Universitat de Lleida

Pig slurry fertilisation in dryland agriculture. Impacts in the air-soil-water system

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http://hdl.handle.net/10803/667350

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TESI DOCTORAL

Pig slurry fertilisation in dryland agriculture. Impacts in the air-soil-water system

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Memòria presentada per optar al grau de Doctor per la Universitat de Lleida
Programa de Doctorat en Ciència i Tecnologia Agrària i Alimentària

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2019

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SUMMARY

The use of pig slurry as fertilizer is a viable alternative in agricultural systems with considerable livestock activity. However, negative impacts of its use on the air, soil and groundwater need to be further evaluated. The objective of this thesis was to evaluate the effects of different slurry fertilization strategies on the soil organic matter (as a quality criterion) and the nitrogen (N) losses applied outside the agricultural system. Work was performed in an experimental site established in 2002 (NE Spain), under rainfed conditions. Factors such as the slurry origin (reproductive mothers or fattening pigs), the dose (from 00 to 120 m^3 ha^{-1}) and the application time (sowing or tillering in winter cereal), were considered. The temporal scale of the observations varied from a specific moment, to weeks and years. The data was obtained through field experiments, laboratory analysis and the use of the LEACHM model. The content and fractions of soil organic matter (SOM) together with ammonia (NH_3) volatilised, were quantified. The humic substances of the soil were characterized spectroscopically. Superficial soil water repellency (SWR) was evaluated using the two most common techniques (with drop of water and ethanol solution). Through a field parallel follow-up, the evolution of the SWR and the volatilization of NH_3 were evaluated. The water dynamics in the soil was assessed with the LEACHM. The results indicate that the continued application of slurry increases the SOM content. The aromatic character of the humic substances of the soil decreased due to the augments of carbon (C) structures related to aliphatic groups. High slurry rates increase the easily available C reservoir, enhancing the risk of being a source of C emissions to the atmosphere. The organic matter applied with the slurry develops a transient SWR. The higher SWR was related to higher contents of dry matter and hydrophobic compounds; although its evaluation (intensity and persistence) requires an adaptation of the classical quantification methods. In the field, the SWR was strongly influenced by the wetting - drying periods of the soil. However, SWR could not be related to the NH_3 emissions that varied between 11% and 18% of the ammonium N (NH_4^+-N) applied, in the slurry. The LEACHM model allowed the evaluation of the soil water dynamics. The fallow periods recharged the soil water content, while the barley crop produced a water reduction in the soil profile below the permanent wilting point. The maximum volume of drained water was 14.3 mm yr^{-1} due to the dryland Mediterranean conditions. Respecting the maximum agronomic doses applicable in areas vulnerable to contamination by nitrates (170 kg N ha^{-1}) are also considered acceptable to reduce negative impacts on air and water and maintain the SOM content in the soil.

Keywords: ammonia emissions, LEACHN model, slurry fertilization, soil hydrophobicity, soil moisture, soil organic matter, water drainage.

RESUM

L'ús de purins de porc com a fertilitzants és una alternativa assequible en sistemes agraris amb important activitat ramadera. No obstant això, el seu ús pot derivar en perjudicis sobre l'aire, el sòl i les aigües subterrànies que necessiten ser avaluats. L'objectiu d'aquesta tesi va ser avaluar els efectes de diferents estratègies de fertilització de purins sobre la matèria orgànica del sòl (com a criteri de qualitat) i les pèrdues del nitrogen (N) aplicat fora del sistema agrícola. Es va treballar en parcel·les experimentals establertes l'any 2002 en un sistema agrari de secà (NE Espanya). Es van considerar factors com l'origen del purí (mares reproductores o porcs d'engreix), la dosi (00-120 m^3 ha^{-1}) i el moment d'aplicació (sembra o cobertora en cereal d'hivern). L'escala temporal de les observacions va variar des d'un moment puntual, a setmanes i anys. Les dades es van obtenir mitjançant experiments en camp, anàlisis de laboratori i també amb l'ús del model LEACHM. Es va quantificar el contingut i les fraccions de matèria orgànica del sòl (SOM) i d'amoníac (NH_3) volatilitzat. Es van caracteritzar espectroscòpicament les substàncies húmiques del sòl. Es va avaluar la repel·lència superficial del sòl (SWR) utilitzant les dues tècniques més comuns (amb gota d'aigua i solució d'etanol). Mitjançant un seguiment de camp en paral·lel, es va avaluar l'evolució de la SWR i la volatilització de NH_3. Es va avaluar la dinàmica de l'aigua al sòl amb el model LEACHM. Els resultats indiquen que l'aplicació continuada de purins augmenta el contingut de SOM. El caràcter aromàtic de les substàncies húmiques del sòl disminueix a causa d'una major presència d'estructures de carboni (C) relacionades amb grups alifàtics. Altes dosis de purins augmenten el reservori de C fàcilment assimilable, incrementant el risc de ser una font d'emissió de C a l'atmosfera. La matèria orgànica aplicada amb els purins desenvolupa una SWR transitòria. La SWR és més evident com més gran és el seu contingut en matèria seca i en compostos hidròfobs, encara que la seva avaluació (intensitat i persistència) requereix l'adaptació del mètodes clàssics de quantificació. En camp, la SWR va ser fortament influenciada pels períodes de humitejat - assecat del sòl. No obstant això, no es va poder relacionar amb les emissions de NH_3 que van variar entre 11% i 18% del N amoniacal (NH_4^+-N) contingut en els purins. El model LEACHM va permetre l'avaluació de la dinàmica de l'aigua en el sòl. Els períodes de guaret permeten una recàrrega de l'aigua del sòl, mentre que el cultiu d'ordi produeix una reducció d'aigua en el perfil per sota del punt de marciment permanent. A causa de les condicions del secà Mediterrani, el màxim volum d'aigua drenada va ser 14.3 mm any^{-1}. El respecte a les dosis agronòmiques màximes aplicables en zones vulnerables a la contaminació per nitrats (170 kg N ha^{-1}) es consideren també acceptables per reduir impactes negatius sobre l'aire i l'aigua i mantenir el contingut de SOM al sòl.

Paraules clau: drenatge d'aigua, emissions d'amoníac, fertilització amb purins, hidrofobicitat del sòl, humitat del sòl, matèria orgànica del sòl, model LEACHM.

RESUMEN

El uso de purines de cerdo como fertilizante es una alternativa asequible en sistemas agrarios con importante actividad ganadera. Sin embargo, su uso puede derivar en impactos negativos sobre el aire, el suelo y las aguas subterráneas que necesitan ser evaluados. El objetivo de esta tesis fue evaluar los efectos de diferentes estrategias de fertilización de purines sobre la materia orgánica del suelo (como criterio de calidad) y las pérdidas del nitrógeno (N) aplicado fuera del sistema agrícola. Se trabajó en parcelas experimentales establecidas en el 2002 en un sistema agrario de secano (NE España). Se consideraron factores como el origen del purín (madres reproductoras o cerdos de engorde), la dosis (00 - 120 m^3 ha^{-1}) y el momento de aplicación (siembra o cobertera en cereal de invierno). La escala temporal de las observaciones varió desde un momento puntual, a semanas y años. Los datos se obtuvieron mediante experimentos en campo, análisis de laboratorio y también con el uso del modelo LEACHM. Se cuantificó el contenido y las fracciones de materia orgánica del suelo (SOM) y de amoniaco (NH_3) volatilizado. Se caracterizaron espectroscópicamente las sustancias húmicas del suelo. Se evaluó la repelencia superficial del suelo (SWR). Mediante un seguimiento paralelo en campo, se evaluó la evolución de la SWR y la volatilización de NH_3. Se evaluó la dinámica del agua en el suelo con el modelo LEACHM. Los resultados indican que la aplicación continuada de purines aumenta el contenido de SOM. El carácter aromático de las sustancias húmicas del suelo disminuye debido a una mayor presencia de estructuras de carbono (C) relacionadas con los grupos alifáticos. Altas dosis de purines aumentan el reservorio de C fácilmente asimilable, incrementando el riesgo de ser una fuente de emisión de C a la atmósfera. La materia orgánica aplicada con el purín desarrolla una SWR transitoria. La SWR es más evidente cuanto mayor es su contenido en materia seca y en compuestos hidrófobos, aunque su evaluación (intensidad y persistencia) requiere la adaptación de dos métodos clásicos de cuantificación (con gota de agua y solución de etanol). En campo, la SWR estuvo influenciada por los periodos de humedecimiento - secado del suelo. Sin embargo, no se pudo relacionar con las emisiones de NH_3 que variaron entre 11% y 18% del N amoniacal (NH_4^+-N) contenido en el purín. El modelo LEACHM permitió la evaluación de la dinámica del agua en el suelo. Los periodos de barbecho permiten una recarga del agua del suelo, mientras que el cultivo de cebada produce una reducción de agua en el perfil por debajo del punto de marchitez permanente. Debido a las condiciones del secano Mediterráneo, el máximo volumen de agua drenada fue 14.3 mm $año^{-1}$. El respeto a las dosis agronómicas máximas aplicables en zonas vulnerables a la contaminación por nitratos (170 kg N ha^{-1}) se consideran también aceptables para reducir impactos negativos sobre el aire y el agua y mantener el contenido de SOM en el suelo.

Palabras clave: drenaje de agua, emisiones de amoniaco, fertilización con purines, hidrofobicidad del suelo, humedad del suelo, materia orgánica del suelo, modelo LEACHM.

CHAPTER 1

General introduction

1. INTRODUCTION

Spain is the biggest intensive livestock pig producer in Europe with almost 30 million heads (Eurostat 2017), whereas the Catalonia region holds a third of the total Spanish pig population (MAPAMA, 2017).

The main by-product of intensive pig farming is pig slurry, which is widely used as a fertiliser because it provides water and plant nutrients (e.g. nitrogen, N). Indeed, the effectiveness of pig slurry fertilisation on crop yields has been reported as a viable agronomic alternative in a number of studies, some of them in cereal in Mediterranean conditions (Guillaumes et al., 2006; Berenguer et al., 2008; Hernández et al., 2013; Bosch-Serra et al., 2015; Domingo-Olivé et al., 2016; Plaza-Bonilla et al., 2017).

Nevertheless, slurry fertilisation without an appropriate management can pollute air, soil and groundwater (Guillaumes et al., 2006). In Catalonia, slurry application is regulated by DECRET 136/2009 (Generalitat de Catalunya, 2009), which includes a list of procedures to assure the correct livestock manure and N-fertilisation management in nitrate vulnerable areas.

The main potential impacts of the use of pig slurry as a fertiliser in agricultural systems are derived from its composition. Ammonium-N (NH_4^+-N) constitutes ~75% of its N content (Yagüe et al., 2012) and can be easily lost to the air by ammonia (NH_3) emissions or to groundwater as nitrate (NO_3^-). Also, the organic matter added can modify the ratio of different soil organic matter (SOM) components or to cause hydrophobicity.

This thesis studied these effects on Mediterranean rainfed crops, which, in spite of being extremely sensitive to climate (Austin et al., 1998; Beguería et al., 2011; Morell et al., 2011), represent 80% of the total Spanish cultivated area (MARM, 2017).

Slurries and the soil organic matter (Objective 1, hypothesis 1)

To maintain the equilibrium in agricultural systems SOM is imperative. The addition of SOM have positive effects on plant and soil as it stabilizes soil surface aggregates, and increases soil quality, water holding capacity and plant available water (Tisdall and Oades, 1982; Chandrasekhar et al., 2018).

Reciprocally, soil characteristics play an important role in the transformation of SOM into humic-like substances (HLS; Ndayegamiye and Côté, 1989; Fernández Ugalde et al., 2011) as well as in their main components.

Semiarid soils, as most in the Mediterranean basin, are low in organic matter, nutrients and water content (Lal, 2004). Soils fertilised with slurries show a small or in some cases not significant increase in SOM (Rochette et al., 2000; Plaza et al., 2002; Domingo-Olivé et al., 2016). However, it has been suggested that the slurry composition (low C:N ratio) enhances its fast transformation in the soil, producing a temporary effect (Ndayegamiye and Côté, 1989; Rochette et al., 2000; Yagüe et al. 2012b).

In addition to its benefits on plant growth, slurry transformation in soil (affected by slurry composition) can increase organic carbon (C) mineralisation, as reported in a four-year study (Plaza et al., 2004). Thus, not only the quantity, but also slurry quality is needed to enhance the positive effects on plant and soils. In this frame, several studies that characterise the main structural groups present in the HLS with spectroscopic techniques have been conducted in Mediterranean areas, comparing different land uses, including cereal crops (Tinoco, 2000; Plaza et al., 2002). Nevertheless, little attention has been devoted so far to changes in SOM quality in long-term slurry fertilised soils.

Soil water repellency due to slurry application (Objective 2, hypothesis 2)

Despite the above-mentioned minor increase of SOM due to slurry fertilisation, a positive and significant effect on the aggregate stability has been observed (Yagüe et al., 2012; Bosch-Serra et al., 2017). It has been proposed that part of this stability would be due to the hydrophobic characteristics of SOM.

Soil hydrophobicity or water repellency (SWR) reduces water infiltration in soils for periods ranging from a few seconds to hours, days or weeks (Doerr et al., 2000; Doerr and Thomas, 2000). It is a transient and dynamic soil property produced by the presence of hydrophobic compounds in the soil (Doerr and Thomas, 2000). Most of the work on SWR has been focused on natural repellency (Doer and Tomas, 2000; Jiménez-Morillo et al., 2016) or fire affected soils (Doerr et al., 2000; Jordán et al., 2014).

However, in natural wettable soils, SWR can be induced by an external addition of products containing hydrophobic compounds, as slurries (Gigliotti et al., 2002; Provenzano et al., 2014). Therefore, the increase of waste water and slurries as organic fertilisers has recently promoted the interest in SWR in agricultural systems (Wallach et al., 2005; González-Peñaloza et al., 2012).

Some studies indicate that slurry transformation through composting results in an increase of the hydrophobic fraction due to the decrease of the labile C compounds (Said-Pullicino et al., 2007; Provenzano et al., 2014). Nevertheless, the focus is still in the SOM amount (González-Peñaloza et al., 2012; Gao et al., 2018) and soil moisture content (Doerr and Thomas, 2000). Quantification of hydrophobic compounds has received little attention so far, probably because soil tillage is a known strategy to remediate SWR (Müller et al., 2011). Moreover, the calcareous nature of many Mediterranean areas limits the SWR development (Cerda and Doerr, 2007; Burget et al., 2016).

Considering the continuous slurry application in some areas and its fast transformation in the soil, there is a high risk of increase in the hydrophobic compounds concentration, promoting the development of SWR in both, short and long-term applications. In rainfed agricultural systems, the presence and persistence of SWR can be a serious problem as crops depend entirely on rainfall. In consequence, a method to quantify and assess SWR in slurry-fertilised soils is very much needed.

Ammonia emissions (Objective 3, hypothesis 3)

Agriculture production is the main NH_3 source at the European level (Sommer and Hutchings, 2001; EUROSTAT, 2017) and slurries are a main contributor to this pollution since around 70% of the total N is in the form of NH_4^+-N (Yagüe et al., 2012; Antezana et al., 2016).

Ammonia is a secondary precursor of the particulate aerosols formation, which has adverse impacts on human health (EUROSTAT, 2017); besides, ammonia losses reduce the slurry fertilisation value (Sommer and Hutchings, 2001).

Differences in NH_3 emissions are due to soil and slurry properties, weather conditions and management (Sommer and Hutchings, 2001; Thompson and Meisinger, 2002; Zavala et al., 2009). Thus, calcareous nature favours NH_3 volatilisation (Kissel and Cabrera, 2005). Traditional wide-spread slurry fertilisation also enhance NH_3 emissions compared to slurry application by injection, trail hoses or its incorporation to soil by tillage (Thompson and Meisinger, 2002; Yagüe et al., 2019). High slurry rates display large amounts of NH_3 emitted (Hernández et al., 2013; Bosch-Serra et al., 2014). On the contrary, low air temperatures, acid pH and rainfalls limit the NH_3 emissions (Sommer et al., 2003; Kissel and Cabrera, 2005). Slurry dry matter is related to crust formation (Sommer and Hutchings, 2001; Sommer et al., 2013). It acts as a diffusion and capillary barrier between the soil and the atmosphere, reducing NH_3 transport (Thompson and Meisinger, 2002; Misselbrook et al., 2005). Nevertheless, low dry matter also reduces NH_3 emission because it enhances infiltration (Bosch-Serra et al., 2014).

Moreover, crust formation would be related to the development of hydrophobic soil properties, linked to the composition of the slurry applied and influence NH_3 emissions (Bosch-Serra et al., 2014; 2015). The reduction of water infiltration capacity because of the hydrophobicity would reduce soil moisture and promote surface erosion.

In consequence, to study the relationship between NH_3 emission and SWR in rainfed Mediterranean systems will improve our understanding about soil water and N dynamics which will translate into better soil and slurry management practices. In spite of this importance, there are still few data regarding NH_3 emissions in rainfed Mediterranean winter cereal systems (Sanz et al., 2010; Bosch-Serra et al., 2014; Yagüe et al., 2019) and the interaction with SWR is unkown.

Soil water movement to estimate nitrate leaching (Objective 4, hypothesis 4)

Nitrate leaching from agricultural activities (N-fertilisation) is a remarkable environmental and human health issue that worries governments and international institutions (European Union, 1991; Generalitat de Catalunya, 2009). Thus, the NO_3^- concentration in water is considered a water quality parameter (UNE, 2018). A water body is contaminated when it overpasses 50 mg L^{-1} of NO_3^- (European Union, 1991). In Spain, this figure has been reached in 21.55% of the waterbodies (European Union, 2018). In Catalonia (Spain), 8.5% stations in non-vulnerable zones overpass the above mentioned threshold (ACA, 2017).

Water transports NO_3^- through soil. Models have to be used in order to study water movement (and, therefore, dissolved chemicals transport) in soil and groundwater (Akinremi and McGinn, 1996; Lidón et al., 2013). Leaching Estimation and Chemistry Model (LEACHM) is a one-dimensional deterministic mechanistic model describing the storage, transport, and distribution of water and solute in an unsaturated soil (Hutson and Wagenet, 1991; Hutson, 2003). It needs to be fed with accurate data to predict water dynamics and, subsequently, the potential nitrate leaching (Czarnomski, 2005). Thus, soil physical properties and rainfall characterisation are essential to evaluate soil water dynamics and the effectiveness of fallow in dryland environments.

In rainfed Mediterranean agricultural systems, precipitation is the main water source entering into the system (Morell et al., 2011). Annual precipitation is low compared to other climates but the extreme variability of rainfall, with high rainfall intensities, few rain events and uneven spatial and temporal distribution are the major limiting factors of crop yields (Rockström et al., 2010) and water drainage during most part of the year.

Traditionally, fallow is a practice in rainfed agricultural systems to store water from rainfall to grow a single crop (Lampurlanés et al., 2002; Moret et al., 2007). Fallow years permit to study the residual effect of N-fertilisation in the soil, as slurries, (Berenguer et al., 2008). During fallow, the risk of N losses by leaching or deposition in deeper layers where the roots do not reach is enhanced. Drainage evaluation on irrigated systems has been widely studied (Lidón et al., 1999; 2013; Quemada et al., 2013). On the contrary, little attention has been devoted to Mediterranean dryland agricultural systems (Akinremi et al., 2005). Therefore, this thesis has studied soil water dynamics and drainage in both cereal and fallow plots in a rainfed Mediterranean area.

Considerable efforts have been performed to shed light about the usefulness of slurries as organic fertilisers as mentioned above, its properties and effects.

As said above, this thesis focuses on the following effects of pig slurry as N fertiliser in rainfed Mediterranean cereal crops: structural changes in soil organic matter, soil water repellency development and persistence; the possible interaction of NH_3 emissions with SWR; and soil water dynamics. The ultimate goal of this thesis is to help in the adoption of best management practices for pig slurry.

1.1.HYPOTHESIS

The main hypothesis is that continued slurry application affects organic matter content in soil over time. The nature of this new organic matter added might change the structure and composition of the SOM but also, it would cause the development of SWR, affecting NH_3 emissions, aside from other N losses as NO_3^- leaching related to water movement through the soil. In more detail, this hypothesis can be divided in the following sub-hypotheses:

H1: Crop-season slurry application over time would change the chemical structure of SOM, and the different HLS fractions respond positively to the SOM applied rate.

H2: The addition of hydrophobic substances contained in pig slurries to the soil surface causes SWR, mainly at cereal tillering, when slurries cannot be buried. Besides, pig slurry composition affects persistence and intensity of SWR. To test this sub-hypothesis, it must be taken into account that SWR is also influenced by the soil sample water content and the drying temperature applied during the evaluation process.

H3: Slurry application at sowing time, increases NH_3 volatilisation in subsequent (topdressing) slurry applications due to its link with SWR.

H4: Drainage occurs in semiarid rainfed areas and fallow periods, as well as irregular rain distribution in time, have an impact in water movement through soil.

1.2. GENERAL AND DETAILED OBJECTIVES

The main aim of this work was to evaluate the effects of different strategies of slurry fertilisation (slurry origin, rate and application time) on the soil-water quality and losses related to the N cycle.

Based on the general objective and the above mentioned hypothesis, the specific objectives of this thesis are:

O1:To characterise the composition of humic-like substances with spectroscopic techniques and to evaluate the transformation on calcimorphic soil of organic matter inputs from long-term slurry addition.

O2:To quantify the impact and the evolution of SWR and to assess the two most common methods for SWR evaluation in different pig slurry fertilisation strategies at cereal tillering.

O3:To evaluate the distribution and persistence of SWR induced by the application of different pig slurries strategies, and its potential influence on NH_3 volatilisation.

O4:To quantify the drainage and to evaluate the soil water dynamics using the LEACHM model in a dryland Mediterranean agricultural soil with winter cereal crop rotation as a first step to assess NO_3 leaching.

1.3. THESIS SCHEME

This thesis was structured in 8 chapters plus 2 annexes.

The first chapter introduces the reader into the frame of the thesis, and lists the hypotheses and the associated objectives.

Chapter 2 describes the experimental context of the thesis.

Chapters 3 to 6 are the core of the work as they answer the stated objectives. These chapters are presented in article format, following the conventional research article sections, and each of them can be considered as an independent unit.

Chapter 7 is devoted to an integrative discussion about the core chapters, which conduct the reader to the general conclusions.

In Chapter 8, general conclusions are presented in relation to the initial objectives.

Finally, annexes display extra information related to the main objectives of the thesis.

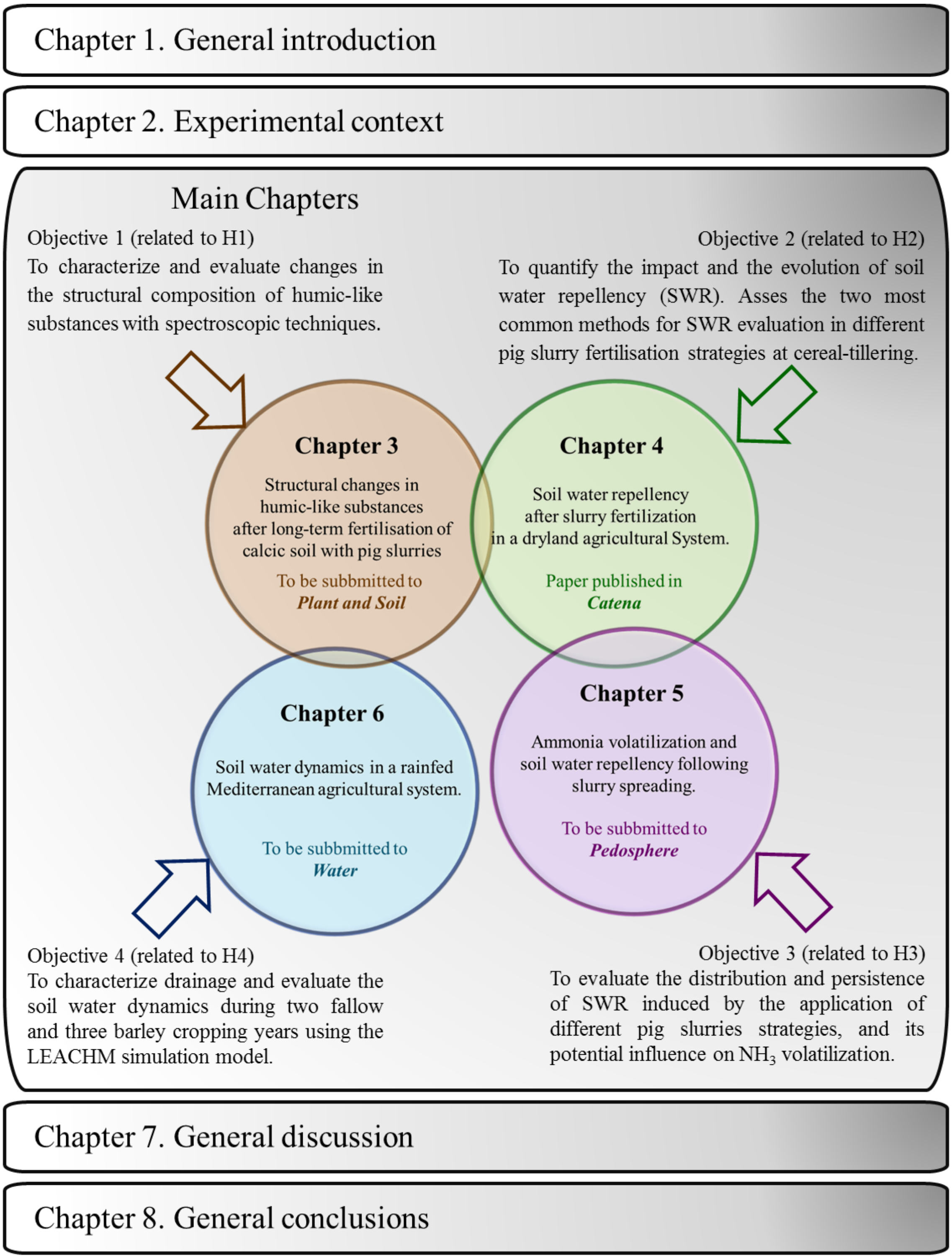

Figure 1.1. Thesis structure including the objectives of the main chapters and their relation with the hypotheses (H1 to H4).

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CHAPTER 2

Experimental site conditions

EXPERIMENTAL CONDITIONS

Site description

The experimental site (Fig. 2.1) is located in the municipality of Oliola NE area of Spain (coordinates 41º52’29”N, 1º09’13”E, 440 m a.s.l.). Climate is semiarid Mediterranean with mean annual temperature of 12.6°C with high summer temperatures. The average annual precipitation is 443 mm. The maximum monthly precipitation occurs in April, followed by October and November.

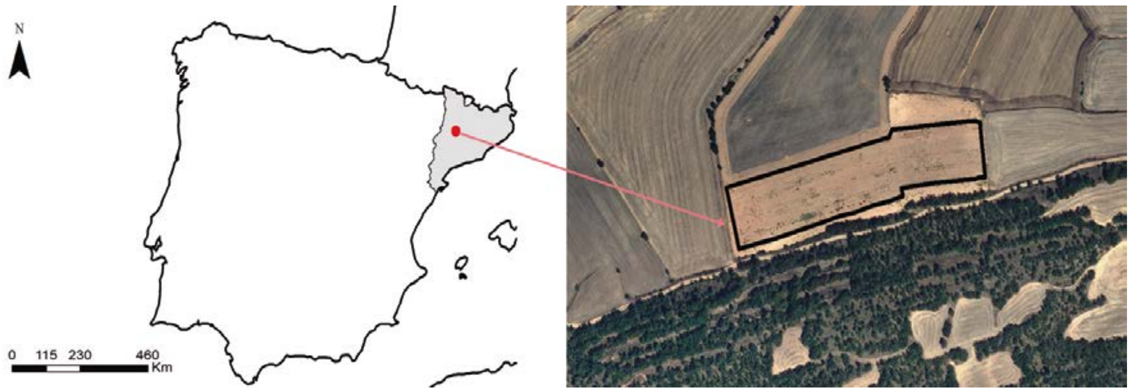

Figure 2.1. Oliola experimental site

Oliola experimental site has a NW-SE orientation. It limits to the north with the folded structures of Serra d’Oliola, to the west with the Serra de Montclar and Pedrós, to the east with the Llobregós combe valley and to the south with the Coscó and Cabanabona platforms of subhorizontal sandstones. From geomorphological point of view the studied area corresponds on a valley bottom developed on an inverted erosional landscape or combe (the Llobregós anticlinal branch, the northern branch of the Barbastro-Balaguer anticline) formed by folded Oligocene sandstones in the flanks and gypsum evaporative sediments of Upper Eocene in the core of the anticline. The soils covering this substratum are red clays and silts from deep alluvial deposits of the Holocene drainage system as shown in Fig. 2.2 (ICGC, 2006).

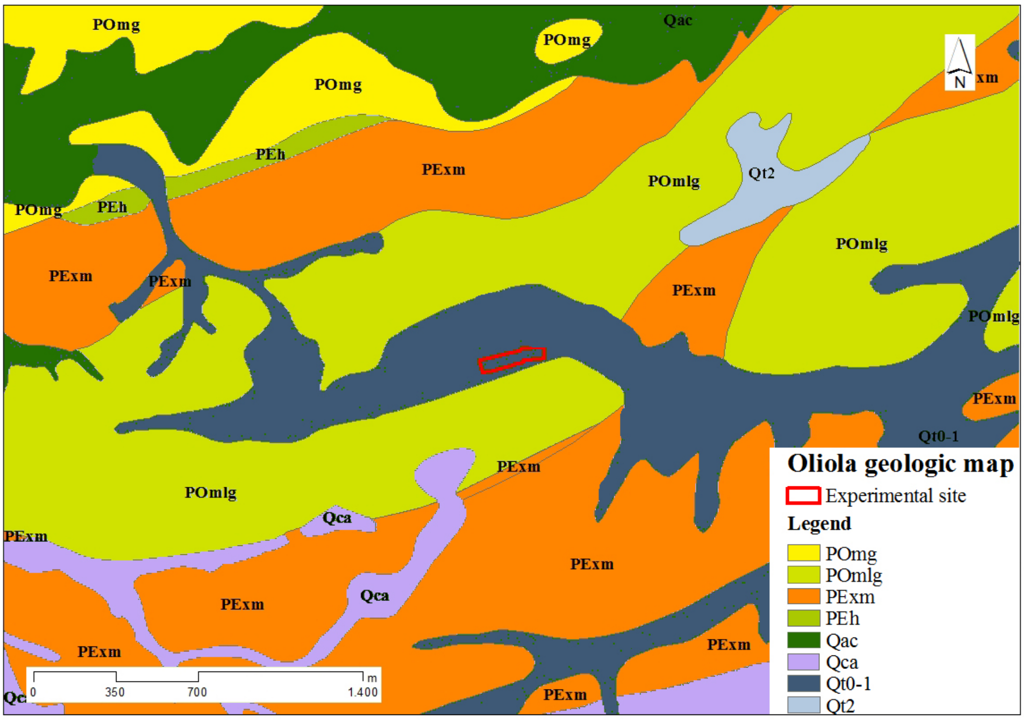

Figure 2.2. Geologic conditions of the experimental site (red rectangle).

The soil was classified as a Typic Xerofluvent (Soil Survey Staff, 2014). It is >2 m deep with few coarse elements, non-saline, and calcareous. The upper layer (0-0.30 m) was characterized as silt loam texture (131 g kg^{-1} sand, 609 g kg^{-1} silt, and 260 g kg^{-1} clay), with a pH of 8.2 (1:2.5; soil: distilled water). The mean organic C content was 11.67 g kg^{-1}, the bulk density 1.65 g cm^{-3}, and the calcium carbonate content 300 g kg^{-1}.

Experimental set up

The framework of this research was a long term fertilization experiment established in 2002 which was maintained from then onwards. Winter cereals were cropped on the experimental site with the exception of 2007/08, 2013/14 and 2016/17 cropping seasons when soil was left under fallow. The experimental design was a split-block design with three blocks (replications). Fertilization treatments at sowing (slurry application or not) were randomized against the block, and treatments at cereal tillering were randomized against the slurry applied (Table 2.1). The rotation was the common one used in the area, with wheat (*Triticum aestivum*) and barley (*Hordeum vulgare*) rotation (maintained during one and three years, respectively) as the main crops. Plot size for treatments was 137.5 m^2 (11 m wide and 12.5 m long) except for the control plots which were 87.5 m^2 (7 m wide and 12.5 m long). Usually, the crops were sown in late October-early November and harvested at the end of June-early July. The agricultural practices related to the use of herbicides and insecticides followed the re-commendations of the farm advisory system of the area.

Table 2.1.

Relation between treatment names used in the different chapters and the slurry rates.

Treatment	Slurry rate (Mg ha^{-1}) at		Plot name in Chapter:			
	Sowing	Cereal tillering	3	4	5	6
N0	0	0		0-0	S00	
N2	0		M120			
N3	0	20	F20			
N4	0	40	F40	0-F4	S04	
N7	0	60	S60			
N8	0	90	S90	0-S8	S08	
PN0	30	0	F30	F2-0	S20	
PN3	30	20	F50			
PN4	30	40	F70	F2-F4	S24	No name
PN5	30	60	F90			
PN8	30	90		F2-S8	S28	

Pig slurry fertilisation

Slurry composition varies due to the animal types, diet, and the farm management including water usage, tank characteristics and time of storage (Sánchez and González. 2005; Antezana et al., 2006; Yagüe et al., 2012). Slurries have neutral to basic pH; and a mean electrical conductivity of 26.8 dSm^{-1} (Yagüe et al., 2012). They are low in dry matter (average of 6%) compared with other fertilisers of organic origin as manure or compost (Ndayegamiye and Côté, 1989). Slurries vary in the NPK composition but nitrogen is mainly present as ammonium-nitrogen form (70% on average). The ammonium-nitrogen (NH_4-N) can be easily transformed in nitric-nitrogen into the soil. Besides, the low C:N ratio can enhance priming effect (Plaza et al., 2004).

The chemical characteristics of the slurries applied during the two crop seasons (2014/2015 and 2015/16), directly related to the field experiments are shown in Table 2.2. There in can be observed that average composition is in the range of the data reported by Yagüe et al. (2012) por this area.

Slurry was applied over the soil surface by the splash-plate machine method. Tractor speed was adjusted and applied doses were supervised by differences of tank weight after each application. Slurry came from two sources: from fattening or from sow pigs. Yearly, slurry was applied twice a crop year. First, slurries were spread prior sowing in late October and at cereal tillering stage in early February. At sowing, slurry was buried the same day after slurry application by disc-harrowing tillage. While at cereal tillering, slurry was left on the soil surface.

Table 2.2

Average physicochemical values of pig slurries applied in Oliola experimental field during the 2014/15 and 2015/16 cropping seasons. Specific organic components for the pig slurry liquid fraction (LIF) and solid fraction (SOF, i.e. dry matter) are also displayed. Total average and means obtained from slurry origin (fattening or sows pigs) are shown.

		Pig Slurry (±SD)	
Parameters	Mean[b] (±SD)	Fattening	Sows
pH (1:5)[a]	8.5 (0.1)	8.55 (0.1)	8.4 (0.2)
Electrical conductivity (1:5, dS m^{-1}, 25ºC)[a]	5.1 (2.1)	6.4 (0.3)	2.5 (0.1)
Dry matter (kg Mg^{-1})	88.3 (27.8)	94.8 (32.5)	75.3 (12.9)
Organic matter (kg Mg^{-1})	63.2 (24.4)	70.4 (28.0)	48.9 (1.4)
Organic N (kg Mg^{-1})	1.9 (0.5)	2.2 (0.5)	1.5 (0.1)
Total N (kg Mg^{-1})	4.9 (2.5)	5.7 (2.7)	3.2 (0.3)
Ammoniacal N (kg Mg^{-1})	3.8 (1.7)	4.8 (0.6)	1.7 (0.2)

Total organic C (kg Mg^{-1})	31.5 (11.9)	34.9 (13.7)	24.5 (0.7)
	LIF	LIF	LIF
Water extractable organic C (kg Mg^{-1})	6.0 (3.3)	8.2 (0.4)	2.5 (2.0)
Hydrophobic organic C (kg Mg^{-1})	2.4 (1.4)	3.4 (0.2)	1.01 (0.6)
Hydrophilic organic C (kg Mg^{-1})	3.5 (2.0)	4.8 (0.4)	1.5 (1.5)
	SOF	SOF	SOF
Water extractable organic C (kg Mg^{-1})	1.4 (0.9)	1.8 (0.9)	0.72 (0.2)
Hydrophobic organic C (kg Mg^{-1})	0.6 (0.5)	0.9 (0.4)	0.26 (0.01)
Hydrophilic organic C (kg Mg^{-1})	0.8 (0.5)	1.0 (0.5)	0.5 (0.2)

[a]Ratio 1:5, slurry: water

[b]Considering both slurry types

The results presented in this thesis were obtained from selected plots during the cropping seasons 2014/15 (chapter 4) and 2015/16 (chapters 3 and 5). Moreover, for chapter 6, moisture data was collected from 2006-2017. Only such treatments are described below. As mentioned in Chapter 1, each of the main chapters aims to be published in a scientific journal. Thus, each chapter has its own treatments nomenclature as shown in Table 2.1. Plots received slurry before sowing were those with code P, while the ones that received slurry at cereal tillering stage were designated with code N. The number after the letters differentiates the slurry dose, ranging from 20 to 90 Mg ha^{-1}. Furthermore, a mineral N fertilized plot (N2, 120 kg N ha^{-1}) applied as ammonium nitrate and a control treatment (N0) received P (40 kg P ha^{-1}) and K (56 kg K ha^{-1}).

METHODS

In order to shed light in the methods followed to obtain the data for each of the main chapters, different schematic illustrations related to each chapter are shown. The article-format of the main chapters includes a specific section to materials and methods. There, the specific techniques and the equipment needed are described.

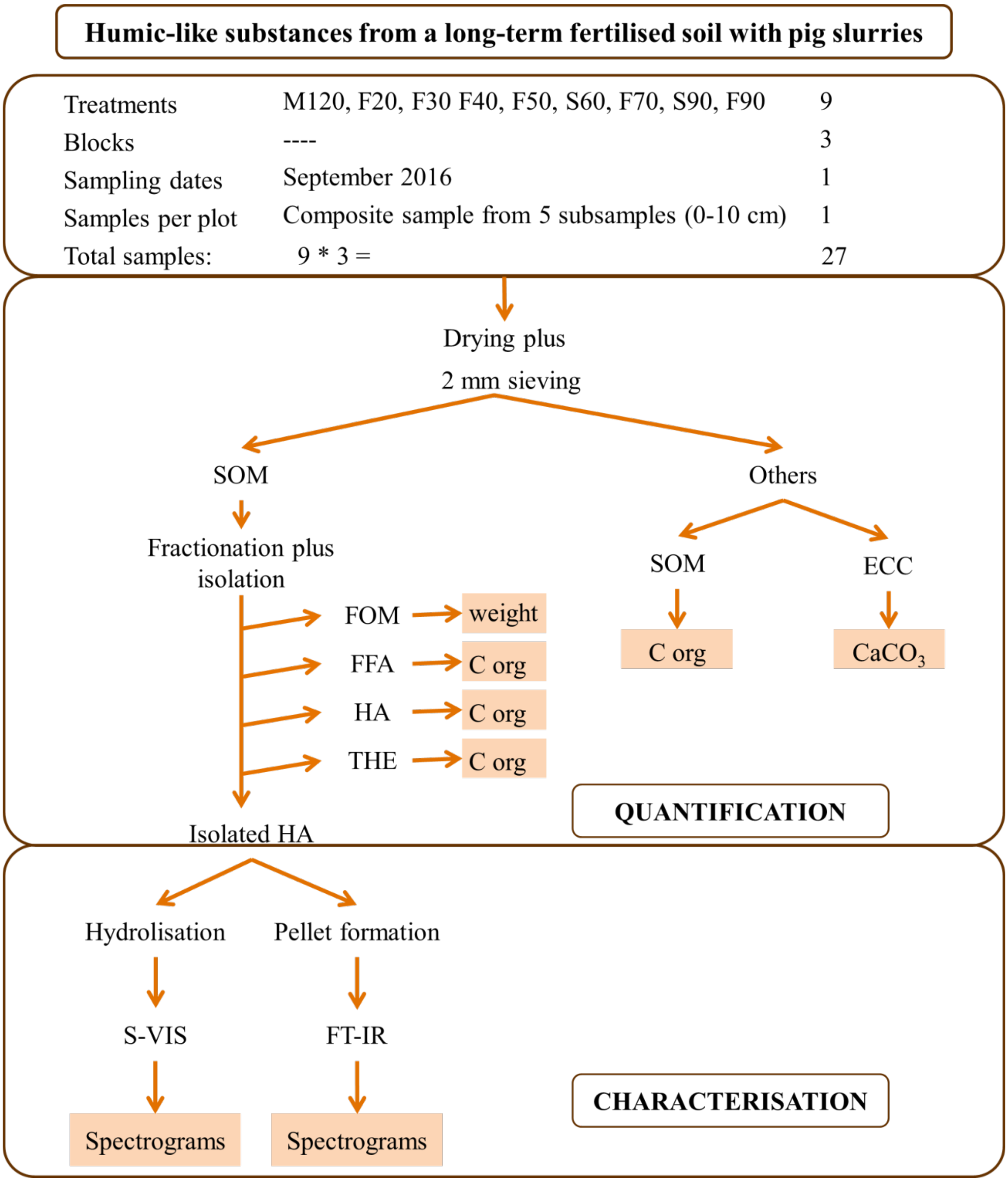

Figure 2.3. Methodological diagram to data acquisition related to Chapter 3. Abbreviations: soil organic matter (SOM), free organic matter (FOM), free fulvic acids (FFA), humic acids (HA), total humic extract (THE), equivalent calcium carbonate (ECC), organic carbon (Corg), Fourier transformed infrared (FT-IR), spectra in the visible range (S-VIS).

