Universitat de Lleida

Assessment of environmental impacts of agricultural practices

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http://hdl.handle.net/10803/689234

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TESIS DOCTORAL

Assessment of environmental impacts of agricultural practices

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Memòria presentada per optar al grau de Doctor per la Universitat de Lleida

Programa de Doctorado en Ciencia y Tecnología Agraria y Alimentaria

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Lleida, November 2020

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List of abbreviations

N: nitrogen

C: carbon

NO_3^-: nitrate

NH_4^+: ammonium

NUE: nitrogen use efficiency

GHGs: greenhouse gas emissions

CO_2: carbon dioxide

CH_4: methane

N_2O: nitrous oxide

SOC: soil organic carbon

SOM: soil organic matter

PRISMA: Preferred Reporting Items for Systematic Reviews and Meta-Analyses

$\overline{lnRR}$: natural logarithm of response ratio

GWP: global warming potential

WFPS: water filled pore space

Q_t: total heterogeneity

NT: no-tillage

CT: conventional tillage

NO_3^--N: nitrate-nitrogen

NH_4^+-N: ammonium-nitrogen

LEACHM: Leaching Estimation and Chemistry Model

LH-OAT: Latin Hypercube-One factor At a Time

MD: mean difference

N_{min}: mineral nitrogen

NRMSE: normalized root mean square error

NSE: Nash and Sutcliffe coefficient of efficiency

RMSE: root mean square error

SWC: soil water content

EU: European Union

ETo: reference evapotranspiration

ACKNOWLEDGMENTS

In the Name of *Almighty ALLAH*, the Most Gracious, the Most Merciful

All praises are for *Almighty ALLAH*, who gave me courage, health, and endurance to complete my studies successfully, and all respects are for the Holy Prophet "*MUHAMMAD*" (peace be upon him), who is an everlasting model of guidance and knowledge for humanity.

It is a humbling experience to acknowledge those people who have, mostly out of kindness, helped along the journey of my PhD. I am indebted to so many for encouragement and support.

First and foremost, I am extremely grateful to my supervisors, *Prof. Dr. Ángela Dolores Bosch Serra* and *Dr. José Ramón Olarieta Alberdi*, for their invaluable advice, continuous support, and patience during my PhD study. Their immense knowledge and plentiful experience have encouraged me throughout my academic research and daily life. One thing I would like to mention here is that *Ángela* took care of me like her own child, and that attitude was very special to me. I will always remember it. I am again deeply grateful to *Olarieta*, who always helped me out of the box not only for academics but also in other matters of life.

This PhD degree would not have been completed without funding. Therefore, my sincere gratitude also extends to the University of Lleida, Spain for providing the funding opportunity to undertake my PhD studies in the Department of Environment and Soil Sciences at the University of Lleida, Spain. The work included in this PhD has been founded by the Spanish Ministry of Economy, Industry and Competitivity and the National Institute of Research in Agriculture and Food Technology. Project: RTA2017-88-C03.

I would also like to offer my special thanks to all my co-authors of the chapters of this thesis. Without you, it would not be possible to obtain the information and its contextual interpretation.

I would like to express my gratitude to *Montse Antunez*, *Silvia Porras,* and *Silvana Nacci* for their technical and valuable support in the laboratory and field work. I will also pass my special thanks to the secretary of the department, *Clara Llena Farrés*, for her kind help in all the documented work in the department. Moreover, I would also like to thank all the teachers in the Department of Environment and Soil Sciences, UdL, who have always been very supportive and kind to me.

I would also like to extend my sincere thanks to *Dr. Sher Muhammad Shahzad* (University of Sargodha, Pakistan) and *Dr. Muhammad Saleem Arif* (Government College University Faisalabad, Pakistan) for their countless help and support in scientific writing or even in daily life matters.

I am deeply grateful to all of my friends who also supported me in writing, and incented me to strive towards my goal. A special mention goes to my beloved and truly honest friends, *Dr. Muhammad Abdullah*, *Dr. Muhammad Aamir Manzoor,* and *Dr. Taimoor Hassan Farooq*; you all were always there with a word of encouragement or listening ear. I would also like to thank *Mr. Ifraz Ahmad*, *Mr. Muhammad Abu Bakar*, and all the Lleida Tigers cricket team members. It is their kind help and support that has made my studies and life in Lleida (Spain) a wonderful and memorable time.

Finally, I would like to express my gratitude to my father (*Abdul Shakoor*), mother (*Suryya Parveen*), my two lovely sisters (*Anum Shakoor* and *Saba Shakoor*), and my late younger brother (*Fahad Shakoor*) for giving me tons of love, prayers, pursuit for higher ideas in life, and confidence to face the ups and downs of life. Without their tremendous understanding and encouragement in the past few years, it would not be possible for me to complete my study.

With immense happiness and love,
Awais Shakoor

Resumen

Las prácticas de manejo agrícola intensivo contribuyen en las emisiones de gases de efecto invernadero (GEIs), al lavado de nitratos del suelo, y al incremento en las concentraciones de metales pesados en el suelo. Por ello, es muy importante evaluar estas prácticas en relación a sus efectos sobre los agroecosistemas.

El meta-análisis de 48 investigaciones muestra que la aplicación de residuos ganaderos junto con fertilizantes nitrogenados de síntesis es el principal causante de las emisiones de GEIs (p.e., CO_2, CH_4, N_2O) en los sistemas agrícolas a escala de parcela. La aplicación de gallinaza origina mayores emisiones que la de estiércol vacuno o del purín porcino. Por otra parte, el meta-análisis de otros 50 estudios indica que el no-laboreo (NL) produce un aumento en las emisiones de GEIs en comparación con el laboreo convencional. Este incremento es de un 7’1% para el CO_2, de un 11’9% para el N_2O, y de un 20’8% para el CH_4. El análisis de aquellos estudios que solo miden las emisiones de los tres gases, permite concluir que el NL reduce en un 7’5% el potencial de calentamiento global (GWP) en comparación con el laboreo convencional. No obstante, son necesarios más estudios para establecer una conclusión definitiva del efecto de estas dos prácticas en las emisiones de GEIs.

En la agricultura mediterránea de secano, el barbecho puede incluirse como práctica agronómica dentro de la política agraria común europea de diversificación de cultivos. Durante tres años de barbecho, se ha evaluado, mediante el modelo LEACHM, los efectos de la fertilización mineral previa sobre el contenido de nitrógeno mineral (N) en el suelo y sobre el potencial de lavado de NO_3^- durante esos períodos de barbecho. Los resultados muestran que el lavado de N aumenta al aumentar la concentración de N mineral durante el barbecho, estimándose unas pérdidas por este proceso de 11-38 kg N ha^{-1}.

Finalmente, mediante un experimento de campo (7 años) se concluyó que la aplicación de purín porcino incrementaba los macronutrientes y metales pesados en suelo y planta. También aumentaba el carbono orgánico del suelo (CO): entre 13’5-24’7 kg ha^{-1} por cada tonelada de CO de purín aplicado. Las concentraciones de B, Cu, y Zn en el suelo también aumentaron, así como la biodisponibilidad de Cu y Zn pero sin alcanzar niveles tóxicos.

De esta investigación se concluye que la eficiencia y los impactos ambientales de las prácticas agrícolas varían en función de las condiciones edafo-climáticas. Éstas deberían incluirse en el marco de las políticas e iniciativas legislativas para incentivar y regular el uso de fertilizantes.

Palabras clave: prácticas de manejo agrícola; meta-análisis, emisiones de GEIs; agricultura mediterránea de secano; modelo LEACHM; lavado de nitratos; metales pesados en el suelo.

Summary

Intensive agricultural management practices contribute to significant greenhouse gas emissions (GHGs), nitrate (NO_3^-) leaching from the soil, and increased soil heavy metal content. Hence, it is extremely important to evaluate these agricultural practices in terms of their ecological feedback effects in agro-ecosystems.

From the data-synthesis (48 peer-reviewed publications) on animal manure, it appears that application of animal manure together with nitrogen fertilizer is the main contributor to higher GHG emissions (i.e., CO_2, CH_4, N_2O). Poultry manure was responsible for higher GHGs emissions from croplands when compared to pig and cattle manure. In another data synthesis, where we selected 50 peer-reviewed publications, no-till (NT) agriculture resulted in an increase in GHGs emissions, CO_2 by 7.1%, N_2O by 11.9% and CH_4 by 20.8%, compared to conventional tillage. However, a meta-analysis of only those studies that measured the emissions of the three gases showed that NT reduces global warming potential (GWP) by 7.5% in comparison to conventional tillage. Therefore, no definite conclusion can be reached, and further work is required to elucidate the effects of both practices in terms of GHGs.

In Mediterranean rainfed agriculture, the fallow periods can be included within the existing EU common policy for crop diversification as an agronomic practice. In this field, this research aimed to quantify the effects of previous mineral fertilization on the soil mineral nitrogen (N) content and on potential NO_3^- leaching during fallow periods of a crop rotation using the LEACHM model. The estimate of N leached ranged from 11 to 38 kg N ha^{-1}.

Finally, a field experiment showed in the mid-term (7 years) that pig slurry significantly increased soil organic carbon (OC) from 13.5 to 24.7 kg ha^{-1} for every ton of slurry OC applied. The concentrations of B, Cu, and Zn increased in the soil surface horizon over time. Moreover, pig slurry also increased the bioavailability of Cu and Zn, but not at toxic levels.

From this research work it can be concluded that the effectiveness and the environmental impacts of different agricultural land use practices will vary depending on soil and climatic conditions. Such conditions may be included in the framework of policy incentives and regulations related to the use fertilizers and manures in order to prevent the negative environmental impacts associated with their management in agriculture.

Keywords: agricultural management practices; meta-analysis; GHGs emissions; Mediterranean rainfed agriculture; LEACHM model; nitrate leaching; soil heavy metal

Resum

El maneig agrícola intensiu contribueix a les emissions de gasos d'efecte hivernacle (GEHs), al rentat de nitrats del sòl, i a l'increment en les concentracions de metalls pesants al sòl. Per això és molt important avaluar aquestes pràctiques en relació als seus efectes en els agroecosistemes.

La meta-anàlisi de 48 treballs de recerca mostra que l'aplicació de fems d'animals, conjuntament amb fertilitzants nitrogenats de síntesi, és la principal font de GEHs (p.e., CO_2, CH_4, N_2O) en sistemes agrícoles a escala de parcel·la. La gallinassa produeix més emissions que els fems bovins o el purí de porcs. D'altra banda, la meta-anàlisi d'altres 50 treballs de recerca indica que la sembra directa (NL) produeix un augment de les emissions de GEHs, en comparació amb el treball del sòl convencional. Aquest increment ve a ser d'un 7'1% per al CO_2, d'un 11'9% per al N_2O, i d'un 20'8% per al CH_4. Analitzant només els estudis que mesuren les emissions dels tres gasos esmentats s'arriba a la conclusió que el NL redueix en un 7'5% el potencial d'escalfament global en comparació amb el treball del sòl convencional. Són necessaris més estudis per tal d'aclarir l'impacte dels diferents tipus de treball de sòl en les emissions de GEHs.

En l'agricultura mediterrània de secà, el guaret es pot incloure com una pràctica agronòmica dins de la política agrària comuna europea de diversificació de cultius. En tres anys de guaret s'ha avaluat els efectes de la fertilització mineral prèvia sobre el contingut de N mineral al sòl i sobre el potencial de rentat de NO_3^- mitjançant el model LEACHM. Les pèrdues per aquest procés oscil·len entre 11-38 kg N ha^{-1}.

Finalment, mitjançant un experiment de camp, es mostra que l'aplicació de purí porcí (durant 7 campanyes agrícoles) augmenta significativament els macronutrients i metalls pesants al sòl. També augmenta el contingut de carboni orgànic (CO) de 13'5 a 24'7 kg ha^{-1} per cada tona de CO de purí aplicat. Les concentracions de B, Cu, i Zn al sòl també augmenten, així com la biodisponibilitat de Cu i Zn però sense arribar a nivells tòxics.

D'aquesta investigació es conclou que l'eficiència i els impactes ambientals de les diferents pràctiques agrícoles variarà en funció de les condicions edafo-climàtiques. Aquestes condicions s'haurien d'incloure en les polítiques per incentivar i/o regular l'ús de fertilitzants minerals i orgànics, a fi de prevenir els seus impactes ambientals.

Paraules clau: Pràctiques de maneig agrícola; meta-anàlisi; emissions de GEIs; agricultura mediterrània de secà; LEACHM model; rentat de nitrats; metalls pesants al sòl.

Chapter 1

General introduction and objectives

Chapter 1: General introduction and objectives

1.1 General introduction

Global agricultural food and feed production faces a major challenge as the world's population continues to rise, and by 2050 it is expected that the world's population will reach up to 9-10 billion people (United Nations, 2015; Barão et al., 2019). Therefore, best agricultural practices should have to be adopted properly to feed the world without other environmental consequences. Agricultural practices such as the application of synthetic fertilizer, tillage practice, manure type, crop rotation, and irrigation method are the major sources that can significantly alter the physiochemical properties of soil (Ascough et al., 2018). However, agriculture contributes to a larger number of environmental issues, for example climate change, global warming, deforestation, land degradation, biodiversity loss, and heavy metal pollution (Suddick et al., 2010; Poonam et al., 2014). Therefore, proper use of agricultural practices should not only enhance soil quality, fertility, and crop productivity but also substantially decrease these environmental concerns.

1.1.1 Impact of agricultural practice on environment

Nitrogen (N) is an essential nutrient for plant growth, reproduction, and high yield (Yang et al., 2018). Most N in soils is in organic forms that are partly converted into small compounds such as nitrate (NO_3^-) and ammonium (NH_4^+) that plants can easily use (Hadden and Rein, 2011; Mohanty et al., 2017). Agricultural N is derived from a number of different sources, but mainly from inorganic fertilizer and animal manures (Syswerda et al., 2012; Perramon et al., 2016). Nevertheless, excessive use of N fertilizer with decreasing nitrogen use efficiency (NUE) has resulted in N surplus (Zhou et al., 2016) and ultimately causing very serious environmental problems, for example, soil acidification, NO_3^- leaching, GHGs emissions (Thangarajan et al.,

2013) and ammonia volatilization (Bosch-Serra et al., 2014). Animal manure application (pig, cattle, and poultry) as an organic amendment to croplands significantly increases N contents, soil fertility, crop yield, and soil organic carbon (SOC) dynamics by improving soil aggregation, but also significantly disturbs the GHGs emissions (Thangarajan et al., 2013; Zhou et al., 2017). Agriculture is an important source of human-caused greenhouse gases (GHGs) emissions into the atmosphere (Paustian et al., 2016), influencing carbon dioxide (CO_2), nitrous oxide (N_2O), and methane (CH_4) fluxes (Liu et al., 2015). Annually, the total GHGs emissions from agricultural soils are 5.3-6.2 petagrams (Pg; 1 Pg = 1 billion metric tons) CO_2-equivalent (Yao et al., 2017). Application of animal manure and synthetic N fertilizer to agricultural soils were projected to emit 1.3 gigatons CO_2-equivalent in 2010, with emissions expected to increase to 1.7 gigatons CO_2-equivalent by 2050 (Searchinger et al., 2019). Animal manure applications on agricultural soils have intensively been studied, however, their effects on GHGs emissions remain uncertain. Different meta-analysis studies conducted by Maillard and Angers, (2014) and Zhou et al., (2017) found that application of animal manure substantially enhanced CO_2 and N_2O emissions from croplands. On the other hand, manure application significantly reduced N_2O emissions from croplands (Velthof et al., 2003). Other studies showed that manure application had no discernible effect on N_2O emissions (Dendooven et al., 1998; Li et al., 2016). Watts et al., (2011) reported that animal manure significantly increased SOC contents, which ultimately increased CO_2 emissions through microbial activities. Animal manure application also increases soil organic matter (SOM) content, which leads to increased methanotrophic activities, resulting in CH_4 emissions (Wang et al., 2013). Phan et al. (2012) reported that animal manure application emitted large amounts of CO_2 and CH_4 from agricultural soils.

The total amount of C in the terrestrial environment is approximately 3170 Pg, with topsoil accounting for nearly 80% (2500 Pg) of this total (Lal, 2004a; Lal, 2008). Soil C and N cycles are closely interlinked and controlled by different biological processes (Zhou et al., 2018). Decomposition of SOM through biological processes is a key part of these cycles. Therefore, any change or disturbance in SOM decomposition would have a direct impact on CO_2, CH_4, and N_2O emissions and global warming (Smith et al., 2014). Conservation tillage practices, including no-tillage (NT) and reduced tillage (RT), are considered the best agriculture practices to improve soil structure, minimize soil erosion, increase SOM contents and reduce GHGs emissions as compared to conventional tillage (CT) (Abdalla et al., 2016; Feng et al., 2018). In 2009 NT was practiced on almost 111 million ha of land worldwide and this figure had risen to 155 million ha in 2014 (Derpsch et al., 2010; Huang et al., 2018). However, the effects of NT practice on GHGs mitigation greatly depend on soil physiochemical properties and climatic conditions that have not been well documented in previous research studies. The effects of NT on GHGs emissions have been debated intensively and considerably vary among individual research studies (Abdalla et al., 2016; Van Kessel et al., 2013; Zhao et al., 2016). For example, the application of NT as compared to CT substantially enhanced GHGs emissions (Yao et al., 2013; Sainju, 2016; Zhang et al., 2016), while some researchers reported that NT significantly mitigated GHGs emissions from agricultural soils (Drury et al., 2006; Li et al., 2011; Tellez-Rio et al., 2015; Lu et al., 2016). Bayer et al., (2015) conducted a seven-year-long experiment and found that NT did not exhibit any significant effect on GHGs emissions. The high variability in the results from individual studies does not to reveal the actual effect of NT practice on GHGs mitigation.

1.1.2 Impact of agricultural practices on water

The agricultural soils of rainfed semiarid Mediterranean regions are characterized by low organic matter and water content (Lal, 2004b). Water availability in the rainfed semiarid Mediterranean regions is directly linked to the amount of rainfall during the cropping season and its distribution, and is the most limiting factor for high productivity (Lopez-Bellido et al., 2000). Moreover, the availability of plant nutrients (N) is limited (Hernanz et al., 2002), and therefore fertilization is a common practice. However, public concern has been raised about ground water contamination caused by NO_3^--N leaching due to intensive agricultural practices for several decades (Ersahin and Rüstü Karaman, 2001). According to the IPCC (Intergovernmental Panel on Climate Change) report, approximately 30% of agricultural N is lost through NO_3^- leaching (IPCC, 2006). The European Nitrate Directive aims to minimize diffuse NO_3^--N contamination of water bodies by identifying Nitrate Vulnerable Zones in which to avoid NO_3^--N accumulation. The threshold concentration of NO_3^--N in surface and ground water established by the European Nitrate Directive is 50 mg l^{-1} (European Union, 1998). Nevertheless, the amount of NO_3^--N leached varied from 4 kg N ha^{-1} to 300 kg N ha^{-1} in Europe (Yang et al., 2018). In Spain, the amount of NO_3^--N leached can attain figures of 150 kg N ha^{-1} or 300 kg N ha^{-1} as a result of high N fertilization rates (Ramos et al., 2002). Under both fertilizer and irrigation treatments, the maximum concentration of NO_3^--N leaching varied from 54 kg N ha^{-1} to 322 kg N ha^{-1} in central Spain (Diez et al., 2000; Daudén et al., 2004b). In a rainfed system, average seasonal rainfall and leachate NO_3^--N concentrationss ranged from 23 mm to 228 mm and 6 kg N ha^{-1} to 78 kg N ha^{-1}, respectively (Diez et al., 2000). So, understanding the NO_3^--N fate and movement is very important for better agricultural management (Stadler et al., 2008). Nowadays, computer-based models are being used as simulation tools for a better understanding of the N cycle (Kersebaum et al., 2007; Cannavo et al., 2008). The main processes which are simulated with these models include NO_3^--N leaching, N mineralization, volatilization, and immobilization, N_2 fixation, water flow, nitrification, and denitrification processes (Asada et al., 2013). The Leaching Estimation and Chemistry Model (LEACHM) developed by Hutson and Wagenet, (1991) and its modified version (Hutson, 2003) is a research-oriented model and has been widely used to examine the impacts of different mineral fertilizers on N cycle, although it is mainly used to quantify the NO_3^--N leaching from agricultural fields. The working performance of LEACHM model has been checked under different N fertilization levels, and different climate and soil conditions (Jabro et al., 1997; Sogbedji et al., 2001).. Model must be calibrated and then validated by adjusting different input parameter values to get a good relationship between model outputs and observations according to the field conditions (Vazquez-Cruz et al., 2014).

1.1.3 Impact of agricultural practices on soil and plant

Heavy metal-polluted soils have become a worldwide problem and agricultural practices have been considered the main source of heavy metal contamination (Chibuike and Obiora, 2014; Alves et al., 2016). Heavy metals can accumulate in soils due to pollution from rapidly developing industrial areas, waste disposal, mine tailings, pesticides and fertilizer application, animal manures, wastewater irrigation, and atmospheric deposition (Wuana and Okieimen, 2011). Heavy metal contamination in soils could be the ultimate threat to the ecosystems, agricultural production, and food safety and henceforth to the human health. Knowledge of the heavy metal content of soils, and the origin of these metals, are priority objectives of the European Union (EU). The European Commission in 2011 published "Towards a thematic strategy for soil protection" (European Commission, 2012), the document that established the basis and guidelines for maintaining or improving soil quality. Recently, different groups have produced reports addressing the state of the soils, impacts, and pressures, and recommendations for soil protection policymaking at the EU level (Micó et al., 2006). Analysis of heavy metal concentrations in agricultural soils is therefore important for policymaking aimed at decreasing heavy metal inputs to soil and ensuring the preservation or even enhancement of soil quality. Pig farming is considered an important industry that plays an important role in the socio-economic development of European rural areas (Daudén et al., 2004a; Martínez et al., 2017). Pig slurry is used as an organic fertilizer because it contains a large amount of macro-micronutrients. The composition of pig slurry varies depending on the animal, diet, and farm management, including water use, storage time, and tank characteristics (Sánchez and González, 2005; Yagüe et al., 2012). Mostly, pig slurry has neutral to basic pH, and a mean electrical conductivity (EC) of 26.8 dSm^{-1}. On average, pig slurry has a dry matter content of 6%, that is very low as compared to other organic fertilizers such as compost and/or manure (Ndayegamiye and Cote, 1989; Yagüe et al., 2012), and almost 70% of total N is present NH_4^+-N.

Application of pig slurry not only increases plant and soil nutrients but also heavy metal concentration as compared with synthetic fertilization (Zhang et al., 2016; Provolo et al., 2018). Despite the importance of agriculture in the Mediterranean region, there is little information on the present state of agricultural soils, as heavy metal studies have mainly referred to northern European countries (Koller et al., 2002) and there are few works on Southern Europe, particularly on the semiarid Mediterranean region after the application of pig slurry. At a national level, Corbí (2009) published a report on heavy metal levels in Spanish agricultural soils.

Plants play a crucial role in ecosystems by transferring materials from the abiotic to the biotic environment. Among all toxic heavy metals in agricultural soils, As, Cd, Hg, and Pb are highly toxic towards plants and play a critical role in food contamination (Rehman et al., 2020). At the same time, excessive concentrations of particular micronutrients (e.g. Cu, Cr, Ni, Zn, Mn) may be hazardous to both plants and human health (Chojnacka et al., 2005). These elements are necessary in sufficient quantities for the plant life cycle. However, when concentrations exceed certain thresholds, the metals become noxious to crops and significantly affect humans and animals (Berenguer et al., 2008; Leclerc and Laurent, 2017). Heavy metal concentrations in plant shoots are significantly affected by pig slurry physiochemical properties, application rate, timing, and storage (Provolo et al., 2018). This risk could induce a future restriction on pig slurry use because it contains a significant amount of micronutrients, and therefore, proper slurry management, application rate, and timing must be considered before its use.

1.2 General and detailed objectives

The general objective of this doctoral thesis was to evaluate the use of different organic and mineral fertilizers in terms of its impact on N losses due to NO_3^--N leaching, soil heavy metal accumulation, and GHG emissions within the framework of a dryland agricultural system in Catalonia, Spain.

This general objective was broken down into different sub-objectives:

Objective I

To calculate the GHG emissions after the application of animal manure and NT practice using meta-analysis techniques of previously published literature.

Objective II

To quantify N dynamics and potential NO_3^--N leaching using LEACHM model in a dryland agricultural system under fallow system when mineral fertilizers are used.

Objective III

To assess micronutrients and heavy metals in soil and in plant when pig slurries are used on barley crop.

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Chapter 2

General methodology and experimental site conditions

General methodology and experimental site conditions

2.1 General Methodology

This thesis work was divided into three parts, 1) meta-analysis to evaluate the GHGs emissions from various agricultural practices using data from the existing literature, 2) analysis of N dynamics in soil through computer modelling, and 3) analysis of nutrient and heavy meal evolution in soil and plant from experimental field data.

2.1.1 Meta-analysis study

A meta-analysis technique was used to fulfil the objective I. Meta-analysis is a useful technique to quantitatively synthesize, analyze, and then summarize the final results of different studies (Ren et al., 2017). The analytical method suggests a proper statistical analysis to combine and compare the collected results of different studies and to draw general models at different spatial scales, considering that the outcomes of already published studies are subject to uncertainties of sampling.

Different meta-analysis studies were conducted to evaluate the effect on the emissions of GHGs and crop yield of, agricultural practices such as animal manure, on the one hand, and NT practice on the other.

Metadata for different meta-analyses were obtained following the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) reporting guidelines (Moher et al., 2009). Here, the general methodologies used to gather the data for each chapter are presented. But all the data collections, specific techniques, and equipment methodologies are presented in the specif chapters (Chapters 3 and 4). Each chapter is represented by a separate set of schematic illustration (Figure 2.1, and 2.2).

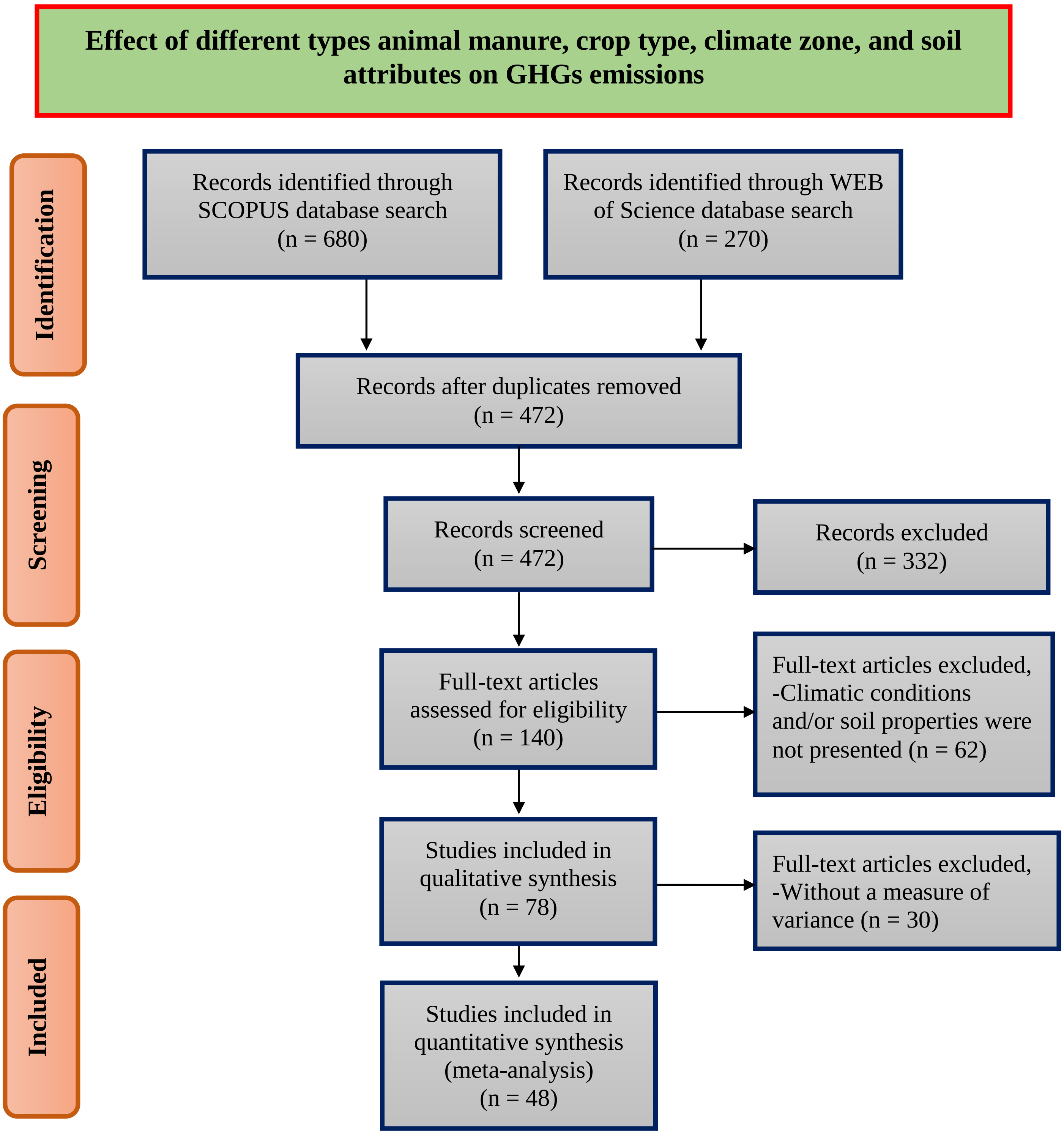

Figure 2.1. Preferred reporting items for systematic reviews and meta-analyses (PRISMA) flow diagram for the collection of the metadata for animal manure and GHGs emissions meta-analysis.

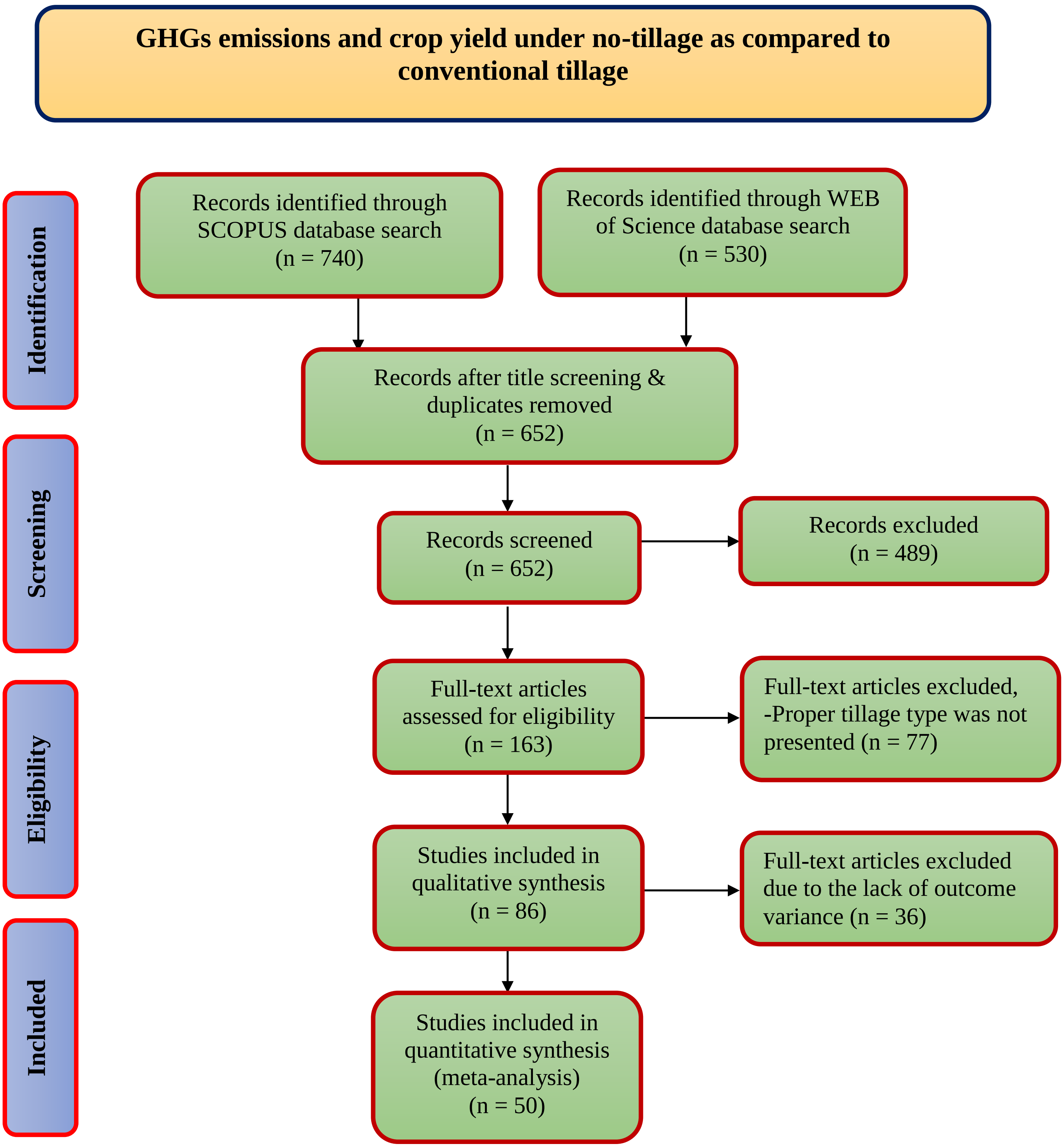

Figure 2.2. PRISMA flow diagram for the collection of the metadata for tillage and GHGs emissions meta-analysis.

2.1.2 Experimental field study

Two field experiments were performed: one for the application of LEACHM (objective II) and another for heavy metal monitoring (objective III). These experiments were run on the same experimental site in Oliola, Spain. This study was based on two long-term fertilization experiments that began in 2000 (Objective III) and 2002 (objective II) and have been ongoing since then. Both experiments were based on rainfed production of barley (*Hordeum vulgare*), mainly, and wheat (*Triticum aestivum*) in two cropping seasons, with 2007-08, 2013-14, and 2016-17 seasons of fallow.

2.2 Study area description and methodology

2.2.1 Description of experimental field

The experimental field was located in Oliola, Lleida, northeastern (NE) Spain. The specific location is 41º52'30" north latitude and 1º09'1" east longitude and is 440 m above sea level (Figure 2.3).

The climate in this area is characterized as semiarid Mediterranean, with dry summers and mild winters. Semiarid Mediterranean regions typically have high average summer temperatures (greater than 20 ºC), average annual rainfall less than 450 mm $yr^{-1,}$ and high average reference evapotranspiration (ET_o) (>1000 mm yr^{-1}) (Figure 2.4). Daily air temperature, evapotranspiration, precipitation, and meteorological data were obtained from an automatic station next to the experimental field.

The soil of the research site is well-drained, flat, non-saline, and calcareous, classified as Typic Xerofluvent (Soil Survey Staff, 2014) with a silty loam texture.

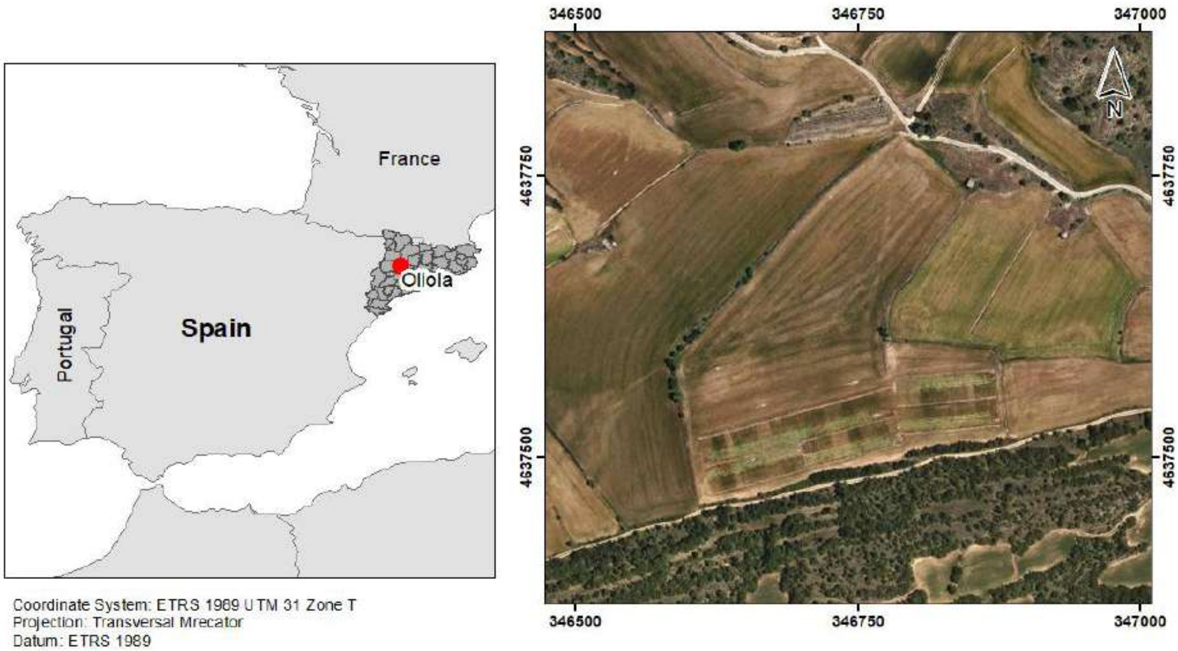

Figure 2.3. Geological location map of the experimental site (Oliola, Lleida, Spain) generated from Arc GIS 9.3 (ESRI, USA) software.

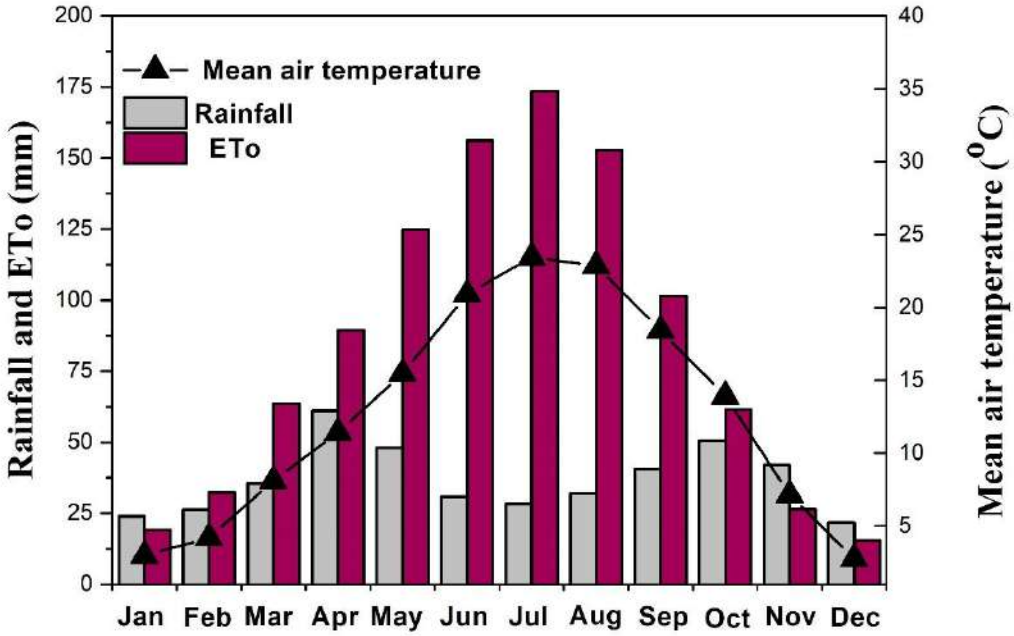

Figure 2.4. Monthly mean rainfall (mm), reference evapotranspiration (ETo) (mm), and air temperature (ºC) in the study area (period 2001-2018).

In the topsoil layer (0–0.3 m), the average organic carbon content is 11.67 g kg^{-1}, the pH is 8.2 (soil: distilled water; 1:2.5), electrical conductivity (EC) is 0.18 dS m^{-1}, the cation exchange capacity (CEC) is 11.1 $cmol^{+}$ kg^{-1}, and calcium carbonate content is 300 g kg^{-1}. Complete soil physicochemical properties for various soil depths are shown in Table 2.1.

Table 2.1. Soil physicochemical properties of the experimental site at different depths.

		Depth (m)		
Soil Properties	**Units**	**0–0.3**	**0.3–0.6**	**0.6–0.9**
Sand (Pipette method)	g kg^{-1}	152	311	115
Silt (Pipette method)	g kg^{-1}	581	486	603
Clay (Pipette method)	g kg^{-1}	267	203	282
Textural class (USDA)		Silty loam	Silty loam	Silty clay loam
pH (1:2.5, soil: water)		8.3	8.5	8.5
Ca CO_3eq (Bernard Calcimeter)	g kg^{-1}	306	329	363
Organic carbon (Walkley-Black method)	g C kg^{-1}	9.5	7.1	5.5
Bulk density (core method)	kg m^{-3}	1650	1600	1550
Cation exchange capacity	$cmol^+$ kg^{-1}	11.1	–	–
Electrical conductivity (1:5)	dS m^{-1}	0.18	–	–

2.2.2 Field management and experimental design (Objective II)

During this long-term experimental period, 2007–08, 2013–14, and 2016–17 seasons were selected as fallow periods with available data on NO_3^- and NH_4^+ in the soil profile. A randomized experimental design was used with three blocks as replications. The dimension of the control and treatment plots were 87.5 m^2. The experiment run between 2002 and 2019. Each season crops were sown in mid-October and harvested at the end of June. Calcium ammonium nitrate (CAN) ($CaNH_4(NO_3)_3$) and ammonium nitrate (NH_4NO_3) were used as sources of inorganic N-fertilizer. The area's farm advisory system guidelines were used for the application of herbicides and insecticides to control weeds and insects, respectively. To achieve objective II, data was collected from two N fertilizer treatments, N0 and N1, which were applied at the tillering stage and contained 0 kg N ha^{-1} and 120 kg N ha^{-1}, respectively. Daily gravimetric soil water contents (SWC) were also measured by the ECH2O sensor that is installed in the field. No irrigation was applied during the whole experimental period.

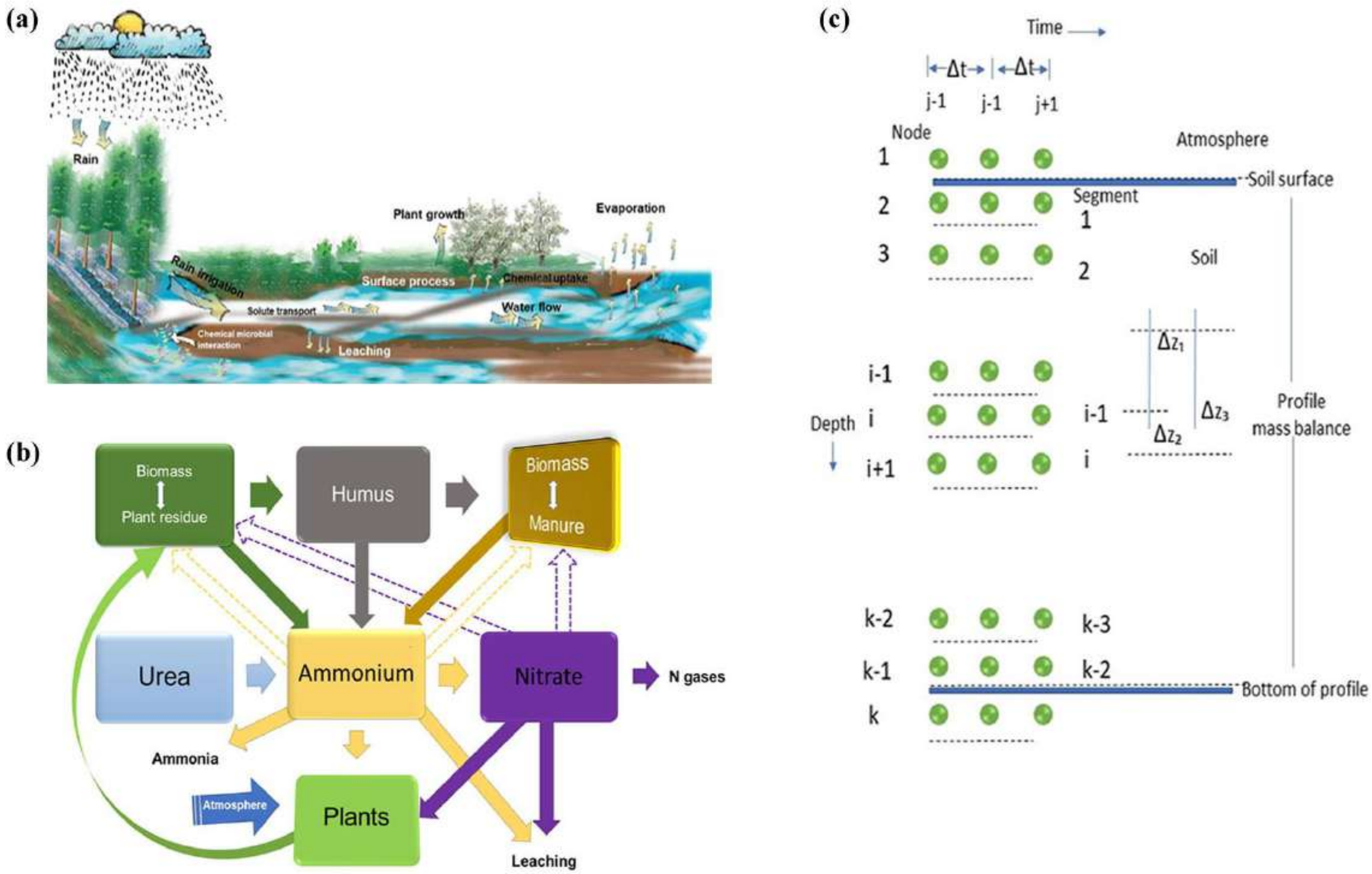

Figure 2.5. Major components and pathways (a), nitrogen cycles (b), and nodes and segments described in LEACHM. Since node spacing is uniform, Δz1 = Δz2. Successive time intervals are not necessarily of equal duration. Two boundary nodes (1 and k) are outside of the profile and are not included in profile mass balance calculations (c).

