

The potential of organic fertilizers and water management to reduce N₂O emissions in Mediterranean climate cropping systems. A review

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A B S T R A C T

Environmental problems related to the use of synthetic fertilizers and to organic waste management have led to increased interest in the use of organic materials as an alternative source of nutrients for crops, but this is also associated with N₂O emissions. There has been an increasing amount of research into the effects of using different types of fertilization on N₂O emissions under Mediterranean climatic conditions, but the findings have sometimes been rather contradictory. Available information also suggests that water management could exert a high influence on N₂O emissions. In this context, we have reviewed the current scientific knowledge, including an analysis of the effect of fertilizer type and water management on direct N₂O emissions.

A meta-analysis of compliant reviewed experiments revealed significantly lower N₂O emissions for organic as opposed to synthetic fertilizers (23% reduction). When organic materials were segregated in solid and liquid, only solid organic fertilizer emissions were significantly lower than those of synthetic fertilizers (28% reduction in cumulative emissions). The EF is similar to the IPCC factor in conventionally irrigated systems (0.98% N₂O-NN applied⁻¹), but one order of magnitude lower in rainfed systems (0.08%). Drip irrigation produces intermediate emission levels (0.66%). Differences are driven by Mediterranean agro-climatic characteristics, which include low soil organic matter (SOM) content and a distinctive rainfall and temperature pattern. Interactions between environmental and management factors and the microbial processes involved in N₂O emissions are discussed in detail.

Indirect emissions have not been fully accounted for, but when organic fertilizers are applied at similar N rates to synthetic fertilizers, they generally make smaller contributions to the leached NO₃⁻ pool. The most promising practices for reducing N₂O through organic fertilization include: (i) minimizing water applications; (ii) minimizing bare soil; (iii) improving waste management; and (iv) tightening N cycling through N immobilization. The mitigation potential may be limited by: (i) residual effect; (ii) the long-term effects of fertilizers on SOM; (iii) lower yield-scaled performance; and (iv) total N availability from organic sources. Knowledge gaps identified in the review included: (i) insufficient sampling periods; (ii) high background emissions; (iii) the need to provide N₂O EF and yield-scaled EF; (iv) the need for more research on specific cropping systems; and (v) the need for full GHG balances.

In conclusion, the available information suggests a potential of organic fertilizers and water-saving practices to mitigate N₂O emissions under Mediterranean climatic conditions, although further research is needed before it can be regarded as fully proven, understood and developed.

Keywords:

Nitrous oxide
Mediterranean cropping systems
Synthetic fertilizer
Organic fertilizer
Irrigated crops
Rainfed crops

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1. Introduction

Nitrous oxide (N₂O) is a powerful greenhouse gas (GHG). It is 298 times stronger than CO₂ at the 100-year time horizon and in 2005, it accounted for 6.1% of combined GHG radiative forcing (Forster et al., 2007). According to the cited authors, the atmospheric N₂O concentration rose from 270 to 319 ppb in the period 1900–2005, after having previously remained relatively stable for the previous two millennia. Agricultural emissions represent about 60% of global anthropogenic N₂O emissions. They increased by 17% from 1990 to 2005 and are projected to increase by 35–60% up to 2030 (Smith et al., 2007).

Nitrogen fertilizer applications to soils, whether organic or synthetic, result in N₂O emissions, as this gas is a by-product of the transformation of N compounds added to the soil. N₂O fluxes from soil are mainly driven by microbial activity, through nitrification and denitrification processes (Firestone and Davidson, 1989). In spite of the existence of a large body of knowledge on the mechanisms that underlie these pathways, there is still an insufficient understanding of the finer details of the process, such as how the composition of organic N fertilizers affects denitrification, nitrification and emission rates (Vallejo et al., 2006).

Besides soil emissions after fertilizer applications (direct emissions), fertilizer-related N₂O production can also result from indirect emissions. Downstream of the cropping system, N₂O is produced when N compounds, and particularly leached nitrate (NO₃⁻) and volatilized ammonia (NH₃), are subsequently transformed into N₂O (IPCC, 2006a). These indirect sources can represent a significant fraction of total agricultural N₂O emissions (Garnier et al., 2009). Upstream of the cropping system, N₂O and other GHG are emitted as by-products of fertilizer production, storage and transport (Snyder et al., 2009). Although these emissions are

very dependent on the methods used to obtain fertilizers, half of synthetic N fertilizer-related GHG emissions could occur in the production phase, whereas the other half occurs from the soil (Tirado et al., 2010). In 2001, fertilizer production accounted for 1% of the global energy demand; 72% of this energy corresponded to N, and a further 16% to compound fertilizers containing N (Ramírez and Worrell, 2006).

There is increasing interest in the application of organic fertilizers to soils (e.g., Hargreaves et al., 2008; Petersen et al., 2003; Singh and Agrawal, 2008; Smil, 1999), as they can contribute to climate change mitigation through C sequestration (Diacono and Montemurro, 2010), at the same time helping to tackle problems associated with waste management and meeting the nutrient and organic matter needs of agricultural soils (Tirado et al., 2010). Nevertheless, the use of organic fertilizers also has a number of drawbacks, which include the energy costs associated with transport and the land spreading of the fertilizers (Wiens et al., 2008), potential pollution with heavy metals and other toxic substances (Petersen et al., 2003), the availability of organic N sources, and GHG emissions (Snyder et al., 2009).

The type and composition of fertilizers have been shown to affect direct N₂O emissions from cropped soils (Stehfest and Bouwman, 2006), although the differences between applying organic and synthetic fertilizers are still not clear. For example, Laegreid and Aastveit (2002) analyzed several databases and found higher direct N₂O emissions from manure than from mineral fertilizers. Although there is great uncertainty in the estimation of the effect of fertilization type on indirect N₂O emissions, overall emissions could actually be slightly lower for organic fertilizers, as calculated in a top-down analysis (Davidson, 2009).

These information gaps are especially relevant for Mediterranean-type cropping systems, where an increasing

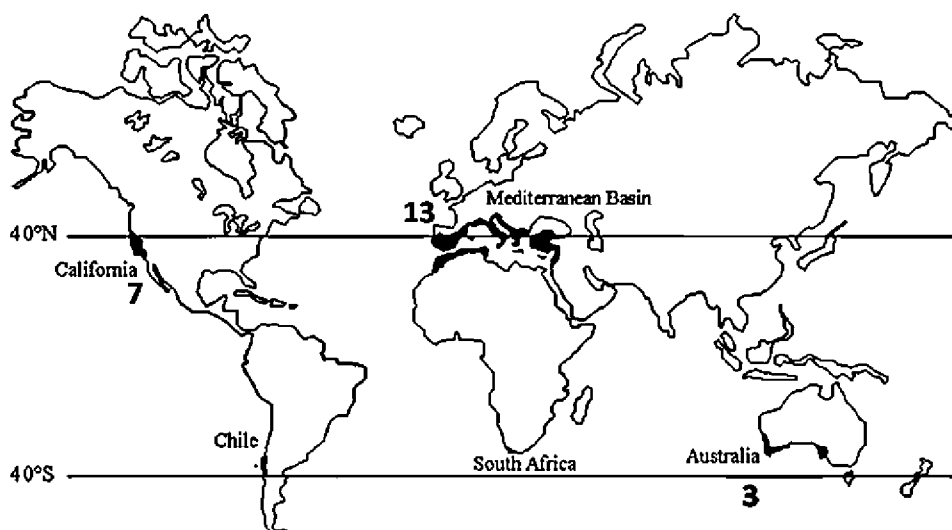


Fig. 1. Regions of the world with a Mediterranean climate and number of papers measuring field N₂O emissions in each region.

body of knowledge is being built. However, the data involved are rather dispersed in the existing literature and no compilations have yet been made. Most N₂O emission studies have been conducted under temperate climatic conditions, but ecological processes in regions with Mediterranean climates are affected in different ways to those subject to other climatic conditions, as has been shown in various fields of research including plant physiology (González-Fernández et al., 2010), N biogeochemistry (Breiner et al., 2007), limnology (Álvarez-Cobelas et al., 2005) and biodiversity (Barriga et al., 2010). Aschmann (1973) defined areas with Mediterranean climates as those in which at least 65% of annual rainfall occurs in winter and in which annual precipitation ranges from 275 to 900 mm. The average winter temperature is below 15 °C, but the number of hours per year with temperatures below 0 °C does not exceed 3% of the total. This climate is characterized by seasonal dryness and many of its subtypes could be classified as semi-arid. This climate type is found in five different parts of the world; they are generally on the west coasts of continents and between latitudes 32° and 40° north and south of the equator. These areas are: the Mediterranean basin; California; Central Chile; the Cape region of South Africa; and South and South-West Australia (Fig. 1). The diversity of soil types is very wide in areas with Mediterranean climates on account of their extensions, variety of geological origins and different land uses. The only common feature shared by these soils is their low organic matter content, while they also often contain low levels of mineral nutrients. The Mediterranean biome is highly biodiverse, but subject to extremely intense development pressure (Underwood et al., 2009). Large increases in yield have been achieved through the intensification of agricultural practices in areas with Mediterranean climates (e.g. Ryan et al., 2009). However, the associated agronomic practices are now undermining both soil and water quality (Zalidis et al., 2002) and are also affecting the natural biodiversity through, for example, N deposition in ecosystems (Ochoa-Hueso et al., 2011).

Research into the effects of N fertilization on N₂O fluxes under Mediterranean conditions has yielded somewhat contradictory results. Moreover, IPCC Tier 1 N₂O emission factors (EF) are mainly based on temperate climate data, and Leip et al. (2011) have recently emphasized the need of more specific EF considering particular parameters such as fertilizer type or climate. The development of Mediterranean climate-specific information on N₂O emission would therefore greatly improve the

accuracy of national GHG inventories for these regions. In this context, we have reviewed and analyzed the currently available scientific information associated with fertilizer-related N₂O emissions under Mediterranean climatic conditions, with the following objectives:

- (1) to compare and contrast direct N₂O emissions from the application of organic and synthetic fertilizers, describing the influence of agricultural practices and environmental factors
- (2) to get an overview of indirect N₂O sources related to fertilizer use, both upstream and downstream of the cropping system
- (3) to identify options for mitigating N₂O emissions, and their respective drawbacks, through the application of organic fertilizers in these agroecosystems and to detect the main gaps in currently available information.

2. Methods

A wide review was performed which included every paper containing data on N₂O emissions in Mediterranean agroecosystems. Articles were consulted on the ISI Web of Knowledge database by simultaneously typing the words “nitrous oxide” or “N₂O”, “emission”, and either the word “Mediterranean” or the name of a country with territory in areas with a Mediterranean climate, according to the map in Fig. 1. This search based on keywords was complemented with a search through the literature cited in the articles found.

N₂O emission data have been expressed as cumulative emissions and EF. Cumulative emission data refer to the sum of N₂O fluxes over the reported measurement period. For measurements covering more than 1 year, the values cited were converted to 1-year references. In some cases, cumulative emissions were estimated through the interpolation of emission values obtained from the figures provided in these papers. Figures were digitized using GetData v.2.24 software (Fedorov, 2002). N₂O EF refers to the proportion of fertilizer N that is released as N₂O-N during the measurement period after discounting emissions from an unfertilized control treatment (equation (1)). Studies covering less than a full growth season were excluded from EF analyses. In many cases, measurement period was extended for a full growth season or more, but was shorter than 1 year; therefore the annual EF may be underestimated. In order to explore different methodologies, we estimated an additional EF (EF_{annual}) and cumulative emissions by

linearly extrapolating average N₂O emission levels during sampling period to the rest of the year.

$$EF = \frac{\text{kg N}_2\text{O-N(F)} - \text{kg N}_2\text{O-N(C)}}{\text{kg N fertilizer applied}} \quad (1)$$

where EF is the emission factor (N₂O-N emitted as % of fertilizer-N applied) and N₂O-N (F) and N₂O-N (C) are the reported cumulative N₂O emissions (kg N ha⁻¹ yr⁻¹) from the fertilized and control (unfertilized) treatments, respectively. N fertilizer applied is the rate of N applied during the study (kg ha⁻¹ yr⁻¹). For slow N release organic amendments (i.e. solid organic fertilizers), “available N” was preferentially chosen as the “N fertilizer applied” value instead of the total N content in the fertilizer; this was in line with the procedure followed by most of the authors whose work was reviewed. The “available N” approach takes into account the fact that only a fraction of the N contained in organic fertilizers mineralizes during the measurement period. The EF for organic fertilizers obtained applying this approach is therefore greater than that obtained with the total N approach recommended by the IPCC (2006a). However, this avoids any possible underestimation of the EF associated with the residual effect of solid organic fertilizers, which is particularly useful for short sampling periods (although this assumption is open to criticism, see Section 6.1). EF based on total N applied was also calculated for some analyses in order to compare the results obtained with the available N method and then discuss them.

