature had a similar trend inside each chamber (data not shown), the whole experiment was assumed to be at standard temperature and pressure (STP) conditions and the molar volume of the air is assumed as 22.4 liters.

N_{leach}: Collection of leaching was performed through cistern located in the ditch between the two rows of tanks after each rainy event. Collected leachate samples were filtered and air-dried to assess sediment concentration. The total N was determined using a CHN elemental analyzer (PerkinElmer's 2400 Series II CHNS/O, PerkinElmer, Waltham, MA) (APHA, 1992). An aliquot of each sample was decanted and dried at 105 °C, then weighed for determining sediment concentration. Then, other unfiltered aliquots were acid-digested for total N (Bremner and Mulvaney, 1982; Napoli et al., 2017) determinations. Quality Control (QC) for N measurements includes triplicate sample analysis for each sample. Moreover, 3 of every 15 samples analysed were known QC samples (distilled water blank, 0.5 and 5 mg L^{-1}).

Table 1 Elementary composition of digestate

	Unit	Liquid fraction of digestate
N	g/Kg	3.14
NH_4^+	g/Kg	2.81
NO_3^-	g/kg	0.081
P	g/Kg	18.44
K	g/Kg	69.46

Table 2 N deposition estimation

Element	Type of deposition	Deposition (kg/ha)
Oxidized Nitrogen (NOx)	dry	2.7
	wet	4.0
	total	6.6
Reduced nitrogen (NHx)	dry	1.6
	wet	3.1
	total	4.7
Total nitrogen	total	11.3

2.3 Data Evaluation

Calculation of the N surplus and N use efficiency

The nitrogen (N) flows were expressed by two different indicators. The N surplus was calculated as the difference between the total nitrogen output (uptake) and the total nitrogen input by fertilizers and deposition ($N_{suplus} = N_{fert} + N_{dep} - N_{harv}$), assuming fixation to be negligible (OECD and EUROSTAT, 2007. Gross Nitrogen Balance, HANDBOOK). This was calculated for both the control plot (no fertilization) and the fertilized plot. In addition, the agronomic nitrogen use efficiency (NUE) was calculated as ($N_{output\ (uptake)\ fertilized\ plot}$- $N_{output\ (uptake)\ control\ plot}$)/$N_{input\ fertilizer\ plot}$

This indicator provides the efficiency level of the added N fertilizer in the considered agricultural system and allows to make a comparison between the different agricultural systems and fertilizers used.

In addition, we calculated the fate of the N surplus in terms of volatilization of NH_3 and N_2O (measured), N leaching, N mineralization (calculated) and denitrification (calculated) according to

$$N_{min} = N_{harv,control} + NH_{3\ control} + N_{leach\ control} + (N_{min\ end} - N_{min\ start})_{control} - N_{dep\ control} \quad (1)$$

$$N_{den} = N_{fert} + N_{dep} + N_{min} - N_{harv} - N_{volatil} - N_{leach} \quad (2)$$

Where

N_{den} : N denitrification losses

N_{min} : soil N mineralization

$N_{min\ end} - N_{min\ start}$: change in N pool in the soil before crop sowing and after harvesting (kg/ha)

N_{fert} : N input by fertilizers

N_{dep} : total (wet and dry) N deposition from the atmosphere

N_{harv} : N uptake by crops

$N_{volatil}$: N lost through volatilization (N_2O + NH_3)

N_{leach} : N losses through leaching

Calculation of the net energy and the energy use efficiency

A simple output/input budget evaluation was performed for the assessment of the energy balance (GJ/ha) on silage maize and barley. The analysis focused on the amount of energy needed by crop cultivation, and totals and net energy produced by the two crops under different fertilization strategies. As with the N flow, the energy flows were expressed by two different indicators. Net energy (NE) gives the gross amount of energy expressed as GJ ha^{-1} and was calculated as the difference between Total Energy Output (GJ ha^{-1}) and the Total Energy Input (GJ ha^{-1}). The Energy Use Efficiency (EUE) was calculated as: ($E_{output\ fertilized\ plot}$- $E_{output\ control\ plot}$)/$E_{input\ fertilizer\ plot}$

This indicator provides the efficiency level of the considered agricultural system and allows to make a comparison between the different agricultural systems.