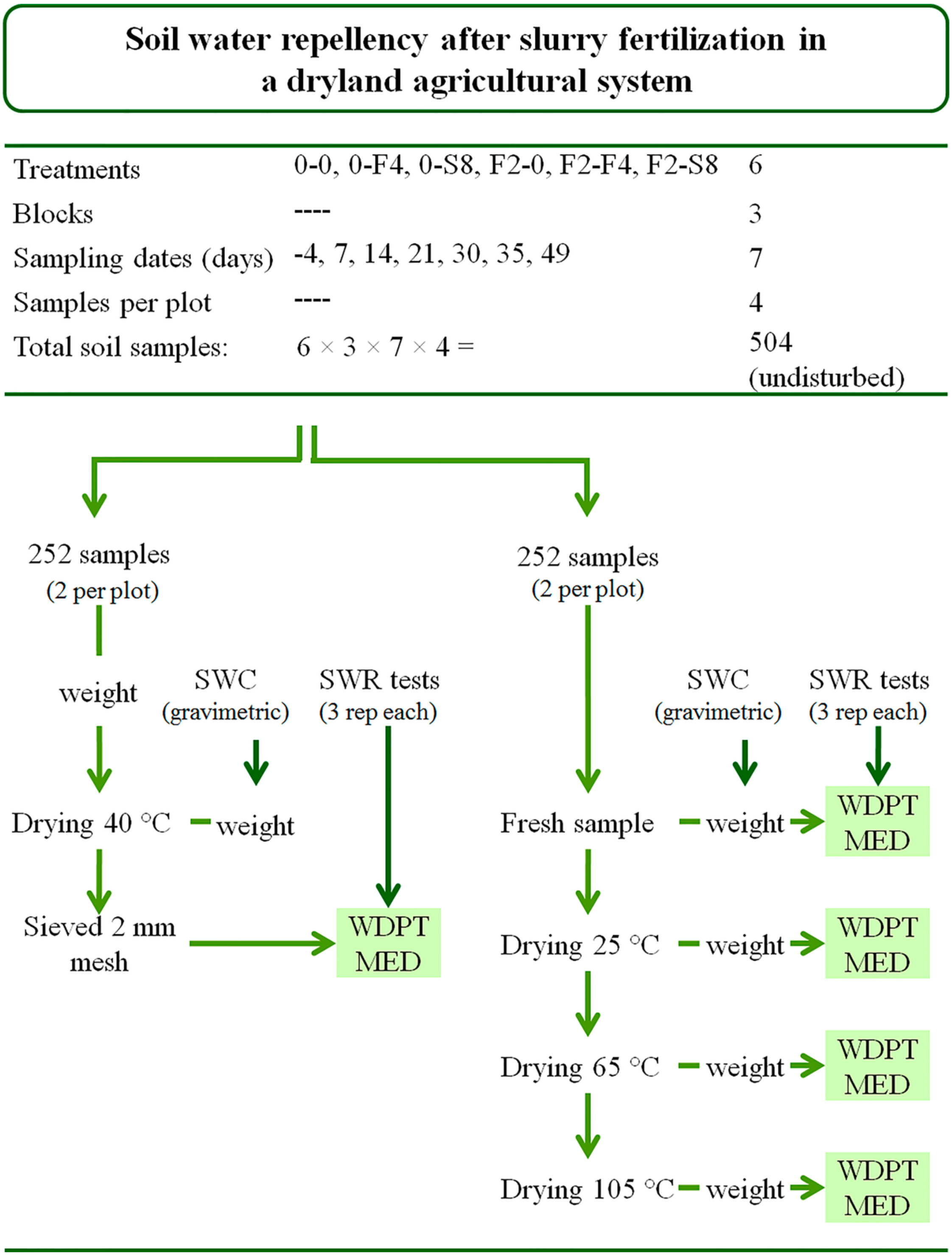

Figure 2.4. Methodological diagram to data acquisition related to Chapter 4. Abbreviations: molarity of ethanol droplet test, MED; soil water content, SWC; soil water repellency, SWR; water drop penetration time test WDPT.

Ammonia volatilisation and soil water repellency following slurry spreading

SOWING (October 2015)		
	NH_3^+ volatilisation	
Treatments	S00, S20	2
Blocks	----	2
Sampling times (h)	9, 24[a], 32, 49[a], 56, 80, 145	7
Samples per plot	---	6
Total samples	2 × 2 × 7 × 6 = 168 168 – (4 × 3)[a] =	156

CEREAL TILLERING (February 2016)						
	NH_3^+ volatilisation		SWR		SWC	
Treatments	S00, S04, S08, S20, S24, S28	6	*idem*	6	*idem*	6
Blocks	---	2	*idem*	2	*idem*	2
Sampling times (h)	7, 24, 31, 48, 55, 72, 79, 103, 144, 168, 192, 216, 240, 312, 360, 408, 480, 528, 576	19	0, 24, 72, 144, 192, 312, 360, 408, 480, 528, 576, 672, 840, 1176	14	*idem* als SWR	14
Samples per plot	---	6	---	6	---	1
Total samples:	6 × 2 × 19 × 6 =	1368	6 × 2 × 14 × 6 =	1008	6 × 2 × 14 =	168

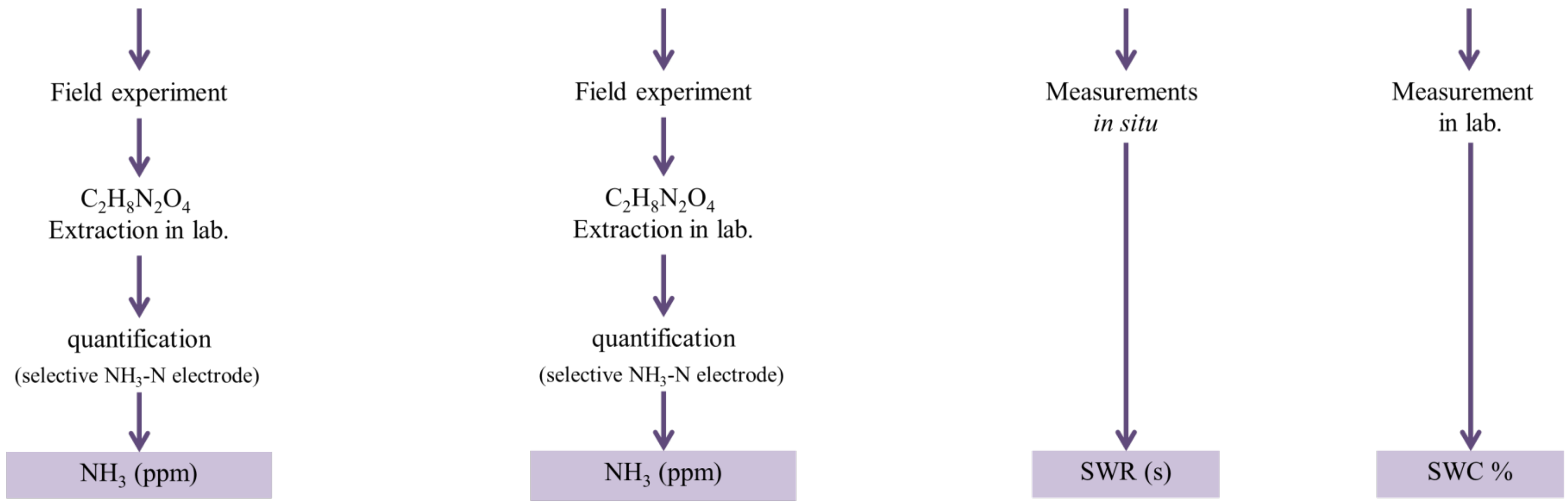

Figure 2.5. Methodological diagram to data acquisition related to Chapter 6. The highlighted purple text identifes the data-type obtained. Abbreviations: ammonia, NH_3^+; ammonium oxalate, $C_2H_8N_2O_4$; soil water content, SWC; soil water repellency, SWR.

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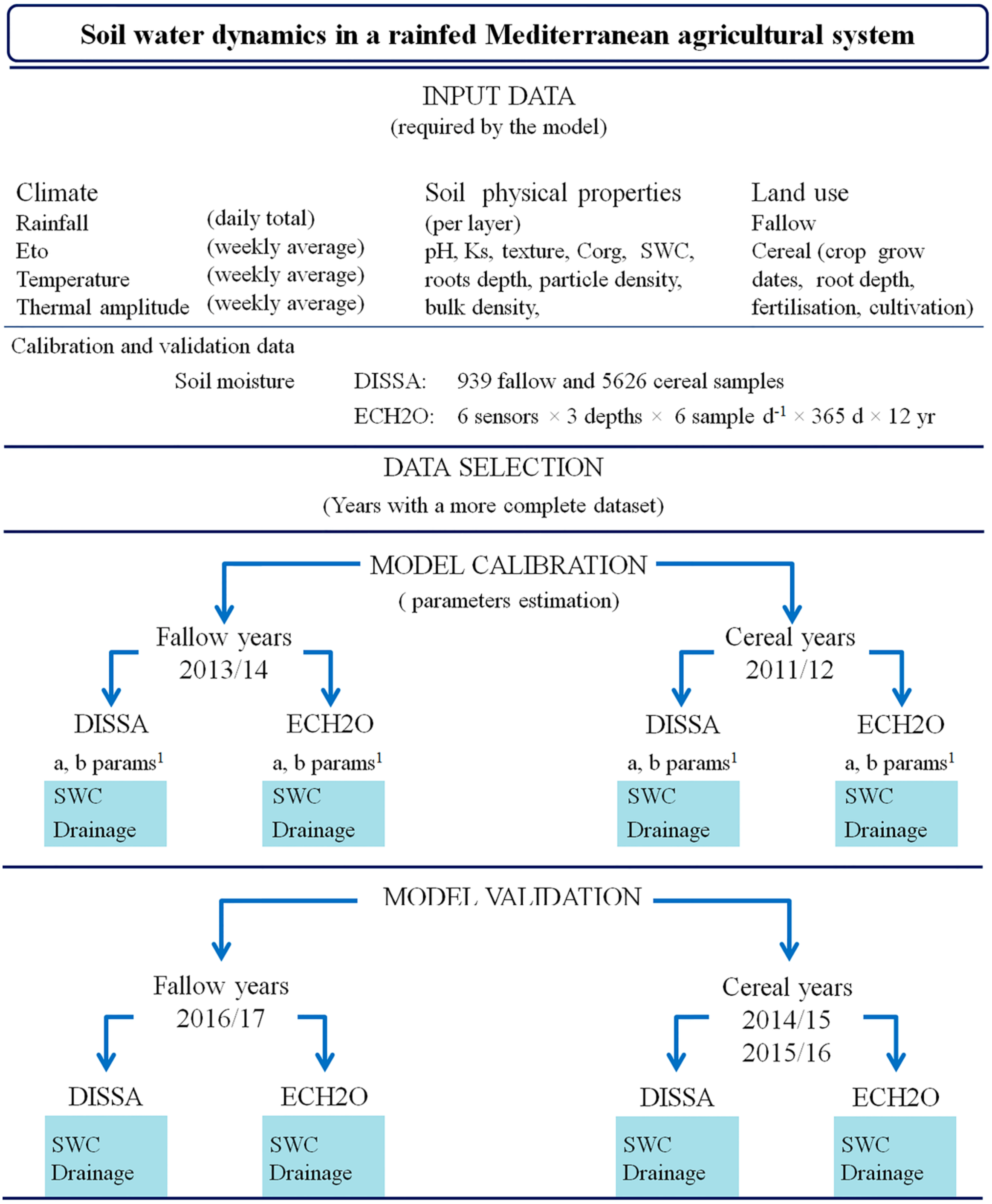

Figure 2.6. General scheme of the applied methodology for data acquisition and the evaluation process to model water dynamics in soil (Chapter 6). Abbreviations: disturbed soil samples, DISSA; Evapotranspiration, Eto; hydraulic conductivity at the saturation point, Ks; organic carbon, Corg; capacitance probes, ECH2O; soil water content, SWC.

[1]Parameters belonging to unsaturated hydraulic conductivity function proposed by Campbell (1974)

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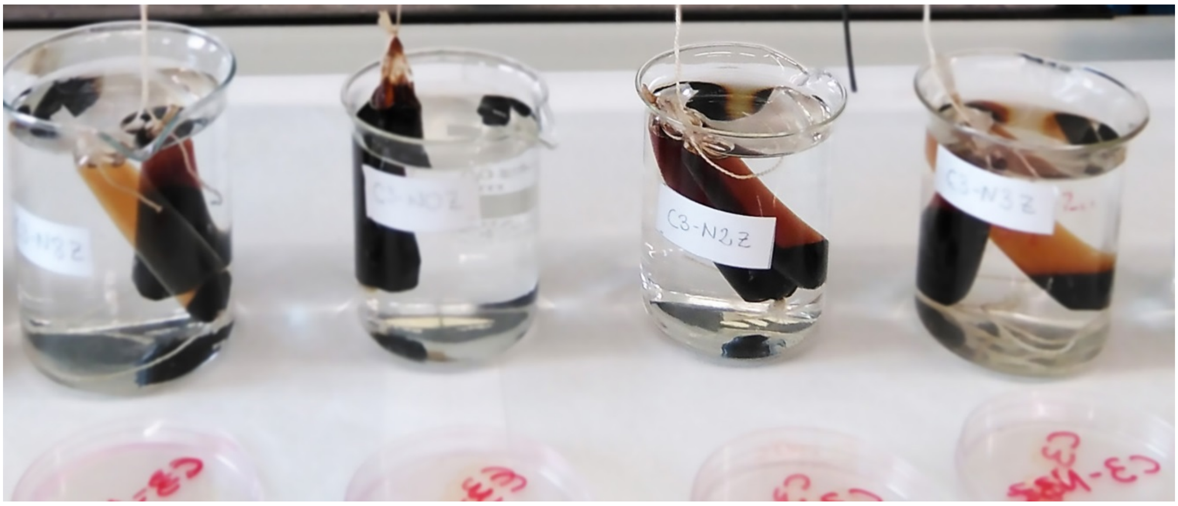
CHAPTER 3

Structural changes in humic-like substances after long-term fertilisation of calcic soil with pig slurries



This chapter contains the manuscript to be submitted to the journal *Plant and Soil*.

STRUCTURAL CHANGES IN HUMIC-LIKE SUBSTANCES AFTER LONG-TERM FERTILISATION OF CALCIC SOIL WITH PIG SLURRIES

ABSTRACT

Sustained slurry applications in dryland Mediterranean calcareous soils with low organic matter (SOM) have positive effects on soil fertility leading to structural changes in the SOM. The objective was to determine potential changes in the structural composition of the most stable SOM fraction: the humic-like substances (HLS). After 14 years of pig slurry fertilisation, eight slurry fertilisation treatments which included a range from 20 to 90 Mg ha^{-1} of slurry applied were evaluated. They were compared with a mineral treatment (no slurry added): N-P-K treatment. Soil organic carbon content was quantified previously to winter cereal sowing (September). The HLS were isolated by alkaline extraction followed by acid precipitation. Visible spectroscopy (800–400 nm) and Fourier transformed infrared spectroscopy (4000–400 cm^{-1}) were used. Soil organic carbon content increased from 9.5 g C kg^{-1} (mineral treatment) to 13.8 g C kg^{-1}, in the highest slurry rate. This increase was reflected in the humic acid fraction due to incorporation mainly of polyalkyl aliphatic structures, reflecting long-term changes in the molecular composition of the SOM, which show a relative decrease of peaks related to the aromatic carbon. These findings suggests structural changes characteristic of a short-term or temporary effect. This is interpreted as HLS from slurry does not represent a stable source of SOM, limiting the SOM contribution to the long-term C sequestration.

Keywords: Aliphatic compounds, organic fertilizers, soil organic matter, Fourier transformed mid-infrared spectroscopy

Abbreviations: Fourier transformed infrared (FT-IR), fulvic acids (FA), humic acids (HA), humic-like substances (HLS), optical density at 465 nm (E4), optical density at 665 nm (E6), principal component analysis (PCA), soil organic matter (SOM), spectroscopy in the visible range (S-VIS), total humic extract (THE).

HIGHLIGHTS

Long-term pig slurry application increased total SOM and in the HA fraction.

Pig slurry increased SOM structures of aliphatic character.

The HA increment rich in aliphatics should not be considered a stable C reservoir.

INTRODUCTION

Pig slurry, the main by-product of intensively-farmed pigs, is a major concern due to the livestock intensification. This production model is rooted in Spain, in such a way that more than 55×10^6 m^3 of pig slurry were produced in 2016. One traditional way to get rid of this substance is to use slurries as an organic fertiliser. Indeed, this practice is widely recognized as an effective strategy to improve crop productions (Bosch-Serra et al., 2015; Domingo-Olivé et al., 2016), and to increase and/or restore the soil organic matter (SOM) (Senesi et al., 2007; Zhang et al., 2017). Slurries are low in dry matter (>90% water) and ammonium-nitrogen is the predominant N form (Antezana et al., 2016; Sanchez and Gonzalez, 2005) despite their wide range of variation in composition (Yagüe et al., 2012). However, the use of pig slurry in agriculture promotes changes in soil quality and fertility over time (Bosch-Serra et al., 2015; Domingo-Olivé et al., 2016; Piccolo et al., 1992).

Organic matter content and nature influences soil quality and fertility. From a structural point of view, humic-like substances (HLS) are the frame of SOM. According to their solubility in acid and basic extractants, HLS are divided into humic acids (HA) or fulvic acids (FA). Both are the ending result of the humification process. The microbial and chemical transformation of 'fresh' organic matter in soil stabilizes organic substances against biodegradation (Kögel-Knabner, 2002; Senesi et al., 1996). Moreover, HLS act as suppliers and storehouses of N for plant and microorganisms as HA contain among 2 to 6% nitrogen (Schnitzer, 1985).

Organic compounds in pig slurry differ to native soil HLS (Cheng et al., 2002; Plaza et al., 2002; Senesi et al., 1996). Despite some authors (Dorado et al., 2003) suggest that inputs of organic fertilisers in general lead to SOM with comparatively low biological stability or maturity than the pre-existing HSL in soil. Other authors (Senesi et al., 1996; 2007) suggest that the course of its progressive transformation in the soil, they are gradually transformed and incorporated into the HLS until they become similar to soil native HLS.

Indeed, short and medium term research on HLS under dryland agricultural environments has been published (Brunetti et al., 2007; Madrid et al., 2004; Plaza et al., 2002). However, long-term studies on HLS composition and N-related chemical bounds are still scarce (Ferrari et al., 2011; Francioso et al., 2000; Zhang et al., 2017).

The aim of this work was to characterize the HLS composition with spectroscopic techniques in order to evaluate the transformation on calcimorphic soil of organic matter inputs from pig slurry, after 14 years of additions at different doses.

We hypothesized that (i) crop-season slurry application over time would change the chemical structure of SOM and (ii) Moreover, the different HLS fractions respond positively to the SOM applied rate.

MATERIALS AND METHODS

Experimental location and design

A long-term field experiment was established in 2002 in NE Spain (41º52’29”N, 1º09’13”E, 440 m a.s.l.). The climate is semiarid Mediterranean with an annual precipitation of 450 mm. Evapotranspiration is higher than precipitation for most of the year (Fig. 3.1), especially in summer, where high temperatures are recorded.

The soil was classified as a Typic Xerofluvent (Soil Survey Staff, 2014), non-saline and calcareous. The upper layer (0-0.30 m) has a silty loam texture (131 g kg^{-1} sand, 609 g kg^{-1} silt, and 260 g kg^{-1}clay); pH of 8.2 (1:2.5; soil:distilled water), mean organic carbon content of 11.67 g kg^{-1}, bulk density 1.65 $kg \cdot m^{-3}$ and calcium carbonate content from 300 g kg^{-1}. The water field capacity was 17.2% (w/w) and the permanent wilting point was 10.2% (w/w).

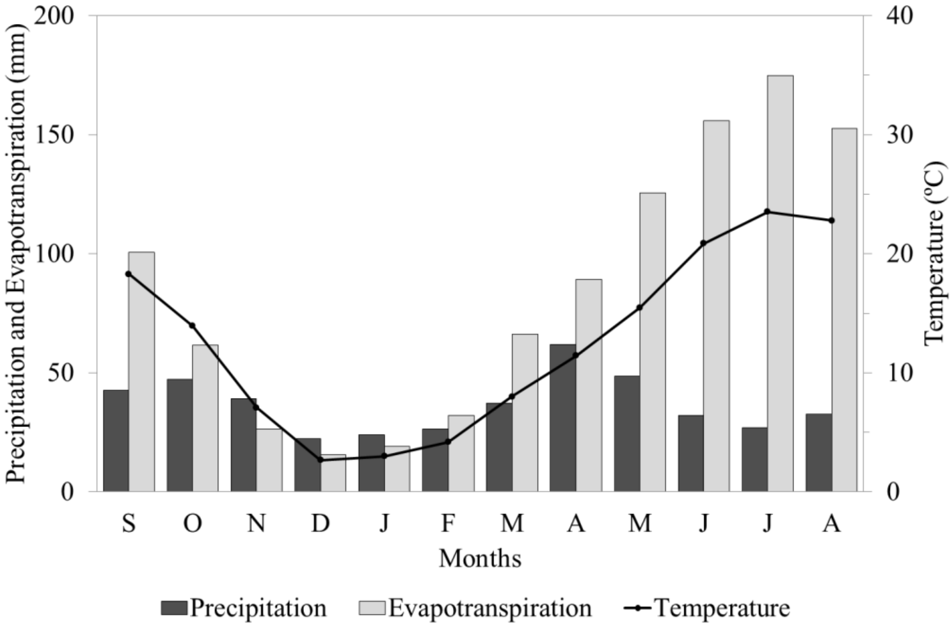


Figure 3.1. Average monthly temperature, precipitation and evapotranspiration from 2001–2018.

A rainfed winter cereal system with barley (*Hordeum vulgare* L.) rotated with wheat (*Triticum aestivum* L.) was maintained since the beginning of the above mentioned experiment. Fertilizer treatments were distributed in three blocks (repetitions). In the 2016–2017 cropping season, nine treatments were chosen. Treatments were designed based on the total annual SOM rate applied with pig slurries (Table 3.1). Slurry came from two sources: fattening (code F) at 20, 30, 40, 50, 70 and 90 Mg ha^{-1} y^{-1} or from sow pigs (code S) at 60 and 90 Mg ha^{-1} y^{-1}. A mineral N fertilized plot (120 kg N ha^{-1} y^{-1}) applied as ammonium nitrate (code M120) received P (40 kg P ha^{-1} y^{-1}) and K (56 kg K ha^{-1} y^{-1}).

Slurry was applied over the soil surface by the splash-plate machine method. Tractor speed was adjusted and applied doses were supervised by differences of tank weight after each application. Yearly, slurries were spread prior sowing in late October and at cereal tillering stage in early February. At sowing, the same day after slurry application it was buried by disc-harrowing tillage but it was left on the soil surface at cereal tillering.

Table 3.1. Fertilisation strategies from 14 cropping seasons (2002–2016). Average and standard deviation (numbers in parenthesis) of total N, organic N and organic matter applied, and accumulated grain yield (0% humidity).

Treatment†	Total N	Organic N	Ammonia N	Organic Matter	Accumulated grain yield
	-------------------	kg ha^{-1} y^{-1}		-------------------	kg ha^{-1}
M120	0 (0)	0 (0)	0 (0)	0 (0)	45040
F20	124 (33)	43 (22)	81 (19)	959 (355)	44303
S60	114 (59)	44 (36)	71 (30)	1136 (1097)	47428
F40	210 (44)	71 (30)	142 (27)	1604 (757)	50481
F30	185 (40)	60 (13)	126 (34)	1611 (530)	47347
S90	190 (88)	74 (50)	116 (49)	2107 (1421)	50340
F50	308 (63)	101 (29)	206 (42)	2563 (741)	53665
F70	403 (72)	130 (37)	271 (47)	3224 (1048)	53215
F90	586 (116)	192 (61)	393 (76)	4802 (1249)	48711

† Treatments codes are as follow: the letter indicates if the slurry comes from fattening or sows (codes F or S, respectively). The number indicates the annual application rate (20, 30, 40, 50, 60, 70 and 90 Mg ha^{-1}), and a mineral fertilized plot with ammonium nitrate (120-40-56 Kg N-P-K ha^{-1} y^{-1}).

Soil sampling

A composite soil sample per treatment (1 kg) was taken the 20th September 2016, prior sowing. It consisted of a mixture of five subsamples (0–0.1 m). It was dried at room temperature and passed through a 2 mm sieve. A total of 30 soil samples, linked to the10 treatments which were present in each of the 3 blocks, were processed.

Organic matter fractionation and quantification

Humic acids were isolated according to Duchaufour and Jacquin (1975) and Velthorst et al. (1999). Each sample was threefold repeated in series of 50 g soil per treatment to obtain at least 0.5 g of isolated HA. Firstly, carbonates were removed with 2*M* H_3PO_4 (100 mL). The supernatant (free fulvic acids) was filtered to separate it from the organic matter light fraction (LF) and from the soil sample. Organic matter light fraction sample was washed with distilled water until pH = 7 was achieved. Both, LF and free fulvic acids were kept for further analysis.

Therefore, a series of 10 consecutive extractions in the soil sample were performed following Dabin (1971). Samples were treated twice with 0.1 *M* $Na_4P_2O_7$ (150 mL each time) and eightfold with 0.1 *M* NaOH (150 mL each time). Each extraction consisted of 4 h stirring, followed by a 5 min centrifugation at 6000 rpm. After each centrifugation step, the NaOH solution with the humic extract was recovered. At the end of the extractions, the volume of the recovered solution was determined and aliquots of 25 and 50 mL of each extract were recovered for the soluble and the total humic extract (THE) quantification, respectively. The remained solution was acidified up to pH = 1 with 6*M* HCl (25 mL) for 24 h to promote HA precipitation and then, HA were decanted. Supernatant (soluble fulvic acids) was discarded. The humic acid fraction was re-dissolved with 0.5 M NaOH (100 mL) and it was centrifuged at 5500 g for 5 min to precipitate clay minerals, which were discarded. The clay-free sodium humate solution was again precipitated with 6*M* HCl (10 mL) until pH = 1, centrifuged at 5500 g for 5 min and decanted. The purified HA were recovered with distilled water and placed into a cellophane dialysis bag for 3–4 d. Distilled water was changed every day until no chloride reaction with silver nitrate was observed. Finally, the resulting HA suspensions were transferred to Petri dishes and dried in an oven at 40 °C. Isolated HA were stored in small glass bottles for further analyses.

Carbon content from the different fractions (free organic matter, free fulvic acids, THE, and HA) was quantified by dichromate oxidation and subsequent titration with ferrous ammonium sulphate (Walkley and Black, 1934; Yeomans and Bremner, 1988).

Fulvic acids were calculated by difference between THE and HA. Soil organic matter from the soil sample was quantified by dichromate oxidation and subsequent titration with ferrous ammonium sulphate (Walkley and Black, 1934; Yeomans and Bremner, 1988).

Spectroscopic analyses

The spectroscopic determinations in the visible range were carried out in solutions adjusted the equal concentration in carbon (Gosh and Schnitzer, 1979). The HA were dissolved into 0.01*M* NaOH at concentration equivalent to 0.2 mg C mL^{-1}.Spectra in the visible range (S-VIS) (400–800 nm) were obtained with a diode array spectrophotometer Hewlett Packard 8452 A VIS- UV. Optical densities at 465 (E4) and 665 (E6) nm were obtained.

Fourier transformed infrared (FT-IR) spectra were obtained with a spectrophotometer Bruker IFS28. Pellets were produced with 2 mg of isolated HA and 200 mg KBr. Spectra in the range of 4000–400 cm^{-1}were baseline-corrected. In addition, and for resolution enhancement, a digital treatment was used based on subtracting the spectrum from a positive multiple of its second derivative (Almendros et al., 1992). Finally, data were full-scale normalized adjusting to 10,000 the highest point of the spectra.

Statistical analysis

The ANOVA analysis was performed for intensity peaks and ratios of interest in S-VIS and FT-IR spectra, according a randomized block design. If significant, differences between treatments were done with Tukey's Studentized Range Test at $\alpha = 0.05$. Analyses were performed with the statistical package SAS version 9.4 (SAS Institute Inc., 2002–2013).

Multivariate approach was used to analyse the information provided by the peak intensities of the FT-IR spectra. One mineral and two slurry treatments were selected (M120, F90 and S90, respectively) to perform a principal component analysis (PCA). Statistical package JMP-Pro version 13 was used (SAS Institute Inc., 2017). Figures from all the analyses were created using MS Excel (2010).

RESULTS

Soil organic matter fractionation showed an increase in the HLS and in SOC with the increase of SOM rate (Fig. 3.2). Fractionation of SOM showed that the main changes were observed in HA, as they increased almost 75%, from 1.5 in the mineral treatment to 2.6 in the highest slurry dose. Humic acids represented between 60 and 80% of the THE. The lowest contribution came from the FOM fraction, which ranged from 0.1 to 0.7 g C kg^{-1} soil, followed by FFA, FA and HA. Significant differences were observed only between the highest SOM rates (F70, F90) and the mineral treatment (M120). It represented an increase of 46% in SOC by the slurry fertilisation. No significant differences between treatments were found, except for HA and THE (S1), which displayed similar tendency to the SOC results.

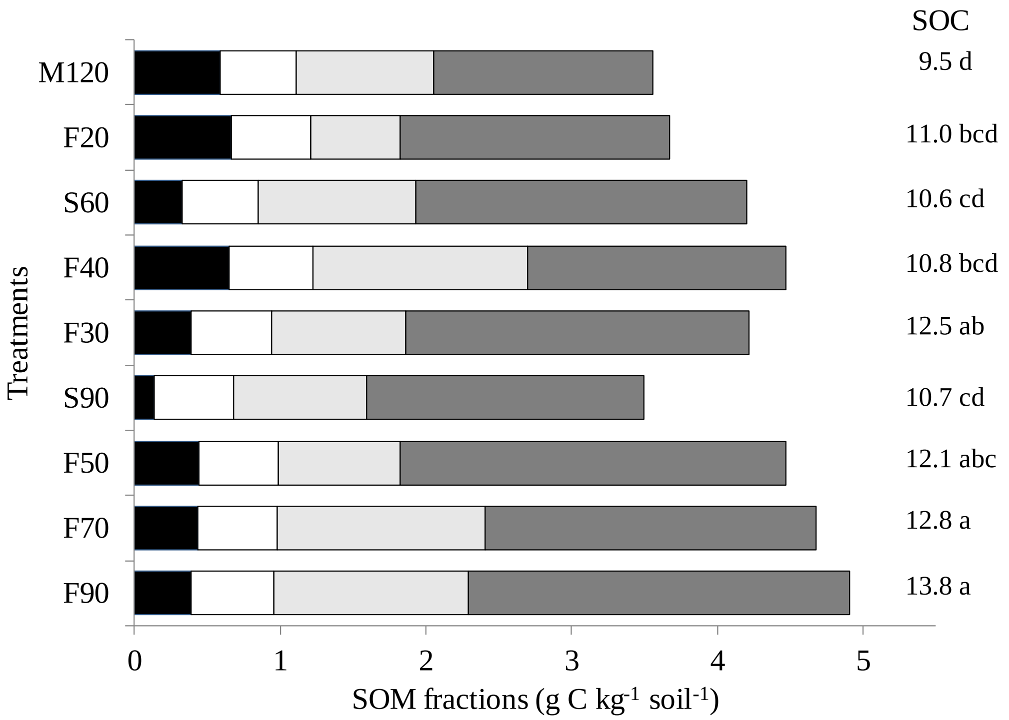


Figure 3.2. Free organic matter (black), free fulvic acids (white), fulvic acids (light grey) and humic acids (dark grey) isolated from different treatments. Differences in the average soil organic carbon (SOC, g C kg^{-1} soil) content per treatment are shown. Means with the same letter are not significantly different (Tukey's Studentised Range Test, $\alpha > 0.05$). Treatments codes are as follow: the letter indicates if the slurry comes from fattening, from sows or from mineral fertiliser (codes F, S or M, respectively). The number indicates the annual application rate 20, 30, 40, 50, 60, 70 and 90 Mg ha^{-1}). The mineral treatment was fertilised plot with ammonium nitrate, phosphorus and potassium (120-40-56 kg ha^{-1} y^{-1}).

An increase in the HLS was observed as there was a positive linear relationship in THE, HA and FA when plotted against the mean SOM rate (Fig. 3.3). The best linear adjustment was found when SOM was plotted against THE (r^2 = 0.70), and the lowest when plotted against FA (r^2 = 0.25).

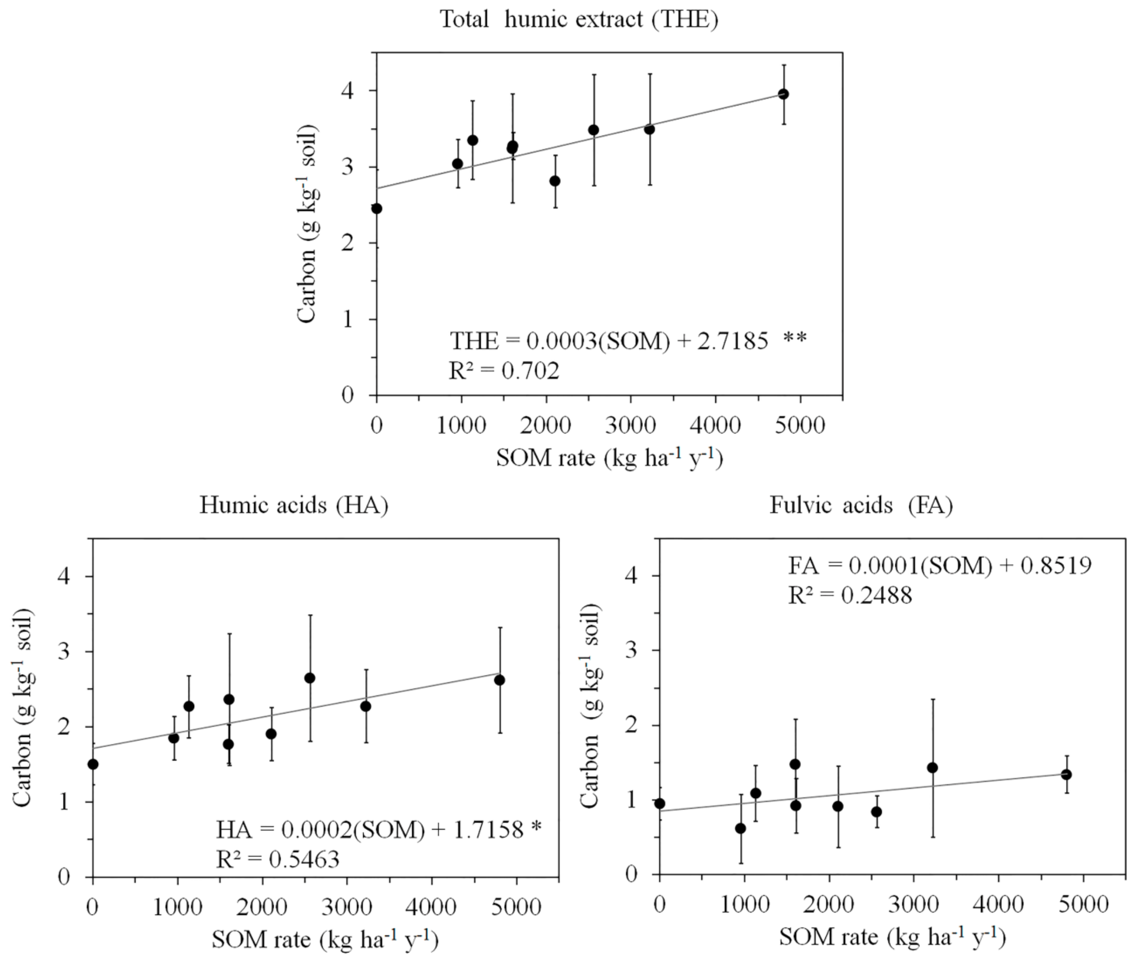


Figure 3.3. Regression relationship between mean soil organic matter (SOM) rate and total humic extract, humic acids, and fulvic acids. Regression significance at: (*) 0.01 probability level, and at (**) 0.001 probability level.

Optical density at E4 slightly decreased with the increase of SOM rate while the E6 remained similar in all treatments (Fig.3.4). Calculated E4/E6 ratio values were higher than 4.8 but they showed high standard deviation. However, there was not a clear trend in the decrease if the molecular size of HA suggested by the E4/E6 ratio and no significant differences were detected in structural aromaticity reflected by E4 and E6 optical densities (S2).

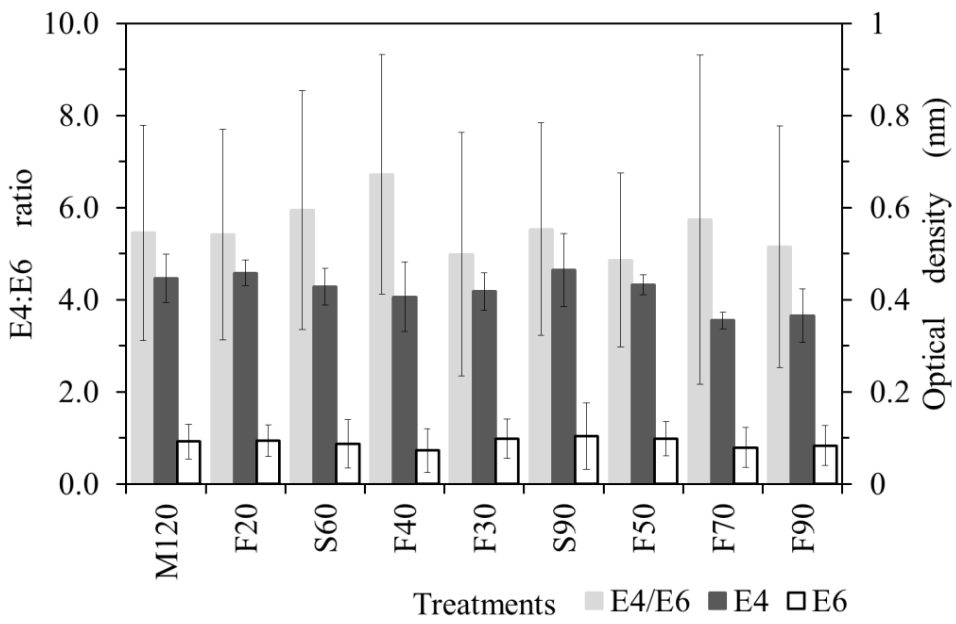


Figure 3.4. Average E4/E6 ratio, optical density at 465 (E4) and at 665 nm (E6) from isolated humic-like substances. Vertical lines indicate the standard deviation (*n* = 3). Treatments codes are as follow: the letter indicates if the slurry comes from fattening, from sows or from mineral fertiliser (codes F, S or M, respectively). The numbers indicates the annual application rate 20, 30, 40, 50, 60, 70 and 90 Mg ha^{-1}). The mineral treatment was fertilised plot with ammonium nitrate, phosphorus and potassium (120-40-56 kg ha^{-1} y^{-1}).