In a first approach, the effect of fertilizer type on cumulative emissions of N₂O and EF was studied using a general matrix containing the results of all the publications reviewed. Fertilizer type was grouped at four levels: (i) synthetic, including urea, ammonium nitrate, ammonium sulfate and NPK compound fertilizers; (ii) organic (solid), including residues of cover crops (legumes and non-legumes), organic manure, composted municipal solid waste, composted cattle and sheep manure, and composted thick fractions of digested pig slurries; (iii) organic (liquid), including raw or digested pig slurries; (iv) organic + synthetic, including mixtures of organic and synthetic sources of N, except when the organic N was only represented by residues of the previous crop, in which case the treatment was classified as “synthetic”.

The influence of water management on N₂O emissions was studied by classifying this factor in three categories: (i) rainfed systems, in which no irrigation water was applied; (ii) high-water systems, including furrow, sprinkler and micro-sprinkler irrigation; (iii) low-water systems, including surface and subsurface drip irrigation techniques.

We have observed a high degree of variability in the published N₂O emissions associated with organic and synthetic fertilization. Therefore, in a second approach, the dataset was further narrowed down by restricting the data used to pairwise comparisons of field emissions from organic and synthetic fertilizers in order to examine them meta-analytically. Weighted meta-analysis requires information on variance and the number of replications of each treatment; studies that did not report these data were therefore also excluded. These pairwise comparisons represent experiments where synthetic and organic fertilizers are compared under similar agro-climatic conditions and application rates. In many occasions, multiple organic fertilizers were compared to a common control (synthetic) group. Therefore, in order to avoid an over-estimation of the precision of the mean effect size (Borenstein et al., 2009; Hungate et al., 2009), the resulting pairs were combined into one composite effect size, which variance is given by equation (2).

$$\text{var} \left(\frac{1}{m} \sum_{i=1}^m Y_i \right) = \left(\frac{1}{m} \right)^2 \left(\sum_{i=1}^m V_i + \sum_{i \neq j} (r_{ij} \times \sqrt{V_i} \times \sqrt{V_j}) \right) \quad (2)$$

where m represents the number of correlated pairs, Y_i and V_i are the effect size and the variance of pair i , and r is the correlation coefficient, which is equal to 0.5 because all pairs share a common control.

No EF standard deviations (SD_{EF}) were provided in any of the reviewed papers, so they were calculated from cumulative emission standard deviations and sample sizes, following equation (3).

$$SD_{EF} = \frac{\sqrt{(n_F - 1) \times SD_F^2 + (n_C - 1) \times SD_C^2 / (n_F + n_C - 2)}}{\text{kg N fertilizer applied}} \quad (3)$$

where n_F and n_C are the number of observations in the fertilized and control (unfertilized) treatments, respectively. SD_F and SD_C are the standard deviations in the fertilized and control treatments, respectively.

We chose the response ratio (RR) as the effect size unit for both cumulative emissions and EF data. This RR-value is the ratio between some measured quantity in the experimental (organic in our case, \bar{X}_{Org}) and control (synthetic, \bar{X}_{Syn}) groups ($RR = \bar{X}_{Org} / \bar{X}_{Syn}$). We used the natural log of RR (L_i) to perform the analysis (equation (4) for its mean, and equation (5) for its variance), because this transformation results in a much more normal sampling distribution in small samples (Hedges et al., 1999).

$$L_i = \ln(\bar{X}_{Org}) - \ln(\bar{X}_{Syn}) \quad (4)$$

$$\text{var}_i = \frac{(SD_{Org})^2}{n_{Org} \times \bar{X}_{Org}} + \frac{(SD_{Syn})^2}{n_{Syn} \times \bar{X}_{Syn}} \quad (5)$$

where SD is the standard deviation and n the number of observations in the organic and synthetic groups. Individual effect sizes were pooled together into a common effect size following a random effects model; this is appropriate for situations in which individual studies are not projected to share a common effect size. This weighted mean effect size and its related statistical parameters were calculated using Comprehensive Meta-Analysis software (Borenstein and Rothstein, 1999). The weighted mean L_i and their variances were transformed back in the presentation of the results.

In order to summarize all the data reviewed, information on cumulative emissions and EF grouped by other factors was also provided: N fertilizer rate, crop type and tillage. Some treatments were excluded from all the analyses: (i) rice paddies, because only one measurement was available (Skiba et al., 2009) and the conditions for N₂O production are very different from those of the rest of the crop types; (ii) experiments employing chemicals or additives such as nitrification inhibitors, because their use is limited on a global scale (Stehfest and Bouwman, 2006); (iii) treatments with N fertilizer rates of more than 300 kg N ha⁻¹ yr⁻¹ of available N, or 500 kg N ha⁻¹ yr⁻¹ of total N (solid organic fertilizers), as higher rates are not considered representative of typical Mediterranean agroecosystems. We only found one such treatment (in Heller et al., 2010); (iv) studies published before 2000, in order to assure a relatively homogeneous measurement methodology. This implied the exclusion of only one paper (Ryden and Lund, 1980a).

3. Direct N₂O emissions in Mediterranean cropping systems

3.1. General overview of the papers reviewed

Published field research into N₂O emissions from Mediterranean agricultural systems began three decades ago in the Santa Maria Valley, Santa Barbara, California (Ryden and Lund, 1980a), although this pioneering study was not followed by any others until very recently, when research results from the La Poveda research station in Central Spain were published (Vallejo et al., 2005). Over the short period from 2005 to mid-2011, a valuable body of knowledge has been acquired. 24 field experiments are now available

Table 1
Characteristics of field experiments measuring N₂O emissions in Mediterranean cropping systems.

Reference	Study site	Crop type	Fertilizer ²	Irrigation ³	Duration (days)	Soil type	Observations
Barton et al. (2011)	Cunderdin, SW Australia	Lupin	Legume CC, none	Rainfed	350	Natric Haploxeralf and Typic Natrixeralf	
Barton et al. (2010)	Cunderdin, SW Australia	Canola	U, none	Rainfed	360	Natric Haploxeralf and Typic Natrixeralf	
Barton et al. (2008)	Cunderdin, SW Australia	Wheat	U, none	Rainfed	365	Natric Haploxeralf and Typic Natrixeralf	
Burger et al. (2005)	Russell Ranch (LTRAS-CIFS ¹), Davis, California, USA	Tomato	Compost, CC, synthetic fertilizers	Furrow		Typic Xerothent and Mollic Haploxeralf	Not included (no data on cumulative emissions)
De Gryze et al. (2010)	Central Valley, California, USA	Various rotations	Compost, legume CC, synthetic fertilizers	Furrow, rainfed			Not included (only simulated N ₂ O emission reported). Tillage comparisons
Garland et al. (2011)	Arbuckle, California, USA	Vineyard, legume mix (cover crop)	Legume CC, U-AN	Drip (vineyard), rainfed (CC)	194	Willows silty clay	Tillage comparisons
Heller et al. (2010)	Volcani, Israel	Maize	NPK, chicken manure	Drip	365	Typic Rhodoxeralf	One treatment with very high N fertilization (not included). Tillage comparisons
Kallenbach et al. (2010)	Russell Ranch, Davis, California, USA	Tomato	LCC, NPK, AS	Furrow, drip	365	Reiff loam and Yolo silt loam	
Kong et al. (2007)	Russell Ranch (LTRAS-CIFS), Davis, California, USA	Maize	Compost, legume CC, U-AS	Furrow	142	Typic Xerothent and Mollic Haploxeralf	Not included (same experiment as Kong et al., 2009)
Kong et al. (2009)	Russell Ranch (LTRAS-CIFS), Davis, California, USA	Maize	Compost, legume CC, U-AS	Furrow	142	Typic Xerothent and Mollic Haploxeralf	Tillage comparisons
Lee et al. (2009)	Yolo County, California, USA	Maize-Sunflower-Chickpea	U-AN, NPK	Furrow	912.5	Myers clay (Entic Chromoxererts)	Tillage comparisons
López-Fernández et al. (2007)	La Poveda, Madrid, Spain	Maize	MSW compost, sheep manure compost, PS, U, none	Furrow	200	Typic Xerofluvent	
Lugato et al. (2010)	Beano, Udine, Italy	Maize	Not specified	Irrigation	1095	Chromi-Endoskeletal Cambisol	Not included (only simulated N ₂ O emission reported)
Meijide et al. (2007)	La Poveda, Madrid, Spain	Maize	PS, DPS, DPS compost, MSW compost, U, none	Furrow	145	Typic Xerofluvent	Nitrification inhibitor used in some treatments (not included)
Meijide et al. (2009)	El Encín, Madrid, Spain	Barley	PS, DPS, SS compost, MSW, U, none	Rainfed	335	Calcic Haploxerepts (USDA) – Calcaric Cambisol (FAO)	
Menéndez et al. (2008)	El Malagón, Córdoba, Spain	Wheat-Sunflower-Faba bean	AN, none	Rainfed	22, 29	Vertisol (Typic Haploxerert)	Not included (short measurement period). Tillage comparisons
Petersen et al. (2006)	Reggio Emilia, Italy	Wheat-Alfalfa-Maize-Grass	Manure, legume CC, synthetic fertilizers	Irrigation	365		
Ryden and Lund (1980a)	Santa Maria Valley, Santa Barbara, California, USA	Horticultural crops	Manure, legume CC, NPK	Furrow	365		Not included (old study)
Sánchez-Martín et al. (2008b)	El Encín, Madrid, Spain	Melon	AN, none	Drip, furrow	140	Calcic Haploxerepts (USDA) – Calcaric Cambisol (FAO)	
Sánchez-Martín et al. (2010a)	El Encín, Madrid, Spain	Melon	DPS, none	Drip, furrow	150	Calcic Haploxerepts (USDA) – Calcaric Cambisol (FAO)	

Table 1 (Continued)

Reference	Study site	Crop type	Fertilizer ²	Irrigation ³	Duration (days)	Soil type	Observations
Sánchez-Martín et al. (2010b)	El Encín, Madrid, Spain	Onion	Manure, DPS, none	Micro-sprinkler	365	Calcic Haploxerepts (USDA) – Calcic Cambisol (FAO)	
Skiba et al. (2009)	Castellaro, Italy	Rice, Fennel and Maize	Not specified	Irrigation	365	Not specified	Not included (N ₂ O emission reported only for rice paddies) Tillage comparisons
Steenwerth and Belina (2008)	Monterey, California, USA	Vineyard cover	CC, none	Rainfed	365	Cumulic Haploxeroll, or Haplic Chernozem	Not included (short measurement period). Tillage comparisons
Steenwerth and Belina (2010)	Monterey, California, USA	Vineyard	U-AN, CC	Drip	33.3	Cumulic Haploxeroll, or Haplic Chernozem	
Townsend-Small et al. (2011)	Irvine and Popoma, California, USA	Maize, horticulture	AP (maize), AN (horticulture) PS, none	Rainfed	365	Sorrento loam and clay loam Typic Xerofluvent	Nitrification inhibitor used in some treatments (not included)
Vallejo et al. (2005)	La Poveda, Madrid, Spain	Maize		Furrow	215		Nitrification inhibitor used in some treatments (not included)
Vallejo et al. (2006)	El Encín, Madrid, Spain	Potato	PS, DPS, DPS compost, MSW, U, none	Furrow	150	Calcic Haploxerepts (USDA) – Calcic Cambisol (FAO)	

¹ ITRAS-CIFS: Center for Integrated Farming Systems, formerly known as the long-term research on agricultural systems experiment.

² Organic fertilizers (solid): CC: cover crops; MSW: municipal solid wastes; SS: sewage sludge; DPS compost: composted thick fraction of digested pig slurry; Organic fertilizers (liquid): PS: raw pig slurry; DPS: digested pig slurry (thin fraction). Synthetic fertilizers: U: urea; AN: ammonium nitrate; NPK: compound fertilizers; AS: ammonium sulfate; AP: ammonium phosphate.