2.2.3 Field management and experimental design for Objective III

The experiment for Objective III was established in 2000 and the last year of this research experiment was 2007. The fertilizer application scheme described in Table 2.2 was adopted.

Table 2.2. Fertilizer application scheme for Chapter 6 (Objective III).

		Application rate (m^3 ha^{-1})	
Fertilizer type	**Treatment code**	**Sowing stage**	**Tillering stage**
Mineral without N	COOO	0	0
Mineral	M090	30*	60*
Pig slurry	S146	20	0
Pig slurry	S281	40	0
Pig slurry	S534	80	0

*represents the application rate in kg N ha^{-1}.

The physiochemical characteristics of the pig slurry used during the experimental period are presented in Table 2.3. Pig slurry was applied to agricultural soils using the splash plate method (Pegoraro et al., 2020; Sisquella et al., 2004). Pig slurry was derived from either fattening and/or sow pigs. Pig slurry was added twice every year. Pig slurry was applied before sowing and at tillering stage in late October and early February, respectively. Pig slurry was buried in the soil with the help of disc harrow plough at the sowing stage, while it was left on the surface of the soil at tillering application.

Table 2.3. Average physiochemical properties (± standard deviation)[a] of slurry used during the whole experimental period (2000-2020).

Parameter	**Units[b]**	**Concentration**
pH		8.2 ± 0.1
EC	mS cm^{-1}	30.7 ± 13.5
DM	g kg^{-1}	88 ± 22
Total OM	g kg^{-1}	690 ± 51
Total N	g kg^{-1}	95.5 ± 19.5
Organic N	g kg^{-1}	27.5 ± 2.5
Ammonia nitrogen	g kg^{-1}	68 ± 16
P	g kg^{-1}	17 ± 0
K	g kg^{-1}	79 ± 23
Ca	g kg^{-1}	30 ± 11.5
Mg	g kg^{-1}	9.5 ± 1.5
Na	g kg^{-1}	16.5 ± 4
S	g kg^{-1}	7 ± 0
Fe	mg ka^{-1}	3415 ± 218.7
Mn	mg ka^{-1}	558.2 ± 138.5
Cu	mg ka^{-1}	556.5 ± 158.5
Zn	mg ka^{-1}	1495.1 ± 471.9

[a] It represents the average and standard deviation of four replications
[b] EC, electrical conductivity; DM, dry matter; OM, organic matter;
parameters are measured over dry weight expect DM which is measured over fresh weight.

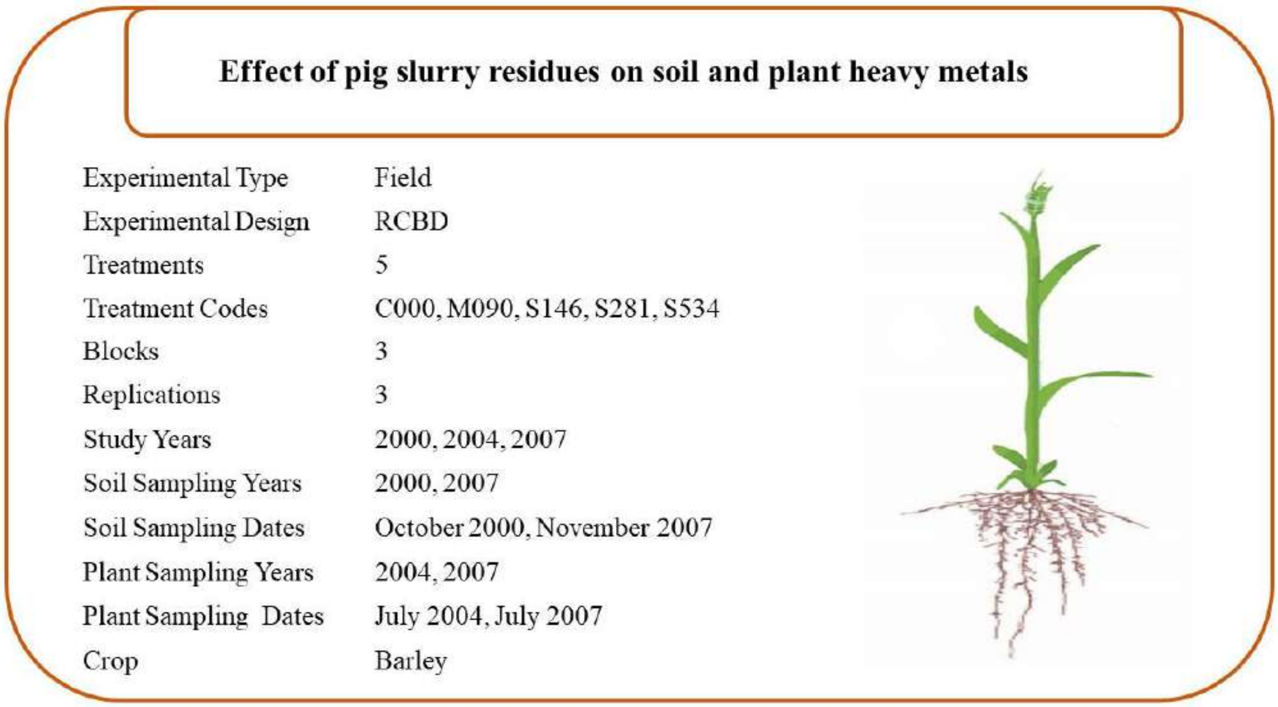

Figure 2.6. Methodology diagram related to Chapter 5 (Objective III). Abbreviations: Randomized Complete Block Design (RCBD), control (C000), mineral fertilizer treatment (M090), pig slurry treatments (S146, S281, S534).

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<u>Chapter 3</u>

This chapter contains the following accepted and already online published paper in the "*Journal of Cleaner Production.*"

Shakoor, A., Shakoor, S., Rehman, A., Ashraf, F., Abdullah, M., Shahzad, S. M., ... & Altaf, M. A. (2021). Effect of animal manure, crop type, climate zone, and soil attributes on greenhouse gas emissions from agricultural soils—A global meta-analysis. *Journal of Cleaner Production*, *278*, 124019. https://doi.org/10.1016/j.jclepro.2020.124019

Effect of animal manure, crop type, climate zone, and soil attributes on greenhouse gas emissions from agricultural soils—A global meta-analysis

Abstract

Agricultural lands, because of their large area and exhaustive management practices, have a substantial impact on the earth's carbon and nitrogen cycles, and agricultural activities consequence in discharges of greenhouse gases (GHGs). Globally, greenhouse gases (GHGs) emissions especially carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) from the agricultural sector are increasing due to anthropogenic activities. Although, the application of animal manure to the agricultural soil as an organic fertilizer not only improves soil health and agricultural production but also has a significant impact on GHGs emissions. But the extent of GHGs emissions in response to manure application under diverse environmental conditions is still uncertain. Here, a meta-analysis study was conducted using field data (48 peer-reviewed publications) published from 1989 to 2019. Meta-analysis results showed that poultry manure considerably increased CO_2, CH_4, and N_2O emissions than pig and cattle manure. Furthermore, application of poultry manure also increased ($\overline{lnRR}$ =0.141, 95% CI =0.526-0.356) GWP (global warming potential) of total soil GHGs emissions. While, the significant effects on CO_2, CH_4, and N_2O emissions also occurred at manure rate > 320 kg N ha^{-1} and > 60% water filled pore space. The maximum concentrations of CO_2, CH_4, and N_2O emissions were observed in neutral soils ($\overline{lnRR}$ =3.375, 95% CI =3.323-3.428), alkaline soils ($\overline{lnRR}$ =1.468, 95% CI =1.403-1.532), and acidic soils ($\overline{lnRR}$ =2.355, 95% CI =2.390-2.400), respectively. Soil texture, climate zone and crop type were also found significant factors to increase GHGs emissions. Thus, this meta-analysis revealed a knowledge gap concerning the consequences of animal manure application and rate, climate zone, and physicochemical properties of soil on GHGs emissions from

agricultural soils.

Keywords: meta-analysis, animal manure, GHGs emissions, soil attributes, crop type

Highlights

Manure application, particularly poultry manure significantly increased GHGs emissions from croplands.

Forty-eight publications were used to conduct a global meta-analysis study.

Overall, manure application had no effect on GWP because confidence interval overlapped with zero.

Soil physiochemical properties had a strong impact on the response of GHGs emissions to manure application.

3.1 Introduction

Emissions of GHGs like carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) from the terrestrial environment have been renowned as the main contributor to global warming (Ren et al., 2017). Agriculture was seen as the first evidence of increased human-made greenhouse gas emissions into the atmosphere (Paustian et al., 2016). It contributes almost 10 to 14% of total global GHG emissions, which includes 50–60% of N_2O and CH_4 that are directly linked with agricultural soil and its inputs like manure application and synthetic fertilizers (Shakoor et al., 2020b).

Application of animal manure to agricultural lands as organic fertilizer improved crop productivity, soil fertility and boosts organic carbon (OC) reserves in the soil, but also affects GHGs emissions (Zhou et al., 2017b). Globally, 7.0 billion tons of animal manure is used annually for agricultural lands (Thangarajan et al., 2013). The total quantity of produced manure, for each type of animal, can be calculated as an average between the quantity of manure produced per animal, and the number of animals (IPCC, 2006). Animal manure contributes up to 37% of global GHGs emissions (Vac et al., 2013). Soil texture (Oertel, et al., 2016), soil pH (Wu et al., 2018), water filled pore space (WFPS) (Säurich, et al., 2019), crop type (Severin, et al., 2015) and crop duration (Tongwane et al., 2016) have also been documented important factors of CO_2, CH_4 and N_2O emissions from the terrestrial environment.

Atmospheric CO_2 plays an important role in the global carbon cycle in the atmospheric system. Human activities such as the burning of fossil fuel and deforestation significantly increased the CO_2 concentration in the atmosphere from around 280 to 387 ppm (parts per million) and, recently, have even exceeded 400 ppm (parts per million). This CO_2 concentration is projected to increase considerably by 2100 (Goldman et al., 2017). In the earth system, this global carbon cycle contributes to a large amount of carbon, which is connected through the exchange of carbon fluxes (Ciais et al., 2013). The terrestrial environment is intimately linked to atmospheric CO_2 levels by the sequestration of carbon in the soil and biomass, which is emitted by the decomposition of organic manure (Drigo et al., 2008). In a research study, it was found that the application of animal manure potentially enhances the carbon content in the soil and then converts into a net CO_2 sink (Gattinger et al., 2012).

Atmospheric CH_4 has received a lot of attention recently, simply because it is a very important and long-lasting GHG also contributing to global warming (Wang et al., 2016), which exhibits relative global warming potential of 265 (Weller et al., 2015), 34 times higher than that of CO_2 present in the atmospheric environment, considered on an equivalent mass basis. The total concentration of CH_4 in the atmosphere is approximately 1,780 ppb, which is higher than pre-industrial levels. Agricultural lands act as anthropogenic sources and contribute about 50% of the total flux of CH_4 emissions into the atmosphere (Wang et al., 2016). The application of animal manure and synthetic fertilizer can be considered the best predictor of CH_4 emission from agricultural lands (Shakoor et al., 2020a).

Following CO_2 and CH_4, N_2O is the third most important GHG, contributing up to 6% in global warming. While, N_2O has 298 times more GWP compared to CO_2 and also favors ozone (O_3) destruction (Charles et al., 2017). The emission of N_2O from agricultural sources is considered to be one of the main contributors to the global warming budget. Agricultural lands approximately contribute up to 68% in the atmospheric N_2O emissions (Shakoor et al., 2018). Application of animal manure cannot only enhance soil pH (Whalen et al., 2000) but also improved soil aggregation, porosity as well as hydraulic conductivity (Haynes & Naidu, 1998), which can control different biotic and abiotic processes leading N_2O production in soils (Shakoor et al., 2016). Several studies show the effects of different animal manures and synthetic fertilizers on N_2O emission from agricultural lands, indicating, that different manures and dung management practices, for example, manure storage, animal houses (Anitha & Bindu, 2016), and application of manure in the field (Ku et al., 2017), causes the emission of N_2O into the atmosphere.

Meta-analysis is a useful technique to quantitatively synthesize, analyze, and then summarize the final results of different studies (Ren et al., 2017). The analytical method suggests a proper statistical analysis to combine and compare the collected results of different studies and to draw general models at different spatial scales, and the outcomes of already published studies are treated as if they are subject to uncertainties of sampling (Freeman et al., 1986). Detailed information about how different animal manures affect GHGs is critical to assessing the potential of manure application to croplands for mitigation the GHGs emissions.

The climate sensitivity of all three GHGs (CO_2, CH_4, and N_2O) emissions is poorly known, which makes it difficult to project how changing manure and/or synthetic fertilizer use and climate will influence radiative forcing and the ozone (O_3) layer. A decent number of research scientists have conducted the meta-analysis about N_2O emissions from soils considering different parameters like animal manure application and rate (Zhou et al., 2017b), urine-derived (López-Aizpún et al., 2020), crop residues (Chen et al., 2013), no-tillage (Zhao et al., 2016), salinization (Zhou et al., 2017a) and climate (Van Kessel et al., 2013). But, a few numbers of meta-analysis studies are available considering the CO_2, CH_4, as well as N_2O emissions simultaneously under the application of animal manures and rates, climate, and soil attributes. So, we conducted a meta-analysis to fulfill this gap.

In this meta-analysis study, we systematically compared the GHGs emissions of the soil under different animal manures, the quantity of manure, climate zone, soil pH, water filled pore space (WFPS), soil texture, crop type, and crop duration. The main objectives of this study were to address the following questions: 1) Do the application and amount of different animal manures affect soil GHGs emissions as compared to control and/or no fertilizer? 2) Which GHG more affected by the application of animal manure and manure rate? 3) Do crop duration and crop species important factors for regulating the GHGs emissions? and finally, 4) How do soil attributes and different climate zones affect soil GHGs emissions?

3.2 Materials and methods

3.2.1 Data collection

A systematic literature search approach was followed to collect research articles for meta-analysis. To cover the main objectives of this meta-analysis, a total of 950 peer-reviewed research publications were collected that reported GHGs emissions in agricultural soils following application of animal manures into the search engines of Google Scholar, Scopus, and Web of

Science to identify relevant research articles for inclusion in the meta-analysis, to a cut-off date of 31st December 2019. The keywords 'manure' 'animal manure' 'pig' 'swine' 'cattle' 'dairy' 'poultry' 'carbon dioxide or CO_2' 'methane or CH_4' and 'nitrous oxide or N_2O' were used to search the publications.

Peer-reviewed publications selected by using the following criteria: a) experiments who had at least one pair of data (control and treatment) and calculated cumulative CO_2, CH_4, and/or N_2O emission fluxes; b) clearly described experimental method with crop type and duration, and c) physiochemical properties of soil. In total, 48 peer-reviewed publications on manure application were selected published from 1989 to 2019 (Table 3.1). Most research publications reported emission flux in tables that could easily be transferred into the dataset directly. Emission data presented in figures, GetData (version 2.26) Graph Digitizer software (http://getdata-graph-digitizer.com/index.php) was used to extract the data. From each research publication, we extracted the cumulative values (kg ha^{-1}) of all three GHGs emissions in the dataset. For manure application and/or synthetic fertilizer, kg N ha^{-1} unit was used and converted all other units (such as Megagram (Mg N ha^{-1})) into kg N ha^{-1} where it needed. We also collected the means, standard deviations (SD), and sample sizes from treatment and control for each research study. If research publications only presented standard errors (SE), then the SD values were calculated from SE.

Table 3. 1. Description of crop type, location, number of observation, soil attributes, manure type and rate included in this meta-analysis.

Study number	Study Reference	Journal	Country	Number of observations	Crop type	Soil pH	WFPS (%)	Soil textural class	Climate zone	Manure type	N rate (kg N ha^{-1})
1	Meijide et al., (2007)	AEE	Spain	7	Maize	8.1	46-70	Sandy loam	Warm temperate	Pig	0-250
2	Van Zwieten et al., (2013)	STE	Australia	4	Maize	4.8	_	Clay loam	Sub-tropical	Poultry	100-120
3	Maris et al., (2016)	STE	Spain	13	Rice	8.1-8.5	_	Silty clay loam and Silty loam	Warm temperate and Semi-arid	Poultry and Pig	0-170
4	Zhang et al., (2018)	STE	China	8	Wheat	7.3-8.7	20-79	Loam	Cool temperate	Pig	0-410
5	De Rosa et al., (2018)	STE	Australia	18	Green beans and Sweet corn	7.8	37-79	Clay loam	Sub-tropical	Poultry	0-367
6	Dambreville et al., (2008)	AEE	France	6	Maize	5.9-6.9	46	Silt loam	Warm temperate	Pig	0-180
7	(Velthof et al., 2011)	AEE	Netherlands	43	Grassland and Maize	4.8-7.1	_	Clay and sandy	Warm temperate	Cattle and Pig	0-460
8	Fangueiro et al., (2008)	BT	England	7	Grassland	6-6.7	_	Clay loam	Cool temperate	Cattle	0-354
9	Sanz-Cobena et al., (2019)	AE	Spain	2	Fallow	8.1	64-70	Sandy loam	Warm temperate	Pig	63-77
10	Thornton et al., (1998)	AE	USA	4	Grassland	5.5	77.3	Silty clay loam	Sub-tropical	Poultry	0-336

Study number	Study Reference	Journal	Country	Number of observations	Crop type	Soil pH	WFPS (%)	Soil textural class	Climate zone	Manure type	N rate (kg N ha^{-1})
11	Rodhe et all., (2012)	BSE	Sweden	7	Fallow	7.1	23.4-31.6	Silty clay loam	Cool temperate	Pig	0-140
12	Severin et al., (2015)	PSE	Germany	21	Maize	4.3-5.8	42-67	_	Warm temperate	Pig	0-150
13	Ball et al., (2004)	SUM	Scotland	6	Grassland	_	_	Clay loam	Cool temperate	Cattle	0-430
14	Collins et al., (2011)	SBB	USA	12	Maize	6.7	36.9-42.1	Silt loam	Warm temperate	Cattle	0-336
15	Chadwick et al., (2000)	JEQ	England	6	Grassland	6.9	38.1-55.1	Sandy loam	Cool temperate	Cattle and Pig	0-295
16	Jarecki etal., (2008)	JEQ	USA	6	Fallow	6.9-7.0	48-54	Sandy loam and Clay	Warm temperate	Pig	0-200
17	Chantigny et al., (2016)	CJSS	Canada	12	Barley	6.5-6.8	_	Sandy loam and Silty clay	Cool temperate	Pig	0-65
18	Li et al., (2013)	EJSB	China	6	Maize	5.76-6.01	47-52	_	Cool temperate	Pig	0-450
19	Mapanda et al., (2011)	PS	Zimbabwe	24	Maize	5.4-6.5	3.3-24.2	Clay and Sandy loam	Sub-tropical	Cattle	0-120
20	Rochette & Côté, (2000)	CJSS	Canada	3	Maize	_	_	Loam	_	Pig	0-252
21	Petersen, (1999)	JEQ	Denmark	10	Barely	5.9	55	Sandy	Cool temperate	Pig and Cattle	80-120

Study number	Study Reference	Journal	Country	Number of observations	Crop type	Soil pH	WFPS (%)	Soil textural class	Climate zone	Manure type	N rate (kg N ha^{-1})
22	Zhou et al., (2014)	ES	China	8	Wheat and Maize	8.3	65-80	_	Sub-tropical	Pig	0-150
23	Das & Adhya, (2014)	GD	India	5	Rice	6.16	_	Sandy clay loam	Tropical	Poultry	0-120
24	Liang et al., (2013)	FCR	China	42	Rice	6.9	_	Clay loam	Sub-tropical	Pig	0-270
25	Wu et al., (2019)	PSE	China	4	Rice	6.9-7.22	_	_	Cool temperate	Pig	180-266
26	Vallejo et al., (2006)	SBB	Spain	7	Potato	7.9	52-60	Clay loam	Warm temperate	Pig	0-300
27	Wang et al., (2013)	JSS	China	5	Rice	7.29-7.41	_	Clay loam	Sub-tropical	Pig	0-180
28	O' Flynn et al., (2013)	JOEM	Ireland	3	Fallow	6.26	53	Sandy loam	Cool temperate	Pig	0-90
29	Sherlock et al., (2000)	JEQ	NewZealand	3	Grassland	5.36	_	Silt loam	Sub-tropical	Pig	0-60
30	Li et al., (2016)	CJSS	Canada	5	Fallow	6.58	6.58	Loam	Cool temperate	Cattle	0-120
31	Grave et al., (2015)	STR	Brazil	5	Wheat	5.3	68	Silty clay loam	Sub-tropical	Pig	0-140
32	X.M.Yang, (2017)	ACS	Canada	14	Fallow	_	30	Clay loam	Cool temperate	Pig	0-165
33	Sampanpanish, (2012)	MAS	Thailand	4	Rice	5.3	_	Clay	Sub-tropical	Cattle	0-156
34	Dendooven et al., (1998)	BFS	Belgium	4	Fallow	6.2	18.7	Silt loam	Warm temperate	Pig	0-250
35	Dinuccio et al., (2011)	AFST	Italy	4	Fallow	7.43	9.8	Loamy sand	_	Cattle	0-21

Study number	Study Reference	Journal	Country	Number of observations	Crop type	Soil pH	WFPS (%)	Soil textural class	Climate zone	Manure type	N rate (kg N ha^{-1})
36	Sistani et al., (2019)	Es	USA	10	Maize	4.7	37-42	Silty clay	Sub-tropical	Poultry	0-224
37	Brennan et al., (2015)	PO	Ireland	4	Fallow	7.45	_	Sandy loam	Sub-tropical	Cattle	295
38	Bourdin et al., (2014)	AEE	Ireland	6	Grassland	5.5	29.4	Sandy loam	Warm temperate	Cattle	0-275
39	Leytem et al., (2019)	SBB	USA	20	Wheat - Barely-Sugar Beet	8	57-75	Silt loam	Tropical	Cattle	0-1315
40	Bertora et al., (2008)	SBB	Italy	6	Maize	7.9	63	Loam	_	Pig	0-170
41	Smith & Owens, (2010)	CSSPA	USA	4	Grassland	_	_	Silt loam	Tropical	Poultry and Pig	0-420
42	Gao et al., (2014)	CJSS	Canada	4	Alfalfa	7.8	50	Sandy loam	Cool temperate	Pig	0-410
43	Cote & Ndayegamiye, (1989)	CJSS	Canada	6	Maize	5.4	_	Silty loam	Cool temperate	Cattle and Pig	0-160
44	Herr et al., (2019)	JPNSS	Germany	8	Maize	7	28-30	Loam	Warm temperate	Cattle	0-170
45	Asgedom et al., (2014)	AJ	Canada	6	Rapeseed	7	_	Clay	Cool temperate	Cattle	0-137
46	Syväsalo et al., (2006)	AEE	Finland	4	Grassland-Cereal	_	_	Sandy	Cool temperate	Cattle	0-200
47	Verdi et al., (2019)	IJAM	Italy	3	Maize	_	_	Silty clay	Warm temperate	Pig	0-150
48	Abagandura et al., (2019)	JEQ	USA	24	Soybean-Maize-	5.2-6.1	28.9-45	Sandy loam-Clay loam	Cool temperate	Cattle	0-150

Journal: AEE (Agricultural, Ecosystems & Environment), STE (Science of the Total Environment), BT (Bioresource Technology), AE (Atmospheric Environment), BSE (Biosystems Engineering), PSE (Plant, Soil and Environment), SUM (Soil Use and Management), SBB (Soil Biology & Biochemistry), JEQ (Journal of Environmental Quality), CJSS (Canadian Journal of Soil Science), EJSB (European Journal of Soil Biology), PS (Plant and Soil), ES (Ecosystems), GD (Geoderma), FCR (Field Crops Research), JSS (Journal of Soils and Sediments), JOEM (Journal of Environmental Management), STR (Soil & Tillage Research), ACS (Acta Ecologica Sinica), MAS (Modern Applied Science), BFS (Biology and Fertility of Soils), AFST (Animal Feed Science and Technology), Es (Environments), PO (Plos One), CSSPA (Communications in Soil Science and Plant Analysis), JPNSS (Journal of Plant Nutrition and Soil Science), AJ (Agronomy Journal), IJAM (Italian Journal of Agrometeorology).

Other informations that were used in the dataset included the following: type of manure, amount of manure, soil pH, WFPS, soil texture, crop type, crop duration time, and climate zone. The manure type grouped as pig, cattle, and poultry; amount of manure, grouped as ≤ 120 kg N ha^{-1} (low), ≤ 320 kg N ha^{-1} (medium) and > 320 kg N ha^{-1} (high) doses as did by Cayuela et al., (2017) ; soil pH, grouped to ≤ 6.5 (acidic), 6.6-7.3 (neutral), > 7.3 (alkaline) (Havlin et al., 2013); WFPS grouped as < 30%, 30-60%, > 60%; soil texture was grouped into different categories following the USDA, (1999) (clay, clay loam, loam, sandy, sandy clay loam, sandy loam, silt clay, silt loam, silty clay loam); crop type and crop duration time grouped as barley, fallow, grassland, maize, rice, soybean, sweet corn, wheat and ≤ 320 days, 321-725 days, > 725 days, respectively; and climate zone divided into 4 groups as cool temperate, semi-arid, tropical, sub-tropical and warm temperate (Zhou et al., 2017b).

3.2.2 Meta-analysis

For the meta-analysis, we used a response ratio (*RR*, natural log of the ratio) as the effect size to calculate the effects of manure application on GHGs emission from agricultural soils (Hedges et al., 1999) by using the following equation:

$$RR = \ln(\overline{xt}/\overline{xc}) = \ln(\overline{xt}) - \ln(\overline{xc}) \qquad (1)$$

Where the subscript of $\overline{xt}$ and $\overline{xc}$ represents the mean value of treatment and control, respectively. If the *RR* value is zero, *RR* > 1 and *RR* < 1, its mean that manure treatment had no, positive and negative effect on GHGs emissions, respectively.

The natural logarithm of *RR* (*lnRR*), the effect size, was calculated for each treatment in every trial/experiment (Hedges et al., 1999). The variance (ν) of each *lnRR* for each study was calculated by using the equation (2);

$$\nu = \frac{St^2}{ntxt^2} + \frac{Sc^2}{ncxc^2} \qquad (2)$$

where St and Sc are the standard deviation of a treatment and reference control, and nt and nc are the number of samples in a treatment and reference control, respectively. For each research study, the weighting factor (ω) was measured as the inverse of the pooled variance $(1/\nu)$.

The mean effect sizes were calculated as;

$$\overline{lnRR} = \frac{\sum(lnRRi \times \omega i)}{\sum \omega i} \quad (3)$$

Where ωi and *lnRRi* were the weight and effect size from the ith comparison, respectively.

The GWP was also calculated when fluxes for all three GHGs emissions (CO_2, CH_4, and N_2O) were reported in every single study. The IPCC factor was used to calculate the GWP (kg CO_2-eq ha^{-1} yr^{-1}) (IPCC, 2013) in over a 100-year time horizon:

$$\mathrm{GWP} = (CO_2 \times 1) + (N_2O \times 298) + (CH_4 \times 34) \quad (4)$$

3.2.3 Statistical analysis

A random-effects meta-analysis model was used to examine the dataset as early as explained by (Michael et al., 2009). METAWIN 2.1 (Rosenberg et al., 2000) and OpenMEE (Wallace et al., 2017) software were used to calculate the mean effect sizes of the dataset and 95% bootstrapped confidence intervals (CIs) were generated using 4999 iterations. The results were considered significant if the 95% CI of cumulative CO_2, CH_4, and N_2O emissions did not overlap with zero and the randomization tests resulted $P < 0.05$. Statistical results such as total heterogeneity (Q_t) in effect sizes among studies were also calculated using OpenMEE software. The relationship is significant if $P < 0.05$.

3.3 Results and discussion

3.3.1 Effects of manure type and manure rate on GHGs emissions

Of the total, 324 and 242 paired-wise observations were selected for manure type and manure rate, respectively. Three types of manure (pig (n=115), cattle (n=101) and poultry (n=28)) and three levels of manure rate ($\leq$ 120 kg N ha^{-1} (n=71), $\leq$ 320 kg N ha^{-1} (n=134) and > 320 kg N ha^{-1} (n=37)) were chosen to check the effect on GHGs emissions. The application of different manure types and manure rates had significantly positive effects on CO_2, CH_4, and N_2O emissions. Based on meta-analysis results, the overall effect sizes ($\overline{lnRR}$) of manure type and manure rate on CO_2, CH_4, and N_2O emissions were significantly greater than zero (Figure. 3.1a, 3.1b and 3.1c), [but slightly negative effects on CO_2 emission related to manure rate was also observed (Figure. 3.1a (i))], showing that application of different manure type and manure rate considerably increased CO_2, CH_4 as well as N_2O emissions from the agricultural soil as compared to controls.

Manure rate and manure type had a strong effect on CO_2 emission ($\overline{lnRR}$ =0.635, 95% CI =0.01-1.26) and ($\overline{lnRR}$ =0.125, 95% CI =-0.925-1.175), CH_4 emission ($\overline{lnRR}$ =2.31, 95% CI =1.161-3.481) and ($\overline{lnRR}$ =1.495, 95% CI =1.135-1.855), and N_2O emission ($\overline{lnRR}$ =1.123, 95% CI =1.004-1.241) and ($\overline{lnRR}$ =0.862, 95% CI =0.035-1.69), respectively (Table S2). The total heterogeneity (Q_t) was also calculated for both parameters (Table S3). The statistical results showed that the manure rate and manure type had a positive effect on CO_2 emissions.

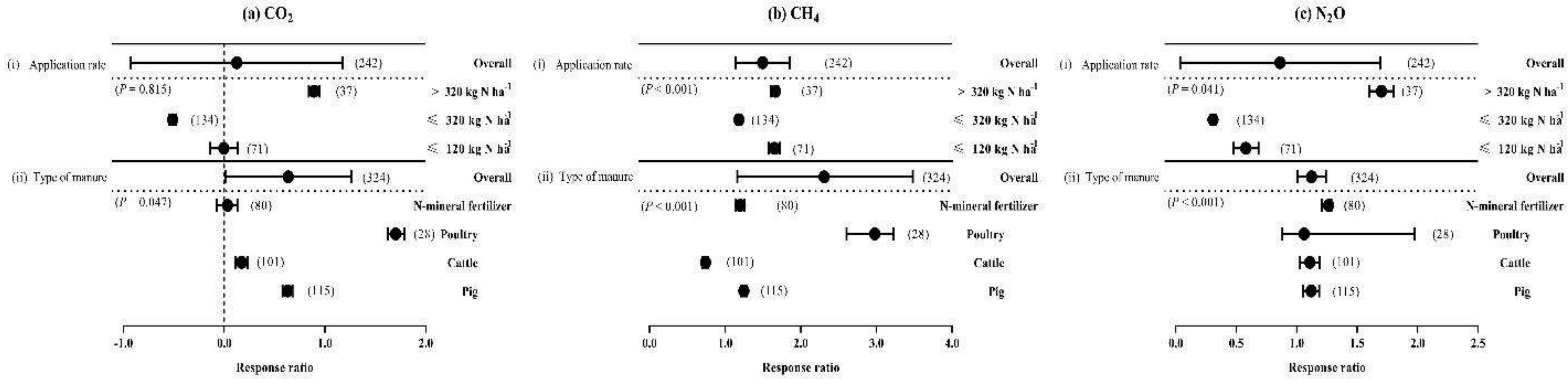

Figure 3.1. Impact of (i) animal manure and mineral fertilizer application rate (kg N ha^{-1}) and (ii) manure type on (a) CO_2, (b) CH_4 and (c) N_2O emissions from agricultural soils. Symbols represent mean effect sizes with 95% confidence intervals. Sample sizes are presented in parentheses and the *P* values are shown in the panel.

In manure rate, > 320 kg N ha^{-1} ($\overline{lnRR}$ =0.891, 95% CI =0.84-0.942) had maximum effects on CO_2 emission than other rates while the negative effect was also observed at ≤ 320 kg N ha^{-1} ($\overline{lnRR}$ =-0.512, 95% CI =-0.546--0.479) (Figure. 3.1a (i), Table (S2)). Alternatively, poultry manure had the notably highest effects on CO_2 emission as compared to pig and cattle manures (Figure. 3.1a (ii)). On the other hand, a significant effect of manure rate and manure type were also observed on CH_4 emissions (Q_t=6445.801, P < 0.011) and (Q_t=389.849, P < 0.001) (Table S4), and on N_2O emissions (Q_t=27.879, P < 0.001) and (Q_t=757.926, P < 0.027) (Table S5), respectively. According to our meta-analysis, the application of poultry manure and manure at the rate of > 320 kg N ha^{-1} also had the maximum effect on CH_4 and N_2O emissions (Figure. 3.1b and 1c).

Animal manure contains nitrogen (N), phosphorus (P), and other micronutrients that plants need to grow. Farmers can often save money by properly using manure as a fertilizer (Cavalli et al., 2017). On the other hand, the application of animal manure has been a big concern worldwide because manure contributes up to 37% of global GHGs emissions (Vac et al., 2013).

The GHGs emissions from agricultural soils mostly depend on soil characteristics, environmental conditions and type and amount of manure. According to our meta-analysis, results revealed that the application of different animal manure significantly enhanced GHGs emissions (Figure. 3.1a, 1b and1c). Our meta-analysis showed that poultry manure significantly enhanced the GHGs emissions from the soil than pig and cattle manures. Emission of CO_2 from agricultural soils is mainly emitted through microbial activities. Autotrophic microbial communities significantly increase the decomposition of soil organic matter (SOM) results in increase soil organic carbon (SOC) as well as CO_2 emission (Watts et al., 2011) because CO_2 is mostly emitted from agricultural soil as a result of the soil microbial respiration and plant root respiration (Ray et al., 2020).

The CH_4 emission from croplands mostly due to anaerobic decomposition of organic matter (Praeg et al., 2016). The application of poultry manure significantly enhanced CH_4 emissions from croplands. This might be because of manure application increase soil microbial biomass and also activities. Therefore, manure application provides more oxidizable C content to the methanotrophs under oxygen limiting conditions, which would increase CH_4 emissions (Pathak, 2015).

Poultry manure also significantly increases N_2O emission from croplands mainly due to their easily decomposable SOC relative to other manures (Zhou et al., 2017b). One main reason for high N_2O emission from agricultural soils may be due to high rates of net N mineralization of the poultry manure (Akiyama et al., 2004), which possibly increased nitrification as well as denitrification rates and, subsequently, N_2O production (Hayakawa et al., 2009).

The manure and mineral nitrogen application rates were directly proportional to the GHGs emissions because C, N, phosphorus (P) and potash (K) contents were increased accordingly in the soil. Zhou, et al., (2017b) also conducted a global meta-analysis and proved that poultry manure produces more GHGs emission as compared to other manures (pig and cattle). Maris et al., (2016) had examined the response of GHGs emission using different animal manures and showed that poultry manure increased GHGs emission than pig and cattle mainly due to the higher application rate. Smith et al., (2010) also showed a similar trend in their research study. Because, poultry manure has high C and N contents than pig and cattle manure (Ahn, et al., 2010). Shen, et al., (2015) also proved that poultry manure has more N content than cattle and pig manure. The rate of manure is also a very important factor for getting the maximum production but the amount of manure is directly proportional to GHGs emissions. De Rosa et al. (2018) conducted research study using different animal manures with different rates. They all found that a higher amount of manure significantly affects GHGs emissions which were similar to our findings.

3.3.2 Water filled pore space (WFPS) and soil pH

Soil pH and WFPS have been recognized as important factors of GHGs emissions (Butterbach-Bahl et al., 2013). Figure 3.2 shows the effect sizes of WFPS and soil pH on GHGs emissions from agricultural soils after manure application. From the total, 260 and 408 observations were chosen for WFPS and soil pH, respectively. WFPS was classified as < 30% (n=53), 30-60% (n=144) and > 60% (n=63), on the other hand, soil pH was also categorized into three classes like ≤ 6.5 (n=189), 6.6-7.3(n=118) and > 7.3 (n=101).

The present meta-analysis showed that overall effect sizes of WFPS on CO_2 ($\overline{lnRR}$ =0.212, 95% CI =0.102-0.323), CH_4 ($\overline{lnRR}$ =0.841, 95% CI =-0.644-2.326), and N_2O ($\overline{lnRR}$ =0.394, 95% CI =-0.394-0.913) emissions were significantly greater than zero (Table S2), indicating that WFPS significantly enhanced CO_2, CH_4, and N_2O emissions. For CO_2, $\overline{lnRR}$ was positive when WFPS was greater than 30%, showing the positive effects on CO_2 emissions and 30-60% WFPS had more effect than > 60% WFPS (Figure 3.2a (i)). Otherwise, maximum emissions of CH_4 and N_2O were observed at > 60% WFPS (Figure. 3.2b (i) and 3.2c (i)). The maximum emission of CO_2 was observed when WFPS 35-55% (Alluvione et al., 2009) which was in the range of our findings. Our results were also similar to those estimates studied by Sakabe et al. (2015). While N_2O and CH_4 emissions were normally low at WFPS levels ≤ 60%.

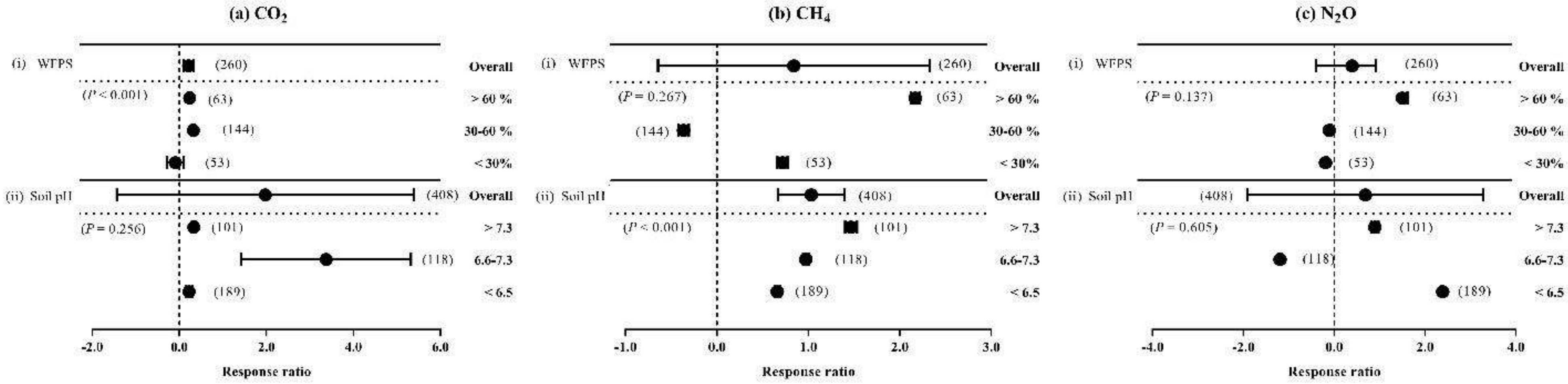

Figure 3.2. Effect of (i) WFPS (%) and (ii) soil pH on (a) CO_2, (b) CH_4 and (c) N_2O emissions from agricultural soils. Symbols represent mean effect sizes with 95% confidence intervals. Sample sizes are presented in parentheses and the *P* values are shown in the panel.

The emission of CO_2 increased at < 50% WFPS indicating the microbial processes like mineralization were less affected by low moisture content. At > 70% WFPS values, soil CO_2 emissions were significantly inhibited by lack of available oxygen (Franco-Luesma et al., 2020), making soil conditions that promote denitrification (Rowlings et al., 2010). Several factors are influencing CH_4 emissions in higher WFPSs. Soil conditions that support methanotrophic rather than a methanogenic activity which was favored by low temperature and the high percentage of WFPS (> 60%) (García-Marco et al., 2014). Another study found that in the anaerobic environmental conditions, a higher amount of SOM would also contribute to the low CH_4 absorption (Sakabe et al., 2015).

Maximum N_2O emissions with increasing the WFPS were frequently reported from different research studies (Ruser et al., 2001). A higher amount of water content significantly improved the denitrification process in soil and maximum activity was observed at a WFPS 70% (Ruser et al., 2006). Another study reported the soil with 90% WFPS had the maximum N_2O emissions. These results show that emissions of N_2O at higher WFPSs were significantly influenced by SOC contents. The greater specific substrate may have preferred the anoxic microsites formation, which is well-known to enhance N_2O emissions (Flessa and Beese, 2000).

The overall effect sizes of soil pH on CO_2 ($\overline{lnRR}$ =1.977, 95% CI =-1.434-5.388), CH_4 ($\overline{lnRR}$ =1.032, 95% CI =0.669-1.396) and N_2O ($\overline{lnRR}$ =0.686, 95% CI =-1.91-3.281) emissions were also significantly > 0 (Table S2), suggested that positive effects on GHGs emissions. The maximum concentrations of CO_2, CH_4, and N_2O emissions were observed in neutral soils (pH = 6.6-7.3), alkaline soils (pH > 7.3) and acidic soils (pH ≤ 6.5), respectively (Figure. 3.2a (ii), 3.2b (ii) and 3.2c (ii)). Wu et al., (2019) studied and showed that the maximum emissions of CO_2 were seen in acidic soils because the manure application increases soil pH.

The CO_2 emission increases in acidic soil after manure application because organic manure generally enhances soil pH and consequently promotes the CO_2 solubility and the formation of bicarbonate acid (Rochette and Gregorich, 1998). In acidic soils, the N_2O reductase (N_2OR) activities inhibited which results in the reduction of N_2O to N_2 (Bakken et al., 2012).

Consequently, in acid soils, the application of manure could significantly promote N_2O than N_2 by the denitrification process and consequently enhance N_2O emissions. Another research found that nitrification as well as denitrification processes are mainly affected by soil pH and result in N_2O emissions. Normally, autotrophic nitrifiers prefer neutral and/or slightly alkaline conditions for oxidizing NH_4^+ to NO_3^-, and consequently, the nitrification process is frequently low in acidic soils (Chen et al., 2013).

It would be needed for the anaerobic situation to activate methanogenesis bacteria (Ball, 2013). The best pH value for this situation is ranged from 6.6 to 7.6 and the ideal value would be at 7.2. The growth of these bacteria will be limited and eliminated less than 5 and more than 8.5 (Staley et al., 2011). Biological degradation of SOM is done with anaerobic bacteria and optimal activity was found with pH 7 (Horn et al., 2003). Wang et al., (1993) also studied and reported that the maximum CH_4 emissions were observed in the pH range of 6.9 to 7.1 (neutral soil pH) because methanogenic is acid sensitive. Normally, the best pH for methanogenesis is considered to be approximate 7.0. Thus, our results were similar to the previous findings of the researchers. According to our meta-analysis results, total heterogeneity showed that WFPS and soil pH had a significantly positive effect on GHGs emissions (Table S3, S4, and S5).

3.3.3 Soil texture

Effect sizes of soil texture on CO_2, CH_4 and N_2O emissions after manure application are shown in figure 3.3. According to our meta-analysis dataset, all soils were classified into different textural classes e.g. clay, clay loam, loam, sandy loam, sandy, sandy clay loam, silt loam, slit clay and silty clay loam.

The overall effect sizes of soil texture on CO_2 ($\overline{lnRR}$ =0.285, 95% CI =0.143-0.427), CH_4 ($\overline{lnRR}$ =0.706, 95% CI =0.342-1.069) and N_2O ($\overline{lnRR}$ =0.946, 95% CI =-0.004-1.897) emissions were significantly positive (Table S2), revealing that soil texture had a very strong effect on GHGs emissions from the terrestrial environment. All textural classes showed significantly positive response to CO_2 emission and maximum emission of CO_2 was observed in silt loam soil (Figure 3.3a). On the other hand, all textural classes also gave a considerably positive response to CH_4 and N_2O (except loamy soil) emissions. The highest concentration of CH_4 and N_2O emissions were found in silty clay loam and sandy loam soils, respectively (Figure 3.3b and 3.3c). The total heterogeneity (Q_t) was also suggested that soil texture had a positive effect on GHGs emissions (Table S3, S4, and S5).

The terrestrial environment serves as a source and sinks for GHGs emissions and soil attributes, in particular, the soil textural classes play a critical role in GHGs emissions (Oertel et al., 2016). Maximum emissions of CO_2 were observed in fine-textured soils compared to coarse-textured soils (Dilustro et al., 2005) which were similar to our results. The mineralization process depends on the bio-availability of organic matter contents. Soils with high clay contents significantly decreased CO_2 emissions because the high capacity of the clay fraction decreased mineralization process (Jäger et al., 2011).