Input components

Energy balance is a useful tool for the evaluation of energy flows into specific systems. However, there is a great potential for misinterpretation about factors quantification. In particular, several issues affect systems performances and the weight of each factor as boundary limits, technological level of considered system etc. Moreover, as previous affirmed, there is no a universally accepted method for the evaluation of energy balance (Zegada-Lizarazu et al., 2010). Several studies are based on assumptions and make use of statistical databases that include a wide range of scenarios but may not represent specific situations. However, there is a lack of studies based on experimental observed data. The main energy inputs of agricultural systems used in order to improve crop production are: (i) energy to produce applied inputs (seeds, fertilizers, herbicides/pesticides); (ii) energy consumed in machinery manufacture, including direct energy cost for manufacturing and the service life ($year^{-1}$); (iii) fuel energy, that considers the energy consumed in seedling, tillage and harvest operations; (iv) energy consumed for irrigation. In the most recent literature, several authors also consider the energy consumed by human labor (Zegada-Lizarazu, 2010).

In this study, a combination of information from recent literature and databases, and experimental data was used to estimate energy flows (Borin et al., 1997; Hülsbergen et al. 2000; Romanelli & Milan, 2005; Mobtaker et al., 2010; Zegada – Lizarazu et al., 2010; Ribaudo et al., 2012), hypothesizing a conventional agricultural management in Central Italy for maize and barley. Crop cultivation was organized in tanks and tillage operations, included fertilization, irrigation, weed control and harvest, were manually performed. On energy input evaluation, we considered the energy consumption of each agricultural operation, included the energy consumption to produce the applied inputs (seeds, fertilizers, herbicides etc.) per hectare. In particular, soil was prepared for maize sowing with plowing and harrowing replacing. Weed control was performed one week after sowing with 4.5 l ha^{-1} of Primagram Gold (Syngenta) and three weeks later mechanically. From the second week irrigation was performed once per day with 8 mm day^{-1} ha^{-1}. Fertilization was performed in two times in correspondence of the maximum crop requirement. After maize harvest, soil was prepared for barley sowing. In particular, plowing and harrowing were performed in the beginning of October and, in the 2nd of November, a second harrowing before sowing. Fertilization was organized in two times in correspondence of the maximum crop requirement and during the first week of April, a chemical weed control was performed using 750 ml ha^{-1} of Axial Pronto 60 (Syngenta) and 37 g ha^{-1} of Logran (Syngenta).

Output components

Total energy produced by agricultural systems is commonly expressed as a function of quantity and quality of crop yields. In this study calculation of total produced energy was performed using the elemental composition of crops from direct laboratory measurements (AOAC, 2012) and the enclosed energy (MJ Kg^{-1} of DM) of each class of components from literature sources (Hülsbergen et al. 2000; Romanelli & Milan, 2005; Brehmer et al., 2008; Zegada-Lizarazu et al., 2010) as reported in Table 5.

Calculation of the total energy produced by the two systems (maize and barley) was performed through the following equation (Romanelli & Milan, 2005):

$$OE = \{(Y \times DM) \times [(CP \times fCP) + (EE \times fEE) + (CF \times fCF) + (NFE \times fNFE)]\} \div 100 \quad \text{(Eq. 2)}$$

OE = Total Output Energy (GJ ha^{-1}); Y = Yield (Kg ha^{-1}); DM = Dry Matter (%); CP = Crude Protein content (%); fCP = Crude Protein enclosed energy (MJ Kg^{-1} DM^{-1}); EE = Ether Extract content (%); fEE = Ether Extract enclosed energy (MJ Kg^{-1} DM^{-1}); CF = Crude Fiber content (%); fCF = Crude Fiber enclosed energy (MJ Kg^{-1} DM^{-1}); NFE = Nitrogen Free Extract content (%); fNFE = Nitrogen Free Extract enclosed energy (MJ Kg^{-1} DM^{-1}).

3. Results

3.1 Nitrogen surplus and Nitrogen Use Efficiency

Maize

Table 3 Maize N mass balance evaluation

	Unit	Control	Digestate	Urea
N_{fert}	Kg ha^{-1}	-	150	150
N_{dep}	Kg ha^{-1}	11.3	11.3	11.3
N_{harv}	Kg ha^{-1}	128.45	208.08	216.03
$N_{surplus/deficit}$	Kg ha^{-1}	-117.15	-46.78	-54.74
N_{vol}	Kg ha^{-1}	0.73	2.87	3.76
$NH_{3\ vol}$	Kg ha^{-1}	0.32	0.72	2.08
$N_2O_{\ vol}$	Kg ha^{-1}	0.41	2.15	1.68
N_{leach}	Kg ha^{-1}	0	0	0
$N_{min\ end} – N_{min\ start}$	Kg ha^{-1}	0.13	-	-
N_{min}	Kg ha^{-1}	117.60	-	-
N_{den}	Kg ha^{-1}	-	67.95	59.10
NUE		-	0.53	0.58

N deposition amount was estimated using EMEP N deposition model for the year 2013. Obtained results provide N deposition amount of 11.3 Kg N ha^{-1} including wet and dry deposition.