³ Rainfed: no irrigation water is applied; high-water: furrow and micro-sprinkler irrigation; low-water: drip (surface or subsurface) irrigation.

in the scientific literature, which relate to 13 different study sites (Table 1). These relate to three of the five areas in the world that have Mediterranean climates. All the field measurements of N₂O emissions were performed using closed chambers, with a sampling frequency of usually between 1 day and 2 weeks, which usually increased after important management events such as fertilization, irrigation or significant rainfall. The measurement frequency was highest in the Australian studies (Barton et al., 2008, 2010, 2011), which used soil chambers connected to a fully automated system and collected samples every 180 min. These field data were complemented by 11 laboratory experiments that addressed N₂O emissions from Mediterranean soils, or under specific Mediterranean conditions, such as the addition of organic matter sources from Mediterranean cropping systems (olive residues) (García-Ruiz and Baggs, 2007).

3.2. Factors influencing N₂O emissions

3.2.1. General effects of fertilizer type and water management

Emissions were highest for slurries (“liquid organic fertilizers”, 4.4 kg N₂O-N ha⁻¹ yr⁻¹ on average, Table 2, Fig. 2a), followed by organic-synthetic mixtures and synthetic fertilizers (respectively, 3.5 and 3.0 kg N₂O-N ha⁻¹ yr⁻¹), whereas solid organic fertilizers and unfertilized treatments (“none” group) showed the lowest values (1.7 and 1.8 kg N₂O-N ha⁻¹ yr⁻¹, respectively).

Despite the high degree of variability in the treatments and conditions included in this analysis, a clear influence of water management on cumulative emissions and EF could be observed in both cases (Fig. 3). Emission levels in rainfed treatments were one order of magnitude lower than those in conventionally irrigated ones (mean cumulative emissions were 0.4 and 4.0 kg N₂O-N ha⁻¹ yr⁻¹ and average EF values were 0.08% and 1.01% for rainfed and high-water irrigation treatments, respectively; Tables 2 and 3). Drip irrigation (low-water category) showed intermediate distributions in emission levels (the averaged cumulative emissions and EF in this category were 1.2 kg N₂O-N ha⁻¹ yr⁻¹ and 0.66%).

The high influence of irrigation can be explained by the fact that in Mediterranean agroecosystems this type of management activity is usually applied during the summer dry period, which leads to optimal moisture and temperature conditions for N₂O production (Section 3.3). In this way, average cumulative N₂O emissions for Mediterranean cropping systems irrigated with conventional techniques were normally slightly higher than the cumulative emissions for high N application rates (200–250 kg ha⁻¹) obtained from the global data compiled by Stehfest and Bouwman (2006), whereas average EFs were generally similar to the default IPCC factor of 1%. Other works have also shown that when semi-arid soils are irrigated, an increase in N₂O emissions can be expected (Horvath et al., 2010; Maraseni et al., 2010). In rainfed systems, different limitations on N₂O production are imposed throughout the cropping cycle, especially when the semi-arid conditions are marked. This result was very much in line with low N₂O emissions linked to fertilizer application reported for semi-arid agroecosystems under different climatic conditions (Dick et al., 2008; Galbally et al., 2008). What limited information is available about drip-irrigated systems suggests intermediate emission levels, which points to a high potential for N₂O mitigation when using this water-saving technique (Section 5.1). The N₂O mitigation effect of applying low-water irrigation techniques also applies to other world climate types, e.g., under temperate continental (Liu et al., 2011) and arid continental climates (Scheer et al., 2008).

3.2.2. Meta-analysis of the fertilizer type effect

N₂O emission levels from organic fertilizers were in many cases lower than those from synthetic fertilizers when compared on a pair-wise basis, even if the variability was sometimes very

Table 2
Number of observations (*N*), mean and standard deviation (SD) of cumulative N₂O emissions (kg N₂O-N ha⁻¹ yr⁻¹) for some of the factors with a significant influence on N₂O emissions from agricultural fields.

	<i>N</i>	Cumulative emissions (experiment period)		Cumulative emissions (year estimate)		Mean N fertilizer rate (kg N ha ⁻¹ yr ⁻¹)	Mean experiment length (days)
		Mean	SD	Mean	SD		
Fertilizer type							
None	18	1.8	1.8	3.9	4.2	0	242
Organic + synthetic	11	3.5	3.3	6.6	8.0	171	234
Synthetic	22	3.0	2.6	5.2	5.9	159	288
Organic (solid)	17	1.7	1.9	3.1	4.3	147	263
Organic (liquid)	16	4.4	3.0	9.0	6.7	163	220
Water management type							
Rainfed	19	0.4	0.5	0.6	1.0	57	316
High-water	54	4.0	2.6	7.8	6.3	137	231
Low-water	11	1.2	1.0	2.0	1.7	128	254
N fertilizer rate (kg N ha⁻¹ yr⁻¹)							
0–75	25	1.4	1.7	2.9	3.9	11	248
75–150	16	1.2	1.1	1.2	1.1	113	356
150–225	29	5.3	2.2	11.2	6.0	178	192
225–500	6	2.9	3.0	3.8	3.0	265	291
Crop type							
Horticulture	21	1.9	1.5	3.4	3.4	100	281
Maize	26	4.5	3.2	9.0	7.4	176	207
Other	12	4.0	2.3	8.0	6.3	113	257
Winter cereals	8	0.3	0.1	0.3	0.1	91	343
Vineyard	5	0.4	0.3	0.4	0.2	35	297
Legume	5	0.7	0.9	0.7	1.8	0	220
None	7	3.2	1.5	5.8	2.7	121	221
Tillage type							
Minimum tillage	10	1.9	2.6	2.7	2.8	133	246
Standard tillage	9	1.1	1.4	1.6	1.4	111	232

N fertilizer rate refers to N applied during the experimental period. In the case of solid organic fertilizers this value corresponds to available N in the experimental period, not to total N applied.

high. The mean response ratio for cumulative emissions was 0.77 ($p < 0.05$), meaning that average emission levels were 23% lower for organic than for synthetic fertilizers (Fig. 4a). When organic fertilizers were segregated in solid and liquid ones, only organic

solid fertilizer emissions were significantly lower than synthetic ($RR = 0.72$, $p < 0.05$). An EF comparison showed a 23% reduction for organic fertilizers ($RR = 0.77$, $p = 0.08$), but the differences were only significant for solid materials ($RR = 0.8$, $p < 0.05$) (Fig. 4b).

Table 3
Number of observations (*N*), mean and standard deviation (SD) of emission factor (EF, %N₂O-N over N applied) for some of the factors that have a significant influence on N₂O emissions from agricultural fields.

	<i>N</i>	EF (experient period)		EF (year estimative)		Mean N fertilizer rate (kg N ha ⁻¹ yr ⁻¹)	Mean experiment length (days)
		Mean	SD	Mean	SD		
Fertilizer type							
Organic + synthetic	3	1.22	0.62	3.04	1.57	175	147
Synthetic	11	0.82	0.73	1.71	1.79	142	251
Organic (solid)	9	0.54	0.48	0.97	1.17	147	261
Organic (liquid)	16	0.91	0.70	1.75	1.34	163	220
Water management type							
Rainfed	7	0.08	0.04	0.09	0.05	114	343
High-water	30	1.01	0.63	2.02	1.48	162	213
Low-water	2	0.66	0.33	1.65	0.75	175	145
N fertilizer rate (kg N ha⁻¹ yr⁻¹)							
0–75	1	0.06		0.06		75	360
75–150	12	0.36	0.31	0.37	0.30	115	353
150–225	26	1.06	0.66	2.31	1.42	175	173
Crop type							
Horticulture	10	0.67	0.31	1.10	0.96	136	277
Maize	12	1.33	0.70	2.74	1.34	177	180
Other	6	1.08	0.71	2.61	1.75	158	185
Winter cereals	6	0.09	0.05	0.10	0.05	121	340
None	5	1.08	0.35	0.91	0.64	170	200

N fertilizer rate refers to N applied during the experimental period. In the case of solid organic fertilizers this value corresponds to available N in the experimental period, not to total N applied.

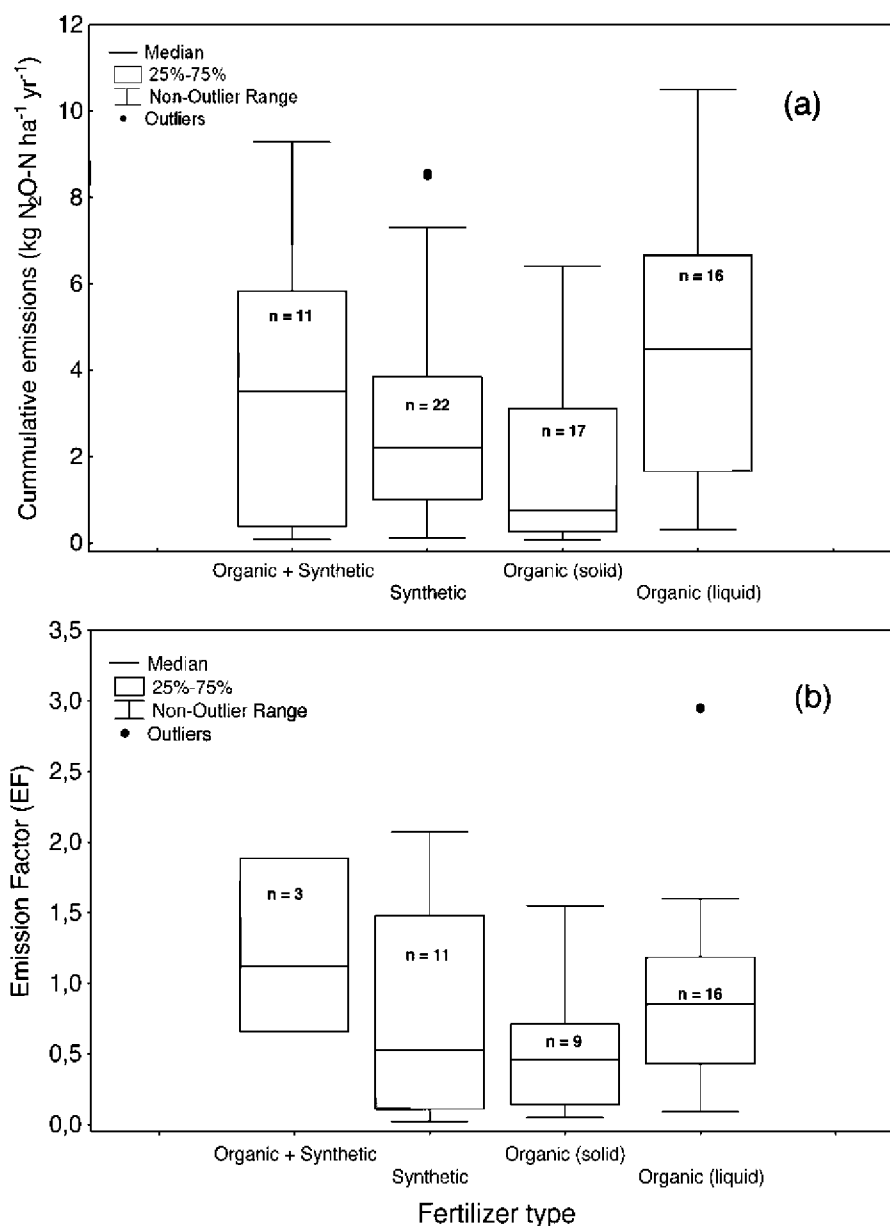


Fig. 2. N₂O emissions from Mediterranean cropping systems according to fertilizer type, expressed as: (a) cumulative emissions during experimental period, (b) emission factor. Numbers in the boxes indicate sample sizes.

When solid organic fertilizer EF was calculated on a total applied N basis, the specific response ratio for this category dropped from 0.8 to 0.37; in other words, from a 20% reduction in N₂O emissions in comparison with synthetic fertilizers, the reduction reached up to 63% with total applied N ($p < 0.001$) (Fig. 4c). These results show that the choice between total applied N and available N is highly relevant for EF calculation (Section 6.1).