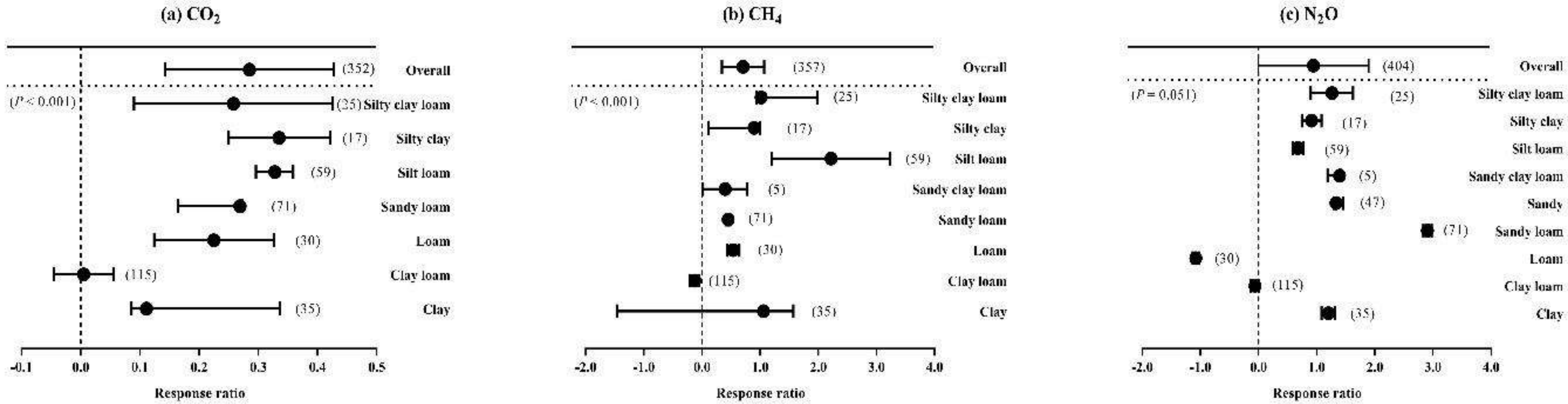

Figure 3.3. (a) CO_2, (b) CH_4 and (c) N_2O emissions from agricultural soils affected by soil textural class. Symbols represent mean effect sizes with 95% confidence intervals. Sample sizes are presented in parentheses and the *P* values are shown in the panel.

Meta-analysis results show that maximum CH_4 emissions were emitted from fine-textured soils after manure application. Fine-textured soils have maximum water holding capacity (USDA, 2008), which alternatively produce anaerobic conditions in the soil. Under anaerobic terrestrial environmental conditions, biological decomposition of the organic material by methanogens emits a significant amount of CH_4 from agricultural soils (Lu, 2011). However, soils with fine pores support the emission of CH_4 under anaerobic conditions (Dutaur and Verchot, 2007). Chen et al., (2013) conducted a meta-analysis and showed that sandy loam soils were produced maximum N_2O emissions. Another research study also reported that sandy loam soil emitted higher N_2O (Manzali-D, 1994).

Soil texture significantly controls the emissions of N_2O through moderating the soil oxygen availability because soil texture has an important impact on the size as well as the distribution of soil pores (Corre et al., 1999). In coarse-textured soils, the nitrification process is the main factor of N_2O emissions (Zhou et al., 2014). Moreover, manure application to agricultural soils provides a sufficient amount of C substrate that can stimulate the denitrification process and consequently enhance N_2O emissions after manure application.

3.3.4 Crop duration and type

The crop species and study duration also played an important role in the differences in GHGs emissions (Huang et al., 2018). Different crop species like barley, grassland, maize, rice, soybean, sweet corn, wheat, and the fallow period between crops were chosen for meta-analysis, while, the study duration was categorized as ≤ 320 days, 321-725 days, > 725 days (Figure. 3.4). In this meta-analysis, the overall effect sizes of crop duration and crop type on CO_2, CH_4 and N_2O emissions were $\overline{lnRR}$ =0.517, 95% CI =0.226-0.807 and $\overline{lnRR}$ =1.138, 95% CI =-0.445-3.00, $\overline{lnRR}$ =0.876, 95% CI =-0.141-

1.893 and $\overline{lnRR}$ =0.919, 95% CI =0.336-1.502 and $\overline{lnRR}$ =0.645, 95% CI =-0.271-1.561 and $\overline{lnRR}$ =1.097, 95% CI =-0.547-2.741, respectively (Table S2).

Based on the results of meta-analysis, the overall effect size for both crop duration and type was significantly greater than zero, presenting that both parameters had positive effects on CO_2, CH_4 and N_2O emissions. Crop duration is also a very important factor in controlling GHGs emissions. Crops that having > 321 days had more CO_2 and N_2O emissions (Figure. 3.4a (i) and 3.4c (i)). While, a higher concentration of CH_4 was observed when crop duration was ≤ 320 days (Figure. 3.4b (i)). Our meta-analysis findings were similar to previous research study (Leytem et al., 2019). According to our meta-analysis, barley produced maximum emission of CO_2 (Figure. 3.4a (ii)) which was similar to Gan et al., (2012) research study. Smith et al., (2019) also studied and reported that barley, which normally requires less manure and/or synthetic fertilizer than other cereals crops, have greater CO_2 emissions per unit production.

The CO_2 emission was produced through microbial respiration after manure application in the agricultural soils (Li et al., 2016). The effects of the heterotrophic microbial community on SOM decomposition significantly increase CO_2 emissions (Bore et al., 2017). Manure application to the cereal crops is capable of stimulating the organic C pool and, in turn, increases CO_2 emissions (Triberti et al., 2008). The decomposition of SOM significantly increased the C mineralization process and consequently increased CO_2 emissions from croplands (Hossain et al., 2017). Terhoeven-Urselmans et al., (2009) studied and assessed that the C mineralization process significantly increased CO_2 emissions from barley crop after manure application.

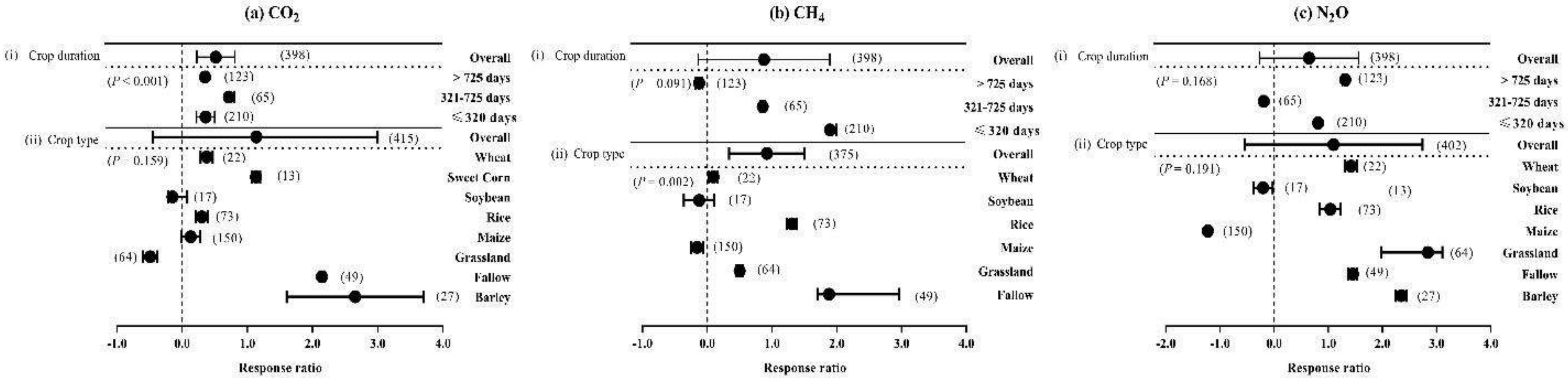

Figure 3.4. Influence of (i) crop duration (days) and (ii) crop type on (a) CO_2, (b) CH_4 and (c) N_2O emissions from agricultural soils. Symbols represent mean effect sizes with 95% confidence intervals. Sample sizes are presented in parentheses and the *P* values are shown in the panel.

The maximum concentration of CH_4 was observed in the fallow and rice crop (Figure. 3.4b (ii)). Rice paddies are considered among the main sources of man-caused CH_4 emission, contributing up to 6% to 20% of the total anthropogenic CH_4 release to the atmosphere (Wang et al., 2017). Wu et al., (2019) also studied and found that rice paddies are significant source of CH_4 emissions. The CH_4 in rice fields is emitted through microbes that respire CO_2, similar humans respire oxygen. The CH_4 emissions from rice paddies depend on the availability of SOC content and anaerobic conditions (Tariq et al., 2017). Continuous flooding in rice paddies significantly affects the microbial activities in the terrestrial environment (Gebremichael et al., 2017) and increases anaerobic conditions. This process significantly affects the decomposition rate of SOM and ultimately alters the CH_4 emissions. Different researchers also studied and explained that CH_4 emission produced as a result of decomposition of SOM by microbial activates in the absence of oxygen (Conrad, 2009). Under anaerobic conditions, flooded rice paddies are considered one of the most important anthropogenic sources of CH_4 emissions (Hurkuck et al., 2012).

In this meta-analysis, grasslands have been found as a significant source of N_2O emissions (Figure. 3.4c (ii)). According to Rafique et al. (2011) research study that approximately 28% of global N_2O was emitted from grasslands. Van Beek et al. (2010) also found similar findings. Maize crop didn't show any significant positive effects on all three GHGs emissions while it showed significantly negative effects on N_2O emissions (Figure. 3.4c (ii)). Microbial nitrification, nitrifier-denitrification (Xu et al., 2017), respiration, and denitrification are the most important processes affecting the N_2O emission from the terrestrial environment (Case et al., 2015). Intensively managed grasslands are considered the main source of N_2O emissions contributing for almost 10% of the global N_2O emissions (He et al., 2020) and this is mainly attributed to higher manure application as well as animal excreta deposition on grassland surface (Dangal et al., 2019). Application of manure in grassland influences soil biochemical conditions and increases microbial activities which significantly affects the nitrification as well as denitrification process and ultimately changes N_2O emissions (Schirmann et al., 2020). The GHGs emissions are strongly affected by the amount as well as properties of manure added to the crops.

According to our meta-analysis results, total heterogeneity also showed that crop duration (Q_t=84.736 with $P < 0.001$ for CO_2, Q_t=8006.292 with $P < 0.001$ for CH_4 and Q_t=3522.244 with $P < 0.001$ for N_2O emissions) and crop type (Q_t=31780.765 with $P < 0.001$ for CO_2, Q_t=1443.669 with $P < 0.001$ for CH_4 and Q_t=18495.592 with $P < 0.001$ for N_2O emissions) had significantly positive effect on GHGs emissions (Table S3, S4 and S5).

3.3.5 Climate zone

Figure 3.5 shows the effect sizes of climate zones on CO_2, CH_4, and N_2O emissions. Climate zones were divided into warm temperate (n=134), cool temperate (n=132), tropical (n=29), sub-tropical (n=131) and semi-arid region (n=4). The overall effect sizes of climate zones were ($\overline{lnRR}$ =0.345, 95% CI =0.218-0.471), ($\overline{lnRR}$ =1.65, 95% CI =-0.302-3.602) and ($\overline{lnRR}$ =0.506, 95% CI =-0.273-1.285) for CO_2, CH_4 and N_2O emissions, respectively (Table S2).

Climate zones had shown significantly positive effects on CO_2, CH_4, and N_2O emissions because the overall effect sizes of climate zones were significantly great than 0. According to our meta-analysis results, tropical and sub-tropical regions emitted more CO_2 and N_2O but on the other hand, the higher concentration of CH_4 was found in cool temperate zone (Figure. 3.5). Van der Werf et al. (2009) found that the maximum concentration of CO_2 is emitted from the tropical zone.

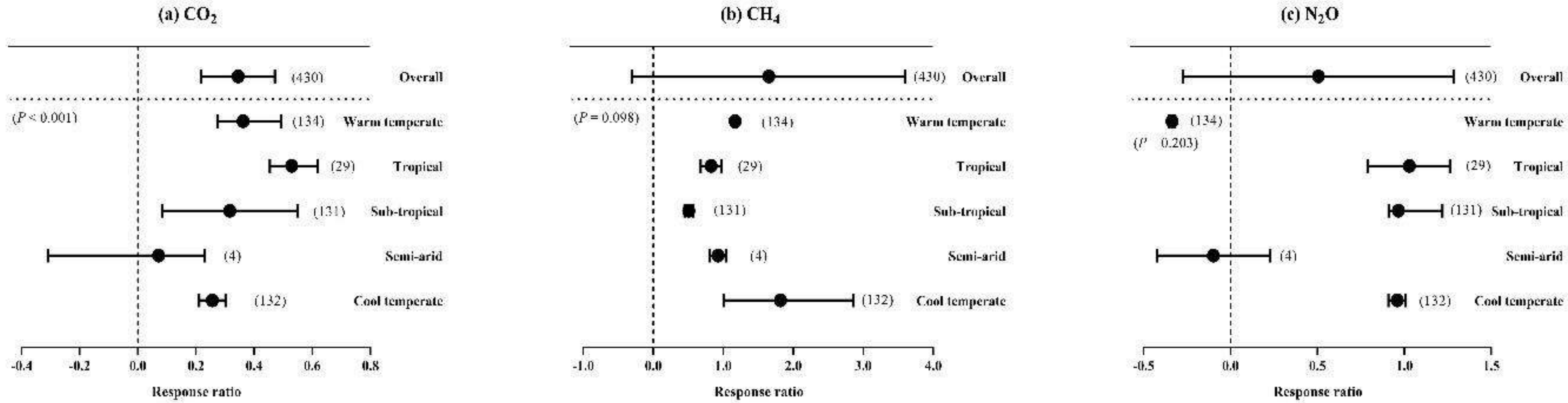

Figure 3.5. Effect of climate zone on (a) CO_2, (b) CH_4 and (c) N_2O emissions from agricultural soils. Symbols represent mean effect sizes with 95% confidence intervals. Sample sizes are presented in parentheses and the *P* values are shown in the panel.

Agricultural soils contain large concentrations of organic C, reaching approximately 1,500 petagrams (Pg) (at 1 m depth) (Paustian et al., 2016) and tropical environment provides favorable conditions to microbial communities for the decomposition of organic C, ultimately increase the CO_2 emissions. Globally, the average temperature is expected to rise (1.5 to 3.9 ºC) near the end of 21st century (IPCC, 2014), so, tropical soils could cause roughly a 9% increase in CO_2 emissions this century (Nottingham et al., 2019).

Different research studies were found that higher N_2O emission emitted from the warm temperate zone (Luo et al., 2013) due to microbial activities (Pärn et al., 2018) but this meta-analysis study revealed that sub-tropical and cool temperate zones produced higher N_2O concentration than other regions (Figure. 3.5c). Welti et al. (2017) also found the higher N_2O emissions from agricultural soils under sub-tropical zones. The sensitivity of climatic conditions of N_2O emission is not well-known, so, it is difficult to project how manure application and climatic conditions will impact the N_2O emission (Griffis et al., 2017). Therefore, there is future research is needed to conduct for better understating how climate zone effects GHGs emissions after manure application. The tropical and sub-tropical climate zones may favor microbial nitrification as well as denitrification processes (Barnard et al., 2005) that are directly linked with CO_2 and N_2O emissions (Xu et al., 2012). Fangueiro et al. (2008) studied and reported that cool temperate also significantly increase N_2O emissions from soils. According to Müller et al., (2003), the emission of N_2O was observed between −1.0 °C to 10.0 °C, the maximum N_2O emission was occurred near 0 °C, probably from increasing the activity of N_2O reductase. Cool temperate soils cause waterlog conditions in the terrestrial environment, generating anaerobic conditions that help in the emissions of CH_4 and CO_2 (Jorgenson et al., 2006). Another study also proposed that maximum CH4 emissions are emitted by paddy fields in snowy temperate regions (Naser et al., 2007). The total heterogeneity between-groups were also showed significant positive effects on GHGs emissions (Table S3, S4, and S5).

3.3.6 Effect of manure application on GWP

With those research studies that simultaneously measured all three GHGs emissions fluxes, manure application positively affected GWP ($\overline{lnRR}$ =0.781, 95% CI =-0.55-2.512) (Figure. 3.6, Table S2). Meanwhile, the application of poultry and cattle manure to agricultural soils significantly increased GWP, whereas a minor negative effect was observed in pig manure (Figure. 3.6). However, with the realization that few research studies were reported fluxes of all three GHGs after manure application, these results were likely affected by publication biases, and therefore should be interpreted cautiously. Ren et al., (2019) also obtained coinciding results. GWP is a basic index to calculate the future impacts of GHGs based on their lifetime and radiative forcing (IPCC, 2013).

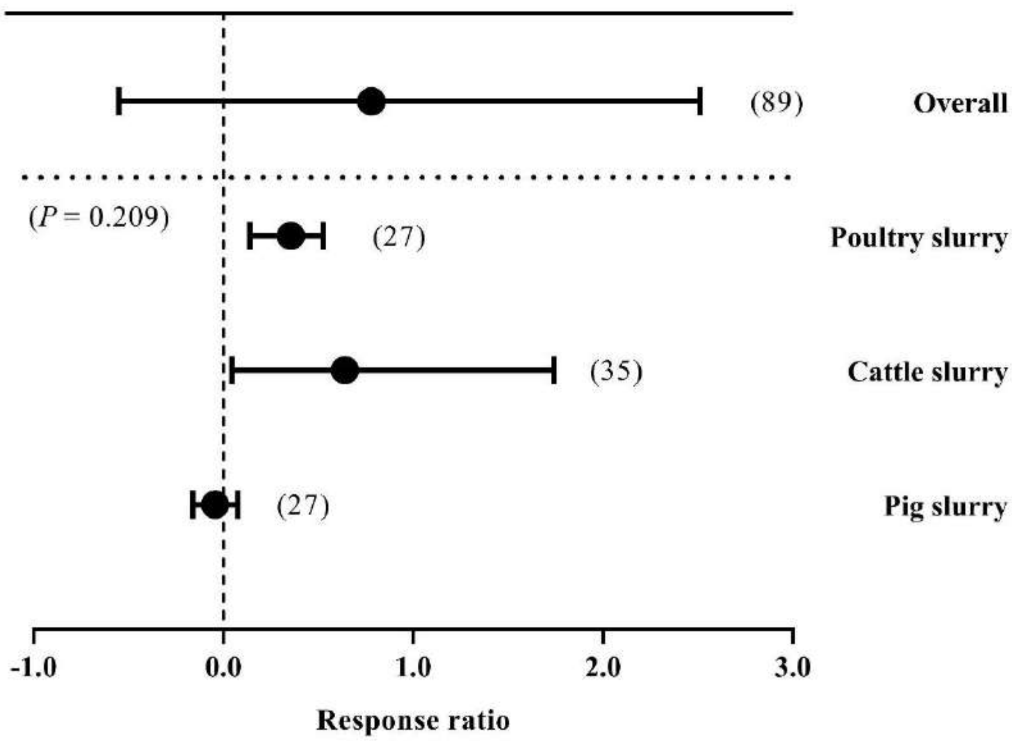

Figure 3.6. Effect of manure application on the global warming potential (GWP) of greenhouse gas (GHG) emissions. Symbols represent mean effect sizes with 95% confidence intervals. Sample sizes are presented in parentheses and the *P* values are shown in the panel.

Agriculture and its related land use contribute to carbon (C) and nitrogen (N) dynamics, affecting the flux of CO_2, CH_4, and N_2O, which represent the GHGs principally linked to agricultural activities. Agricultural soils released a significant amount of GHGs emissions to the atmosphere (He et al., 2017), which estimated for approximately one-fifth of the annual increase in radiative forcing of climate change (Cole et al., 1997). GHGs emissions would increase significantly after animal manure was applied, particularly in croplands (Thers et al., 2020). In 2011, the emissions of GHGs from crops were approximately 5.3 Pg of CO_2eq (FAO, 2014). Agricultural management practices significantly change the GWP (Shang et al., 2011). Although the application of manure significantly increased the annual N_2O and CH_4 emissions, they increased the SOC sequestration in this cropping system through microbial activities, ultimately increased GWP.

3.4 Limitations and concluding remarks

In this meta-analysis, most of the experiments had been studied in China, Europe and North America. There remains a lack of experimental studies in other continents, like South America, South-East Asia, Africa and Australia. Therefore, long-term experimental research studies are needed with proper manure application rate in these regions to estimate the GHGs emissions. Several research studies had measured GHGs emissions using different animal manures but did not report the summary of statistics that are required for meta-analysis. So, we urge that research scientists must report the proper manure type, complete soil attributes like soil pH, bulk density, soil texture, WFPS, air temperature, proper climate zone, and rainfall, flux type and unit, number of observations and control treatment in their future research studies. This will greatly assist in future meta-analyses which can hopefully provide far greater insights into the range and variability of GHGs emissions than any individual study.

This meta-analysis provided a comprehensive and quantitative synthesis of animal manure, climate zone, and soil attributes effects on GHGs emissions. Evidence presented in this meta-analysis shows that the application of animal manure and N-mineral fertilizer significantly increased CO_2, CH_4 and N_2O emission as compared to control treatment from soils. Moreover, this meta-analysis study revealed that poultry manure had significantly positive effects on CO_2, CH_4, and N_2O emissions from the soil than pig and cattle manures. Moreover, the amount/rate of animal manure and N-mineral fertilization also had strong effects on CO_2, CH_4, and N_2O emissions. The effect of animal manure and N-mineral fertilize on CO_2, CH_4 and N_2O emissions were considerably depended on soil attributes like soil pH, WFPS, soil texture, crop types, and climate zones, indicating that these factors need to be fully considered to optimize the fertilization strategies to reduce the emissions of GHGs. Stimulatory positive effects occurred at the rate of > 60% WFPS, while negative effects were found at the rate of < 30% WFPS. Soil pH and soil texture are very important factors for predicting the GHGs emissions. Hence, this meta-analysis suggests that some experimental strategies, for example, selecting the manure type and proper rate need to be planned correctly to mitigate GHGs emissions from soil. Finally, the application of different types of animal manure in agricultural soils (as shown by our meta-analysis results) can be useful for calibrating and validating computer-based models and also filling the knowledge gaps about GHGs emissions that are derived from agricultural soils.

Acknowledgments

Awais Shakoor would like to express his gratitude for the grant provided by the University of Lleida, Spain. The authors would like to appreciate the valuable comments from the editors and anonymous reviewers to improve the quality of this study.

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SUPPLEMENTARY SUPPORTING INFORMATION

Table S2. Summary of effect sizes (lnRR) with upper and lower values for all variables

	Upper value	lnRR	Lower value
Type of manure and CO_2			
	Upper value	**lnRR**	**Lower value**
Pig slurry	0.677	0.628	0.579
Cattle slurry	0.232	0.173	0.115
Poultry slurry	1.787	1.702	1.621
N-mineral fertilizer	0.13	0.032	-0.073
Overall	1.26	0.635	0.01
Type of manure and CH_4			
	Upper value	**lnRR**	**Lower value**
Pig slurry	1.284	1.248	1.212
Cattle slurry	0.779	0.741	0.703
Poultry slurry	3.23	2.605	2.979
N-mineral fertilizer	1.257	1.2	1.144
Overall	3.481	2.31	1.161
Type of manure and N_2O			
	Upper value	**lnRR**	**Lower value**
Pig slurry	1.186	1.12	1.053
Cattle slurry	1.189	1.109	1.029
Poultry slurry	1.062	1.972	0.882
N-mineral fertilizer	1.264	1.286	1.209
Overall	1.241	1.123	1.004
Amount of manure and CO_2			
	Upper value	**lnRR**	**Lower value**
≤ 120	0.135	-0.004	-0.143
≤ 320	-0.479	-0.512	-0.546
> 320	0.942	0.891	0.84
Overall	1.175	0.125	-0.925
Amount of manure and CH_4			
	Upper value	**lnRR**	**Lower value**
≤ 120	1.723	1.65	1.578
≤ 320	1.209	1.182	1.156
> 320	1.7	1.665	1.609
Overall	1.855	1.495	1.135
Amount of manure and N_2O			
	Upper value	**lnRR**	**Lower value**
≤ 120	0.684	0.579	0.475
≤ 320	0.328	0.308	0.289
> 320	1.799	1.701	1.603
Overall	1.69	0.862	0.035

Soil pH and CO_2			
	Upper value	**lnRR**	**Lower value**
< 6.5	0.295	0.224	0.152
6.6-7.3	1.428	3.375	5.323
> 7.3	0.371	0.332	0.292
Overall	5.388	1.977	-1.434

Soil pH and CH_4			
	Upper value	**lnRR**	**Lower value**
< 6.5	0.689	0.659	0.63
6.6-7.3	1.003	0.973	0.943
> 7.3	1.532	1.468	1.403
Overall	1.396	1.032	0.669

Soil pH and N_2O			
	Upper value	**lnRR**	**Lower value**
< 6.5	2.39	2.355	2.39
6.6-7.3	-1.165	-1.193	-1.22
> 7.3	0.976	0.895	0.813
Overall	3.281	0.686	-1.91

WFPS and CO_2			
	Upper value	**lnRR**	**Lower value**
< 30%	0.102	-0.093	-0.288
30-60 %	0.352	0.323	0.294
> 60 %	0.276	0.237	0.197
Overall	0.323	0.212	0.102

WFPS and CH_4			
	Upper value	**lnRR**	**Lower value**
< 30%	0.773	0.717	0.662
30-60 %	-0.307	-0.365	-0.423
> 60 %	2.215	2.17	2.125
Overall	2.326	0.841	-0.644

WFPS and N_2O			
	Upper value	**lnRR**	**Lower value**
< 30%	-0.166	-0.192	-0.192
30-60 %	-0.07	-0.11	-0.11
> 60 %	1.613	1.499	1.499
Overall	0.913	0.394	-0.394

Soil texture and CO_2			
	Upper value	**lnRR**	**Lower value**
Clay	0.336	0.111	0.086
Clay loam	0.055	0.005	-0.045
Loam	0.326	0.225	0.124
Sandy loam	0.273	0.269	0.165

Silt loam	0.359	0.328	0.296
Silty clay	0.421	0.335	0.25
Silty clay loam	0.425	0.258	0.09
Overall	0.427	0.285	0.143
Soil texture and CH_4			
	Upper value	**lnRR**	**Lower value**
Clay	1.571	1.056	-1.459
Clay loam	-0.042	-0.125	-0.208
Loam	0.644	0.539	0.434
Sandy loam	0.483	0.45	0.417
Sandy clay loam	0.778	0.398	0.017
Silt loam	3.235	2.219	1.202
Silty clay	0.896	1.004	0.111
Silty clay loam	1.017	1.978	0.939
Overall	1.069	0.706	0.342
Soil texture and N_2O			
	Upper value	**lnRR**	**Lower value**
Clay	1.318	1.201	1.085
Clay loam	0.01	-0.059	-0.127
Loam	-1.024	-1.078	-1.132
Sandy loam	2.977	2.906	2.835
Sandy	1.451	1.302	1.334
Sandy clay loam	1.423	1.395	1.187
Silt loam	0.769	0.677	0.584
Silty clay	1.084	0.915	0.746
Silty clay loam	1.627	1.264	0.902
Overall	1.897	0.946	-0.004
Crop type and CO_2			
	Upper value	**lnRR**	**Lower value**
Barley	2.701	2.652	2.604
Fallow	2.18	2.144	2.109
Grassland	-0.383	-0.489	-0.596
Maize	0.277	0.131	-0.014
Rice	0.393	0.302	0.21
Soybean	0.08	-0.147	-0.213
Sweet Corn	1.196	1.132	1.068
Wheat	0.47	0.377	0.284
Overall	3	1.138	-0.445
Crop type and CH_4			
	Upper value	**lnRR**	**Lower value**
Fallow	1.88	2.964	1.698
Grassland	0.543	0.499	0.455

Maize	-0.067	-0.16	-0.252
Rice	1.384	1.308	1.232
Soybean	0.112	-0.125	-0.362
Wheat	0.164	0.095	0.027
Overall	1.502	0.919	0.336

Crop type and N_2O

	Upper value	lnRR	Lower value
Barley	3.452	2.352	1.251
Fallow	1.539	1.454	1.37
Grassland	3.108	2.84	1.973
Maize	-1.198	-1.225	-1.251
Rice	1.232	1.039	0.845
Soybean	-0.024	-0.204	-0.385
Wheat	1.533	1.422	1.311
Overall	2.741	1.097	-0.547

Crop duration and CO_2

	Upper value	lnRR	Lower value
≤ 320 days	0.499	0.36	0.221
321-725 days	0.718	0.801	0.718
> 725 days	0.352	0.385	0.352
Overall	0.807	0.517	0.226

Crop duration and CH_4

	Upper value	lnRR	Lower value
≤ 320 days	1.991	1.896	1.882
321-725 days	0.882	0.855	0.827
> 725 days	-0.068	-0.125	-0.182
Overall	1.893	0.876	-0.141

Crop duration and N_2O

	Upper value	lnRR	Lower value
≤ 320 days	0.852	0.812	0.772
321-725 days	-0.162	-0.189	-0.215
> 725 days	1.362	1.312	1.262
Overall	1.561	0.645	-0.271

Climate zone and CO_2

	Upper value	lnRR	Lower value
Cool temperate	0.301	0.256	0.211
Semi-arid	0.071	0.231	-0.31
Sub-tropical	0.549	0.316	0.084
Tropical	0.529	0.619	0.454
Warm temperate	0.362	0.492	0.275
Overall	0.471	0.345	0.218

Climate zone and CH_4			
	Upper value	**lnRR**	**Lower value**
Cool temperate	2.855	1.819	1.002
Semi-arid	1.048	0.927	0.806
Sub-tropical	0.568	0.507	0.446
Tropical	0.973	0.826	0.68
Warm temperate	1.195	1.17	1.145
Overall	3.602	1.65	-0.302
Climate zone and N_2O			
	Upper value	**lnRR**	**Lower value**
Cool temperate	1.009	0.959	0.909
Semi-arid	0.226	-0.099	-0.424
Sub-tropical	1.22	0.966	0.91
Tropical	1.262	1.029	0.788
Warm temperate	-0.318	-0.336	-0.355
Overall	1.285	0.506	-0.273
GWP of GHGs emissions			
	Upper value	**lnRR**	**Lower value**
Pig slurry	0.077	-0.042	-0.161
Cattle slurry	0.641	1.543	0.046
Poultry slurry	0.526	0.141	0.356
Overall	2.512	0.781	-0.55

Supplementary Table S3. Statistical results were reported as total heterogeneity (Q_t) in effect sizes among studies from continuous randomized-effects model meta-analysis for CO_2. The relationship is significant if $P < 0.05$.

Parameter	**Q_t**	***P***
Type of manure	996.635	< 0.001
Amount of manure	2047.082	< 0.001
Soil pH	24867.565	< 0.001
WFPS	26.737	< 0.001
Soil texture	138.288	< 0.001
Crop type	31780.765	< 0.001
Crop duration	84.736	< 0.001
Climate zone	70.084	< 0.001

Supplementary Table S4. Statistical results were reported as total heterogeneity (Q_t) in effect sizes among studies from continuous randomized-effects model meta-analysis for CH_4. The relationship is significant if P < 0.05.

Parameter	**Q_t**	***P***
Type of manure	6445.801	< 0.001
Amount of manure	389.849	0.011
Soil pH	571.537	< 0.001
WFPS	4812.705	< 0.001
Soil texture	2558.770	< 0.001
Crop type	1443.669	< 0.001
Crop duration	8006.292	< 0.001
Climate zone	29693.307	< 0.001

Supplementary Table S5. Statistical results were reported as total heterogeneity (Q_t) in effect sizes among studies from continuous randomized-effects model meta-analysis for N_2O. The relationship is significant if P < 0.05.

Parameter	**Q_t**	***P***
Type of manure	27.879	< 0.001
Amount of manure	757.926	< 0.001
Soil pH	25088.042	< 0.001
WFPS	812.905	< 0.001
Soil texture	9090.584	< 0.001
Crop type	18495.592	< 0.001
Crop duration	3522.244	< 0.001
Climate zone	3828.746	< 0.001

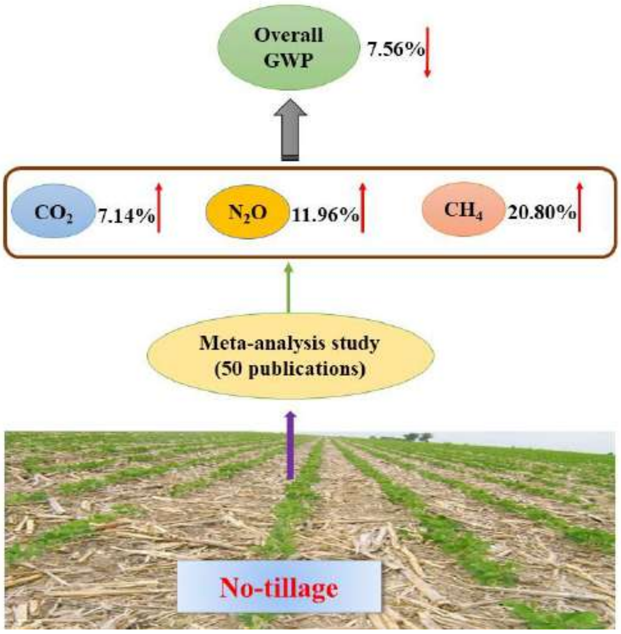
Chapter 4

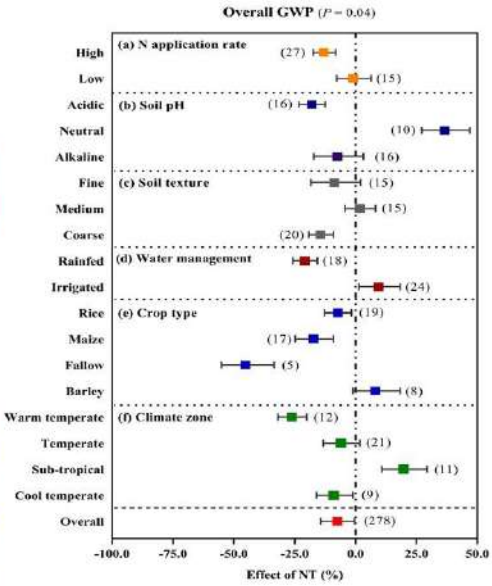
This chapter contains the following accepted and already online published paper in the "*Science of The Total Environment*"

Shakoor, A., Shahbaz, M., Farooq, T. H., Sahar, N. E., Shahzad, S. M., Altaf, M. M., & Ashraf, M. (2021). A global meta-analysis of greenhouse gases emission and crop yield under no-tillage as compared to conventional tillage. *Science of The Total Environment*, *750*, 142299. https://doi.org/10.1016/j.scitotenv.2020.142299

A global meta-analysis of greenhouse gases emission and crop yield under no-tillage as compared to conventional tillage

Graphical abstract





Abstract

No-tillage (NT) practice is extensively adopted with aims to improve soil physical conditions, carbon (C) sequestration and to alleviate greenhouse gases (GHGs) emissions without compromising crop yield. However, the influences of NT on GHGs emissions and crop yields remains inconsistent. A global meta-analysis was performed by using fifty pee-reviewed publications to assess the effectiveness of soil physicochemical properties, nitrogen (N) fertilization, type and duration of crop, water management and climatic zones on GHGs emissions and crop yields under NT compared to conventional tillage (CT) practices. The outcome reveals that compared to CT, NT increased CO_2, N_2O, and CH_4 emissions by 7.1, 12.0, and 20.8%, respectively. In contrast, NT caused up to 7.6% decline in global warming potential as compared to CT. However, absence of difference in crop yield was observed both under NT and CT practices. Increasing N fertilization rates under NT improved crop yield and GHGs emission up to 23 and 58%, respectively, compared to CT. Further, NT practices caused an increase of 16.1% CO_2 and 14.7% N_2O emission in the rainfed areas and up to 54.0% CH_4 emission under irrigated areas as compared to CT practices. This meta-analysis study provides a scientific basis for evaluating the effects of NT on GHGs emissions and crop yields, and also provides basic information to mitigate the GHGs emissions that are associated with NT practice.

Keywords: Crop yield; GHGs emission; No-tillage; Meta-analysis; Mitigation

Highlights

- Fifty peer-reviewed publications were used to conduct a global meta-analysis.
- No-tillage (NT) significantly increased CO_2, N_2O, and CH_4 emissions by 7.14%, 11.96%, and 20.80%.
- Overall, NT significantly reduced GWP by 7.56% as compared to (conventional tillage) CT.
- In NT, barley and wheat yields increased by 43.76% and 4.49%, respectively.

4.1 Introduction

Global warming is one of the major consequences of the human activities associated with increasing concentration of atmospheric greenhouse gases (GHGs) emission, such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) (Paustian et al., 2006). Among anthropogenic activities, agriculture is estimated to be accountable for 12% of total GHGs emissions (IPCC, 2014). This reveals the importance of agricultural management practices, particularly soil tillage, in emitting or mitigating GHGs emission (WRI, 2014). Soil stores 3-4 times more carbon (C) than is present in vegetation and atmosphere combined (Lal, 2004a). Total C in the terrestrial environment is ~ 3170 Pg and nearly 80% (2500 Pg) of this C is found in topsoil (Jobbagy and Jackson, 2000; Lal, 2008, 2004b). Soil C and nitrogen (N) cycles are closely interlinked and controlled by different biological processes (Martínez et al., 2017). The decomposition of soil organic matter (SOM) through biological processes is a key part of both C and N cycles. Therefore, any change or disturbance in SOM decomposition would have direct impact on GHGs emission such as CO_2, CH_4, and N_2O and thus global warming (Shakoor et al., 2020b). No-tillage (NT) as compared to conventional tillage (CT) is becoming popular with an aim to improve soil C sequestration, soil physiochemical conditions without compromising crop yield (Lal, 2015; Lal et al., 2007). In addition, NT management practice can also significantly alter the concentrations of GHGs emissions from agricultural soils. However, net effect of NT on GHGs emissions and crop yields remains variable.

Worldwide, NT was practiced on ~111 million ha land in 2009 (Derpsch et al., 2010), and in 2014, this number touched ~155 million ha (Huang et al., 2018). No-tillage is extensively used to protect soil degradation and erosion (Krauss et al., 2017), to improve soil aggregation ability (Quiroga et al., 2010), to increase SOM stocks (Stewart et al., 2016) and to mitigate the GHGs emissions (Kong et al., 2009) as compared to CT practice.

The effects of NT on GHGs emissions have been intensively debated and ominously vary among individual research studies (Abdalla et al., 2016; Van Kessel et al., 2013; Zhao et al., 2016). Previous research studies showed that NT, as compared to CT, significantly increased (Sainju, 2016; Zhang et al., 2016), decreased (Lu et al., 2016; Tellez-Rio et al., 2015b) and/or did not affect (Bayer et al., 2015) CO_2, CH_4, and N_2O emissions from agricultural soils. The high inconsistency in the results from individual studies are challenging to reveal the main effect of soil tillage on GHGs mitigation. Though some research studies have been conducted to evaluate the effect of NT as compared to CT on GHG mitigation, but they only focused on N_2O and/or CH_4 emissions (Van Kessel et al., 2013; Zhao et al., 2016). The effect of NT on the global warming potential (GWP) of GHGs emissions has not also been well addressed, keeping GHGs mitigation possibilities with NT indeterminate.

Different hypotheses have been suggested to describe the GHGs emissions in responses to NT as compared to CT. For example, it is estimated that SOM decomposition is significantly affected by soil tillage (Lal, 2003). However, this estimation is uncertain, due to the lack of detailed site-level meta-analysis for soil types, different climatic conditions, and management practices. Tillage practices may induce soil disruption and disturbance of soil aggregates and soil moisture content. This increased microbial decomposition of SOM and consequently causing C and N loss in the form of CO_2 and N_2O (Plaza-Bonilla et al., 2014b; Six et al., 2004). On the other hand, CO_2 emission decreased after NT practice and this might be due to C protection associated with improved soil aggregations and reduced soil temperature (Lu et al., 2016; He et al., 2011).

Soil acts as a source and/or sink of CH_4 emissions, depending on the tillage practice, microbial activity, amount of fertilizer, and SMC (Pareja-Sánchez et al., 2019; Shakoor et al., 2020a). Tillage practices significantly affect the CH_4 emissions from agricultural soils through SMC. Generally, SMC shows strong control over CH_4 emissions, usually through soil structure. Therefore, degradation of soil structure, mainly through soil compaction, that is a common problem particularly in intensively tilled soils, can adversely affect CH_4 emissions (Ball et al., 1999). Zhang et al., (2015) studied that CH_4 emission increased might have been due to excess of soil organic substrates that consequently increase anaerobic microsites.

In order to better understand the effect of soil tillage practice on N_2O emission, soil nitrification, and denitrification processes need to be studied. Under aerobic conditions, ammonia is converted to nitrate along with N_2O emission as the gaseous product of nitrification by autotrophic nitrifiers. In contrast to the aerobic conditions, nitrate converted into N_2O as well as dinitrogen (N_2) as a result of the denitrification process (heterotrophic denitrifiers activities) under anaerobic conditions (Mei et al., 2018; Shakoor et al., 2016). NT practice significantly increases soil C and SOM that could promote the denitrification process (Sheehy et al., 2013; Ma et al., 2013). Another research study found that NT significantly increased denitrification rates due to the abundance in denitrifiers as compared with CT fields (Attard et al., 2011). While, a reduction in N_2O emission could be due to improved soil structure, limited availability of decomposable SOC as well as mineral N to microbial communities (Grandy et al., 2006; Ruan and Philip Robertson, 2013).

Meta-analysis is a useful technique to quantitatively synthesize, analyze, and summarize the findings presented in the literature (Ren et al., 2017). The analytical method suggests a proper statistical analysis to combine and compare the collected results of different studies and to draw general models at different spatial scales, and the outcomes of already published studies are treated as if they are subject to uncertainties of sampling (Freeman et al., 1986).

Recently, several meta-analysis studies have been reported on GHGs emissions and crop yield with NT versus CT (Abdalla et al., 2016; Mei et al., 2018; Van Kessel et al., 2013; Zhao et al., 2016). However, these studies have mainly focused on individual specie of GHGs (i.e. CO_2, or N_2O or CH_4) under a specific region, and/or a specific crop type, which highlight the need of global meta-analysis. Accordingly, we conducted a global meta-analysis by measuring all three GHGs emission to fulfill the knowledge gap. The main objectives of this meta-analysis study were to: a) examine the responses of GHGs emissions, GWP, and crop yield to NT, b) check the impact of soil physicochemical properties (i.e. soil pH, C: N ratio, and soil texture), climatic zones and crop management (N application rate, crop types and growth duration and water management) on GHGs emission and crop yield under NT as compared to CT practices.

4.2 Materials and methods

4.2.1 Database generation

The data used in this meta-analysis were collected from peer-reviewed publications, which measured the GHGs emissions under NT compared to CT from the search engines of Web of Science, Scopus and Google Scholar to a cut-off date of April 2020. The search keywords 'soil tillage' OR 'no-tillage' OR 'zero-tillage' and 'GHGs' 'carbon dioxide' OR 'CO_2' 'AND 'methane' OR 'CH_4' and 'nitrous oxide' OR 'N_2O' were used to search the peer-reviewed articles. Peer-reviewed articles were selected using the following criteria; a) research studies conducted in the field; b) studies measuring cumulative emissions (kg ha^{-1}) of GHGs either CO_2, CH_4, and/or N_2O under both NT and CT treatments at the same study site; c) means, standard deviations (or standard errors), and the number of replications that was either reported and/or could be calculated; d) experimental duration, N application rate, and water management practices that were clearly reported. According to the above criteria, in total, 50 peer-reviewed publications with 431 observations (due to multiple treatments included within individual research articles) were selected (Table 4.1). Most research publications reported emission data in tables that could be transferred into the dataset directly. Data were also retrieved directly from graphs using GetData (version 2.26) Graph Digitizer software.

Table 4.1. Description of crop type, climate zone, soil physiochemical properties (texture, pH, C: N ratio), number of observation, N application rate, water management and GHGs included in this meta-analysis.