In maize, crop uptake represents the main part of N output and exceed the amount provided with fertilization (Tab. 3). No statistical differences were observed in yields between fertilization treatments; however, N uptake was higher in urea than in digestate. N surplus calculation on maize provide a deficit in both treatments, -46.78 Kg N ha^{-1} and -54.74 Kg N ha^{-1} for digestate and urea respectively, due to the high N uptake by crops and the small amount of residues incorporated into the soil (Grignani et al., 2007). N volatilization was higher from urea than from digestate, mainly due to the high temperatures occurred during the fertilizers spreading (Fig. 1a), and to the irrigation regimes that encouraged emissions (Vallejo et al., 2005; Pezzolla et al., 2012). In particular, N_2O emissions were higher in digestate (2.15 Kg N ha^{-1}) than urea (1.68 Kg N ha^{-1}). However, the great part of N volatilization losses were represented by NH_3 that was roughly three times higher in urea (2.08 Kg N ha^{-1}) than digestate (0.72 Kg N ha^{-1}). N leaching were negligible in both treatment and this factor did not affected N dynamics. Likewise, change in N pool in the soil before crop sowing and after harvesting was 0.13 Kg N ha^{-1} and its weight on N dynamics has little impact. Mineralized N rate was derived in eq. 1 from N fluxes at control plots and obtained results was 117.60 Kg N ha^{-1}. Moreover, denitrification was calculated in eq.2 for both treatments and digestate provide higher amount of N denitrification losses (67.95 Kg N ha^{-1}) than urea (59.10 Kg N ha^{-1}).

Comparison between the two agricultural systems and fertilizers use were performed using NUE evaluation. However, we observed similar NUE performances between digestate and urea on maize (Tab.9).

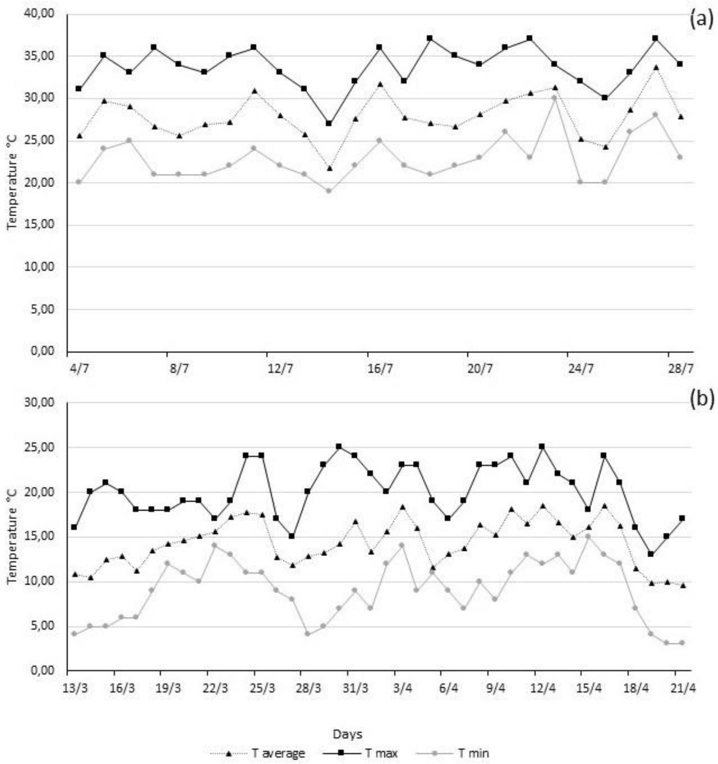

Figure 1 Temperature trend on maize (a) and barley (b)