The resolution-enhanced FT-IR spectra led to identify the characteristic bands in both, the slurries and the experimental plots (Fig. 3.5). The aliphatic groups were the C–H stretching (2920 cm^{-1}); the C-H asymetric deformation (1460 cm^{-1}); and the C–H from OCH_3 or the C–O stretching of polysaccharides (1030 cm^{-1}). The amide bands were the amide I and the amide II C=N stretching (1650 and 1550 cm^{-1}, respectively). The O-related functional groups were the carboxylic C=O stretching (1720 cm^{-1}); the CH_3 symmetric deformation from carboxylic acids (1380 cm^{-1}); and the 1550 cm^{-1} which besides the amide II, it would also refers to conjugated carboxylic groups in the aromatic rings. Finally, the aromatic and lignin bands were the C=C aromatic (1620 cm^{-1}); the lignin aromatic C (1510 cm^{-1}); the aromatic substitution of lignin structures (1420 cm^{-1}), syringyl (1330 and 1130cm^{-1}); and guaiacyl (1270 cm^{-1}).

Following Hernández (2009) and Fengel and Wegener (1989), the lignin pattern was identified. It included the absorption bands at 2920, 1620, 1510, 1460, 1420, 1330, 1270 and 1030 cm^{-1}. However, spectra intensities were quite similar in all treatments. The slurry bands (Fig. 3.5a) were different in intensity to those in the treatments (Fig. 5b). The main differences were observed in the slurries that showed a marked peaks at in the amide band (1550 cm^{-1}), which appear as a shoulder in the fertilised soil. On the contrary, the lignin aromatic C (1510 cm^{-1}) and the carboxylic C=O stretching (1720 cm^{-1}) were quite small in the slurries compared against the one in the slurry fertilised soil.

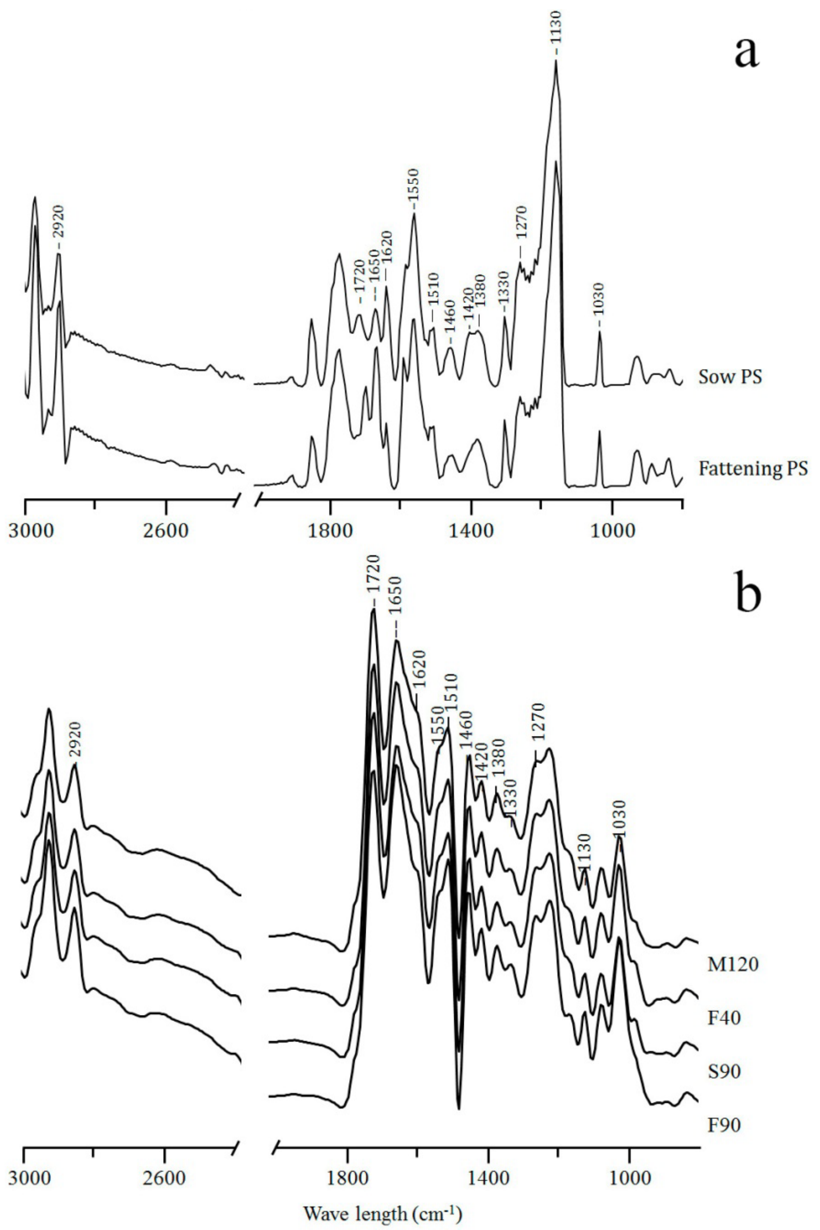


Figure 3.5. Resolution-enhanced infrared spectra in the range of 3000 to 800 cm^{-1} from pig slurries (PS, a) and from humic acids in a cultivated soil (b). Treatments codes are as follow: the letter indicates if the slurry comes from fattening, from sows or from

mineral fertiliser (codes F, S or M, respectively). The number indicates the annual application rate (40 and 90 Mg ha^{-1}). The mineral treatment was fertilised plot with ammonium nitrate, phosphorus and potassium (120-40-56 kg ha^{-1} y^{-1}).

Significant relationships between certain peaks intensities of the treatments and the SOM rate were found (Fig. 3.6). The C–H aliphatic stretching (1460 cm^{-1}), and the peak for lignocellulosic structures (methyl groups, carbohydrate polysaccharide-like substances and Si-O from silicate ; 1030 cm^{-1}) were positively related to the SOM rate.

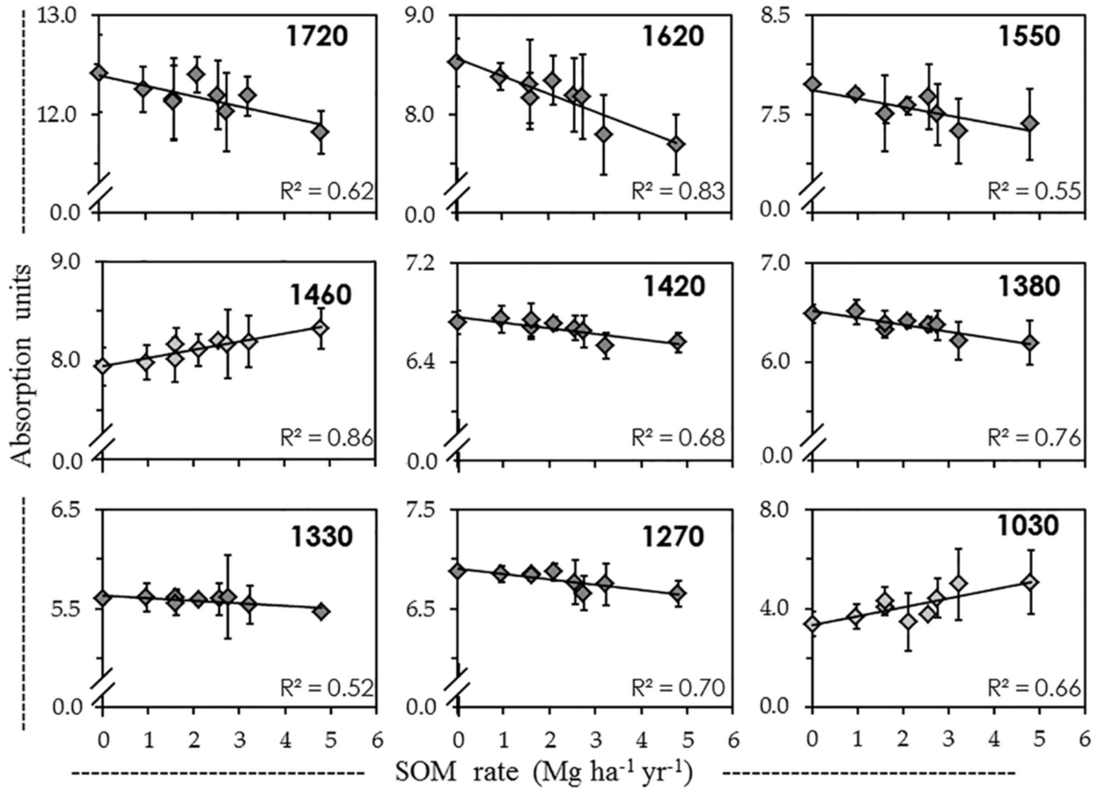


Figure 3.6. Linear regression relationship between mean soil organic matter (SOM) rate and the normalized intensity of peaks of interest at 1720, 1620, 1550, 1460, 1420, 1380, 1270 and 1030 cm^{-1}. Regressions were significant at 0.05 probability level.

On the contrary, a decrease in the SOM oxidation degree, related to the peak intensity in the C=O tension (1720 cm^{-1}) was observed. Furthermore, a structural aliphatic enhancement with the increase of SOM rate was found, with the concomitant relative decrease in the intensity of aromatic structures peaking at e.g. (1620 cm^{-1}), which is also observed with the most prominent aromatic peaks of the lignin pattern ,e.g. peaks at (1420 cm^{-1} and 1270 cm^{-1}).

The PCA analysis showed that two factors explained 69.2% of the variance (Fig. 3.7). The treatments position in chart *A* display the gradual changes in HLS due to the slurry fertilisation. It can be observed that mineral treatment (M120) is on the right side, the highest slurry rate treatment (F90) is the left side, while the treatment with slurry medium dose (S90) is placed in between the other two treatments. According to chart *B*, the absorption peaks of interest were separated in two groups, the right side was dominated by peaks related to aromatic groups, and the left one was clearly related to aliphatic groups.

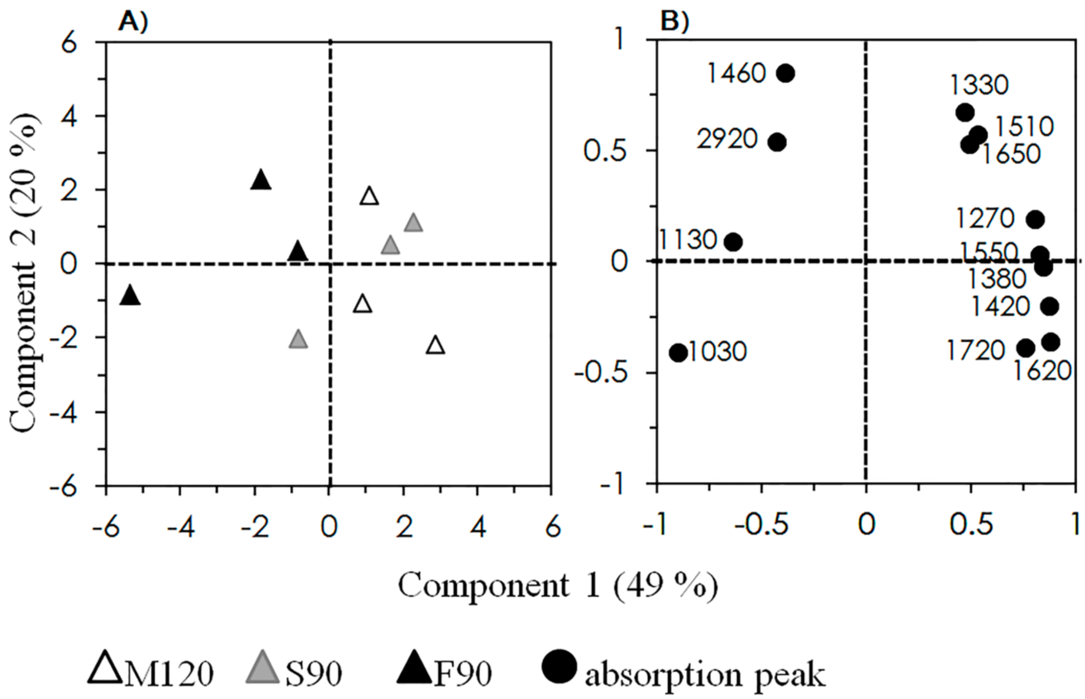


Figure 3.7. Factor loadings plot for the two main components obtained from the principal component analysis (B). Treatments used for the analysis are shown (A). Plots fertilised with slurry from fattening and from sows pigs with 90 Mg ha^{-1} (F90 and S90, respectively) and a mineral treatment fertilised with ammonium nitrate, phosphorus and potassium (120-40-56 kg ha^{-1} y^{-1}) were evaluated.

DISCUSSION

Long-term slurry application led changes in SOC content and in HA molecular characteristics. Significant increases were only observed at the highest SOM application rates. Soil organic carbon and THE raised in 4.26 and 1.5 g C kg^{-1} soil in the F90 treatment, meaning an increment of 45 and 61% compared to the mineral treatment (M120). Other authors reported small or in some cases not significant increase in SOM (Ndayegamiye and Côté, 1988; Plaza et al., 2002; Domingo-Olivé et al., 2016). In our case, the mean annual temperature and precipitation amount would reduce the SOM mineralisation rate, enhancing the significant differences. Moreover, the grain yields were similar between mineral and slurry fertilised treatments (Table 3.1), indicating that changes in SOM and THE could be related to the slurry fertilisation.

The THE, which is the sum of HA plus FA, was related to the increase of HA instead of the FA (Fig. 3.3). These results are contrary to Plaza et al. (2002), who found a significant increase in FA with the slurry application. It could mean that long-term slurry fertilisation lead to quantitative and structural changes in the soil HA pool in agricultural soil. Such changes were observed in the spectroscopic analysis, in N, soil aromaticity and aliphaticity.

We expected to find N in the spectrograms related to the SOM application rate as they were clearly observed in the slurry spectrograms (Fig. 3.5). However, no changes in the N-related peak intensities were detected with the FTIR method, as the linear regressions hold big standard deviations. On the one hand, N applied with slurries would be used by plants, easily lost by volatilisation or moved to deeper layers in the soil profile as reported in other investigations (Antezana, et al. 2016; N'dayegamiye and Côté, 1989; Sánchez and González, 2005; Yagüe et al., 2012). On the other hand, N would be masked by other bands, as the aromatic C=C and C=O in the 1650 cm^{-1} band as suggested by Konnonova (1982). In fact, in the PCA analysis, 1650 cm^{-1} absorption band was located next to the C=C aromatic and the 1550 cm^{-1} band was suited between the syringyl and the guaiacyl absorption bands (Fig. 3.7b).

Aromaticity was negatively related to the SOM application rate. It was forecasted because the slurries are considered raw materials with low humification degree (Provenzao et al., 2014). The UV-VIS results corroborated these assumptions, as the E4/E6 ratios higher than five in most of the cases because of the slurry composition (low C content). It has been reported that organic structures rich in carbon and poor in oxygen show high absorbance at 665 nm (Tinoco et al., 2015). Furthermore, high values in E4/E6 ratio indicates the presence of aromatic humic components with a low degree of condensation and low molecular weight infer the presence of relatively large proportions of aliphatic structures (Chen et al., 1977; Gosh and Schnitzer, 1979).

Aromatic components of the HLS seemed to decrease while a significant enhance in the intensity of the alkyl peaks with the increase of SOM rates agree with U-VIS results (Fig. 3.6). An enrichment of the less stable compounds added with the slurries would explain the corresponding relative decrease in the intensity of the aromatic structures including the characteristic FT-IR lignin pattern but not the C mineralisation.

The addition of raw material as slurries increased SOM, due to incorporation of structures of aliphatic character, mainly polyalkyl. After 14 years of slurry application the biological transformation through the development of an important bacterial biomass, whose lipoproteic composition is reflected in the long-term, would change the molecular composition pre-existing SOM, which show a relative decrease in its original aromaticity. Some authors have reported that HLS of organic fertilisers are characterized by higher aliphatic character and molecular heterogeneity, and low aromaticity (Brunetti et al., 2007; Piccolo et al., 1992; Senesi et al., 2007) and the resulting relative decrease in the aromatic peak intensities in long-term experiments has been observed (Almendros et al., 1989; Dorado et al., 2003).

The PCA analysis (Fig. 3.7) highlighted the differences in HLS composition among the mineral treatment (M120) and the one with the highest slurry rate (F90). The bands related to aromatic and lignin structures were located in the same quadrant as M120, while the aliphatic bands were in the same quadrant to the F90. These findings agree to the negative relation between SOM and some aromatic or lignin aromatic peaks (1620, 1420, 1270 cm^{-1}), as well as to the positive relation between SOM and the aliphatic peak intensity (1460 cm^{-1}). The enhanced intensity of the aliphatic peaks with pig slurry fertilisation was previously reported (García-Gil et al., 2004; Plaza et al., 2002). Plaza et al. (2002) suggested that aliphatic structures, are partially accumulated by incorporation into the soil HAs.

Slurry composition enhanced its transformation into the soil and its assimilation by plants, leaving few signs at the structural level. In our case, these changes were observed only in the treatments with the highest slurry rates (F70 and F90), which overpass the recommended dose for those areas.

The slurries are useful as nutrients source in a short-term period, and the importance of following good management practices in order to maintain the equilibrium in the system. The recommended dose (170 kg N ha^{-1} y^{-1}) is adequate to maintain the equilibria between agronomical productions and SOM maintenance in these dryland Mediterranean conditions. The increase of HA by slurry fertilisation should not be accounted as a long-term stable C reservoir because aliphatic structures would be easily degraded if conditions are favourable because it increases the mineralisation rate, as reported in other experiments (Madrid et al., 2004, Almendros et al., 2018).

CONCLUSIONS

Long-term slurry application produced changes in total SOM and in the HA. According to the FT-IR analysis, this increase was mainly due to incorporation of structures of aliphatic character, mainly polyalkyl, as would be expected of the contribution of a raw material after biological transformation is reflected in the long-term, in changes in the molecular composition of the pre-existing SOM, which show a relative decrease in its original aromaticity.

Easily degradable compounds coming from slurry produced a fast mineralisation into the soil, thus as small changes were observed after 14 years of slurry fertilisation. These changes were only observed in highest SOM rates (F70 and F90), which overpass the recommended doses. It strengthens the need of follow the recommended rates in these areas to maintain grain yield. Finally, these findings suggest that the quantitative increase of HA by slurry fertilisation should not be accounted as a long-term stable C reservoir.

ACKNOWLEDGMENTS

Lab assistance: M. Antúnez and S. Porras from University of Lleida and to the Nationa Museum of Natural Sciences, for the support in the perform of the spectroscopic analyses. Funding: Spanish Ministry of Economy and Competitiveness and the Spanish

National Institute for Agricultural Research and Experimentation (MINECO-INIA) through the projects RTA2013-57-C5-5 and RTA2017-88-C3-3. D.E. Jiménez-de-Santiago also acknowledges the JADE-Plus scholarship from Bank of Santander-University of Lleida for PhD studies.

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SUPPLEMENTAL MATERIAL

Table 3.S1.

Concentration of soil humic acids (HA), fulvic acids (FA),) and total humic extract (THE) in calcimorphic agricultural soil, Mean content and standard deviation (*n* = 9). Means with the same letter and columns without letter are not significantly different (Tukey's Studentized Range Test, α > 0.05).

Treatment	FA	SD	HA	SD	THE	SD
		------------------ -- (g C·kg^{-1} soil) --------------------				
M120	0.95	0.22	1.50 c	0.28	2.45 c	0.31
F20	0.61	0.46	1.85 bc	0.29	3.04 bc	0.52
S60	1.08	0.37	2.27 ab	0.41	3.35 ab	0.18
F40	1.47	0.60	1.77 bc	0.26	3.24 abc	0.71
F30	0.92	0.36	2.36 ab	0.88	3.28 ab	0.73
S90	0.91	0.55	1.90 bc	0.35	2.81 bc	0.34
F50	0.84	0.21	2.65 a	0.84	3.48 ab	0.73
F70	1.42	0.92	2.27 ab	0.49	3.49 ab	0.39
F90	1.34	0.25	2.62 a	0.70	3.95 a	0.65

Treatments codes are as follow: the letter indicates if the slurry comes from fattening, from sows or from mineral fertiliser (codes F, S or M, respectively). The number indicates the annual application rate 20, 30, 40, 50, 60, 70 and 90 Mg ha^{-1}). The mineral treatment was fertilised plot with ammonium nitrate, phosphorus and potassium (120-40-56 kg ha^{-1} yr^{-1}).

Table 3.S2.

Analysis of variance of the different fractions of soil organic matter in a calcimorphic agricultural soil. Free organic matter (FOM), free fulvic acids (FFA), humic acids (HA), and total humic extract (THE) were evaluated (*n* = 9).

		---- FOM ----		----- FFA -----		----- HA -----		---- THE ----	
Source	df	MS	*P*	MS	*P*	MS	*P*	MS	*P*
block	2	0.0132	0.0002	$4.43E^{-06}$	0.9442	0.0490	<0.0001	0.0059	0.1361
treatment	8	0.0025	0.0750	$2.99E^{-05}$	0.9236	0.0141	<0.0001	0.0168	<0.0001
Error	70	0.0013		0.0001		0.0017		0.0029	

df: degree freedom

MS: mean square values

P: probability

Table 3.S3.

Analysis of variance of the V-VIS analysis for E4, E6 and E4/E6 ratio (*n* = 9).

		--------- E4 ---------		--------- E6 ---------		------- E4/E6 -------	
Source	df	MS	P	MS	P	MS	P
Block	2	0.008	0.035	0.013	0	30.936	0.003
Treatment	8	0.004	0.069	0	0.92	0.956	0.968
Error	16	0.002		0.001		3.582	

df: degree freedom

MS: mean square values

P: probability

CHAPTER 4

Soil water repellency after slurry fertilization in dryland agricultural system

This chapter contains the following accepted and already online published paper in the journal *CATENA*.

Jiménez-de-Santiago, D.E., M.R. Yagüe, and À.D. Bosch-Serra. 2019. Soil Water Repellency after Slurry Fertilization in a Dryland Agricultural System. *Catena* 174: 536–45. doi:10.1016/j.catena.2018.11.040.

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SOIL WATER REPELLENCY AFTER SLURRY FERTILIZATION IN A DRYLAND AGRICULTURAL SYSTEM

ABSTRACT

In the context of the circular economy, the use of animal excrements as fertilizers is encouraged, but the addition of such organic materials can develop soil water repellency (SWR) or hydrophobicity. There is a lack of consensus about how to assess SWR in agricultural soils. This work evaluated SWR when pig slurries were applied onto soil using the two most common testing methods: the water drop penetration time (WDPT) and the molarity of ethanol droplet (MED) tests. The experiment consisted of five different slurry treatments plus a control (no slurry added). At sowing, slurry from fattening pigs (SF) or no slurry application was combined with a second application at the cereal tillering stage, in which SF, slurry from sows (SS) or no-slurry were the treatments. Soil water repellency was tested at cereal tillering before slurry application and then during the following 47 days. At each sampling date, hydrophobicity was tested in undisturbed samples at field-moist and after 25 °C, 65 °C, and 105 °C oven drying. Disturbed samples were tested after 40 °C oven drying. Soil disturbance removed SWR. Under field conditions, undisturbed samples attained the maximum SWR expression 7d from pig slurry application; moderate and very severe scores using WDPT and MED were respectively attained. From 14d to the end of the experiment, the highest SWR was observed after 105 °C oven drying and when SF applications at sowing (900 kg TOC ha^{-1}) had been combined with SS applications at cereal tillering (1894 kg TOC ha^{-1}). Slurry hydrophobic compounds rather than slurry dry matter influenced SWR expression which is enhanced as the soil dries. The persistence of repellency (WDPT test) was more sensitive to detecting changes in SWR between treatments than the changes in its severity (MED test). The importance of the SWR described hereafter slurry application will depend on plant cover over the soil and the effects in slaking prevention in order to avoid superficial water runoff.

Abbreviations: LIF, slurry liquid fraction; MED, molarity ethanol droplet; OChi, hydrophilic organic carbon; OCho, hydrophobic organic carbon; TOC, total organic carbon; SF, slurry from fattening pigs; SOF, slurry solid fraction; SS, slurry from sows; SWR, soil water repellency; WDPT, water drop penetration time; WEOC, water extractable organic carbon.

Keywords: hydrophobicity, land use, organic materials, soil moisture, water repellency tests

HIGHLIGHTS

Pig slurry develops transitory soil water repellency (SWR) lasting for 47 days.
The strongest SWR is recorded seven days after pig slurry addition.
Hydrophobic compounds in solid and liquid slurry fractions explain SWR persistence.
Soil sample management and moisture content influenced SWR expression.

INTRODUCTION

Manures and slurries produced in intensive livestock farming systems are used as organic fertilizers (i.e. in the circular economy). Under conventional tillage, slurries applied to winter cereals are buried, but they remain on the soil surface when applied as topdressing at the cereal tillering stage.

This fact could contribute to soil water repellency (SWR), since the SWR is generally caused by the presence of organic compounds, such as humic and fulvic acids and fatty waxes, which can coat individual soil particles and aggregates (Bisdom et al., 1993). In particular, pig (*Sus strofa domesticus*) slurries contain hydrophobic organic compounds (Gigliotti et al., 2002; Leelamanie, 2014). They can be present as phenols, hydrocarbons, fatty acids and quinones in soil, which produce SWR, also called soil hydrophobicity (Doerr et al., 2000).

Soil water repellency is considered a transient property (King, 1981; Doerr et al., 2000; Laudicina et al., 2015), although, in some cases, such as in fire-affected soils, it can last for many years (Mataix-Solera et al., 2011). Extensive research has been conducted on hydrophobic soils in different geographical areas (Cerdà and Doerr, 2007; Burguet et al., 2016) in natural (Zavala et al., 2009; Jiménez-Morillo et al., 2016) or under induced conditions which can be subdivided into land uses (Doerr et al., 2006), waste water for irrigation (Abegunrin et al., 2016), tillage management (Blanco-Canqui and Lal, 2009), fire affected soils (Jordán et al., 2014) and fertilization management under laboratory (Pagliari et al., 2011; Leelamanie, 2014) or under field conditions (Hassouna et al., 2010; Laudicina et al., 2015).

Soil water repellency development has many impacts (Doerr et al., 2000), such as to decrease plant water availability through a reduction in water infiltration (Wallach et al., 2005). The impact is more relevant in rainfed agricultural systems where water availability is the main limiting factor for crop growth and development. Moreover, SWR could change the soil's ability to sequester carbon as it increases the soil organic matter stability against microbial decomposition (Goebel et al., 2011).

Some studies have demonstrated that SWR has beneficial consequences in stabilizing soil aggregates (Cosentino et al., 2010), and subcritical or light-moderate water repellency in soils can improve the resistance of aggregates against slaking (Eynard et al., 2004; Blanco-Canqui and Ruis, 2018). In this dryland system, slaking is the main agent for aggregate breakdown (Bosch-Serra et al., 2017).

Quantification of SWR has been addressed in several different studies (DeBano, 2000; Dekker et al., 2003). Different methodologies have been compared (King, 1981; Doerr, 1998) and variations of their parameters have been tested (Dekker et al., 1998, 2009). The most frequently methods used are: i) the water drop penetration time test (WDPT; Letey, 1969), which determines how long water repellency persists in the contact area of a water droplet, and ii) the molarity of an ethanol droplet test (MED) (King, 1981; Roy and McGill, 2002), which indirectly measures how strongly water is repelled. The SWR evaluation can vary according to the procedure used, as SWR is sensitive to sample disturbance and soil moisture (Dekker et al., 1998; Badía et al., 2013). Water repellency measured on field-moist samples has been referred to as “actual water repellency,” whereas that measured on 105 °C dried samples has been called “potential water repellency” (Dekker and Ritsema, 1994).

A previous step in SWR evaluation after slurry application over soil is to choose the most suitable test, because not all methods are suitable for all kinds of samples (Papierowska et al., 2018). There is a lack of information about actual and potential

SWR related to slurry application and it is difficult to compare results between different methods. Zavala et al. (2009) reported a low correlation between WDPT and MED methods in cultivated soils in which olives are grown but a stronger one in soils under forest vegetation. Other studies (Badía et al., 2013) re- ported a good correlation between WDPT and the MED test applied over natural soils with natural SWR. Miller et al. (2017) showed similar repellency findings using WDPT and MED measured on disturbed samples. Thus, the varied findings of these authors indicated that when a soil has a moderate or severe water repellency it may persist for a long time, but it does not always do so.

As slurries are applied before sowing (buried before 24 h after application) and at cereal tillering stage, the initial slurry spreading might enhance SWR at tillering. Nevertheless, in conventional tillage, since the slurries are buried at sowing, we do not expect to find any serious immediate SWR because tillage has been reported as a physical solution to SWR (Müller and Deurer, 2011; Laudicina et al., 2015). In addition, soil hydrophobicity might quickly disappear during the cropping season compared with fire-affected or waste-water irrigated soils, in which SWR can last up to 6 years (Mataix-Solera et al., 2011).

The aims of this work were: i) to quantify the impact of pig slurries of different composition, applied as topdressings on a winter cereal crop, on SWR and its evolution, with or without a previous slurry application at sowing; ii) to assess the two most common methods for SWR evaluation when fertilizing with PS. Our hypothesis is that the addition of hydrophobic substances contained in pig slurries to the soil surface can cause SWR, mainly at cereal tillering, although its persistence will be reduced in time and the intensity may vary according to origin of the pig slurry. The general assessment will be also influenced by the soil water content of the sample and the drying temperature applied in the evaluation process.

MATERIALS AND METHODS

Soil and climate conditions

The experimental field was located in Oliola, Lleida, NE of Spain: the coordinates are 41° 52′ 30″ N, 1° 09′ 17″ E, with altitude of 440 m a.s.l. The region has a semiarid Mediterranean climate. During the 2002–2016 period, the mean daily temperature of the hottest month (July) was 23.4 °C and of the coldest month (January) it was 2.9 °C. The daily meteorological data, also for the winter cereal growing season (2014/15) were obtained from the field's automatic meteorological station (Fig. 4.1). The soil is deep (> 1 m) and calcareous. It is classified as a Typic Xerofluvent (Soil Survey Staff, 2014). Some relevant characteristics of the upper layer (0–0.30 m) are: silty loam texture (131 g kg^{-1} sand, 609 g kg^{-1} silt, and 260 g kg^{-1} clay); pH of 8.2 (1:2.5; soil:distilled water), average organic carbon content of 11.67 g kg^{-1} and calcium carbonate content of 300 g kg^{-1}.

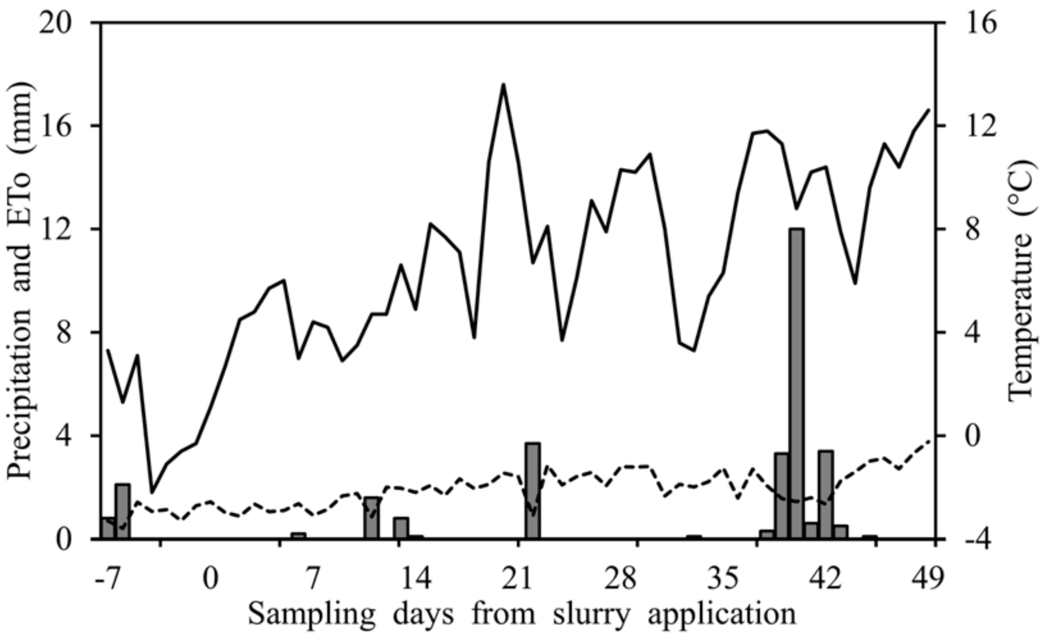

Fig. 4.1. Daily meteorological conditions from slurry application at cereal tillering. Precipitation (gray bars), evapotranspiration, (ET0; dotted line) and mean air temperature (uninterrupted line) are shown.

Description of the experiment

The framework of the research described is an experiment dealing with pig slurry fertilization established in 2002, where treatments have been maintained in the same positions on the plots since then. Winter cereals were cropped on the experimental site with the exception of 2007/08 and 2013/14 cropping seasons when it was left under fallow. The rotation was the common one used in the area, with barley (*Hordeum vulgare L.*) and wheat (*Triticum aestivum L.*) as the main crops. Usually, the crops were sown in late October-early November and harvested at the end of June-early July. The agricultural practices related to the use of herbicides and insecticides followed the re-commendations of the farm advisory system of the area. The experiment was carried out during the 2014/15 winter barley cropping season. Sowing was done on the 30th October 2014 and harvest on the 12th June 2015.

Pig slurry treatments (Table 4.1) were always spread by the splash-plate method. Slurry rates were applied by an adjustment of tractor speed and supervised by differences of tank weight after each application. They were split prior to sowing (23th October 2014) and at cereal tillering stage (21–24 of Zadoks-Chang-Konzak decimal scale; Zadoks et al., 1974) on the 10th February 2015. The field was disc harrowed on the same day after slurry application pre-sowing but it was left on the soil surface at cereal tillering. Treatments were established according to a split-block design with three blocks (repetitions). At sowing, half of the experimental plots received slurry from fattening pigs at rate of 25.1 Mg ha^{-1} (code F2) and the other half did not (code 0). At cereal tillering, the slurry application type was randomized against the block. Treatments at sowing were combined or not with slurry from fattening pigs applied at a topdressing a rate of 42.1 Mg ha^{-1} (code F4) and with slurry from sows at a rate of 75.8 Mg ha^{-1} (code S8). In the control (code 0-0), no slurry was applied but P (40 kg ha^{-1}) and K (56 kg ha^{-1}) were added as mineral fertilizer. Treatments were done in triplicate (three blocks). Thus, a total of 18 plots: six treatments in three blocks were set up. The plot size was 137.5 m^2 (11 m wide and 12.5 m long) with the exception of the control, which was 87.5 m^2 (7 m wide and 12.5 m long).

Table 4.1.

Pig slurry (PS) rates, total N (TN), organic N (ON) and total organic carbon (TOC) applied at sowing and at cereal tillering stage for the different slurry treatments (TRTM). At tillering, specific organic components: water extractable organic carbon (WEOC), hydrophobic (OCho) and hydrophilic organic compounds (OChi); are shown for the PS and for its liquid fraction (LIF).

Treatments[a]	Sowing				Tillering				Raw slurry components at tillering			LIF slurry components at tillering			
	Rate	TN	ON	TOC	Rate	TN	ON	TOC	WEOC	Ochi[b]	OCho[b]	LIF	WEOC	OChi[b]	OCho[b]
	Mg ha^{-1}	kg ha^{-1}			Mg ha^{-1}	kg ha^{-1}						Mg ha^{-1}	kg ha^{-1}		
0-0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0-F4	0	0	0	0	42	240	72	682	325	200	125	40	323	199	124
0-S8	0	0	0	0	76	258	114	1894	287	187	100	71	283	184	99
F2-0	25	171	48	900	0	0	0	0	0	0	0	0	0	0	0
F2-F4	25	171	48	900	42	240	72	682	325	200	125	40	323	199	124
F2-S8	25	171	48	900	76	258	114	1894	287	187	100	71	283	184	99

[a] Codes for treatments. The number before the hyphen indicates the rate of slurry applied at sowing: 0, no slurry applied; 2, slurry from fattening pigs (F) applied at a rate of 25 Mg ha^{-1}. The number after the hyphen indicates the rate of slurry applied at tillering: 0, no slurry applied; 4, slurry from fattening pigs (F) applied at a rate of 42 Mg ha^{-1}; 8, slurry from sows (S) applied at a rate of 76 Mg ha^{-1}.

[b] Obtained from the associated WEOC fraction in raw slurry on in the liquid slurry fraction.

A composite slurry sample was taken from each tank at the time of application and it was analyzed in laboratory for chemical composition (Table 4.2). The analyzed parameters were: pH, electrical conductivity at 25 °C (1:5, slurry: distilled water), gravimetric dry matter content at 105 °C, total N and $NH4^{+}$-N by the Kjeldahl method (APHA, 1998) being the difference between both the organic-N.

Table 4.2

Physicochemical values of pig slurries applied at sowing from fattening pigs and at cereal tillering from fattening pigs or sows during the 2014/15 cropping season. At tillering, specific organic components for the pig slurry liquid fraction (LIF) and solid fraction (SOF, i.e. dry matter) are shown.

Parameters	Sowing (Oct.)	Tillering (Feb.)			
	Fattening	Fattening		Sows	
	Raw	Raw		Raw	
pH (1:5)[a]	8.7	8.4		8.3	
Electrical conductivity (1:5, dS m^{-1}, 25ºC)[a]	6.0	6.4		2.5	
Dry matter (kg Mg^{-1})	101.9	49.4		66.2	
Organic N (kg Mg^{-1})	1.9	1.7		1.5	
Total N (kg Mg^{-1})	6.8	5.7		3.4	
Total organic C (kg Mg^{-1})	35.9	16.2		25.0	
		LIF	SOF	LIF	SOF
Water extractable organic C (kg Mg^{-1})	--	8.1	0.9	4.0	0.8
Hydrophobic organic C (kg Mg^{-1})	--	3.1	0.4	1.4	0.3
Hydrophilic organic C (kg Mg^{-1})	--	5.0	0.5	2.6	0.6

[a]Ratio 1:5, slurry: water

Total organic carbon (TOC) was analyzed by combustion from pig slurry samples (TruSpec CN, LECO instruments). The solid (SOF) and liquid (LIF) slurry fractions from the fresh slurry samples were separated by centrifugation. Afterwards, SOF was freeze-dried, milled with an Agatha mortar, dissolved for 24 h in water (1:20, milled slurry: distilled water), and centrifuged prior the 0.45 μm filtration. The filtrates contained the water-ex- tractable organic carbon

(WEOC). Then, the hydrophobic (OCho) and the hydrophilic (OChi) carbon compounds were obtained from the WEOC for each fraction (LIF and SOF) with amberlite XAD-8 resin, following the method proposed by Gigliotti et al. (2002). The WEOC concentrations in the bulk SOF and LIF solutions and the OChi were obtained from the resin column effluents and they were measured by using Pt-catalyzed, high temperature combustion (800 °C) followed by infrared detection of the CO2 produced (MULTI N/C 2100/2100S, Analytik Jena AG, Jena, Germany). The OCho was calculated by the difference between the WEOC and the OChi.

Soil water repellency analyses

The first soil sampling was done the 6th February 2015, four days before slurry spreading at cereal tillering. Further samplings were taken at 7, 14, 21, 30, 35 and 47 days after pig slurry application. Samplings stopped when the canopy fully covered the plot surface. At each sampling date, four steel cylinders of 0.06 m diameter and 0.05 m depth full of soil were taken per plot. Soil samplings were performed following two theoretical lines; 3 m inside each plot and perpendicular to the pig slurry application for minimizing eventual heterogeneity in slurry application over plots. Samplings did not overlay each other as each sampling cylinder was always taken from close neighboring areas to the previous sampling and following the theoretical lines. Cylinders were pressed vertically into the soil, then carefully removed from the surface, avoiding superficial disturbance, packed into plastic bags and closed to maintain field soil moisture content until they arrived at the laboratory. Soil water repellency was quantified in undisturbed soil samples using two cylinders, and after soil disturbance using the two additional ones.