The smaller N₂O emissions from solid compared to liquid organic materials is probably related to their lower concentrations of ammonium (NH₄⁺) and their low rate of N mineralization, which usually prevent very high soil mineral N contents being reached. This reduction also seems to be influenced by the semi-arid features which are very common in Mediterranean soils, in which C and N contents are usually low (Section 3.3.1). Relatively high emission levels for liquid organic fertilizers (pig slurries) may be influenced by the highly mineralized nature of the N contained in these materials. NH₄⁺ levels could actually represent as much as 81% and 78%, respectively, of the total N in raw and digested pig slurries (Meijide

et al., 2009). Low N₂O emissions for solid organic as opposed to synthetic or liquid organic fertilizers have also been reported in temperate areas (Gregorich et al., 2005).

3.2.3. Other factors influencing N₂O emissions

3.2.3.1. N application rate. To our knowledge, there were no studies comparing EF as affected by N application rates under Mediterranean conditions. The IPCC approach proposes a linear relationship between N₂O fluxes and fertilizer application rates. However, many experimental data suggest that this relationship may be non-linear, with EF being lowest at low N fertilizer rates and highest at high rates. Accordingly, the global data compiled by Stehfest and Bouwman (2006) suggest a N-shaped curve for N₂O responses to N fertilizer applications, while other studies point to an exponential curve (i.e. Cardenas et al., 2010; Hoben et al., 2011).

In our review, a clear relationship between fertilizer dose and N₂O emissions could be observed in EF (Table 3), but not in cumulative emissions (Table 2), where high-emitting, irrigated control

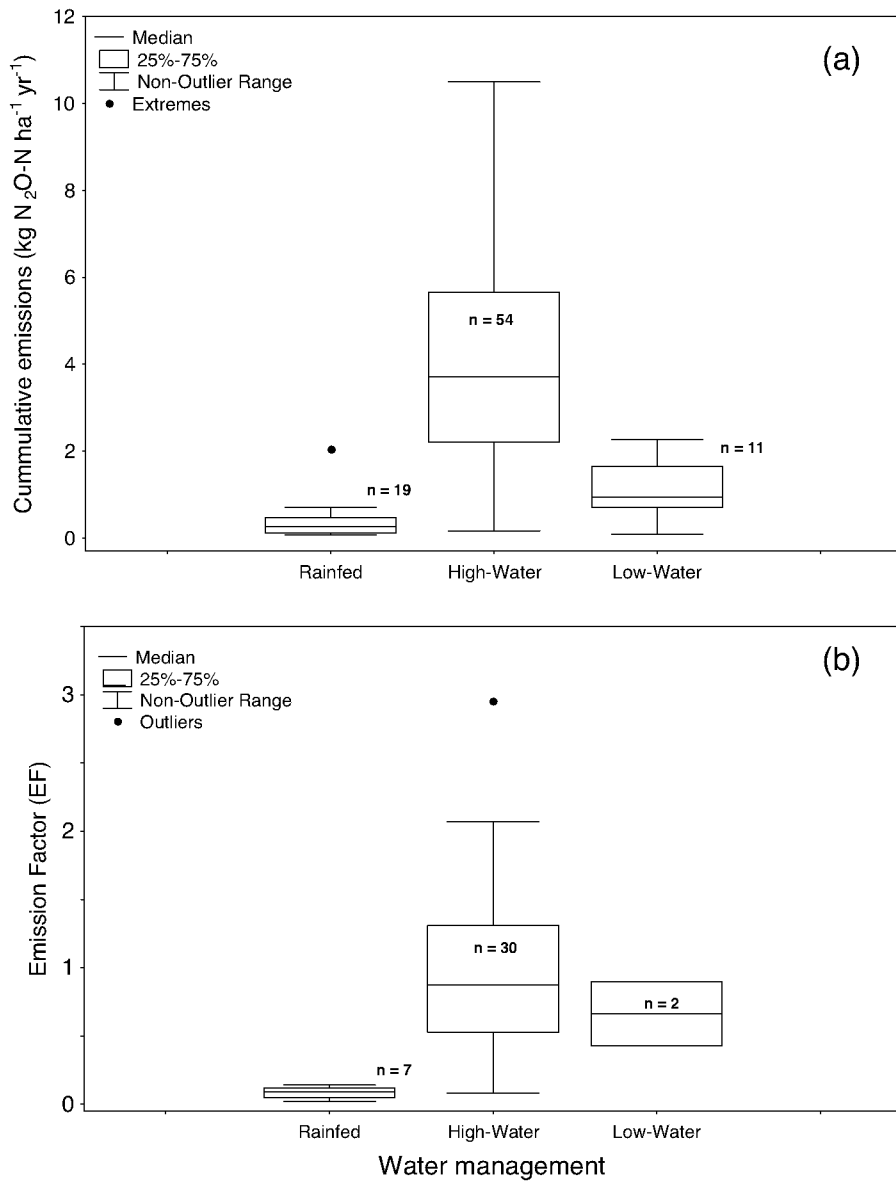


Fig. 3. N₂O emissions from Mediterranean cropping systems according to water management type. Rainfed: no irrigation; high-water: conventional irrigation systems (furrow and sprinkler); low-water: drip irrigation. Emissions are expressed as: (a) cumulative emissions, (b) emission factor. Numbers in the boxes indicate sample sizes.

treatments in the lowest dose group (0–75 kg N), and low sample size in the highest dose one (225–500 kg N) may have hidden the underlying trend. 1.8 kg N₂O-N ha⁻¹ yr⁻¹ was emitted on average from non-fertilized agricultural soils (Table 2). These “background emissions”, which occurred on unfertilized control plots, averaged 63.5% of the fertilized treatment emissions ($N=42$). Similar results were obtained by Kroeze and Seitzinger (1998) in their top-down analysis; they estimated that in the Mediterranean basins of Europe, 210.7 Mt of background N₂O was emitted from agricultural soils, while only 132.9 Mt of N₂ was associated with the use of manure and synthetic fertilizers. Background emissions are discussed in Section 6.2.

3.2.3.2. Crop type. Although none of the studies analyzed compared emissions from different crop types in the same year, cumulative N₂O emissions varied in a range of from 1 to 4 in function of the crop type assessed in the database analyzed (Tables 2 and 3). The main reason for this was the fact that the influence of crop type is closely related to other important factors that

control N₂O production such as the N fertilizer rate and irrigation regime. For example, winter cereals and legumes exhibit exceptionally low N₂O emission levels. Both crops are grown under similar conditions: as rainfed crops during the cool rainy season, with low N fertilizing rates for winter cereals and no fertilizer applications for legumes. Low N₂O emissions have also been observed for cereals in temperate systems (Dobbie et al., 1999). Low N₂O fluxes in vineyards could similarly be related to very low N and water inputs. These systems are rainfed or drip-irrigated. In the latter case, the water applied is limited to the soil next to the vine, representing roughly one-third of the total surface area (Garland et al., 2011). The highest emissions were registered for maize. N fertilizer application rates and water inputs are normally very high for maize fields, which are cultivated under conventional irrigation techniques and high summer temperatures.

3.2.3.3. Tillage. The lower mean cumulative emissions registered for tilled as opposed to no-tilled or minimum-tilled treatments, shown in Table 2, were corroborated by the results of most of the

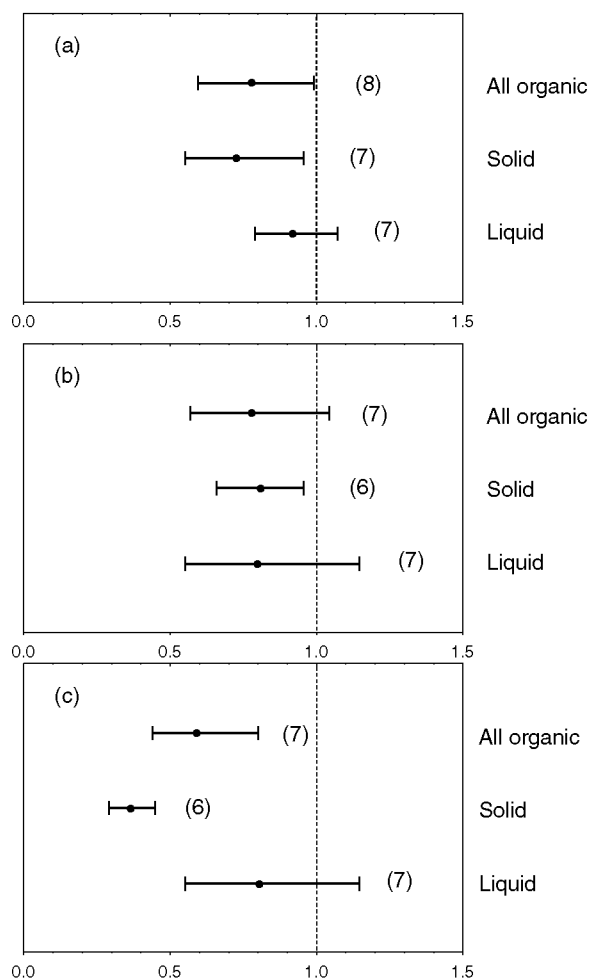


Fig. 4. Effect of fertilizer type (organic vs. synthetic) on (a) cumulative N₂O emissions; (b) N₂O emission factor (EF) calculated considering available N in solid organic fertilizers; (c) EF calculated considering total N in solid organic fertilizers. The effect is expressed as the response ratio ($RR = \bar{X}_{org}/\bar{X}_{syn}$) and categorized into solid and liquid organic fertilizers. Mean values and 95% confidence intervals of the back-transformed response ratios are shown (number of comparisons in parentheses). Emissions are significantly different if confidence intervals do not overlap. 1. Number of aggregated paired comparisons are indicated in parentheses (see Section 2 for independence criteria).

studies that specifically addressed this question (Garland et al., 2011; Kong et al., 2009; Lee et al., 2006; Menéndez et al., 2008; Steenwerth and Belina, 2008, 2010), although in some cases the differences were not significant (Garland et al., 2011). There was only one exception to this general trend (Heller et al., 2010), in which emissions were twice as high for the tilled compared to the no-tilled treatment. Tillage events themselves showed no clear effect on N₂O emissions. Thus, whereas in a vineyard soil N₂O pulses occurred after tillage events (Steenwerth and Belina, 2008), in a laboratory experiment there was no N₂O flux response nor any response in the denitrification rate to a simulated tillage event (Calderón et al., 2000). Higher emission rates under minimum or no-tilled treatments were mainly attributed to less aeration, which could have enhanced denitrification, particularly as most of the emissions occurred after irrigation events (Lee et al., 2009; Kong et al., 2009). Studies specifically measuring denitrification show heterogeneous responses of this microbial activity to different tillage practices, ranging from lower (Menéndez et al., 2008) to higher (Melero et al., 2011) denitrification activity under no-tillage, despite both studies were performed under similar conditions (rainfed systems on Vertisol soils). Researchers have also reported higher N₂O emissions

from no-tilled plots in both humid and dry climates of the world (Six et al., 2004). In the long term, however, this relationship could disappear or even reverse (Omonode et al., 2011; Six et al., 2004).

3.2.3.4. Soil mineral N. Soil mineral N can generally be found either in the form of NH₄⁺ or NO₃⁻. These two compounds are respectively the substrates of nitrification and denitrification and therefore they both can stimulate N₂O emissions. In accordance with this, some authors have reported a positive correlation between N₂O flux and NO₃⁻ concentration in the soil (Lee et al., 2006; López-Fernández et al., 2007; Sánchez-Martín et al., 2010b). In some cases, this positive correlation only existed during certain periods (e.g. after the onset of irrigation, López-Fernández et al., 2007) or for certain values of NO₃⁻ content (e.g. >6.5 mg N kg soil⁻¹ for temperate climates, Vilain et al., 2010). This last result may explain why many authors have not found any correlation between N₂O emissions and soil NO₃⁻ (Garland et al., 2011; Sánchez-Martín et al., 2008b; Steenwerth and Belina, 2008; Vallejo et al., 2005, 2006).

Soil NH₄⁺ concentration has been significantly and positively correlated with N₂O emissions in many cases (Garland et al., 2011; Heller et al., 2010; Mejjide et al., 2007, 2009; Petersen et al., 2006; Sánchez-Martín et al., 2008b; Vallejo et al., 2005). A significant relationship between the NH₄⁺ content of the applied fertilizer and N₂O emissions has also been reported (Mejjide et al., 2009). In many other cases, however, the correlation is not significant (Barton et al., 2008, 2010, 2011; Steenwerth and Belina, 2008; Vallejo et al., 2004, 2006). There have even been cases in which negative correlations have been found; this occurred in two different experiments involving no-tilled treatments (Garland et al., 2011; Lee et al., 2006). These somewhat contradictory findings suggest that other factors could be limiting N₂O production in cases in which no evident relationship between emissions and soil mineral N has been found. A lack of synchrony between N₂O flux measurement and soil sampling could also have been responsible for some of these results (Barton et al., 2008).