Barley

Table 4 Barley N mass balance evaluation

	Unit	Control		Digestate		Ammonium Nitrate	
		Straw	Grain	Straw	Grain	Straw	Grain
$\mathbf{N_{fert}}$	Kg ha^{-1}	-	-	150	150	150	150
$\mathbf{N_{dep}}$	Kg ha^{-1}	11.3	11.3	11.3	11.3	11.3	11.3
$\mathbf{N_{harv}}$	Kg ha^{-1}	10.33	70.11	28.05	152.91	22.36	133.82
Total	Kg ha^{-1}	80.44		180.96		156.18	
$\mathbf{N_{surplus/deficit}}$ [a]	Kg ha^{-1}	-58.81		8.39		27.48	
$\mathbf{N_{surplus/deficit}}$ [b]	Kg ha^{-1}	-69.14		-19.66		5.12	
$\mathbf{N_{vol}}$							
$\mathbf{N_2O}$	Kg ha^{-1}	0.007		0.27		0.02	
$\mathbf{NH_3}$	Kg ha^{-1}	0		0		0	
$\mathbf{N_{leach}}$	Kg ha^{-1}	0	0	0	0	0	0
$\mathbf{N_{min\ end} - N_{min\ start}}$	Kg ha^{-1}	0.27		-	-	-	-
$\mathbf{N_{min}}$	Kg ha^{-1}	69.40	59.07	-	-	-	-
$\mathbf{N_{den}}$ [a]	Kg ha^{-1}	-	-	67.20		86.53	
$\mathbf{N_{den}}$ [b]	Kg ha^{-1}	-	-	49.48		74.50	
NUE[a]		-	-	0.55		0.42	
NUE[b]		-	-	0.67		0.51	

[a] straw incorporation into the soil
[b] straw harvesting

As for maize, N deposition estimation was performed using EMEP N deposition model for the year 2013, the same result was obtained (11.3 Kg N ha^{-1}).

Crop N uptake was higher in digestate (180.96 Kg N ha^{-1}) than in ammonium nitrate (156.18 Kg N ha^{-1}) in accordance to the differences in crop growth and yields (Tab. 10). In accordance to Alburquerque et al. (2012), Walsh et al. (2012), Koszel & Lorencowicz (2015), Riva et al. (2016) digestate was able to produce higher yields due to the high N-ready components content as phosphorus (P) and potassium (K) supply (Tab. 1) and the ability of digestate (liquid fertilizer) to infiltrate into the roots zone.

From N surplus evaluation we obtained contrasting results based on crop residues management (Tab. 4). In particular, the "a" scenario, that hypothesize straw incorporation into the soil after harvesting, ensure N accumulation into the soil. Ammonium nitrate-fertilized barley provide higher amount of N stored in soil (27.48 Kg N ha^{-1}) than digestate-fertilized barley (8.39 Kg N ha^{-1}). From "b" scenario, that assume straw harvest without incorporation into the soil, was observed as digestate treatment provide N deficit in soil (-19.66 Kg N ha^{-1}) at the end of cultivation season. Contrarily, ammonium nitrate ensured an increment of N rate into the soil. Nevertheless, straw removal from field reduce the amount of stored N (5.12 Kg N ha^{-1}).

N volatilization in both treatments was negligible (Tab. 4) compared to the other factors due to the low temperature during fertilizer spreading (Fig. 1b) that radically reduced N emissions (Huang et al., 2004; van Groenigen et al., 2004; Stehfest & Bouwman, 2006). We did not observed any NH_3 emissions and the entire N losses through volatilization were represented by N_2O (0.27 Kg N ha^{-1} and

0.02 Kg N ha^{-1} for digestate and ammonium nitrate, respectively). N leaching losses were negligible in both treatment and this factor did not affected N dynamics of the systems. Similarly, difference between N soil content before crop sowing and after harvesting was 0.27 Kg N ha^{-1} and its weight on N dynamics has little impact. In eq. 1 mineralized N rate was derived from N fluxes at control plots and obtained results were 59.07 Kg N ha^{-1} and 69.40 Kg N ha^{-1} for "a" and "b" scenario, respectively. N denitrification losses were evaluated by eq. 2 for different fertilizers and scenario. Independently to crop residues management, digestate-fertilization strategy provide less N losses than ammonium nitrate. In particular, in scenario "a" denitrification was 67.20 Kg N ha^{-1} for digestate and 86.53 Kg N ha^{-1} for ammonium nitrate. In "b" scenario, denitrification decrease to 49.48 Kg N ha^{-1} for digestate and 74.50 Kg N ha^{-1} for ammonium nitrate. N utilization at different fertilization strategies and crop residues management was finally evaluated using NUE. Generally, digestate provide greater N utilization performances in the agricultural systems. Hypothesizing barley straw incorporation into the soil digestate provide NUE values of 0.55 than ammonium nitrate that reach 0.42. Likewise, with harvest of barley straw NUE were 0.67 in digestate and 0.51 in ammonium nitrate.