The two most common methods (WDPT and MED) for assessing persistence and intensity of SWR were used. The WDPT consisted of placing a water droplet using a dropper on a soil sample surface. The time spent until the drop infiltrated into the soil was recorded. The SWR persistence was classified according to the infiltration time expressed in seconds: ≤ 1, non-repellent; 1–10, very low; 10–50, low; 50–260, moderate; > 260, moderate to very severe

(Hazelton and Murphy, 2007 adapted from King, 1981). The MED was performed following Roy and McGill (2002) in order to quantify the severity of SWR. Solutions were prepared at different molar concentrations using ethanol (99.5% v/v) and distilled water. In order to better define differences between fertilization treatments, a concentration scale was adapted. The molarity range used was 0.2, 0.4, 0.6, 0.8, 1, 2, 3, 4 and 5 M. The method consisted of a drop of the ethanol solution being placed on a soil surface and recording its infiltration time. Repellency was defined by the lowest drop of alcohol molarity that penetrated the soil in 10 s or less. Classical grading (in sandy soils) follows the classification: ≤1, low; > 1–2.2, moderate; > 2.2–3.0, severe; > 3.0, very severe (King, 1981) and where the droplet entry time of 10 s represents the linear regression between $\log_{10}$ droplet entry time and molarity of ethanol.

In undisturbed samples the soil surface was randomly divided into two areas. As soil water content influences repellency, WDPT and MED were evaluated at field-moist sample conditions and after successively drying the soil at different temperatures for 48 h (25 °C, 65 °C, and 105 °C) in a ventilated oven, followed by 24 h of cooling down using a desiccator. Soil moisture content was calculated and analyzed for each drying temperature (Fig. 4.2, Table 4.S1).

In the two cylinders of the disturbed samples, soil in each cylinder was mixed and dried in an oven at 40 °C for 48 h and cooled down for 24 h. Afterwards, these samples were sieved through a 2 mm mesh and the repellency was also measured applying WDPT and MED.

All the tests were done in triplicate in each cylinder in disturbed and undisturbed samples and at different temperatures, always avoiding any superposition between the droplets.

Considering that 72 cylinders (36 disturbed and 36 undisturbed samples) were taken in each of the 7 sampling dates, and the application of WDPT and MED tests at the 5 drying temperatures was done in triplicate (3 droplets), > 7500 repellency measurements were done.

Statistical analysis

The normal distribution and homogeneity of the data were evaluated. Data (x) from WDPT, was normalized using the log (x + 1) transformation. In MED scores, the average of the measurements (n = 3) in each cylinder was calculated, which implies that the absolute number of values to be analyzed was reduced to a third when compared with WDPT. No data transformation was performed for these MED averages as they fitted normality. The differences in SWR between treatments at each sampling day and temperature were evaluated by ANOVA (Tables 4.3 and 4.4). If the interaction between treatments was statistically significant, each combination of treatments was compared with the rest of the combinations with the multiple comparison analysis of Tukey (Tables 4.S2 and S4). If the interaction was not statistically significant, the effect of slurry application at sowing or at tillering on SWR was independently checked (Tables 4.S3 and 4.S5) according to Duncan's multiple range test ($\alpha = 0.05$). The statistical analyses were performed with the statistical package SAS version 9.4 (SAS Institute Inc., 2002–2013).

RESULTS

Slurry from sows (76 Mg ha^{-1}) was applied at cereal tillering stage at a higher rate than SF (42 Mg ha^{-1}) based on N criteria. In practice, it resulted in 240 and 258 kg N ha^{-1} being applied with SF (F4) and SS (F8), respectively. Although these TN numbers were very close (8% difference) it resulted in bigger ON and TOC differences in SS, when compared with SF (Table 4.1), 58% and 178% higher, respectively. The distribution of the organic compounds in the slurry WEOC indicates that OChi components predominate over the OCho ones (Table 4.1) in raw slurries and in their LIF. The slurry LIF fraction accounted for 99% of the total raw slurry WEOC component (Table 4.1).

After slurry spreading, mean soil water content decreased during the 35 following days and it rose following rainfall events (Fig. 4.1). Slurry treatments led to differences in the superficial (0–0.05 m) field soil water content at 7 and 21 days after slurry spreading at tillering (Fig. 4.2). One week after spreading, plots not receiving slurries were the driest (11%, w/w) and plots receiving SS the wettest (15%, w/w). Two weeks later (21d after spreading), SS plots still maintained the highest soil water content (9%, w/w). When testing for SWR, most of the water content in soil samples was eliminated after 25 °C drying and no significant differences were found between slurry treatments in soil water content after drying at different temperatures (analysis not shown).

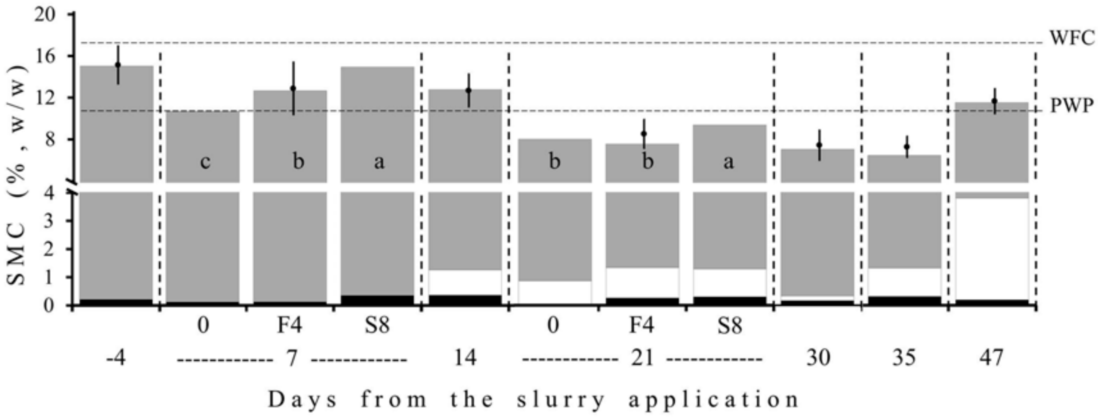

Fig. 4.2. Mean (n = 36) soil water content SWC at the field-moist (gray bars) and after 25 °C (black + white) or 65 °C (black) oven drying. Data for 25 °C drying at the first two sampling days was lost. For samplings done 7 and 21 days from slurry application, SWC was broken down according to the slurry rate applied at cereal tillering (F4: 42 Mg ha^{-1}, S8: 76 Mg ha^{-1}) as ANOVA analysis indicated significant differences between treatments. Different letters at the top of the columns indicate significant differences ($\alpha = 0.05$) in SWC. Soil water content at field capacity (WFC) and at permanent wilting point (PWP), are represented by long dash lines parallel to the *x* axis.

The disturbed samples did not show repellency at any sampling date or methodology (WDPT and MED), whatever the treatment was. No repellency was detected four days before pig slurry application at tillering, as a consequence of SF application at sowing ~3.5 months previously (F2–0), nor in the control (0–0), whatever the method of evaluation was (Figs. 4.3 and 4.4).

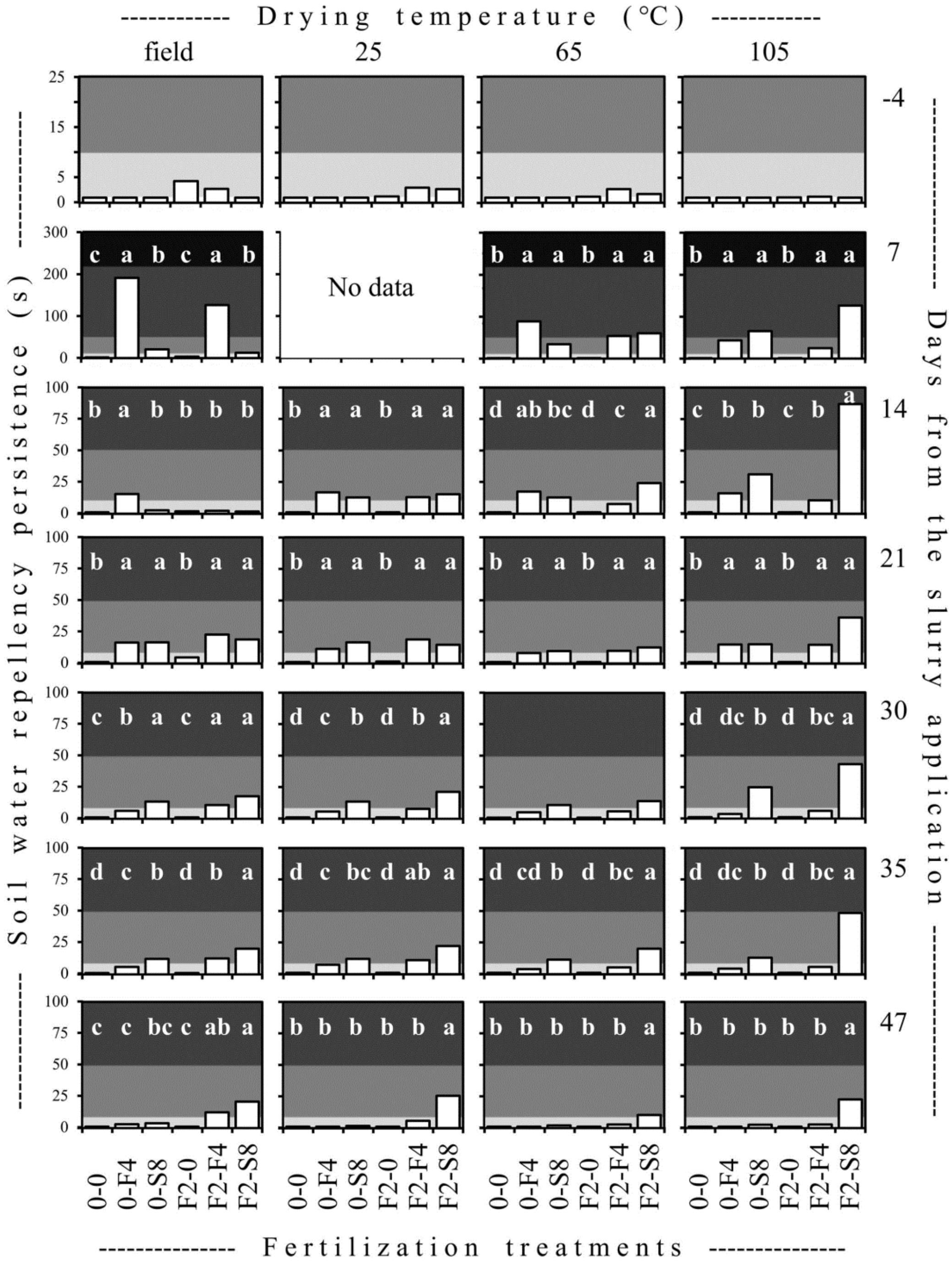

Fig. 4.3. Soil water repellency accordingly to the applied WDPT test at seven sampling dates (−4, 7, 14, 21, 30, 35 and 47 days) before and after the slurry application, at cereal tillering stage, and for the different fertilization treatments. Background colors indicate the degree of water repellency according to King (1981): non-repellent (white), very low (light gray), low (gray), moderate (dark gray) and, moderate to very severe (black). Bars with different letters indicate significant differences between pairs of means ac- cording to the Least Squares Means adjustment for multiple comparisons: Tukey test ($\alpha < 0.05$) when an

interaction between slurry rates applied at sowing and at tillering was detected. When no interaction was detected differences were established according to the Duncan multiple range test ($\alpha = 0.05$). Codes for treatments: the number before the hyphen indicates the rate of slurry applied at sowing: 0, no slurry applied; 2, slurry from fattening pigs (F) at a rate of 25 Mg ha^{-1}. The number after the hyphen indicates the rate of slurry applied at tillering: 0, no slurry applied; 4, slurry from fattening pigs (F) at a rate of 42 Mg ha^{-1}; 8, slurry from sows (S) at a rate of 76 Mg ha^{-1}.

The degree of SWR changed with time and soil moisture. The highest hydrophobicity was found in both tests, at 7d from slurry application at tillering and at field moisture, being qualified as in the moderate or very severe class with WDPT and MED, respectively (Figs. 4.3 and 4.4). It decreased at 14d sampling to a low and very low class (WDPT and MED grades, respectively). From 21d sampling, low SWR class (moderate for F2-S8) was maintained until the end of the experiment in the WDPT (Fig. 4.3) and very low for MED (Fig. 4), no matter which drying temperature was applied.

Furthermore, pig slurry application at tillering led to an interaction with slurry applied at sowing. When WDPT was used (Fig. 4.3), the interaction was detected at 14d (except at 25 °C), 30d (except at 65 °C), 35d, and 47d samplings (Table 4.3). When using the MED method (Fig. 4.4) the interaction was detected at 7d (field conditions), 14d (105 °C), 21d (field conditions), and 35d (25 °C, 65 °C, 105 °C) samplings (Table 4.4). In both cases, the general trend was that the application at sowing enhanced SWR in S8 when WDPT and MED tests were done after drying at the highest (105 °C) temperature, which was not the case in F4. In F4 applications the described interaction was mainly observed at field moisture or at the lowest drying temperature but with a more erratic behavior depending upon the time from slurry application, although it was mainly observed from 14d onwards samplings (WDPT, Fig. 4.3) and at 21d sampling (MED, Fig. 4.4). The persistence of the SWR (WDPT method) was more sensitive to differences between treatments and temperatures than the initial severity of the SWR (MED method) (Figs. 4.3 and 4.4).

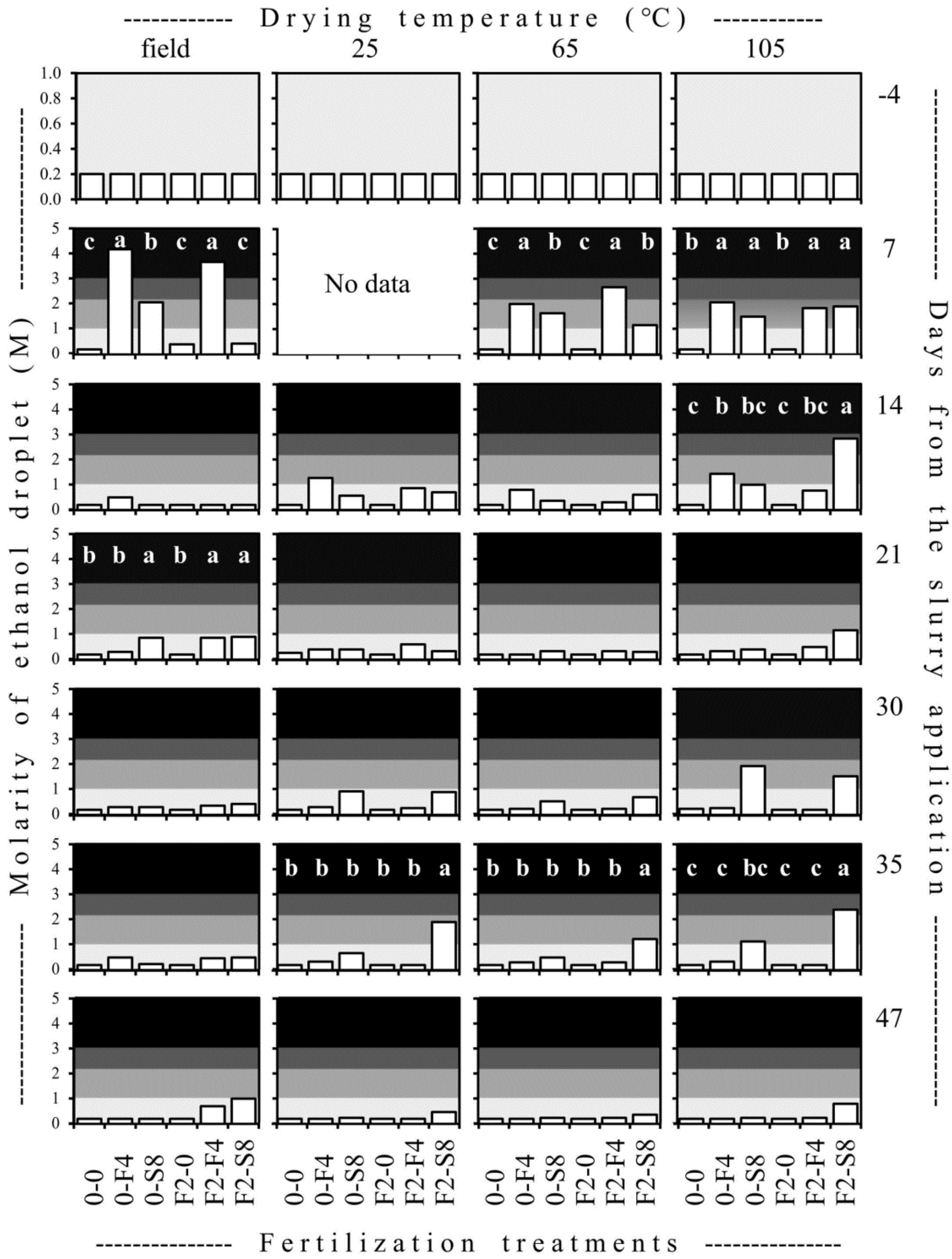

Fig. 4.4. Soil water repellency accordingly to the MED test at seven sampling dates (−4, 7, 14, 21, 30, 35 and 47 days), from the slurry application at tillering stage and for different fertilization strategies. Background colors indicate the degree of water repellency according to King (1981): low (light gray), moderate (gray), severe (dark gray) and, very severe (black). Different letters on columns indicate significant differences between pairs of means according to the Least Squares Means adjustment for multiple comparisons: Tukey test (α < 0.05) when an interaction between slurry rates applied at sowing and at tillering was

detected. When no interaction was detected differences were established according to the Duncan multiple range test (α = 0.05). Codes for treatments: the number before the hyphen indicates the rate of slurry applied at sowing: 0, no slurry applied; 2, slurry from fattening pigs (F) at a rate of 25 Mg ha^{-1}. The number after the hyphen indicates the rate of slurry applied tillering: 0, no slurry applied; 4, slurry from fattening pigs (F) at a rate of 42 Mg ha^{-1}; 8, slurry from sows (S) at a rate of 76 Mg ha^{-1}.

Table 4.3

Soil water repellency ANOVA analysis (simplified output) when the water drop penetration time test was used at different drying temperatures and sampling days (S- DAY) from slurry spreading before sowing (BS) or at cereal tillering (CT). Data was normalized using the log (WDTP + 1) transformation.

Temperature		Mean squares for field-moist samples						
S-DAY	df	-4[a]	7	14	21	30	35	47
Block	2	0.38	1.70	5.36***	3.48***	4.33***	2.74***	2.23*
Block * BS	2	0.38	0.52	0.38	0.72	0.44	1.16*	0.06
Block* CT	4	0.75**	3.41*	0.70	1.02**	1.54**	2.00***	2.26**
BS * CT	2	0.40	1.33	2.92**	0.64	1.28*	2.16***	2.99**
Error	94	0.17	1.19	0.39	0.28	0.32	0.29	0.54
BS[b]	1	1.52	0.60	2.64	3.54	4.23	8.63	10.83**
CT[c]	2	0.40	91.98**	3.20	45.51**	30.33**	34.30*	12.55
Temperature		Mean squares for 25ºC dried samples						
S-DAY	df	-4[a]	7	14	21	30	35	47
Block	2	0.57*	--	1.60**	4.46***	12.03***	2.48**	1.99*
Block * BS	2	0.57*	--	0.76*	0.20	0.73	1.73**	0.53
Block* CT	4	0.25	--	0.91**	1.99***	4.00***	5.37***	1.19
BS * CT	2	0.18	--	0.29	0.54	1.42**	2.45**	3.41**
Error	94	0.15	--	0.22	0.21	0.29	0.35	0.54
BS[b]	1	1.28	--	0.33	0.45	5.32	9.79	11.30*
CT[c]	2	0.18	--	41.90**	40.74**	26.20	27.62	6.31
Temperature		Mean squares for 65ºC dried samples						
S-DAY	df	-4 [a]	7	14	21	30	35	47
Block	2	0.61***	2.18*	1.21*	4.488***	10.51***	1.52*	0.86
Block*BS	2	0.61***	2.86**	0.13	0.24	0.61	2.06**	0.11

Block* CT	4	0.33**	1.63*	1.42**	1.82***	4.61***	4.93***	0.67
BS * CT	2	0.23	0.48	3.08***	0.39	0.51	3.01**	1.83**
Error	94	0.07	0.51	0.34	0.19	0.26	0.39	0.32
BS[b]	1	1.14	1.88	0.001	1.44	1.91	7.93	4.79*
CT[c]	2	0.23	117.69***	40.65**	26.80*	16.98	24.41	4.05

Temperature		Mean squares for 105ºC dried samples						
S-DAY	df	-4[a]	7	14	21	30	35	47
Block	2	0.02**	4.30**	2.16*	3.46***	15.74***	8.05***	1.08
Block * BS	2	0.02**	5.99**	0.14	0.21	0.81	5.65***	0.41
Block* CT	4	0.01	1.14	3.66***	1.80**	6.81***	11.72***	0.99
BS * CT	2	0.01	0.42	5.20***	0.50	1.32*	2.57*	2.72**
Error	94	0.004	0.83	0.60	0.36	0.36	0.66	0.51
BS[b]	1	0.02	0.78	1.42	1.41	4.62	7.09	6.59
CT[c]	2	0.01	100.93***	60.66*	45.38**	27.68	43.18	4.92

df: degrees of freedom.

* Significant at 0.05 probability level.

** Significant at 0.01 probability level.

*** Significant at 0.001 probability level.

a Sampling before slurry application.

b Tests of hypothesis using the Block * BS as an error term.

c Tests of hypothesis using the Block * CT as an error term.

Table 4.4

Soil water repellency ANOVA analysis (simplified output) evaluated using the molarity ethanol droplet for different drying temperatures and sampling days (S-DAY) from slurry spreading before sowing (BS) or at cereal tillering (CT).

Temperature		Mean squares for field-moist samples					
S-DAY	df	7	14	21	30	35	47
Block	2	1.15	0.09	0.82***	0.12**	0.06	0.37
Block * BS	2	0.45	0.09	0.12	0.01	0.11	0.37
Block * CT	4	0.63	0.09	0.78***	0.04	0.11	0.34
BS * CT	2	2.57*	0.09	0.30**	0.01	0.08	0.49
Error	22	0.73	0.09	0.06	0.02	0.11	0.49
BS[a]	1	3.74	0.09	0.36	0.04	0.05	1.69

CT[b]	2	42.19***	0.09	1.41	0.09	0.24	0.49
Temperature		Mean squares for 25ºC dried samples					
S-DAY	df	7	14	21	30	35	47
Block	2	--	1.10***	0.16	1.03**	1.20*	0.02
Block * BS	2	--	0.15	0.03	0.17	0.63	0.01
Block * CT	4	--	0.53**	0.25	0.61**	1.64**	0.02
BS * CT	2	--	0.23	0.07	0.001	1.70**	0.05
Error	22	--	0.01	0.09	0.14	0.29	0.03
BS[a]	1	--	0.07	0.004	0.004	1.21	0.05
CT[b]	2	--	2.25	0.21	1.84	4.42	0.09
Temperature		Mean squares for 65ºC dried samples					
S-DAY	df	7	14	21	30	35	47
Block	2	0.3	0.31	0.05	0.30*	0.38	0.004
Block * BS	2	0.02	0.39	0.003	0.07	0.51	0.004
Block * CT	4	0.46	0.55*	0.02	0.26*	0.51*	0.01
BS * CT	2	0.97	0.42	0.02	0.03	0.54*	0.01
Error	22	0.52	0.17	0.02	0.07	0.16	0.02
BS[a]	1	0.04	0.07	0.01	0.03	0.54	0.03
CT[b]	2	13.72**	0.41	0.04	0.64	1.55	0.03
Temperature		Mean squares for 105ºC dried samples					
S-DAY	df	7	14	21	30	35	47
Block	2	1.33	1.03	0.61	5.61***	3.97***	0.11
Block * BS	2	2.53	0.38	0.25	0.16	0.64	0.09
Block * CT	4	0.67	1.28	0.61	5.23***	4.60***	0.10
BS * CT	2	0.31	5.03***	0.49	0.12	1.79*	0.30
Error	22	0.79	0.46	0.31	0.21	0.40	0.16
BS[a]	1	0.03	1.36	0.87	0.25	1.28	0.36
CT[b]	2	10.75*	8.85	1.04	9.10	9.42	0.38

df: degrees of freedom.

* Significant at 0.05 probability level.

** Significant at 0.01 probability level.

*** Significant at 0.001 probability level.

[a] Test of hypothesis using the Block * BS as an error term.

[b] Test of hypothesis using the Block * CT as an error term.

DISCUSSION

Fertilization effect on SWR

In calcareous soils, Ca^{2+} can be linked to aromatic structures (Hassouna et al., 2010) which reduces the natural presence of SWR in these soils (Cerdà and Doerr, 2007). In our case, SWR is mainly due to farming activity linked to slurry applications.

Slurry composition was in the range of the results reported by Yagüe et al. (2012) in the North-Eastern part of Spain, although our dry matter values for SF and SS (Table 4.2) were representative of the low and the high values inside ranges for each slurry origin. The C:N ratio in the SF (2.8) and SS (7.3) slurries was low (Table 4.2). Usually the ratio is much lower than in other organic fertilizers such as urban waste composts or cattle manure (Paetsch et al., 2016; Gómez-Muñoz et al., 2017). A low C:N ratio favors faster degradation. The higher C:N ratio values in SS vs. SF are related to the farm system management, as in Spain, sawdust can be spread over the floor for pregnant sows close to delivery. Higher slurry C:N of the dry matter might increase SWR, as the ratio increases when the labile organic components diminish (Mao et al., 2014), although in our case slurries applied at tillering were close to a liquid product (dry matter < 70 kg Mg^{-1}, Table 4.2). The amount of liquid applied with slurries at tillering (2.1 or 2.6 L m^{-2} in F4 and S8, respectively) were similar but they were associated with differences in the total amount of dry matter applied: 2.1 Mg ha^{-1} in F4 and 5.0 Mg ha^{-1} in S8. These differences were sufficient to lead to significant and gradual differences in soil water content (0–0.05 m) seven days after superficial application although they temporarily disappeared after a low rainfall event (14d, Fig. 4.1). Slurry influences over soil water content reappeared in S8 treatment at the 21d sampling and despite the superficial layer being very dry (below PWP), the small difference in soil water content was enough to smear the interaction with previous slurry applied at sowing (0-S8 vs. F2-S8) which was clearly shown, under field conditions (Fig. 4.3), in the F4 treatment (0-F4 vs. F2-F4). However, in all slurry treatments (21d sampling) SWR was qualified as moderate. The temporary changes in SWR were influenced by the drying-wetting soil pattern, in agreement with Doerr et al.

(2006), Keizer et al. (2007) and Burguet et al. (2016). Nevertheless, the drying-wetting pattern did not restore SWR to the initial level because of the organic matter trans- formation (crust degradation) and pig slurry dilution during the wetting period.

The hydrophobic compound percentages in the WEOC of the raw slurries (38% in SF and 35% in SS, Table 4.1) were similar to those of organic amendments evaluated by other authors (Gigliotti et al., 2002; Said-Pullicino et al., 2007). The amounts of OChi and OCho are mainly present in the slurry liquid fraction but the slurry dry matter content cannot be underestimated as the total amount of OCho applied diminishes as it increases. In our case (Table 4.1), differences in the applied amount of OCho at tillering were found: 100 (S8) vs. 125 kg ha^{-1} (F4) but with very large differences in the total TOC applied: 682 (F4) vs. 1894 kg ha^{-1} (S8). Thus, the amount of OCho compounds is not proportional to the organic matter in pig slurries in agreement with other findings in different organic materials (Doerr et al., 2000, 2006; Contreras et al., 2008; Dekker et al., 2009; Mataix-Solera et al., 2011). This means that higher hydrophobicity is expected in F4 treatments, as was initially recorded (7 days, Figs. 4.3 and 4.4) and also because only a small amount of OCho is necessary to induce changes in soil wettability (Zavala et al., 2009).

As soil dries, the main agent in crust development and the associated hydrophobicity is the SOF, as can be seen when dried at 105 °C (Figs. 4.3 and 4.4) where S8 treatments became SWR relevant, due to their higher dry matter content. As LIF is the only fraction considered in the chemical characterizations (Gigliotti et al., 2002), the potential impact on SWR is not properly accounted for. In our case, the interactions with previous applications (Table 4.S2 and 4.S4) are also important. They can be related to the presence of higher or not fully degraded organic matter, as a positive relation between SWR and Table 4.4. soil organic matter content has also been described (Vogelmann et al., 2013; Leelamanie, 2014; Gao et al., 2018).

Soil sample disturbance by sieving led to a totally wet Table 4.4. soil for any of the sampling dates as it modifies and dilutes the slurry distribution in the soil sample. If slurries develop a crust when drying, soil sieving also breaks it. In the field, a similar process can occur by tillage at sowing time (Blanco-Canqui et al., 2007) which is recommended as a management practice to reduce SWR (Müller and Deurer, 2011; Müller et al., 2016). As disturbance changes the surface roughness and morphology, the OCho compounds arrangement on the surface (Buczko et al., 2006) and consequently the contact between the water droplets, it underestimates potential SWR (Doerr, 1998; Graber et al., 2006; Badía et al., 2013).

Under field conditions (undisturbed soil samples) SWR was a transient soil property although it lasted for 47 days in plots receiving slurries at sowing plus at tillering (F2-F4 and F2-S8, Figs. 4.3 and 4.4). Transitory SWR has also been reported for other organic amendments (Keizer et al., 2007; Leelamanie, 2014). The SWR persistence in soil means a potential reduction of soil water infiltration, mainly during the first week after slurry spreading. A reduction in crop water availability is especially noteworthy in dryland environments, as it is a constraint on maximum yields. Nevertheless, SWR also has a positive effect in these environments as it helps to reduce the superficial soil disaggregation by slaking, acting as a protective coating at the soil surface. The balance between both consequences for actual crop production requires further research.

Methodological approach on SWR

Sample drying causes a superficial slurry crust which is enhanced as the slurry dry matter content increases according to Bosch-Serra et al. (2014). Increasing drying temperatures leads to the rearrangement of hydrophobic compounds and the denaturing of hydrophilic ones, producing a relative increase in the hydrophobic fraction (Dekker and Ritsema, 1994; Dekker et al., 2001) as we observed with different samplings over time, mainly after drying at 105 °C (Figs. 3 and 4). The leverage effect of drying temperature on SWR has been reported (Mirbabaei et al., 2013) and drying soil samples is a widely recommended practice to compare them with respect to their sensitivity to water repellency, because differences in water content are minimized (Dekker and Ritsema, 1994; Dekker et al., 2003). On the other hand, we observed that soil wetting by different rainfall events also reduces SWR (Figs. 4.2 and 4.3).

However, there is no consensus about a specific drying temperature. Actual

SWR, obtained under field moisture conditions, and in agreement with other authors (Dekker et al., 1998; Ziogas et al., 2005; Dekker et al., 2009), allowed us to find a real effect of the pig slurry on hydrophobicity and differences between treatments, although soil water content at each sampling date must be quantified to interpret the results. Dekker et al. (2009) suggested SWR testing in the driest period of the year, but this would not be easily applicable for slurries as they are commonly applied close to rainy periods in dryland systems (if irrigation is not available), as they contain > 90% water and finally, because the strongest SWR effects were found close to slurry spreading (Figs. 4.3 and 4.4). As repellency also depends on the initial soil water content, the 25 °C drying temperature led to erratic results as reported by Ziogas et al. (2005). The 65 and 105 °C drying temperatures showed similar SWR results, with exception of the SS treatments (0-S8, F2-S8) which might reflect the stimulating dry matter effect (when is dried) on SWR. Moreover, the 105 °C drying temperature shows the potential SWR but it would be unrealistic to recommend this from an agronomic point of view. In fact, some authors mentioned the 105 °C drying temperature as a potential but artificial measurement of SWR (Franco et al., 1995; Dekker et al., 1998), which in our case could be also related to some denaturing effect of the organic compounds applied with slurries.

The WDPT was accurate while MED was not sufficiently sensitive to detect differences between treatments over the different sampling days. As MED uses ethanol, it might act as an organic compound solvent, removing low molecular weight polysaccharides and other water-ethanol soluble components (Lawther et al., 1995) which are present in slurries. The results (Table 4.4, Fig. 4.3) showed that MED is not able to detect potential differences in the severity of the actual SWR in pig slurry fertilized soils, as significant differences were only observed after the 105 °C drying temperature.

CONCLUSIONS

In a dryland agricultural system, the use of pig slurries as fertilizer develops transitory SWR although its expression is prevented by soil disturbance.

At cereal tillering, when slurries are not buried, the WDPT test allowed us to detect differences in SWR between treatments over the whole experimental period, but MED did not.

Under field conditions, maximum SWR was observed seven days from slurry spreading, being classified as moderate or very severe according to WDPT and MED procedures, respectively. Repellency was associated with WEOC and OCho compounds, enhancing it as they increased (F4 vs. S8). If samples were dried at 105 °C before repellency testing, the SWR expression was enhanced in treatments with the lowest WEOC but with the highest dry matter (S8). An interaction with a previous slurry application at sowing (F2) was detected. It increased repellency for F4 applications under field conditions or in S8 treatments after drying at 105 °C.

In dryland systems, as the ratio WEOC/TOC diminishes (F4 vs. S8), potential persistence of the water repellency in soil could be measured using the WDPT test at 105 °C oven drying followed by a 24 h cool down period.

ACKNOWLEDGEMENTS

Field assistance from J.C. Estruga, J.M. Llop, B. Martínez and N. Mateo and laboratory assistance from M. Antúnez and S. Porras (University of Lleida); D. Pezzolla, G. Gigliotti and “Laboratorio di Chimica Agraria – Chimica delle Biomasse di Uso Agrario” (University of Perugia) is fully acknowledged. Funding: 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 projects RTA2013-57-C5-5 and RTA2017-88-C3-3. JADE-Plus scholarship from Bank of Santander-University of Lleida for D.E. Jiménez-De-Santiago PhD studies. Grant for linguistic revision from the Language Institute of the University of Lleida.

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SUPPLEMENTAL MATERIAL

Table 4.S1

Soil moisture ANOVA analysis for different sampling days (S-DAY) from slurry spreading before sowing or at cereal tillering.

S-DAY	-4d		7d		14d		21d		30d		35d		47d	
	MS[a]	*P*	MS	*P*	MS	*P*	MS	*P*	MS	*P*	MS	*P*	MS	*P*
Sowing	4.96	0.42	10.72	0.31	11.79	0.11	6.59	0.14	0.06	0.92	0.01	0.96	0.41	0.53
Error term	9.93		11.79		3.01		2.43		8.58		3.08		1.38	
Tillering	1.50	0.83	54.18	0.004	10.41	0.10	10.81	0.03	4.73	0.27	0.95	0.63	2.81	0.23
Error term	3.10		6.40		1.82		1.11		3.75		2.70		0.64	

[a] MS: mean squares.

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Table 4.S2

Statistical differences between treatments in soil water repellency (SWR) transformed data (log (SWR + 1)), according to the multiple comparison analysis of Tukey, when the water drop penetration time test was used at different temperatures and sampling dates after slurry application at cereal tillering. Comparisons were only used when the interaction between the slurry rates applied at sowing and at cereal tillering was significant.

Sampling day	4 days before the slurry application at tillering																			
Temperature	Field					25 °C					65 °C					105 °C				
Treatment[a]	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8
0-0	1.00	1.00	0.05	0.26	1.00	1.00	1.00	1.00	0.40	0.11	1.00	1.00	0.99	0.001	0.27	1.00	1.00	0.92	0.04	1.00
0-F4		1.00	0.05	0.26	1.00		1.00	1.00	0.40	0.11		1.00	0.99	0.001	0.27		1.00	0.92	0.04	1.00
0-S8			0.05	0.26	1.00			1.00	0.40	0.11			0.99	0.001	0.27			0.92	0.04	1.00
F2-0				0.97	0.05				0.70	0.28				0.01	0.61				0.35	0.92
F2-F4					0.26					0.98					0.39					0.04
Sampling day	7 days after the slurry application at tillering																			
Temperature	Field					25 °C					65 °C					105 °C				
Treatment[a]	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8
0-0	<.0001	0.0002	0.95	<.0001	0.003	nd[b]	nd	nd	nd	nd	<.0001	<.0001	1.00	<.0001	<.0001	<.0001	<.0001	1.00	<.0001	<.0001
0-F4		0.002	<.0001	0.86	<.0001		nd	nd	nd	nd		1.00	<.0001	0.47	0.73		0.50	<.0001	1.00	0.03
0-S8			0.004	<.0001	0.97			nd	nd	nd			<.0001	0.40	0.65			<.0001	0.71	0.75
F2-0				<.0001	0.05				nd	nd				<.0001	<.0001				<.0001	<.0001
F2-F4					<.0001					nd					1.00					0.07

Sampling day	14 days after the slurry application at tillering																			
Temperature	Field					25 °C					65 °C					105 °C				
Treatment[a]	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8
0-0	<.0001	0.39	0.92	0.89	0.95	<.0001	<.0001	1.00	<.0001	<.0001	<.0001	<.0001	1.00	<.0001	<.0001	<.0001	<.0001	1.00	<.0001	<.0001
0-F4		0.01	0.0003	0.0004	0.0002		0.98	<.0001	1.00	0.75		0.95	<.0001	0.05	0.26		0.99	<.0001	0.66	0.0001
0-S8			0.93	0.96	0.90			<.0001	0.97	0.32			<.0001	0.30	0.03			<.0001	0.33	0.0009
F2-0				1.00	1.00				<.0001	<.0001				<.0001	<.0001				<.0001	<.0001
F2-F4					1.00					0.80					<.0001					<.0001
Sampling day	21 days after the slurry application at tillering																			
Temperature	Field					25 °C					65 °C					105 °C				
Treatment[a]	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8
0-0	<.0001	<.0001	0.35	<.0001	<.0001	<.0001	<.0001	0.99	<.0001	<.0001	<.0001	<.0001	1.00	<.0001	<.0001	<.0001	<.0001	1.00	<.0001	<.0001
0-F4		0.30	<.0001	0.01	0.10		0.03	<.0001	0.12	0.12		0.42	<.0001	0.08	0.003		0.19	<.0001	0.19	0.01
0-S8			<.0001	0.70	0.99			<.0001	0.99	0.99			<.0001	0.96	0.35			<.0001	1.00	0.90
F2-0				<.0001	<.0001				<.0001	<.0001				<.0001	<.0001				<.0001	<.0001
F2-F4					0.95					1.00					0.85					0.90
Sampling day	30 days after the slurry application at tillering																			
Temperature	Field					25 °C					65 °C					105 °C				
Treatment[a]	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8
0-0	0.0002	<.0001	1.00	<.0001	<.0001	0.01	<.0001	1.00	<.0001	<.0001	0.001	<.0001	1.00	<.0001	<.0001	0.15	<.0001	1.00	<.0001	<.0001
0-F4		0.004	0.0002	0.002	<.0001		0.002	0.01	0.02	<.0001		0.16	0.001	0.36	<.0001		0.0005	0.15	0.17	<.0001
0-S8			<.0001	1.00	0.20			<.0001	0.98	0.0006			<.0001	1.00	0.08			<.0001	0.39	0.004

F2-0				<.0001	<.0001				<.0001	<.0001				<.0001	<.0001				<.0001	<.0001
F2-F4					0.32					<.0001					0.03					<.0001
Sampling day	35 days after the slurry application at tillering																			
Temperature	Field					25 °C					65 °C					105 °C				
Treatment[a]	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8
0-0	<.0001	<.0001	1.00	<.0001	<.0001	0.01	<.0001	1.00	<.0001	<.0001	0.52	<.0001	1.00	0.002	<.0001	0.61	<.0001	1.00	0.02	<.0001
0-F4		0.02	<.0001	0.0001	<.0001		0.06	0.01	0.0002	<.0001		0.02	0.52	0.22	<.0001		0.0005	0.61	0.51	<.0001
0-S8			<.0001	0.71	0.0001			<.0001	0.51	0.0002			<.0001	0.90	<.0001			<.0001	0.11	0.002
F2-0				<.0001	<.0001				<.0001	<.0001				0.002	<.0001				0.02	<.0001
F2-F4					0.02					0.06					<.0001					<.0001
Sampling day	47 days after the slurry application at tillering																			
Temperature	Field					25 °C					65 °C					105 °C				
Treatment[a]	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8
0-0	0.42	0.19	1.00	<.0001	<.0001	1.00	0.95	1.00	0.05	<.0001	1.00	0.89	1.00	0.39	<.0001	1.00	0.98	1.00	0.56	<.0001
0-F4		1.00	0.42	0.03	<.0001		0.95	1.00	0.05	<.0001		0.89	1.00	0.39	<.0001		0.98	1.00	0.56	<.0001
0-S8			0.19	0.08	0.0002			0.95	0.35	<.0001			0.89	0.95	0.0001			0.98	0.94	0.0002
F2-0				<.0001	<.0001				0.05	<.0001				0.39	<.0001				0.56	<.0001
F2-F4					0.41					0.04					0.003					0.01

[a] Codes for treatments. The number before the hyphen indicates the rate of slurry applied at sowing: 0, no slurry applied; 2, slurry from fattening pigs (F) at a rate of 25 Mg ha^{-1}. The number after the hyphen indicates the rate of slurry applied tillering: 0, no slurry applied; 4, slurry from fattening pigs (F) at a rate of 42 Mg ha^{-1}; 8, slurry from sows (S) at a rate of 76 Mg ha^{-1}.