Study No.	Country	Crop type	Climate zone	Soil texture	Soil pH	Soil C: N	N application rate (kg N ha^{-1})	Water management	Number of observations	GHGs			Reference
										CO_2	N_2O	CH_4	
1	Poland	Maize	Temperate	Coarse-Medium	Acidic	10.4	120	Irrigated	8	✓	-	-	Rutkowska et al., (2018)
2	India	Rice	Sub-tropical	Coarse	Neutral	4.46	150	Irrigated	4	✓	✓	✓	Pandey et al., (2013)
3	Spain	Fallow	Warm temperate	Coarse	Alkaline	9.3-10.3	150	Rainfed	2	-	✓	✓	Tellez-Rio et al., (2015)
4	China	Rice	Sub-tropical	-	Acidic	10.1	180	Irrigated	6	-	✓	✓	Liu et al., (2020)
5	China	Rice-Wheat	Sub-tropical	-	Alkaline	12.6	250	Irrigated	6	-	✓	✓	Yao et al., (2013)
6	France	Fallow	Warm temperate	-	Acidic-Neutral	9.1-11.7	0-158	Irrigated	4	✓	✓	-	Oorts et al., (2007)
7	Denmark	Barley	Cool temperate	Coarse	Acidic	-	117	Rainfed	3	✓	✓	-	(Chatskikh and Olesen, (2007)
8	USA	Maize	Temperate	Medium	-	9.2	187	Irrigated	2	-	✓	✓	Ussiri et al., (2009)
9	China	Rice	Sub-tropical	Medium	Acidic	5.12	0-210	Irrigated	4	✓	✓	✓	Ahmad et al., (2009)
10	Finland	Barley	Cool temperate	Medium -Fine	-	13.5 - 18.6	0-105	-	12	✓	✓	✓	Regina and Alakukku, (2010)
11	China	Rice	Sub-	Medium	Acidic	9.33	112.5	Irrigated	4	-	-	✓	Li et al.,

			tropical										(2011)
12	China	Wheat-Rice	Sub-tropical	Medium	Acidic	10.05	210-240	Irrigated	18	-	✓	✓	Zhang et al., (2015)
13	Belgium	Cereals	Temperate	-	-	11	122	Rainfed	2	✓	✓	-	Lognoul et al., (2017)
14	China	Wheat	Sub-tropical	Medium	Alkaline	-	375	-	2	-	-	✓	Wang et al., (2019)
15	Italy	Soybean-Maize	Temperate	Medium	Neutral	10.6	0-200	Irrigated	5	-	-	✓	Fiorini et al., (2020)
16	Spain	Maize	Warm temperate	Medium	Alkaline	-	0-400	Irrigated	6	✓	-	✓	Pareja-Sánchez et al., (2019)
17	China	Wheat	Sub-tropical	-	Alkaline	11	0-166	Irrigated	8	-	✓	-	Niu et al., (2019)
18	New Zealand	Maize	Cool temperate	Medium	Acidic	10.8	120	-	2	-	-	✓	Choudhary et al., (2002)
19	Denmark	Barley-Rapeseed	Cool temperate	Coarse	Acidic-Neutral	-	100	Rainfed	8	✓	✓	-	Chatskikh et al., (2008)
20	Spain	Barley	Warm temperate	Coarse	Alkaline	-	-	Rainfed	8	✓	-	-	Morell et al., (2010)
21	USA	Fallow	Temperate	Medium	-	13.6	-	-	2	✓	✓	✓	Datta et al., (2013)
22	UK	Barley	Cool temperate	Coarse	-	-	-	Irrigated	4	-	✓	✓	Ball et al., (2014)
23	Spain	Fallow	Warm temperate	Coarse	Alkaline	-	-	Rainfed	2	✓	✓	✓	Guardia et al., (2016)
24	India	Rice-Wheat	Sub-tropical	Medium	Alkaline	-	120	Irrigated	24	-	✓	✓	Gupta et al., (2016)
25	China	Rapeseed-Fallow	Sub-tropical	-	Acidic	-	273	Irrigated	12	-	✓	✓	Hao et al., (2016)

26	Switzerland	Wheat	Neutral	Fine	-	-	-	Rainfed	8	-	√	√	Krauss et al., (2017)
27	USA	Temperate	Maize-Soybean-Wheat	Medium	Acidic-Neutral	12.8	0-246	Rainfed	10	√	√	√	Behnke et al., (2018)
28	China	Maize	Sub-tropical	Medium	Alkaline	10.1	150	irrigated	2	√	-	-	Wang et al., (2020)
29	USA	Maize-Soybean	Sub-tropical	Coarse	-	-	310	-	2	√	√	√	Smith et al., (2012)
30	China	Rice	Sub-tropical	Medium	Acidic	-	0-210	Irrigated	8	√	-	-	Li et al., (2010)
31	China	Rice-Wheat	Sub-tropical	Coarse	Acidic	7.67	180	Irrigated	16	-	-	√	(Zhang et al., (2015)
32	Spain	Wheat-Rapeseed - Barley - Fallow	Warm temperate	Coarse	Alkaline	-	-	Rainfed	26	√	-	-	Álvaro-Fuentes et al., (2008)
33	China	Fallow-Rice	Sub-tropical	-	Acidic	10.2	144	Irrigated	48	-	√	√	Zhang et al., (2016)
34	Canada	Maize	Cool temperate	Medium	-	-	0-180	Rainfed	4	√	√	-	Almaraz et al., (2009)
35	UK	Fallow	Cool temperate	Medium	Acidic	-	0-200	-	16	√	√	-	Baggs et al., (2003)
36	China	Rice	Sub-tropical	Coarse	Acidic	10.1	180	Irrigated	10	-	-	√	Fan et al., (2020)
37	China	Fallow	Sub-tropical	Coarse	Alkaline	17.5	0-225	Irrigated	4	-	√	√	Liu et al., (2015)
38	USA	Maize	Temperate	Fine	Alkaline	8.09	0-202	Irrigated	24	√	√	√	Mosier et al., (2006)

39	USA	Rice	Sub-tropical	-	-	-	118	Irrigated	2	-	✓	✓	Joshua et al., (2018)
40	Brazil	Rice	Tropical	-	Acidic	13.5	33	Rainfed	4	✓	✓	-	Passianoto et al., (2003)
41	Spain	Barley	Warm temperate	-	Alkaline	11.1	0-120	Rainfed	20	✓	-	✓	Plaza-Bonilla et al., (2014)
42	China	Rice	Sub-tropical	Medium	Acidic	17.4	0-126	Irrigated	4	✓	-	✓	Cheng-Fang et al., (2012)
43	China	Rice	Sub-tropical	-	Acidic	-	375	Irrigated	6	-	✓	-	Zhang et al., (2013)
44	Canada	Maize	Cool temperate	Medium	-	-	199	Rainfed	18	✓	✓	-	Drury et al., (2006)
45	New Zealand	Soybean-Maize	Temperate	Medium	-	-	168	-	10	-	✓	✓	Smith et al., (2011)
46	Spain	Cereals	Warm temperate	Coarse	Alkaline	9.31	-	Rainfed	2	-	✓	✓	Tellez-Rio et al., (2015a)
47	UK	Fallow	Cool temperate	Coarse	-	-	-	Rainfed	2	✓	✓	✓	Yamulki and Jarvis, (2002)
48	Japan	Fallow-Soybean	Sub-tropical	Fine	Neutral	-	-	-	4	-	✓	✓	(Yonemura et al., 2014)
49	India	Rice	Sub-tropical	Coarse	Neutral	4.46	-	Irrigated	8	✓	✓	✓	Pandey et al., (2013)
50	Portugal	Rice	Warm temperate	Coarse	Acidic	10.9	550	Rainfed	15	✓	✓	✓	Fangueiro et al., (2017)

Other pieces of information that were used in this meta-analysis study grouped by the following categories: soil texture, soil pH, soil C: N ratio, N application rate, study duration, crop type, water management, and climatic conditions (Table 4.2). The three categories of soil texture were classified as coarse (sandy clay loam, loamy sand, sandy loam), medium (clay loam, loam, silt, silty clay loam, silt loam), and fine (silt clay, clay, sandy clay) based on USDA, (1999). Soil pH was grouped into a) acidic (⩽ 6.5), b) Neutral (6.6-7.3), and c) Alkaline (> 7.3) (Havlin et al., 2013). The N application rates were divided into two subgroups: low (⩽ 120 kg N ha^{-1}) and high (> 120 kg N ha^{-1}) levels of N. Water management practices were categorized into irrigation and rainfed subgroups. Crop type and climatic conditions were also divided into different subgroups (Table 4.2).

Table 4.2. Factors categorized as predictive variables in this meta-analysis study.

	Factors	**Levels**
Soil properties	Soil texture[a]	Coarse; Medium; Fine
	Soil pH[b]	Acidic (< 6.6); Neutral (6.6-7.3); Alkaline (> 7.3)
	Soil C: N ratio[c]	⩽ 10; > 10
Experimental conditions	N application rate (kg N ha^{-1})[d]	Low (⩽ 120); High (> 120)
	Study duration (days)	⩽ 320; 321-725; > 725
	Crop type	Barley; Maize; Rice; Rapeseed; Fallow; Soybean; Wheat
	Water management[e]	Irrigated; Rainfed
	Climate zone[f]	Cool temperate; Sub-tropical; Temperate; Warm-temperate

[a](USDA, 1999)
[b](Havlin et al., 2013)
[c](Zhang et al., 2013)
[d](Huang et al., 2018)
[e](Feng et al., 2018)
[f](Zhou et al., 2017)

4.2.2 Analysis

For this meta-analysis study, a continuous randomized-effects meta-analysis was performed to assess the GHGs emissions under NT versus CT (Michael et al., 2009; Skinner et al., 2014). The response ratio (*RR*) was used to compare the GHGs emissions, crop yield and overall GWP under NT and CT. We used a natural log-transformed response ratio (ln*RR*) as the effect size to calculate the effects of NT and CT on GHGs emissions from agricultural soils (Hedges et al., 1999).

$$\ln RR = \ln(X_{NT}/X_{CT}) = \ln(X_{NT}) - \ln((X_{CT}) \quad (1)$$

Where, the subscript of X_{NT} and X_{CT} are the mean values of the GHGs emissions, crop yield and overall GWP under NT and CT, respectively. If the *RR* value is zero, *RR* > 1 and *RR* < 1, its mean that treatment had no, positive and negative effect on GHGs emissions, respectively. The variance (v) of each *lnRR* for each study was calculated by using the equation (2);

$$v = \frac{SDt^2}{ntX_{NT}{}^2} + \frac{SDc^2}{ncX_{CT}{}^2} \quad (2)$$

Where, SDt and SDc are the standard deviation of treatment and control, and nt and nc are the number of replicates in treatment and control, respectively. For each research study, the weighting factor (ω) was measured as the inverse of the pooled variance $(1/v)$.

The mean effect sizes were calculated as;

$$\overline{lnRR} = \frac{\Sigma(lnRRi \times \omega i)}{\Sigma\, \omega i} \quad (3)$$

Where, ωi and *lnRRi* were the weight and effect size from the ith comparison, respectively.

The GWP is used to calculate the CO_2 equivalent emissions to measure all three GHG with the same measure (Tellez-Rio et al., 2017). We used the IPCC factors (IPCC, 2013) to calculate the GWP (kg CO_2-eq ha^{-1} yr^{-1}) in over a 100-year time horizon:

$$GWP = (CO_2 \times 1) + (N_2O \times 298) + (CH_4 \times 34) \quad (4)$$

4.2.3 Statistical analysis

METAWIN 2.1 (Rosenberg et al., 2000) software was used to calculate the mean effect sizes of the dataset and 95% bootstrapped confidence intervals (CIs) were generated using 4999 iterations. The results were considered significant If the 95% CI of cumulative CO_2, N_2O and CH_4 emissions did not overlap with zero and the randomization tests resulted $P < 0.05$. To ease interpretation, the percentage changes in selected variables were calculated following the equation:

$$(e^{\overline{lnRR}} - 1)\times 100\% \quad (5)$$

4.3 RESULTS

4.3.1 Overall effect on GHGs emissions and crop yield

Figure 4.1 shows the overall effect sizes ($\overline{lnRR}$) of NT as compared to CT on CO_2 (n=116), N_2O (n=181), CH_4 (n=168) emissions and crop yield (n=156). Overall, NT showed significantly positive effect on all three GHGs emissions as compared to CT. On average, NT significantly increased CO_2, N_2O, and CH_4 emissions by 7.1% (95% CI = 4.3%, 9.8%), 11.9% (95% CI = 8.3%, 15.7%), and 20.8% (95% CI = 18.0%, 10.8%), respectively (Fig. 4.1). In contrast, crop yields were not significantly different ($\overline{lnRR}$ = 2.1%, 95% CI = -0.8%, 5.2%) between NT and CT because 95% CI overlapped with zero (Fig. 4.1).

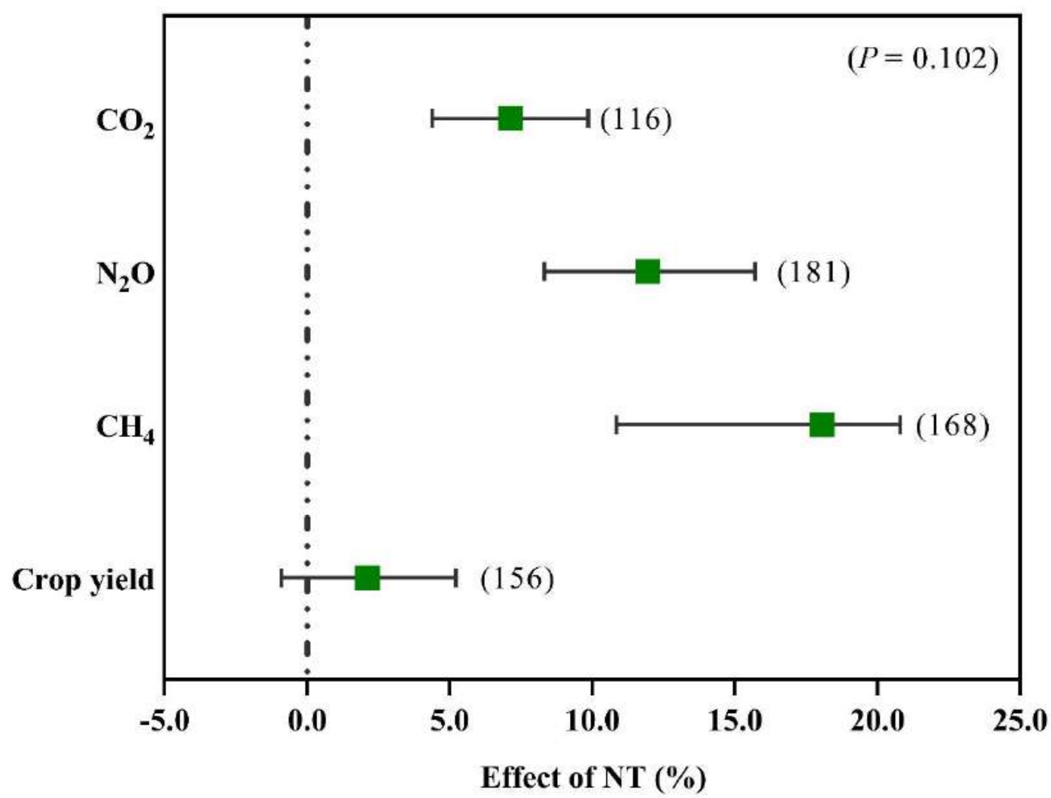


Figure 4.1. The overall effects of NT on GHGs emissions and crop yield. Parentheses numbers

indicate the number of observations and error bars represent 95% confidence intervals. The relationship is considered significant if $P < 0.05$.

4.3.2 Soil texture

Effect sizes of soil texture on CO_2, N_2O, and CH_4 emissions as well as crop yield are shown in Figure 4.2. According to our meta-analysis results, overall, soil texture did not show any significant effect on CO_2, and N_2O emissions as well as crop yield. In contrast, NT significantly enhanced CH_4 emissions as compared to CT (Fig. 4.2).

For CO_2 emissions, medium textured soils significantly increased CO_2 emissions by 8.0% (95% CI = 4.7%, 11.4%), whereas coarse ($\overline{lnRR}$ = 0.6%, 95% CI = -1.8%, 3.1%) and fine ($\overline{lnRR}$ = -5.5%, 95% CI = -13.0%, 2.6%) textured soils did not show any significant difference between NT and CT (Fig. 4.2(a)).

On the other hand, fine textured soils significantly reduced N_2O emissions by 24.2% (95% CI = -34.1%, -12.8%)) under NT as compared to CT (Fig. 4.2(b)). In contrast, N_2O emissions significantly increased in coarse ($\overline{lnRR}$ = 11.9%, 95% CI = 7.1%, 17.1%) and medium ($\overline{lnRR}$ = 11.9%, 95% CI = 6.7%, 17.4%) textured soils under NT (versus CT) (Fig. 4.2(b)).

Moreover, on average, NT as compared to CT significantly enhanced CH_4 emissions by 40.6% (95% CI = 10.7%, 78.6%) (Fig. 4.2(c)). Maximum emission was observed in fine textured soils ($\overline{lnRR}$ = 86.6%, 95% CI = 44.4%, 141.0%). While, NT also significantly increased CH_4 emission by 10.8% (95% CI = 7.3%, 14.4%) and 46.3% (95% CI = 41.1%, 51.7%) in coarse and medium textures soils, respectively (Fig. 4.2(c)).

Additionally, crop yield significantly increased in coarse textured soils by 9.4% (95% CI = 4.1%, 14.7%). In contrast, a significant reduction was observed in fine texture soils ($\overline{lnRR}$ = -17.5%, 95% CI = -21.9%, -13.4%). However, no significant difference between CT and NT in medium textured soils (Fig. 4.2(d)).

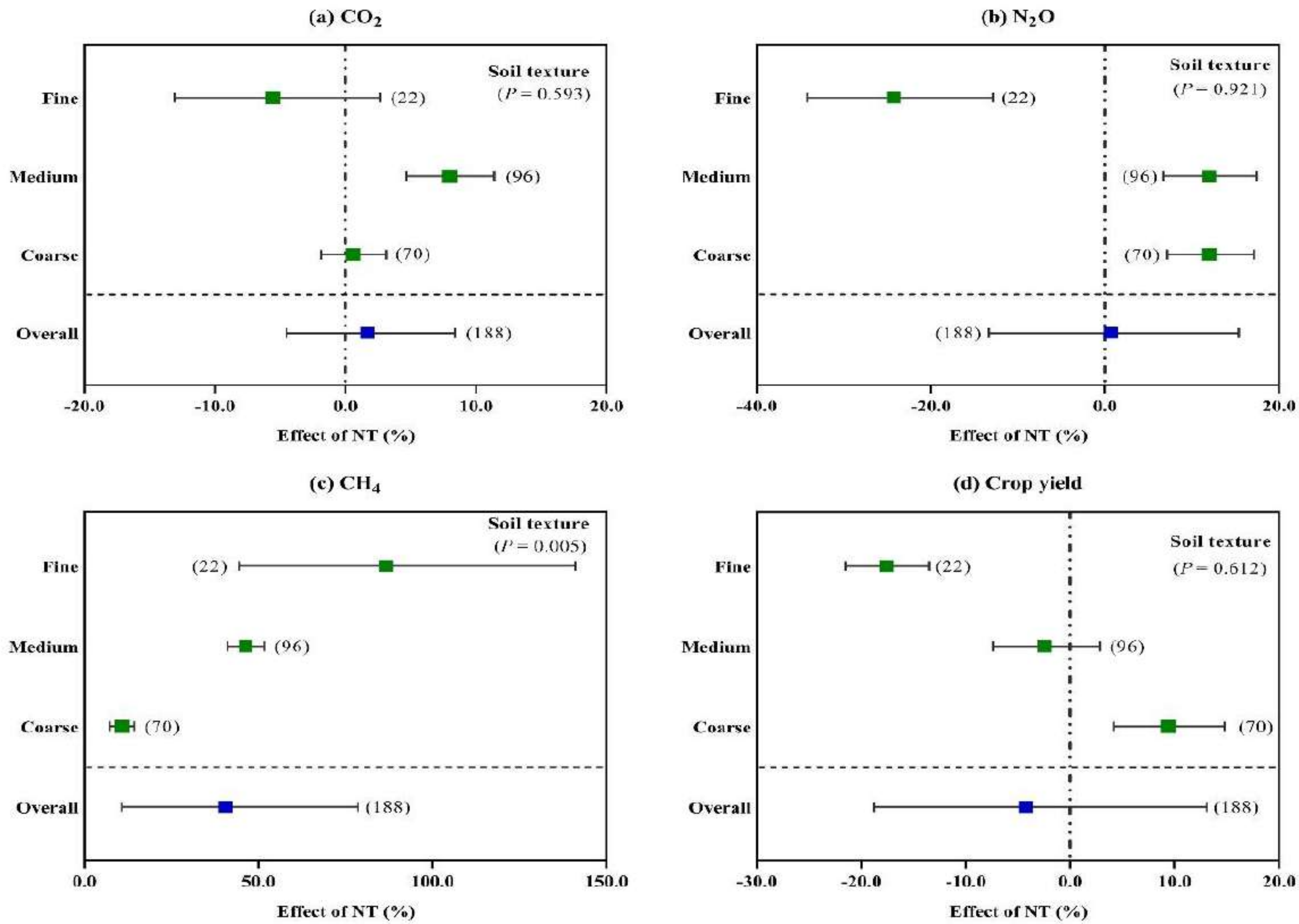


Figure 4.2. The effect soil textural classes on a) CO_2, b) N_2O, c) CH_4 emissions and d) crop yield following the application of NT. Parentheses numbers indicate the number of observations and error bars represent 95% confidence intervals. The relationship is considered significant if $P < 0.05$.

4.3.3 Soil pH and C: N ratio

Figure 4.3 shows the overall effect sizes of soil pH and C: N ratio on CO_2, N_2O and CH_4 emissions as well as crop yield from agricultural soils.

On average, the NT significantly enhanced CO_2 emission as compared to CT under soil pH ($\overline{lnRR}$ = 8.6%, 95% CI = 0.1%, 18.0%) and soil C: N ratio ($\overline{lnRR}$ = 7.4%, 95% CI = 3.5%, 11.6%) (Fig. 4.3(a)). The NT as compared to CT significantly increased CO_2 emissions by 16.8% (95% CI = 12.6%, 21.4%) and 7.7% (95% CI = 3.4%, 12.1%) in alkaline and neural soils, respectively (Fig. 4.3(ai)). On the other hand, soil C: N ratios also significantly affected CO_2 emissions under NT (Fig. 4.3(aii)). Overall, soil C: N ratio enhanced CO_2 emissions by 7.4%. The maximum positive effect for NT (versus CT) was occurred with > 10 C: N ratios ($\overline{lnRR}$ = 8.8%, 95% CI = 6.6%, 11.1%). However, no significant effect was observed in ⩽ 10 C: N ratios (95% CI overlapped with zero) ($\overline{lnRR}$ = 4.6%, 95% CI = -0.6%, 10.1%) (Fig. 4.3(aii)).

For N_2O emissions, overall, there was no significant difference for N_2O emissions ($\overline{lnRR}$ = 1.1%, 95% CI = -24.6%, 35.6%) between NT and CT in soil pH (Fig. 4.3(bi)). Similarly, overall, soil C: N ratios had no significant effect on N_2O emissions (95% CI overlapped with zero) (Fig. 4.3(bii)). The maximum N_2O emission was observed in acidic soils ($\overline{lnRR}$ = 30.0%, 95% CI = 24.8%, 35.6%). In contrast, NT as compared to CT significantly mitigated N_2O emissions under alkaline ($\overline{lnRR}$ = -12.3%, 95% CI = -16.5%, -7.9%) and neutral ($\overline{lnRR}$ = -9.6%, 95% CI = -18.4%, 0.1%) soils (Fig. 4.3(bi)). Similarly, overall, soil C: N ratios had no significant effect on N_2O emissions (95% CI overlapped with zero) (Fig. 4.3(bii)). On the other hand, NT significantly reduced N_2O emissions by 15.8% (95% CI = -24.1%, -6.4%) under ⩽ 10 C: N ratios. In contrast, a significant increment in N_2O emission ($\overline{lnRR}$ = 24.9%, 95% CI = 20.5%, 29.5%) was observed with > 10 C: N ratios under NT as compared to CT (Fig. 4.3(bii)).

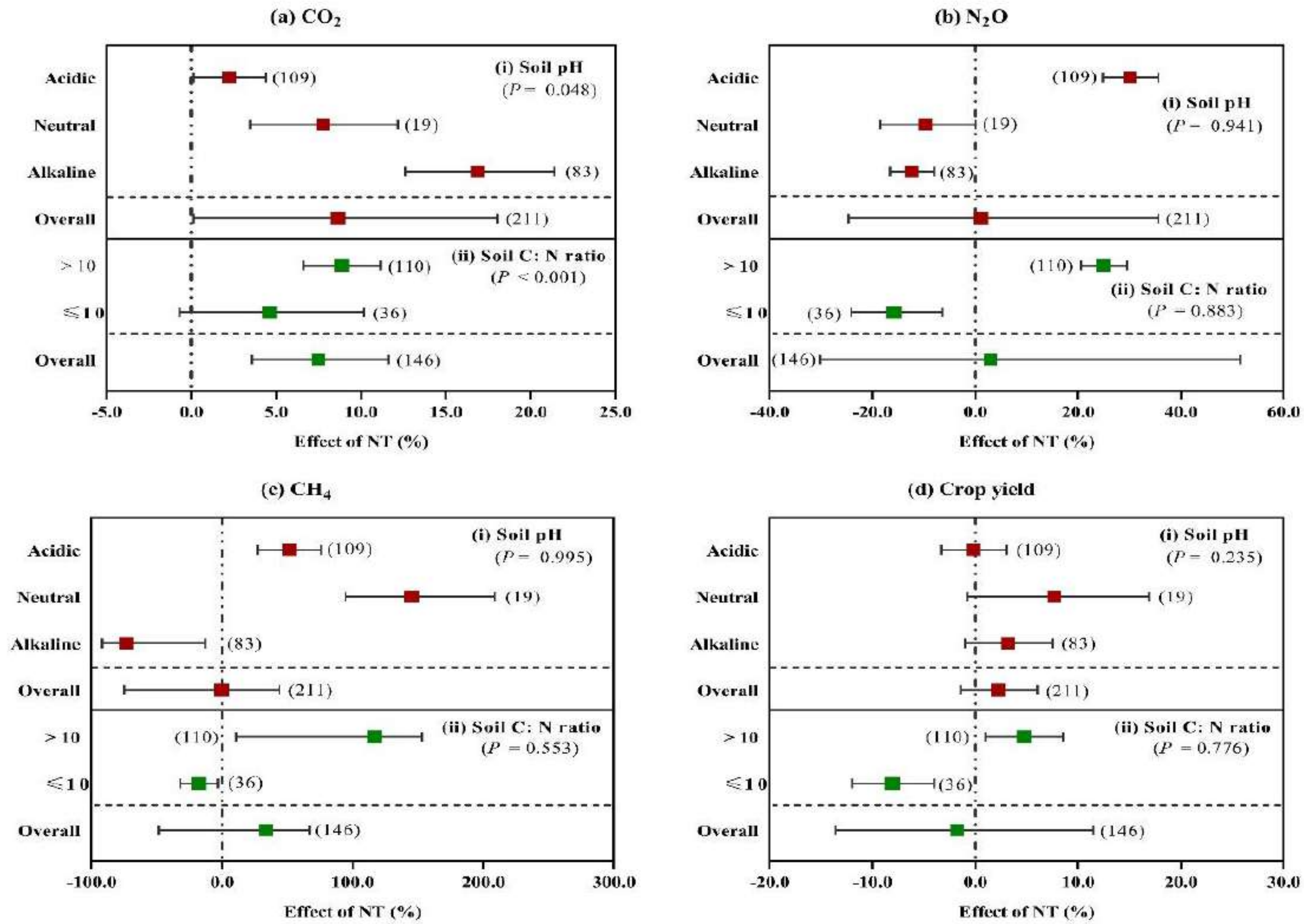


Figure 4.3. The impact of (i) soil pH and (ii) soil C: N ratio on a) CO_2, b) N_2O, c) CH_4 emissions and d) crop yield following the application of NT. Parentheses numbers indicate the number of observations and error bars represent 95% confidence intervals. The relationship is considered significant if $P < 0.05$.

The overall effect sizes of soil pH and C: N ratio for CH_4 emissions were ($\overline{lnRR}$ = -0.3%, 95% CI = -74.6%, 43.9%) and ($\overline{lnRR}$ = 33.6%, 95% CI = -48.3%, 26.9%), respectively (Fig. 4.3(c)) showing that both variables had not effect on CH_4 emission (because 95% CI overlapped with zero in both cases) under NT as compared to CT. Acidic and neutral soils significantly stimulated CH_4 emissions by 51.7% (95% CI = 47.5%, 55.8%), and 145.2% (95% CI = 94.6%, 208.6%), respectively. On the other hand, NT significantly reduced CH_4 emission by 73.2% (95% CI = -12.7%, -71.8%) in alkaline soils as compared with CT (Fig. 4.3(ci)). For C: N ratio, similar results were found as in N_2O emission (Fig. 4.3(cii)).

For crop yield, overall effect sizes of soil pH ($\overline{lnRR}$ = 2.2%, 95% CI = -1.3%, 6.0%) and C: N ratio ($\overline{lnRR}$ = -1.7%, 95% CI = -13.5%, 11.5%) were not shown significant difference between NT and CT (Fig. 4.3(d)). No significant difference between NT and CT was observed in all soil pH classes (Fig. 4.3(di)). While a significant reduction ($\overline{lnRR}$ = -8.0%, 95% CI = -11.9%, -0.9%) and increment ($\overline{lnRR}$ = 4.7%, 95% CI = 1.0%, 8.5%) in crop yields were occurred with $\leqslant$ 10 and > 10 C: N ratios, respectively (Fig. 4.3(dii)).

4.3.4 N application rate and crop duration

Figure 4.4 shows the response of GHGs emissions with crop yield to NT as compared with CT. For N application rate and crop duration, 200 and 245 paired observations were sorted from the database, respectively. Different N application rates significantly affected GHGs emissions and crop yield. Overall, CO_2, N_2O, CH_4 emissions, and crop yield significantly increased by 6.6%, 13.0%, 57.9%, and 23.3%, respectively with NT as compared to CT (Fig. 4.4).

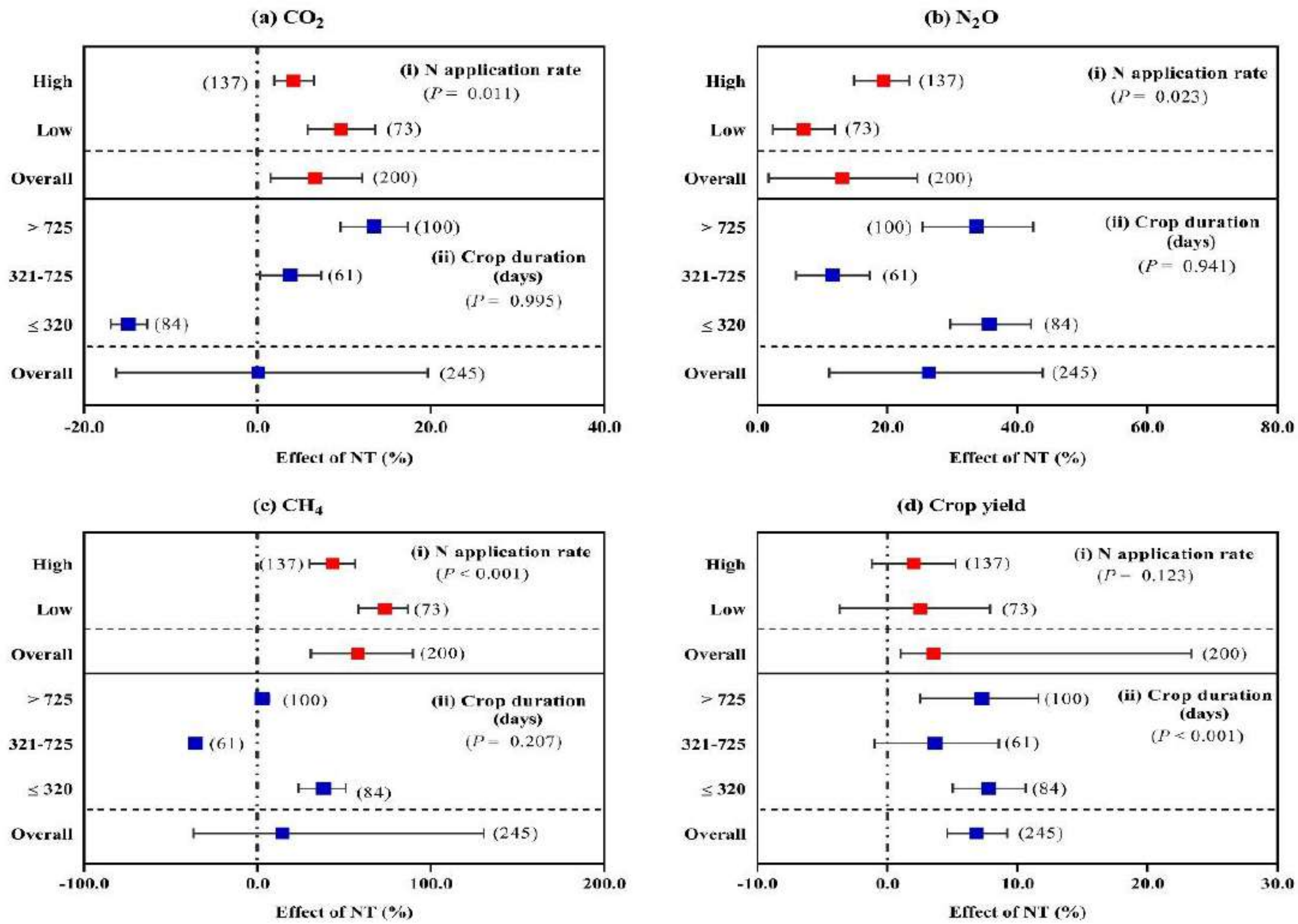


Figure 4.4. The effect of (i) N application rate and (ii) crop duration on a) CO_2, b) N_2O, c) CH_4 emissions and d) crop yield following the application of NT. Parentheses numbers indicate the number of observations and error bars represent 95% confidence intervals. The relationship is considered significant if $P < 0.05$.

On average, maximum CO_2 emission ($\overline{lnRR}$ = 9.6%, 95% CI = 5.7%, 13.5%) was observed in low N application rate with NT CT (Fig. 4.4(ai)). In contrast, high N application rate significantly enhanced N_2O emission by 19.3% (95% CI = 14.7%, 23.3%) (Fig. 4.4(bi)). On the other hand, low N application rate showed a strong positive effect ($\overline{lnRR}$ = 73.6%, 95% CI = 68.2%, 76.8%) on CH_4 under NT as compared to CT (Fig. 4.4(ci)). However, there was no significant difference in crop yield in both low ($\overline{lnRR}$ = 2.5%, 95% CI = -23.6%, 7.8%) as well as high ($\overline{lnRR}$ = 2.0%, 95% CI = -1.1%, 5.2%) N application rate (because 95% CI overlapped with zero) (Fig. 4.4(di)).

Overall, crop duration had no significant effect on CO_2 ($\overline{lnRR}$ = 0.1%, 95% CI = -16.3%, 19.6%) and CH_4 ($\overline{lnRR}$ = 130.0%, 95% CI = -37.0%, 14.3%) emissions (95% CI overlapped with zero) (Fig. 4.4(aii, cii)). In contrast, overall crop duration significantly increased N_2O emission and crop yield by 26.3% (95% CI = 11.0%, 43.9%) and 6.8% (95% CI = 4.6%, 9.1%) (Fig. 4.4(bii, dii)).

On average, maximum CO_2 emission ($\overline{lnRR}$ = 13.4%, 95% CI = 9.6%, 17.3%) was observed in > 725 days, whereas maximum mitigation effects ($\overline{lnRR}$ = -14.8%, 95% CI = -6.8%, -12.7%) were seen in ⩽ 320 days under NT versus CT (Fig. 4.4(aii)). In contrast, ⩽ 320 days significantly increased CH_4 emission by 150.9% (95% CI = 143.7%, 158.0%) and significant reduction was detected in medium-term duration (321-720) (Fig. 4.4(cii)). On the other hand, NT significantly increased N_2O emission and crop yield in all duration periods (Fig. 4.4(bii, dii)).

4.3.5 Crop type

Crop species showed significant positive and negative effects on GHGs emissions and crop yield (Fig. 4.5). Overall, NT exhibited no significant effects on GHGs emissions as well as crop yield (all 95% Cl overlapped with zero) compared to CT (Fig. 4.5). On average, barley, rice and soybean significantly increased CO_2 emissions by 18.2% (95% CI = 15.4%, 21.1%), 8.5% (95%

CI = 6.5%, 10.5%) and 27.6% (95% CI = 21.2%, 34.1%), respectively (Fig. 4.5(a)). In contrast, fallow soils significantly decreased CO_2 emissions by -36.9% % (95% CI = -40.7%, -32.9%). On the other hand, there were no changes in CO_2 emissions with maize, rapeseed and wheat crop species in NT as compared with CT (Fig. 4.5(a)).

After NT, N_2O emissions significantly increased in barley, fallow, rice and soybean crops by 29.0%, 50.9%, 21.2% and 29.5%, respectably (Fig. 4.5(b)). Alternatively, N_2O emissions significantly lower in rapeseed (-27.4%) and wheat (-12.3%) crops in NT (versus CT) (Fig. 4.5(b)). For CH_4 emission, maize ($\overline{lnRR}$ = 87.7%, 95% CI = 36.3%, 155.9%) and rice ($\overline{lnRR}$ = 43.9%, 95% CI = 39.0%, 47.6%) had strong positive effects after NT (Fig. 4.5(c)). Fallow soils, wheat and barley crops significantly reduced CH_4 emissions by -43.8%, -25.0% and -17.7%, respectively (Fig. 4.5(c)).

However, crop yields were not changed in NT as compared to CT in all crop species except barley and wheat (Fig. 4.5(d)). Maximum crop yields were observed in barley ($\overline{lnRR}$ = 43.7%, 95% CI = 34.1%, 54.1%) and wheat ($\overline{lnRR}$ = 4.4%, 95% CI = 0.8%, 8.3%) after NT as compared to CT (Fig. 4.5(d)).

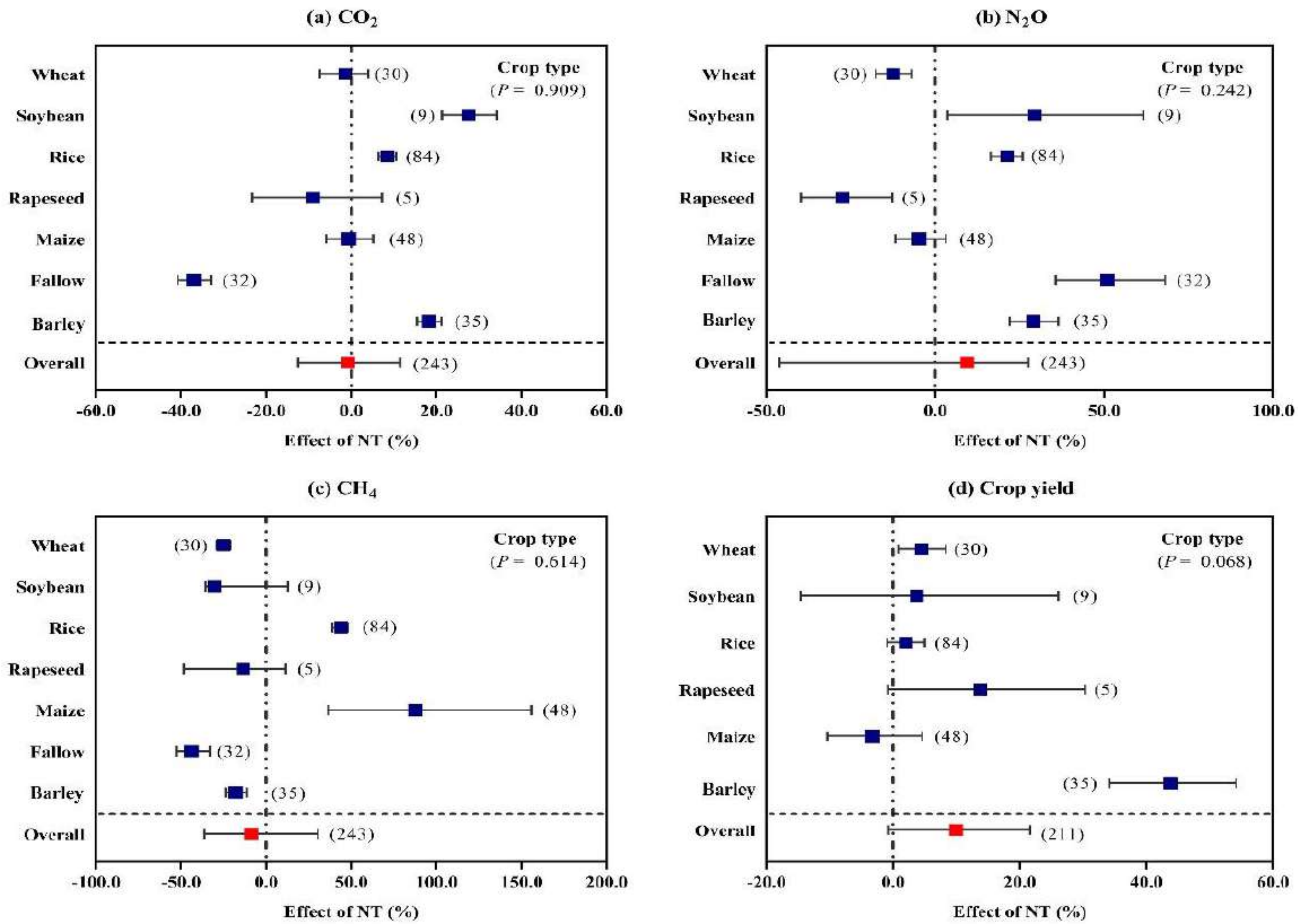


Figure 4.5. The Influence of crop types on a) CO_2, b) N_2O, c) CH_4 emissions and d) crop yield following the application of NT. Parentheses numbers indicate the number of observations and error bars represent 95% confidence intervals. The relationship is considered significant if P < 0.05.

4.3.6 Water management and climate zone

Water management practices and climate zones significantly affected GHGs emissions and crop yield. Overall, there were no significant differences between NT and CT in GHGs emissions and crop yield because overall effect sizes overlapped with zero in water management practices (Fig. 4.6(ai, bi, ci, di)).

On average, rainfed significantly increased CO_2 emissions by 16.0% (95% CI = 12.9%, 19.2%), however, no effect was observed in the irrigation system ($\overline{lnRR}$ = -1.3%, 95% CI = -4.2%, 1.6%) (Fig. 4.6(ai)). Similarly, rainfed also had strong positive effects on N_2O emission (14.6%) in NT as compared to CT (Fig. 4.6(bi)). However, NT in irrigated soils significantly increased CH_4 emission ($\overline{lnRR}$ = 53.5%, 95% CI = 49.7%, 56.8%), whereas maximum reduction was observed in rainfed agricultural soils ($\overline{lnRR}$ = -42.7%, 95% CI = -45.7%, -39.5%) as compared to CT (Fig. 4.6(ci)). On the other hand, crop yield significantly increased by 17.2% in the rainfed system, while significant reduction (-4.5%) was seen in irrigated soils after NT practice as compared with CT (Fig. 4.6(di)). Furthermore, warm and cool temperate climate zones significantly enhanced CO_2, N_2O emissions as well as crop yields (Fig. 4.6(aii, bii, dii)). Whereas, CH_4 emission significantly increased in sub-tropical climate zone ($\overline{lnRR}$ = 59.0%, 95% CI = 54.8%, 63.5%) after NT practice (Fig. 4.6(cii)).

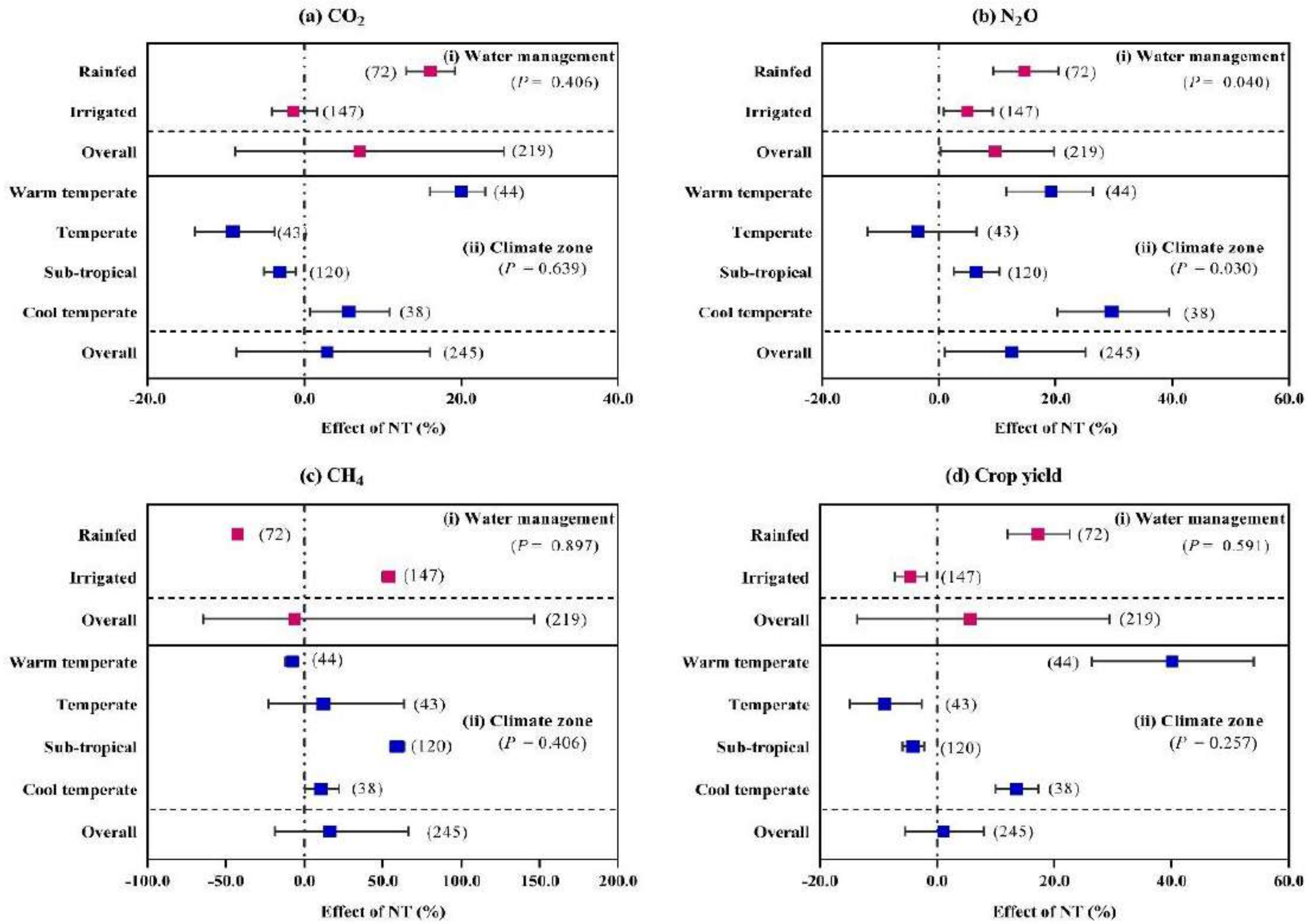


Figure 4.6. The impact of (i) water management and (ii) climate zones on a) CO_2, b) N_2O, c) CH_4 emissions and d) crop yield following the application of NT. Parentheses numbers indicate the number of observations and error bars represent 95% confidence intervals. The relationship is considered significant if $P < 0.05$.