3.2.3.5. Soil organic carbon (SOC) and dissolved organic carbon (DOC). In the studies analyzed, SOC concentration was within a narrow range around 1% of soil mass (7–11.3 g C kg soil⁻¹); as a result, we could not study its relationship with N₂O emissions. DOC is a more dynamic parameter than SOC and its relationship with N₂O emissions was studied in some of the papers reviewed, although they did not show a homogeneous response. Thus, whereas some studies reported a positive correspondence between the two parameters (López-Fernández et al., 2007; Sánchez-Martín et al., 2010b; Vallejo et al., 2006), this relationship was only verified during the irrigation period, and sometimes only at the beginning of this period (Vallejo et al., 2006), while in others, it was absent throughout the experiment (Mejjide et al., 2007). In a laboratory experiment, Sánchez-Martín et al. (2008a) showed that labile C (glucose) added to a low-carbon, basic Mediterranean soil strongly reduced N₂O emissions when a mineral N source was applied. Similar results were obtained with temperate soils and added acetate (Laverman et al., 2010). This effect was not, however, so evident in a high-carbon, acid Scottish soil, where emissions were reduced under high-water conditions (90% water filled pore space) but not under low-water conditions (40% WFPS) (Sánchez-Martín et al., 2008a). On the other hand, DOC also has an influence on the denitrification rate and N₂O/N₂ ratio, and high-carbon content does not necessarily mean that this substrate is biodegradable for denitrification (see Section 3.3.1).

3.2.3.6. Water filled pore space (WFPS). The general association between water inputs and N₂O emissions described in Section 3.2.1 is not so clear in the relationship between the WFPS and

N₂O fluxes presented in the individual studies. In some cases, N₂O emissions were reported to have increased linearly, with WFPS values increasing from 20% to 70% (Lee et al., 2006), whereas in many other cases this relationship was not found (Garland et al., 2011; Sánchez-Martín et al., 2008b; Steenwerth and Belina, 2008; Vallejo et al., 2005, 2006); this apparently contradicts results reported for temperate climates (Vilain et al., 2010). The lack of correlation between WFPS and N₂O emissions at a temporal scale of days or weeks suggests that WFPS only imposes the upper and lower limits to the microbial processes of nitrification and denitrification; in consequence, within a certain WFPS range, N₂O emissions could be largely unlinked to soil water content (Vilain et al., 2010). Accordingly, increases in WFPS were significantly related to N₂O emission pulses from Mediterranean soils when changes in soil water content were very marked, such as when rainfall or irrigation occurred after a dry period (Barton et al., 2008, 2010, 2011; Garland et al., 2011; López-Fernández et al., 2007; Meijide et al., 2009; Steenwerth and Belina, 2008, see Section 3.3 in this paper).

3.2.3.7. Temperature. The annual temperature range across different sites (13.2–20.9 °C) was too narrow to divide into categories, so the information was qualitatively reviewed. Temperature is a key factor for microbial activity and is therefore considered to have a pronounced effect on N₂O emissions. Moreover, soil temperature indirectly affects N₂O production through its influence on soil water evaporation rate, and subsequently on WFPS. In accordance, the studies reviewed here suggest that this factor, along with water and N inputs, was responsible for the large differences in N₂O emissions that were observed between winter-cropped (usually rainfed) and summer-cropped (irrigated) Mediterranean soils. A positive, significant correlation between temperature and N₂O flux was generally identified (Heller et al., 2010; Lee et al., 2009; Meijide et al., 2007; Petersen et al., 2006; Vallejo et al., 2006). In some cases, such a relationship was not evident throughout the whole experimental period, but only under certain circumstances. For example, low temperatures (below 10–12 °C) were associated with very low (Lee et al., 2009) or even negative (Meijide et al., 2009; Sánchez-Martín et al., 2010b) N₂O fluxes. In the study by López-Fernández et al. (2007), temperature only influenced N₂O flux during the irrigation period; this was probably due to restrictions on N₂O production imposed by low-water availability in the pre-irrigation period. Sánchez-Martín et al. (2010a) observed rapid soil desiccation after slurry application due to high temperatures, which delayed nitrification until the onset of irrigation. Other studies found no correlation between N₂O fluxes and temperature during the experimental period (e.g. Sánchez-Martín et al., 2008a; Steenwerth and Belina, 2008). In other climates, Horvath et al. (2010) found a link between N₂O emissions and soil temperatures up to 20 °C. Schaufler et al. (2010) reported a non-linear increase in N₂O emissions with temperature for a large set of soil cores studied under laboratory conditions.

3.2.3.8. pH. The magnitude and origin of N₂O emissions can be markedly affected by soil pH. At low pH, N₂O reduction is usually inhibited, which results in increased emissions (Baggs et al., 2010; Sánchez-Martín et al., 2008a), although this effect may only be apparent in the long term (Baggs et al., 2010). In the experiments reviewed, the soils had pH values ranging from 5.2 to 8.1 (with an average of 7.7 for all the treatments). Only two trials were performed in slightly acid soils: one in Australia (pH 6, Barton et al., 2008, 2010, 2011) and one in California (pH 5.2–7.2, Garland et al., 2011). The N₂O emissions in those trials were lower than average, but they all related to extensive systems with low or zero water and N inputs.

3.2.3.9. Texture. Soil texture affects soil N₂O production through its influence on soil aeration which, in turn, conditions nitrification and denitrification processes. For sediment, denitrification was shown to increase with the proportion of fine-textured sediment, <50 µm (Garnier et al., 2009). In this study, most of the soils analyzed were medium-textured, with only one study site corresponding to a fine-textured soil (Garland et al., 2011) and two corresponding to light-textured soils, one of which was in Australia (Barton et al., 2008, 2010, 2011) while the other was in California (Steenwerth and Belina, 2008). N₂O emissions were lower than average in the three mentioned sites, but the differences cannot be attributed to soil texture due to the low number of studies.

3.3. *The influence of fertilization type and irrigation management on biochemical processes driving the annual pattern of N₂O emissions*

The production of N₂O, whether in soils, wastewater treatment plants, sediments or water bodies, mainly results from biological transformations of nitrogenous compounds (Wrage et al., 2001). As Firestone and Davidson (1989) reported, soil aerobic microorganisms can nitrify soil NH₄⁺ to NO₃⁻, with N₂O being emitted as a by-product of this transformation. This NO₃⁻ can then be sequentially reduced to nitric oxide (NO), N₂O and finally N₂ by anaerobic denitrifiers; N₂O emissions occur when the reduction is incomplete. Finally, nitrifier denitrification has been proposed as a third pathway for N₂O production in the soil (Kool et al., 2011; Wrage et al., 2001). Through this pathway, autotrophic nitrifiers oxidize NH₃ to nitrite (NO₂⁻) and then reduce NO₂⁻ to NO, N₂O and N₂ (Wrage et al., 2001).

In real agroecosystems, there is rapid shifting between the different pathways in line with changes in environmental factors and management activities. The typical Mediterranean climate pattern includes a very marked drought period during summer and usually has mild temperatures and an erratic distribution of rainfall over the rest of the year; this contributes to the existence of several wetting and drying cycles. When the soil is rewetted, without reaching complete anoxia, microbial activity is recovered, leading to a pronounced peak in N₂O and CO₂ emissions; this is what has been called the “pulse” or “Birch” effect (Birch, 1958; Beare et al., 2009; Davidson et al., 1993). This sub-optimal activity is enhanced by the availability of large quantities of C and N substrates that have been accumulated in the soil due to the death of soil microorganisms during the previous dry period. A large proportion of the annual N₂O fluxes in Mediterranean cropping systems is comprised of pulses that occur after rainfall or, when present, irrigation events, especially when the soil was previously dry. N₂O pulses after rainfall events are also common in temperate climates, where they may be driven by denitrification (Davidson et al., 1993; Vilain et al., 2010). Pulses may also be driven by aerobic processes (nitrification) when the climate conditions are semi-arid (Galbally et al., 2008). Pulses driven by nitrification are, however, usually of lower intensity, in absolute terms, than those driven by denitrification (see Section 3.3.2).

On the other hand, all of these biochemical processes can also occur in the soil simultaneously due to the high complexity of soil structure, where adjacent microsites can show very different levels for such soil parameters as WFPS, NH₄⁺, NO₃⁻ or C accumulation. This spatial and temporal heterogeneity has already been specifically studied in Mediterranean cropping systems. Kong et al. (2010) studied the abundance of ammonia oxidizing bacteria (AOB), denitrifiers and total bacterial communities in different soil microenvironments under different long-term management regimes. They showed that despite the fact that AOB and denitrifier community abundances were affected by management practices, they were largely decoupled from N cycling. Nitrifier and denitrifier

communities were larger and fluctuated more in microaggregates than in particulate organic matter (POM) and silt-and-clay fractions. These findings suggest that microaggregates are potential hotspots for N_2O production in the soil (Kong et al., 2010).

Although nitrification and denitrification are the processes responsible for N_2O production in the soil, they may not be correlated with N_2O flux. Denitrification activity could actually shift from being a source to a sink for N_2O , depending on its efficiency for N_2O reduction to N_2 . This efficiency has sometimes been shown to be enhanced under Mediterranean conditions, thus potentially decreasing N_2O emissions. This process may occur at relatively low WFPS (Menéndez et al., 2008), but it is usually enhanced when N_2O diffusivity is low due to very high WFPS (Lee et al., 2009; Sánchez-Martín et al., 2010b; Vallejo et al., 2005) and when soil NO_3^- content is low (Ryden and Lund, 1980b; Sánchez-Martín et al., 2008a, 2010b). Labile organic C sources could also increase denitrification efficiency (Section 3.3.1). Whether driven by this or by another process, a net N_2O uptake has been observed on some occasions (Barton et al., 2008, 2011; Garland et al., 2011; Meijide et al., 2009; Sánchez-Martín et al., 2010b). N_2O uptake events occurred at the end of spring, coinciding with low WFPS and low mineral N levels and/or high DOC (Barton et al., 2008; Garland et al., 2011). The information related to the different biochemical pathways for N_2O production that were influenced by seasonal changes in environmental factors is reviewed in the following sections and grouped according to fertilizer type and water management regime.

3.3.1. Fertilizer type

Organic fertilizers are very heterogeneous materials, whose properties can vary widely depending on their origin and processing. As a general trend, however, adding organic matter to the soil provides the labile C substrates needed for denitrification, which is further enhanced by the creation of anaerobic microsites, even when soil WFPS is <55% (García-Ruiz and Baggs, 2007). The positive effect of a range of different organic fertilizers on the denitrification rate has been verified by López-Fernández et al. (2007), Meijide et al. (2007) and Vallejo et al. (2006), in irrigated arable plots in Central Spain, in which a larger proportion of N_2O fluxes were driven by denitrification in soils amended with organic matter than in synthetic N fertilized soils. On the contrary, in drip-irrigated treatments (Sánchez-Martín et al., 2008b), digested NH_4^+ -enriched pig slurry-amended plots produced proportionally less N_2O by denitrification (56%) than the unfertilized control (92%).

DOC (see Section 3.2.3) is a soil parameter which is affected by the type of fertilizer employed. Applying mineral N promotes the consumption of DOC by soil microbial biomass (Sánchez-Martín et al., 2008b) and applying urea is usually related to a temporal (1–2 months) increase in DOC (Meijide et al., 2007; Vallejo et al., 2006). Complex organic materials like composts release labile C compounds during their mineralization process, even though their DOC promoting effect could be delayed until 3–4 months after application (Meijide et al., 2007). DOC concentrations have been correlated with the denitrification rate in numerous cases (López-Fernández et al., 2007; Meijide et al., 2007; Vallejo et al., 2006) and especially during the irrigation period. High DOC during irrigation promoted anoxia, which favored denitrification, but not necessarily N_2O emissions (López-Fernández et al., 2007; Meijide et al., 2007). This implies that labile C could also reduce the N_2O/N_2 ratio. Indeed, enhanced denitrification efficiency due to the availability of labile C resulted in a reduction in net N_2O emissions in a Cumulic Haploxeroll in California (Steenwerth and Belina, 2010).