[b] nd: no data.

Table 4.S3

Soil water repellency (SWR) transformed data (log (SWR + 1))[a] when the water drop penetration time test was used at cereal tillering[a] for each sampling date (S-DAY) and at different oven drying temperatures, after slurry spreading at different rates.

	Field-moist samples				25 ºC oven drying samples			
Slurry rate[b]/S-DAY	7d		21d		14d		21d	
0	1.09	c	0.87	b	0.69	b	0.74	b
F4	4.28	a	2.76	a	2.54	a	2.45	a
S8	2.47	b	2.87	a	2.58	a	2.69	a
	65 ºC oven drying samples				105 ºC oven drying samples			
Slurry rate[b]/S-DAY	7d		21d		7d		21d	
0	0.69	b	0.69	b	0.69	b	0.69	b
F4	3.86	a	2.06	a	3.19	a	2.44	a
S8	3.79	a	2.29	a	3.88	a	2.79	a

[a] Means (n=36) within a column followed by a different letter are significantly different ($\alpha = 0.05$) according to Duncan's multiple range test.

[b] The number indicates the rate of slurry applied at cereal tillering: 0, no slurry applied; 4, slurry from fattening pigs (F) at a rate of 42 Mg ha^{-1}; 8, slurry from sows (S) at a rate of 76 Mg ha^{-1}.

Table 4.S4

Statistical differences between treatments in soil water repellency (SWR) according to the multiple comparison analysis of Tukey, when the molarity of ethanol droplet test was used at different temperatures and sampling dates after slurry application at cereal tillering. Comparisons were only used when the interaction between the slurry rates applied at sowing and at cereal tillering was significant.

Sampling day	7 days after the slurry application																			
Temperature	Field					25 °C					65 °C					105 °C				
Treatment[a]	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8
0-0	<.0001	0.01	1.00	<.0001	1.00	nd[b]	nd	nd	nd	nd	0.003	0.02	1.00	<.0001	0.23	0.02	0.16	1.00	0.04	0.03
0-F4		0.004	<.0001	0.91	<.0001		nd	nd	nd	nd		0.95	0.003	0.61	0.37		0.87	0.02	1.00	1.00
0-S8			0.03	0.04	0.03			nd	nd	nd			0.02	0.17	0.87			0.16	0.99	0.97
F2-0				<.0001	1.00				nd	nd				<.0001	0.23				0.04	0.03
F2-F4					<.0001					nd					0.02					1.00
Sampling day	14 days after the slurry application																			
Temperature	Field					25 °C					65 °C					105 °C				
Treatment[a]	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8
0-0	0.53	1.00	1.00	1.00	1.00	<.0001	0.35	1.00	0.01	0.10	0.16	0.98	1.00	1.00	0.55	0.05	0.35	1.00	0.70	<.0001
0-F4		0.53	0.53	0.53	0.53		0.01	<.0001	0.26	0.05		0.47	0.16	0.32	0.96		0.87	0.05	0.54	0.02
0-S8			1.00	1.00	1.00			0.35	0.56	0.97			0.98	1.00	0.92			0.35	0.99	0.001
F2-0				1.00	1.00				0.01	0.10				1.00	0.55				0.70	<.0001
F2-F4					1.00					0.93					0.80					0.0003

Sampling day	21 days after the slurry application																			
Temperature	Field					25 °C					65 °C					105 °C				
Treatment[a]	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8
0-0	0.98	0.002	1.00	0.002	0.001	0.97	0.97	1.00	0.44	1.00	1.00	0.67	1.00	0.67	0.87	1.00	0.99	1.00	0.93	0.06
0-F4		0.01	0.98	0.01	0.01		1.00	0.86	0.86	1.00		0.67	1.00	0.67	0.87		1.00	1.00	0.99	0.14
0-S8			0.002	1.00	1.00			0.86	0.86	1.00			0.67	1.00	1.00			0.99	1.00	0.21
F2-0				0.002	0.001				0.25	0.97				0.67	0.87				0.93	0.06
F2-F4					1.00					0.66					1.00					0.34
Sampling day	30 days after the slurry application																			
Temperature	Field					25 °C					65 °C					105 °C				
Treatment[a]	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8
0-0	0.80	0.80	1.00	0.32	0.07	1.00	0.03	1.00	1.00	0.04	1.00	0.27	1.00	1.00	0.03	1.00	<.0001	1.00	1.00	0.0009
0-F4		1.00	0.80	0.96	0.56		0.08	1.00	1.00	0.10		0.38	1.00	1.00	0.05		<.0001	1.00	1.00	0.001
0-S8			0.80	0.96	0.56			0.03	0.06	1.00			0.27	0.38	0.87			<.0001	<.0001	0.67
F2-0				0.32	0.07				1.00	0.04				1.00	0.03				1.00	0.0007
F2-F4					0.96					0.08					0.05					0.0007
Sampling day	35 days after the slurry application																			
Temperature	Field					25 °C					65 °C					105 °C				
Treatment[a]	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8
0-0	0.62	1.00	1.00	0.73	0.62	1.00	0.66	1.00	1.00	0.0002	1.00	0.77	1.00	1.00	0.002	1.00	0.15	1.00	1.00	<.0001
0-F4		0.73	0.62	1.00	1.00		0.88	1.00	1.00	0.001		0.95	1.00	1.00	0.01		0.29	1.00	1.00	0.0001

0-S8			1.00	0.82	0.73			0.66	0.66	0.01			0.77	0.95	0.04			0.15	0.15	0.02
F2-0				0.73	0.62				1.00	0.0002				1.00	0.002				1.00	<.0001
F2-F4					1.00					0.0002					0.01					<.0001
Sampling day	47 days after the slurry application																			
Temperature	Field					25 °C					65 °C					105 °C				
Treatment[a]	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8	0-F4	0-S8	F2-0	F2-F4	F2-S8
0-0	1.00	1.00	1.00	0.82	0.39	1.00	1.00	1.00	1.00	0.15	1.00	1.00	1.00	1.00	0.23	1.00	1.00	1.00	1.00	0.15
0-F4		1.00	1.00	0.82	0.39		1.00	1.00	1.00	0.15		1.00	1.00	1.00	0.23		1.00	1.00	1.00	0.15
0-S8			1.00	0.82	0.39			1.00	1.00	0.26			1.00	1.00	0.46			1.00	1.00	0.19
F2-0				0.82	0.39				1.00	0.15				1.00	0.23				1.00	0.15
F2-F4					0.97					0.15					0.46					0.19

[a] Codes for treatments. The number before the hyphen indicates the rate of slurry applied at sowing: 0, no slurry applied; 2, slurry from fattening pigs (F) at a rate of 25 Mg ha^{-1}. The number after the hyphen indicates the rate of slurry applied tillering: 0, no slurry applied; 4, slurry from fattening pigs (F) at a rate of 42 Mg ha^{-1}; 8, slurry from sows (S) at a rate of 76 Mg ha^{-1}.

[b] nd: no data.

Table 4.S5

Soil water repellency (SWR) when the molarity of ethanol droplet test was used at cereal tillering[a] for each sampling date (S-DAY) and at different oven drying temperatures, after slurry spreading at different rates.

Temperature	65 ºC		105 ºC	
Slurry rate[b]/S-DAY	7d		7d	
0	0.20	c	0.20	b
F4	2.33	a	1.95	a
S8	1.40	b	1.70	a

[a] Means (n = 12) within a column followed by a different letter are significantly different (α = 0.05) according to Duncan's multiple range test.

[b] The number indicates the rate of slurry applied at cereal tillering: 0, no slurry applied; 4, slurry from fattening pigs (F) at a rate of 42 Mg ha^{-1}; 8, slurry from sows (S) at a rate of 76 Mg ha^{-1}.

CHAPTER 5

Ammonia volatilisation and soil water repellency following slurry spreading

This chapter contains the manuscript to be submitted in the journal *Pedosphere*

AMMONIA VOLATILISATION AND SOIL WATER REPELLENCY FOLLOWING SLURRY SPREADING

ABSTRACT

Slurries produced in animal rearing farms are one of the main NH_3 emission sources. The potential relationships of NH_3 emissions after slurry addition and soil fertility are poorly understood. In a rainfed Mediterranean agricultural system, the aim was to evaluate the persistence of soil water repellency (SWR) at the soil surface, and how this affects NH_3 emissions. Five N fertilization treatments plus a control (no N added, S00) were established. One treatment was slurry from fattening pigs (PSF) applied before cereal sowing (S20), two treatments were PSF or from sows (PSS) applied at cereal tillering stage (S04 and S08, respectively); and two more treatments received slurries twice, at sowing and at tillering (S24 and S28). Ammonia emission was quantified with semi-static chambers during 145 (at sowing) and 576 h (at cereal tillering) after slurry application. At topdressing SWR was also quantified by the water drop penetration time test. Slurry burying controlled NH_3-N emissions at sowing. At topdressing, maximum NH_3-N emissions accounted for 18 and 11% of total NH_4-N applied as PSF or PSS, respectively. Superficial SWR lasted less than 49 d. It followed a wetting-drying pattern between rain events. An inverse time pattern between SWR and NH_3-N emission rate was found. The liquid slurry fraction hydrophobic compounds and slurry DM combined with soil moisture content, controlled NH_3 emissions and further SWR. In dryland Mediterranean rainfed systems, further research is needed to determine the initial SWR caused by periodic slurry applications which could enhance NH_3 emission.

Key words: ammonia emission rate, fattening pig slurry, soil hydrophobicity, sow slurry

Abbreviations: AN, ammonium nitrogen; DM, dry matter; DOC, dissolved organic carbon; MD, molecular diffusion; OC_{hi}, hydrophilic organic carbon; OC_{ho}, hydrophobic organic carbon; PSF, slurry from fattening pigs; PSS, slurry from sows; PWP, permanent wilting point; SD, standard deviation; SWR, soil water repellence; SWA, soil water availability to plants; AN, total ammonium nitrogen; TD, turbulent diffusion; TN, total nitrogen; TON, total organic nitrogen; WDPT, water drop penetration time; WEOC, water extractable organic carbon; WEOM, water extractable organic matter; WFC, water field capacity.

HIGHLIGHTS

Pig slurry (PS) burying controls soil water repellency (SWR) after its spreading.

If slurry is not buried, PS develops a transitory SWR lasting less than 49 days.

Drying-wetting cycles drive SWR and inversely affect NH_3 emissions.

INTRODUCTION

Ammonia (NH_3) emissions from fertilizers are an important environmental issue (Sutton et al., 2011). They also represent a cost for farms because they reduce N use efficiency from the manure applied. In Europe, the agricultural sector contributes an estimated 94% of NH_3 emissions to the atmosphere (EUROSTAT, 2017a). In Spain, NH_3 emissions increased by 11.9% from 1990 to 2015, mainly caused by a significant growth of the national cattle herd (EEA report, 2017). An important source of NH_3 emission comes from pig (*Sus strofa domesticus*) slurries, as Spain is the leading European pig producer (EUROSTAT, 2017b) with a herd of 30 million pigs in 2016 (MAPAMA, 2017). Ammonium N (AN) accounts for 70% of total N (TN) in slurries (Yagüe et al., 2012), which are mainly spread over agricultural land (92%) as organic fertilizers (MARM, 2010).

In the dryland Mediterranean rainfed systems of Spain, farmers apply slurries when available and they sow winter cereals in autumn despite the lack of water, waiting for the later rains of the winter. Sowing after rain periods is not advisable because of some difficulties in land preparation during cold winter periods.

Ammonia volatilisation from soil is associated with the chemical and physical properties of the material added, but also with the method and time of application, the soil properties and the meteorological conditions. The increase of air temperature, wind speed, solar radiation, application rate and high content of AN, or dry matter (DM) concentration in the slurry could all increase NH_3 emissions (Thompson et al., 1990; Braschkat et al., 1997). Regarding the environmental conditions, rises in relative humidity and in rainfall (which increase slurry infiltration), reduce NH_3volatilisation (Misselbrook et al., 2005a; Holcom et al., 2011).

Slurry DM changes the hydraulic properties of the soil surface (Garnier et al., 2004). High DM content can enhance NH_3 emission when moist (Thompson and Meisinger, 2002), but it favors crust formation when dried (Bosch-Serra et al., 2014). Emissions can be reduced as fast as the slurry dries because ion diffusion resistance increases (Thompson et al., 1990). Furthermore, DM could enhance SWR as it is the case in other liquid wastes (Wallach et al., 2005).

Soil hydrophobicity is a dynamic and transient soil property, which reduces the affinity of soils for water with irregular moisture patterns (Dekker and Ritsema, 1994). Soil is not completely wettable as SWR increases. Hydrophobic organic substances can coat individual soil particles and aggregates leading to SWR (Müller and Deurer, 2011). Those compounds can be from natural origin, such as the ones present in soils under certain vegetation types, or in the presence of fungi or microorganisms (Benito et al., 2015) or can derived from external sources such as the use of waste water for irrigation (Wallach et al., 2005; Vogeler, 2009) or organic fertilization (González-Peñaloza et al., 2012). The main mechanism causing SWR is the imbalance between the organic matter input and its decomposition rate (Müller and Deurer, 2011). The hydrophobic compounds are characterized by their low degradation potential and can be enhanced by the increase in the transformation of hydrophilic components into hydrophobic moieties (Said-Pullicino et al., 2007). It can significant impact on soil-water related processes that occur at the interface between the pedosphere and atmosphere, such as the reduction in the rate of water infiltration into the soil surface (Dekker and Ritsema, 1994), the decrease in the availability of water in the root zone (Wang et al., 2000), the increase in water runoff (Benito et al., 2015), and the potential risk of nutrient and pesticide loss by preferential flow (Clothier et al., 2000).

Soil water repellency is usually tested under moist field conditions (Müller and Deurer, 2011). Moreover, it has been proved that SWR monitored over time supplies information about temporal changes with minimal soil disturbance (Doerr and Thomas, 2000; Benito et al., 2015).

In the present work, it was hypothesized that slurries led to soil hydrophobicity. As a consequence, applications at sowing time could enhance NH_3 volatilisation in subsequent (topdressing) slurry applications. The basis of this influence is of interest because it could improve our understanding about soil water and N dynamics in dryland Mediterranean conditions. It will also be useful to advise farmers and policy makers regarding soil management when slurries are spread over the surface.

The aim of this work is to evaluate SWR when pig slurries are applied in a dryland Mediterranean agricultural system, and its potential influence on NH_3 volatilisation. Slurries from different origins applied at different rates and times were used to assess the distribution and persistence of SWR and potential differences in NH_3 emissions resulting from their use. The evaluation was done in the context of conventional agricultural practices where slurries are buried before sowing and left on the surface when the slurries are applied as topdressing at the cereal tillering stage.

MATERIALS AND METHODS

Experimental location and design

The experiment was set up in a NE area of Spain (coordinates 41º52’29”N, 1º09’13”E). The climate is semiarid Mediterranean with a mean annual precipitation of 450 mm. Daily climatic data were obtained from the automatic meteorological station installed next to the experimental area. The soil was classified as a Typic Xerofluvent (Soil Survey Staff, 2014), non-saline and calcareous. The upper layer (0-0.30 m) was characterized as silt loam texture (131 g kg^{-1} sand, 609 g kg^{-1} silt, and 260 g kg^{-1} clay), with a pH of 8.2 (1:2.5; soil: distilled water), mean organic C content of 11.67 g kg^{-1}, bulk density 1.65 g cm^{-3}, and calcium carbonate content of 300 g kg^{-1}. The water field capacity (WFC) was 17.2% (w/w), the permanent wilting point (PWP) was 10.2% (w/w), and the soil water availability to plants (SWA) was defined as the difference between WFC and PWP.

The framework of our research was a fertilization experiment established in 2002 which was maintained from then onwards. Fertilization treatments at sowing were randomized against the block and treatments at cereal tillering were randomized against the slurry applied. The experimental design was a split-block design with two blocks (replications). Winter cereals, barley (*Hordeum vulgare* L.) and wheat (*Triticum aestivum* L.) were the main crops in a rotation system. Plot size for treatments was 137.5 m^2 (11 m wide and 12.5 m long) except for the control plots which were 87.5 m^2 (7 m wide and 12.5 m long).

In the 2015-2016 cropping season, six treatments from the two blocks were chosen for this study. Distance between blocks was 100 m. Two treatments were based on the same amount of N applied at cereal tillering stage (2 of Feekes scale; Large, 1954) (ca. 250 kg N ha^{-1}), but from different types of pig slurry: fattening pigs (35 Mg ha^{-1}) (code 4) or sows (77 Mg ha^{-1}) (code 8). They were combined (codes S24 and S28) or not (codes S04 and S08) with fattening pig slurry applied at sowing (20 Mg ha^{-1}). Slurry applied only at sowing (code S20, 20 Mg ha^{-1}) was the fifth treatment. A control with no N-addition (code S00), but receiving P (40 kg ha^{-1}) and K (56 kg ha^{-1}) was included. Slurry application was done over the soil surface by the splash-plate machine method. At sowing, slurry was incorporated 9 h after application by superficial disc harrowing. At tillering, slurries were left on the surface. In the experimental cropping season Barley was sown the last week of October and harvested in the fourth week of June.

Field ammonia emission measurements

Slurry application was done the 20th October 2015 before sowing, and the 2nd February 2016 at cereal tillering stage, respectively. Immediately after slurry spreading, NH_3 emission measurements were started. They were followed for 145 h before sowing and 576 h after topdressing. Semi-static chambers adapted from Grant et al. (1996), three for each treatment, were used. Each semi-static chamber consisted of a plastic cylinder (0.2 m diameter and 0.2 m high) made of LD PET (Low Density PolyEthylene Terephthalate) with a pair of removable low density (20 kg m^3) polyfoam sponges. One sponge was situated at the top, and the second one was placed 0.1 m high inside the cylinder, sustained by a cross of metal wire. The upper foam disc was protected with a plastic mesh and fixed with elastic bands to the cylinder. The foam discs were previously soaked in an acid solution of 80 mL oxalic acid in acetone (3% w/v), well dried and preserved in hermetically sealed plastic bags up until their placement in the field.

The inner sponge discs (foam I) trapped the NH_3 emitted from the soil surface (molecular diffusion, MD). The upper sponge (foam II) was isolated from the inner one and it trapped part of the emission related to turbulent diffusion (TD) from the adjacent surface of the plot.

Immediately after the slurry was applied to each plot, the semi-static chambers were vertically introduced 25 mm deep into the soil and following the sowed line, avoiding soil surface disturbance. Foam discs were periodically changed according to the schedule. On rainy days, the semi-static chambers were closed with a transparent plastic bag. Thus, no data was obtained from these foams during the rainy period. Foam disc I was renewed at 9, 24, 32, 49, 56, 80 and 145 h after sowing slurry application; and foam disc II was replaced more sparsely at 9, 32, 56, 80 and 145 h. At cereal tillering, foams I and II were renewed at 7, 24, 31, 48, 55, 72, 79, 103, 144, 168, 192, 216, 240, 312, 360, 408, 480, 528 and 576h after topdressing slurry. Foam discs were individually stored in plastic bags, carried to the laboratory and kept in the fridge for the NH_3 extraction and quantification.

Ammonium oxalate was extracted from the foam disc by five successive washes with 0.1 L of distilled water. Each time, the water was collected in a volumetric flask, adjusted to 0.5 L and homogenized. A 25 mL aliquot was taken for the NH_3 quantification. For the quantification, the pH of the aliquot was increased with 25 µL of NaOH (40%) to enhance the presence of NH_3 gas in the solution. A selective NH_3-N electrode (Crison, GLP 22) was used for quantifications. A total of 156 foams were analysed at sowing and 1368 at topdressing.

Soil water repellency

At tillering crop stage, soil water repellency was quantified in the field, matching up the timings with NH_3 volatilisation samplings. The water drop penetration time test (WDPT, King, 1981) was implemented. A droplet of distilled water was placed on the soil surface and the time spent until the droplet infiltrated was recorded using a chronometer. The WDPT test was performed prior to slurry application (called time zero) to evaluate the SWR associated to previous slurry applications at sowing time. It was also performed at 24, 72, 144, 192, 312, 360, 408, 480, 528, 576, 672, 840 and 1176 h after slurry spreading. Six measurements per plot were done.

Soil was sampled (0 – 0.1 m) at each SWR test time to measure soil moisture content.

Slurry sampling and analyses

Slurries were collected before each application and stored in a portable fridge until their arrival at the laboratory. Fresh samples were analysed for pH (water 1:5), electrical conductivity (1:5; dS m^{-1}, 25 ºC), dry matter (DM; Gravimetry, 105 °C) and organic matter content (Walkley-Black). Fresh samples were also used to analyse total N and NH_4^+ (TN, AN respectively) by Kjeldahl method. Organic N (TON) was calculated as the difference of the TN and AN contents. The slurry liquid fraction was isolated and quantified. Hydrophilic (OC_{hi}) and hydrophobic (OC_{ho}) organic C were only analysed in the liquid fraction of slurries, because of minimal contribution of the slurry solid fraction to OC_{hi} and OC_{ho}. Water-extractable organic matter (WEOM) was extracted by filtering the fresh samples through a 0.45 µm membrane filter. Amberlite XAD-8 resin was used to obtain the hydrophilic and hydrophobic fraction of WEOM, following the method proposed by Gigliotti et al. (2002). The hydrophilic fraction was obtained from the resin column effluents and the hydrophobic fraction was calculated by difference between the water-extractable organic C (WEOC) and OC_{hi} concentration in the hydrophilic fraction. The C content in the WEOM and the hydrophilic fraction were measured by using Pt-catalysed, high temperature combustion (800°C) followed by infrared detection of the CO_2 produced (MULTI N/C 2100/2100S, Analytik Jena AG, Jena, Germany).

Statistical analysis

Control treatments showed minimal and constant NH_3 emissions (between 0.002 and 0.04 kg N-NH_3 $ha^{-1}h^{-1}$) and no SWR. As the aim was to compare NH_3 volatilisation between fertilization strategies, values obtained in foam I from the control treatment were treated as the natural soil emission. They were and were subtracted from the other values in order to correct the baseline and were not included in the statistical analysis.

Data were normally distributed. Linear and logarithmic distributions were fitted to establish the best data adjustment for NH_3 emissions in each treatment using the mean values of each sampling date. Differences among treatments using all repetitions were evaluated when N losses reached 100% of the total recorded emissions. Soil water repellency data were classified according to King (1981), transformed to categorical values and plotted to show their percentage distribution over time. As SWR data did not fit normality, normalization was performed with the Log (SWR + 1) transformation. Four sampling dates before a rainfall event were selected to perform an ANOVA (192, 408, 576 and 840 h after slurry application); the general lineal model procedure from the statistical package SAS version 9.4 (SAS Institute, 2013) was used. Means were compared with the studentized range test of Tuckey ($\alpha = 0.05$).

RESULTS

During the initial period of measurements before sowing, maximum wind speed reached 1.7·m s^{-1} and no rain events occurred; mean air temperature and humidity were 12 °C (SD 3) and 76% (SD 7), respectively. Soil moisture, tested just before the slurry addition, was 11.3% (SD 2) which equalled 16% of SWA (Fig. 5.1a).

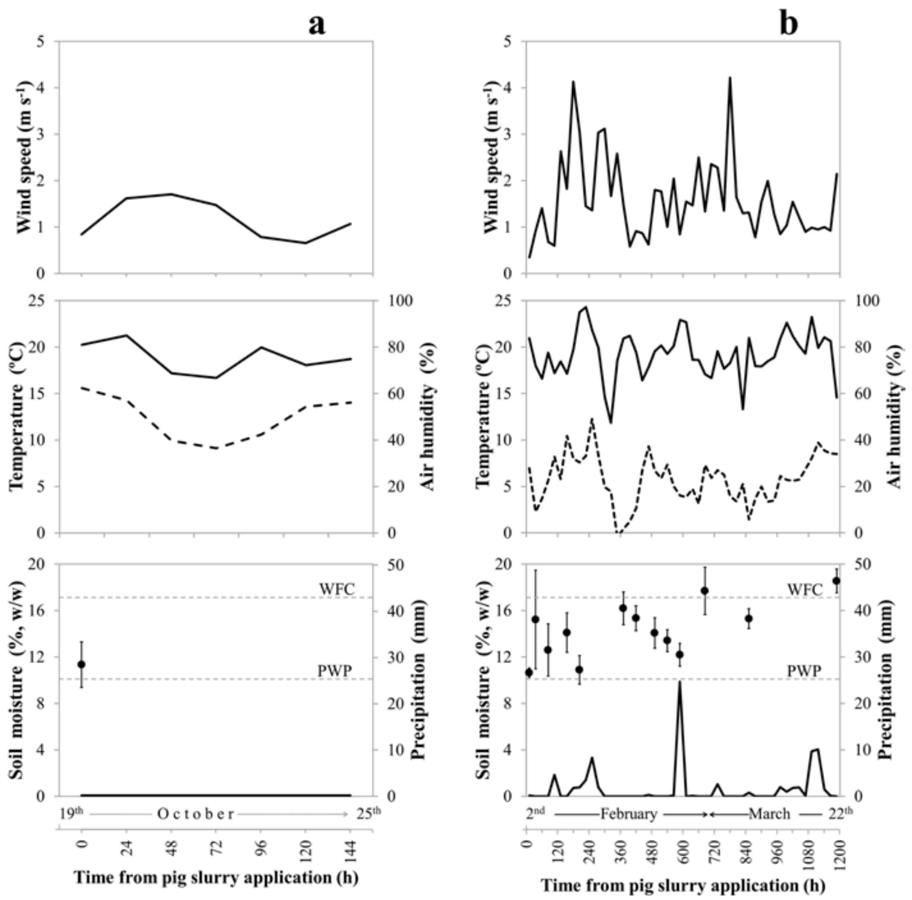

Figure 5.1. Mean meteorological conditions (temperature in dotted line) and available soil moisture from 0-0.1 m (black points) after pig slurry application during two

periods: a) before sowing and b) at cereal tillering stage. At sowing, soil sampling was only done just before slurry application. Available soil moisture is plotted with two references: permanent wilting point (PWP) and water content at field capacity (WFC). The difference between WFC and PWP is the soil water available to plants.

Pig slurry analyses from fattening pigs (PFS) showed higher values of DM, EC, TN and AN, than slurry from sows (PSS) (Table 5.1). Slurries PFS also had a higher ratio of organic matter over DM: 0.8 for PFS and 0.6 for PSS. The WEOC was eight times higher in PSF than in PSS and the ratio between OC_{hi} and OC_{ho} was higher in PSF .

Table 5.1.

Slurry rates, total nitrogen and ammonium nitrogen added to the different treatments. Other physicochemical values of pig slurry applied at sowing (October 2015) and at cereal tillering (February 2016) from fattening pigs (PSF) and sows (PSS) are included.

Parameters	Sowing	Tillering	
	PSF	PSF	PSS
Slurry rate (Mg ha^{-1})	20†	35‡	77§
Total N added (kg N ha^{-1})	152†	265‡	233§
Total ammonium N added (kg N ha^{-1})	101†	183‡	119§
pH (water 1:5)	8.5	8.6	8.5
Electrical conductivity (1:5; slurry: distilled water; dS m^{-1}, 25ºC)	6.7	6.6	2.4
Dry matter (kg m^{-3})	127	101	84
Organic matter (kg m^{-3})	98	78	48
Organic N (kg m^{-3})	2.6	2.4	1.5
Total N (kg m^{-3})	7.7	7.6	3.1
Total ammonium N (kg m^{-3})	5.1	5.3	1.6
Total organic C (kg m^{-3})	49	39	24
Water extractable organic C (kg m^{-3})	8.6	7.9	1.1
Hydrophobic organic C¶ (kg m^{-3})	3.5	3.5	0.6
Hydrophilic organic C¶ (kg m^{-3})	5.1	4.4	0.5

† Rate applied at sowing to treatments S20, S24, S28

‡ Rate applied at tillering to treatments S04, S24

§ Rate applied at tillering to treatments S08, S28

¶ Fraction obtained from the dissolved organic carbon

At cereal tillering stage, from the slurry application up to 1170 h later, rain events contributed with 79.4 mm. During the volatilisation experiment, rainfall contributed 23 mm (up to 576 h after spreading). A heavy rain at the end of February added 25 mm, and rainfall events increased towards the end of the experiment (Fig. 5.1b). Wind speed ranged from 0.3 to 4.2 m s^{-1}. The relative humidity and temperature of the air ranged from 47 to 97% and between 0 to 12 °C, respectively. Soil moisture (0-0.1 m) was between 9 and 21% (w/w).

At sowing time, the highest NH_3 flux rates (1.15 kg N ha^{-1} h^{-1}) were measured 9 h after PSF application, just before incorporation by disking. A rapid decline in NH_3 emission followed, being close, after 24 h, to the control treatment: 0.06 kg N ha^{-1} h^{-1} from S20 vs. 0.01 kg N ha^{-1} h^{-1} from S00 (Fig. 5.2a and Fig. 5.2b).

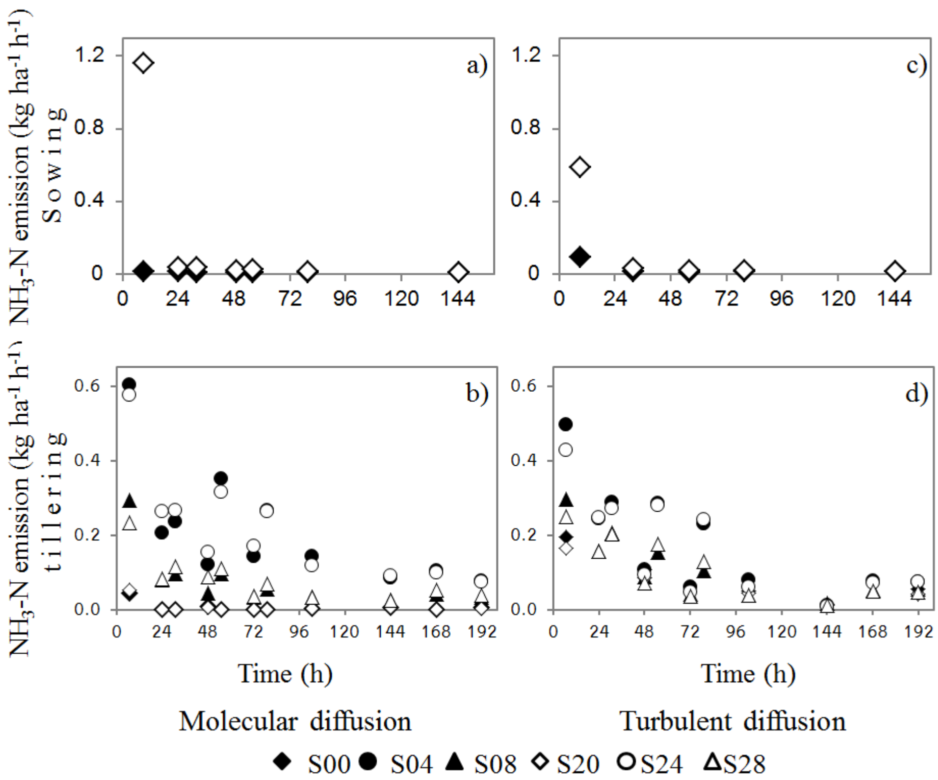

Figure 5.2. Ammonia (NH_3-N) volatilisation rate before sowing and at cereal tillering. Molecular and turbulent diffusion are shown. Results from treatments S00 and S20

overlap (2d). Code treatment number is related to the timing of slurry (S) application and N dose. The first number indicates treatment at sowing: 0, no N applied; 2, slurry from fattening pigs applied at a rate of 152 kg N ha^{-1}. Second number indicates the treatment at tillering: 0, no N applied; 4, slurry from fattening pigs at a rate of 265 kg N ha^{-1}; 8, slurry from sows at a rate of 233 kg N ha^{-1}.

At tillering, both fluxes (MD, TD) showed a similar trend in the NH_3 emission rates (Fig. 5.3a and Fig. 5.3c) and in the associated accumulated values (Table 5.2). However, statistical differences were found in the total amount of NH_3 volatilized by MD according to the slurry application method (Table 5.3), (Fig. 5.3a and Fig. 5.3c). The highest NH_3 emission rates for all treatments were recorded during the first 7 h after slurry application, decreasing by a half after 48 h and gradually matching the control from 192 h onwards. During the 72 h after slurry application, 50% of AN applied was emitted. It means that NH_3 losses were confined to one week.

Table 5.2.

Accumulated ammonia volatilisation (y, NH_3-N kg ha^{-1}) over time (x, hour) according to the slurry treatment at sowing and/or at cereal tillering.

Application time	Flux diffusion	Treatment codes†	Equation	R^2
Sowing	Turbulent	S00	y= 0.0046x + 0.0999	0.96
	Molecular	S20	y= 1.1875·ln(x) + 8.1362	0.94
	Turbulent	S20	y=0.7242·ln(x) + 3.5072	0.96
Tillering	Molecular	S04	y=6.8756·ln(x) - 12.372	0.97
	Molecular	S08	y=2.3432·ln(x) - 3.6139	0.97
	Turbulent	S20	y=0.0033x + 0.3548	0.97
	Molecular	S24	y=6.9631·ln(x) - 11.721	0.97
	Molecular	S28	y=2.8267·ln(x) - 5.1685	0.98
	Turbulent	S04	y=5.1321·ln(x) - 7.2218	0.98
	Turbulent	S08	y=3.3897·ln(x) - 5.0529	0.99
	Turbulent	S24	y=4.8738·ln(x) - 7.117	0.98
	Turbulent	S28	y=3.3546·ln(x) - 5.3658	0.99

† Code numbers are related to the timing of slurry (S) application and N dose. First number indicates the treatment at sowing: 0, no N applied; 2, slurry from fattening pigs applied at a rate of 152 kg N ha^{-1}. Second number indicates the treatment at tillering: 0,

no N applied; 4, slurry from fattening pigs at a rate of 265 kg N ha^{-1}; 8, slurry from sows at a rate of 233 kg N ha^{-1}.

Table 5.3.

Analysis of variance of total ammonia nitrogen emitted by molecular or turbulent diffusion, after slurry application at cereal tillering.

Diffusion	Source	df	Sum of squares	Mean square	F ratio	P
Molecular	Between treatments	3	2135.832	711.944	26.11	<0.0001
	Between blocks	1	0.016	0.016	0.00	0.98
	Between samples within treatments	8	605.739	75.717	2.78	0.06
	Within samples (residual)	11	299.927	27.266		
	Total	23	3041.514			
Turbulent	Between treatments	3	358.294	119.431	19.02	0.0001
	Between blocks	1	50.158	50.158	7.99	0.02
	Between samples within treatments	8	48.160	6.020	0.96	0.51
	Within samples (residual)	11	456.613	38.051		
	Total	23	69.078	6.280		

Maximum NH_3 emission rate from MD was below 0.7 kg N ha^{-1} h^{-1} for PSF and 0.3 kg N ha^{-1} h^{-1} for PSS, accounting for a total emission average of 33 and 13 kg N ha^{-1}, respectively (Fig. 5.3c). Their emissions in TD reached 25 and 17 kg NH_3-N ha^{-1} h^{-1} for PSF and PSS (Fig. 5.3a), respectively. For control treatments (S00 and S20), a threshold loss of 2.5 kg NH_3-N ha^{-1} was recorded. Finally, accumulated emissions by MD (foam I) were above TD records (foam II) (Fig. 5.3a and Fig. 5.3c). Also, at tillering, no significant influence of previous slurry applications at sowing was detected on NH_3 volatilisation. Nevertheless, when accounting for losses linked to MD, the total emitted NH_3 on treatments receiving slurry previously at sowing (S24, S28) was slightly higher than the ones which did not (S04, S08) (Fig. 5.3c, Table 5.2).

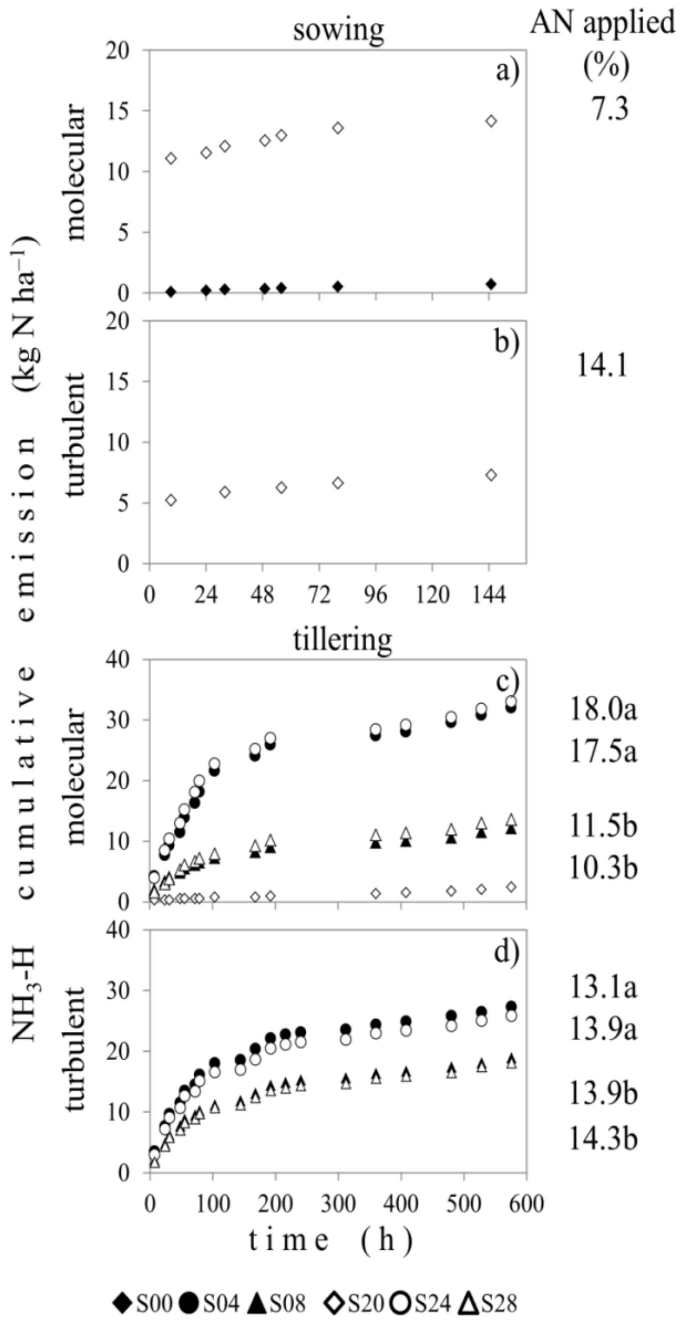

Figure 5.3. Ammonia (NH_3-N) cumulative values before sowing and at cereal tillering. Molecular and turbulent diffusion are shown. Cumulative emissions as a percentage of the ammonium nitrogen applied (AN) are also included. At tillering, losses as a percentage of AN applied, followed by the same capital letter, are not statistically different according to Tukey test ($\alpha = 0.05$). Code treatment number is related to the timing of slurry (S) application and N dose. The first number indicates treatment at sowing: 0, no N applied; 2, slurry from fattening pigs applied at a rate of 152 kg N ha^{-1}. Second number indicates the treatment at tillering: 0, no N applied; 4, slurry from fattening pigs at a rate of 265 kg N ha^{-1}; 8, slurry from sows at a rate of 233 kg N ha^{-1}.