4.3.7 NT and overall GWP

Figure 4.7 shows the responses GWP to NT as compared to CT. For GWP analysis, only those research studies were included who simultaneously reported CO_2, N_2O and CH_4 emissions. Overall, NT significantly reduced GWP by 7.5% (95% CI = -14.3%, -0.3%) as compared to CT (Fig. 4.7). Only 11 publications were used to measure the GWP (Table 4.1) and it might be the reason in the reduction of overall GWP.

On average, the low N application rate did not exhibit any difference between NT and CT. In contrast, high N application rate significantly decreased GWP ($\overline{lnRR}$ = -13.0%, 95% CI = -17.3%, -8.1%) (Fig. 4.7(a)). On the other hand, neutral soils significantly increased GWP ($\overline{lnRR}$ = 36.6%, 95% CI = 27.1%, 46.8%), whereas acidic soils reduced GWP by 17.9% (Fig. 4.7(b)). Similarly, coarse textured soils also mitigated the GWP after NT as compared to CT ($\overline{lnRR}$ = -14.3%, 95% CI = -19.2%, -9.1%) (Fig. 4.7(c)). However, rainfed and irrigated soils significantly decreased and increased GWP by 20.7% and 9.5%, respectively (Fig. 4.7(d)). Significant reductions in GWP after NT (versus CT) were observed in fallow (45.2%), rice (7.3%) and maize (17.3%) crops, whereas barley increased GWP by 8.1% (Fig. 4.7(e)). Furthermore, warm temperate climate zone significantly deceased GWP ($\overline{lnRR}$ = -26.2%, 95% CI = -31.8%, -20.0%), while sub-tropical increased GWP by 19.7% (95% CI = 10.7%, 29.4%) after NT as compared to CT (Fig. 4.7(f)). Though a few studies reported all three GHGs emissions as well as crop yield after NT as compared with CT. These all results were probably affected through publication bias, and so should be understood cautiously.

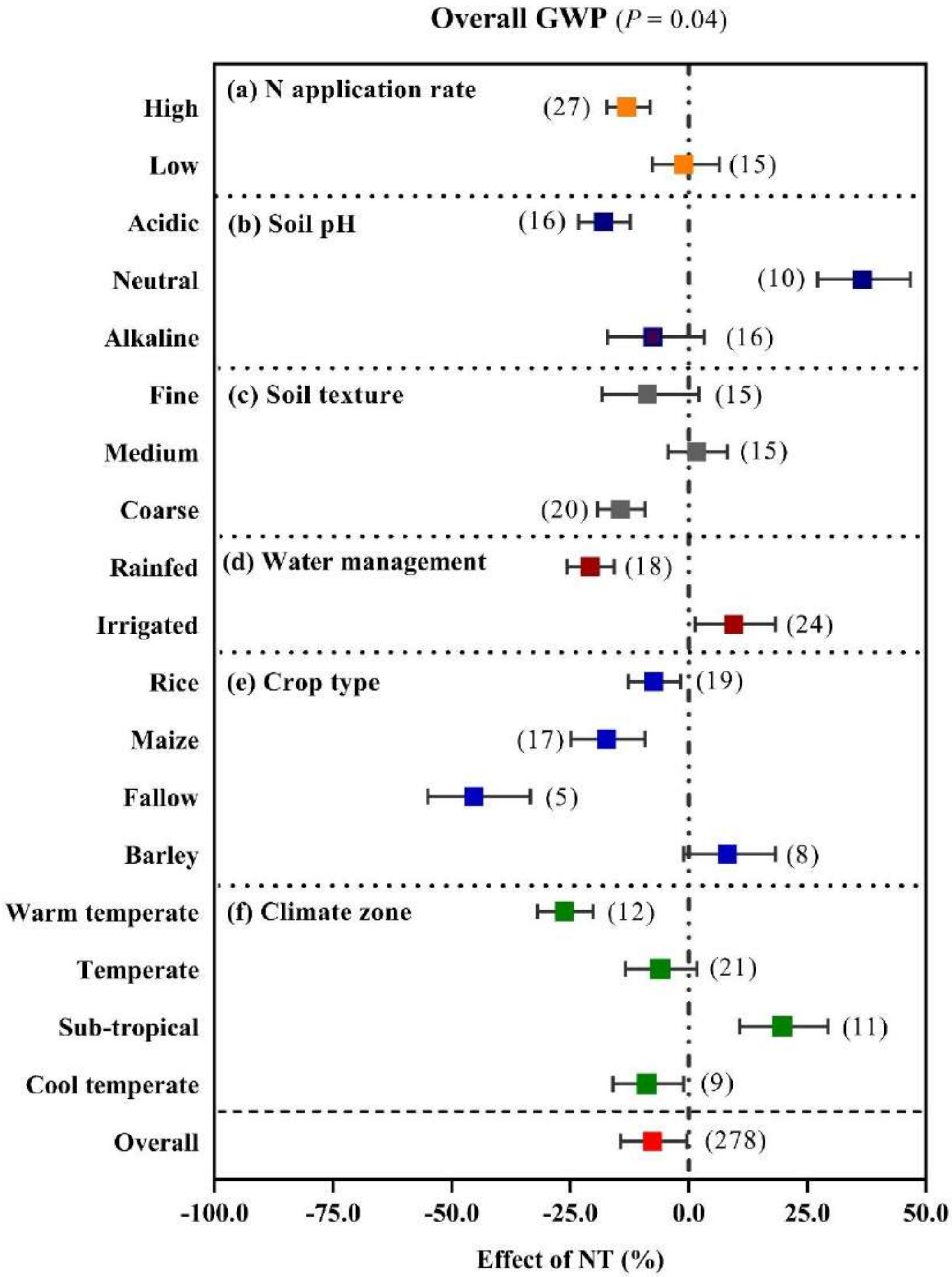


Figure 4.7. The effect of NT on the overall GWP of GHGs emissions. Parentheses numbers indicate the number of observations and error bars represent 95% confidence intervals. The relationship is considered significant if $P < 0.05$.

4.4 Discussion

4.4.1 Effect of tillage on GHGs emissions and crop yield

Conservation tillage especially NT is becoming an effective and popular practice for decreased investment costs with improved soil fertility as well as C sequestration (Alvarez et al., 2014; Lal, 2004c). NT is considered as an effective technique to mitigate climate change. However, the effect of GHGs emissions and crop yield under NT practice is still controversial. Some research studies reported that NT significantly increased GHGs emissions (Oorts et al., 2007; Pandey et al., 2012; Yao et al., 2013b), whereas some studies showed that GHGs emissions significantly decreased under NT as compared to CT (Rutkowska et al., 2018; Tellez-Rio et al., 2015b).

According to our meta-analysis results, overall, NT significantly increased CO_2, N_2O and CH_4 emissions as compared to CT, whereas crop yield was similar between CT and NT (Fig. 4.1). Long-term application of NT practice significantly alters GHGs concentration through SOM stocks, soil physicochemical properties, and microbial composition and population. Huang et al., (2018) conducted a meta-analysis study and found that N_2O emissions significantly increased without affecting crop yield in NT as compared to CT. Oorts et al., (2007) and Chatskikh and Olesen, (2007) reported that CO_2 and N_2O emissions significantly enhanced with NT as compared to CT. According to Ussiri et al., (2009), NT as compared to CT increased N_2O emission but significantly decreased CH_4 emission in the winter cropping season. Li et al., (2011) studied and found that CH_4 emissions increased in early rice after NT practice as compared to CT.

Tillage practices have an important influence on CO_2 emissions. Usually, CT brings drastic changes to soil physical conditions that lead to increased CO_2 emissions (e.g. by 50%) due to stimulated SOM decomposition processes (Lal, 2006; Rutkowska et al., 2018). Furthermore, crop residues also significantly affect CO_2 emissions under NT. Crop residues provide ready available C and N substrates for microbial community and consequently enhances heterotrophic respiration due to increased soil microbial activities (Plaza-Bonilla et al., 2014b; Zhang et al., 2016), thus enhancing CO_2 emissions. Moreover, under long-term NT, decomposition of crop residues significantly increases because short-term field studies might not be significant source of CO_2 emissions associated with crop residues under NT practice (Oorts et al., 2007).

N_2O emissions are significantly affected by nitrification and de-nitrification processes (Rodríguez, 2019; Shakoor et al., 2018). Some research studies have found that NT (versus CT) acts as a significant sink and/or source for N_2O emissions (Almaraz et al., 2009b; Pandey et al., 2012) due to irrigation, high precipitation, N fertilization rate and placement. Moreover, crop residues might also have an important factor to stimulate the N_2O emission under NT as compared to CT.

CH_4 emissions can be influenced by tillage practices (Canadell and Schulze, 2014; Smith et al., 2008; Zhao et al., 2016). Long-term NT practice increases soil bulk density, compaction and water-filled pore spaces (WFPS) (Bayer et al., 2012) which ultimately favors the anaerobic decomposition of SOM. On the other hand, long-term field experiments under NT practice also significantly increases water-stable macroaggregates with increases in SOM concentration and consequently increases methanotrophic activities resulting in CH_4 emissions (Álvaro-Fuentes et al., 2008a; Plaza-Bonilla et al., 2013).

In addition, fertilizer application rate and placement also play an important role in GHGs emissions under NT practice as compared to CT (Liu et al., 2020). For example, surface broadcast of N fertilizer under NT practice not only emits CH_4 but also significantly increases CO_2 and N_2O emissions through temperature, moisture content and other environmental factors (Fan et al., 2020; Jian-She et al., 2011). Surface placement of chemical fertilizers provides sufficient substrate to the population of denitrifiers under NT (Liu et al., 2006). Nitrifiers and denitrifiers activities significantly decreased with depth under NT practice because deep N placement may reduce inorganic N substrates supply to these microbial community (Groffman, 1985; Venterea and Stanenas, 2008).

4.4.2 Effects of soil physicochemical properties on GHGs emissions and crop yield

4.4.2.1 Soil texture

Emissions of GHGs and crop yield were significantly regulated by soil texture in NT practice. For CO_2, the maximum emission was observed in medium textured soils in NT as compared to CT, whereas fine and coarse textured soils did not show any effect on CO_2 emission (Fig. 4.2(a)). Aslam et al., (2000) studied and observed that CO_2 emission significantly increased in silt loam soil with NT as compared to CT. Ahmad et al., (2009) and Pareja-Sánchez et al., (2019) also found that medium textured soil significantly increased CO_2 emission in NT (versus CT). Generally, medium textured soils contain more nutrients and soil moisture content. Under NT as compared to CT, the existence of crop residues (from the previous crop) on the soil surface increases water availability by reducing water loss through evaporation (Lampurlanés et al., 2016). The increased concentration in moisture contents observed under NT as compared to CT was accompanied by maximum CO_2 emissions indicating enzymatic activities stimulated by SOM contents (Pareja-Sánchez et al., 2019).

According to our meta-analysis results, coarse and medium textured soils significantly increased N_2O emission with NT management practice (Fig. 4.2(b)). Ball et al., (2014), Sheehy et al., (2013) and Zhang et al., (2015) also came to the similar conclusions. Soil texture significantly controls the emissions of N_2O through moderating the soil oxygen availability because soil texture has an important impact on the size as well as the distribution of soil pores (Corre et al., 1999). In coarse textured soils, the nitrification and denitrification processes significantly influenced N_2O emissions (Zhou et al., 2014). Consumption of oxygen following SOM decomposition may enhance oxygen stress in microsites and significantly affect denitrification process and therefore N_2O emissions might be less in fine textured soils as compared to coarse textured soils (Chen et al., 2013). Moreover, crop residues and N fertilizer application to agricultural soils provide a sufficient amount of C substrate that can stimulate the denitrification process and consequently enhance N_2O emissions in NT as compared to CT.

Furthermore, coarse, medium, and fine textured soils significantly increased CH_4 emission by 10.8%, 46.3%, and 86.6% (Fig. 4.2(c)). Kim et al., (2016) conducted a long-term field experiment in fine silty soil and observed a much higher CH_4 emission in NT (36.0%) than the CT plot. Fine textured soils have maximum water holding capacity (USDA, 2008), which alternatively produce anaerobic conditions in the soil. Under anaerobic terrestrial environmental conditions, biological decomposition of the SOM by methanogens emits a significant amount of CH_4 from agricultural soils (Lu, 2011). However, soils with fine pores support the emission of CH_4 under anaerobic conditions (Ball, 2013; Dutaur and Verchot, 2007). On the other hand, the long-term application of NT can significantly alter the physical properties of soil, which may also change the microbial composition as well as the population (Elliott et al., 1988). Particularly, the bacterial communities which convert the biological polymers (for example hemicellulose and cellulose to carbohydrates) may supply more methanogenic substrates and ultimately affect the methanogenesis process and CH_4 emission under long-term NT practice as compared to CT (Demirel and Scherer, 2008).

Crop yield was also significantly affected by textural classes under NT. Our results revealed that coarse textured soil had a significant positive effect on crop yield in NT as compared to CT (Fig. 4.2(d)). Beyaert et al., (2002) studied and found that crop yield significantly increased in coarse textured soils in NT management practice as compared to CT. The increment in the crop yield in coarse textured soil can be attributed to the maximum availability of the water contents to plants in NT practice due to higher crop residues cover and precipitation.

4.4.2.2 Soil pH and C: N ratio

Soil pH and C: N ratios significantly affect GHGs emissions and crop yield with the application of NT. In this meta-analysis, in NT, alkaline soils significantly enhanced CO_2 emission, whereas acidic and natural soils positively correlated with N_2O and CH_4 emissions, respectively (Fig. 4.3(ai, bi, ci)). Huang et al., (2018) conducted a meta-analysis study and also found that acidic soils decreased CO_2 and CH_4 emissions, while significant stimulation was observed in N_2O emission in NT as compared to CT. Mei et al., (2018) also performed a meta-analysis study and reported similar findings. Maximum N_2O emissions from acidic soil under NT (versus CT) were also reported by other researchers (Liu et al., 2010; Samad et al., 2016).

Microbial activities significantly contribute to the global CO_2 emission and their activities are sensitive to soil pH. Increasing soil pH significantly improves basal respiration and consequently affect CO_2 emissions (Lundström et al., 2003). The activity of N_2O reductase (N_2OR) decreases significantly in acidic soils than alkaline soil as it is more sensitive to acidic soils which could inhibit N_2O conversion to N_2, leading to enhance in N_2O (Liu et al., 2010; Liu et al., 2014). Other researchers studied and reported that nitrification as well as denitrification processes are influenced by soil pH and resulted in N_2O emissions. Generally, autotrophic nitrifiers prefer neutral and/or slightly alkaline conditions for oxidizing NH_4^+ (ammonia) to NO_3^- (nitrate), and therefore, the nitrification processes are also frequently lower in acidic soil conditions (Chen et al., 2013). Similarly, heterotrophic denitrifiers activities also slow in acidic soils as compared to alkaline soils. On the other hand, N_2O fractions might be higher at low pH, mainly with an adequate NO_3^- supply. This is normally attributed to the sensitivity of N_2O reductase to proton activity (Bouwman, 2001).

Methanogenesis bacterial activities simulated under anaerobic soil conditions and ultimately increases CH_4 emission (J. Liu et al., 2015). According to Linn and Doran, (1984) research study, the population of anaerobic microorganisms in the topsoil of NT soils was greater than CT soils might be due to higher crop residues on surface. Generally, the best soil pH for the methanogenesis process is considered closer to neutral. The growth and activity of these bacteria will be reduced at < 5 and > 8.5 soil's pH (Staley et al., 2011). Biological degradation of SOM is done with anaerobic bacteria and optimal activity was found with pH 7 (Horn et al., 2003). Wang et al., (1993) also found that the maximum CH_4 emissions were observed in the pH range of 6.9 to 7.1 (neutral soil pH) because methanogenic is acid sensitive. Thus, our meta-analysis study results were similar to previous research studies.

Higher soil C: N ratios (>10) had a strong positive effect on GHGs emissions (Fig. 4.3(aii, bii, cii)). Zhang et al. (2016) and Lin et al. (2015) found that maximum CO_2 and N_2O emissions occurred in high soil C: N ratios (> 10). Crop residues increase soil C: N ratio in NT soils as compared to CT, also enhance microbial activities, and alternatively increase GHGs emissions (Mosier et al., 2006a; Muñoz et al., 2019).

According to our meta-analysis results, there was no significant difference between NT and CT in crop yield at soil pH. While, higher soil C: N ratio increased crop yield (Fig. 4.3(di, dii)). There would be several environmental factors like climate, temperature, water content, textural class, and SOM content that can affect the crop yield and should be considered properly in future research studies.

4.4.3 N application rate and crop duration

GHGs emissions and crop yield significantly influenced by N application rate and duration of study. Generally, it is considered that N application rate is directly proportional to GHGs emissions and crop yield. According to our study, low rate of N application ($\leqslant$ 120 kg N ha^{-1}) significantly increased CO_2 and CH_4 emissions by 9.6% and 73.6%, whereas a high level of N application rate significantly enhanced N_2O emissions in NT plots as compared to CT (Fig. 4.4(ai, bi, ci)). In contrast, N application rate did not show any significant difference between NT and CT on crop yield (Fig. 4.4(di)).

Mosier et al., (2006) also found that plot with a low level of N fertilizer and /or control plot produced more CO_2 and CH_4 emissions under NT as compared to CT. Aronson et al., (2010) conducted a meta-analysis study and found that a low level of N application significantly increased CH_4 emissions. However, Huang et al., (2018), Plaza-Bonilla et al., (2017) and Abdalla et al., (2016) studied and found no significant difference between NT and CT on CO_2 emissions with N fertilizer application rate as well as placement. . In our case, firstly, it might be possible that the plot with a low level of N application rate has more crop residues and moisture contents which favor the CO_2 emissions. Secondly, duration of the tillage operation particularly NT can also be an important factor to stimulate CO_2 emission. Concentration of soil organic carbon (SOC) significantly increased under NT during long-term (4 and 50 years) field experiments (Lemke et al., 2010; Morell et al., 2010) because application of N fertilizer stimulated biological activities and resulting more CO_2 emissions. Therefore, it is highly recommended that in future studies these factors should be reported properly.

Generally, it is expected that the application of NH_4^+ containing synthetic fertilizer will lead to reduced CH_4 oxidation (Bedard et al., 1989; Sylvia et al., 2005). Nevertheless, this response is totally rate dependent; a low level of N application tends to increase CH_4 emission while a high rate of N application significantly reduces CH emission from agricultural soil (Aronson et al., 2010).

Zhao et al., (2016) conducted a meta-analysis study and found that a high level of N application significantly increased N_2O emission under NT as compared to CT. Shakoor et al., (2018) also conducted a field experiment and reported that N_2O emission increased with a higher level of N application rate. High level of N application significantly stimulates the denitrification process and ultimately releases more N_2O. Moreover, type and time of N fertilizer also influences the nitrification as well as denitrification processes. For example, anhydrous ammonia, which is commonly injected, shows maximum losses as compared to other fertilizers. Furthermore, soil physiochemical conditions are also expected to be favorable to increase denitrifying activities in NT as compared to CT (Venterea et al., 2005).

On the other hand, crop duration with NT management significantly affects GHGs emissions as well as crop yield. In this study, crops that are having > 725 days had a strong positive effect on CO_2, N_2O emissions and crop yield (Fig. 4.4(aii, bii, dii)), whereas CH_4 emission was significantly affected with ⩽ 320 days in NT as compared to CT (Fig. 4.4(cii)). Mei et al., (2018) and Huang et al., (2018) had also found similar findings. Long-term application of NT practice may decrease and/or resist the microbial activities (Alluvione et al., 2009). According to Oorts et al., (2007), the long-term application of NT significantly increased C stocks and then ultimately stimulated CO_2 emission. Duration of study with NT practice as compared to CT were also affected by soil physiochemical conditions, like soil compaction, water-filled pore spaces, aeration and soil structure which can significantly alter the microbial communities as well as activities to produce GHGs.

4.4.4 Crop type

The crop species also played an important role in the emissions of GHGs and crop yield (Huang et al., 2018). Barley and soybean crops significantly increased CO_2 emissions, while rice, soybean, barley and fallow soils had strong positive effects on N_2O emissions in NT as compared to CT (Fig. 4.5(a, b)). Moreover, rice and maize crops significantly enhanced CH_4 emissions (Fig. 4.5(c)). On the other hand, NT did not show any effect on crop yield except barley (Fig. 4.5(d)). Behnke et al., (2018) conducted a long-term field experiment and observed that soybean produced more CO_2 emissions than maize under NT management compared with CT. Gan et al., (2012) studied and reported a barley significantly enhanced CO_2 emission. According to Zhang et al., (2016) and Hurisso et al., (2016) studies, the maximum N_2O emission was observed in the fallow season. Pareja-Sánchez et al., (2019) and Wu et al., (2019) also studied and reported that maize and rice fields are a significant increase in CH_4 emissions in NT.

In NT management fields, microbial activities are the key factor for stimulating the GHGs emissions (Banger et al., 2012; Wang et al., 2019). The heterotrophic microbes significantly increase decomposition SOM (Bore et al., 2017). The decomposition of SOM significantly enhance C mineralization and ultimately increases CO_2 emissions from croplands (Hossain et al., 2017). Higher N_2O emission from the fallow seasons might be due to the increased mineralization process. The maximum N_2O fluxes from rice, soybean, and barley crops may be associated with the higher N application rate, higher soil water contents (SWC), temperatures and crop residues, which increased nitrifier as well as denitrifier activities in NT as compared to CT (Hu et al., 2019). On the other hand, biological N fixation by leguminous crops, like soybean, alfalfa, and Cereals, also provides an important impact on N level in agricultural soils. For example, transformation of organic N in soybean nodules is mineralized into NH_4^+ that will be converted into N_2O by nitrifier and denitrifier activities (Sánchez and Minamisawa, 2019). The CH_4 emissions from croplands depend on the availability of SOC content and anaerobic conditions (Tariq et al., 2017). In addition, soil temperature, bulk density and water contents also play a vital role in methanogens activity under NT management fields (Mitra et al., 2002) that significantly affected CH_4 emission.

Furthermore, the maximum yield was observed in barley crops under NT (Fig. 4.5(d)). A meta-analysis study reported that barley yield increased in NT practice (Huang et al., 2018). Another researcher studied in the Mediterranean climate and found that yield significantly increased in NT as compared to CT due to maximum WUE (water use efficiency) (Plaza-Bonilla et al., 2014a).

4.4.5 Water management and climate zone

According to our meta-analysis results, the rain-fed system significantly stimulated CO_2 and N_2O emission, whereas irrigated lands produced more CH_4 emissions (Fig. 4.6((ai, bi, ci)). De Sanctis et al., (2012) studied and reported that long-term NT management practice significantly increased SOC in the rain-fed region and consequently enhanced CO_2 emission. Another researcher studied and found that NT management as compared to CT significantly increased SOC particularly in topsoil (0-20cm) in the rain-fed system (Álvaro-Fuentes et al., 2008c). Plaza-

Bonilla et al., (2014a) and Tellez-Rio et al., (2015a) found maximum N_2O emission from the rain-fed Mediterranean region under NT as compared with CT. Previous research studies describe that emission of N_2O from continuous flooded croplands was negligible (Fangueiro et al., 2017; Liu et al., 2010; Zou et al., 2005). Greater N_2O emission under NT as compared to CT may be due to fertilizer placement (topdressing) and crop residues. In addition, soil wetting and drying conditions also favored nitrification as well as denitrification processes. In rainfed agricultural system, wetting and drying cycles produced in soil by rainfall that provide ideal conditions for both nitrification and denitrification processes (Shi et al., 2013). Feng et al., (2018) conducted a meta-analysis study and found that continuous irrigation significantly affected CH_4 emissions in NT as compared to CT. Continuous flooding significantly affects the microbial activities in the terrestrial environment (Gebremichael et al., 2017) and increases anaerobic conditions. This process significantly affects the decomposition rate of SOM and ultimately alters the CH_4 emissions.

Warm temperature significantly increased CO_2 and N_2O emissions by 20.2% and 19.2%, respectively, while sub-tropical environment had a strong positive effect on CH_4 emission (Fig. 4.6((aii, bii, cii)). Oorts et al., (2007) studied and reported that warm and dry climate significantly enhanced CO_2 emission under NT. Soil moisture and higher temperature stimulate the decomposition of crop residue and SOM that ultimately effect CO_2 emissions. Warm-temperate climate zone with high surface temperature may also increase nitrifiers activities, resulting in CO_2 emission (Feng et al., 2013). Under NT, maximum soil water contents were reported in the topsoil layer (0-5cm) (Al-Kaisi and Yin, 2005; Alvarez et al., 2001). This shows that climatic conditions and zones partly control CO_2 emission flux in NT as compared with CT.

According to Mei et al., (2018) meta-analysis study, tropical and warm-temperature climate zones significantly increase N_2O emission in NT. Van Kessel et al., (2013) also conducted a meta-analysis study and found that warm dry climate significantly enhanced N_2O emission.

Mostly, rainfall and temperature are the key factors in regulating N_2O emissions across climate zones. Higher rainfall leads to increase soil moisture content and ultimately reduce the concentration of soil oxygen (O_2), which significantly enhance nitrification as well as denitrification dynamics. In warm-temperate climate zone, decomposition rate of SOM and co-efficient of N turnover significantly higher, which can increase heterotrophic microbial activities and ultimately improve soil respiration (Zhou et al., 2011). Sub-tropical climate zone had strong positive effects on CH_4 emission through extreme precipitation events (Cheng-Fang et al., 2012; Li et al., 2013). Basically, most of the studies that are used in this meta-analysis were conducted in sub-tropical regions. Soil moisture level, temperature, precipitation and N fertilizer application rate might be considered as the key factors in regulating CH_4 emission in sub-tropical regions.

Responses of crop yield to water management and climate zone significantly affected in NT as compared with CT (Fig. 4.6((di, dii)). According to our results, rain-fed regions and warm temperate climate zones enhanced crop yield. Pittelkow et al., (2015) conducted a meta-analysis study and came to similar conclusions. In a long-term field experiment, it has been reported that wheat yield under NT as compared to CT in the rain-fed Mediterranean region increased (Amato et al., 2013). Another researcher also reported similar results (Toliver et al., 2012). According to Plaza-Bonilla et al., (2014a), better WUE is the key factor for getting maximum yield in rain-fed regions. In warm temperate climate zone, application of N fertilizers and soil water contents play an important role in crop growth and yield (Stuecker et al., 2018). According to Pittelkow et al., (2015) study, NT management practice performs better as compared to CT in warm and dry climates.

4.4.6 NT and overall GWP

GWP is a basic index to calculate the future influences of GHGs based on their lifetime and radiative forcing (IPCC, 2013). Overall, NT significantly decreased GWP by 7.5% (Fig. 4.7). GWP only calculated from those publications who simultaneously measured all three GHGs emission fluxes. According to our meta-analysis results, soil physicochemical properties, crop types, climate zones, N application rate and water management significantly affected GWP in NT as compared to CT. On average, all the variables significantly mitigated GHGs emissions. In contrast, neutral soil pH, irrigated lands, barley crop and sub-tropical climate zones had strong positive effects on GWP of GHGs emissions (Fig. 4.7). Huang et al., (2018) and Feng et al., (2018) conducted meta-analysis studies and found similar findings. Generally, it is considered that NT as compared to CT can increase soil C sequestration, reduce C mineralization rate and soil disturbance, which helps in GHGs mitigation (Sainju, 2016). Soil aggregates are significantly affected by RT and/or NT management practices that inhibit N mineralization process, consequently mitigate the N_2O emission (Chen et al., 2013). Continuous irrigation may also weaken the efficiency of NT practice by enhancing soil water contents and anaerobic conditions, which increases methanotrophic activities (Feng et al., 2018). Non-legumes crop, such as barley increased GWP than legumes crop (lentil and pea) because non-legumes crop required high amount of N fertilizer to sustain crop production and high amount of N fertilizer significantly increases N_2O emission (Sainju et al., 2014a, 2014b).

Agriculture and its related land use contribute to C and N dynamics, affecting the flux of CO_2, N_2O, and CH_4, which represent the GHGs principally linked to agricultural activities. Agricultural soils released a significant amount of GHGs emissions to the atmospheric environment, which estimated for one-fifth (approximately) of the annual increase in radiative forcing (Cole et al., 1997; He et al., 2017). According to the FAO (2014) emissions of GHGs from crops were approximately 5.3 Pg of CO_2eq in 2011. Although agricultural management practices under NT significantly change the GWP of GHGs emissions (Guardia et al., 2016).

4.5 Limitations

In this meta-analysis study, numerous limitations should be considered in future research studies. Many meta-analysis studies have already been published but they did not found any significant difference between NT and CT (Abdalla et al., 2016; Feng et al., 2018; Huang et al., 2018; Mei et al., 2018). Our study reveals that differences in GHGs emissions and crop yield do exist between NT and CT management practices. Normally, NT management practice is adopted on sloping soils (Pittelkow et al., 2015). But, long-term implementation of NT management practice on field experiments can significantly contribute to GHGs mitigation. In our dataset, most of the studies have been conducted in China, North America and Europe. There remains a lack of experimental studies in other continents, like South America, South-East Asia, Africa and Australia. Thus, long-term field experimental research studies are needed to be conducted with NT management practice in these regions. This meta-analysis study only measured GHGs fluxes during the cropping and/or fallow seasons. In future research, non-cropping seasons particularly in regions with snow covers and freezing and thawing conditions must be included. Additionally, most of the studies that are comprised in this meta-analysis study did not report soil physiochemical properties, crop management practices and weather conditions. So, we urge that researchers should include proper timing of NT practice, complete soil physiochemical properties like soil pH, bulk density, soil texture, water filled pore spaces, air temperature, climate zone, timing and amount of rainfall, N fertilizer rate and timing, flux type and unit, number of observations and control treatment in their future research studies. This will greatly assist in future meta-analyses which can hopefully provide far greater insights into the range and variability of GHGs emissions than any individual study. Furthermore, it would also be very helpful to understand the difference between CT and NT management practice if the researcher could measure GHGs emissions fluxes during the whole year with specific time intervals, with and without cropping seasons. Last but not the least; researchers must measure all three GHGs fluxes under NT practice in a single study with the same treatments to calculate the GWP.

4.6 Conclusions

In different climatic zones, NT management practice as compared to CT significantly increased CO_2, N_2O and CH_4 emissions by 7.1%, 11.9% and 20.8%. However, these increments in GHGs emissions can be reduced under long-term NT practices. On the other hand, NT decreased overall GWP of GHGs emissions by 7.5% as compared to CT. Soil physicochemical properties such as soil textural class, pH, and C: N ratio also play an important role in regulating GHGs emissions in NT (versus CT). Moreover, the application rate of N fertilizers also had strong positive effects on CO_2, CH_4, and N_2O emissions in NT and these effects were mostly dependent upon soil physicochemical properties, indicating that these factors need to be fully considered to optimize the fertilization strategies to reduce the emissions of GHGs in NT management lands. Crop yield did not show any difference between NT and CT in N application rate. On the other hand, overall, no difference was observed in crop yield. In NT practice, water management also considered an important factor that controlling GHGs emissions and crop yields as compared to CT. To check the detailed effect of NT on GHGs emissions and crop yields, climate zones should not be ignored. The results of this meta-analysis study provides both support and a caution to adopt the NT practice. Agricultural management practices such as tillage type, N application rate, crop type and water management should be planned properly to mitigate GHGs emission without reducing the crop yield in NT management practice.

Acknowledgments

Awais Shakoor would like to express his gratitude for the grant provided by the University of Lleida, Spain. The authors would like to appreciate the valuable comments from the editors and anonymous reviewers to improve the quality of this study

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<u>Chapter 5</u>

This chapter contains the following accepted paper in the "*Pedosphere*"

Shakoor A, Àngela D. Bosch-Serra, Antonio Lidon, Damián Ginestar and Jaime Boixadera (2021). Soil nitrogen dynamics in fallow periods in a rainfed semiarid Mediterranean system.

Soil nitrogen dynamics in fallow periods in a rainfed semiarid Mediterranean system

Abstract

Rainfed agricultural systems in semiarid Mediterranean environments are subject to erratic but often heavy rainfall events. As an agronomic practice, fallow periods can be included even within the existing EU common policy for crop diversification. This research aimed to quantify the effects of a previous mineral fertilization on the soil mineral nitrogen (N_{min}) content and on potential nitrate leaching during no-tilled fallow periods of a crop rotation. Water and Nmin soil measurements obtained during three fallow seasons were used. Data were also used to check if the Leaching Estimation and Chemistry Model (LEACHM) can be used for the soil N_{min} prediction after fallow. During these periods, the Nmin measured in the soil profile increased on average by 125 kg N ha^{-1}, while the model averaged an increase of 95 kg N ha^{-1}. The estimate of N leached ranged from 11 to 38 kg N ha^{-1}. The N balance simulated using LEACHM might differ from the actual processes. After a drought period followed by a soil water replenishment, the calibrated LEACHM underestimated soil N_{min} probably due to the "Birch effect". After occasional rainy spells when soil quickly became saturated, LEACHM overestimated soil N_{min} probably due to occasional N_2O emissions not being fully accounted by the model and to specific preferential water flow which might produce a greater nitrate leaching than that simulated by LEACHM using the convection-dispersion equation. The results show that soil N_{min} measurements by sampling after the fallow period cannot be replaced by LEACHM simulations. These samplings are of interest in fallow established inside a rotation and to avoid over-

fertilization in the following cropping season, while reducing N environmental impacts.

Key Words: LEACHM model, LH-OAT, mineral fertilizer, N leaching, soil water, soil mineral N.

Highlights

- The fallow period increases soil water and soil mineral nitrogen content
- N leaching losses might not be negligible in fallow periods of semiarid areas
- Mineralization is enhanced following drying-rewetting summer periods
- LEACHM is not sufficient to properly predict Nmin values in semiarid rainfed systems

5.1 Introduction

The agricultural systems of rainfed semiarid Mediterranean regions are characterized by low rainfall (250–450 mm) with a high annual variability (Bosch-Serra, 2010). Water availability, linked to the amount of rainfall during the crop growth season and its distribution, is the most important limiting factor for high yields (Lopez-Bellido *et al*., 2000). The availability of plant nutrients (mainly N) is also a constraint because there is a very long history of cultivation in the area and soil organic matter is usually low (Hernanz *et al*., 2002), therefore fertilization is a common practice. However, dry periods after N fertilization might result in N surplus which decreases the N use efficiency (Angás *et al*., 2006). Despite the low precipitation, and the general assumption that N leaching is close to zero (Angás *et al*., 2006; Fan *et al*., 2010), N losses through leaching can occur. In rainfed Spanish systems, a leaching loss of 78 kg NO_3^--N ha^{-1} $year^{-1}$ has been reported for 228 mm of seasonal rainfall (Diez *et al*., 2000).

In rainfed Spanish areas devoted to cereals, various tillage systems cover 89% of the cultivated areas and no-till covers the remaining 11% (MAPAMA, 2017). Fallow has been a long lasting option since Roman times (García-Badell, 1951) and it is also a common practice in dryland areas worldwide (Koohafkan and Stewart, 2008). The objectives of fallow are to increase water and also N availability for the next cropping season. Currently, and mainly in tilled areas, leaving a field fallow for a cropping season is an option for crop diversification within the framework of the European Agricultural Policy (European Commission, 2017). In the European Union, the conditioning factors for fallow establishment and the context have changed (i.e. N fertilizer availability is not a constraint for the preceding or the following crop after a fallow period, and weeds can be controlled without tillage). Thus, during fallow, residual N may be important while soil mineral N can further increase as organic-N mineralizes and no plant N uptake occurs. In this new scenario, it is therefore necessary to understand the N dynamics in order to reduce potential N impacts on underground waters and to increase N use efficiency in the rotation as a whole.

Soil N content can be determined by soil sampling and analysis, but some N processes in the soil are difficult to quantify. Nowadays, process-oriented models are being used as simulation tools for a better understanding of the N cycle (Kersebaum *et al*., 2007; Cannavo *et al*., 2008). The main processes which are simulated with these computer-based models include N mineralization, N immobilization, nitrification, denitrification, volatilization, dinitrogen (N_2) fixation, root uptake, water flow and nitrate leaching (Asada *et al*., 2013). Although several modelling studies compare continuous versus fallow systems under semi-arid conditions (e.g. Roloff *et al*., 1998; Kersebaum *et al*., 2008), it is valuable to clarify the function of the fallow period in terms of N dynamics.

Under fallow, evaporation from soil becomes the main process of soil water loss. However, evaporation can easily be overestimated when it is simulated, as has been described by Cantero-Martínez *et al*. (2016) when using the CropSys model. Consequently, soil water content might not be simulated with the required precision and this may hamper the understanding of N dynamics in the system.

Computer based-models must be calibrated by adjusting some parameters to get a good agreement between the simulated and measured values according to the field conditions (Vazquez-Cruz *et al*., 2014). The selection of the most influential parameters is made by means of a sensitivity analysis. The Latin Hypercube-One Factor at a Time (LH-OAT) is a global sensitivity method based on a scalar output variable that has been used to calibrate different agricultural models (Jung *et al*., 2010; Sánchez de Oleo, 2016). Afterwards, a validation process using another set of measurements is required.

The Leaching Estimation and Chemistry Model (LEACHM) is a research-oriented model. It has been widely used to examine the impacts of different mineral fertilizers on the N cycle, although it is mainly used to quantify NO_3^--N leached from fields. LEACHM has been used and checked under a variety of different climate and soil conditions (Mahmood, 2018; Roy *et al.*, 2000; Sogbedji *et al*., 2001), different fertilizer management systems in different crops (Jabro *et al*., 1997; Singh and Sondhi, 2001) and under different tillage systems (Ng *et al*., 2000). However, few research studies have been done using LEACHM to estimate soil water content and solute transport in dryland cropping systems (Akinremi *et al*., 2011) or in semiarid environments (Kumar *et al.*, 2013). In a recent study, Jiménez-de-Santiago *et al*., (2019), using soil moisture measurements and a soil water simulation model, found that drainage losses exist, and that they are mainly recorded after a period of heavy rainfall events, with a long term recurrence.

Our research work was set up in the framework of three fallow periods in a rainfed semiarid Mediterranean agricultural system, where soil is tilled at sowing and mineral N fertilizers are usually applied at cereal tillering. Our hypothesis for the work is that fallow increases soil water and mineral N (N_{min}) contents but it can also lead to a N_{min} leaching, thus, reducing its theoretical availability to the following crop. This N loss by leaching can be enhanced by specific N processes leading to further N mineralization, while other N losses (i.e. denitrification in sporadic rainy spells) will probably be less important. The main objective of this research work was to evaluate, by means of soil sampling and measurements of mineral N and soil water content, the role of a fallow period in a crop rotation in relation to N dynamics for the following crops and for environmental issues in Mediterranean systems. The evaluation was divided i) in terms of the soil N_{min} variation, ii) in terms of nitrate leaching that may occur with this set-aside agricultural management scheme and iii) in terms of substitute data from further soil samplings by the N_{min} outputs from the LEACHM Model.

5.2 Materials and methods

5.2.1 Description of the study area

The experimental field was located in Oliola, Lleida, in northeastern Spain. The specific location is 41º52'30" N, 1º09'1" E, with an altitude of 440 m a.s.l. The site is located in a slightly sloping (< 2%) valley. The soil water regime is non-percolating (Gerasimov, 1965) which means an accumulation of water soluble salts (e.g. calcite, gypsum), but the low leaching is still sufficient to prevent salinization as the soil is non-saline (Table 5.1). The soil is classified as Typic Xerofluvent (Soil Survey Staff, 2014) with a silty loam texture. The soil profile was divided into three different depth layers: 0–0.3 m, 0.3–0.6 m and 0.6–0.9 m for characterization of physicochemical properties (Table 5.1).

The climate in the area is characterized as semiarid Mediterranean, with an average annual rainfall lower than 450 mm and with a high average reference crop evapotranspiration (ET_o) of 1013 mm yr^{-1} obtained from the Penman-Monteith equation (Allen *et al.*, 1998). Daily and weekly air temperature, thermal amplitude, ET_o and daily precipitation data were collected from an automatic station next to the experimental field. From 2001 to 2018, the average annual rainfall was 439 mm and it ranged from 284 mm (2001) to 662 mm (2018). The highest monthly rainfall normally occurs in April, October and November. The probability of cumulative rainfall for the 2001–2018 period shows that the accumulative probability to exceed 525 mm yr^{-1} of rainfall is 22% (humid year) but 374 mm yr^{-1} will be exceeded with a 78% probability (Table 5.SI). During the winter cereal-cropping season (Table 5.SI; see Supplementary Material), 276 mm will be surpassed with an accumulative probability of 78% but the probability to surpass 430 mm is just 22%.

Table 5.1. Soil physicochemical properties of the experimental site at different depths

		Depth (m)		
Soil properties	**Units**	**0–0.3**	**0.3–0.6**	**0.6–0.9**
Sand (Pipette method)	g kg^{-1}	152	311	115
Silt (Pipette method)	g kg^{-1}	581	486	603
Clay (Pipette method)	g kg^{-1}	267	203	282
Textural class (USDA)		Silty loam	Silty loam	Silty clay loam
pH (1:2.5, soil: water)		8.3	8.5	8.5
$CaCO_3$eq (Bernard calcimeter)	g kg^{-1}	306	329	363
Organic carbon (Walkley- Black method)	g C kg^{-1}	9.5	7.1	5.5
Bulk density	kg m^{-3}	1650	1600	1550
Cation exchange capacity	$cmol^{+}$ kg^{-1}	11.1	–	–
Electrical conductivity (1:5)[a)]	dS m^{-1}	0.18	–	–
Infiltration rate	mm h^{-1}	1.54	–	–
Saturated hydraulic conductivity[b)]	mm d^{-1}	233	524	457
Soil water retention at:				
-33 kPa	m^3 m^{-3}	0.269/0.223[c)]	0.266/0.232[c)]	–
-100 kPa	m^3 m^{-3}	0.234/0.194[c)]	0.237/0.213[c)]	–
-500 kPa	m^3 m^{-3}	0.173	0.168	–
-1500 kPa	m^3 m^{-3}	0.163	0.170	–

[a)] Soil: distilled water.
[b)] Value measured from field study when calculating saturated hydraulic conductivity.
[c)] Values on the left measured from samples disturbed by sieving (2 mm); values on the right from undisturbed samples.

5.2.2 Experimental design, soil sampling and soil mineral N measurement

The framework in which the work was done is a rainfed long-term field experiment on N fertilization established in 2002. The main crops are winter cereals sown between late October and early November and harvested at the end of June or early July. Straw is removed from the field for animal bedding and feed. A fallow period is included in between the different sequences of winter cereal crops. In this research project, three fallow periods with available data on nitrate and ammonium contents in the soil were studied (2007–08, 2013–14 and 2016–17). From a previous winter cereal cropping season, plots from two N-fertilizer treatments were chosen: no applied N (N0) and 120 kg N ha^{-1} applied at the cereal tillering stage as calcium ammonium nitrate (N1). In the field, treatments had been distributed according to a randomized block design with three replicates. The plot size was 12.5 m length and 7 m width. Rainfall distribution determined yields, which averaged 2989, 7488 and 5211 kg ha^{-1} (0% humidity) for N1 in 2008, 2014 and 2017 harvests respectively. For the same years, N0 yielded 2035, 3443 and 3799 kg ha^{-1}, respectively. Straw was baled after harvest. No tillage was performed during the fallow period; if necessary, weeds were controlled by herbicide (glyphosate®) spraying.

During fallows, the NO_3^--N, NH_4^+-N and soil water content were monitored. The soil was sampled at the beginning and at the end of the fallow periods, with additional sampling during each period. In 2007–08, three samples were taken at three dates: 16 July 2007, 21 November 2007 and 21 October 2008, which were identified as 0, 132 and 464 simulation days, respectively (Fig. 5.1a). In 2013–14, six samples were taken at six dates: 14 October and 27 November 2013, and 7 February, 25 April, 4 June and 2 September 2014 that were identified as 0, 45, 117, 194, 234 and 324 simulation days, respectively (Fig. 5.1b). In 2016–17, five samples were taken at five dates: 30 October and 12 December 2016, and 8 February, 5 April and 21 June 2017, which were identified as 0, 80, 129, 185 and 262 simulation days, respectively (Fig. 5.1c). A composite soil sample was obtained from two points in each plot and soil taken from 0-0.9 m depth in the three layers (0-0.3 m, 0.3-0.6 m, and 0.6-0.9 m). An Edelman auger (7 cm diameter) was used. The nitrate and ammonium contents were measured by extracting 20±0.5 g of soil with 50 mL of 1M potassium chloride. These soil extracts were examined with a continuous flow autoanalyzer (Seal Analytical, SealAutoanalyzer3, Norderstedt, Germany). Nmin contents (kg ha^{-1}) were then calculated considering average bulk density for each depth and its soil moisture. The gravimetric soil moisture was determined in a subsample by oven-drying at 105 ºC until constant weight. Gravimetric soil moisture of each layer was multiplied by soil bulk density to obtain the volumetric soil moisture.