A second possible explanation for N_2O reduction by organic fertilizers was pointed to by Dick et al. (2008) for semi-arid cropping systems in Mali, where lower N_2O emissions were measured in plots receiving mixtures of urea and organic manure as opposed to those that only received urea. These authors suggested that N could

be immobilized more efficiently by the existing microbial biomass when easily available C and N are simultaneously added to a soil lacking C and N. For example, adding different organic residues to Mediterranean soils fertilized with synthetic N reduced denitrification losses as a percentage of applied N (Coskan et al., 2002), which could perhaps be explained by more efficient N immobilization. However, this immobilization would not necessarily explain the results obtained in Mediterranean systems, where denitrification is usually promoted by organic fertilizers.

The nitrifier denitrification pathway is favored at low concentrations of available C and sub-anoxia (Wrage et al., 2001, see next section); these are common characteristics of Mediterranean soils. The addition of organic C sources to the soil could therefore influence this pathway. An increase in C availability could reduce the contribution of this pathway to overall N_2O emissions, as compared to that of other pathways, and this could help to explain the reduction in cumulative N_2O emissions observed in our analyses.

3.3.2. Rainfed systems

Low N_2O emission levels in Mediterranean rainfed cropping systems are conditioned by the typical agro-climatic features of these systems. During the winter season, N_2O production is usually limited by temperature but also by other factors such as low levels of WFPS (Barton et al., 2008, 2010), soil organic matter (Sánchez-Martín et al., 2008a) or mineral N (Lee et al., 2009). A strong coupling between N mineralization and immobilization has been reported at low soil temperatures (Barton et al., 2010). Moreover, the N fertilization rate in rainfed systems under these climatic conditions is generally low (Kroeze and Seitzinger, 1998; Ryan et al., 2009) due to crop growth limitations driven by climate. This practice could also contribute to low N_2O emissions.

In late spring, during maturation of winter crops, high temperatures favor microbial processes, but N_2O production may be limited by low NH_4^+ content and low WFPS (Meijide et al., 2009).

During summer, dry soil conditions usually prevent N_2O emissions, except when significant rainfall occurs (Barton et al., 2008, 2010, 2011). Rainfall events after the summer are usually related to significant N_2O pulses due to N mineralization and the subsequent accumulation of mineral N in the soil during this period (Meijide et al., 2009). This seasonal pattern of soil N dynamics also occurs in Mediterranean natural ecosystems (Ochoa-Hueso et al., 2011).

In Mediterranean rainfed systems, and especially in those cultivated in well-aerated soils, low rainfall leads to low WFPS and therefore to a high redox potential which is unsuitable for denitrification (Lugato et al., 2010). According to most of the studies reviewed, this makes nitrification the most usual pathway for N_2O production in low organic matter, non-irrigated Mediterranean soils (Barton et al., 2008, 2011; Lugato et al., 2010; Meijide et al., 2009; Menéndez et al., 2008). This hypothesis is also supported by the positive relationship between N_2O fluxes and soil NH_4^+ levels (Meijide et al., 2009). N_2O pulses due to nitrification are relatively small (Sánchez-Martín et al., 2010a), which is in line with the typically low cumulative N_2O fluxes found in Mediterranean rainfed systems.

N_2O emissions due to denitrification can be common in rainfed systems after heavy rainfalls or when the rainy season is especially wet (Meijide et al., 2009; Sánchez-Martín et al., 2010b). Complete anoxia promoting the reduction of N_2O to N_2 is unlikely or very transient in Mediterranean rainfed systems. Therefore, wetter-than-average cropping years usually lead to higher N_2O emissions than drier ones (Sánchez-Martín et al., 2010b), which may also happen under temperate climatic conditions (Laville et al., 2011).

Kool et al. (2011) showed that the nitrifier denitrification pathway for N_2O production could be responsible for a significant fraction of N_2O emissions in agricultural soils, especially

under moisture conditions that are sub-optimal for denitrification. Following this logic, this pathway could be important in N_2O production under Mediterranean conditions (Mondini et al., 2007; Sánchez-Martín et al., 2008a), particularly in rainfed and drip-irrigated systems, where the moisture content required for denitrification is not often reached. For example, Sánchez-Martín et al. (2008a) hypothesized that most N_2O was produced by nitrifier denitrification in a Mediterranean soil incubated under laboratory conditions at 40% WFPS and identified it as a significant source at 90% WFPS. Nitrifier denitrification has also been proposed as a possible pathway for N_2O uptake when conditions are not suitable for anaerobic denitrification (Chapuis-Lardy et al., 2007; Meijide et al., 2009). If nitrifier denitrification plays an important role in N_2O production and consumption in Mediterranean soils, this would imply that a significant fraction of N_2O emissions currently attributed to denitrification or nitrification could actually be driven by this biochemical pathway. Such uncertainty points to the need for more research in order to accurately understand the biochemical processes underlying N_2O emissions in Mediterranean agroecosystems.

3.3.3. Irrigated systems

Irrigation is associated to the intensification in N inputs, and in Mediterranean cropping systems it usually takes place in late spring and summer, when temperatures are highest. Therefore, the most relevant physical properties of the soil (temperature and water and N availability) are optimal for N_2O production during the cropping season. During the winter fallow period, the conditions are similar to those described for rainfed systems, though more residual N can be available in the soil due to the higher application rates of N fertilizers. In summer-irrigated Mediterranean systems, it is therefore usual for significant N_2O fluxes to occur throughout the annual cycle.

In the case of high-water irrigation techniques, such as furrow irrigation, near-saturation conditions are transiently reached for one or more days after irrigation. These conditions usually lead to a very high initial N_2O pulse after the first irrigation event (López-Fernández et al., 2007; Sánchez-Martín et al., 2008b, 2010a; Vallejo et al., 2005). This can then be followed by two or more large pulses in the course of the irrigation period (Kallenbach et al., 2010; Vallejo et al., 2006). Denitrification is usually the prevailing N_2O production pathway under this type of irrigation (Sánchez-Martín et al., 2008b); this is usually a minor pathway before the onset of irrigation and then becomes the main source during the irrigation period (López-Fernández et al., 2007; Vallejo et al., 2005), accounting for up to 99% of N_2O fluxes (Sánchez-Martín et al., 2010a). Nitrification is likely to occur in these systems when a high concentration of NH_4^+ is reached in the soil; this is sometimes the case when synthetic or liquid organic fertilizers are applied (Meijide et al., 2007; Sánchez-Martín et al., 2010b,c; Vallejo et al., 2006), providing aerobic conditions are met, which can be the case in high-water irrigated systems, where WFPS fluctuations are very large.

N_2O fluxes are generally lower in drip-irrigated soils than in those receiving high-water applications, and the emission patterns also differ. Drip irrigation promotes a small but steady flux of N_2O throughout the cropping season (Kallenbach et al., 2010), which could be accompanied by small N_2O pulses after each irrigation event (Sánchez-Martín et al., 2008b, 2010a) instead of one or various large pulses of the sort typically associated with furrow irrigation systems. As in rainfed systems, low-water availability in drip-irrigated soils results in nitrification becoming the most important source of N_2O (Kallenbach et al., 2010). This assumption is supported by papers that report a lack of relationship between N_2O fluxes and NO_3^- concentrations (Garland et al., 2011; Steenwerth and Belina, 2008) and large increases in the size of the

soil NO_3^- pool after the NH_4^+ peak (Sánchez-Martín et al., 2008b). Indeed, N_2O production by denitrification is prevented by low-water availability, as the soil rarely exceeds 60% WFPS, either with subsurface (Kallenbach et al., 2010) or surface (Sánchez-Martín et al., 2008b, 2010a) drip irrigation techniques. However, according to the latter works, the spatial distribution of soil humidity, and subsequently of N_2O fluxes, stress the need for a stratified sampling of N_2O fluxes and soil parameters. For example, wet areas near drippers may lead to a N_2O source, but a WFPS of >80% can be locally reached in dripping points, which may promote denitrification to N_2 .

4. Indirect sources of N_2O emissions

4.1. Upstream emissions

Emissions during the production, manufacturing and transport of fertilizers play a key role in total fertilizer emissions. It is not reasonable to consider these processes from a specifically Mediterranean perspective given the wide range of conditions under which fertilizers are produced in these areas. Nonetheless, there are general differences in the emission of GHG during the production of synthetic and organic fertilizers that are worth noting.

4.1.1. Synthetic fertilizers

The production of synthetic fertilizers requires a high consumption of fossil energy to reduce N_2 to NH_3 . According to the IPCC (2006b), average CO_2 emissions due to NH_3 production in European plants range between 2.55 and 3.57 kg CO_2 per kg of fixed N, depending on the technology employed. In comparison, N_2O emissions from the soil calculated using IPCC EF are equivalent to 4.68 kg CO_2 per kg of applied N. In Mediterranean rainfed and drip-irrigated cropping systems, where N_2O EF is lower than the IPCC default EF, these pre-farm GHG emissions related to fertilizer production may actually be much greater than the on-farm N_2O emissions. For example, Biswas et al. (2008) performed a life cycle assessment (LCA) of rainfed wheat production in the Mediterranean climate region of Western Australia. They estimated that to produce one ton of wheat, 103.87 kg CO_2 -eq was emitted as a result of urea production, whereas N_2O emissions from the field represented 26.98 or 175 kg CO_2 -eq, according to whether region-specific (Barton et al., 2008) or IPCC (2006b) N_2O EF was employed.

4.1.2. Organic fertilizers

The use of organic materials as fertilizers requires the management of organic wastes. When the residual organic matter is not produced in the field, it needs to be handled, stored, transported, and sometimes transformed into more stable and easier to handle compounds. This management process is associated with GHG emissions. In the EU-27, N_2O emissions during the housing and storage of animal manure are estimated to be only slightly lower than those associated with their land application (Oenema et al., 2009). GHG emissions related to the production of organic fertilizers from organic waste should be accounted for by comparison with the emissions associated with conventional residue management (e.g., Kim and Kim, 2010; Prapasongsa et al., 2010). A careful and site-specific assessment of GHG emissions is required during waste management in order to quantify upstream GHG emissions by organic fertilizers.

Legumes are virtually the only organic source of newly fixed N. N_2O emissions during N fixation by legumes are generally taken to be zero or negligible (IPCC, 2006a) and this has been verified under Mediterranean conditions (Barton et al., 2011). Nonetheless, N_2O emissions that occur during legume crop growth and indirect GHG emissions related to their cultivation should be taken into account in full GHG comparisons when legumes are used as green

manure. Furthermore, land occupation associated with biological N fixation calls into question the possibility of a considerable substitution of Haber-Bosch-produced N. Indeed, some authors have shown that the internalization of energy and nutrient fluxes in sustainable agriculture may also have a “land cost” that is externalized in fossil fuel-based systems (Guzmán Casado and González de Molina, 2009). Even so, there is still great potential for reducing the N surplus and increasing N fixation in Mediterranean agroecosystems without needing to occupy any extra land (Section 5), even if the extent to which sources of organic N can replace synthetic ones still remains unclear.

4.1.3. Transport

The use of organic fertilizers (i.e. slurries, manures) requires large amounts of energy due to their weight. However, their production sources tend to be more local to the end user than synthetic fertilizers, which are generally produced in a few large manufacturing plants. Even without taking into account transport costs for synthetic fertilizers, Wiens et al. (2008) estimated that the distance that liquid pig manure was transported could be increased to 8.4 and 12.3 km, respectively, before the energy cost per kg of available N associated with this manure was equivalent to that of anhydrous ammonia or urea N. Nearby land could therefore receive the resulting manure at an appropriate rate and without high transport costs, as long as the concentration of livestock is not very high (Section 5.3).

4.2. Downstream emissions

NO_3^- leaching and NH_3 and oxidized N compounds (NO_x) volatilization are considered the main processes responsible for fertilizer-associated N_2O emissions outside the cropping system and are the only ones classified as “indirect fertilizer N_2O emissions” in the IPCC guidelines for GHG inventories (IPCC, 2006a). Downstream indirect emissions were estimated to represent about 13–17% of direct emissions in one temperate river basin (Garnier et al., 2009).