Slurry treatments influenced the SWR distribution. Control treatments remained totally wettable during the whole experiment. Besides, a day after slurry application no hydrophobicity was recorded, whatever the slurry treatment was (Fig. 5.4 and Fig. 5.5). Maximum values of SWR were classified as moderate. Treatments with PSF at tillering showed three (S04) and four (S24) episodes with moderate SWR, and the highest presence accounted for 33 and 83% of the total samples at 192 h after slurry application. Treatments with PSS, only S28 showed once, at 72 h, a moderate SWR (Fig. 5.4).

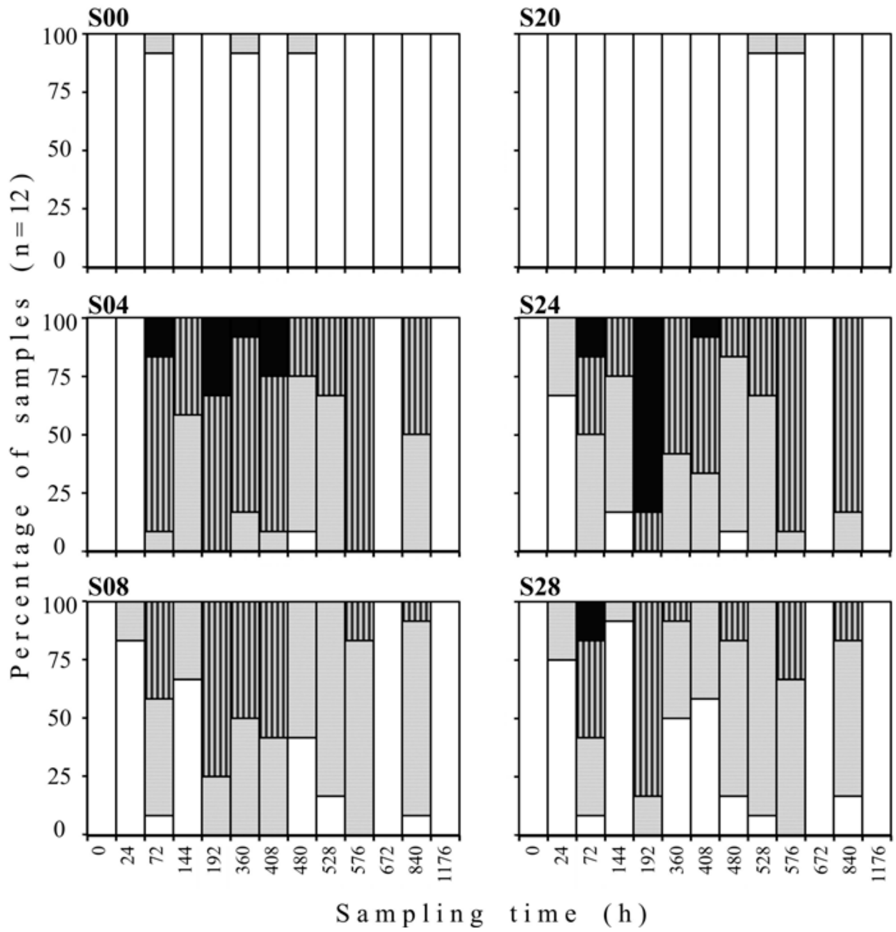

Figure 5.4. Frequency distribution (%) of soil water repellency persistence for each treatment and sampling date from slurry application. The colour bars indicate the degree of water repellence following King (1981): Not significant (white), very low (light grey), low (vertical stripes) and moderate (black bars). Code numbers are related to the moment of slurry (S) application and N dose. The first number indicates treatment at sowing: 0, no N applied; 2, slurry from fattening pigs applied at a rate of 152 kg N ha^{-1}. Second number indicates the treatment at tillering: 0, no N applied; 4, slurry from fattening pigs at a rate of 265 kg N ha^{-1}; 8, slurry from sows at a rate of 233 kg N ha^{-1}.

Plots with two fattening pig slurry applications (S24, S28) were more hydrophobic than those with only one application (S04, S08) and statistical differences were found (Fig. 5.5b, Table 5.4). Nevertheless, a drying – wetting pattern linked to rainfall events at 200, 400, 600 and 800 h constrained the maintenance of such differences. Consecutive rains at the end of the experiment led to the disappearance of the SWR (Fig. 5.5a). The increase in SWR coincided with the progressive decline of the NH_3 emission rate during the period of 192 h after slurry fertilization (Fig. 5.3a, Fig. 5.3c, and Fig. 5.5a). From 192 h until the end of the experiment, drying-wetting cycles clearly influenced SWR, but no changes in emission rates were registered.

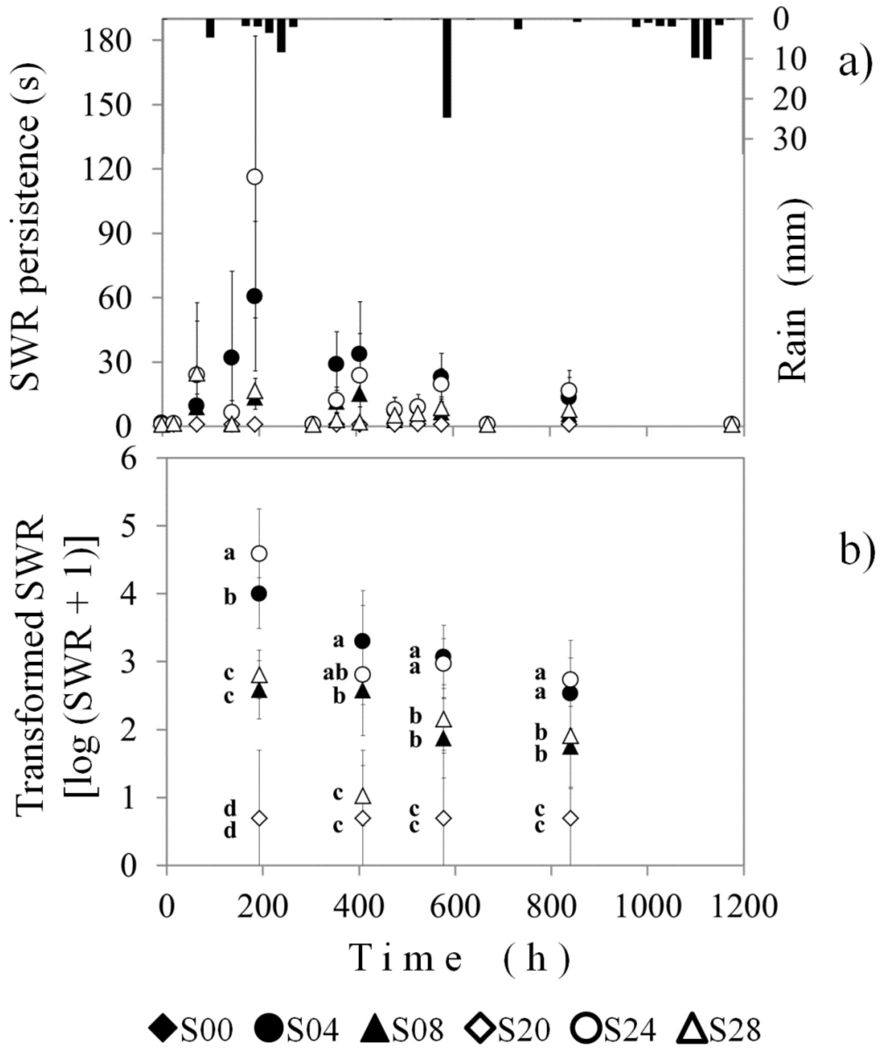

Figure 5.5. Soil water repellency (SWR) persistence averages (n = 12) following the water drop penetration time test (a) and their transformed values (b), during the evaluation period at tillering. Standard deviations are included. Precipitation events are represented by the vertical lines from the top (a). Transformed values followed by the

same capital letter, are not statistically different according to Tukey test ($\alpha = 0.05$). Code numbers are related to the moment of slurry (S) application and N dose. First number indicates treatment at sowing: 0, no N applied; 2, slurry from fattening pigs applied at a rate of 152 kg N ha^{-1}. Second number indicates treatment at tillering: 0, no N applied; 4, slurry from fattening pigs at a rate of 265 kg N ha^{-1}; 8, slurry from sows at a rate of 233 kg N ha^{-1}.

Table 5.4.

Analysis of variance of transformed values (log (SWR + 1)) of soil water repellency by sampling time after slurry application at cereal tillering.

Time (h)	Source	df	Sum of squares	Mean square	F ratio	P
192	Between treatments	5	29.928	5.986	193.37	<0.0001
	Between blocks	1	0.010	0.010	0.34	0.56
	Between samples within treatments	30	0.970	0.032	1.04	0.45
	Within samples (residual)	35	1.083	0.031		
	Total	71	31.992			
408	Between treatments	5	15.647	3.130	44.20	<0.0001
	Between blocks	1	0.335	0.335	4.73	0.04
	Between samples within treatments	30	1.822	0.061	0.86	0.66
	Within samples (residual)	35	2.478	0.071		
	Total	71	20.281			
576	Between treatments	5	12.458	2.492	89.39	<0.0001
	Between blocks	1	0.0001	0.0001	0.02	0.8814
	Between samples within treatments	30	0.989	0.033	1.18	0.35
	Within samples (residual)	35	0.976	0.028		
	Total	71	14.423			
840	Between treatments	5	8.682	1.736	30.82	<0.0001
	Between blocks	1	0.126	0.126	2.23	0.14
	Between samples within treatments	30	1.159	0.039	0.69	0.85
	Within samples (residual)	35	1.972	0.056		
	Total	71	11.938			

DISCUSSION

Ammonia volatilisation

At sowing, the prompt abatement of NH_3 emissions to control levels by burying the slurry applied was a successful measure (Fig. 5.2). In fact, it was higher than other successful abatement data (80 and 50%) recorded by Rochette et al. (2001). It was probably because they reported values of soil water content above field capacity during the whole experiment, while our soil just reached a 16% of SWA at the soil surface (Fig. 5.1a). Lack of water constrained volatilisation as water sustains the reaction of NH_3 emission (Kissel and Cabrera, 2005), reducing potential losses when soil dries (Yagüe and Bosch-Serra, 2013). Slurry burying prevented the reliable detection of SWR previous to the second application (Fig. 5.5). It was due to the inherent mixture of the material added between the top and the bottom of the superficial layers. However, a light influence was observed on accumulated emissions from MD (Fig. 5.3c), enhancing emission when slurries had been previously applied at sowing. This trend has also been recorded by other authors (Bosch-Serra et al., 2014) in dryland systems.

At cereal tillering, the changes in NH_3 emission fluxes over time were affected by diurnal air temperature. Samples collected at 31, 55 and 79 h (traps fitted in the field from 10 AM to 17:00 PM) after slurry application had higher fluxes than those collected at 24, 48, 72 h, after the night period (Fig 3c). As temperature increases, the equilibrium gas-phase NH_3 concentration increases (Hafner and Bisogni, 2009). In contrast, as wind speed increases (Fig. 5.1b), it enhances evaporation and soil surface drying, as reported by Sommer et al. (1991). Thus, the reduction of the superficial (0-0.1 m) soil water content below 10% of SWA (Fig. 5.1b) was followed by a general decrease in flux NH_3 emission (Fig. 5.3a and Fig. 5.3c). As stated, NH_3 does not volatilize from dry soils because of lack of reactions (Kissel and Cabrera, 2005). Re-wetting by a light rainfall (4.6 mm on the fifth day after application (Fig. 5.1b) did not stop the tendency, probably because the main losses had already occurred (Fig. 5.2b).

Despite the similar TN dose applied with both slurries at tillering, higher accumulated NH_3 emissions generated from PSF can be associated to the higher amounts of AN applied (Table 5.1), as absolute emissions are positively correlated with the $\log_{10}$ of manure AN concentration (Hafner et al., 2017). Nevertheless, our records were in the low range of emissions described by these authors. The model pattern of accumulated

NH_3 was similar for both foams (Table 5.2) although differences in total Figure 5.s (higher in MD) were more acute when PSF were used, because the major incidence of turbulent mixing transfer with height at higher NH_3 emissions.

Soil water repellency

Hydrophobic compounds in pig slurries accounted for 45% in PSF and 56% in PSS of the WEOC. These Figure 5.s are in the upper range or rather higher than records from other studies which reported: 47% OC_{ho} (Gigliotti et al., 2002) and 27% OC_{ho} (Provenzano et al., 2014). This variability can be due to the differences in animal waste management. Slurries also showed lower OC_{ho} values than other organic fertilizers such as sewage sludge (92%), urban waste compost (59%) or pig slurry compost (69%) because of the predominance of labile compounds in OC_{hi} in less stabilized organic materials such as pig slurry (Gigliotti et al., 2002; Said-Pullicino et al., 2007; Provenzano et al., 2014),

Water-extractable organic C fractionation in slurries permitted us to obtain the first rough estimation of the OC_{ho} compounds to evaluate the potential risk of SWR development when high doses are applied in soils. Nevertheless, disc harrowing before sowing would be acting as a strategy to avoid SWR persistence, as all treatments were totally wettable at cereal tillering prior to slurry application (Fig. 5.4 and Fig. 5.5). In conventional tillage systems, as this experimental site, tilt has been reported as an effective management practice to avoid hydrophobicity (Jarvis et al., 2008; Müller and Deurer, 2011).

After slurry spreading as topdressing, SWR changes were governed by the variations of soil moisture content (Fig. 5.1b). A decrease in soil moisture content produced SWR peaks at 192, 408, 576 and 840 h after the slurry application (Fig. 5.1b and Fig. 5.5). The lowest soil moisture content coincided with the highest hydrophobicity expression at 192 h after slurry spreading, and treatments with PSF developed higher SWR than PSS. Despite the lower percentage of hydrophobic components in PSF than in PSS, the higher WEOC, total organic matter and DM content in PSF favoured repellency. These differences in DM content were within the range reported for slurries produced in NE Spain (Yagüe et al., 2012; Antezana et al., 2016).

Soil became hydrophilic after rain events when moisture was close to or above the soil water field capacity (360, 672 and 1176 h). Our results are in agreement with Doerr and Thomas (2000) who reported that after a wetting-drying period, SWR was not necessarily restored to the initial values, even in sandy loam to loamy sand soils with high hydrophobic persistence (>1 h). Other authors also have reported wettability in fine sand, sandy loam and loam sand soils when moisture content exceeded the soil WFC (Ritsema and Dekker, 1994; Doerr and Thomas, 2000). We suggest that the wetting periods after rainfalls allowed favourable conditions of soil moisture to enhance the transformation of organic compounds added with slurries. It may result in a first degradation of the organic matter added, especially the OC_{hi} fraction, followed by OC_{ho} compounds re-distribution in the soil surface which gradually decrease over time. Furthermore, it means that SWR can be minimized with a proper control of soil moisture and soil tillage, thus being reversible over time. The opposite was found under long term conservative practices (Blanco-Canqui and Lal, 2009; González-Peñaloza et al., 2012), which increased SWR in soils.

The amount of hydrophobic compounds applied was six times higher in PSF than PSS (Table 5.1) even if the OC_{ho}: OC_{hi} ratio showed the predominance of hydrophobic compounds in PSS. However, the total amount of WEOC added with PSF may have influenced the increase of SWR values (Table 5.3) and its higher persistence up to 840 h after the slurry application (Fig. 5.5).

This persistence creates an alert about the potential for negative SWR effects at the soil surface, such as on water infiltration, laminar erosion and preferential flux in historical applications where slurries are not buried (e.g. no-till systems). A proper management of soil moisture above a critical moisture point, if irrigation systems are available, would limit these negative impacts. Tarchitzky et al. (2007) recommended irrigation, preferably with fresh water, which will also help in the NH_3 emissions abatement (Holcom et al., 2011), mainly in high water irrigation demanding systems (Wallach et al., 2005).

Ammonia volatilisation and soil water repellency patterns

Total organic matter, WEOC, DM and hydrophobic slurry compounds affected SWR and NH_3 emission. Physical and chemical properties of the soil surface in a two-phase process changed. During an initial period, the highest NH_3 volatilisation rates were produced, while the soil was predominantly wettable (Fig. 5.2 and Fig. 5.5a), by the temporary increase in the top soil water content (0-24 h) (Fig. 5.1b). Emissions were higher as the OC_{ho} and DM increased (Table 5.1, Fig. 5.3c). The described effect of DM coincided with Thompson and Meisinger (2002). The second phase started as the soil surface dried, in our case from 24 to 192 h (Fig. 5.1b). Ammonia volatilisation decreased as the superficial crust raised the liquid phase resistance, while SWR was promoted (Fig. 5.2 and Fig. 5.5). Misselbrook et al. (2005a) reported a 50% decrease of NH_3 emissions when a slurry crust was formed in slurry tanks and Bosch-Serra et al. (2014) associated the treatments with thicker crust formation over soil with low NH_3 emission rates. In our case, as slurries were applied in early February, the drying-phase period was prolonged until 192 h due to meteorological conditions (Fig. 5.1b).

At cereal tillering, the first rainfall (4.5 mm) occurred at 120 h after slurry spreading. It caused a decrease of the NH_3 emission rate, as observed also by Sommer and Olesen (1991) and Misselbrook et al. (2005), who found reduced NH_3 emissions after rain simulations. However, 4.5 mm rain was not enough to make the soil become wettable. A higher volume of rainfall (8.3 mm) after 192 h considerably reduced the SWR but without significant effect on NH_3 emission because by then, more than 75% of AN had already been emitted.

Slurry properties, such as DM and its hydrophobic compounds, combined with soil moisture content at fertilization time, controlled NH_3 emissions and further SWR. It is difficult to control soil moisture in dryland systems but in other agricultural systems, mainly under no-till, water management will be a key practice to control volatilisation while avoiding SWR. The hydrophobic compounds in the organic materials affects the variation of SWR development, but in this case the risk of NH_3 emissions may also be avoided by using more stabilized organic materials with a low AN content, e.g. co-composted pig slurry, as suggested by other authors (Sommer and Hutchings, 2001). Beyond the dynamic of superficial crust formation (when slurries are not buried) and its decomposition, the water cycle and laminar erosion when SWR develops, are a matter of concern. In this scenario, attempting to retain critical soil water content would be of interest to avoid such problems.

CONCLUSIONS

At tillering, when slurries were not buried, 50% of NH_3-N emission from AN applied was reached during the 72 h after application. Losses were equivalent to 8.7 to 15.2 kg

N ha^{-1} for PSS and PSF, respectively. Emissions were lower than those cited in the literature, probably because of the influence of low soil water content.

Fattening pig slurry liquid fraction had the highest WEOC content, which increased the soil water repellency, despite the predominance (56 to 59%) of the OC_{hi} fraction. The maximum SWR persistence on soil surface was 242 s at 192 h (8 d). Nevertheless, SWR was a transitory phenomenon not lasting more than 49 d after slurry spreading. It is also true that the drying-wetting pattern in the soil surface affects the soil water repellency, which increases when the soil is dry.

Finally, it is necessary to define the initial SWR after periodic slurry applications that could enhance NH_3 emission (e.g. at tillering slurry spreading or in tillage systems where slurries are not buried).

ACKNOWLEDGMENTS

Field assistance: A. Bureu, E. Edo, J. Llop, J. Rumí, M. Vilarrasa and M.R. Yagüe. Lab assistance: M. Antúnez, S. Maris and S. Porres, as well as G. Gigliotti and “Laboratorio di Chimica Agraria – Chimica delle Biomasse di Uso Agrario”, Department of Civil and Environmental Engineering, University of Perugia for the support in slurry fractionation and analyses. Funding: Spanish Ministry of Economy and Competitiveness and the Spanish National Institute for Agricultural Research and Experimentation (MINECO-INIA) through the projects RTA2013-57-C5-5 and RTA2017-88-C3-3. D.E. Jiménez-de-Santiago also acknowledges the JADE-Plus scholarship from Bank of Santander-University of Lleida for PhD studies.

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CHAPTER 6

Soil water dynamics in a rainfed Mediterranean agricultural system

This chapter contains the following accepted and already online published paper in the journal *Water.*

Jiménez-de-Santiago, D.E., A. Lidón, and À.D. Bosch-Serra. 2019. Soil Water Dynamics in a Rainfed Mediterranean Agricultural System. Water, 11(4), 799, https://doi.org/10.3390/w11040799

SOIL WATER DYNAMICS IN A RAINFED MEDITERRANEAN AGRICULTURAL SYSTEM

ABSTRACT

Rainfed Mediterranean agriculture is characterized by low water input and by soil water content below its field capacity during most of the year. However, erratic rainfall distribution can lead to deep drainage. The understanding of soil-water dynamics is essential to prevent collateral impacts in subsuperficial waters by leached pollutants and to implement suitable soil management (e.g., agronomic measures to avoid nitrate leaching). Soil water dynamics during two fallow years and three barley crop seasons was evaluated using the Leaching estimation and chemistry model in a semiarid Mediterranean agricultural system. Model calibration was carried out using soil moisture data from disturbed soil samples and from capacitance probes installed at three depths. Drainage of water from the plots occurred in the fall and winter periods. The yearly low drainage values obtained (<15 mm) indicate that the estimated annual nitrate leaching would be also small, regardless of the nature of the fertilizer applied (slurries or minerals). In fallow periods, there is a water recharge in the soil, which does not occur under barley cropping. However, annual fallow included in a winter cereal rotation, and a period with substantial autumn-winter rains (70–90 mm) can enhance nitrate leaching, despite the semiarid climate.

Keywords: drainage; ECH2O probes; fallow system; LEACHM; soil water content

INTRODUCTION

Soil water dynamics and solute transport studies are gaining ground due to the interest in solving environmental issues as nitrates in ground waters [1], mainly in intensive rearing agricultural areas [2,3]. Rainfed agriculture in semiarid Mediterranean areas around the world faces limitations on plant water availability related to soil properties (i.e., low soil organic matter content) and climate, mainly due to the variability in precipitation and extreme erosive rainfall events [4]. Rainfall is a critical input and the main source of risk and uncertainty in these agricultural systems [4]. In Spain, 78% of the arable land is used for rainfed agriculture [5]. Soil water content (SWC) is below its field capacity for almost the whole year. Thus, the amount and distribution of seasonal precipitation influences growth, water use efficiency and yield of cereals such as winter barley [6].

Winter cereal production in dryland Mediterranean areas is improved by agricultural practices. Soil fallowing is a traditional practice that saves water and nutrients for the next crop season [7]. In north eastern Spain, an increment of 49% in barley yield has been reported when compared with continuous cropping systems, probably due to the additional soil water storage under the annual fallow system between winter sowings [6]. However, the practice of fallowing to increase cereal crop yields is no longer recommended [6]. Heavy rains could transport nutrients through erosion or by percolation to the deepest layers, easily removing solutes as nitrates (NO_3^-) from the root zone to the groundwater. As rainfed areas are linked to an important animal rearing activity, nitrogen (N) is fully available from livestock wastes and the potential contamination of groundwater by nitrates is feasible despite extended drought periods.

Monitoring SWC, water drainage and its dynamics in cropland areas is useful to quantify water use and potential leaching in order to implement agronomic measures that mitigate the possible groundwater contamination. Soil water content can be quantified from a number of direct or indirect procedures [8,9]. The most common one is the gravimetric method. It consists in oven-drying soil samples until constant weight [10]. Indirect SWC measurements can be obtained from capacitance probes, known as frequency domain reflectometry, based on soil and water dielectric properties [11]. Detailed field sampling in depth and over time is costly. Soil moisture sensors easily provide soil-water data but they require an initial calibration to assure proper measurements. There is no direct way of measuring drainage, except when using lysimeters. However, it is difficult to install them without changing soil hydraulic behavior, which constraints drainage comparisons against other methods [12]. Hence, numerical models represent a feasible option to evaluate soil drainage.

Numerical models are a mathematical approach to obtain soil-water dynamics but they always require accurate field data to obtain high quality outputs [13]. A number of models have been developed [14–16] and some researchers have reviewed them [17–19]. Soil water content models can be applied in agronomy at different scales, and they are coupled with nutrient models for simulating the soil-water-plant system. Models are classified as lumped or distributed, with distributed models being deterministic or stochastic. According to Addiscott and Wagenet [17], deterministic models presume that a system or process operates such that the occurrence of a given set of events leads to a uniquely-definable outcome. The stochastic models are based on the assumption that the outcome will be uncertain, thus the model structure is constructed to account for this uncertainty. Furthermore, deterministic models can be subdivided into mechanistic and functional. The mechanistic models refer to the incorporation of the most fundamental process or mechanisms that in the case of soil-water dynamics involves the use of equations derived from Darcy’s Law, usually based on rate parameters driven by time. The functional models are based on a tipping buckets approach and they are simple and discrete in time, simulating changes in the amount of water content (rather than rates of change).

Leaching Estimation and Chemistry Model (LEACHM) is a one-dimensional deterministic mechanistic model describing the storage, transport and distribution of water and solute in an unsaturated soil [14,20]. The model solves Richards’ equation by finite differences to describe the one-dimensional water flow in the unsaturated zone. It is especially useful in environments with transient conditions as is the case with dryland agriculture. The model is written in FORTRAN code, allowing subroutines to be independently improved or modified, which makes adaptation to different environments easier [14,21]. The input parameters required are the soil hydraulic properties, boundary conditions and input water. These can be measured, estimated or obtained from standard data. The LEACHM model has been evaluated and widely used in diverse geographic settings under various conditions [22–24] not only for N leaching but for soil water dynamics [25,26]. Thus far, few examples of its use have been carried out under dryland environments [26] where it can be useful to quantify water recharge in the soil profile, potential drainage in rainy or fallow seasons and the derived nitrate leaching.

Our hypothesis is that drainage occurs in semiarid rainfed areas and that fallow periods could account for the most important losses. The objective of this work is to characterize drainage and to evaluate the soil-water dynamics using the LEACHM model in a Mediterranean dryland agricultural system. We focused on the minimum, maximum and seasonal values of soil-water drainage and soil water recharge in a winter cereal crop rotation where fallow is included.

MATERIALS AND METHODS

Study Area

The experiment was located in Oliola, Lleida, NE Spain (Fig. 6.1). Coordinates are 41°52”30’ N, 0°09”11’ E with altitude of 440 m above sea level. The experimental site is flat and open. The soil is deep (>1 m), non-saline and calcareous, classified as Typic Xerofluvent [27] with a silty loam texture, an average organic carbon content of 11.67 g kg^{-1}, calcium carbonate content of 300 g kg^{-1}, and pH of 8.2 (1:2.5 soil: distilled water).

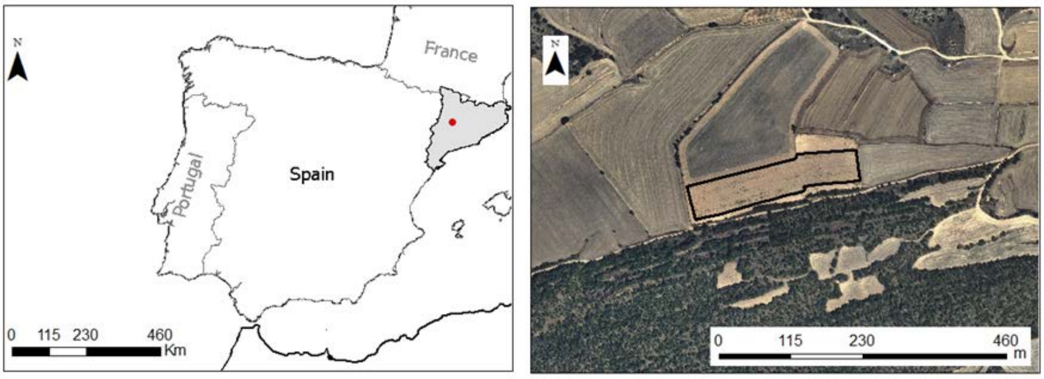

Figure 6.1**.** Geographical location of the experimental field in Oliola (Lleida), in the northeast part of Spain.

A detailed study on soil physical characterization and instrumentation was performed in a plot representative of the area. The experimental field had a four year rotation which included wheat (*Triticum aestivum* L.) and barley (*Hordeum vulgare* L.) maintained during one and three years, respectively, as the main crops. Fallow years were also present. Usually, the crops were sown in late October and harvested at the end of June–early July.

Climate Conditions

The area has a semiarid Mediterranean climate with a mean annual temperature of 12.6 °C with a maximum monthly average of 19.8 °C in August and a minimum monthly average of 5.8 °C in January. Daily meteorological data, precipitation, air temperature and evapotranspiration were obtained from an automatic station next to the field. The mean annual precipitation was 443 mm, and ranged from 291 mm to 593 mm (years 2006 and 2003, respectively) for the period 2002–2017. Within the year, maximum monthly precipitation occurs in April, followed by October and November. The probability of cumulative precipitation for the mentioned period indicates that for half of the years, annual precipitation was 390 mm or lower and in 25% of the years the cumulative precipitation exceeded 500 mm (Fig. 6.2A). During the crop cycle, less than 350 mm of water are available to plants. This amount can be reduced to less than 190 mm (Fig. 6.2B). Extreme events range between 60 and 100 mm in a 100-year return period (Table 6.1). Rainfall data come from the local estimation proposed by Santamaría [28] and they were compared against the proposed rainfall values from Casas [29]. These data were considered in order to detect maximum potential leaching.

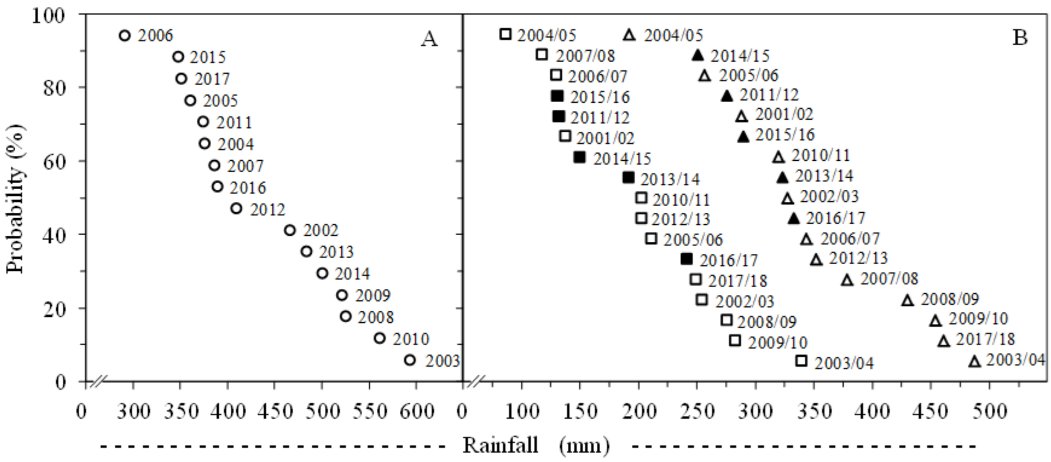

Figure 6.2. Annual (A) and seasonal (B) rainfall probability in the study area based on available rainfall data from 2002–2017. In seasonal evaluation, the whole crop cycle (triangles) and the autumn–winter period (squares) are shown. In black: the years used in this work.

Table 6.1. Maximum 24-hour precipitation, for different return periods (years), at a regional scale calculated by different approaches.

Approach	Maximum 24-h precipitation (mm)		
	25 years	50 years	100 years
Santamaría [28]	72	82	93
Casas [29]	60–80	80–100	100

Soil Properties

Soil physical and chemical characteristics are shown in Table 6.2. Two main horizons were described from 0 to 32 cm and from 32 to 138 cm. The soil profile was divided into three depths, 0–30, 30–60 and 60–90 cm. The second horizon was divided in two for soil water records because root winter cereal density between 30–60 cm (data not shown) is higher than between 60–90 cm [30]; the latter was considered the limit for cereal rooting depth in the area.

Table 6.2. Soil physical and chemical properties of the experimental site.

Properties	Units	Depth (cm)		
		0–30	30–60	60–90
Sand	%	15.2	31.1	11.5
Silt	%	58.1	48.6	60.3
Clay	%	26.7	20.3	28.2
Textural class		Silty loam	Silty loam	Silty clay loam
pH (1:2.5 soil:water)		8.3	8.5	8.5
Organic carbon	g C kg^{-1}	9.9	4.6	4.6
Bulk density	kg m^{-3}	1650	1600	1550
Infiltration velocity	mm h^{-1}	1.54	–	–
Saturated hydraulic conductivity	mm d^{-1}	233	524	457
Soil water retention[1] at:				
−33 kPa	cm^3 cm^{-3}	0.269/0.223	0.266/0.232	–
−100 kPa	cm^3 cm^{-3}	0.234/0.194	0.237/0.213	–
−500 kPa	cm^3 cm^{-3}	0.173	0.168	–
−1500 kPa	cm^3 cm^{-3}	0.163	0.170	–
Soil water content at saturation[2]	cm^3 cm^{-3}	0.37	–	–

[1] Values measured from disturbed and undisturbed samples respectively (before and after the forward slash, respectively).

[2] Value obtained from field sampling when measuring saturated hydraulic conductivity.

Soil texture was obtained from the particle size analysis (Pipette method, [31]). Organic carbon was assessed with the Walkey-Black method [32]. Soil bulk density (ρb) was determined from the soil dry weight of a known soil volume sample (100 cm^3) and the average value of each layer was calculated (n = 4). Saturated hydraulic conductivity (K_s) and infiltration velocity were obtained from field measurements in the experimental plot with the Guelph permeameter (model 2825KI, Soil Moisture Equipment Corp.), and with a tension infiltrometer (model 2826D20, Soil Moisture Equipment Corp.), respectively. The soil water retention was determined in the two upper layers using the pressure plate apparatus at different matric potentials ψ (kPa). At the higher matric potentials (−33 and −100 kPa) it was done in disturbed and undisturbed soil samples to identify differences associated to the soil structure or potential compaction.

Data Acquisition

Soil water content data was obtained from 2011/12, 2013/14, 2014/15, 2015/16 and 2016/17 cropping seasons although the field was maintained under fallow in 2013/14 and 2016/17 (Fig. 6.3).

Data came from two sources: by means of frequency domain reflectometry probes (ECH2O soil moisture probes, Decagon Devices, Pullman, Washington, USA, 2002); hereafter, it will be referred as “ECH2O” sensors, and by disturbed soil samples (DISSA). The ECH2O sensors are devices that measure volumetric water content via the dielectric constant of the soil using capacitance technology [33]. In 2006, the ECH2O sensors were installed at six points of the experimental field in the four soil layers (0–30, 30–60, 60–90 and 90–120 cm) and calibrated using field soil water measurements obtained weekly during three months (data not shown). One of them was located in the plot where the soil characterization was carried out. Daily SWC was automatically recorded at four-hour intervals and converted on a daily basis, since then. The output signals of the probes were transformed according to the manufacturer’s advice to obtain volumetric SWC values for each layer.

From the beginning of the experiment, SWC was monitored at three depths (0–30, 30–60 and 60–90 cm) from disturbed soil samples. Soil samples were collected periodically throughout the crop cycle. Samplings were made with a soil auger close to the ECH2O sensors. In each sampling date, between 3–6 soil samples were taken in different points of the experimental site. Gravimetric SWC was determined by oven drying 20 g of disturbed soil sample at 105 ˚C until constant weight. Then, the volumetric water content (θv) was calculated multiplying gravimetric water content (θg) by the ρb. Soil water storage (mm) was calculated by multiplying θv for the thickness of the soil layer. Finally, total water content was obtained from the sum of the partial water content of the three layers.

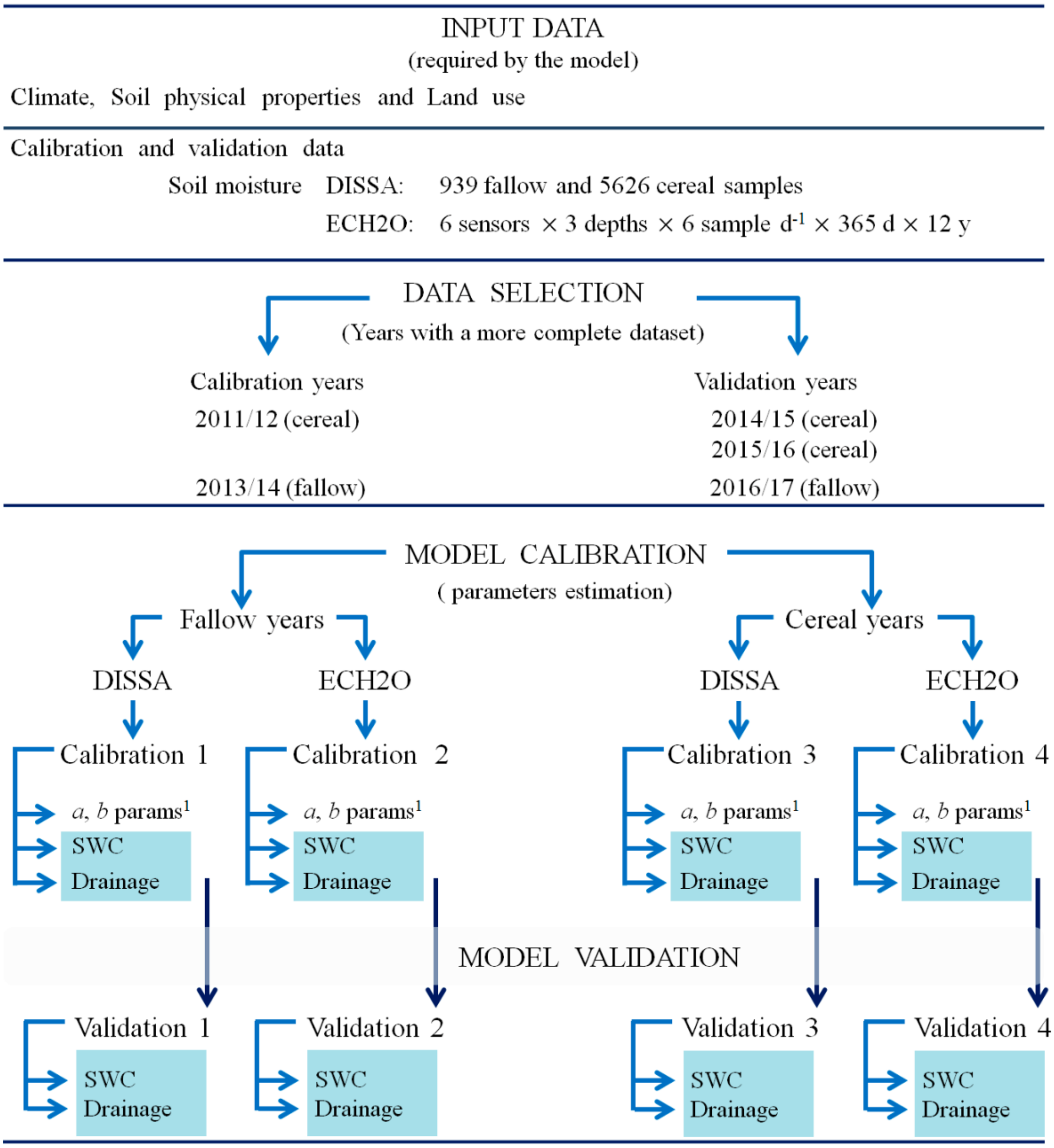

Figure 6.3. General scheme of the applied methodology for data acquisition and the evaluation process to model water dynamics in soil (drainage and soil water content (SWC)) from disturbed soil samples (DISSA) and from frequency domain reflectometry probes (ECH2O). The *a* and *b* parameters[1] belong to the functions defining soil water retention and hydraulic conductivity.

Samplings were done before sowing, at cereal tillering and after crop harvest. During the 2011/12, 2013/14, 2014/15, 2015/16 and 2016/17 cropping seasons, soil samples were taken before sowing (September or October) and in the following month: at cereal tillering stage (late January, early February), at spring time (between March–May) and after crop harvest (June).

Soil water dynamics were evaluated with the LEACHM model. Two cropping seasons under fallow (2013/14 and 2016/17) were included in the study. Barley was cropped in the 2011/12, 2014/15 and 2015/16 seasons, which were used in the evaluation. The later cropping seasons covered the rainfall variability (Fig. 6.4) and yield variability (from 5 to 8 Mg ha^{-1}).