3.2 Energy balance

Table 5 Maize energy Output

	Enclosed Energy (MJ kg^{-1} DM) *(Hülsberg et al., 2001)*	Control	Digestate	Urea
DM (t ha^{-1})		12.13	14.45	14.12
Crude Protein (%)	23,9	8.22	8.20	8.37
Ether Extract (%)	39,8	1.98	2.15	2.19
Crude Fiber (%)	20,1	22.27	21.30	21.60
N-Free Extract (%)	17,5	62.02	63.57	62.80
Ash (%)	-	5.51	4.78	5.04
Energy Content (GJ ha^{-1})		204.41	248.51	241.01

Table 6 Barley energy Output

	Enclosed Energy (MJ kg^{-1} DM)*	Control		Digestate		Ammonium Nitrate	
		Straw	Grain	Straw	Grain	Straw	Grain
DM (t ha^{-1})		3.45	5.76	4.52	7.53	3.90	6.46
Crude Protein (%)	23,9	2.14	7.63	3.71	12.33	3.68	12.38
Ether Extract (%)	39,8	1.43	2.26	1.45	1.99	1.51	2.21
Crude Fiber (%)	20,1	39.95	4.66	36.77	4.32	37.23	4.79
N-Free Extract (%)	17,5	48.17	82.71	49.97	78.85	48.72	77.85
Ash (%)	-	8.31	2.74	8.11	2.51	8.86	2.77
Energy Content (GJ ha^{-1})		41.89	86.46	50.95	103.73	42.53	87.07
		128.35		154.68		129.6	

* *Hülsberg et al., 2001*

Table 7 Maize energy balance Input

	Digestate	Urea	Control	References
Energy to produce applied inputs				
Seeds (GJ ha^{-1})	0.28	0.28	0.28	Zegada-Lizarazu et al. (2010)
Herbicides/Pesticides	0.85	0.85	0.85	Zegada-Lizarazu et al. (2010)
Fertilizer	-	21.16	-	Mobtaker et al. (2010); Zegada-Lizarazu et al. (2010)
Energy for machinery manufacture	7.67	7.67	7.67	Borin et al. (1997)
Fuel energy	53.15	4.67	4.59	Zegada-Lizarazu et al. (2010); Ribaudo (2012)
Energy consumed by human labor	-	-	-	-
Energy for irrigation	20.80	20.80	20.80	Zegada-Lizarazu et al. (2010)
Total Input	34.92	55.44	34.19	

Table 8 Barley energy balance Input

	Digestate	Ammonium Nitrate	Control	References
Energy to produce applied inputs				
Seeds (GJ ha^{-1})	2.8	2.8	2.8	Zegada-Lizarazu et al. (2010)
Herbicides/Pesticides	0.85	0.85	0.85	Zegada-Lizarazu et al. (2010)
Fertilizer	-	12.43	-	Mobtaker et al. (2010); Zegada-Lizarazu et al. (2010)
Energy for machinery manufacture	4.71	4.71	4.71	Borin et al. (1997)
Fuel energy	5.31	4.67	4.59	Zegada-Lizarazu et al. (2010); Ribaudo (2012)
Energy consumed by human labor	-	-	-	-
Total Input	13.67	25.46	12.95	Zegada-Lizarazu et al. (2010)

The energy balance was performed for the evaluation of the effect of the two different fertilization strategies (Tab. 9) on the energy flows of the two crops. The main observed differences between the two treatments on maize were related with the production process of fertilizers. We assumed that digestate, as a by-product of biogas process, has a zero energy production cost, instead urea production consume energy in terms of 21.16 GJ ha^{-1} (Mobtaker et al., 2010). However, energy consumption for the production of the other applied inputs (seeds and herbicides/pesticides) was constant between all treatments.