4.2.1. NO_3^- leaching

This is a source of major concern in many areas in Mediterranean countries, such as Spain (Lassaletta et al., 2009, 2010; Peña-Haro et al., 2010), because of its eutrophication potential and the negative impact on drinking water from surface or ground waters. In Mediterranean cropping systems, NO_3^- leaching can occur either in irrigated fields (Allaire-Leung et al., 2001) or be related to rainfall events during the rainy season (Angás et al., 2006), and it can be responsible for the loss of up to 25% of applied synthetic N in a normal winter fallow period (Sánchez-Martín et al., 2010b).

Very large N surpluses can occur from organically fertilized soils, resulting in NO_3^- leaching and related aquifer pollution. For example, the application of high rates of slurries has caused high N losses, in the form of NO_3^- , in intensive livestock production areas in NE Spain (Peñuelas et al., 2009). Even so, when organic and synthetic fertilizers are compared at similar N application rates, NO_3^- leaching is generally significantly lower with organic fertilizers (Antoniadis et al., 2010; Díez et al., 1997, 2000; Celik, 2009; Sánchez-Martín et al., 2010a). Some authors have even found N leaching to be lower in soils fertilized with compost than in unfertilized plots (Tejada and Gonzalez, 2006). In general, low (Sánchez-Martín et al., 2010a) or null (Díez et al., 2004) NO_3^- leaching reductions are associated with liquid, highly mineralized organic fertilizers, such as pig slurries. On the other hand, other approaches to nutrient management based on organic matter cycling, such as cover cropping, have also proved capable of strongly reducing NO_3^- leaching in Mediterranean environments

(Salmerón et al., 2010; Steenwerth and Belina, 2008; Wyland et al., 1996).

The lower N leaching associated with organic amendments could be driven by a decrease in soluble N in the soil due to the increased performance and efficiency of denitrifiers (Kramer et al., 2006; Steenwerth and Belina, 2010), the immobilization of NO_3^- by a larger microbial biomass (Burger and Jackson, 2003), or the capture of N in the SOM which is built up by the addition of organic matter. For example, Kong et al. (2007) reported that an additional 590 kg N ha^{-1} had been stored in the soil after 11 years of organic management, along with the sequestration of 5.7 Mg C. Applying organic matter to the soil could also reduce the subsoil NO_3^- pool by enhancing the activity of denitrifying microorganisms in the subsoil or groundwater (Sánchez-Martín et al., 2010a), as organic C is the main limiting factor for denitrification in the subsoil (Haag and Kaupenjohann, 2001). In an experiment performed under Mediterranean conditions, DOC leaching of 2.3–4.8 kg C ha^{-1} helped to complete the reduction of 2.1–4.5 kg NO_3^- -N ha^{-1} to N_2 (Sánchez-Martín et al., 2010a), implying capacities for subsoil NO_3^- removal of 100%, 13.2%, 10.4% and 6.7% for organic manure, control, digested pig slurry and urea treatments, respectively. These results should, however, be interpreted with care since incomplete subsoil denitrification could also release N_2O , which could be transported by drainage water due to its high solubility (Van Cleemput, 1998).

4.2.2. NH_3 volatilization

We did not find any field studies that compared NH_3 volatilization after organic and synthetic fertilization under Mediterranean climatic conditions, although some separate data are available. Various different synthetic fertilizers applied to wheat under simulated Mediterranean conditions were reported to have released 12–38% of their N (mostly as NH_3) (Buresh et al., 1990), whereas at arid and semi-arid sites in Syria, slightly lower gaseous N losses, of 11–18% (again mostly as NH_3), were recorded after urea application (Abdel Monem et al., 2010). The only micrometeorological studies conducted that specifically measured NH_3 losses reported: (i) 10.1% NH_3 -N losses from urea (Sanz-Cobena et al., 2008); (ii) 5% losses after green manuring (Rana and Mastroianni, 1998) and (iii) 20% of the Total Ammonium Nitrogen applied with a pig slurry spread at the soil surface (Sanz et al., 2010). The first two values, for synthetic and organic fertilization, are below the 20% default EF value established by the CORINAIR Emission Inventory Guidebook for regions with spring temperatures $>13.8^\circ\text{C}$ (CORINAIR, 2006). Contrastingly, measured NH_3 losses, from synthetic and liquid organic manures, will be in accordance with the values proposed by the IPCC (10% and 20% for synthetic and organic fertilizers, respectively). Existing discrepancies could be associated with local climatic, soil and management conditions, e.g. dry conditions during the experimental period, the presence of vermiculites as the main clay mineral, and the application of 10 mm of irrigation immediately after fertilizing, all possibly favor large decreases in the availability of exchangeable NH_4^+ , which can be potentially lost as NH_3 (Sanz-Cobena et al., 2008).

4.2.3. N_2O emissions

There is very little information about which fraction of the N lost from the cropping system in the form of NO_3^- , NH_4^+ or NH_3 is finally transformed into N_2O in Mediterranean environments. The available data suggest that this fraction could be very significant but variable. Measurements performed in the Douro Estuary in Portugal (Teixeira et al., 2010) revealed that 0.5–47% of the N gases produced were in the form of N_2O , and that emissions were correlated with sediment organic matter. On the plain of the River Po, in Northern Italy, springs were found to be supersaturated with N_2O and were subject to a significant degassing process. As a result this area had a very high potential as a source of N_2O and other GHG

gases (Laini et al., 2011). In one stream in the Doñana National Park, SW Spain, NO_3^- pollution which originated in nearby agricultural fields, mostly from synthetic N sources, was associated with N_2O production, but also with that of CH_4 and CO_2 (Tortosa et al., 2011).

5. Mitigation options with organic fertilizers

5.1. Water-saving agricultural systems

The significant reduction in N_2O fluxes in rain-fed and drip-irrigated systems as opposed to conventionally irrigated systems (Sections 3.2.1 and 3.3) implies a high potential to mitigate N_2O emissions through the optimization of water use. However, the reduction in N_2O fluxes achieved by applying drip irrigation may only occur when a source of organic matter is applied (Kallenbach et al., 2010). Drip-irrigated systems foster water and N_2O emission savings while maintaining yields (Tognetti et al., 2003; Kallenbach et al., 2010), whereas in rainfed systems, yield-scaled emissions may be affected by a lower productivity (Section 6.3). However, a full GHG accounting should also consider the higher fossil energy consumption in irrigated systems (Alonso and Guzmán, 2010).

5.2. Minimization of bare soil

Bare fallows in herbaceous crop rotations and bare soils in woody perennial systems are usually maintained in Mediterranean environments in order to increase water and nutrient availability for commercial crops. This assumption has been challenged by research data, which show that bare fallows may not contribute to overall productivity as much as legume cover crops (López-Bellido et al., 2000; Martín-Rueda et al., 2007), as has also been reported in other dry environments (Rinnofner et al., 2008). Bare fallows and other bare soils may therefore represent stages, or areas, of the cropping systems capable of releasing large quantities of reactive N compounds (which are responsible for both direct and indirect N_2O emissions) without contributing to overall productivity.

Fallow and bare soil emissions can be avoided by system intensification, in which cash crops substitute bare fallows, and also through the cultivation of cover crops, either in crop rotations or in perennial systems. Cover crops have a large potential for increasing N retention in cropping systems and thereby reducing indirect N_2O emissions, mainly through (i) N immobilization by catch crops (e.g., McSwiney et al., 2010; Gabriel and Quemada, 2011), (ii) biological N fixation with legume green manures (e.g. Rinnofner et al., 2008) and (iii) soil protection against erosion (Boellstorff and Benito, 2005; Gómez et al., 2009). Their effect on direct N_2O emissions may vary according to the specific case. Legume cropping in the Mediterranean semi-arid environment of Western Australia yielded similar emission rates as bare soils (Barton et al., 2011). In California, Kallenbach et al. (2010) recorded higher N_2O emissions from a legume cover cropped treatment than from bare soil. These authors suggested that non-legume cover crops could help to reduce N_2O emissions due to their higher C:N ratio and deeper roots, which could extract soil N more efficiently. However, in order to maintain the benefits of biological N fixation, we would propose trials with mixtures of legumes and non-legumes and also their combination with low-quality organic residues (Section 5.4).

5.3. Improved waste management

The high population densities in most Mediterranean areas suggest that urban wastes could represent a significant source of organic matter for agricultural fields. Municipal solid waste and sewage sludge, especially if composted, usually show good agronomic performance, and they also promote an increase in soil organic carbon (Diacono and Montemurro, 2010). As we have

already seen in this review, the use of these materials as fertilizers can also help to reduce direct and indirect N_2O emissions. In spite of these advantages, heavy metals and other toxic compounds may call into question their safe application to soils, which points to the need to appropriately separate urban organic wastes at source.

In the case of livestock farming, the continued specialization of livestock production units leads to increasing problems with the safe recycling of manure nutrients (Petersen et al., 2007), and encourages their application to nearby soils in high doses, which boosts N losses, and particularly N_2O ones. In some parts of Israel, for example, organic manures are applied at rates of over 1000 kg N ha^{-1} , which increases emissions to 34.4 kg $\text{N}_2\text{O-N ha}^{-1}$ (Heller et al., 2010). The minimization of N surpluses that cause both pollution and dependence can be achieved by the circulation of materials between livestock and cropping systems, as demonstrated in other regions (Nekomoto et al., 2006). Biogas production is another integrated approach to waste management that can help to reduce GHG emissions.

5.4. Tightening the N cycle through N immobilization

Typical woody crops cultivated under Mediterranean climatic conditions include vines, olives, almonds, walnuts, citrus and other fruit trees. They occupy large areas and produce high quantities of pruning residues, which are normally burned in the field, resulting in emissions of trace GHG and also stored C. Proposals have recently been made for their use as energy sources (e.g. Di Giacomo and Taglieri, 2009; Kroodsma and Field, 2006). An alternative, or complementary option, is to incorporate these residues into the soil; this could greatly enhance soil carbon storage and biodiversity (Holtz and Caesar-Ton That, 2004) and would also protect the soil against erosion (Rodríguez-Lizana et al., 2008), while fostering a reduction in N losses. Indeed, N retention through N immobilization during fallow periods cannot only be achieved with catch crops (Section 5.2), but also through the addition of low-quality organic residues (Muhammad et al., 2011; Sakala et al., 2000). To be more specific, lignin and polyphenol rich materials, such as pruning residues, have been associated with reductions in N_2O fluxes over a broad range of conditions due to their strong N immobilization effect (Frimpong and Baggs, 2010; García et al., 1997; Gomes et al., 2009). In a laboratory experiment, García-Ruiz and Baggs (2007) demonstrated that N fertilizer application did not increase N_2O emissions if the soil had been mixed with olive leaves; this was related to the high lignin (11%) and polyphenol (2%) contents of olive residues.

The major concern here, is that N immobilization may negatively affect crop production (Frimpong and Baggs, 2010; Soumare et al., 2002), especially during the first months after application (Soumare et al., 2002). Potential reductions in crop productivity due to N immobilization could, however, be remedied by appropriately combining and timing the application of N sources with different mineralization kinetics. In this sense, mineralization kinetic parameters could be used to evaluate the most suitable N release pattern for organic fertilizers (Marinari et al., 2010). Successful examples of soil protecting practices in three different Mediterranean orchards, including the addition of pruning residues, led to a significant increase in fruit yield compared with conventional management strategies (Montanaro et al., 2009; Sofó et al., 2010).

6. Information gaps

We found a number of knowledge gaps that we would recommend addressing in future field research.

6.1. Length of the experiment

The studies included in this review were carried out on average for 243 days. The average experiment length was consistently higher in rainfed systems than in irrigated ones, where cropping period is usually shorter. Measurement periods of less than 1 year do not account for total annual emissions, e.g. those of the residual effects of fertilizers, which could lead to a possible underestimation of EF. An estimation of yearly cumulative emissions and EF based on simple modeling of measured emission levels resulted in a great increase in emissions in irrigated groups (Tables 2 and 3). This procedure, however, could overestimate yearly emissions because N_2O flux is usually highest during cropping period, when fertilizers and water are applied.

Significant emissions during the post-harvest fallow period have been recorded in Mediterranean cropping systems. In the summer fallow period of rainfed systems, emissions are relatively low, most of the time, due to the dry soil conditions (Steenwerth and Belina, 2008), and isolated summer rainfall only stimulates N_2O emissions very transiently due to rapid soil desiccation (Sánchez-Martín et al., 2010a). Large or multiple rainfall events during summer can, however, increase summer fallow emissions to 55% of yearly emissions (Barton et al., 2008, 2010, 2011). Significant quantities of N_2O may also be lost during the winter fallow periods of summer-cropped, irrigated fields (Burger et al., 2005; Kallenbach et al., 2010; Lee et al., 2009; Sánchez-Martín et al., 2010a).