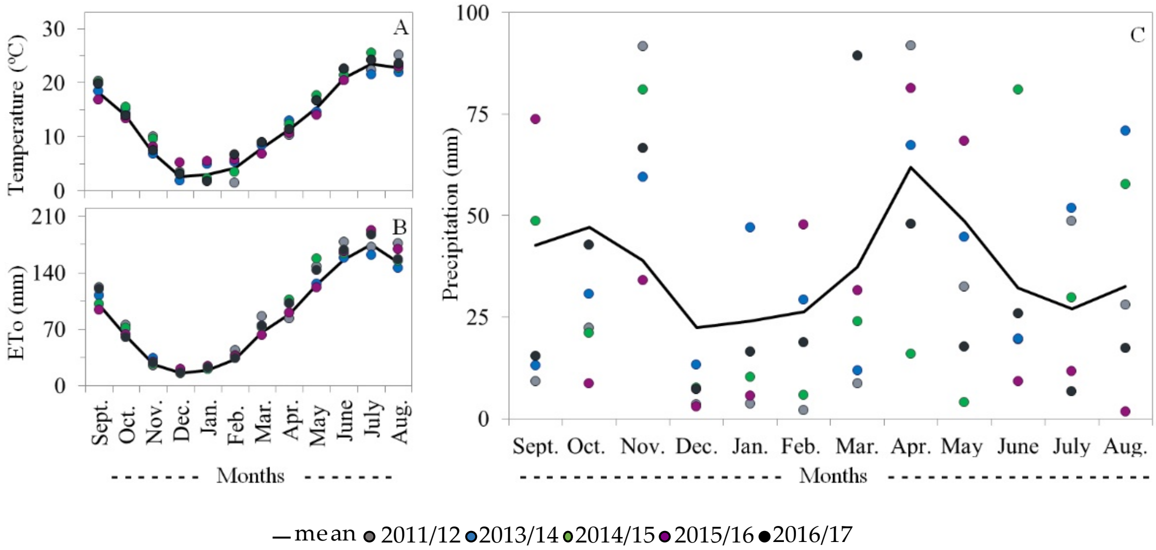

Figure 6.4. Monthly average temperature (A), total monthly evapotranspiration (Penman-Monteith equation) (B) and total monthly precipitation (C) for the experimental period (2002–2017). Specific values for the evaluated years are also shown.

Soil water content from DISSA provided more precise measurements, but daily records were lacking. Thus, for daily records, ECH2O sensor data were used. Soil water content values from midday were chosen and data were taken from 2011 onwards. Data were obtained for the five years from the sensors' installation, meaning that there was enough time to obtain a robust SWC data set. Before the model evaluations, ECH2O sensor data were compared against DISSA data using linear regressions to decide the time period to be used in the LEACHM model.

LEACHM Model

As our dryland agricultural system is characterized by transient water fluxes, the water module belonging to the LEACHM model was used to evaluate the water drainage below 90 cm and the water balance in the soil profile. It is considered a vertical unidimensional mesh, which is divided into an equal number of horizontal layers, and time is split into intervals shorter than a day. This model describes the one-dimensional water flow in the unsaturated zone using the diffusivity form of the Richards' equation, solved by the Crank and Nicolson method [34]. For this, it is necessary to know the relations between hydraulic conductivity, volumetric moisture and matric potential. Those are based on the moisture retention function (Equation 1) and the unsaturated hydraulic conductivity function (Equation 2) proposed by Campbell [35]:

$$h = a(\frac{\theta}{\theta_s})^{-b}, \quad (1)$$

$$K = K_s\left(\frac{\theta}{\theta_s}\right)^{2b+2+p}, \quad (2)$$

where h is the matric potential, a is the air entry water potential and b is an empirically determined constant, θ_s is the volumetric water content at saturation, K_s is the saturated hydraulic conductivity and p is an interaction parameter about pore size, the value of which is assumed to be 1 for the LEACHM model. In addition, LEACHM uses the wet-end modification of Hutson and Cass [36] which introduced a sigmoidal function without discontinuities. The calculated θ_s value from 0 to 30 cm coincided with our field measurements (Table 2). A free-draining lower boundary was assumed because no plough layers or equivalent limiting drainage, have been described in this plot.

Weekly potential evapotranspiration (crop reference evapotranspiration ET_0, obtained with Penman-Monteith equation [37]) was introduced in the input data file of the LEACHM model. Daily potential evapotranspiration (ET) is calculated as one-seventh of the weekly potential ET. The LEACHM model uses the crop cover fraction to separate potential ET into potential evaporation and potential transpiration. Potential ET for a time step is calculated following Childs and Hanks [38]. It was also assumed that both evaporation and transpiration start at 0.3 day (7h 12) and they end 12 hours later

(0.8 day). A sinusoidal variation of potential ET flux density (mm day^{-1}) was included with the final aim to calculate the fraction of total ET lost during a determined time interval. The potential evaporation and the maximum evaporative flux density were considered to calculate the actual evaporation. The plant water uptake at z depth and a time interval t was calculated following Nimah and Hanks [39] as:

$$U(z,t) = \frac{[H_{root} + z(R_c + 1) - h(t) - s(t)]}{\Delta x \Delta z} \times RDF \times K(\theta, t) \quad (3)$$

where $U(z,t)$ is the transpiration sink term in the Richards equation (day^{-1}), H_{root} is the water potential at the root-soil interface (mm), z is depth (mm), $(Rc + 1)$ is a root resistance term (mm), $h(t)$ is the soil water pressure head (mm), $s(t)$ is the osmotic potential (mm), RDF is the fraction of total active roots in the soil layer, $K(\theta,t)$ is hydraulic conductivity (mm day^{-1}) for soil water content θ and Δx is the conceptual distance from the point where h and s are calculated to the plant root (fixed at 10 mm in the code). Richard's equation is solved for each soil layer an each flow interval with a periodicity of 0.05 day or less depending on the water flow. The model requires input data about soil physical properties, water inputs (rain events), weather and crop data. Soil physical properties, such as texture, organic carbon, ρb, water retention curve and Ks at the three soil layers, were selected from Table 2. Daily accumulated rainfall figures were the water inputs and were taken from the meteorological station. Meteorological data were the weekly values of potential evapotranspiration, mean temperatures and thermal amplitude. They were calculated from the daily data sets. Finally, crop data referring to plant characteristics (planting, emergence, plant and root maturity, crop cover fraction at maturity, harvest dates), crop growth (crop cover fraction) and fertilizer applications were obtained from the experiment's field observations.

Model Calibration and Validation

The approach for evaluating water dynamics with the LEACHM model was from the simple case study (fallow period) to a more complex assessment (cropping period). The selected simulation periods were chosen to account for the lowest and the highest SWC data linked to a driest cropping season and a rainy period (under fallow). Soil water dynamics using DISSA were evaluated for the whole crop cycle. The starting simulation day was selected according to the first sampling day, related to the sowing time. The end day was considered to be a week after the last sampling day at harvest. Only for the fallow year 2013/14, a longer period was considered: from September 2013 to October 2014, when barley was sown. Meanwhile, soil water dynamics using ECH2O sensor data were evaluated for a six-month period from 1st October to 31th March of each cropping season. No longer period was selected because under dry summer conditions of the experimental site (Fig. 6.4) ECH2O sensors do not work properly because the pores have not a required minimum water content. During the 2015/16 crop year, data entry from the ECH2O sensors stopped for part of the time; thus, only 119 d of SWC were recorded. Selected ECH2O data were adjusted according to the field moisture data, as they were obtained from independent devices located in the soil at different depths. Once data were collected and properly organized, LEACHM model evaluation was performed (Fig. 6.3). It consisted in calibration and evaluation. First, two fallow seasons were calibrated-validated and then, plants were introduced with three barley cropping seasons. In both cases, observed and modeled SWC data were compared.

Sensitivity analysis evaluates the effect of different parameters on the modeling of the volumetric SWC with the LEACHM model [21,40,41]. Sánchez-de-Óleo [21] found that the most highly influencing parameter was the *b* coefficient of the Campbell equation, and he gave less importance to the *a* coefficient of the equation. According to this author, the saturated hydraulic conductivity was not a sensitive parameter. Calibration was performed by running LEACHM with two data sets, the 2013/14 period for fallowing and the 2015/16 period for cropping land use (Fig. 6.3). An optimization procedure based in the Nelder-Mead simplex method was used to adjust the parameters of the Campbell equation [42]. This is a direct search method that does not use numerical or analytic gradients and minimize an objective function in a multidimensional space according to values of the function. The measured SWC values for each land use and data origin was used for calibration (Fig. 6.3). A range in the coefficient values and an initial input value for each coefficient were needed. To calibrate the *b* coefficient, it ranged from 3 to 15 in the upper layer and from 5 to 15 in the other two deeper layers. The *a* coefficient calibration values ranged from −5 to −2 kPa only for the upper layer. The variation ranges chosen for parameters *a* and *b* were similar to those used in other calibrations of the LEACHM model [21,41]. The second and the third layer were manually adjusted, according to the *a* upper coefficient. Calibration was finished when the *a* and *b* adjusted parameters did not significantly change after the iterations. At that point, the error differences between observed and simulated SWC in profile were minimized.

Five statistical parameters were used to evaluate the model. The mean difference (*MD*) and the determination coefficient (R^2) criteria served to compare model predictions between observed (*Oi*) and simulated (S_i) values:

$$MD = \frac{1}{N}\sum_{i=1}^{N}(O_i - S_i), \tag{4}$$

$$R^2 = \left[\frac{\sum_{i=1}^{N}(O_i-\bar{O})(S_i-\bar{S})}{\sqrt{(\sum_{i=1}^{N}(O_i-\bar{O})^2)(\sum_{i=1}^{N}(S_i-\bar{S})^2)}}\right]^2, \tag{5}$$

where $\bar{O}$ and $\bar{s}$ are the average of the observed and simulated values, respectively. Additionally, other statistical parameters were used. The root mean square error (*RMSE*) evaluated the differences between observed and simulated SWC, the normalized root mean square error (*NRMSE*) set the differences and compared differences between years, and the agreement index (*d*) evaluated the model fitting [21,43]:

$$RMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(O_i - S_i)^2}, \tag{6}$$

$$NRMSE = \frac{RMSE}{\bar{O}}, \tag{7}$$

$$d = 1 - \frac{\sum_{i=1}^{N}(O_i-S_i)^2}{\sum_{i=1}^{N}(|S_i-\bar{O}|+|O_i-\bar{O}|)^2}, \tag{8}$$

Validation was done by running LEACHM with three different data sets, 2016/17 for fallow land and 2011/12 and 2015/16 for cropping land use (Fig. 6.3). The *a* and *b* coefficient values obtained from the calibration were maintained for validation in the following seasons. Drainage and volumetric SWC for each layer were obtained from the model. Observed and simulated values were also evaluated as mentioned above.

The water balance components we used were the soil water storage, the initial and final soil water depth, rainfall, evaporation (fallow periods) evapotranspiration (cropping periods) and drainage. They were calculated for all the evaluated years. These terms were obtained from the simulations performed with the calibrated model using ECH2O sensor data.

RESULTS

Parameters Calibration

Initial and calibrated coefficient values are shown in Table 6.3. The range of variation of the calibrated parameter *a* was lower under fallow conditions than with the barley crop (−4.95–−5.00 kPa and −2.00–−3.00 kPa, respectively). The most pronounced change corresponded to parameter *b* in fallow conditions (6.08–9.87) than under cropping (6.63–8.81). The highest values of *b* correspond to the calibration made with the data set of soil moisture obtained by soil sampling. However, the values obtained using the ECH2O data set provide a characteristic curve for the soil very similar to that obtained with the pressure plates (Table 6.2).

Table 6.3. Initial and optimal values of the hydraulic parameters adjusted through mathematical iterations for a soil under fallow and under barley cultivation during the seasons 2013/14 and 2015/16 seasons, respectively, with soil samples (DISSA) and soil moisture sensors (ECH2O).

Cycle	Data origin	Iterations number	Error	Parameter	Depth (cm)		
					0–30	30–60	60–90
	Initial			*a* (kPa)	−2.500	−5.000	−5.000
				b	7.400	9.600	9.600
2013–14	DISSA[1]	65	0.22	*a* (kPa)	−4.946	−4.982	−4.982
Fallow				*b*	9.873	9.143	8.376
	ECH2O[2]	112	0.28	*a* (kPa)	−4.995	−4.995	−4.995
				b	7.813	7.210	6.084
2015–16	DISSA[3]	134	0.51	*a* (kPa)	−2.000	−2.500	−2.500
Barley				*b*	7.591	6.513	6.895
	ECH2O[4]	68	0.20	*a* (kPa)	−2.382	−3.000	−3.000
				b	8.819	8.677	6.635

[1]n (number data) = 6; [2]n = 182; [3]n = 8; [4]n = 183.

In the fallow period, the calibration increased the value of parameter *b* and decreased the parameter *a* in the upper layer with respect to the initial values, regardless of the data origin. In the deeper soil layers, the values of *b* decreased and those of the parameter *a* slightly increased. In the crop cycle, the calibration supposes, in all cases, a reduction of the parameter *a* with respect to the initial values, while the parameter *b* increased in the superficial layer and decreased in the other two layers. The calibration led to similar *a* values in the three layers, and a *b* value staggering, corresponding the highest value to the surface layer.

Hydraulic parameters calibration of the model when plants were established resulted in higher values of the parameter *b* in the three layers of the soil profile when the ECH2O data set was used, with a smaller error in the adjustment to the measured data.

Soil Water Content Modelling in a Fallowing Period

Statistical parameters from the soil under fallow showed a better data adjustment for the calibration than the validation cycle (Table 6.4). A general overestimation of the SWC was found, except for the 30–60 cm soil layer. Differences in the total SWC ranged between 11 and 25 mm of water according to the *RMSE* (Table 6.4). A good match between observed and simulated data was confirmed with the *NRMSE* (<0.3) and the agreement index (>0.5) in most of the cases. The biggest differences in *NRMSE* were observed in the upper layer, except for the deepest layers with ECH2O sensor data. For the soil profile, the error ranged between 5% and 14%, corresponding to the lowest *NRMSE* values of the calibration period.

Finally, when the ECH2O data set was used, *d* coefficient was higher for the calibrated than for the validated fallow cycle; however, when using soil sampling data, this coefficient was higher for the validation period. In the fallowing seasons the model explained the variability of observed data, with some exceptions mainly in one layer (60–90 cm) during the 2013/14. Aside from those low values, the R^2 from modeling with the DISSA data set doubled the values from the modeling with the ECH2O sensor data.

Table 6.4. Statistical comparisons between observed and simulated soil water depth for fallow period. Observed data came from field disturbed soil samples (DISSA) and soil moisture sensors (ECH2O).

Statistic	Depth	Calibration (13/14)		Validation (16/17)	
	(cm)	DISSA	ECH2O	DISSA	ECH2O
MD (mm)	0–30	0.19	−0.22	13.92	5.86
	30–60	−0.08	−0.49	1.77	−4.40
	60–90	0.22	5.12	−1.05	−21.86
	0–90	0.33	4.41	14.65	−20.41
RMSE (mm)	0–30	7.52	8.85	18.53	8.38
	30–60	5.07	4.63	5.33	6.02
	60–90	3.37	7.82	2.47	23.37
	0–90	11.21	13.47	23.00	24.82
NRMSE	0–30	0.11	0.14	0.23	0.12
	30–60	0.07	0.06	0.07	0.09
	60–90	0.05	0.11	0.04	0.56
	0–90	0.05	0.06	0.10	0.14
R^2	0–30	0.91	0.28	0.49	0.00
	30–60	0.72	0.70	0.56	0.42
	60–90	0.02	0.10	0.94	0.24
	0–90	0.89	0.49	0.64	0.37
d	0–30	0.52	0.66	0.57	0.26
	30–60	0.50	0.86	0.83	0.65
	60–90	0.40	0.20	0.97	0.06
	0–90	0.65	0.81	0.78	0.31

Graphical evaluation showed differences in the calibration (Fig. 6.5) and the validation seasons (Fig. 6.6), using both data sets. Soil water dynamics were higher in the upper layer and decreased with depth over time. The SWC was better simulated during the calibration than the validation seasons. Both data sets were independently calibrated but similar simulated SWC was observed in the calibration season (Fig. 6.5). On the contrary, the validation season showed considerable differences between observed and simulated SWC (Fig. 6.6).

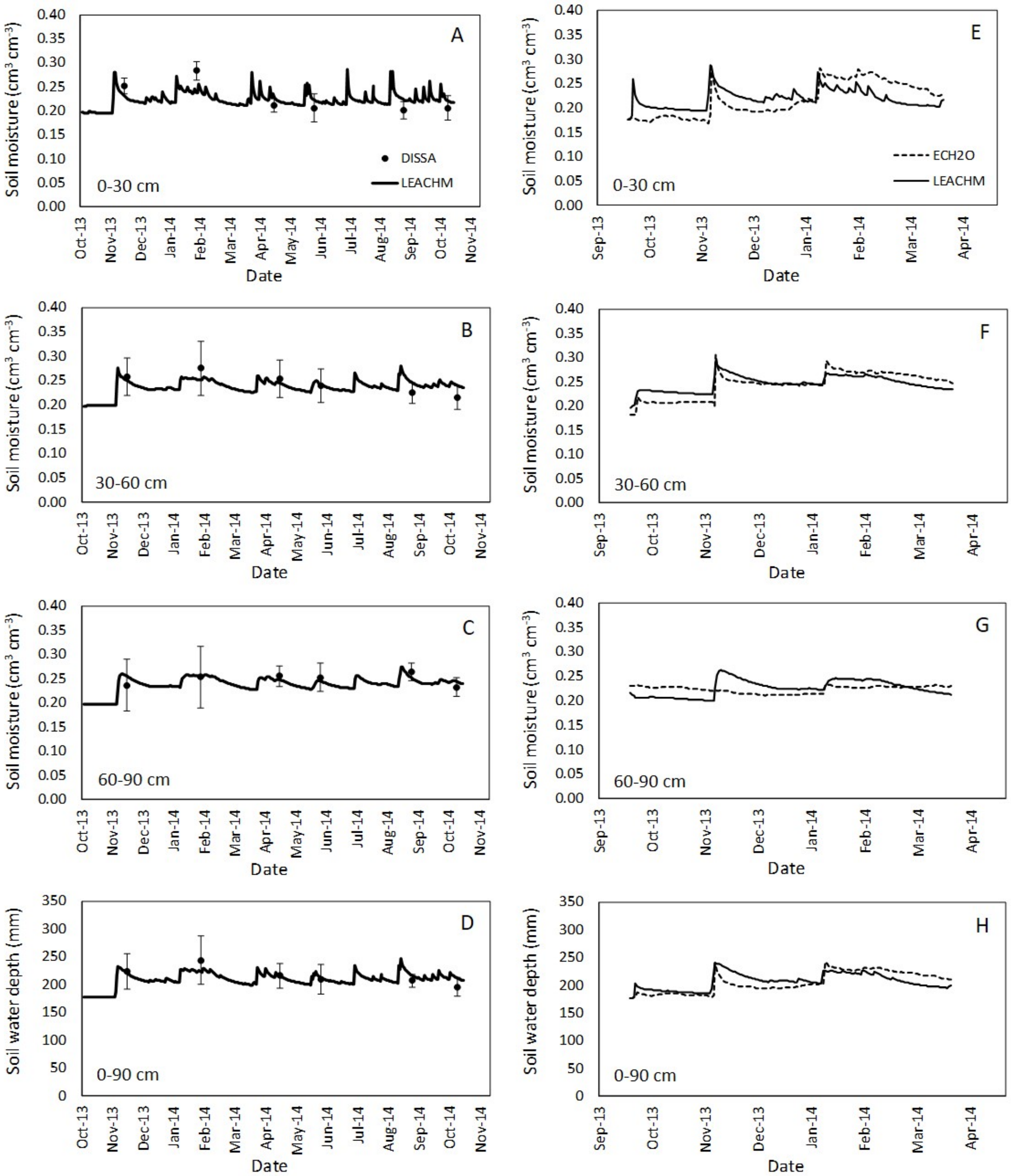

Figure 6.5. Soil moisture in the three soil layers (A, B, C, E, F and G) and soil water depth in the soil profile (D and H) measured from disturbed soil samples (A–D, circles), with ECH2O sensor (E–H, dashed line) and simulated with Leaching Estimation and Chemistry Model (LEACHM) (continuous line) for calibration period under fallow system. Vertical bars represent the standard deviation.

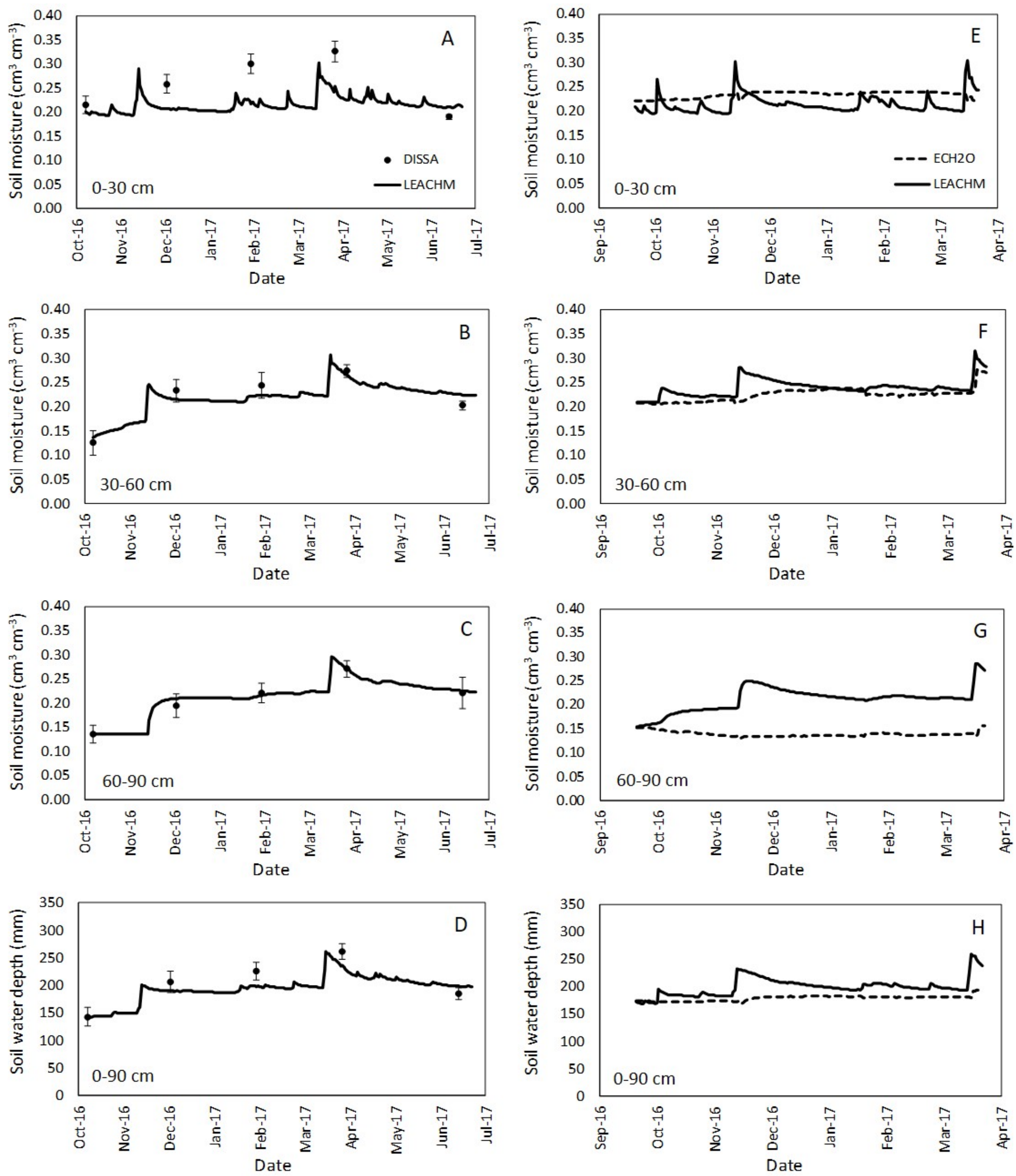

Figure 6.6. Soil moisture in the three soil layers (A, B, C, E, F and G) and soil water depth in the soil profile (D and H) measured from disturbed soil samples (A–D, circles), with ECH2O sensor (E–H, dashed line) and simulated with LEACHM (continuous line) for validation under fallow system. Vertical bars represent the standard deviation.

The main differences between measured and simulated SWC occurred in the superficial layer of soil during the validation period (Fig 6.6). The LEACHM model underestimated the moisture values in the upper layer measured with both sets of SWC input data. The values recorded by the soil moisture probes in the three soil layers during 2016/17 season were anomalous, as they hardly changed over time. Therefore, the dynamics of water in the soil did not reproduce well, since there was almost no response to water inputs in the soil profile due to rain. In the fallow periods, SWC values at the end of the period (June) are of the order of 0.20 $cm^3\ cm^{-3}$, while the highest values are 0.30 $cm^3\ cm^{-3}$, regardless of the soil layer considered. This range of soil moisture was similar in the three layers, confirming the homogeneity of the soil profile in this area.

Cumulative drainage at 90 cm was related to the rainfall events (Fig. 6.7). The 2013/14 season displayed a continuous increase in the drainage over time, while the 2016/17 season followed a sigmoidal function. Changes in water losses increased when rainfall was higher than 20 mm, and these precipitation events generally occurred in autumn and early spring. Drainage below the root zone (>90 cm depth) was from 3.0 to 14.5 mm. Considerable differences were obtained from the LEACHM evaluation respect to the dataset type used. Simulations made with ECH2O calibration displayed drainage values which were three times greater than those obtained with DISSA calibration. These differences are due to the different values of parameter b obtained with each data set. The higher values provided by the calibration with DISSA resulted in a higher water retention capacity of the soil and, therefore, a lower drainage.

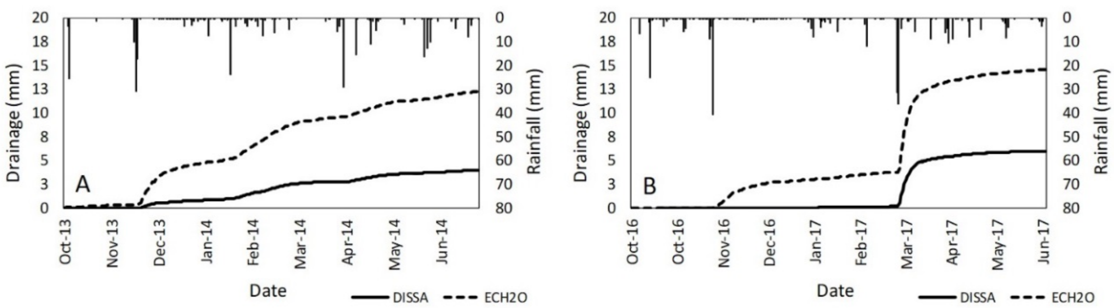

Figure 6.7. Accumulated drainage (90 cm depth) simulated with LEACHM for the calibration (A) and the validation (B) periods using different data sets (continuous line from disturbed soil samples and dashed line from ECH2O sensors) in a fallow soil. Bars indicate daily rainfall values for each season.

SWC Modelling in a Barley Crop Soil

Statistical parameters of SWC simulations showed that LEACHM modelling in barley cropping seasons (Table 6.5) did not fit as well as in the fallow seasons (Table 6.4). The R^2 results were considerably lower than those obtained during the fallow seasons. The smallest values were obtained from modeling with ECH2O data for the calibration period.

Table 6.5. Statistical comparisons between observed and simulated soil water depth for barley cropping period. Observed data came from field disturbed soil samples (DISSA) and soil moisture sensors (ECH2O).

Statistic	Depth	Calibration (15/16)		Validation (11/12)		Validation (14/15)	
	(cm)	DISSA	ECH2O	DISSA	ECH2O	DISSA	ECH2O
MD	0–30	−0.12	−0.47	5.17	−1.38	10.24	−1.58
(mm)	30–60	−0.80	−0.67	7.56	3.91	5.27	3.97
	60–90	−0.97	0.35	7.55	1,57	3.44	6.22
	0–90	−1.89	−0.80	20.27	4.10	18.94	8.61
RMSE	0–30	9.48	4.41	17.51	10.44	13.03	6.06
(mm)	30–60	8.71	3.80	14.35	7.75	7.89	6.87
	60–90	9.09	2.56	12.00	9.46	11.95	8.97
	0–90	25.45	6.73	41.77	17.76	25.84	18.46
NRMSE	0–30	0.18	0.08	0.32	0.18	0.19	0.10
	30–60	0.17	0.07	0.26	0.12	0.13	0.10
	60–90	0.16	0.05	0.20	0.16	0.19	0.13
	0–90	0.16	0.04	0.25	0.12	0.13	0.09
R^2	0–30	0.23	0.05	0.69	0.54	0.66	0.16
	30–60	0.33	0.12	0.62	0.54	0.62	0.50
	60–90	0.21	0.36	0.36	0.09	0.42	0.28
	0–90	0.28	0.31	0.56	0.57	0.52	0.47
d	0–30	0.50	0.50	0.48	0.80	0.74	0.55
	30–60	0.73	0.15	0.63	0.80	0.81	0.46

60–90	0.68	0.68	0.64	0.12	0.70	0.44
0–90	0.68	0.63	0.61	0.86	0.72	0.54

There was a general SWC underestimation in the upper soil layer and in the total SWC. Soil water modeling using the ECH2O data set showed better adjustment than those made with DISSA, although the agreement index was similar in all cases regarding to the soil profile. Mean differences between observed and simulated water depth varied from 1 to 20 mm, and were supported by the *NRMSE* results, which ranged from 0.04 to 0.25 for water depth at 0–90 cm.

Crop seasons calibration fitted better than validation over time (Fig. 6.8). LEACHM overestimated water content predictions at the end of the 2011/12 season: they were 95% higher than the values obtained from DISSA samples. A similar result occurred at the end of the period 2015/16. When the LEACHM model was run with the DISSA data set, it was observed a SWC under and overestimation at the wettest and driest periods of the cropping season. The last of these coincided with the summer period when evapotranspiration was the highest (Fig. 6.2).

The rainfall effect on the SWC evolution over time was marked in the simulations performed with DISSA dataset. Measured SWC with the ECH2O sensor did not detect important changes over time, limiting the accuracy of the LEACHM simulations. The best fit was observed during the wettest period but differences among simulated and observed values increased up to the end of the validation period.

The accumulated drainage predictions with barley varied according to the dataset used for the calibration (Fig. 6.9). Cumulative drainage followed a sigmoidal function and ranged between 0.3 and 14.3 mm of water (2015/16 and the 2014/15 seasons, respectively). The barley crop cycles received on average 20% less rainfall than the fallow cycles (Figs. 6.7 and 6.9), which together with the presence of plants resulted in less drainage. In two out of three evaluated cropping seasons, the highest water losses were obtained from the simulation with DISSA data, probably as a consequence of the lower retention capacity obtained with DISSA data set in the barley season.

The water losses were observed during the first 100 days, which corresponded to the period between sowing and cereal tillering but also coincided with a marked precipitation period. After that, soil water drainage reached a plateau up to the end of the crop cycle. Soil water content at the end of summer affects the drainage amount as it mainly occurs because of autumn rains. Rains of the same amount in the months of October and November can produce different drainage dynamics depending on the existing water content in the upper soil profile.

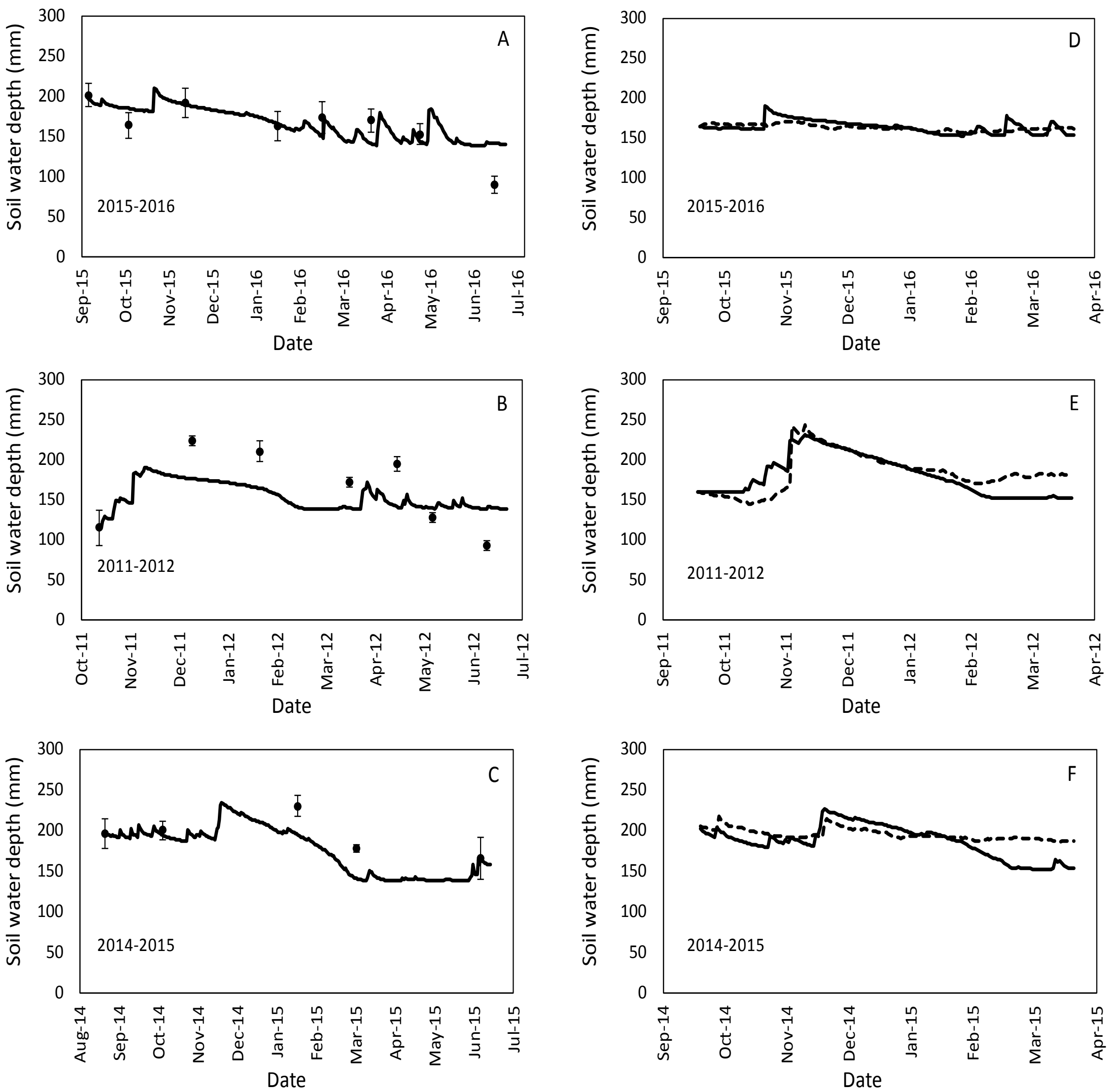

Figure 6.8. Total soil water content (0-90 cm) in the soil profile measured from disturbed soil samples (A–C, circles), with ECH2O sensor (D–F, dashed line) and simulated with LEACHM model (continuous line). Calibration (2015/16) and validation (2011/12 and 2014/15) periods under barley cropping are shown (vertical bars represent the standard deviation).

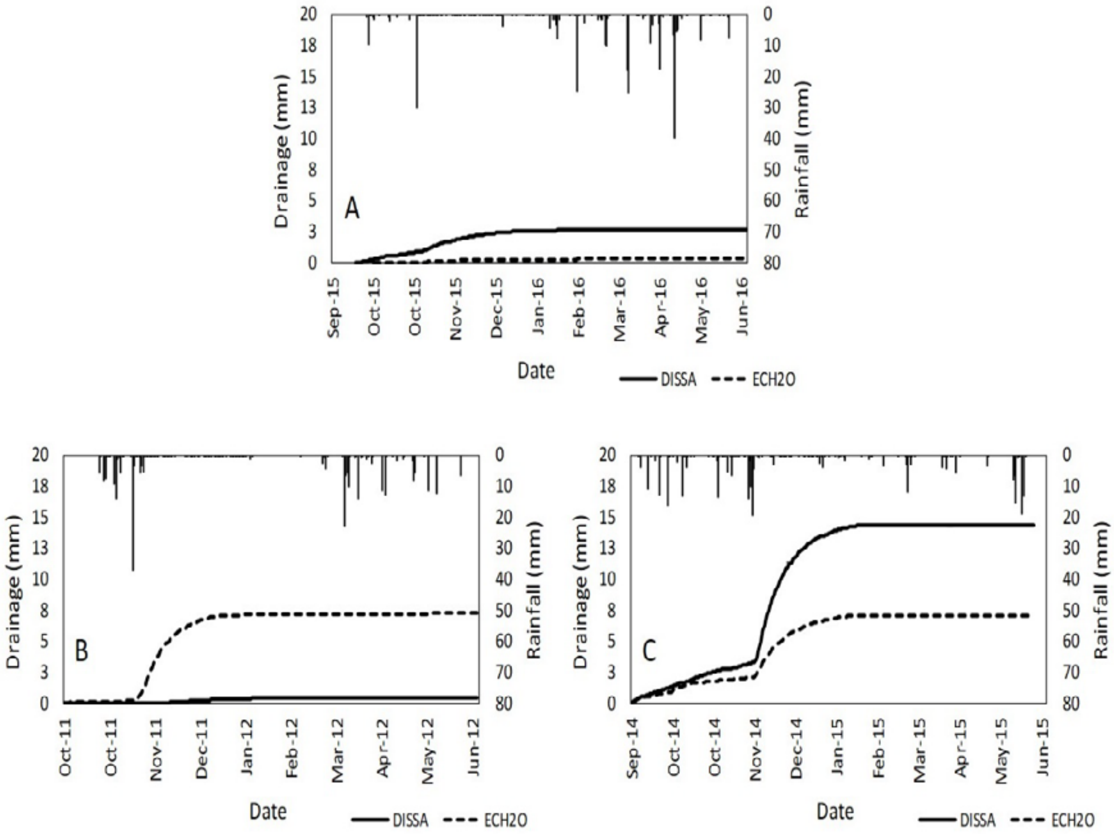

Figure 6.9. Accumulated drainage at 90 cm depth simulated with LEACHM model for calibration (A) and validation (B,C) periods using different data set (continuous line from disturbed soil samples and dashed line from ECH2O sensors) during three barley crop seasons.

Water Balance

The water balance components from the simulations performed with the calibrated model using ECH2O data are shown in Table 6.6. During the two years under fallowing, the soil increased its water content by around 20 mm, while in the periods with barley there was a decrease in the amount of water stored in the soil profile. The net water recharge represented 10% of the water content in the soil profile. Higher percentages (over 20%) were obtained when the calibrated model was used with the DISSA moisture data set (data not shown). Water drainage oscillated between 0.3–14.5 mm, representing less than 10% of the water in the soil and less than 5% of the rainfall.

Table 6.6. Water balance components (mm) simulated with LEACHM model for five different periods (fallow and barley crop) using ECH2O data set for calibration. Simulation period: 1st October–30th June.

Component (mm)	Fallow		Barley		
	2013–2014	2016–2017	2011–2012	2014–2015	2015–2016
Initial water depth	176.1	173.4	159.9	205.2	164.1
Final water depth	196.1	191.1	153.0	171.9	152.9
Soil water storage	20.0	17.7	−6.9	−33.3	−11.2
Rainfall	323.2	332.8	275.7	250.8	289.7
Evaporation-Evapotranspiration[1]	290.0	299.8	274.8	277.5	299.6
Accumulated drainage	12.2	14.5	7.3	6.2	0.3
Drainage for Oct.–Feb. period	7.0	3.1	7.2	5.9	0.2
Drainage for Feb.–Jun. period	5.2	11.3	0.1	0.3	0.1

[1] Evaporation refers to fallow period and evapotranspiration for the cropping season.

DISCUSSION

Soil Water Dynamics

Using the optimal parameters obtained in the rainfed system, the SWC predictions obtained for soil water depth are quite reasonable with both data sets for calibration taking into account that the driest periods were omitted for ECH2O sensors. Soil water dynamics simulations with LEACHM model fitted better in the fallow seasons (Table 6.4) than when crop season data were included (Table 6.5), according to the statistical evaluation. However, differences in water content estimation were lower than 25 and 15 mm for the crop and fallow seasons, respectively, indicating a good SWC estimation using LEACHM model in a dryland system.