5.2.3 Description of LEACHM model

The LEACHM model, version 4.1 (Hutson, 2003), uses the diffusivity form of the Richard's equation, solved by the Crank and Nicolson (1947) method, to describe the one-dimensional water flow in the unsaturated zone divided into a number of horizontal layers of equal thickness chosen by the user. The relationships between soil volumetric water content, saturated hydraulic conductivity and potential pressure are based on Campbell, (1974) equations (Eq. 1):

$$h = a\left(\frac{\theta}{\theta_s}\right)^{-b},\ K(\theta) = K_s\left(\frac{\theta}{\theta_s}\right)^{(2b+2+p)} \tag{1}$$

where h is the matric potential (kPa); K_s is the saturated-hydraulic conductivity (mm d^{-1}); $\theta_s$is the volumetric water-content (m^3 m^{-3}), while a parameter is the air entry water potential in kPa and b parameter is a dimensionless fitting parameter; and p represents the pore interaction parameter and generally set to be 1 for LEACHM. Thus, textural class and K_s are the key parameters for measuring the soil water content (SWC), as a and b parameters of the LEACHM totally depend on these parameters.

Daily potential evapotranspiration is obtained as 1/7th of the weekly ETo calculated with the Penman Monteith method as LEACHM uses weekly ETo. Potential evaporation is obtained as the difference between daily ETo and potential transpiration (zero in our case). For each time step, potential evaporation is calculated assuming that potential evaporation flux density varies in a sinusoidal way throughout the day (starting at 7h12' and ending at 19h12'). The potential evaporation flux density during a time step is compared to the maximum possible evaporative flux density obtained with the Richards' equation applied to the first soil layer. The actual evaporation rate is calculated as a function of the potential evaporation rate and the maximum possible evaporative flux density.

The convection dispersion equation (Eq. 2) is used for solute transport in the soil profile:

$$(\theta + \rho K_d)\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left[\theta \mathcal{D}(\theta, q)\frac{\partial c}{\partial z} - qC\right] - \Phi \tag{2}$$

where ρ is the bulk density of soil (kg m^{-3}); θ is the volumetric water-content (m^3 m^{-3}); K_d is the distribution coefficient for NH_4^+ or NO_3^- (L kg^{-1}); $\mathcal{D}(\theta, q)$ is the apparent dispersion coefficient (mm^2 d^{-1}); q is the water flux (mm d^{-1}); C is the concentration of NH_4^+-N and/or NO_3^--N in the soil solution (mg m^{-3}); and Φ represents all source or/and sink terms (mg m^{-3} d^{-1}).

The original LEACHM version had three soil organic N pools: humus-N, manure-N as well as plant-residue-N and three mineral pools (ammonium, nitrate and urea) in the model. The rate of mineralization for each organic pool totally depends on the decomposition rate for the associated soil organic C pools. The mineralization rate for soil organic N depends upon the rate of decomposition for organic C pools and also depends on the C/N ratio, temperature changes and/or water content of these pools. The rates of decomposition for these soil organic C pools are calculated by a simple first-order decay reaction equation (Eq. 3).

$$\frac{dSOC_i}{dt} = -\mu_{mi} SOC_i \tag{3}$$

where SOC_i shows the soil organic-C contents (mg kg^{-1}) of plant-residue $(i = 1)$, manure $(i = 2)$ and humus $(i = 3)$, and, μ_{mi} $(i = 1 \text{ to } 3)$ is the first-order decomposition rate constant of these SOC pools (d^{-1}). The relation among the three carbon pools is given by the efficiency factor (f_e) and the humification fraction (f_h). The f_h factor is the fraction of the humus-C produced to the biomass-C produced. The f_e factor is the fraction of mineralized C that is converted into biomass as well as humus rather than converting into CO_2. After calibration, we used a constant rate of decomposition for the humus pools in the different soil layers. In our case plant-residue was composed just by roots and no manure was previously applied. The mineral N pools considered were ammonium and nitrate.

Other processes modelled with LEACHM are volatilization, and denitrification, using first-order kinetics. This simplicity in the description of N transformation kinetics might underestimate various N processes which contribute to complex N dynamics, such as soil calcium carbonate (or soil pH) in ammonia volatilization (Kissel and Cabrera, 2005) or the amount of dissolved organic carbon in the soil solution or all soil microbial processes leading to nitrogen emissions, as occurs in N_2O emissions (Smith, 2017). In fact, different additional N pathways (i.e. anaerobic ammonium oxidizing bacteria, reduction to ammonium) contribute to the N transfer to the environment, although in this semiarid environment with short periods of wetting and fast drying, denitrification rates might be reduced (Abbas *et al.*, 2020). Ammonium adsorption and desorption by clay minerals is modelled by a linear sorption isotherm. Similarly, all transformation equations are corrected to account for the influence of soil water content and soil temperature. The mineralization rates are decreased on either side of an optimum range of water content between a high end of optimum water content (air-filled porosity, 0.08 in our case) and a lower end of optimum water content (-100 kPa). The water content correction factor is set to 1 if the water content is in the optimum water content range. Above or below these values the correction factor is less than 1, and transformation rates are zero at the wilting point. A Q_{10} type function response is assumed and the temperature correction factor (T_{cf}) at a temperature t (ºC) is calculated as (Eq. 4):

$$T_{cf} = Q_{10}^{0.1\cdot(t-t_{base})} \tag{4}$$

where t_{base} is the base temperature for which the rate constants are specified in the input file.

5.2.4 The LH-OAT sensitivity analysis method

In this work, the LH-OAT method is used to find the most sensitive as well as the most important parameters for the calibration process of LEACHM. Generally, the OAT (One factor-At a Time) method is used to perform the sensitivity analysis. The OAT method simply changes one parameter value at a time while keeping the other parameters fixed. The LH-OAT global sensitivity analysis combines Latin Hypercube (LH) sampling and OAT design by taking LH sampling as a starting point for an OAT design (Jung *et al.*, 2010). The LH-OAT sensitivity analysis method was performed (Eq. 5):

$$S_i = \sum_{j=1}^{n} \frac{\left|M(e_{1,j},\dots e_{i,j}(1+f_i),\dots,e_{p,j}) - M(e_{1,j}\dots e_{i,j},\dots,e_{p,j})\right|}{n \times f_i \times M(e_{1,j}\dots e_{i,j},\dots,e_{p,j})} \tag{5}$$

where S_i is the sensitivity index for each parameter e_i, M is the model function used to calculate the sensitivity, f_i is the fraction by which the parameter e_i is changed, *j* is the initial point for LH and for P parameters *n* represents the number of intervals considered in the range of variation of each parameter.

Sensitivity analysis was carried out with LEACHM to determine the most significant parameters of N-dynamics influencing the soil N_{min} content in the soil profile (0–0.9 m). In our case, eleven LEACHM parameters related to the N cycle were included in the sensitivity analysis (Table 5.2). Humus mineralization, nitrification and denitrification rate constants were considered along with efficiency parameters and temperature correction factors. According to Jung *et al*., (2010), other chemical properties such as the adsorption coefficient for NH_4^+-N and the molecular diffusion coefficient have also been taken into account in the analysis. The intervals (n) considered in the range of variation of each parameter were 50, and the fraction of change (f_i) in each interval was 5%. The model function (ε_N) used for obtaining the sensitivity indices of the N parameters was (Eq. 6):

$$\varepsilon_N = \sum_{i=1}^{n_l} \frac{\left(\sum_{j=1}^{n_m}\left(N_{i,j} - N_{i,j}^*\right)^2\right)^{\frac{1}{2}}}{\sum_{j=1}^{n_m}(N_{i,j})^{\frac{1}{2}}} \tag{6}$$

where n_l is the number of soil layers considered, n_m is the number of measures available in each layer, $N_{i,j}$ is the *j-th* measure of the soil mineral content (kg ha^{-1}) in the *i-th* layer and $N_{i,j}^*$ is the *j-th* value of the soil mineral content (kg ha^{-1}) in the *i-th* layer computed by the model.

The LH-OAT analysis was repeated five times, taking the average of the five repetitions as the sensitivity index of each parameter (Table 5.2). Thus, taking into account that the runs required in the LH-OAT method are given by the expression n x (P+1), 3000 simulations were carried out to complete the N sensitivity analysis. The sensitivity analysis of the hydraulic parameters of the soil was not carried out, as the previous information obtained by Jiménez-de-Santiago *et al*.,

(2019) in this same area was used (Table 5.3).

Table 5.2. Range of values for the different soil N transformations in soil profile used in the LEACHM sensitivity analysis, sensitivity indices and adjusted values after calibration

Parameters	Units	Upper Value	Lower value	References	Sensitivity index[a)]	Fitted value
Nitrogen cycle parameters						
Adsorption coefficient NH_4^+–N	L kg^{-1}	9.000	0.975	(Hutson, 2003)	0.0078±0.0013	4.9
Molecular diffusion coefficient	mm^2 d^{-1}	166	17	(Hutson, 2003)	0.0054±0.0016	91.50
Synthesis efficiency factor	–	0.7	0.5	(Asada et al., 2013)	0.0000±0.0000	0.60
Humification fraction	–	0.462	0.200	(Coleman and Jenkinson, 1997)	0.0000±0.000	0.33
Base temperature	°C	40.0	2.0	Parameterization	0.3227±0.0385	26.57
Q_{10} factor	–	5.0	0.5	Parameterization	0.2533±0.0439	4.5
Nitrification rate (0–0.3 m)	d^{-1}	1.5	9.2×10^{-4}	(Hutson, 2003)	0.0044±0.0011	7.5×10^{-1}
Denitrification (0–0.3 m)	d^{-1}	0.12	2.0×10^{-5}	(Hutson, 2003)	0.0142±0.0009	1.0×10^{-3}
Humus mineralization rate (0–0.3 m)	d^{-1}	1.0×10^{-4}	1.0×10^{-5}	Parameterization	0.0471±0.0103	7.6×10^{-4}
Humus mineralization rate (0.3–0.6 m)	d^{-1}	1.0×10^{-4}	1.0×10^{-5}	(Coleman and Jenkinson, 1997)	0.1481±0.0121	1.0×10^{-5}
Humus mineralization rate (0.6–0.9 m)	d^{-1}	1.0×10^{-4}	1.0×10^{-5}	(Coleman and Jenkinson, 1997)	0.1947±0.149	1.0×10^{-5}

[a)] Mean value ± standard deviation (n=5).

Table 5.3. Range of values for the different hydraulic parameters in the soil profile (0–0.9 m) used in the LEACHM sensitivity analysis, previously performed by Jiménez-de-Santiago et al. (2019), and the fitted values obtained after calibration which have been used in this work.

Parameters	Units	Upper Value	Lower value	Fitted value
Parameter *a* Campbell equation (0–0.3 m)	kPa	-0.149	-10.000	-2.838
Exponent *b* Campbell equation (0–0.3 m)	-	10.000	0.140	8.561
Saturated hydraulic conductivity (0–0.3 m)	mm d^{-1}	1000	1	52
Parameter *a* Campbell equation (0.3–0.6 m)	kPa	-0.149	-10.000	-5.116
Exponent *b* Campbell equation (0.3–0.6 m)	-	10.000	0.140	5.825
Saturated hydraulic conductivity (0.3–0.6 m)	mm d^{-1}	500	1	115
Parameter *a* Campbell equation (0.6–0.9 m)	kPa	-0.149	-10.00	-4.995
Exponent *b* Campbell equation (0.6–0.9 m)	-	10.000	0.140	4.684
Saturated hydraulic conductivity (0.6–0.9 m)	mm d^{-1}	150	1	119

5.2.5 LEACHM model calibration and validation

Simulations of soil N_{min} content were done with the LEACHM model for a total of 1050 days distributed in the three fallow periods. In each fallow period, simulation periods lasted from the first up to the last soil sampling for soil N measurement (described earlier in section 2.2.). First, the hydraulic parameters of the LEACHM model were adjusted. For this purpose, the values of soil hydraulic parameters obtained by Jiménez-de-Santiago *et al.*, (2019) were used for recalibration of the LEACHM model. Since the main water output during the fallow period is evaporation, it was calculated in the top layer (0-0.3 m) for comparison with the evaporation simulated with LEACHM model. To do this, the volumetric moisture measured during the period with more intense rains

(2016–17) and a simple compartmental model based on a water balance (Contreras *et al.*, 2009) were used. This model estimates evaporation (E) as (Eq. 7):

$$E = K_e \times ET_o, \tag{7}$$

where K_e takes a value between 0 and 1, affected by a reduction coefficient depending on the water content in the soil (Allen *et al.*, 1998). The K_e coefficient is determined by the evaporation layer (Z_e, 0.1 m in this case), the easily evaporable water content depending on soil texture (REW, 10 mm), and a total evaporable water content (TEW, 20.5 mm) depending on moisture capacity at field capacity (0.27 m^3 m^{-3}), the moisture at permanent wilting point (0.13 m^3 m^{-3}) and Z_e. When the soil water depth measured during the period 2016–17 and simulated with the capacity model were similar, the hydraulic parameters of the LEACHM model at 0–0.3 m (*a*, *b* and K_s, Table 5.3) were adjusted using the soil water depth reported by the compartmental model. Once the parameters of the first layer had been calibrated, the parameters of the second and third layers were adjusted. In this case, only the measurements of volumetric water content obtained in the soil samples taken during the 2016–17 period were used.

After water calibration, the most sensitive parameters related to the N cycle (Table 5.2) were calibrated. To do this, the error function (ε_N) (Eq. 6) was minimized using the Nelder-Mead simplex algorithm as described in Lagarias *et al.*, (1999). In this case, the 2013-14 fallow period was chosen for calibration of N parameters because more nitrate and ammonium measurements were available. The rest of the nitrogen mineral measurements were used for validation of the calibrated model. The longest time interval within a day in the LEACHM model was adjusted to 0.05 days, but the results of the simulation were daily. Values of the calibrated parameters of the nitrogen and water of the LEACHM model are shown in Table 5.2 and Table 5.3, respectively. Different statistical indices were applied to assess the agreement between simulated and measured values and the LEACHM model performance:

1) Mean difference (MD)

$$\mathrm{MD} = \frac{1}{n}\sum_{i=1}^{n}(\mathrm{O}_i - \mathrm{S}_i) \tag{8}$$

2) Root mean square error (RMSE)

$$\mathrm{RMSE} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(\mathrm{O}_i - \mathrm{S}_i)^2} \tag{9}$$

3) Normalized RMSE (NRMSE)

$$\mathrm{NRMSE} = \frac{RMSE}{\overline{\mathrm{O}}} \tag{10}$$

4) Agreement index (d) (Willmott, 1981)

$$\mathrm{d} = 1 - \frac{\sum_{i=1}^{n}(\mathrm{O}_i - \mathrm{S}_i)^2}{\sum_{i=1}^{n}(|\mathrm{S}_i - \overline{\mathrm{O}}| + |\mathrm{O}_i - \overline{\mathrm{O}}|)^2} \tag{11}$$

5) Nash-Sutcliffe modeling efficiency (NSE) (Nash and Sutcliffe, 1970)

$$\mathrm{NSE} = 1 - \frac{\sum_{i=1}^{n}(\mathrm{O}_i - \mathrm{S}_i)^2}{\sum_{i=1}^{n}(\mathrm{O}_i - \overline{\mathrm{O}})^2} \tag{12}$$

where, *n* is the number of data, S_i and O_i are the simulated and observed values, respectively, while, $\overline{\mathrm{S}}$ and $\overline{\mathrm{O}}$ are the average of simulated and observed values during the evaluated period, respectively.

Low absolute values of MD (mean difference) indicate a good agreement between measured and simulated values, RMSE = 0 shows a perfect fit, and the NRMSE showed good, moderate and poor agreement between measured and simulated values if NRMSE ≤ 0.15 (equivalent to a 15% error), NRMSE = 0.15–0.30, and NRMSE ⩾ 0.3, respectively (Li *et al*., 2015a; Lidón *et al*., 2019). In addition, the agreement index and NSE values close to 1 indicate good predictive ability of the model, while values close to zero indicate that the measured mean value is a similar predictor to the model. These statistical indices were calculated for the periods 2013–14 and 2016–17. They were not calculated for the period 2007–08, as only three sampling dates were available for that season.

5.3 Results

5.3.1 Meteorological conditions during fallow periods

In fallow periods, there were no differences in water inputs between the N fertilizer treatments (applied at the preceding cropping season) because rainfall was the same in both treatments and no irrigation was provided. During the evaluated fallow periods, 2007–08 (464 days), 2013–14 (324 days) and 2016–17 (262 days), the rainfall and ET_o were 525 and 1364 mm, 417 and 925 mm, 324 and 496 mm, respectively (Fig. 5.1). The rainfall records during the studied fallow periods fell in a humid range for 2007-08 as the probability to surpass the accumulated precipitation was just 27.7%, and was close to the median for 2013-14 and 2016-17 with an accumulated probability of 55.5% and 44.4%, respectively (Table 5.SI). Rainfall distribution indicates that the 2007–08 fallow (Fig. 5.1a) started with a nine-month drought period (only 151 mm of rain were recorded from 16 July 2007 to the end of April 2008), followed by a three-month humid period (from April to June 2018, 260 mm were recorded). The 2013–14 fallow season (Fig. 5.1b) coincided with an almost uniform rainfall distribution. The 2016–17 fallow (Fig. 5.1c) included a snow event on the 25th March 2017 when the field received snow; the snow records in the area vary but might be averaged at around an equivalent of 40 mm rainfall.

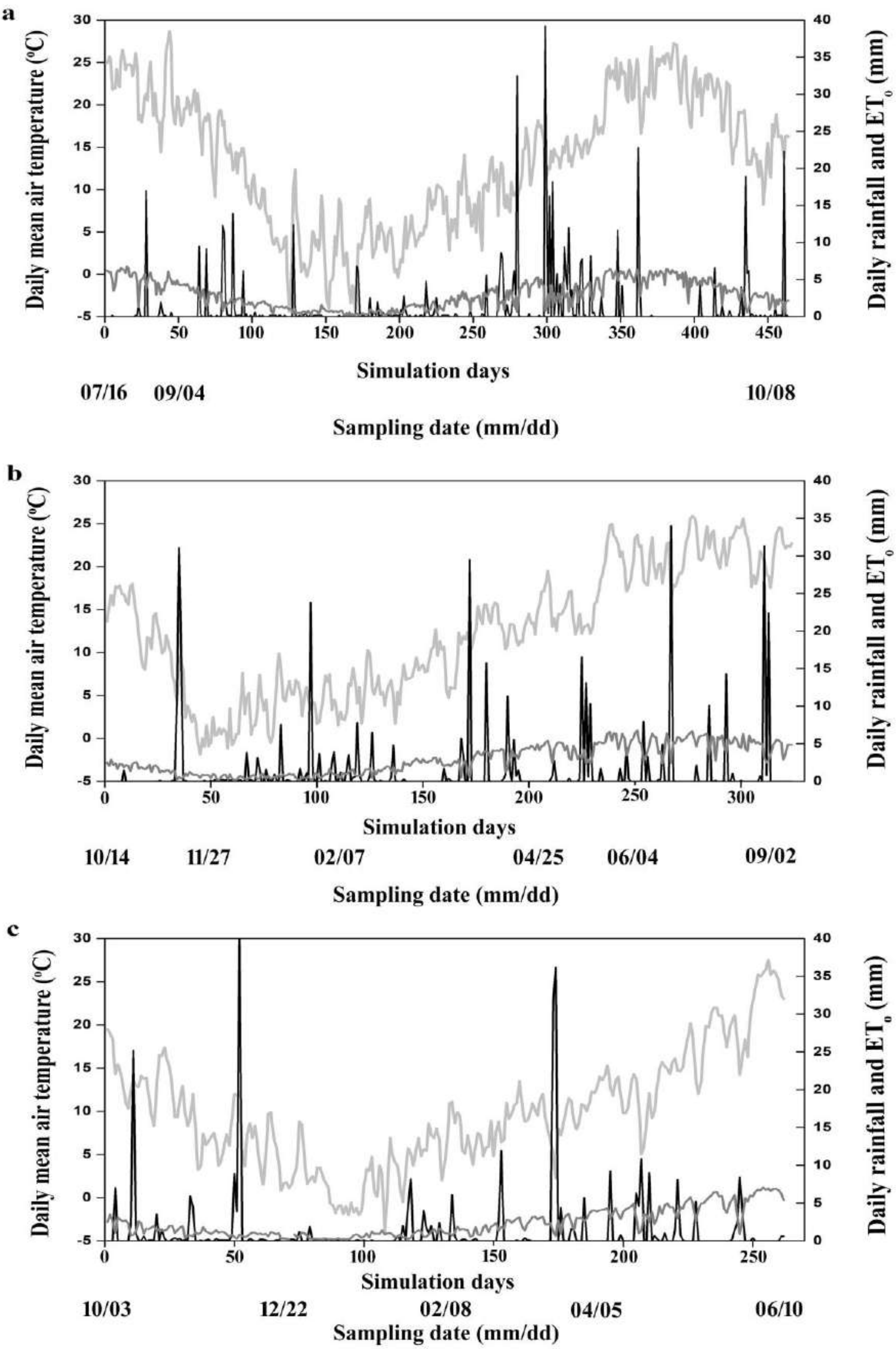

Figure 5.1. Daily meteorological data of mean air temperature (——), rainfall (——) and reference crop evapotranspiration (——, ET$_o$, Penman-Monteith equation) for the

studied periods: a) 2007-08, 464 days from 16th July2007 to 21st October 2008; b) 2013-14, 324 days from 14th October 2013 to 2nd September 2014; and c) 2016-17, 262 days from 3rd October 2016 to 21st June 2017; in Oliola, Lleida, Spain. Information about sampling days is included.

5.3.2 Mineral nitrogen content measured in fallow periods

Mineral nitrogen in the soil profile (0-0.9 m) increased after the fallow periods, except in the N0 treatment during the period from October 2016 to June 2017 when there was a small decrease (Table 5.4). The increase in N_{min} was uneven and was not so much related to the length of the period considered but rather to whether the period covered the full period of summer months or not. Thus, for the longest period from July 2007 (after June harvest) to 21st October 2008 (before winter cereal sowing on the 27th), the N_{min} increase was 183 kg N ha^{-1} in the N0 treatment and 264 kg N ha^{-1} in the N1 treatment (Table 5.4 and Fig. 5.3). However, during the period 2016–17, which included the common cropping period (from October to the end of June), the increase of N_{min} was only 19 kg N ha^{-1} in the N1 treatment, and even decreased by 39 kg N ha^{-1} in the N0 treatment (Table 5.4 and Fig. 5.4). Initially, in the 2013–2014 cropping season, the increase from October to June was 49 and 34 kg N ha^{-1} for N0 and N1, respectively. However, if the period accounted for was lengthened from October 2013 to the next September, the figures went up to 136 and 211 kg N ha^{-1} for N0 and N1, respectively. The variability of the mineral N content in the soil (measured as standard deviations) was higher in the plots that had been fertilized the previous season (N1), before the fallow began (Table 5.4 and Figs. 5.2, 5.3, 5.4).

Table 5.4. Mineral nitrogen measured for each sampling date and for each soil layer in both treatments. In bold type, average and standard deviation (n=3) in the soil profile.

Sampling date	Treatment N0 (kg N ha^{-1})				Treatment N1 (kg N ha^{-1})			
	0-0.3 m	0.3-0.6	0.6-0.9	0-0.9 m	0-0.3 m	0.3-0.6	0.6-0.9	0.0-0.9 m
16/07/07	33.8	23.9	20.3	**80 ± 14**	53.3	32.6	42.9	**129 ± 27**
21/11/07	33.2	17.6	11.0	**62 ± 14**	49.8	45.5	53.2	**149 ± 19**
21/10/08	130.6	92.6	37.6	**261 ± 24**	190.8	123.0	79.2	**393 ± 28**
14/10/13	60.8	34.7	18.3	**114 ± 14**	92.3	54.6	61.5	**208 ± 16**
27/11/13	43.5	22.4	16.9	**83 ± 11**	55.2	52.9	79.6	**188 ± 100**
07/02/14	33.8	32.8	18.9	**86 ± 15**	45.7	51.1	62.2	**159 ± 45**
25/04/14	55.1	40.5	13.9	**110 ± 19**	83.8	68.1	72.9	**225 ± 68**
04/06/14	93.2	43.8	26.7	**162 ± 36**	109.0	49.8	62.7	**221 ± 54**
02/09/14	142.0	72.0	35.4	**249 ± 47**	186.3	153.7	59.1	**399 ± 91**
03/10/16	87.5	49.5	39.4	**176 ± 10**	125.3	89.3	66.1	**281 ± 32**
12/12/16	57.4	50.3	50.2	**158 ± 2**	71.4	94.1	90.1	**256 ± 160**
08/02/17	46.9	41.8	15.3	**106 ± 21**	52.2	101.9	44.6	**199 ± 19**
05/04/17	24.3	21.1	22.0	**67 ± 22**	37.9	37.6	61.1	**137 ± 26**
21/06/17	57.3	26.8	53.6	**138 ± 1**	113.3	89.7	93.0	**296 ± 2**

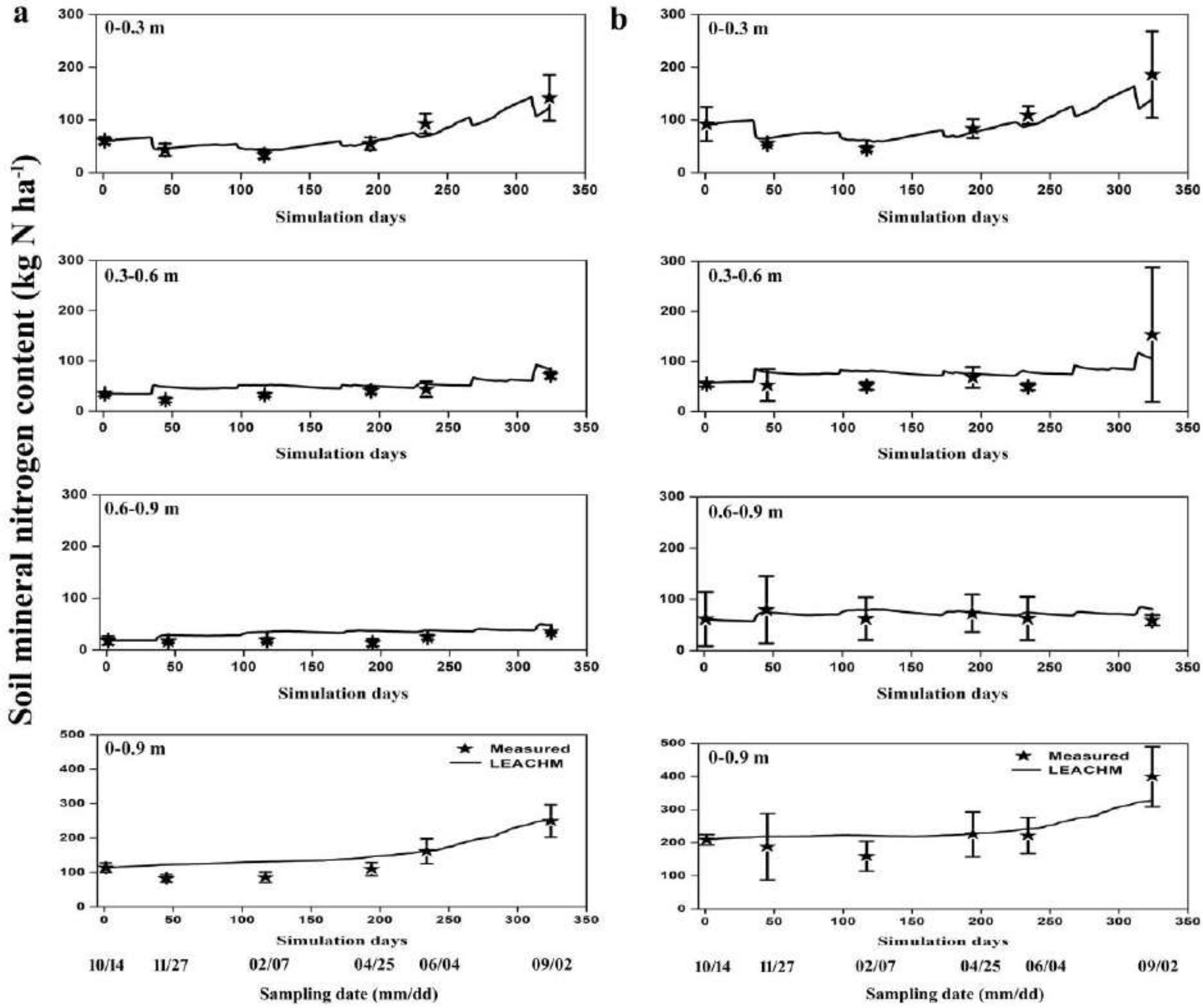

Figure 5.2. Comparison between measured (star points, vertical lines are the standard deviation) and simulated (continuous line) soil mineral N contents within a soil profile (at different depths), for the 324-days calibration period of the 2013-14 fallow season. Starting day was the 14th October 2013 and the period finished the 2nd September 2014. Previous 2012-13 treatments were a) control with no N applied and b) mineral N annual treatment (120 kg N ha^{-1} as ammonium calcium nitrate) at winter cereal tillering stage.

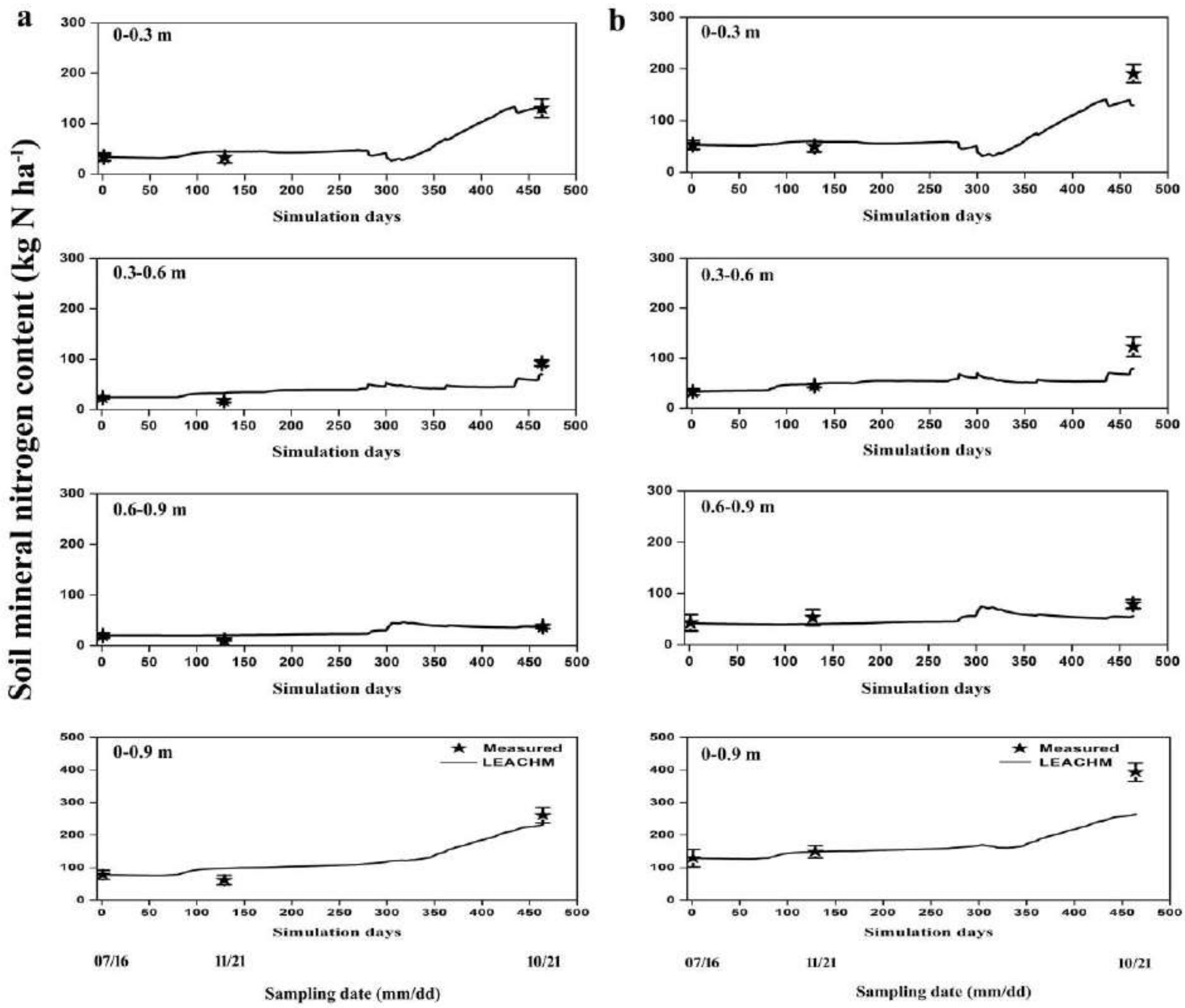

Figure 5.3. Comparison between measured (star points, vertical lines are the standard deviation) and simulated (continuous line) soil mineral N contents within a soil profile (at different depths), for the 464-days validation period of the 2007-08 fallow season. Starting day was the 16th July 2007 and the period finished the 21st October 2008. Previous 2006-07 treatments were a) control with no N applied and b) mineral N annual treatment (120 kg N ha^{-1} as ammonium calcium nitrate) at winter cereal tillering stage.

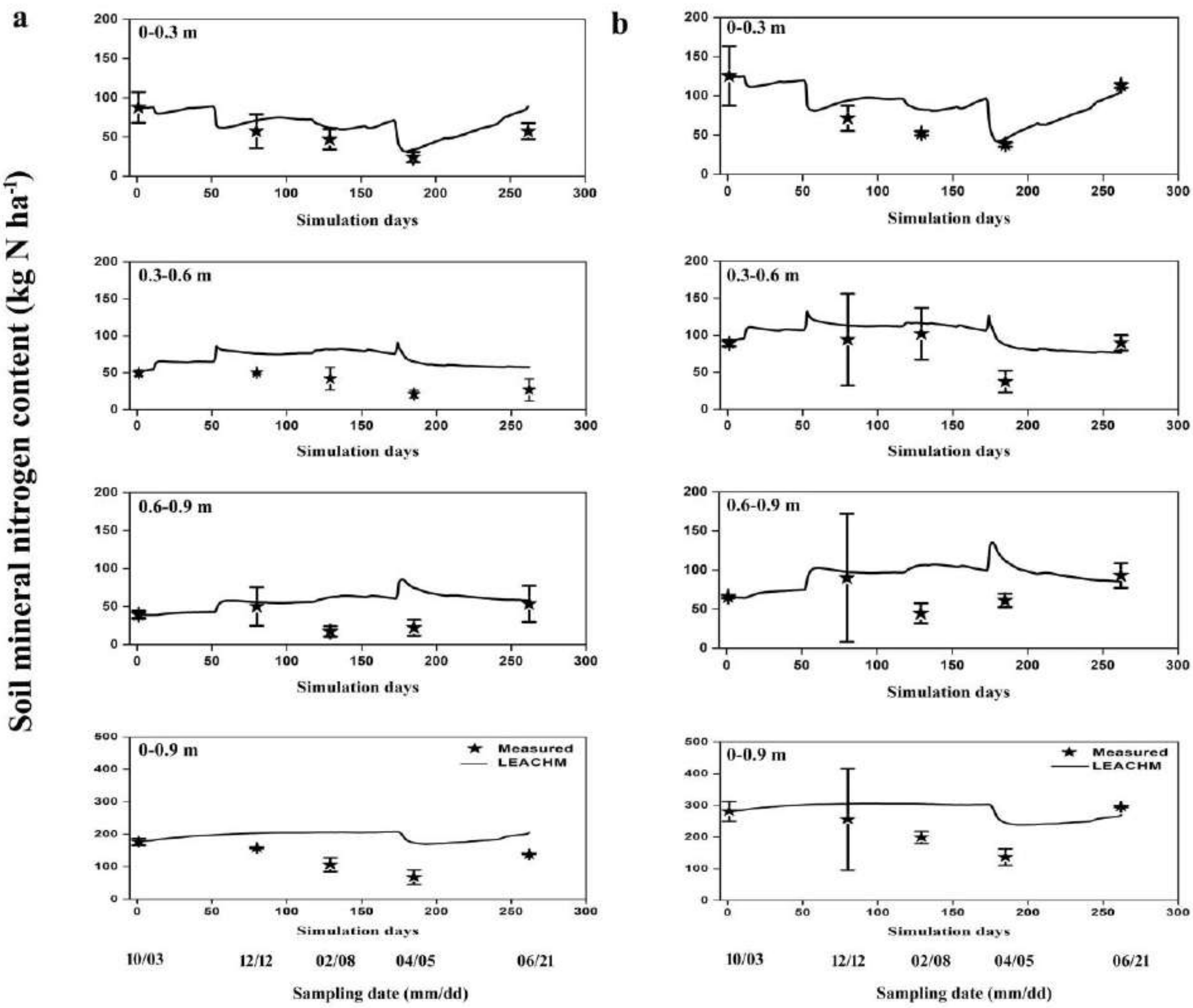

Figure 5.4. Comparison between measured (star points, vertical lines are the standard deviation) and simulated (continuous line) soil mineral N contents within a soil profile (at different depths), for the 262-days validation period of the 2016-17 fallow season. Starting day was 3rd October 2016 and the period finished the 21st June 2017. Previous 2015-16 treatments were a) control with no N applied and b) mineral N annual treatment (120 kg N ha^{-1} as ammonium calcium nitrate) at winter cereal tillering stage.

Most of the N_{min}, *ca*. 45–50%, was found in the first 0.3 m of soil, but the vertical distribution of N_{min} in the soil profile changed over the fallow periods. In the periods including the summer (2007–08 and 2013–14), the behavior was similar, with an increase in the percentage of N_{min} in the soil layers of 0–0.3 and 0.3–0.6 m at the end of the period, and a decrease in that percentage in the deep soil layer (0.6–0.9 m) (Table 5.4 and Figs. 5.2, 5.3). The percentage of N_{min} in the 0–0.6 m layer increased on average by about 10%, stressing the importance of the mineralization process at this soil depth, in which most roots develop when a crop is grown. However, in the shorter period (2016–17), which ended at the beginning of summer, a decrease in the percentage of N_{min} in the upper layers (0–0.30 and 0.3–0.6 m) was observed, while the percentage in the deeper layer (0.6–0.9 m) increased.

The predominant chemical form of mineral nitrogen in the soil throughout the year during fallow periods was the nitrate form. The average percentage of nitrate in relation to total N_{min}, considering all available measures, was 75% for the N0 treatment and 87% for the N1 treatment (Fig. 5.5). However, the percentage of nitrate throughout the year was not uniform. A significant decrease in the percentage of NO_3^--N was observed, coinciding with the dry periods of the summer months. The highest percentages of ammonium were found in July 2007, after a very dry period, with values of 52% and 30% in the N0 and N1 treatments, respectively. These values are equal to 45 and 38 kg NH_4^+-N ha^{-1} for N0 and N1, respectively. There was also a relatively small decrease in the percentage of NO_3^--N during the period from October to December.

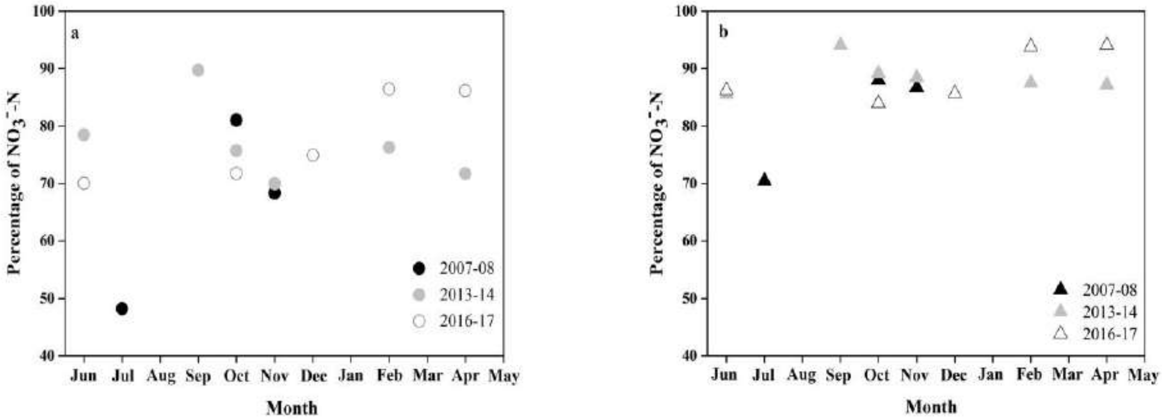

Figure 5.5. Monthly evolution of the percentage of NO_3^--N with respect to total mineral nitrogen (NO_3^--N and NH_4^+-N) in the soil profile (0–0.9 m) in the a) control with no N applied (circles) and b) mineral N annual treatment (120 kg N ha^{-1} as ammonium calcium nitrate) at winter cereal tillering stage (triangles). Information from the three fallow seasons: 2007-08 (grey), 2013-14, (black) and 2016-17 (white) is included.

5.3.3 Soil water content

The LEACHM model adequately predicts the soil water content at 0.9 m depth, with a good adjustment of the soil moisture simulated and measured in each of the three soil layers considered (data not shown). All the statistical indices results (Table 5.5) suggest a good agreement between measured and simulated SWC for the LEACHM model (Fig. 5.6). Regarding the water balance, in all cases, the fallow period led to a recharge (variation) that ranged between 28 mm and 98 mm depending on the period considered (Fig. 5.6).

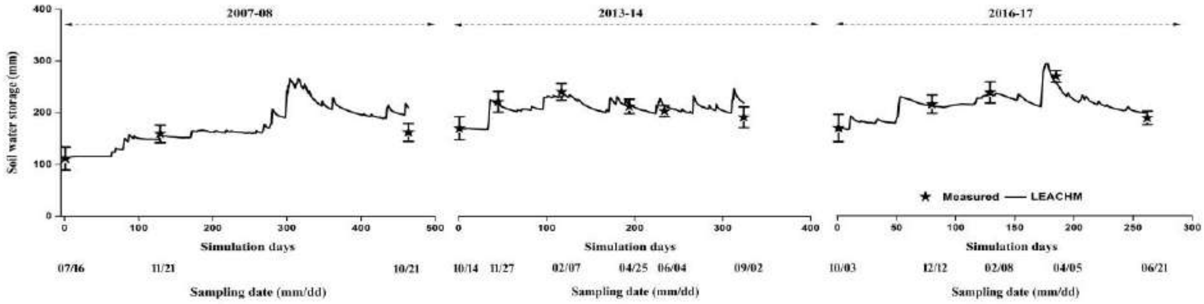

Figure 5.6. Comparison between measured (star points, vertical lines are the standard deviation) and simulated (continuous line) soil water content within a soil profile during the three experimental periods: a) 2007-08, 464 days from 16th July2007 to 21st October 2008; b) 2013-14, 324 days from 14th October 2013 to 2nd September 2014; and c) 2016-17, 262 days from 3rd October 2016 to 21st June 2017; in Oliola, Lleida, Spain.

Figure 5.7 shows the cumulative drainage simulated at 0.9 m during the whole experimental study. In the 2013–14 fallow, according to the results of the simulation a continuous drainage over time was observed, while the 2007–08 fallow showed the sigmoidal form. In the period 2016-17 there was a continuous drainage over time until March (day 174 of simulation) followed by a sigmoidal response after the heavy rains and snowfall that took place at the end of that month. The simulated drainage below 0.9 m mainly occurred after a sustained period of rainfall events. It varied between 33 mm to 86 mm (Table 5.6) and normally, evaporation accounted for 71–80% of the water output from soil.

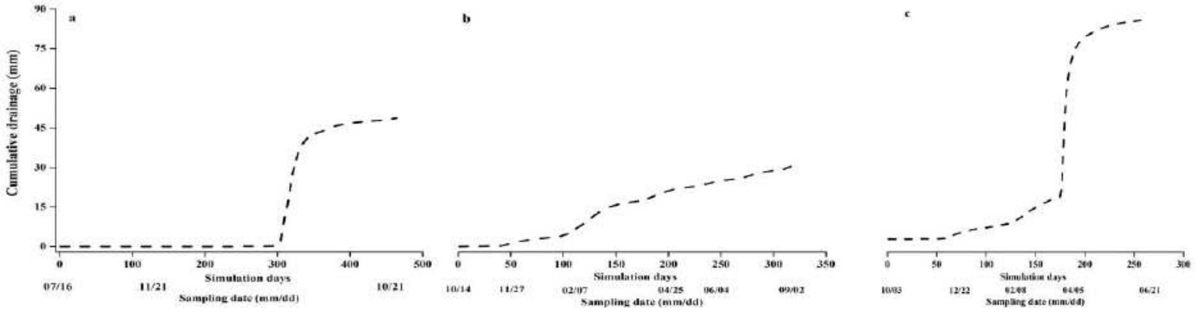

Figure 5.7. Accumulated drainage simulated with LEACHM below 0.9 m during the three experimental periods: a) 2007-08, 464 days from 16th July2007 to 21st October 2008; b) 2013-14, 324 days from 14th October 2013 to 2nd September 2014; and c) 2016-17, 262 days from 3rd October 2016 to 21st June 2017; in Oliola, Lleida, Spain.