Due to the high water content of digestate, fuel consumption for its spreading on field were higher than those for urea. The liquid state of digestate, in fact, requires a specific slurry spreader that consumes more fuel compared to the spreader used for urea. Moreover, the higher N content of urea (46%) involves a lower amount of fertilizer and less energy for the transport and spreading in field. Transport from farm to field, in this case, is the main weakness of the use of the liquid fraction of digestate (Zegada-Lizarazu et al., 2010). In this sense, fuel energy consumption were more than ten times higher than urea, in particular digestate consumed 53.15 GJ ha^{-1} while urea 4.67 GJ ha^{-1}. Energy consumption in irrigation was the same for each treatment (20.80 GJ ha^{-1}). Despite this, digestate still has less energy input requirement than urea.

Comparing elemental composition of yields, we observed that differences between the two treatments were small (Tab. 5). Nevertheless, yields obtained from digestate (14.45 t DM ha^{-1}) were higher than yields from urea (14.12 t DM ha^{-1}) and hence the cumulative energy output were higher in digestate (248.51 GJ ha^{-1}) than urea (241.01 GJ ha^{-1}). Higher yields in digestate was due to several factors as a high rate of ready-N component (Tab. 1), a high water content that ensures a better soil infiltration and diffusion into the root zone, and P and K supply. Due to these characteristics, digestate was able to provide higher yields than urea, which brings only N to the crops and, because of the hydrolysis process, need a few days to be absorbed by plants. The lowest energy requirement of digestate and the highest energy production was confirmed by EUE (Tab. 9). Based on NE results, we also observed that digestate was able to produce roughly one fourth more energy than urea (213.59 GJ ha^{-1} and 185.57 GJ ha^{-1}, respectively).

Regarding barley, we observed again that the weight of energy consumption during fertilizer production process is predominant on the total energy balance (Tab. 8). In particular, we assumed zero energy consumption in digestate production process while 12.43 GJ ha^{-1} for ammonium nitrate. Fuel consumption for spreading was lower in ammonium nitrate, 4.67 GJ ha^{-1}, than digestate, 5.31 GJ ha^{-1}, due to the different N grade and water content of the two products. As on maize, digestate had a positive effect on grain yields (7.53 t DM ha^{-1} while 6.46 t DM ha^{-1} of ammonium nitrate) but differences in their composition were slight (Tab. 6). However, higher yields on digestate-fertilized barley provided higher energy production compared to ammonium nitrate. EUE evaluation demonstrated that barley performed better under digestate than ammonium nitrate (Tab. 9), meaning that digestate provided a higher energy use efficiency. Further, NE highlighted that digestate-fertilized barley produced roughly one third more energy that ammonium nitrate (141.02 GJ ha^{-1} and 104.15 GJ ha^{-1}, respectively).

Comparison between NUE and EUE results for each crop provide information about impact mitigation potential of different agricultural strategies (Fig. 2).

Table 9 Energy Balance evaluation, Net Energy (NE) and Energy Use Efficiency (EUE)

	Maize			Barley		
	Digestate	**Urea**	**Control**	**Digestate**	**Ammonium Nitrate**	**Control**
Total Input Energy (GJ ha^{-1})	34.92	55.44	34.19	13.67	25.45	12.95
Total Output Energy (GJ ha^{-1})	248.51	241.01	204.41	154.68	129.61	128.35
NE (GJ ha^{-1})	213.59	185.57	170.22	141.02	104.15	115.4
EUE	1.26	0.02	-	1.93	0.05	-

Table 10 Maize and Barley yields

	Maize		Barley			
	Digestate	**Urea**	**Digestate**		**Ammonium Nitrate**	
			Grain	Straw	Grain	Straw
DM (%)	64.55	60.37	74.93	64.08	72.64	61.92
DM Kg $tank^{-1}$	1.45	1.41	0.75	0.45	0.65	0.39
t DM ha^{-1}	14.45	14.12	7.53	4.52	6.46	3.91