Simulations under fallow fitted better as LEACHM uses simple relationships related to water demand (evapotranspiration) and plant growth. The increase of SWC by 20 mm of water recharge could be higher since the evaporation simulated by the model could be overestimated [26]. The soil tillage carried out during the fallow cycle would break the pores continuity in the surface layer and decrease the evaporative flow from the deeper layers of the soil to the surface [44,45]. In fallow periods, the amount of rainfall mainly determines the recharge at the begin46ning of spring, since the simulated drainage in this period is similar to that of the periods with barley cultivation despite having greater precipitation (50 mm).

Predictions on soil water dynamics offered a global overview about how water moves through the soil profile, despite the $R^2 < 0.62$ in crop barley simulations. During the growing periods, the water recharge is negative in the rainfed systems that have rainfall below 340 mm per year.

Soil characteristics played an important role in modeling. Texture and *Ks* are key parameters in the assessment of SWC and drainage, as the estimation of the *a* and *b* parameters depend on these variables. Texture would influence the underestimation of SWC in the 30–60 and 60–90 cm soil layers in this experiment, because of the silt content in both layers (49 and 60% respectively). Johnson et al. [46] reported that coarse fractions enhanced water movement through the soil profile, producing an overestimation in SWC from 45 to 75 cm depth, but an underestimation for the upper 30 cm in sandy-loam fallow plots. It must be pointed out that at the end of the growing season the soil moisture is below even the permanent wilting point. The barley crop seems to be adapted to these dryness levels. However, neither the ECH2O probes nor the LEACHM model are capable of reproducing these low values of soil moisture.

Data origin also affected LEACHM simulations. Soil water content obtained from DISSA adjusted better than those obtained from the ECH2O, mainly during the fallow seasons. Other authors pointed to more accurate predictions with the LEACHM model when the K-θ-ψ relationships derived from the in-situ measurements were used [23]. Moreover, the ECH2O probes did not easily detect changes in SWC over time as observed with DISSA samplings. The ECH2O probes are used for irrigated fields where water is usually kept above 50% of the water pore fill capacity. In rainfed systems, this condition was not achieved during the whole crop cycle because of the low precipitation amounts or the air temperature increases.

After prolonged dry periods, the lack of soil moisture would lead to a reduction of the contact area between the soil and the ECH2O sensor. In our case, there was no response from the sensors to the rains during the autumn-winter period of the 2016–2017 years, but the increase of soil moisture, due to the rains of the following months, restored accurate measurements of the sensors (data not show). This process is not immediate, and it is very dependent on the season and the amount of rainfall recorded. The rewetting of the sensors after these periods of low rainfall is very slow and may be the cause of the lack of response that can be prolonged over time. Thus, the resonance frequency used by the sensors to calculate the dielectric constant would be wrongly measured and so would the volumetric water content. Similar findings were reported by Czarnomski et al. [11] who found that the ECH2O device underestimated the soil moisture when the temperature increased from 22 to 31 °C. They found a 1.9% data deviation, but the experiment was performed under controlled conditions, meaning that bigger differences in the field, such as ours, would be expected. This limitation of the ECH2O probes to measure SWC in very dry soil conditions reduces the goodness of the calibration process with this data set. A retroactive calibration of the humidity sensors may be necessary. Incorporating soil physical information using pedotransfer functions can be improve sensor accuracy, as established by Gasch et al. [47]; however, the lack of contact between the sensor and the soil can hardly be corrected by an adequate calibration. Additional data set of soil water content obtained from field measurements can be very useful to recalibrate these sensors. In addition, inverse calibration could be carry out using the adjusted model for obtain realistic measures of the sensors in prolonged dry periods.

The rainfall regime is very important for soil water dynamics. Heavy rains concentrated in the period of low crop coverage increased the recharge, compared to periods with little rainfall much more spread over time. Water moved through the soil profile following the precipitation events. Crop presence or absence showed differences in SWC variations along depth and over time. In fallow seasons, rainfall events promoted changes in SWC even at the deepest layer. On the contrary, in barley cropping seasons, the upper layer was the most prone to SWC changes, due to the direct soil contact with the atmosphere (rainfall, wind, solar exposure). In the second layer, the soil system interacted with plant roots and living organisms, reducing the variations in SWC. Finally, in the third layer, the soil system had few interactions with the barley roots and the atmosphere, leading to a stable soil system with few fluctuations in water content over time.

Land use resulted in a total water gain or lost at the end of the crop cycle. The fallow period was a recharge period because soil gained water at the end of the season. After the barley crop, SWC diminished as plants took water from the soil for their growth. Moret et al. [6] reported similar results in another dryland Mediterranean environment with lower mean precipitation than this site. In dryland environments with erratic rainfall distribution, such as this experimental site (Fig. 6.4), fallow increased the available water for the next cropping season. Thus, it would reduce the risk of plant mortality in case of drought at sowing time and an increase in grain yield compared with a continuous cropping system [6].

Drainage Modelling

Drainage estimate with the LEACHM model is acceptable as the model explains the SWC in profile satisfactorily. Rainfall (amount and distribution) and land use drove the volume of water loss over time. Effective rainfall can be considered lower than 20 mm as drainage was mostly produced above this precipitation value.

Cumulative drainage was higher at fallow than at barley cropping seasons, as there were no plants to take water for growth in the first scenario. Average precipitation in fallow years was higher than for the barley crops. However, only in the 2016/17 fallow season precipitation was above the mean values for the area (Fig. 6.2) probably related to the previous dry and warm summer season (Fig. 6.7). According to probability figures, the results mean that at least one out of two seasons, the system can lose 5.9 mm of water per fallow period.

In the 2014/15 season, drainage was considerably higher than all the other years. A marked increase in water losses was registered during a two-month period (December 2014 and January 2015) which recorded 33 days with rainfall. In 29 of them, daily precipitation was <1 mm (Fig. 6.9). Consecutive precipitation values <1 mm would lead into a problem calculation in the LEACHM.

Maximum water losses were observed at the beginning of the season, from sowing until cereal tillering stage, because it is a period with no plants or when they are not large enough to use the water entering into the soil system. It also coincides with a high precipitation amount period and with the two most common N applications.

Considering the return period of the precipitation, there is a probability between 60–70% of drainage from 6.1–7.2 mm of water during the winter season, the most prone to leach NO_3^--N to the groundwater. The results alert about drainage in dryland agriculture systems and the potential associated impacts, contrary to the premised by other authors [48]. This scenario reinforces the importance of our results for environmental impacts over underground waters by solutes than can be leached.

Minimal or zero water loss values were obtained from cereal tillering until the end of the season. Lack of drainage can be explained by meteorological and agronomic reasons. After cereal tillering, plants increase their water consumption. From spring onwards, temperatures started to rise as well as evapotranspiration.

Compared to other rainfed environments, estimated drainage values (<15 mm) can be considered as small water losses [23,49]. Data accuracy is a key factor in model calibration [12] but data are difficult to obtain due to the soil heterogeneity, porous complexity, water spatial and temporal water dynamics [9]. Without drainage field measurements, appropriate SWC monitoring would lead to proper drainage estimation. The ECH2O probes were easily managed devices, which would be monitored and corrected with periodical field measurements over time and along soil depth but their use is limited over the year in semiarid environments.

In general, the losses during the fallow years were higher, coinciding with the greater amounts of drainage, showing the importance of the water balance as an indicator of the leaching potential of the system.

Despite the finding that estimated drainage is small and the potential for leaching is also low, it is necessary to maintain adequate agronomic practices such as fertilization guidelines in these areas to prevent the NO_3^--N accumulation in the soil profile. The maximum 24-hour precipitation in the set of years considered corresponded to the period 2016/17 was 41 mm, while the drainage for this period was 14.5 mm. However, for a return period of 25 and 50 years, the maximum expected precipitation is 70 and 90 mm, respectively (Table 6.1). The simulations carried out, replacing the 41 mm rainfall by these predicted values, would cause an increase in the drainage of between 2.1 and 3.3 times that obtained with the current maximum 24-hour value. These figures are meaningful in a context of climate change, in which forecasts in the Mediterranean area indicate that short but heavy rainfalls are liable to increase in number [4,50]. Thus higher amounts of drainage could occur, which would increase the risk of groundwater contamination in a huge vast world area [5].

CONCLUSIONS

The LEACHM is a robust model to simulate soil water dynamics in a fallow period in the 0–90 cm depth in a semiarid rainfed agricultural system. As crops were introduced, LEACHM lost accuracy in predicting SWC at the different layers, but an acceptable overview of the soil water was obtained and can be used for environmental purposes linked to drainage. Fallow periods resulted in a little soil water recharge, which did not occur in years with barley cultivation. Drainage losses in this system are small (<15 mm) and usually occur in the autumn-winter period. Under these conditions, the potential impact of water solutes on underground water will be mainly related to their concentration in soil-water solution. Field soil moisture measurements could be more realistic than capacitive sensors when feeding data into models in dryland systems due to the lack of response after prolonged dry periods.

ACKNOWLEDGMENTS

The authors would like to thank the anonymous referees for their suggestions and comments. J. Llop and S. Martínez are fully acknowledged for their field assistance and M.F. Mor, J.C. Balasch and D. Ginestar for cabinet assistance.

This research was funded by the Spanish Ministry of Economy and Competitiveness and the Spanish National Institute for Agricultural Research and Experimentation (MINECO-INIA) through the projects [RTA2013-57-C5-5] and [RTA2017-88-C3-3]. The PhD studies of D.E. Jiménez-de-Santiago were funded by the JADE-Plus scholarship from Bank of Santander-University of Lleida.

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SUPPLEMENTAL MATERIAL

Table 6.S1. Soil physical properties and crop data parameters as the input for the LEACHM model.

Property	Specification	Units	Value
Soil physical property	Soil bulk density	kg dm^{-3}	1.65/1.60/1.55
	Clay	%	27/20/28
	Silt	%	58/49/60
	Organic carbon	%	0.99/0.46/0.46
	Particle density (clay, silt and sand)	kg dm^{-3}	2.65
	Particle density (organic matter)	kg dm^{-3}	1.10
	Air entry value	kPa	Calibrated
	Exponent for Campbell's equation	-	Calibrated
	Hydraulic conductivity	mm d^{-1}	233/524/457
	Dispersivity	mm	100
	Wilting point	kPa	−1500
Crop data	Maximum ratio of actual to potential T	-	1.1
	Minimum root water potential	kPa	−3000
	Root resistance	-	1
	Crop cover fraction	-	1
	Pan factor	-	1.50

CHAPTER 7

General discussion

GENERAL DISCUSSION

The results obtained confirmed the main hypothesis of this study, that slurry application modifies soil properties with impacts on soil quality and on external systems over time. The effcts can be changes on soil through organic matter composition, on air by means of NH_3 emissions, and on groundwater because of the water leached components.

Nevertheless, the impact on SOM content (Chaper 3) was only, significant at the highest slurry rates (70 and 90 Mg ha^{-1} yr^{-1}), when compared to a mineral fertilisation. These results underline the usefulness of long-term experiments as in other studies changes in SOM were not dectected in rainfed conditions, probably due to the shorter periods of experimentation (Plaza et al., 2002; Domingo-Olivé et al., 2016).

In addition, SOM changes were not only quantitive but qualitative (hypothesis H1) as the organic matter added through the slurries has a different composition from that naturally developed in the soil (Senesi et al., 1996). The E4/46 ratio in SOM decreased which is indicator of changes in aromaticity in the macromolecular structure linked to slurry fertilisation. These results suggest the enrichment of humic components with a low degree of condensation and infer the presence of relatively large proportions of aliphatic structures (Gosh and Schnitzer, 1979; Dorado et al., 2003; Senesi et al., 2007). Thus, the increment in the SOM was related to a change into an easily mineralizable structural composition.

Special attention is needed when high slurry doses or slurries rich in organic matter are applied as the increase of HA should not be considered as a stable C reservoir. Aliphatic structures would be transformed if moisture and temperature increase. That is important in irrigated agricultural systems, where a faster mineralisation rate has been reported (Madrid et al., 2004). As average grain yields indicate that the highest slurry rates (F70 and F90) do not increase productivity. Thus, slurry fertilisation beyond the established upper threshold of 170 kg N ha^{-1} yr^{-1} in vulnerable nitrate areas could lead to negative effects related to the increase of available mineral N.

However, the organic matter added at advised rates produces transient soil water repellency, mainly when applied at cereal tillering when slurries are not buried (Chapter 4, hypothesis H2). Until now, little attention had been devoted to dry matter hydrophobic compounds, probably because slurries are mainly water (>90%). This work confirmed that only a small amount of OCho was necessary to induce changes in soil wettability. Besides SWR showed temporal variations influenced by the drying-wetting soil pattern, in agreement with other findings (Doerr et al., 2006; Keizer et al., 2007; Burguet et al., 2016). Dry matter created a superficial crust, which increased SWR during dry periods, but it was dissolved during the wetting period (after rainfalls). By the other hand, these easly degradable compounds can act as transitory binding agents (Tisdall and Oades, 1982). Our results would explain the increase in aggregate stability reported by other authors (Yagüe et al., 2012; Domingo-Olivé et al., 2016) although their reported changes in SOM content were not significant. Slurry advantatges are the equilibrium between soil repellency and aggregate stability. The final balance is related to general management (i.e. irrigation, tillage) and climate (i.e. rainfall). However, the correct assessement requires the use of adapted SWR tests as the ones evaluatedin this research.

From an agronomic point of view and in agreement with other authors (Dekker et al., 1998; 2009; and Ziogas et al., 2005), the WDPT test under field moisture conditions showed a more realistic effect of the pig slurry on hydrophobicity persistence but SWC must be quantified to interpret the results properly. Conversely, SWR intensity measurements can be performed with MED test but the lack of sensitivess to detect differences between treatments should be considered.

In the field, this induced SWR did not signifincantly affect NH_3 emissions as stated in the hypothesis H3 (Chapter 5). Changes in SWR were related to soil water evolution (drying-wetting periods) controlled by rainfalls. The lowest soil moisture content coincided with the highest hydrophobicity value. However, the drying-wetting periods enhanced the degrataion of OCho compounds and slowly restored soil wettability due to the transient SWR effect over time. These findings indicate that a proper SWC management (e.g. irrigation) is also a feasible strategy to avoid the development SWR in agricultural soils when tillage is not possible, as suggested by Holcom et al. (2011).

Otherwise, slurries infiltrated faster in dry soil conditions, previous to SWR development, acting as the main process (quick infiltration) to reduce NH_3 volatilization. The AN concentration in slurries was linked direct and positively to the biggest NH_3 emissions to the atmosphere, instead of the TN concentration rates in the slurries. Other factors as diurnal temperature and slurry burying, also limited NH_3

losses, conforming to the literature reports (Rochette et al., 2001; Kissel and Cabrera, 2005; Yagüe et al., 2012). The findings in this research highlight the importance of AN concentration whith regarding to the fertilisation rates. They are imperative in a context where maximum losses are quantified in the first 7 hours and their values are below the 18% of the NH_4-N applied. These losses are low compared to other agricultural systems (Hafner et al., 2017). However, its importance at the environmental level should be underestimated

The above mentionated indicates that the impact of the more mineralisable organic matter (OCho compounds) added with slurries is negligible in terms of N losses through the NH_3 emissions. However, it might be important through water lixiviation as NO_3.

The soil water distribution and the drainage estimations in the studied Mediterranean dryland agricultural system was well performed by the LEACHM model (Chapter 6), no matter the data origin used (DISSA or ECH2O probes). The model fitted better under fallow because the plants absence reduced the number of parameters to be estimated. Fallow years saved water in soil profile as other authors reported (Lampurlanés et al., 2002; Moret et al., 2007). However, this does not necessarily mean that more water was drained during fallow due to the high soil water holding capacity. Maximum drinage figures ranged from 2.3 to 14.3 mm, reflecting the effect of rainfall amount as the main factor over soil cover. They are low when compared to e.g. to irrigated systems (80-232 mm), where water is not a limiting factor (Lidón et al., 1999).

The water limitation in such environments would limit de N-NO_3 leaching as mentioned above. The potential nitrate to be leached below 90 cm depth will depend on the N-NO_3 concentration in the soil solution. Considering the maximum 24-hour precipitation amount for different return periods (Table 6.1), the risk of NO_3^- losses could be drastically increased. A maximum recorded concentration from other authors working in the agricultural system is 200 kg N-NO_3 ha^{-1} (Quemada et al., 2013) meaning that the estimations for NE Spain are still needed. Moreover, following the recommended slurry application rates are noteworthy as well as the use of models as LEACHM are a suitable tool to work together in the United Nations sustainable development objectives (EU, 2018).

As mentioned in the previous chapters (from 3 to 6), the agronomic benefits and environmental impacts of slurry application are a highly sensitive issue and, consequently, the object of a lengthy and deep research since quite long ago in many parts of the world. The results of this study contribute to a better understanding of the air-soil-water in dryland Mediterranean systems; marked by low and erratic precipitation. The results could help in the amelioration and the adoption of best management practices for pig slurry fertilisation as they confirmed that the maximum agronomic slurry rates applicable in areas vulnerable to nitrates pollution (170 kg N ha^{-1}, Generalitat de Catalunya, 2009) can also help reduce negative impacts on air and water and maintain the SOM content in the soil.

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CHAPTER 8

General conclusions

GENERAL CONCLUSIONS

The impacts on soil, air, and water due to a long-term slurry fertilisation in a dryland agricultural system were evaluated in this Thesis. According to the findings in the main chapters (3 to 6) and the general discussion, the main conclusions are the following:

- Long term slurry application changed the soil organic matter quantity and quality (Hypothesis 1 and Objective 1). Soil organic matter increased and became richer in aliphatic groups, reflected in a relative aromaticity lost. Further attention to the soil management, as C stored under these conditions could be easily mineralizable, should be a matter of concern.

- Pig slurry fertilisation developed transitory SWR. When slurries were not buried, the WDPT test allowed us to detect differences in SWR between treatments over the whole experimental period, but MED did not (Hypothesis 2 and Objective 2). Repellency was associated with slurry composition as WEOC and OCho compounds, enhancing it as they increased. In some cases, an interaction with a previous slurry application at sowing was detected. Moreover, processing factors as drying temperature of the sample drawn differences in SWR for a same sampling day.

- At tillering, when slurries were not buried, 50% of NH_3 emission from AN applied was reached during the 72 h after application. The maximum SWR persistence on soil surface was found 8 days from slurry spreading but it remained less than 49 days. The drying-wetting pattern in the soil surface affected the SWR, which increased when the soil dried (Hypothesis 3 and Objective 3). It is still necessary to define the initial SWR after periodic slurry applications that could enhance NH_3 emission (e.g. at tillering slurry spreading or in tillage systems where slurries are not buried).

- LEACHM was a robust model to simulate soil water dynamics in soil under fallow (Hypothesis 4 and Objective 4). Drainage usually occurred in fall and winter and maxima accumulated values ranged from 2.3 – 14.3 mm, coinciding with the slurry application at sowing.

ANNEX 1

Ammonia emission assessment after slurry spreading in winter cereal at tillering stage

This annex contains the following already presented summary in the Jornada sobre la Recerca en Sòls a Catalunya (Workshop on Soil Research in Catalonia), Barcelona 29th May 2015.

Original summary was in Catalan but here is provided the English version.

Poster presented is shown at the end of this annex (Catalan).

AMMONIA EMISSION ASSESSMENT AFTER SLURRY SPREADING IN WINTER CEREAL AT TILLERING STAGE

SUMMARY

In dryland Mediterranean systems, agricultural activity is complemented by important pig production. Pig slurry is usually applied before sowing and to a lesser extent on the cereal at tillering stage. About 75% of the nitrogen (N) contained in the pig pigs is in ammonium form. Thus, the loss of N as volatilised ammonia (NH_3) could be relevant in a short-time period after application. These losses become more significant in the application at cereal tilleing, since the slurries are not buried. The objective of this work was to evaluate the effect of the slurry application from different origins (pig fattening, maternity) and the antecedent or not slurry application on the NH_3 volatilization, immediately after the application at cereal tillering (February-March). The NH_3 quantification was performed using the photo-acoustic technique (Innova 1412). The application of sewage slurry did not have an effect on NH_3 losses. Pork slurry from fattening showed higher NH_3 losses compared to maternity purine.

Keywords: Mediterranean environment, dryland farming, fertilization with livestock byproducts, nitrogen losses.

Volatilització d'amoníac després de l'aplicació de purins en cobertora de cereal d'hivern

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INTRODUCCIÓ

- L'us de ***purí de porc com a fertilitzant*** és comú a les zones productores de porcí.
- El purí ***conté el 75% del N en forma amoniacal*** (Yagüe *et al.*, 2012), susceptible de perdre per volatilització de NH_3 a les primeres hores després de l'aplicació.
- La aplicació de ***purí en cobertora (febrer-març)***, abans de l'encanyissat del cereal d'hivern:
  - *contribueix a una millor gestió del purí* (evita l'acumulació en fossa) i, a un us agronòmic més eficient (Bosch-Serra *et al.*, 2015).
  - *no permet l'enterrat*, roman en superficie fins que s'infiltra, amb les possibles pèrdues de NH_3 (Bosch-Serra et al., 2014).

OBJETIUS

Avaluar les pèrdues de volatilització d'amoníac després de l'aplicació de purins de porc (engreix i mares) en la cobertora (febrer i març) de cereal d'hivern en el context de l'agricultura de secà, en clima semiàrid Mediterrani.

MATERIALS Y MÉTODES

• *Tractaments*

PN4: 30 t ha^{-1} purí d'engreix en pre-sembra (120 kg NH_4^+-N ha^{-1}) + 40 t ha^{-1} purí d'engreix en cobertora (160 kg N-NH_4^+ ha^{-1}).
PN8: 30 t ha^{-1} purí d'engreix en pre-sembra (120 kg NH_4^+-N ha^{-1}) + 90 t ha^{-1} purí de mares en cobertora (170 kg N-NH_4^+ ha^{-1}).

N4: sense purí en pre-sembra + 40 t ha^{-1} purí d'engreix en cobertora (160 kg N-NH_4^+ ha^{-1}).
N8: sense purí en pre-sembra + 90 t ha^{-1} purí de mares en cobertora (170 kg N-NH_4^+ ha^{-1}).

• *Purins*

- Els purins en camp s'apliquen amb el mètode del ventall (Fig. 1).
- La dosis se estableix en funció del contingut de N-NH_4

• *Temps d'aplicació*

- Cobertora en febrer
- Cobertora en març

Figura 1. Aplicació de purí en cobertora en cereal d'hivern amb el mètode del ventall.

• *Mesures d'amoníac en laboratori*

- Les pèrdues de NH_3 se quantifiquen amb un mètode fotoacústic: Innova 1412 (Fig. 2).
- El purí s'aplica a una mostra inalterada de sòl. Es mesura la temperatura ambient i la pressió atmosfèrica.
- Es mantenen quatre repeticions per tractament.
- Les lectures de NH_3 es realitzen cada deu minuts durant quatre hores després de l'aplicació del purí.

Figura 2. Vista general de l'experiment (Innova 1412).

RESULTATS PRELIMINARS

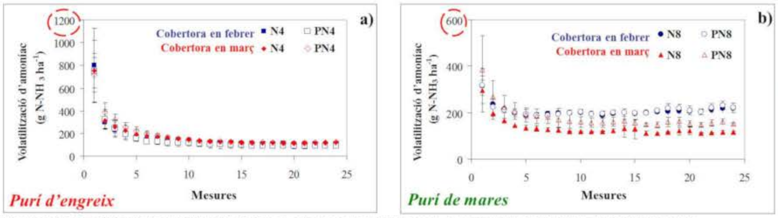

Figura 3. Valors obtinguts de volatilització de NH_3 en cobertores de febrer i març: a) tractaments de purí d'engreix; b) tractaments de purí de mares. Les barres indiquen la desviació estàndard (n=4).

El purí d'engreix ocasiona majors pèrdues de NH_3, durant les primeres mesures, que equivalen casi al doble respecte de les obtingudes amb purí de mares reproductores.

CONCLUSIONS

- **El tipus de purí afecta a las pèrdues de NH_3. Les pèrdues de NH_3 son majors quan s'aplica purí d'engreix.**
- **L'aplicació de purí en fons (engreix) no afecta a las pèrdues de NH_3 en aplicacions en cobertora (independentment del tipus de purí).**
- **El purí de mares és la millor opció en termes de reducció de la volatilització de NH_3, durant les primeres hores després de l'aplicació.**

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Agraïments: Aquest treball ha estat finançat pel Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria MINECO-INIA mitjançant el projecte RTA2013-00057-C05-05 i fons FEDER

Fig. A1.1. Poster presented in the Jornada sobre la Recerca en Sòls a Catalunya (Workshop on Soil Research in Catalonia)

ANNEX 2

Soil water modelling in a dryland agricultural system

This annex contains the following already published chapter in the conference 1st World Conference on Soil and Water Conservation under Global Change-CONSOWA

Jiménez-De-Santiago, D.E.; M.F. Mor-Ruiz, À.D. Bosch-Serra, and A. Lidón. 2017. Soil water modelling in a dryland agricultural system. In: Proceedings of the 1st World Conference on Soil and Water Conservation under Global Change-CONSOWA. Lleida 12-16 June 2017

Poster presented is shown at the end of the annex..

SOIL WATER MODELLING IN A DRYLAND AGRICULTURAL SYSTEM

ABSTRACT

In Spain, dryland agriculture covers 84% of the area devoted to grain cereals. Slurry applications are used widely as fertilizers in order to reduce costs. Slurries have a high nitrogen content and low C:N ratio. Consequently, there is a risk of groundwater contamination by nitrates, through the leaching process in the soil profile. Soil water content (SWC) can be simulated with mathematical models that allow us to predict drainage and leaching losses. They also help to set up decisions regarding agricultural practices and the reduction of environmental impacts. The aim of this work was to model the SWC and its dynamics in a winter cereal crop rotation (barley, wheat) in a dryland Mediterranean agricultural system. One layer, from 0–90 cm, was used in the modelling process. Daily temperature and precipitation were collected from an experimental plot in Oliola municipality (NE Spain). Model simulation was applied for a three year period (2012–2015) and was validated with field data obtained from the 2012/13 cereal cropping season. A small quantity of drainage water was obtained, equivalent to 4% of mean annual precipitation (MAP). Nitrate leaching only occurred on those days in which annual precipitation was higher than the MAP (443mm). The one layer model was useful for SWC quantification in dryland agricultural systems. Nevertheless, a more detailed approach involving different soil layers is recommended to accurately represent SWC dynamics and to quantify nitrate leaching.

INTRODUCTION

Intensive livestock farming has environmental impacts on landscape, air quality, climate change and subsuperficial water quality. Agro-hydrologic modelling, because of its physical base, is a key element of environmental impact prediction. In dryland agricultural systems from Mediterranean areas, one of the strategies to mitigate such environmental impacts is to reuse animal slurries as fertilizers. Slurry application is done on winter cereals at sowing and at tillering development stage. Slurries are composed of more than 90% of a liquid fraction (Yagüe *et al.*, 2012). In consequence, monitoring their movement throughout the soil profile together with water displacement is important to reduce environmental risks in groundwater, such as nitrogen leaching.

Different reference models on soil water monitoring exist (Groot, 1987; Eckersten and Jansson, 1991; Porter, 1993). Some models use dozens of parameters to describe SWC dynamics in soil, which include many physiological processes. Simpler compartmental models can help to monitor soil water dynamics as drainage or SWC. They treat the soil as different layers and make the calculations using soil properties, crop characteristics and weather information.

The aim of this work was to model the drained water and its dynamics in the soil in a winter cereal crop rotation in a dryland Mediterranean agricultural system as a first step to model N leaching.

MATERIALS AND METHODS

Study area

A long term experimental field located in Oliola, Lleida, NE Spain. Coordinates are 41º 52” 34’N, 0º 19” 17’ E with altitude of 440 m a.s.l. was studied. It was set up in a 3-year rotation of barley (*Hordeum vulgare*) and one of wheat (*Triticum aestivum*), with 18 strategies of nitrogen fertilization, including combinations of mineral nitrogen fertilizers, pig slurry and control (no nitrogen applied). The region has a semiarid Mediterranean climate with low annual precipitation (443mm), a mean annual temperature of 12.6°C with high temperatures in summer. The soil is deep (>1 m), it has a silty loam texture, the organic matter content is below 2%. The soil is non-saline and calcareous with pH of 8.2 (1:2.5 soil: distilled water). It is classified as a Typic Xerofluvent.

Data acquisition

Daily precipitation, air temperature and evapotranspiration (ETo) were recorded from an automatized meteorological station next to the field. For modelling, data from three year cropping seasons (2012-2015) were collected. Core samples to measure the real values of water content were collected in the 2012/13 growing season.

Compartmental model

The model was developed in MatLab. The maximum ETo, stored soil water and drainage were calculated. The program took the information from an Excel file. It required initial edaphic conditions, daily precipitation, reference crop ETo, the percentage of the soil surface covered and the crop coefficients. Crop data introduced in the model were adapted from a work under similar conditions (Villar, 1989). One layer of 90 cm deep (0-90cm from the top soil surface) was used. As it is a dryland environment, precipitation is the unique water source. Calculations were done daily for the cropping seasons.The results appeared in an output Excel file. The program plots the drainage versus time and the water layer versus time. As a first approach, results were evaluated with graphical representations from observed and simulated data.

RESULTS

Climatic conditions for the evaluated years are shown in Fig. A2.A and in Fig. A2.2. ETo is higher than the precipitation for the main part of the year. It can be four times the rainfall figure in the hottest month of the year. The variability of precipitation among the studied years was important and directly affected the drainage results. The 2012/13 cropping season was the wettest year with 30% more rainwater received than the 2014/15 season. The latter one was the hottest year.

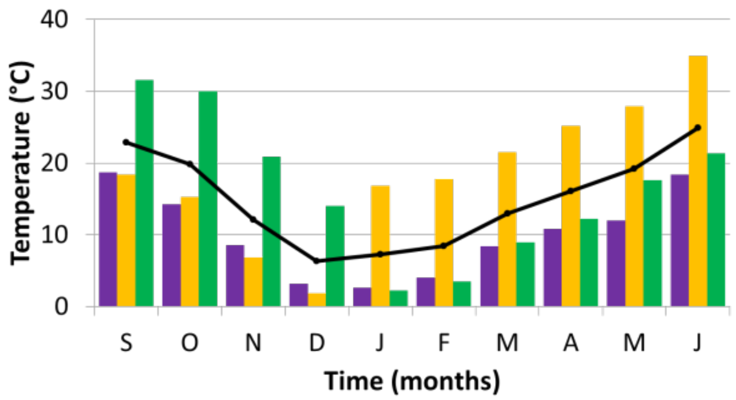

Figure A2.1. Mean monthly temperature (°C) (black line) and precipitation (vertical bars), for each cropping season evaluated: purple, 2012/13; yellow, 2013/14; green, 2014/15.

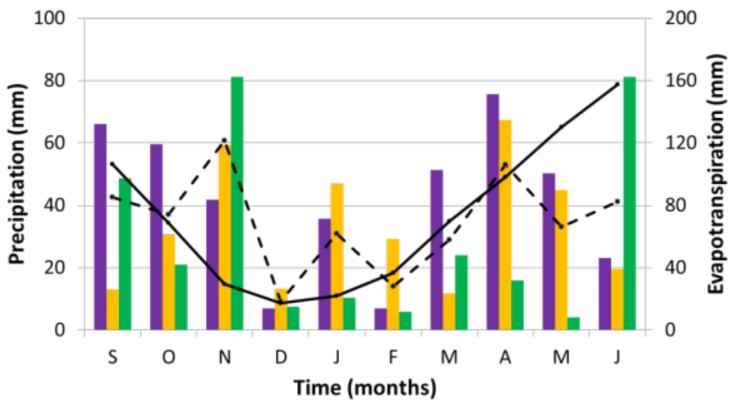

Figure A2.2. Mean monthly precipitation (bars and dotted line), evapotranspiration (continuous line) and total precipitation (vertical bars) for each cropping season: purple, 2012/13; yellow, 2013/14; green, 2014/15.

Soil water content

Soil water dynamics of the soil reservoir in the Oliola study area are shown in Fig. A2.3. The water reservoir graph can be divided in two big groups based on time of year. From September to February, all years had the same tendency. However, from March to June, the water reservoir was different for each year studied.

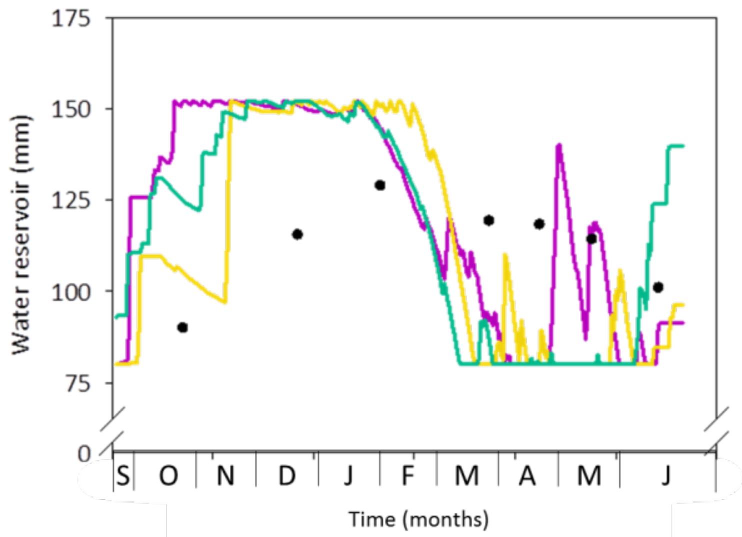

Figure A2.3. Water reservoir (mm) in a soil layer (0-90cm) for three cropping years. Color lines mean; purple, 2012/13; yellow, 2013/14; green, 2014/15; black points, field data (2012/13).

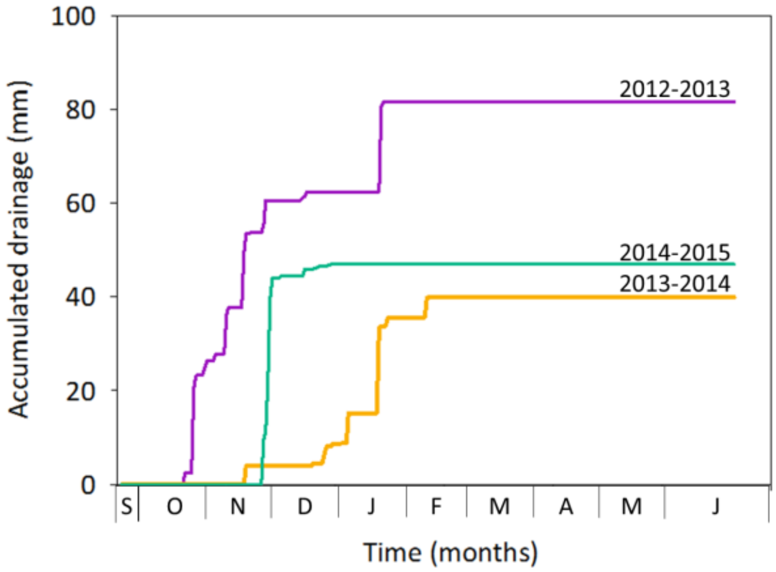

Figure A2.4. Monthly accumulated drainage (mm) for three years of the experimental model period

Accumulated values for water drainage are shown in Fig. 4. Results were associated with rain events. The highest drainage was found in the months where precipitation was higher than ETo (November and January). Because of the low precipitation during the cropping year 2014/15, drainage only occurred during November and December.

The maximum quantity of soil water was achieved during November, December and January. Water content decreased the fastest from February to March, probably because of the growing period of the barley crop. Plant growth was encouraged by fertilization with slurries and the increase in temperature. From March to June, there was no drainage in spite of the rain events (Fig. 2) and the changes observed in the water reservoir (Fig. 3). Precipitation was the unique source of water in the dryland areas, thus the water stored in the soil profile was used for the crop necessities.

A common fertilization practice in Oliola fields is the application of slurries before sowing, at the end of September, and as a top-dressing at the beginning of February. According to these results, the application of slurries as top-dressing could enhance nitrogen leaching from the soil surface in rainy periods.

CONCLUSIONS

In rainy years, water losses calculated with the compartmental model were up to 4% of the annual precipitation.

Compartmental modelling was a practical method to simulate water movement in the soil. Nevertheless, a more detailed approach is suggested to improve the results and contribute to decreasing the environmental hazards of N losses.

ACKNOWLEDGMENTS

This study 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 RTA2013-57-C5-5.

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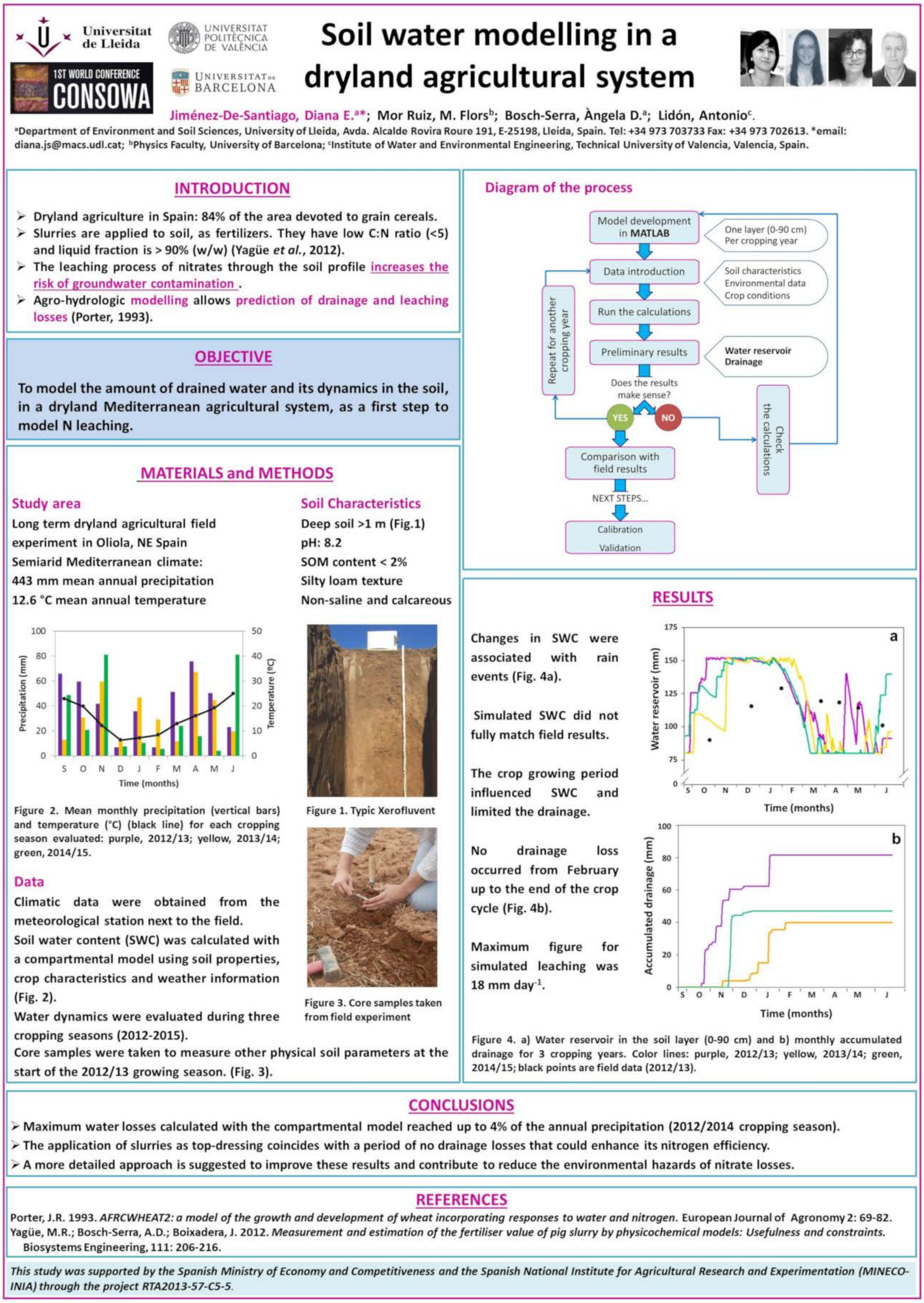

Fig. A2.5. Poster presented in the 1st World Conference on Soil and Water Conservation under Global Change-CONSOWA