As previously mentioned, there is particular concern about the residual effect of organic fertilizers, given their typically slow and extended N release, which can prolong their N_2O emission period (Jones et al., 2007) and would justify the use of “available N” rather than “total N” when calculating their EF (e.g., Vallejo et al., 2006, see Section 2 of this paper). For example, Meijide et al. (2009) found various N_2O emission peaks during the post-harvest period in organic-fertilized soils as opposed to only one peak in the control and synthetic treatments. Conversely, releasing labile C compounds during the mineralization of organic fertilizers in soils poor in organic matter could help to prevent N_2O emissions (Sánchez-Martín et al., 2010a). These findings challenge the assumption that N_2O fluxes would tend to be extended by the residual effect of organic fertilizers and underline the need for longer sampling periods and more long-term studies.

Moving beyond short term residual effect, Li et al. (2005) argued that techniques that promote C sequestration could enhance N_2O emissions in the long term due to the increase in soil organic carbon (SOC). Under Mediterranean conditions, long-term experiments comparing organic and synthetic fertilization have only been performed at one site: Russell Ranch in Davis, California (Burger et al., 2005; Kong et al., 2007, 2009). None of these studies reported increases in N_2O emissions, despite the fact that SOC pool increased significantly after up to 11 years of organic management. We therefore hypothesize that under Mediterranean conditions there may be a SOC content threshold above which fertilizer-related N_2O emissions would start to increase. In spite of this, at relatively low SOC levels around 1%, such as those studied by Kong et al. (2007, 2009), organic fertilizers would help to reduce N_2O fluxes.

6.2. Background emissions

Unfertilized control treatment N_2O emissions on average represented 63.5% of fertilized treatment emissions in the reviewed studies. This implies that a very large fraction of soil N_2O emissions cannot be explained by the fertilizer EF approach. The pulsing effect probably contributes to these high background emissions. Changes in management practices, such as irrigation methods, may also induce distinct changes in emissions from control and fertilized treatments, which would also affect N_2O EF. For example,

Sánchez-Martín et al. (2010b) reported a sharp reduction in N_2O emissions with drip irrigation, as opposed to furrow irrigation. The reduction was, however, much greater in the control treatment; it produced greater EF values for drip-irrigated treatments, while cumulative emissions were actually lower than for furrow-irrigated treatments.

These data suggest that background emissions are influenced by management and consequently require specific accounting, as they are susceptible to improvement. The calculation of EF, by dividing cumulative N_2O emissions by the applied N rate, without subtracting unfertilized control emissions (e.g. Dobbie and Smith, 2003), is an approach that includes background emissions in estimations based on applied fertilizer. This method would be less useful, however, if these background emissions were affected by other management operations. We therefore recommend complementing EF data with cumulative emission data for every treatment, including unfertilized controls, when presenting research results.

6.3. N_2O EF and yield-scaled EF

EF was only provided in 52% of the reviewed studies that measured field N_2O emissions. In the other cases, it was not possible to calculate EF because unfertilized treatments were absent. Despite its limitations, EF provides a useful simplified tool for upscaling the emissions of a given region based on fertilization rates, provided that background emissions are also accounted for. Although N_2O emissions vary greatly, the EF approach is fairly well supported by field data (Stehfest and Bouwman, 2006; Petersen et al., 2006). However, the results analyzed in this review suggest that it needs region-specific modulations for such factors as fertilizer type and irrigation type.

Yield-scaled EF is also a very informative parameter for understanding site-specific trade-offs between fertilization type, N_2O fluxes and yield performance. Full GHG accounting methodologies such as LCA could greatly benefit from this information, as they are usually product based. When applied to a single type of fertilizer, yield-scaled EF usually reveals that N_2O emissions are smaller at intermediate N application rates (Hoben et al., 2011; Van Groenigen et al., 2010). When comparing management schemes, yield-scaled EF shows that environmental benefits may disappear if they are associated to lower yields (De Backer et al., 2009). In the Mediterranean context, Meijide et al. (2009) found that the performance of organic and synthetic fertilizers slightly differed according to whether they were evaluated on an applied N basis or on a yield basis. The authors also warned about the annual variability of crop yield, which should be taken into account when applying yield-scaled index.

Other studies comparing yields associated with organic and synthetic fertilization in Mediterranean cropping systems have obtained heterogeneous results, although most of the authors consulted reported similar yields for the two types of fertilization (Altieri and Esposito, 2008; Bilalis et al., 2010a,b; Caporali and Onnis, 1992; Clark et al., 1999; Díez et al., 1997, 2000; Deria et al., 2003; Drinkwater et al., 1995; Efthimiadou et al., 2009; Herencia et al., 2007; Lithourgidis et al., 2007; Madejón et al., 2001; Meijide et al., 2007; Montanaro et al., 2009; Montemurro et al., 2005, 2008; Montemurro, 2010; Morra et al., 2010; Pardo et al., 2009; Vallejo et al., 2006). Higher yields for organic fertilization have also been reported (Campiglia et al., 2011; Curuk et al., 2004; Deria et al., 2003; Karamanos et al., 2004; Madejón et al., 2001; Melero et al., 2006; Montemurro et al., 2008; Sofu et al., 2010), while other authors discovered yield reductions related to organic as opposed synthetic fertilizers (Annicchiarico et al., 2010; Denison et al., 2004; Deria et al., 2003; García-Martín et al., 2007; Kavargiris et al., 2009; Montemurro et al., 2006, 2007; Montemurro, 2009, 2010;

Morra et al., 2010). The disparity in the relative yield performance of organic and synthetic fertilization is understandable given the variety of types of organic fertilizers, management techniques and agro-climatic conditions. This complexity further emphasizes the need for yield data in specific N₂O emission studies.

6.4. Cropping systems that require more research

Different crop types have been unevenly studied. Maize, open-air horticultural crops and winter cereals have been studied under a fairly wide range of conditions and we now have a rough picture of the behavior of N₂O emissions in these systems, but information about other very important Mediterranean crop types is almost nonexistent. Despite the importance of many of the woody perennial crops grown in this biome, vines are the only crop in this category for which N₂O emissions have been measured. Greenhouse horticulture must also be studied, as its particular environmental conditions, including high humidity and temperature throughout the year, would probably affect the pattern of N₂O emissions.

Organic management systems also require specific research, as they not only exclude synthetic fertilization, but also the use of other synthetic compounds which may either increase or reduce N₂O emissions (Kinney et al., 2005; Spokas et al., 2006). Organic farming is a very important management option in Mediterranean areas. For example, the two European countries with the largest surface areas under organic farming are Spain and Italy (Willer and Kilcher, 2011), whereas California is the state with the largest organic acreage in the USA (USDA, 2011). Lower N₂O fluxes have been reported for organic fields under Mediterranean conditions (Burger et al., 2005; Kong et al., 2007, 2009; Petersen et al., 2006), but the available data is very limited and yield-scaled performance may be reduced by lower yields (Kong et al., 2009).

6.5. Full accounting of GHG emissions

Management recommendations based only on direct emissions may not meet abatement objectives if they are based on techniques that increase emissions at any other point in the life cycle of the fertilizers in question. There is a distinct absence of comparisons of full upstream GHG emissions between synthetic and organic fertilizers for Mediterranean cropping systems. Research into downstream emissions has mainly focused on NO₃⁻ leaching, as NH₃ volatilization has hardly been studied at all. Furthermore, there is very little data on which fraction of this N finally forms N₂O, although the available evidence suggests that it may be very significant (Section 4.2). The simultaneous estimation of the emissions of all of the GHG involved in the GWP of cropping systems can be facilitated by modeling approaches. For example, the DAYCENT model has been shown to be capable of accurately predicting soil GHG emissions for a series of Mediterranean cropping systems (De Gryze et al., 2010), and DNDC is another interesting option (Lugato et al., 2010). At the farm or final product level, LCA methodologies should be adjusted to Mediterranean environments using a specific EF (Biswas et al., 2008, 2011).

7. Concluding remarks

The data reviewed suggest that organic fertilizers and water-saving techniques could reduce agricultural N₂O emissions under Mediterranean climatic conditions. However, the number of experimental sites at which emissions from organic and synthetic fertilizers have been compared is very limited. In the first part of our analysis, which included the majority of the published data, cumulative N₂O emissions were lower for solid organic fertilizers than for synthetic and liquid organic fertilizers. In a more detailed approach,

a meta-analysis of compliant studies revealed that direct N₂O emissions after the application of organic fertilizers were lower than emissions after the addition of synthetic fertilizers (an average 23% was observed for cumulative emissions and EF). When organic fertilizers were segregated in solid and liquid materials, only solid fertilizer emissions were significantly lower than synthetic. When total N instead of available N was used for EF calculations, solid organic fertilizers achieved a 67% reduction in EF compared to synthetic fertilizers. A slower mineral N release from organic fertilizers could prevent high soil N levels prone to N₂O losses. Moreover, the differences observed seem to be related to the semi-arid features that are very common in Mediterranean soils, where C and N contents are usually low.

High-water irrigated systems showed the largest losses of fertilizer N as N₂O, whereas these losses were reduced under water-saving irrigation techniques (i.e. surface or subsurface drip irrigation), and were minimal in rainfed systems, in which the N₂O emission response to N fertilizers was reduced by one order of magnitude compared to conventional irrigation and Tier 1 IPCC EF.

Indirect N₂O emissions have not been fully accounted for, but sectorial information suggests a large reduction in N₂O emissions for organic fertilizers. Upstream of the cropping system, substantial reductions in fossil energy and N₂O emissions can be achieved, given that organic fertilizers usually employ waste materials that have not been produced specifically for this purpose. Downstream of the cropping system, Mediterranean data suggest that indirect N₂O emission savings could be achieved by using organic fertilizers on account of their reduced NO₃⁻ exports.

Options to enhance N₂O mitigation by organic fertilizers include: (i) water management strategies, comprising drip irrigation and rainfed systems; (ii) the minimization of fallow and bare soil emissions through the intensification of crop rotation and the use of cover crops; (iii) improved waste management to reduce indirect emissions, including waste separation at origin, decentralized livestock farming and biogas production; (iv) tightening the N cycle through N immobilization with woody residues in order to minimize emissions during fallow and low crop demand periods.

Identified limitations to the mitigation of N₂O emissions by organic fertilizers include: (i) the residual effect as organic fertilizers could prolong the N₂O emission period due to slower N release; (ii) the long-term addition of organic fertilizers to soil could enhance N₂O emissions through an increase in SOM content; (iii) yield-scaled performance, since organic fertilization could be linked to lower yields, although yield reduction is not the most common response to the substitution of synthetic N sources by organic ones in Mediterranean systems; (iv) the availability of total N from organic sources may be constrained by the land cost of legume cultivation. This land cost would be minimized if N fixing crops were cultivated during inter-cropping periods and N losses were reduced, but the extent to which organic fertilizers can replace synthetic ones is so far unknown.

We found a number of knowledge gaps that should be addressed by future field research: (i) experiment length is usually <12 months, which can lead to the underestimation of N₂O EF due to failure to account for the residual and long-term effects of fertilizers; (ii) background N₂O emissions sometimes represent a large percentage of fertilized treatment emissions; (iii) N₂O EF and yield-scaled EF were not always provided in the studies reviewed; (iv) some types of cropping system need to be studied in greater depth, including rainfed, drip-irrigated, woody perennial, greenhouse horticulture and organic farming; (v) more full cropping system GWP estimations are needed, including indirect emissions and other GHG.

Overall, this review has demonstrated that there is still potential to mitigate N₂O emissions in Mediterranean agriculture through the use of both organic fertilizers and low-water management

systems. In the first case, the potential lies in comparatively lower N₂O fluxes of organic fertilizers with respect to the use of synthetic fertilizers and in the reduction of indirect emissions both upstream and downstream of the cropping system. In the second, the restriction of water availability that occurs in rainfed and drip-irrigated cropping systems has been shown to effectively reduce N₂O emissions by limiting the microbial processes responsible for N₂O production. Further research is needed to bridge the knowledge gaps in current information and to develop strategies that can fully exploit this N₂O reduction potential without burdening environmental and yield performance.

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