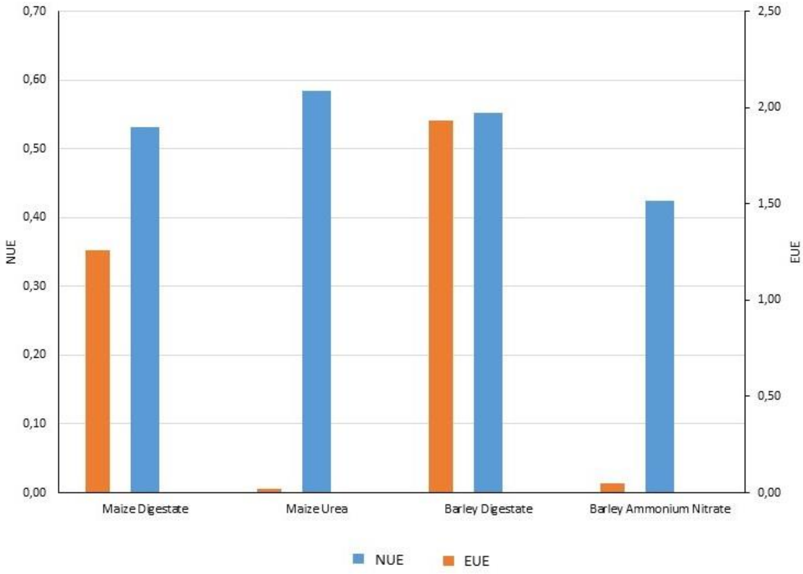

Figure 2 Energy Use Efficiency (EUE) and Nitrogen Use Efficiency (NUE) performances of maize and barley at each fertilization treatment

4. Discussion

N mass balance is a useful tool for a quantitative understanding of N dynamics and for assessing its overall availability for crops and the efficiency of utilization by crops (Gentry et al. 2009). Obviously, the main N output of the systems is represented by crop uptake. However, due to the difficulties on monitoring denitrification during the experiment, N volatilization losses might be underestimated, especially on barley that was fertilized between March and May when low average temperatures and under wet conditions occurred.

A further consideration must be made about N losses by leaching. In this experiment, leachate samples were collected from all tanks and negligible N losses by leaching were observed. The depth soil profile (1 m) had probably reduced the leaching with a consequent accumulation of N into the bottom layers of soil.

The N deficit on maize, in accordance to Grignani et al. (2007), can be explained by the high crop uptake and the low amount of residues incorporated into the soil after harvesting (maize for silage). The inability of both treatments to maintain a positive N rate into the soil demonstrate that agriculture still has heavy impact on soil fertility and more in depth experimentations are needed to reduce this detrimental process. This is in accordance to EU Policies (EU, 2008) that strongly encourage the research of new agricultural strategies for the improvement of soil fertility maintenance. N mass balance assessment on barley suggested that the management of crop residues is a key-point on the soil fertility preservation. Considering that crops N uptake strongly affects the total balance, the incorporation of straw after barley harvesting ensures the preservation of a positive N balance. This is confirmed by straw analysis, which showed that N uptake by straw was roughly one fifth of the N uptake by the entire plant.

The higher Output Energy production of digestate on both crops, coupled to the lowest energy requirement during the production process, make digestate an alternative to mineral fertilization able to improve energy use efficiency and to reduce the impact of the agricultural systems. However, energy balance strongly depends on a wide range of factors that makes each system different to the other. For this reason, specific researches should be implemented. In particular, elemental characterization of crops is fundamental to define the potential energy production of the specific system studied and for the Output Energy assessment. Elemental characterization of crops gives the opportunity for a more precise calculation of the energy production potential from agricultural systems, compared with methodologies that adopt generic values based on total crop yields reported in literature. Finally, the use of existing databases is adoptable for a general overview but, for a better understanding of each specific system, the use of data from laboratory analysis is suggested (Zegada-Lizarazu, 2010). In contrast to Zegada-Lizarazu et al. (2010), we observed that the main factors affecting Energy Balance of the agricultural systems are the energy consumption during fertilizer production process, and the energy consumed by irrigation.

In addition, several authors include human labor on Energy Balance assessment as relevant factor of energy consumption. However, this factor strongly depends on the agricultural systems and its impact on the energy balance is negligible in high-mechanized systems of industrialized countries. For this reason, in this work energy consumption from human labor was considered negligible. Nevertheless, developing countries that are characterized by limited mechanization and low efficient energy-supply systems, represent a different situation where these factors can have greater impacts on the energy balance (Conforti et al. 1997; Nguyen et al. 2007; Zegada-Lizarazu et al., 2010). The sum of each mentioned factor represents the Total Input of the system.

Due to crop composition, maize based systems normally produces more energy compared to barley based systems (Tab. 5 and Tab. 6). However, barley was able to use more efficiently the available energy resources. In both crops, digestate had higher EUE than mineral fertilizers (Tab. 9 and Fig. 2). This was mainly due to the lowest energy requirement in the production process of the fertilizer and to the higher crop yields obtained (Tab. 10).