5.3.4 Soil mineral nitrogen

The sensitivity analysis obtained for the eleven evaluated parameters related to the N cycle (Table 5.2) showed that the most influential parameters were those related to the mineralization of soil organic matter; specifically, the mineralization rates of each of the three soil layers and the parameters related to the influence of temperature on the mineralization process. The most influential parameter was the base temperature, with a sensitivity index of 0.323, followed by the Q10 factor with a value of 0.253. Mineralization rates averaged a sensitivity that ranged from 0.047 to 0.195 (Table 5.2). According to available measurements of mineral N, only three parameters were selected for calibration, leaving the other parameters fixed. The calibrated parameters were the base temperature (26.6 ºC), the Q10 factor (4.5) and the mineralization rate of the first layer (7.58 x 10^{-4} d^{-1}) where most of the organic matter is found (Table 5.1). Other parameters such as the humification fraction, nitrification and denitrification were also very important because they were very useful to measure the mineral N content as well as leaching.

During the calibration process, the simulated soil N_{min} content fitted well with measured values in all three soil layers and for the soil profile, both for the control and previous N mineral fertilized plots (Fig. 5.2; Table 5.5). However, the MD values ranged from -25.4 to -8.8 kg N ha^{-1} for N0 and N1, respectively (Table 5.5), quantifying the overestimation of the soil mineral N content in the soil profile by LEACHM.

Table 5.5. Statistical indices[a)] for comparison between measured and LEACHM simulated soil mineral nitrogen content according to the previous N mineral fertilization and soil water storage in the soil prolife (0–0.9 m).

Statistic index	Mineral nitrogen (kg N ha^{-1})				Soil water storage (mm)	
	2013–14[b)]		2016–17			
	N0[c)]	N1[d)]	N0	N1	2013–14	2016–17
Mean difference	-25.4	-8.8	-79.5	-59.2	-5.9	2.1
RMSE	31.6	45.9	83.3	80.8	14.7	7.5
NRMSE	0.23	0.19	0.71	0.36	0.07	0.03
d	0.92	0.86	0.43	0.49	0.63	0.98
NSE	0.74	0.70	-3.74	-0.45	0.22	0.94

[a)] RMSE, Root mean square error; NRMSE, Normalized RMSE; d, Agreement index; NSE, Nash-Sutcliffe modeling efficiency.
[b)] The N0 treatment measurements for the period 2013-14 were used for the calibration.
[c)] No N was previously applied in the N0 treatment.
[d)] N1 treatment received 120 kg N ha^{-1} as ammonium calcium nitrate at cereal tillering of the previous cropping season.

The predictive ability of the calibrated model varied according to the period and treatment considered (Figs. 5.3, 5.4). In the period 2007–08, the model predicted the dynamics of N_{min} in the N0 treatment and for the three soil layers correctly, it just underestimated by 30 kg N ha^{-1} the N_{min} content of the soil profile at the end of the period (Fig. 5.3a). However, the model was not able to properly predict the final N_{min} content of the soil in the N1 treatment. In this case, the model underestimated the soil N_{min} by 130 kg N ha^{-1}, mainly due to the mismatch in the first two soil layers (Fig. 5.3b).

In contrast, the model tended to overestimate the soil mineral N content throughout the period 2016–17, with a difference at the end of the period of 67 kg N ha^{-1} in the N0 treatment. However, in the N1 treatment the model predicted at the end of the period a slightly lower amount than that measured (27 kg N ha^{-1}, Fig. 5.4). This overestimation occurred on almost all dates sampled, resulting in an MD of -79 and -59 kg N ha^{-1} for N0 and N1, respectively (Table 5.5), although the prediction error almost doubled in N0 *vs.* N1, as shown by NRMSE (Table 5.5).

Fallow seasons implied an increase in the N_{min} content in the soil profile that ranged from 56 kg N ha^{-1} to 152 kg N ha^{-1}, depending on the fertilizer treatment prior to fallow and the length of the period evaluated (Table 5.6). During the whole experimental study, the maximum amount of mineral N content was accumulated in the first soil layer (0–0.3 m) (in almost all study years) and very high amounts of N_{min} content can be available in the soil profile (0–0.9 m), from 205 up to 327 kg N_{min} ha^{-1} (Table 5.6). The peaks of soil N_{min} content in soil profiles were observed after a rainfall event and mainly in September (Figs. 5.1a, 5.1c, 5.3, 5.4), although it increased from early June.

Table 5.6. Mineral nitrogen (N_{min}) and soil water balances (0–0.9 m) obtained from the simulations carried out with the LEACHM model in each of the three fallow studied periods and for the two N fertilization scenarios (N0, N1).

Period	2007-2008		2013-2014		2016-2017	
	N0[a]	N1[b]	N0	N1	N0	N1
Simulation days	464	464	324	324	262	262
N_{min} (kg N ha^{-1})						
Initial content	80	129	114	211	176	281
Final content	232	270	254	327	205	269
Variation	152	141	140	116	29	-11
Mineralization	191	201	167	165	92	93
Nitrification	174	178	144	133	95	88
Volatilization	20	22	16	18	5	6
Denitrification	0.1	0.2	0.2	0.2	0.1	0.1
Leaching	18	38	11	31	59	98
Water (mm)						
Initial content	112	132	174	169	167	166

Final content	210	210	219	219	196	196
Variation	98	78	45	50	29	30
Rainfall	505	505	417	417	402	402
Evaporation	357	368	335	333	286	290
Drainage	49	57	36	33	86	81

Modelled nitrogen leaching below the soil profile (0.9 m) in the calibration period (Table 5.6) ranged from 11 (N0) up to 31 kg N ha^{-1} (N1) (Fig. 5.2, Table 5.6). Mineralization ranged between 165 kg N ha^{-1} and 167 kg N ha^{-1}, and nitrification accounted for 83% of the mineralized N on average. Volatilization losses averaged about 17 kg N ha^{-1} and they were not dependent on previous fertilization treatment. Denitrification losses were negligible (Table 5.6). In the validation periods, nitrate leaching ranged from 18 kg N ha^{-1} (N0 2007-08) to 98 kg N ha^{-1} (N1 2016-17) and mineralization was 92 kg N ha^{-1} in the period 2016-17 and 196 kg N ha^{-1} in the period 2007-08 (Table 5.6). The gaseous losses were similar to those obtained in the calibration period.

5.3.5 Comparison of soil water and mineral nitrogen balances

For the purposes of comparison between the three study periods, a fallow period of the same duration was considered. The period between October 14 and July 2 was selected, which corresponds to a fallow period of 262 days. For this period, the simulation shows that the fallow represented a water recharge in the profile, measured as the difference between the water content at the beginning and end of the period, which ranged between 26 mm to 60 mm, the highest value corresponding to the plot with the lowest water content at the beginning of the period. The average recharge was 36 mm (± 14 mm) and it did not depend much on the amount of precipitation but on the frequency and intensity of the precipitation. The evaporation of water from the soil averaged about 254 mm (± 26 mm), and accounted for 70–72% of precipitation in the 2007–08 period and 81% in another period (2013–14). The estimated drainage varied between 26 mm to 86 mm, with an average value for the 262 days considered to be of 53 mm (± 26 mm), representing 14%, 9.2% and 20.8% of the precipitation registered between October-June in 2007–08, 2013–14 and 2016–17, respectively.

Considering the period of 262 days, fallow led to an average increase in mineral N content of up to 67 kg N ha^{-1} (± 12 kg N ha^{-1}) in areas with a lower fertilizer contribution prior to fallow (N0). In the areas that received the higher amount of fertilizer (N1), in the soil profile the average increase was 47 kg N ha^{-1} (± 10 kg N ha^{-1}). The mineralization during that period was similar in both treatments (90 ± 9 kg N ha^{-1} on average). The average leaching from the N0 plots was 27 kg N ha^{-1} (± 27 kg N ha^{-1}) while in the N1 plots it was 52 kg N ha^{-1} (± 40 kg N ha^{-1}). Volatilization losses accounted for 8 kg N ha^{-1} (± 3 kg N ha^{-1}) and 11 kg N ha^{-1} (± 2 kg N ha^{-1}) for N0 and N1, respectively.

5.4 Discussions

5.4.1 Mineral nitrogen content in fallow periods

The increase of mineral N in the soil profile as a consequence of fallow was dependent on the period considered and the previous fertilization treatment. On average, the increase was 93 kg N ha^{-1} for the N0 treatment and 157 kg N ha^{-1} for the N1 treatment. These amounts are higher than the N requirements of the following crop in the rotation and should be taken into account when planning fertilization. For the entire studied periods and averaging for both treatments, there was an increase in N_{min} over the initial content of 220% in 2007–08, 106% in 2013–14 and 7% in 2016–17 (in this case only for the N1 treatment). This increase in soil Nmin is due to the mineralization of soil organic matter and residues from the previous crop (mainly roots).

An important part of the mineralization in this area coincides with the summer months of July, August and September when temperatures (Fig. 5.1) are more favorable for nitrifying microorganisms as their optimal temperature ranges between 24ºC and 32ºC (Hagin and Tucker, 1982). However, in these rainfed systems, soil water potential is a key issue.

During a two-month period in 2007 from July sampling, soil moisture went down to 132.6 mm for a depth of 0.9 m (Fig. 5.6) thus, below the permanent wilting point. Water content below the permanent wilting point stops the activity of nitrifying bacteria, although ammonifying microflora, less sensitive to lack of water, can increase NH_4^+-N in the soil (Dommergues, 1977). However, diffusion limitations would reduce microbial access to resources and their activity might diminish. Our results (mainly during the 2008 summer drought) on the increment of NH_4^+-N *vs*. NO_3^--N in the summer months (Fig. 5.5) agree with the meta-analysis performed by Homyak *et al.*, (2017), where NH_4^+ increased significantly with decreased rainfall. Low rainfall also tends to build up the extractable ammonium (Parker and Schimel, 2011). Ammonia is quickly transformed to nitrate when water becomes available and exchangeable NH_4^+ concentrations then drop, likely because exchangeable NH_4^+ is nitrified (Schaeffer *et al.,* 2017). This probably also explains the faster nitrate increase after the first autumn rainfall (Figs. 5.1a, 5.3 and 5.1b, 5.2). Growth of nitrifiers lasts less than 24 hours, e.g. by *Nitrobacter,* with a generation time of about 8–16 hours (Schmidt, 1982). In November 2007 after soil rewetting and in both treatments, the amount of ammonium was reduced by half, with a figure of 20 kg NH_4^+-N ha^{-1}.

Furthermore, Fierer and Schimel (2002) found that drying-rewetting events induce changes in C and N dynamics, and C and N mineralization rates increase (wetting pulse), although the effects diminish as the frequency of the drying-rewetting stress increases. Hess *et al*., (2020) found that this effect can lead to differences in soil nitrate concentrations which can be around 32% higher in drying-rewetting stressed soils compared with frequently wetted soils. Rewetting after a drought period immediately stimulates decomposition of low quality substrate (Manrubia *et al.*, 2019) or relatively labile substrate which includes either dead microbial biomass or osmoregulatory substances released by soil microorganisms in response to hypo-osmotic stress in order to avoid cell lyses (Unger *et al*., 2010). It is mainly observed in the upper layers where water availability controls their persistence (Schaeffer *et al.,* 2017). This burst of nitrification observed on rewetting was first described in dry regions by Birch (1958). Furthermore, drying and rapid rewetting of soils causes slaking (Bosch-Serra *et al*., 2017) by the penetration of water into dry aggregates (implosion) exposing previously unavailable organic substrates for decomposition (Denef *et al*., 2001). In fine-textured soils such as the one in the experimental field, N mineralization might increase much more rapidly due to the size of C and N pools which is higher than those found in coarse soils in similar semi-arid environments (Austin *et al*., 2004).

The nitrification activity linked to water soil profile refill in early autumn also explains the recommendations for delaying sowing time (from October to November) in these Mediterranean rainfed areas (Plaza-Bonilla *et al*., 2017).

5.4.2 Evaluation of the LEACHM model in fallow periods

The statistical indices comparing the measured and the simulated SWC by LEACHM showed an acceptable agreement between both data sets. The latter was observed for the calibration and with some constraints for the validation period. The results also agreed with those found by other authors (Akinremi *et al*., 2011; Lidón *et al*., 2019, Asada *et* *al*., 2013; Jiménez-de-Santiago *et al*., 2019). The increase in SWC at the end of the fallow period fulfills one of the functions of this agricultural practice. Thus, it entails capturing rainfall during the fallow period and storing it in the soil for use during the subsequent cropping period (Koohafkan and Steward, 2008). The distortion related to the 2017 snow event (174 simulation day) was not so evident in SWC as it was followed by a rainy period (Figs. 5.1c, Fig. 5.6), leading to the sigmoidal function (Fig. 5.7). Drainage less than 15 mm is considered a small water loss in rainfed regions (Parsinejad and Feng, 2003; Jabro *et al*., 2011) but our numbers at least doubled this amount. However, the loss of water by drainage during the fallow periods is assumed to be higher than in cropping seasons (Jiménez-de-Santiago *et al*., 2019). During fallow periods, transpiration is avoided and evaporation from the first soil layer is reduced as the soil dries. Thus, soil water content increases. After rainy periods, the probability to surpass the soil water content at field capacity is higher under fallow than when crops are established. Water above FC drains due to gravitational forces.

In the N cycle, the importance of humus mineralization as a sensitive parameter was underlined by Schmied *et al*., (2010) and the base temperature parameter by Jung *et al*., (2010). Both parameters were also placed in the group of the most sensitive parameters by other authors (Sogbedji *et al*., 2001; Mahmood *et al*., 2002; Akinremi *et al*., 2011). Their importance is reinforced in a fallow period as no manure and/or plant residues (only roots from a previous crop) are introduced as an N source.

Denitrification shows low numbers, as befits a usually unsaturated soil, as in LEACHM denitrification rates decrease as water content diminishes from saturation following a Michaelis-Menten equation. However, in this silty loam soil, as the flow of soil water is 0.97 cm h^{-1} in the first layer (Table 5.1), nitrification can be stopped in some small pores filled with water within soil aggregates (due to constraints in oxygen diffusion rates) and nitrogen emissions can follow.. Denitrification at anaerobic microsites possibly occurs simultaneously with nitrate ammonification (one of the N_2O pathways). As N_2/N_2O emission ratio decreases with soil pH and in soils with high NO_3^- concentrations (Sun *et al*., 2012), some additional N_2O production might have occurred, mainly when 80% of water filled pore space was attained in April 2017 and in May 2007 (Fig. 5.6, Table 5.1). As the soil oxygen concentration decreases, greater N_2O emissions through nitrifier denitrification, carried out by ammonia-oxidizing bacteria, are produced (Smith, 2017). Besides, N_2O emissions can be enhanced by soil temperature (logarithmic relationship). Although the temperature threshold varies between climatic regions, air average temperatures of 11.3 ºC in April 2017 and 15.7 ºC in May 2007 were prone to N_2O emissions (Cosentino *et al*., 2013). The described factors could be translated to maximum emission values of 0.2-0.5 kg N_2O-N ha^{-1} day^{-1} while conversely, our results account for denitrification values of 0.1-0.2 kg N ha^{-1} for each fallow period (Table 5.5). Despite the described chance of occasional high daily N_2O emissions, the expected numbers of N losses from soil to the air are still low as the April-May period also coincides with a rapid evaporation enhancement (Figs. 5.1a, 5.1c).

The statistics obtained for soil N_{min} (Table 5.5) are in the range of those reported by other authors using LEACHM (Jung *et al*., 2010; Li *et al*., 2015b; Lidón *et al*., 2013; Lidón *et al*., 2019; Sogbedji *et al*., 2006; Vazquez-Cruz *et al*., 2014; Zhang *et al*., 2019). During the calibration process (2013–14, Table 5.5), the RMSE values in the soil profile were also in the same range as the ones found by Lidón *et al*., (2013) and Katou *et al.*, (2015) and the NRMSEs were below 0.40, indicating a good agreement between simulated and observed values (Li *et al*., 2015b; Van Liew and Garbrecht, 2003). After calibrating the LEACHM model, the agreement index value (d) was higher than 0.70

which, according to Van Liew and Garbrecht (2003), is acceptable. The obtained d values are included in the LEACHM model calibration range (0.77 to 0.91) indicated by several researchers (Hu *et al*., 2010; Li *et al*., 2015b), as also were the NSE values (Lidón *et al*., 2019; Ritter and Muñoz-Carpena, 2013; Zhang *et al*., 2019).

N transformation processes (mineralization and nitrification) were influenced not only by temperature but also by soil moisture. In 2007–08, SWC was *ca*. below 156 mm (*c*. below -500 kPa) throughout the first half of the studied period, and it was followed by an important rainy period where 80% of water-filled pore space was attained (Fig. 5.3, Table 5.1). Then, until June 2008 (~ 310 simulation day), optimum soil conditions for nitrification were not attained, but from then onwards, it proceeded very fast. As LEACHM considers the current moisture content and not the drying-rewetting stress history, it underestimates net mineralization in such situations. This fact could explain why in the 2007–08 fallow season LEACHM underestimated N_{min} content from the 0–0.6m depth.

During the validation process (2016–17), the differences in the mineral N overestimation occurred during the winter and spring months (January to April), when a significant decrease in the mineral N content of the soil was observed in both treatments, which the LEACHM did not reproduce. This observed decrease might be linked to an important snowfall event on the 25th March 2017 followed by several rainy days that could promote N_2O emissions (unaccounted) but also drainage and N leaching.

As recorded in June 2016 (Table 5.6), at the start of the 2016-17 validation period there was an important amount of residual N_{min}, as high as 281 kg N ha^{-1} in N1 (176 kg N ha^{-1} in N0). When soil parameters (moisture, temperature) are not limiting (i.e. in April 2017) and mineral N is over 10 mg N kg^{-1} (*ca.* 50 kg N ha^{-1} in the first 0.3 m depth),

N_2O fluxes are usually higher than 10 g N_2O ha^{-1} day^{-1} and a great proportion might be in the range of 0.1-1 kg N_2O-N ha^{-1} day^{-1} (Smith, 2017). Thus, unaccounted N_2O emissions might contribute to the reduction of soil mineral N, although to a much lesser quantitative extent than potential lixiviation. Leaching importance is corroborated by the mineral N increase at a depth between 0.6–0.9 m (Fig. 5.4a). This increase also indicated the prevalence of Nmin transport (from the shallowest soil layer to the deepest) over mineralization. However, simulations carried out show that a higher rainfall (>100 mm) than that recorded in the weather station at that time, would be necessary in order to result in a decrease in mineral N of the same order as that measured (data not shown) and which can raise the final amount of leached N (Table 5.5). It must be pointed out that during this period, nitrification was not constrained by low temperatures as the temperature limitations appear below 5ºC (Dommergues, 1977) and average daily temperatures were always higher than 5ºC (Fig. 5.1c). The disagreement between measured and simulated N_{min} values can be further explained by the effect of preferential transport on leaching of nitrate to drainage (Cheng *et al.*, 2014). The experimental field is characterized by compacted aggregates and the bulk density is high (Table 5.1), being similar to values found in nearby areas (Cantero-Martinez *et al.*, 1995). Besides, the qualitative assessment of porosity by micromorphology showed that both the soil treated with mineral fertilizer and the control had fissures and vughs (Bosch-Serra *et al.*, 2017). As many models including LEACHM do not account for preferential transport of water and nitrates from the upper layer to deeper layers in the soil profile, mainly when a fast saturation of the wet plow layer occurs, they underestimate the leaching of nitrate (Nagy *et al.*, 2020). The importance of such transport (higher than a dispersive-convective flow) diminishes in the other fallow periods when rainfall follows a period of drying. It is difficult to predict this nitrate mass flux in field experiments because of spatial variation in preferential flow (Williams *et al*., 2003). However, its existence in our field leads to an underestimation of water drained figures (Fig. 5.6) and the amount of NO_3^--N leached (Fig. 5.4) in 2006-17. Higher leaching in N1 *vs.* N0 was not due to a higher mineralization or nitrification but to the higher N_{min} initial content at the start of the fallow period (Table 5.6).

5.4.3 Implications of fallow for N in a rainfed semiarid system

The mineral N contents present in the soil profile at the end of the fallow period can be used for the next cropping season, saving N fertilizer, but as recommended by Stanford (1982), soil should be sampled shortly before sowing to determine the available N supply. The omission of such sampling can lead to over-fertilization in rainfed Mediterranean areas (López-Bellido *et al.*, 2013), mainly when fallow is introduced into the rotation. Besides, the high amounts detected in the soil profile at the beginning of the next cropping season (between 232 up to 337 kg N_{min} ha^{-1}) are a potential environmental hazard for groundwater but also for climate change related aspects (N_2O emissions) due to erratic precipitation amounts (Fig. 5.1). Mineralized N indicates that in rainfed Mediterranean systems it is necessary to establish the fallow period within a rotation according to the N balance. Soil sampling and the use of models such as LEACHM might be useful, although models must be adjusted for mineralization enhancement after a drying-rewetting cycle, and even further when ending in periods with favorable temperatures for mineralization. Also, it might be interesting to set up another approach which includes a more complex dimensional water flow, mainly when soil regularly becomes saturated.

5.4 Conclusions

By measurements taken during three fallow periods in crop rotation in a rainfed

Mediterranean area, N input by mineralization was higher than N losses (through gaseous emissions or leaching). The N_{min} increment occurred mostly when temperatures were more favorable for the mineralization process; thus, during the end of the summer months if enough water is available, or in early autumn. Additional nitrate pulses appeared after drying-rewetting periods linked to rainfall shifts and N_{min} soil values close to 130 kg N ha^{-1} in previously N fertilized plots were measured. In these plots, the maximum amount of N_{min} that was accumulated in the soil profile (0–0.9 m) attained 400 kg N ha^{-1}. Numbers draw attention to the need to consider such amounts of mineral nitrogen in the N fertilization schedule for the next cropping season or in the decision to be taken about the introduction of a fallow in a rotation. The simulated results with LEACHM show that the amount of mineral N leached below 0.9 m depth, in previously mineral fertilized plots, ranged from 11 kg N ha^{-1} to 38 kg N ha^{-1}. Nitrogen losses might be higher (including N_2O emissions) as LEACHM underestimates soil N_{min} after a drying-rewetting period, and also it does not take into account additional preferential flows when soil saturates very quickly. The LEACHM version used has some deficiencies, meaning that there are limitations to its usefulness in semiarid rainfed environments to evaluate N losses out of the system, and therefore it cannot fully substitute for soil N_{min} sampling at the end of a fallow period prior to crop establishment.

Acknowledgements

This work was supported by the Spanish Ministry of Economy and Competitiveness and the Spanish National Institute for Agricultural Research and Experimentation (MINECO-INIA) through the project RTA2017-88-C3-3. The field maintenance of the experimental site by the Ministry of Agriculture, Livestock, Fisheries and Food (Generalitat de Catalunya), in the framework of the improvement of fertilization practices in Catalonia (Spain), is fully acknowledged.

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Supplementary material

Table 5.SI. Cumulative rainfall probability for a yearly period and during the winter cereal cropping season (from first October to end of June) in the experimental area

Yearly period	Rainfall (mm)	Probability (%)	Cropping season	Rainfall (mm)	Probability (%)
2018	662.4	5.5	2003-04	487.4	5.5
2003	593.2	11.1	2017-18	461.0	11.1
2010	561.4	16.6	2009-10	453.6	16.6
2008	525.5	22.2	2008-09	429.6	22.2
2009	521.4	27.7	2007-08	378.3	27.7
2014	500.6	33.3	2012-13	352.0	33.3
2013	484.2	38.8	2006-07	343.5	38.8
2002	466.4	44.4	2016-17	332.7	44.4
2012	409.6	50.0	2002-03	327.0	50.0
2016	402.0	55.5	2013-14	323.1	55.5
2007	389.4	61.1	2010-11	319.8	61.1
2004	386.6	66.6	2015-16	289.6	66.6
2011	375.7	72.2	2001-02	287.6	72.2
2005	374.2	77.7	2011-12	275.6	77.7
2017	360.9	83.3	2005-06	256.5	83.3
2015	347.9	88.8	2014-15	250.7	88.8
2006	291.6	94.4	2004-05	191.6	94.4

Calculations were based on available rainfall data from the field automatic meteorological station (2001–18).

Chapter 6

This chapter contains the manuscript to be submitted in the journal of "*Environmental Science and Pollution Research*"

Changes in soil properties and heavy metal content after 7 years of winter cereal fertilized with pig slurry

Abstract

The intensification of pig farming produces large amounts of slurry which is applied to agricultural soils as fertilizer. A 7-year field study was performed to check the mid-term residual effect of pig slurry on soil properties, the accumulation (0-0.3 m) of some essential nutrients and heavy metals in soil. Five fertilization treatments such as control (no N applied), mineral fertilizer (90 kg N ha^{-1}), and different N doses of pig slurry (146, 281, 534 kg N ha^{-1}) were applied at sowing of a winter cereal crop. Pig slurry significantly increased soil OC increased by an average between 1.3- 2.5% of the slurry OC applied Phosphorous (Olsen P and total P), and exchangeable potassium concentration in soil. Similarly, pig slurry residues significantly affected Zn and Cu uptake concentration in grains in both harvesting years and uptake concentrations ranged from 92.7 g ha^{-1} to 110.0 g ha^{-1} and 0.8 g ha^{-}1 to 21.9 g ha^{-1}, respectively. In 2004, pig slurry resides significantly increased grain yield biomasses and ranged from 3512 kg ha^{-1} to 3970 kg ha^{-1}, while grain yield biomasses slightly decreased in 2007 and varied from 2474 kg ha^{-1} to 3125 kg ha^{-1}. The results of this research study provide both support and a caution to adopt the mid-term agricultural practice of pig slurry residues.

Keywords: pig slurry residues, heavy metals, contamination, plant uptake, crop yield

Highlights

Mid-term pig slurry significantly increased macronutrients in soil and plant

Concentrations of B, Cu, and Zn have been enhanced in the soil profile over time.

Pig slurry also increased the bioavailability of Cu and Zn, but not at a toxic level.

6.1 Introduction

Pig farming plays an important role in the socio-economic development of European rural areas (Daudén et al. 2004; Martínez et al. 2017), mainly in Spain (which is the European leading country) with 29 million heads (MAPAMA 2016; Eurostat 2017; Rivero-Juarez et al. 2020). Application of pig slurry at a recommend rate is considered a suitable agricultural practice to increase soil quality and to avoid agricultural and environmental pollution (Mallmann et al. 2012; Qaswar et al. 2020) by nitrate leaching, ammonia volatilization (Bosch-Serra et al. 2014) or greenhouse gas emissions (Chethan et al. 2020). Pig slurry is also considered an important source of macronutrients (N,P, K, Ca, Mg S) and micronutrients specially copper (Cu) and zinc (Zn) (Grohskopf et al. 2016). The high concentrations of Cu and Zn in pig slurry are mainly due to their traditional use in animal feed to improve animal performance, and for preventing bacterial infections (Suresh et al. 2009; Grohskopf et al. 2016). However, when pig slurry is applied to soils, these elements may accumulate, but their uptake by plant may also increase (Jakubus et al. 2013; Provolo et al. 2018).

The bioavailability and solubility of micronutrients in the soil profile behave differently when pig slurry is used instead of synthetic fertilizers, because of their complexation with soil organic matter (SOM) (Grohskopf et al. 2016). Mineral fertilisation, mainly with P fertilizers, is also a source of additional micronutrients (e.g. Ni, Zn) and heavy metals (Cr, Ni, Pb, Zn) according to the fertilizer origin (Mortvedt, 2005).

The objective of this research work was to assess the mid-term effect of pig slurry fertilisation when compared with mineral fertilisation on: 1) soil properties (pH, salinity, organic carbon) including soil nutrients (N, P, B, Cu, Fe, Mn, Ni, Zn, K) and heavy metal concentrations (Co, Cr, Pb), 2) the concentration of nutrients (N, P, K, Ca, Mg, Cu, Mn, Zn) in straw and grain of barley (*Hordeum vulgare* L.) and 3) plant biomass (grain yield and straw biomass).

6.2 Materials and methods

6.2.1 Experimental site and study design

A mid-term field experiment (2000-2007) was conducted in Oliola, Lleida, northeastern Spain. The specific location is 41º52’30” N, 1º09’1” E, with an altitude of 440 m a.s.l. The site is located in a slightly sloping (< 2%) valley. No slurry fertilisation was applied before the establishment of the experiment. Five different treatments with three replications were used during the whole experiment according to a randomized complete block design. The five treatments included a control (C000); a mineral N fertilizer (M090) applied at 120 kg N/ha and pig slurry applied at 20 m^3/ha (S146), 40 m^3/ha (S281) and at 80 m^3/ha (S534). Pig slurry (PS) was spread using a conventional splash-plate system before sowing and it was incorporated into the soil by disc-harrowing within 24 hours of spreading. Phosphorus (P) and potassium (K) were applied annually at sowing in C000 and M090 treatments at 42 kg P ha^{-1} and 89 kg K ha^{-1}. Ammonium nitrate was used as a mineral N fertilizer in M090. From 2000 to 2004, annual doses of PS were complemented with 60 kg N ha^{-1} as ammonium nitrate at cereal tillering stage. Experimental plots were 12 m long and 7 m wide for C000 and M090 while the rest of the plots were 20 m long and 12 m wide.

Winter cereals were sown under rainfed conditions following a rotation of barley (with wheat (*Triticum aestivum* L.). Wheat was established in 2002/2003 and 2005/2006 cropping seasons. The winter cereal was sown at early November, and harvested at the end of June. Cereal straw was annually removed from the field and the stubble was buried by tillage before sowing.

6.2.2 Climatic conditions of study site

The climate in the area is characterized as semiarid Mediterranean, with an average annual rainfall lower than 450 mm and an average reference crop evapotranspiration (ET_o) of 1013 mm yr^{-1} (Penman-Monteith equation; Allen et al., 1998). Daily and weekly air temperature, thermal amplitude, ET_o and daily precipitation data were collected from an automatic station next to the experimental field. From 2001 to 2007 annual rainfall ranged from 284 mm (2001) to 593 mm (2003). Within a year, the maximum monthly rainfall occurs in April, October or November.

6.2.3 Soil sampling and analysis

The soil samples were collected from 0 to 0.3 m of depth using a soil auger. To check the effect of pig slurry, soil samples were taken in October 2000 (before any fertilization treatment) and in June 2007. Three samples were taken per plot randomly distributed to make a composite sample. Bulk density was measured with the ring method and its average value was 1650 kg m^{-3} in the top layer (0-0.3m). The texture was silty loam. The soil is classified as Typic Xerofluvent (Soil Survey Staff ,2014). The soil physicochemical properties were determined as follows (Porta Casanellas et al. 1986): texture by pipette method, pH in aqueous solution using a 1:2.5 sample/water ratio, salinity (EC) by conductimetry (1:5), total N by the Kjeldahl method, oxidizable organic carbon by the Walkley and Black (1934) method, available P content by the Olsen method, availability of K was measured by extraction with ammonium acetate with 1N solution and determination by atomic absorption spectrophotometry. A Bernard Calcimeter was used for the estimation of calcium carbonate ($CaCO_3$) and the average values was 300 g kg^{-1}. Extraction with 3 mL HNO_3 (69%) and 2 mL H_2O_2 (30%) followed by determination by inductively coupled plasma mass spectrometry (ICP-MS (UNE-EN 15763) (Agilent Technologies Model: 7700x) was used for total element analysis.

6.2.4 Application of pig slurry

Pig slurry, always collected from a nearby fattening pig farm, was applied every year before sowing. The amount of nutrients (N, P, K, Ca, Mg, S, Fe, Mn, Cu, Zn) and sodium (Na) applied with pig slurry were calculated for two periods from October 2000 to October 2003 and from October 2004 to October 2006 (Table 6.1). The slurry samples were collected at application time, just before sowing. Slurry analyses (pH; dry matter, ammonia nitrogen and total Kjeldahl N content) were carried out according to standard methods. The total contents of calcium (Ca), copper (Cu), manganese (Mn), zinc (Zn), and chromium (Cr) in the slurries were evaluated using ICP-MS spectroscopy after acid mineralization.

Table 6.1. Average chemical properties (± standard deviation)[a] of pig slurry used during two periods of the seven whole experiment period.

Period	**Four applications**	**Three applications**
Parameter (units)	**Oct 2000Oct 2003**	**Oct 2004-Oct 2006**
pH (1:5; potentiometry)	7.8 ± 0.1	8.6 ± 0.1
EC (dS cm^{-1}, 1:5 conductimetry)[b, c]	35.7 ± 3.0	25.8 ± 24.3
DM (g kg^{-1}, gravimetry 105 °C)[b]	74 ± 36	102 ± 9
Organic matter (g kg^{-1}, Walkey-Black)	644 ± 71	736 ± 31
Nitrogen (g kg^{-1}, Kjeldahl)	100 ± 36	91 ± 3
Organic N (g kg^{-1}, Kjeldahl)	28 ± 4	27 ± 1
Ammonia N (g kg^{-1}, Kjeldahl)	72 ± 31	64 ± 1
P (g kg^{-1}, ICP)[d]	20 ± 0	14 ± 0
K (g kg^{-1}, ICP)	83 ±40	77 ± 16
Ca (g kg^{-1}, ICP)	26 ± 6	34 ± 17
Mg (g kg^{-1}, ICP)	9 ± 3	10 ± 0
Na (g kg^{-1}, ICP)	19 ± 7	14 ± 1
S (g kg^{-1}, ICP)	-	7 ± 0
Fe (mg kg^{-1}, ICP)	3871.7 ± 161.4	2958.3 ± 271.0
Mn (mg kg^{-1}, ICP)	492.0 ± 127.0	624.4 ± 150.2
Cu (mg kg^{-1}, ICP)	751.6 ± 183.4	361.5 ± 133.6
Zn (mg kg^{-1}, ICP)	1661.1 ± 678.0	1330.7 ± 265.9

[a] It represents the average and standard deviation of the applied pig slurry for each period. Parameters are referred to dry matter.
[b] EC, electrical conductivity; DM, dry matter.
[c] Soil: distilled water.
[d] ICP: inductively coupled plasma atomic emission spectrometry (U.S. EPA, 2014)

6.2.5 Plant sampling and analysis

Barley plant samples were taken from the 2004 and 2007 harvests. The homogenized plants straw and grain samples were analyzed for N according to the Kjeldalh method. Other samples were digested with a mixture of HNO_3 and $HClO_4$ at a ratio of 9:4 v/v on hot plate at 150-180 ^oC until the clear liquid colour appeared, and the total concentrations of elements and heavy metals were determined by inductively coupled plasma mass spectrometry (ICP-MS (UNE-EN 15763) (Agilent Technologies Model: 7700x). Plant uptake was estimated by multiplying straw and grain biomass by their element or nutrient concentration.

6.2.6 Statistical analysis

Mixed-effects models using the experimental blocks as a random variable, followed by LSD tests using SAS software (SAS Institute, 2002–2012) were performed to analyze the effects of treatments and sampling year on soil variables, and element concentrations and contents in the aerial crop biomass.

6.3 Results

The amount of nutrients and OC applied in the different treatments are summarized in Table 6.2.

Table 6.2. Amount of organic carbon (OC) and nutrients applied in the different treatments[a] (seven cropping seasons from October 2000 to June 2007[b] and divided in two periods according to plant sampling (June 2004 and June 2007).

		Accumulated OC applied (kg ha^{-1})			
Treatment	**C000**	**M090**	**S146**	**S281**	**S534**
Application time					
Oct00-Oct01-Oct02-Oct03	—	—	2469.5	4318.5	8285.4
Oct04-Oct05- Oct06	—	—	1544.6	3174.1	6285.0
Total	—	—	4014.1	7492.6	14570.4
		Accumulated N applied (kg ha^{-1})			
Treatment	**C000**	**M090**	**S146**	**S281**	**S534**
Application time					
Oct00-Oct01-Oct02-Oct03	0	360	513.9	1016.2	1913.2
Oct04-Oct05- Oct06	0	270	284.2	625.8	1215.0

Total	0	630	798.1	1642.0	3128.2
Accumulated P applied (kg ha^{-1})					
Treatment	**C000**	**M090**	**S146**	**S281**	**S534**
Application time					
Oct00-Oct01-Oct02-Oct03	169	169	116.9	231.0	433.0
Oct04-Oct05- Oct06	126	126	44.3	98.1	200.0
Total	295	295	161.2	329.1	633.0
Accumulated K applied (kg ha^{-1})					
Treatment	**C000**	**M090**	**S146**	**S281**	**S534**
Application time					
Oct00-Oct01-Oct02-Oct03	357	357	388.5	855.7	1515.3
Oct04-Oct05- Oct06	268	268	234.7	518.5	1107.8
Total	625	625	623.2	1374.2	2623.1
Accumulated Ca applied (kg ha^{-1})					
Treatment	**C000**	**M090**	**S146**	**S281**	**S534**
Application time					
Oct00-Oct01-Oct02-Oct03	—	—	172.7	305.9	605.1
Oct04-Oct05- Oct06	—	—	107.3	240.0	503.2
Total	—	—	280.0	545.9	1108.3
Accumulated Mg applied (kg ha^{-1})					
Treatment	**C000**	**M090**	**S146**	**S281**	**S534**
Application time					
Oct00-Oct01-Oct02-Oct03	—	—	64.1	116.8	232.8
Oct04-Oct05- Oct06	—	—	32.0	70.9	144.0
Total	—	—	96.1	187.7	376.8
Accumulated Na applied (kg ha^{-1})					
Treatment	**C000**	**M090**	**S146**	**S281**	**S534**
Application time					
Oct00-Oct01-Oct02-Oct03	—	—	99.1	213.5	372.3
Oct04-Oct05- Oct06	—	—	43.5	93.2	195.8
Total	—	—	142.6	306.7	568.1
Accumulated S applied (kg ha^{-1})					
Treatment	**C000**	**M090**	**S146**	**S281**	**S534**
Application time					
Oct00-Oct01-Oct02-Oct03	—	—	1.2	2.5	5.0
Oct04-Oct05- Oct06	—	—	21.4	48.6	100.6
Total	—	—	22.6	51.1	105.6
Accumulated Fe applied (kg ha^{-1})					
Treatment	**C000**	**M090**	**S146**	**S281**	**S534**
Application time					
Oct00-Oct01-Oct02-Oct03	—	—	25.5	51.1	98.6
Oct04-Oct05- Oct06	—	—	8.9	19.9	40.1
Total	—	—	34.4	71.0	138.7

Accumulated Mn applied (kg ha^{-1})					
Treatment	**C000**	**M090**	**S146**	**S281**	**S534**
Application time					
Oct00-Oct01-Oct02-Oct03	—	—	3.1	5.7	11.3
Oct04-Oct05- Oct06	—	—	1.9	6.9	8.8
Total	—	—	5.0	12.6	20.1
Accumulated Cu applied (kg ha^{-1})					
Treatment	**C000**	**M090**	**S146**	**S281**	**S534**
Application time					
Oct00-Oct01-Oct02-Oct03	—	—	4.6	9.6	17.7
Oct04-Oct05- Oct06	—	—	1.0	2.3	4.7
Total	—	—	5.6	11.9	22.4
Accumulated Zn applied (kg ha^{-1})					
Treatment	**C000**	**M090**	**S146**	**S281**	**S534**
Application time					
Oct00-Oct01-Oct02-Oct03	—	—	10.8	22.4	41.3
Oct04-Oct05- Oct06	—	—	3.9	8.7	18.0
Total	—	—	14.7	31.1	59.3

[a]The letter in the acronym indicates the fertilizer origin: mineral fertilizer (M), pig slurry (S) and the control (C). The numbers indicate the average of N rate applied annually (kg ha^{-1}).
[b]Slurries and mineral were always applied in October except in the M090 where 30 kg N ha^{-1} were applied in October and the rest (60 kg N ha^{-1}) at cereal tillering stage in February.

6.3.1 Pig slurry effects on soil properties and fertility

In the experimental period of seven years, no significant changes appeared in soil pH or CEC (Table 6.3), with mean values ranging between 8.1 and 8.3, and 7.7 and 9.1 cmol^{+} kg^{-1}, respectively. Fertilisation (whatever the origin) tended to increase soil EC with time (from 0.2 up to 0.3 dS m^{-1}). Soil organic carbon (OC) concentration, when compared with the control and at slurry rates higher than 281 kg N ha^{-1}, increased by an average of 20% (Table 6.3). No differences were found at lower rates or when compared with M090. The C: N ratio remained around 9.1 – 9.2. Pig slurry applications higher than 281 kg N ha^{-1} increased available P by an average of 4.6 mg P kg $^{-1}$ soil for every 100 kg P ha^{-1} applied. At the lower rate of 146 kg N ha^{-1}, the increment still existed at a rate of 3.1 mg P kg $^{-1}$ soil. The increment in the relation between available P and total P was 10%, 12% and 17% for S146, S281 and S534, respectively. Available P Olsen concentrations significantly increased and varied from an initial average of 10.7 mg kg^{-1} in 2000 to 27.0 mg kg^{-1} in 2007, with a highest value of 41.0 mg kg^{-1} for the S534 treatment in 2007. Available K concentrations in soil also increased from an average of 96.1 mg K kg^{-1} in 2000 to 209.1 mg K kg^{-1} in 2007, with a highest value of 302 mg K kg^{-1} in the S534 treatment (Table 6.3).

Table 6.3. Values of physicochemical properties of soils and macronutrient concentrations according to pig slurry treatments maintained for seven cropping seasons (2000-2007).

Parameter	Treatment	2000	2007	Marginal Mean	SED[a]	LSD[b]
pH	C000	8.3	8.1	8.2 ± 0.05		
	M090	8.2	8.2	8.2 ± 0.05		
	S146	8.1	8.2	8.2 ± 0.05		
	S281	8.3	8.2	8.3 ± 0.05		
	S534	8.3	8.2	8.2 ± 0.05		
	Marginal Mean	8.2 ± 0.03	8.2 ± 0.03			
Soil EC 1:5 (dS m^{-1}, 25ºC)	C000	0.2	0.3	0.2 ± 0.02		
	M090	0.2	0.3	0.2 ± 0.02		
	S146	0.2	0.3	0.2 ± 0.02		
	S281	0.2	0.2	0.2 ± 0.02		
	S534	0.2	0.3	0.2 ± 0.02		
	Marginal Mean	0.2 ± 0.01y	0.3 ± 0.01x			
	SED/ LSD		0.01/0.01			
Soil CEC ($cmol^{+}$ kg^{-1})	C000	7.8	7.9	7.9 ± 0.68		
	M090	-	-	-		
	S146	7.7	8.8	8.2 ± 0.68		
	S281	9.1	9.1	9.1 ± 0.68		
	S534	8.5	7.7	8.1 ± 0.68		
	Marginal Mean	8.3 ± 0.54	8.4 ± 0.54			
Soil OC (g kg^{-1})	C000	10.0	11.0	10.5 ± 0.49b	0.54	0.37
	M090	10.0	12.0	11.0 ± 0.49ab		
	S146	10.0	12.0	11.0 ± 0.49ab		
	S281	11.0	13.0	12.0 ± 0.49a		

	S534	10.0	14.0	12.0 ± 0.49a		
	Marginal Mean	10.1 ± 0.38y	11.6 ± 0.38x			
	SED/ LSD		0.34/0.23			
N (g kg^{-1}, Kjeldahl method)	C000	1.1ax	1.2cx	1.1 ± 0.05	0.06	0.04
	M090	1.1ay	1.3bcx	1.2 ± 0.05		
	S146	1.1ay	1.3bcx	1.2 ± 0.05		
	S281	1.1ay	1.4abx	1.2 ± 0.05		
	S534	1.0ay	1.6ax	1.3 ± 0.05		
	Marginal Mean	1.0 ± 0.04	1.3 ± 0.04			
	SED/ LSD		0.003/0.002			
C: N ratio	C000	9.4	9.1	9.3 ± 0.36		
	M090	9.5	9.3	9.4 ± 0.36		
	S146	8.9	9.0	9.0 ± 0.36		
	S281	9.3	9.2	9.3 ± 0.36		
	S534	9.8	8.8	9.3 ± 0.36		
	Marginal Mean	9.2 ± 0.27	9.1 ± 0.27			
Available P Olsen (mg kg^{-1})	C000	11.0a	35.67ab	23.33 ± 1.94	2.75	1.89
	M090	10.3a	17.67c	14.00 ± 1.94		
	S146	9.7a	14.7c	12.2 ± 1.9		
	S281	11.3a	26.0bc	18.7 ± 1.94		
	S534	11.3a	41.0a	26.2 ± 1.94		
	Marginal Mean	10.7 ± 1.23y	27.0 ± 1.23x			
	SED/ LSD		1.74/1.19			
Available K (mg kg^{-1})	C000	81.0a	205.0b	143.0 ± 12.45	16.72	11.51
	M090	102.3a	178.0bc	140.2 ± 12.45		

	S146	94.7a	154.7c	124.7 ± 12.45		
	S281	104.3a	205.7b	155.0 ± 12.45		
	S534	98.3a	302.0a	200.2 ± 12.45		
	Marginal Mean	96.1 ± 8.43y	209.1 ± 8.43x			
	SED/ LSD		10.57/7.28			
Total P (mg kg^{-1})	C000	480.7	719.7	600.2 ± 32.23ab	45.58	31.45
	M090	-	-	-		
	S146	566.3	607.3	586.8 ± 32.23b		
	S281	621.0	770.3	695.7 ± 32.23a		
	S534	607.3	779.7	693.5 ± 32.23a		
	Marginal Mean	568.8 ± 22.79y	719.3 ± 22.79x			
	SED/ LSD		32.23/22.24			

[a]SED, standard error of a difference; [b]LSD, least significant difference; all for *P*=0.05; means followed by the different letter are significantly different. Number with letter a, b, c and x, y showed significantly difference between treatments and time, respectively.

For micronutrients and heavy metals, differences between years and fertilisation treatments were only detected in Zn concentration (Table 6.4). The application of slurries increased soil Zn concentration by an average of 22% for every 100 kg Zn ha^{-1} applied. In 2007, the slurry treatments showed a higher B concentration (average of 12.6 mg kg^{-1}) than the control (9.0 mg kg^{-1}). Significant changes in Cu concentrations were detected between years with an average increment of approximately 24% for every 100 kg Cu ha^{-1} applied (Table 6.4). Changes in the concentration of the rest of elements with time or between treatments were not significant.

Table 6.4. Micronutrient and soil heavy metal contents according to pig slurry treatments maintained for seven cropping seasons (2000-2007).

Nutrient	Treatment	2004	2007	Marginal Mean	SED[a]	LSD[b]
B (mg kg^{-1})	C000	17.3ax	9.0cy	13.2 ± 1.27	1.79	1.23
	S146	12.7abx	11.7by	12.2 ± 1.27		
	S281	11.3by	14.7ax	13.0 ± 1.27		
	S534	10.3by	11.3bx	10.8 ± 1.27		
	Marginal Mean	13.0 ± 0.89	11.7 ± 0.89			
	SED/LSD		1.25/0.87			
Co (mg kg^{-1})	C000	8.1	8.5	8.3 ± 0.34		
	S146	8.8	8.8	8.8 ± 0.34		
	S281	8.9	8.9	8.9 ± 0.34		
	S534	8.4	8.4	8.4 ± 0.34		
	Marginal Mean	8.5 ± 0.27	8.6 ± 0.27			
Cr (mg kg^{-1})	C000	17.7	12.7	15.2 ± 1.07		
	S146	15.0	14.7	14.8 ± 1.07		
	S281	15.0	17.3	16.2 ± 1.07		
	S534	13.7	14.3	14.0 ± 1.07		
	Marginal Mean	15.3 ± 0.71	14.8 ± 0.71			
Cu (mg kg^{-1})	C000	20.0	20.0	20.0 ±1.31		
	S146	19.7	23.0	21.3 ±1.31		
	S281	16.0	22.7	19.3 ±1.31		
	S534	17.0	24.7	20.8 ±1.31		
	Marginal Mean	18.2 ±1.03y	22.6 ±1.03x			
	SED/LSD		1.16/0.80			
Fe (mg kg^{-1})	C000	20987.4	21486.1	21236.7 ± 604.23		

	S146	22112.9	22065.6	22089.2 ± 604.23		
	S281	22573.0	22671.7	22622.3 ± 604.23		
	S534	21577.2	21217.3	21397.3 ± 604.23		
	Marginal Mean	21813 ± 461.2	21860 ± 461.2			
Mn (mg kg^{-1})	C000	564.3	588.0	576.2 ± 24.27		
	S146	604.3	626.7	615.5 ± 24.27		
	S281	598.3	596.3	597.3 ± 24.27		
	S534	568.3	547.7	558.0 ± 24.27		
	Marginal Mean	583.8 ± 21.75	588.7 ± 21.75			
Ni (mg kg^{-1})	C000	21.3	23.3	22.3 ± 1.06		
	S146	23.3	24.0	23.7 ± 1.06		
	S281	24.0	24.7	24.3 ± 1.06		
	S534	22.7	23.0	22.8 ± 1.06		
	Marginal Mean	22.8 ± 0.91	23.7 ± 0.91			
Pb (mg kg^{-1})	C000	18.7	18.7	18.7 ± 0.81		
	S146	19.0	19.7	19.3 ± 0.81		
	S281	19.3	19.7	19.5 ± 0.81		
	S534	18.3	19.0	18.7 ± 0.81		
	Marginal Mean	18.8 ± 0.67	19.3 ± 0.67			
Zn (mg kg^{-1})	C000	61.0	67.3	64.2 ± 3.68b	4.63	3.20
	S146	68.7	74.3	71.5 ± 3.68ab		
	S281	70.7	85.0	77.8 ± 3.68a		
	S534	67.0	89.7	78.3 ± 3.68a		
	Marginal Mean	66.8 ± 2.86y	79.1 ± 2.86x			
	SED/LSD		3.27/2.26			

[a]SED, standard error of a difference; [b]LSD, least significant difference; all for P=0.05; means followed by the different letter are significantly different. Number with letter a, b, c or/and with letters x, y showed significantly differences between treatments or/and time, respectively.

6.3.2 Pig slurry effects on element concentrations in plants and uptake

In the 2004 cropping season grain yield biomass, straw biomass and total biomass were higher than in 2007 cropping season (Figure 6.1). In the 2004 harvest, the grain yield biomass and straw biomass ranged from 2312 kg ha^{-1} to 3974 kg ha^{-1} and from 4535 kg ha^{-1} to 6104 kg ha^{-1}, respectively. However, the total biomass for S146, S281, and S534 treatments were 8216 kg ha^{-1}, 10342 kg ha^{-1}, and 8354 kg ha^{-1}, respectively (Figure 6.1a). In the 2007 harvest, the grain yield biomasses were 3125 kg ha^{-1}, 2825 kg ha^{-1}, and 2474 kg ha^{-1} for S146, S281, and S534 treatments, respectively (Figure 6.1(b)). In contrast, straw biomass significantly increased and ranged from 3500 kg ha^{-1} to 4982 kg ha^{-1}. The total biomasses for S146, S281, and S534 treatments were 6625 kg ha^{-1}, 6119 kg ha^{-1}, and 7456 kg ha^{-1}, respectively (Figure 6.1(b)).

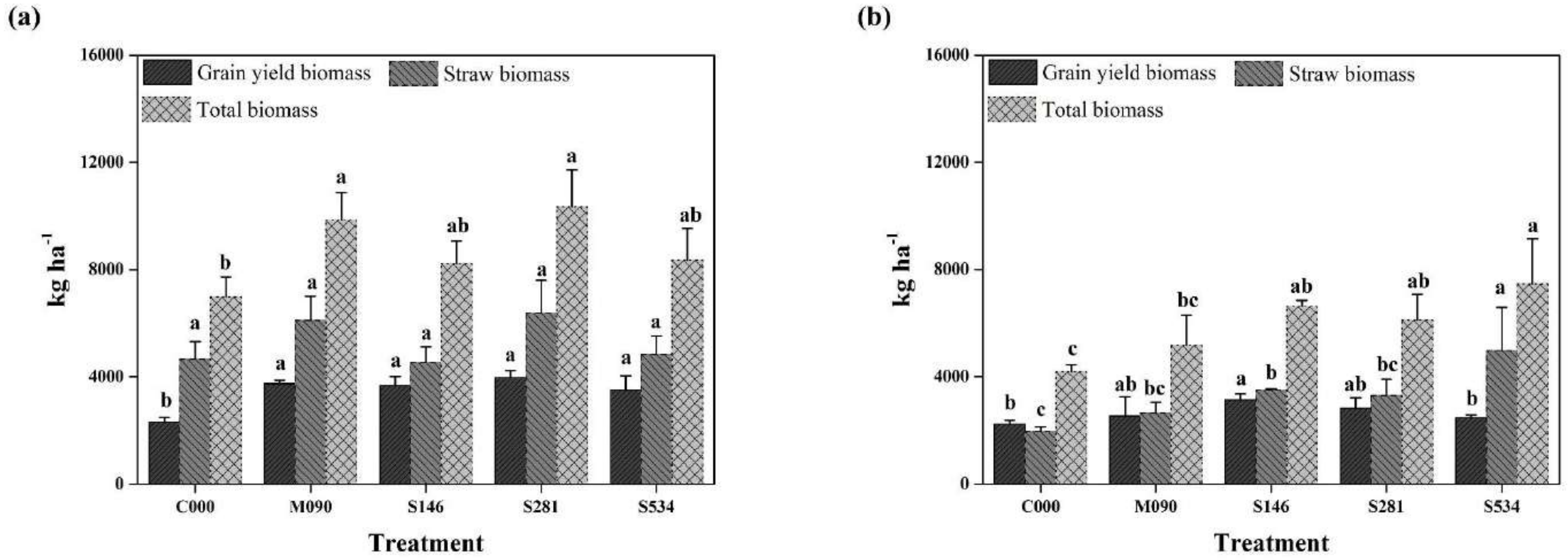

Figure 6.1. Grain yield biomass, straw biomass and total biomass according to pig slurry treatments maintained for (a) 2004 and (b) 2007 cropping seasons.

The concentrations of N and P in grain increased with the highest slurry doses (Table 6.5). The N concentration in grain increased approximately 35% and 53% for S281 and S534 for every 100 kg N ha^{-1} applied, respectively. Similarly, the increment of P concentration in grain for S281 and S534 treatments were 8% and 21% for every 100 kg P ha^{-1} applied, respectively (Table 6.5). Mean increments in N (14%), Mg (18%), Cu (59%) and Mn (10%) concentrations in grain were also observed between 2004 and 2007. In contrast, the mean P and K concentrations in grain decreased 7% and 20%, respectively in the last cropping year (Table 6.5). On the other hand, there was a interaction between treatments and time for Zn concentration in grain; concentration increase between 2004 and 2007 was only significant for the mineral treatment and the two highest doses of slurry (Table 6.5).

Table 6.5. Changes on nutrient concentration contents in barley (*Hordeum vulgare* L.) grain in 2004 and 2007 harvests and according to different annual pig slurry treatments after four (2004) and seven (2007) cropping seasons.

Nutrient	**Treatment**	**2004**	**2007**	**Marginal Mean**	**SED**[a]	**LSD**[b]
N (g kg^{-1})	C000	14.9	23.0	19.0 ± 1.11c	1.40	1.00
	M090	16.9	31.4	24.1 ± 1.11b		
	S146	17.4	28.3	22.9 ± 1.11b		
	S281	19.3	32.0	25.7 ± 1.11b		
	S534	21.2	36.9	29.1 ± 1.11a		
	Marginal Mean	17.9 ± 0.80y	30.3 ± 0.80x			
	SED/LSD		0.9/0.6			
P (g kg^{-1})	C000	4.2	3.5	3.8 ± 0.11c	0.15	0.10
	M090	4.1	3.9	4.0 ± 0.11bc		
	S146	4.3	3.7	4.0 ± 0.1bc		
	S281	4.3	4.0	4.1 ± 0.11b		
	S534	4.5	4.7	4.6 ± 0.11a		
	Marginal Mean	4.2 ± 0.07x	3.9 ± 0.07y			
	SED/LSD		0.10/0.06			
K (g kg^{-1})	C000	5.6	4.2	4.9 ± 0.10		
	M090	5.3	4.6	4.9 ± 0.10		
	S146	5.5	4.3	4.9 ± 0.10		
	S281	5.7	4.3	5.0 ± 0.10		
	S534	5.3	4.5	4.9 ± 0.10		
	Marginal Mean	5.4 ± 0.07x	4.3 ± 0.07y			
	SED/LSD		0.08/0.06			
Ca (g kg^{-1})	C000	0.6	0.4	0.5 ± 0.04		

	M090	0.5	0.6	0.5 ± 0.04
	S146	0.5	0.5	0.5 ± 0.04
	S281	0.6	0.6	0.5 ± 0.04
	S534	0.6	0.7	0.6 ± 0.04
	Marginal Mean	0.5 ± 0.03	0.5 ± 0.03	
Mg (g kg^{-1})	C000	1.2	1.2	1.2 ± 0.04
	M090	1.1	1.3	1.2 ± 0.04
	S146	1.2	1.3	1.2 ± 0.04
	S281	1.1	1.3	1.2 ± 0.04
	S534	1.1	1.4	1.2 ± 0.04
	Marginal Mean	1.1 ± 0.02y	1.3 ± 0.03x	
	SED/LSD		0.03/0.02	
Cu (mg kg^{-1})	C000	2.6	3.7	3.3 ± 0.52
	M090	2.5	5.0	3.7 ± 0.47
	S146	2.3	5.3	3.8 ± 0.47
	S281	4.7	5.3	5.0 ± 0.48
	S534	3.8	6.3	5.0 ± 0.52
	Marginal Mean	3.2 ± 0.29y	5.1 ± 0.26x	
	SED/LSD		0.34/0.23	
Mn (mg kg^{-1})	C000	17.9	18.3	18.1 ± 0.62
	M090	18.1	19.7	18.9 ± 0.62
	S146	19.9	19.0	19.4 ± 0.62
	S281	16.8	20.7	18.7 ± 0.62
	S534	18.2	22.0	20.1 ± 0.62
	Marginal Mean	18.2 ± 0.39y	20.0 ± 0.39x	
	SED/LSD		0.55/0.38	

Zn (mg kg^{-1})	C000	25.2bx	23.7cx	24.4 ± 2.11	2.98	2.10
	M090	23.4by	30.0bcx	26.7 ± 2.11		
	S146	29.7ax	29.7bcx	29.8 ± 2.11		
	S281	23.5by	35.0abx	29.2 ± 2.11		
	S534	27.1aby	41.3ax	34.2 ± 2.29		
	Marginal Mean	25.8 ± 1.23	31.9 ± 1.18			
	SED/LSD		1.46/1.02			

[a]SED, standard error of a difference; [b]LSD, least significant difference; all for *P*=0.05; means followed by the different letter are significantly different. Number with letter a, b, c or/and with letters x, y showed significantly differences between treatments or/and time, respectively.

The nutrient concentration contents in barley straw were also significantly influenced by fertilization and the application of pig slurry (Table 6.6). The N concentration increased in 2007 vs. 2004 when N fertilization was applied; maximum increment from 7 g kg^{-1} to 15.2 g kg^{-1} was observed in the S534 treatment. The P concentration in straw for S534 was significantly higher than for the rest of treatments with an increment of 117% for every 100 kg P ha^{-1} applied. Concentrations of Cu and Zn increased by 39% between 2004 and 2007. In contrast, the mean Ca concentration in straw decreased 12% in 2007 compared to 2004 (Table 6.6). Changes in the concentrations of other nutrients were not statistically significant, but there was a tendency for an increment in the concentrations with higher slurry application rates.

Table 6.6. Changes on nutrient concentration contents in barley (*Hordeum vulgare* L.) straw in 2004 and 2007 harvests and according to different annual pig slurry treatments and after four (2004) and seven (2007) cropping seasons.

Nutrient	Treatment	2004	2007	Marginal Mean	SED[a]	LSD[b]
N (g kg^{-1})	C000	4.3bx	4.5cx	4.4 ± 0.60	0.90	0.60
	M090	5.1aby	7.7bcx	6.4 ± 0.60		
	S146	4.7by	6.4bcx	5.5 ± 0.60		
	S281	6.8ay	8.7bx	7.8 ± 0.60		
	S534	7.0ay	15.2ax	11.1 ± 0.60		
	Marginal Mean	5.6 ± 0.40	8.5 ± 0.40			
	SED/LSD		0.5/0.40			
P (g kg^{-1})	C000	1.1	0.5	0.6 ± 0.11c	0.15	0.10
	M090	0.8	0.8	1.0 ± 0.11b		
	S146	0.8	0.6	0.7 ± 0.11bc		
	S281	0.9	0.8	0.9 ± 0.11bc		
	S534	1.2	1.4	1.3 ± 0.11a		
	Marginal Mean	1.1 ± 0.07	0.8 ± 0.07			
K (g kg^{-1})	C000	14.2	13.5	13.8 ± 1.40		
	M090	18.7	17.4	18.1 ± 1.40		
	S146	15.7	14.2	15.0 ± 1.40		
	S281	14.7	17.7	16.2 ± 1.40		
	S534	20.5	20.4	20.4 ± 1.40		
	Marginal Mean	16.7 ± 0.80	16.6 ± 0.80			
Ca (g kg^{-1})	C000	6.7	5.4	6.1 ± 0.3ab	0.4	0.3
	M090	7.3	6.4	6.8 ± 0.30a		

	S146	6.8	5.8	6.4 ± 0.30a
	S281	4.9	5.5	5.2 ± 0.30b
	S534	7.4	6.1	6.7 ± 0.30a
	Marginal Mean	6.6 ± 0.20x	5.8 ± 0.20y	
	SED/LSD		0.2/0.10	
Mg (g kg^{-1})	C000	1.1	0.8	1.0 ± 0.12
	M090	1.2	1.0	1.0 ± 0.13
	S146	1.0	0.7	0.8 ± 0.12
	S281	0.9	1.1	1.0 ± 0.12
	S534	1.0	0.7	0.8 ± 0.12
	Marginal Mean	1.0 ± 0.09	0.8 ± 0.08	
Cu (mg kg^{-1})	C000	3.4	4.7	4.1 ± 0.55
	M090	4.0	5.3	4.7 ± 0.49
	S146	3.9	5.3	4.6 ± 0.55
	S281	3.9	6.7	5.2 ± 0.49
	S534	5.4	6.3	5.8 ± 0.49
	Marginal Mean	4.1 ± 0.34y	5.7 ± 0.31x	
	SED/LSD		0.46/0.31	
Mn (mg kg^{-1})	C000	39.6	32.0	35.8 ± 6.90
	M090	32.6	37.0	34.8 ± 7.55
	S146	42.7	52.0	35.3 ± 6.90
	S281	42.6	51.6	48.3 ± 6.90
	S534	53.7	60.0	39.5 ± 6.90
	Marginal Mean	42.2 ± 4.76	35.2 ± 4.60	
Zn (mg kg^{-1})	C000	5.8	7.5	6.6 ± 0.21
	M090	5.4	8.6	7.0 ± 0.32

S146	8.9	8.7	8.8 ± 0.42
S281	7.0	11.0	9.0 ± 0.55
S534	10.7	17.0	13.9 ± 0.69
Marginal Mean	7.56 ± 0.65y	10.6 ± 0.31x	
SED/LSD		0.36/0.21	

[a]SED, standard error of a difference; [b]LSD, least significant difference; all for *P*=0.05; means followed by the different letter are significantly different. Number with letter a, b, c or/and with letters x, y showed significantly differences between treatments or/and time, respectively.

The fertilization treatments influenced the amounts of Cu, Mn and Zn taken up by the aerial parts (straw or gain) of barley plants (Figure 6.2) as a consequence of differences in element concentration and biomass produced. However, uptake differences between treatments were not always detected in all harvests. In general terms and related to Cu uptake it tends to decrease between 2004 (Figure 6.2a) and 2007 (Figure 6.2d) in the control and mineral treatments whereas those contents remain similar (or may increase in some cases) in the slurry treatments. In the case of Mn, the graphs show a very clear pattern of decrease in all cases (at least for straw and total contents) between 2004 (Figure 6.2b) and 2007 (Figure 6.2e). The opposite seems to happen for Zn, as the contents seem to increase from 2004 (Figure 6.2c) to 2007 (Figure 6.2f) in all the slurry treatments while in the control and mineral treatments the contents seem to remain similar between the two years.

In 2004 harvest, only the S281 treatment had a grain Cu uptake higher than the control (Figure 6.2a). However, all fertilization treatments (whether organic or mineral) showed higher Mn uptake (Figure 6.2b) than the control, while no differences were found on Zn grain uptake (Figure 6.2c). No differences were found in Cu, Mn or Zn straw uptake.

In 2007 harvest, the straw Cu uptake was higher in S534 (31.5 g ha^{-1}) than in S146 (22.3 g ha^{-1}), M090 (14.2 g ha^{-1}) and C00 (9.1 g ha^{-1}) but it was not the case for grain uptake (Figure 6.2d). Straw Mn uptake increased by 80% vs. the control in the S534 treatment, while grain Mn uptake increased by 40% in S146 and S281 vs. the control (Figure 6.2e). Zn uptake was enhanced as fertilization rates increased and it did at a higher rate than in 2004. Zn straw uptake significantly increased from 26.7 g ha^{-1} to 188.5 g ha^{-1}. Similarly, Zn uptake by grains ranged from 72.1 g ha^{-1} to 154.7 g ha^{-1}.

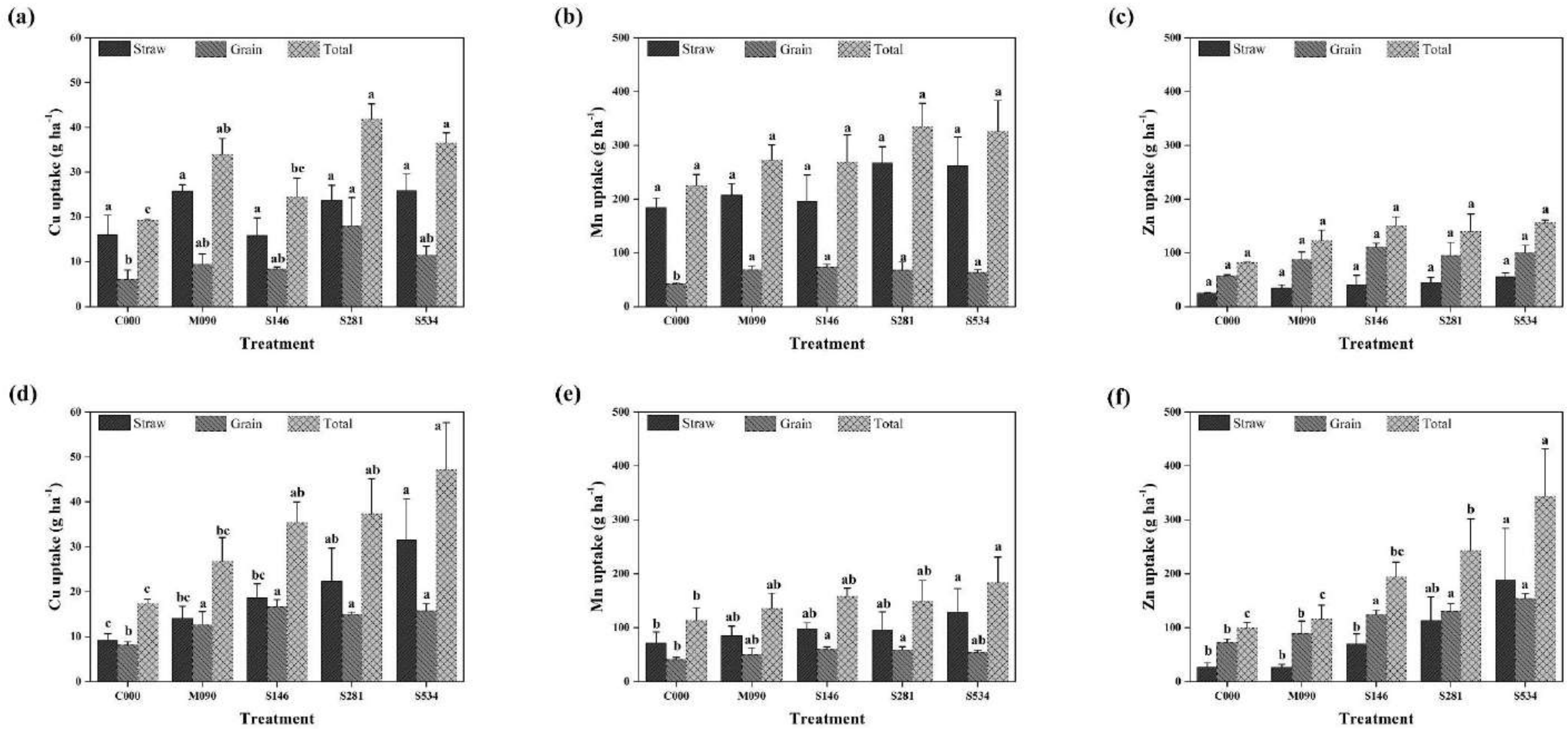

Figure 6.2. Uptake concentrations of Cu, Mn and Cu by straw, grain and total in 2004 (a, b, c) and 2007 (d, e, f) cropping seasons according to different annual pig slurry treatments.

6.4 Discussion

In soil, the results from this study demonstrate that the mid-term application of pig slurry residues significantly increased macronutrients and improved physiochemical properties of the soil (Table 6.3). A significant amount of macronutrients (N, P, and K) reserved in the soil profile after the application of pig slurry, which is gradually released over the time period (Zhang et al. 2016; Provolo et al. 2018). The increment in the concentrations of N, P and K might be due to the higher application rate of pig slurry. These N forms may remain in the soil profile at the end of the cropping season, benefitting subsequent crops, and improving soil quality (Wentzel et al. 2015), which is known as the residual effect (Albuquerque et al. 2017). Mahmood et al. (2017) studied and found that organic manure residues significantly increased total N, P and K contents in soil profile, which was similar to our findings. It has also been reported that pig slurry residues may increase soil productivity, above and over their nutrient contents, when large inputs are applied to soil over several years (Edmeades 2003). Oliveira et al. (2014) also studied and reported that soil physiochemical properties significantly affected by the application of pig slurry. Mainly, application of pig slurry to agricultural soils acts as an organic amendment that contains beneficial nutrients. Over the time period, these beneficial nutrients slowly available to soil and then plant by the help to microbial activities. According to the Teixeira et al. (2012) study, pig slurry residues quickly increased nutrients contents in leaves, whereas soil productivity enhanced a year after the application.

The results of this study show that the concentrations of soil heavy metals influenced by application of pig slurry (Table 6.4, Figure 6.1). Different research studies that have been used pig slurry and/or pig slurry residues showed that concentration of soil heavy metals significantly affected (Kumaragamage et al. 2016; Provolo et al. 2018). Qaswar et al. (2020) studied and found that B and Cr concentrations significantly increased after pig slurry first year. According to this study results, B, Cr and Fe concentrations decreased in the last year because pig slurry that was applied, didn’t have significant amount of B, Cr and Fe contents and this might be the main reason in the reduction

B, Cr and Fe contents in soil. According to our results, no significant differences were observed in Mn, Ni and Pb concentrations (Table 6.4, Figure 6.1). Qaswar et al. (2020) studied and reported that Pb concentration slightly changed after pig slurry application. Organic amendments (manure, or slurry) contains several heavy metals and other elements. Some are micronutrients that are essential to plant growth. The Cu content in soil significantly increased upto 25% with time. The Cu contents were constant in both study years (Table 6.4). Moreover, no difference was observed between the treatments because initial condition was the constant. A significant difference between the treatments as well as with time was observed in Zn content. As compared to control, S534 increased Zn content in soil upto 22% and it is due to the higher application rate of pig slurry. Alternatively, the Zn content in the control increased upto 10% (Table 6.4), which is related to the addition of P, as rock phosphate contains a considerably high quantity of Zn. Compared to other types of slurry, pig slurry has higher levels of Cu and Zn because these nutrients are added to feed (Augenstein et al. 1994; Sommer et al. 2015). Soil levels of Cu and Zn may build up after long term or heavy manure applications. Excessive levels of Cu and Zn can also induce deficiencies of Fe and other nutrients contents in soil profile (Marschner 1995; Larbi et al. 2002).

In plant, in the present study, mid-term application of pig slurry residues significantly increased macronutrients in plant (Table 6.5, 6.6, Figure 6.2). The greater application rate of pig slurry may be responsible for the increase in N, P, and K contents both in grain. According to Greenwood & Draycott (1989), there is a dilution effect between N content and crop yield. In our study, the N contents in grain were more in the 2007 cropping season as compared to 2004 cropping season (Table 6.5). It is only because we had more crop yield in 2004 cropping season than 2007 cropping season. In our study, the concentration of P contents decreased in the last cropping season as compared to 2004 cropping season (Table 6.5). Greenwood et al. (2008) studied and reported the constant relationship between N and P when crop yield increased. However, when crop yield decreases then N contents significantly increases and ultimately decreased the P content and it is happened in our study. K the contents in grain significantly decreased upto 20% and it could be exchangeable K level. Exchangeable K significantly decreased as the time duration increased (Barber 1995) and it might be the reason in the reduction of K content in the last study year. Mg contents in grain increased with time. In control, the Mg contents remained constant, however, there was a tendency in the increment with application rates. In our study, a significant increment was observed in Cu and Mn contents. It might have been due to soil pH, as soil pH greater than 8, it increases the Cu availability (Barber 1995) or might be due to the dilution effect as N, however, whole mechanism is still unclear. The Zn contents in grain significantly increased with treatment. The maximum Zn contents in 2004 and 2007 cropping seasons were 29.7 mg ka^{-1} (S146) and 41.3 mg ka^{-1} (S534) and both treatments had significant amount of Zn content. Banik and Nandi (2004) studied and found that the manures contain are rich amount of in mineral nutrient contents like N, P, K, Ca, and Mn. It is reported that residual slurry manures are more effective in plant growth, which could be due to the presence of higher nutrients content in pig slurry.

Pig slurry residues significantly increased the N and P content of straw. There was a significant difference observed in treatments both for N and P. As the application of pig slurry increased, it significantly increased N and P consents in straw (Table 6.6). N content with S534 treatment increased upto 60% as compared to control. Similarly, P content with S534 treatment enhanced upto 110% as compared to control. According to our study results, pig slurry residues significantly increased Ca contents in straw. There was significant different was observed between the study years and treatments. The concentration of the Ca contents in straw was more in 2004 cropping season than 2007 cropping season and it is might be due to low biomass yield in 2007 when compared with 2004 cropping season. On the other hand, the Ca concentration increased in S534 treatment and it is might be due to higher application rate of this nutrients. Alternatively, Mg and Ca belong to elements whose deficiency is a factor limiting both the quantity and quality of plants (Brodowska et al. 2017). The role of Mg in plant organisms arises from its ability to interact with nucleophilic ligands (Shaul 2002). Mg also acts the central atom of a chlorophyll molecule and forms bridge bonds in the aggregation of ribosome subunits necessary for protein synthesis. This element is also essential for the functioning of many enzymes which include ATPases, RNA polymerases, phosphatases, protein kinases, carboxylases, and glutathione cytases (Williams et al. 2000; Brodowska et al. 2017) that significantly increase the nutritional value in fodder. In turn, the role of Ca in plant fertilization most frequently consists of improving soil physicochemical properties, whereas its contribution to yield formation is ignored in most cases. Nevertheless, Ca performs a number of important functions in the metabolism of plants, which affect their growth and development (Gilliham et al. 2011). Ca also contributes to prolonged photosynthetic activity and extends the time of production of assimilates, owing to which the plant produces a higher yield and growth (Brodowska et al. 2017), which significantly rise the nutritional value in fodder for animal. There was also a significant difference observed between the study years in the concentration of Cu in straw. In straw, the Cu concentration was higher in the 2007 cropping season than in 2004 (Table 6.6). The increase in Cu in straw might be attributable to laboratory process and analytical precision. Moreover, there was no significant difference between the treatments. However, a clear tendency in the increment was observed and it was due to the higher application rate of pig slurries. In straw, the concentration of Zn also increased in 2007 than 2004 cropping season because 2007 cropping season had higher Zn availability (Figure 6.2 (c, f)). Although, there was no significant difference between the treatment, however, clear tendency in the increment was seen due to higher pig slurry rates. On the other hand, in control, the Zn concentration increased upto 29% (Table 6.6) and it is due to the application of P because rock phosphate contained a significant amount of Zn (De López Camelo et al. 1997) and almost 20 kg P ha^{-1} contained approximately 31 mg Zn kg^{-1}.

Many research studies have been suggested that application of organic amendments, such as animal manure and/or slurries, significantly enhances nutrients contents in soil (Park et al. 2011; Wang et al. 2018) and this might be the main reason for the greater uptake of heavy metals when pig slurry residues are applied. According to our study results, maximum uptake of heavy metals by plant happened with pig slurry residue treatments as compared to control or chemical fertilizer and this is in accordance with findings by Provolo et al. (2018). According to Provolo et al. (2018) study, the soils with a long history of pig slurry application were associated with higher contents of Zn Cu and Mn in plant shoots. On the other hand, pig slurry has large amount of Zn and Cu contents than other slurries (cattle and poultry) and that could also be the main reason for more Zn and Cu uptake by plant.

Mid-term application of pig manure and slurry enhances the soil OM content, which directly supports the better plant growth and increase the crop yield, due to the presence of high nutrient contents in slurry such as N, P, and carbon (C) (Pan et al. 2009; Cai et al. 2019; Qaswar et al. 2020). We also reported similar results in this study; nutrient contents and soil organic C (SOC) were highest under pig slurry residual treatments as compared to control (Figure 6.2, Table 6.3). Cai et al. (2019) also found high nutrient contents in soil under the application of slurry, compared to the chemical fertilization, which resulted in high crop yield.

6.5 Conclusions

In a seven-year period of pig slurry application at different rates, soil pH and CEC was not modified although the average OC soil content significantly increased. The measured soil OC increases (0.3 m) were equivalent to c. 13.5 to 24.7 kg ha^{-1} for every 1 ton of the slurry OC applied, where maximum increase value was obtained when 4 t OC $ha^{–1}$ were applied (over a 7-year period). The current study demonstrated that the long-term residual effects of pig slurry significantly improved the physio-chemical properties of soil, increased crop yield, enhanced total and available nutrients contents. In addition, pig slurry residues significantly affected concentration of heavy metals contents in soil as well as in plant. The long-term effects of pig slurry residues significantly increased the concentrations of B, Cu, Zn, and Mn contents in soil profile. Moreover, availability of macronutrients such as N, P, and K by plants were increased by increasing the pig slurry rate. The Ca and Mg contents in straw significantly increased after pig slurry residues and ranged from 17.9 kg ha-1 to 29.5 kg ha-1 and 6.4 kg ha-1 to 10.9 kg ha-1, respectively, which may increase the nutritional level in the animal feed. Furthermore, long-term effects of pig slurry residues significantly influenced and affected the uptake concentration of soil heavy metal by plant. In the case of straw, pig slurry residues significantly enhanced the uptake of B, Cu, Fe, and Zn concentrations, whereas Fe uptake decreased as pig slurry rate increased. The uptake concentrations of Cu and Zn under pig slurry residues treatments were surpassed the maximum permissible limit in the grain, which may cause serious threat to the environment and food safety. The long-term effects of pig slurry residues significantly increased grain yield biomass, straw biomass and total biomass. Our findings propose that long-term residual effects of pig slurry significantly affect the soil heavy metal contents and crop yield.

Acknowledgements

This work was supported by the Spanish Ministry of Economy and Competitiveness and the Spanish National Institute for Agricultural Research and Experimentation (MINECO-INIA) through the project RTA2017-88-C3-3. A special thanks to Montse Antunez for her kind help in the laboratory work. We would also like to extend our sincere thanks to the Ministry of Climate Action, Food and Rural Agenda, Catalan Government, for the field maintenance.

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Chapter 7

General discussion

General discussion

Although it is frequently stated that implementation of agricultural management practices (i.e. application of animal manure and no-tillage practice) on cropland can provide short and long-term reductions in GHGs emissions and resilient cropping systems (Duan et al., 2020; Maucieri et al., 2021; Nyagumbo et al., 2020), definitive conclusions have not been reached due to the lack of comprehensive data synthesis. The results of Chapter 3 indicate that poultry manure application produce the largest GHG emissions from agricultural soil (Chapter 3, Fig. 3.1). As highlighted in this data synthesis, CH_4 and N_2O were the most prevalent GHGs emissions, when soil was amended with either poultry or pig manure. Typically, labile C and N constituents in livestock manures are the significant sources of CH_4 and N_2O emissions (Petersen, 2018).

Nevertheless, as manures with a high content of decomposable C are added into the soil, they provide food substrate for heterotrophic microbial activity, including methanogens, and thus enhance CH_4 emissions. Furthermore, the use of liquid manures, such as pig slurry, can create anaerobic conditions due to the higher water content, and the presence of C substrates promotes methanogenic activities (Wang et al., 2020). Such feedback response of methanogens to C-substrate after manure amendment is in line with previous studies (Nguyen et al., 2020; Zhang et al., 2018a; Zhang et al., 2020). Potentially, increases in net N mineralization and subsequent nitrification promote N_2O release from the soil; however, substrate-driven heterotrophic microbial activity tends to consume abundant O_2, resulting in anaerobic conditions favorable to high N_2O emissions through the denitrification pathway (Aita et al., 2015; de León et al., 2021). Importantly, literature on the effects of repeated manure application demonstrated significant soil organic carbon buildup, which promotes soil denitrifiers and, as a result, increases N_2O emissions (Guenet et al., 2020; Zhang et al., 2018b; Lazcano et al., 2021). In a recent study, the presence of antibiotics from poultry litter altered the soil microbiome assembly (e.g., bacterial diversity), and the associated metabolic functions were suggested as sources of N_2O and other GHGs emissions from the soil (Parente et al., 2021).

No-tillage agriculture has been promoted as an important soil conservation measure against climate change because of its ability to bolster soil health, reduce soil erosion, and increase C-sequestration potential (Hao et al., 2020; Huang et al., 2020; Nunes et al., 2020). No-tillage practices, according to our meta-analysis, caused a significant increase in GHG emissions, particularly CH_4 and N_2O (Chapter 4, Fig. 4.1). This is significant when considering agricultural emissions reduction targets, because N_2O and CH_4 are 296 and 34 times more potent global warmers than CO_2 (Myhre et al., 2013). In no-tillage agroecosystems, decreased soil disturbance coupled with crop residue retention is strongly linked to heterotrophic microbial activity, where CH_4-oxidizing bacteria could be driving towards increased CH_4 emissions (Smith et al., 2001), while greater residue-derived microbial biomass and SOC buildup could entice soil nitrifying-denitrifying bacteria, triggering greater N_2O emissions (Mangalassery et al., 2014). A possible explanation for increased GHGs emissions from no-tillage soil is that less soil contact with surface clay reduces nutrient adsorption compared to conventional tillage, resulting in higher availability of labile C and N constituents, which contributes to higher GHG emissions (Ma et al., 2021). Furthermore, higher emissions from no-tillage soil may result from changes in soil properties (e.g., pH, temperature, bulk density), which are quite often fostered by increased residue decomposition in the surface soil (Vanzolini et al., 2017). In a recent meta-analysis on CH_4 emissions, Maucieri et al., (2021) found a weak mitigating response against emissions in no-tilled crops of the dryland region, whereas significant reductions in the emissions were possible in flooded soils. Other studies focusing on no-tillage have documented the uncertainties of the results, which are specifically dependent on soil, climate conditions, and crop types, and suggested that no-tillage management may be viewed as a countermeasure against soil erosion and land degradation, while the associated SOC accrual could be considered as an additional benefit to mitigate GHGs emissions (Gong et al., 2021; Ogle et al., 2019).

The world's population is growing very fast and expected to reach up to 9 to 10 billion by 2050, and almost 35% already use N fertilization to increase crop yield and total biomass productivity (Yang et al., 2006). However, a significant amount of N is lost through gases (N_2O & NH_3) (Bosch-Serra et al., 2014; Pan et al., 2016) or leached into groundwater (Li et al., 2015). According to Directive 91/676/EEC, the European Union has established NO_3^- vulnerable zones to protect the groundwater, and the threshold value for N in form of NO_3^- in groundwater should not exceed to 11.3 mg N-NO_3 l^{-1} (EEC, 1991). Therefore, to protect the atmospheric environment and groundwater quality, proper agricultural management practices (N fertilizer rate, timing, crop type and crop rotation cycle) should be adopted.

In semiarid rainfed agricultural systems, fallow can be included as an agronomic practice, supported in EU countries by the Common Agricultural Policy. During this period, soil N dynamics is linked to soil water content and its fluctuations. The results of Chapter 5 show a good agreement between measured and simulated soil water content (SWC) (LEACHM model) and with the results found by other authors (Akinremi et al., 2011; Lidón et al., 2019, Asada et al., 2013; Jiménez-de-Santiago et al., 2019). Moreover, the values obtained for soil mineral N content ($N_{m)}$ are in the interval of those reported by other authors using LEACHM model (Asada et al., 2018; Jung et al., 2010; Li et al., 2015a; Lidón et al., 2013; Lidón et al., 2019; Plaza-Bonilla et al., 2015; Sogbedji et al., 2006; Vazquez-Cruz et al., 2014; Zhang et al., 2019) for both calibration as well as validation periods. The distortion related to the 2017 snow event was not evident in the SWC as it was followed by a rainy period (Chapter 5, Fig. 5.1 c, Fig. 5.9), when the soil became saturated. However, a difference of 48 mm between simulated and measured SWC was recorded in the soil profile at the end of the 2008 simulation period, minimizing the real leaching. Estimation of drainage with LEACHM model (with the previous exception) is satisfactory because the model predicted the SWC within acceptable ranges. Precipitation less than 20 mm could not be affect the drainage because mostly drainage occurred above this rainfall range. Generally, the loss of water during the fallow periods is higher than in cropping seasons (Jiménez-de-Santiago et al., 2019), which significantly increased leaching.

Mineral nitrogen (N_m) in the soil profile increased after the fallow period in all cases considered, except in the N0 treatment during the period 2016-17, when there was a small decrease (Chapter 5, Fig. 5.3). This increase indicates that processes involving an input of N_m to the soil predominate over processes that result in an output of N_m from the soil profile during fallow. In non-crop periods, this result shows that atmospheric deposition, net mineralization of soil organic matter and of harvest residues and roots from the previous crop is higher than the gaseous and leaching losses produced during fallow in rainfed semiarid Mediterranean system.

In general, thus, the LEACHM model has been shown to be a useful tool for evaluating different processes related to soil water content and the N cycle.

Heavy metal pollution of agricultural land is a major environmental issue all over the world (Xu et al., 2019). Many anthropogenic wastes, such as mining wastes, agricultural wastes, fertilizers, pesticides, manure, toxic chemicals, and wastewaters end up in the soil environment, making it a more vulnerable environment in terms of elemental contamination (Bolan et al., 2004; Mench et al., 2010). Heavy metal pollution in soils might pose a serious danger to ecosystems, agricultural output, food safety, and, ultimately, human health. Pig slurry is used as an organic fertilizer because it contains a high concentration of macro-micronutrients such as N, P, K, Zn, Cu, Fe, and Mn, as well as heavy metals such as Ni and Pb (Pegoraro et al., 2020; Terrero et al., 2020). However, the intensification of the use of pig slurry acts as a risky agricultural management practice for the croplands when it is not adequately treated (Daudén and Quílez, 2004; Terrero et al., 2020). Results of Chapter 6 showed that the long-term residual effect of pig slurry considerably increased macronutrients in soil and plant, improved soil physiochemical properties, and increased soil heavy metal concentrations. Provolo et al., (2018) and Mahmood et al., (2017) reported that pig slurry residues substantially enhanced total N, P, and K contents in the soil profile. According to Qaswar et al., (2020), B and Cr contents increased considerably following pig slurry in the first year. Moreover, Pb concentration also slightly increased after the application of pig slurry, which was similar to our findings. According to Provolo et al. (2018), the soils with a long history of pig slurry application were associated with higher contents of Zn, Cu and Mn in plant shoots. Pig slurry has higher concentrations of Zn and Cu than other slurries (cattle and poultry) because these nutrients are added to feed (Augenstein et al., 1994; Sommer et al., 2015), and that could be the main reason for the increased Zn and Cu contents in soil and plant recorded in our experiment.

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Chapter 8

General conclusions

General conclusions

Different agricultural practices, for example, the application of different organic and inorganic fertilizers, tillage operations, and crop rotations, may have significantly different effects on crop productivity but also significantly different environmental consequences. According to our objectives, the main conclusions of this thesis are as follows:

- ❖ Evidence presented in Chapter 3 shows that the application of animal manure (as a N source) significantly increased CO_2, CH_4, and N_2O emission as compared to control treatment from croplands. Soil pH, soil textural classes, crop types, and climate zones are very important factors for predicting GHGs emissions. Selecting the manure type and proper N application rate are required to mitigate the GHGs emissions.
- ❖ No tillage (NT) practice, as compared to conventional tillage (CT), significantly increased CO_2, N_2O, and CH_4 emissions by 7.1%, 11.9%, and 20.8%, respectively. On the other hand, NT decreased the overall GWP of GHGs emissions by 7.5% (Chapter 4). Agricultural management practices such as tillage type, N application rate, crop type, and water management should be planned properly to mitigate GHGs emissions without reducing the crop yield in NT management practice.
- ❖ The LEACHM model applied in a rainfed Mediterranean region to a winter-cereal rotation, showed that the mineral N content of soil (N_{min}) during the fallow period (??)increased mostly when temperatures were more favorable for the mineralization process. But the calibrated LEACHM model underestimated soil N_{min} probably due to the "Birch effect". The simulated results with LEACHM show that the amount of mineral N leached below 0.9 m depth, during fallow in previously mineral fertilized plots, ranged from 11 kg N ha^{-1} to 38 kg N ha^{-1} (Chapter 5).
- ❖ The Mid-term residual effects of pig slurry on this agroecosystem significantly improved the physio-chemical properties of soil, increased crop yield, and enhanced total and available nutrients contents. Mid-term effects increased grain yield biomass, straw biomass, and total

biomass. Moreover, concentration of B, Cu, and Zn have been enhanced in the soil profile over time. Pig slurry residues also increased significantly increased the bioavailability of Cu and Zn, but not at a toxic level (Chapter 6).