5. Conclusion

N mass balance allows understanding the dynamics of different agricultural strategies and input/output factors budget. In this sense, strengths and weaknesses of each system were evaluated. Obtained information may be used by governance organization to assess the guidelines for the evolution of national or EU agriculture. Digestate is a valid alternative to mineral fertilizers (urea) for the reduction of cumulative N losses. Crop uptake represents the main output of the systems. However, the assessment of N soil content showed that the management of crop residues might be fundamental for the preservation of soil fertility. Simulating barley straw incorporation, with N uptake by crop represented only by grains, the N mass balance calculation provide positive N surplus. Silage maize leaves a low amount of residues and N deficit occurred. Further experiments focused on N mass balance on maize for grain, and with incorporation of residues into the soil, are suggested for a more in-depth understanding of the potential of crop management for the maintenance of soil fertility. Moreover, the in field monitoring of denitrification would provide a more accurate N mass balance, especially for those crops having a large part of their growing cycle during the wet conditions that encourage denitrification losses.

Digestate induced higher yields demonstrating a better resources utilization (nutrients and energy) and higher energy production from the systems, also confirmed by the energy balance. Nevertheless, more accurate data are needed regarding production process of agricultural input for a complete and exhaustive evaluation of efficiency on energy use in agriculture.

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Chapter 4. General Conclusions

During the PhD project, three experiments were carried out.

The first experiment focused on the role of organic matter on GHGs emissions from fertilized soil. To this aim two different organic fertilizers, liquid fraction of digestate from pig slurries and compost from organic fraction of municipal solid waste, and urea as conventional organ-mineral fertilizer were tested on bare soil. Obtained results showed that in correspondence of higher soil organic matter content, emissions from urea also increase. Results on cumulative emissions showed that digestate provided the highest emissions. However, digestate and compost had a different trend of emissions that were higher in correspondence of the lower organic matter content. This requires further investigation that consider the microorganism population into the soil. Compost represents the best opportunity to replace mineral fertilizers having lower CO_2 and NH_3 emissions, and comparable levels of CH_4 and N_2O emissions, that allow to reduce overall GHGs emissions and preserve N source into the soil. However, further experiments on the role of compost on final yield are needed.

The second experiment dealt with the use of the different fertilization methods on a summer crop (*Zea mays L.*). We observed that digestate was an effective method to lower total emissions of N compared to urea. In particular, application of digestate instead of urea led to a significant reduction of NH_3 emission from soil. Nevertheless, N_2O emissions were higher and we hypothesized that this was due to the higher organic C content of the digestate. Further studies on the effect of nitrification inhibitors might provide useful information for reducing N_2O emissions from the use of digestate as fertilizer. However, digestate N content is low and several passes in field are needed to spread the high amount of digestate necessary for fertilization. This of course causes further emissions that should be taken into account. At the same time urea is a product of an industrial process that also produces significant emissions. Hence, as for digestate further experiments that include environmental impacts of each production step are needed for a better understanding of the system. The assessment of total N content into the soil before sowing and after harvest provided information about additional N losses. The lower total N content of tanks treated with digestate than those with urea can be considered as N losses through denitrification. However, the lack of direct measurement and the difficulties in denitrification measurements could led to an underestimation of N losses from tested fertilizers. Comparison on yields proved that digestate and urea provided similar results. Crop N uptake confirms that with comparable N content in both treatments.

Future experiments should focus on factors affecting N losses. In particular, attention should be focused on factors responsible to direct N_2O emissions from the soil and the spreading of digestate (DM, organic C, soil moisture, spreading methods and nitrification inhibitors). Moreover, a study that consider environmental impacts of digestate and urea production chains is suggested for a better understanding of the system.

Finally, the assessment of nutrient mass balances and energy balance provided useful information about sustainability of the agricultural systems tested. Through the study of these indicators, we observed that digestate is a valid alternative to mineral fertilizers for maintaining soil fertility. On the other hand, the management of crop residues plays a key role in the N use efficiency of the system and has a direct impact on the sustainability of the process. However, soil fertility maintenance depends on a wide range of factors and fertilization is only one of them. A more complex study, which considers the entire agricultural system from inputs production processes to crop residues management, is required in order to obtain a complete overview of the system. The lowest requirement of energy for digestate production makes this strategy the most sustainable among those studied.