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Direct nitrous oxide emissions in Mediterranean climate cropping systems: Emission factors based on a meta-analysis of available measurement data

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Highlights

A meta-analysis of $N_{\rm 2}O$ EFs in Mediterranean cropping systems was conducted.

Mediterranean EFs (average of 0.5%) were lower than the IPCC default value (1%).

Annual rainfall, water management and crop type highly affected EFs.

Drip irrigation (EF = 0.51%) is a promising measure to mitigate N₂O emissions.

The use of new EFs would reduce the estimation of Spanish N_2O emissions 2-fold.

Abstract

Many recent reviews and meta-analyses of N₂O emissions do not include data from Mediterranean studies. In this paper we present a meta-analysis of the N₂O emissions from Mediterranean cropping systems, and propose a more robust and reliable regional emission factor (EF) for N₂O, distinguishing the effects of water management, crop type, and fertilizer management. The average overall EF for Mediterranean agriculture (EF_{Med}) was 0.5%, which is substantially lower than the IPCC default value of 1%. Soil properties had no significant effect on EFs for N₂O. Increasing the N fertilizer rate led to higher EFs; when N was applied at rates greater than 400 kg N ha⁻¹, the EF did not significantly differ from the 1% default value (EF: 0.82%). Liquid slurries led to emissions that did not significantly differ from 1%; the other fertilizer types were lower but did not significantly differ from each other. Rain-fed crops in Mediterranean regions have lower EFs (EF: 0.27%) than irrigated crops (EF: 0.63%). Drip irrigation systems (EF: 0.51%) had 44% lower EF than sprinkler irrigation methods (EF: 0.91%). Extensive crops, such as winter cereals (wheat, oat and barley), had lower EFs (EF: 0.26%) than intensive crops such as maize (EF: 0.83%). For flooded rice, anaerobic conditions likely led to complete denitrification and low EFs (EF: 0.19%). Our results indicate that N₂O emissions from Mediterranean agriculture are overestimated in current national greenhouse gas inventories and that, with the new EF determined from this study, the effect of mitigation strategies such as drip irrigation or the use of nitrification inhibitors, even if highly significant, may be smaller in absolute terms.

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Keywords N₂O Greenhouse gases Field studies Mitigation Systematic review

1. Introduction

More than half of the global Mediterranean climate zone is located on the Mediterranean Sea Basin (Aschmann, 1973); the remainder is on the Pacific coast of North America, south-western Australia, the Cape region of South Africa and the central coast of Chile (Olson et al., 2001). One of the most distinctive features of Mediterranean climates is the summer drought and relatively mild temperatures in winter. However, annual precipitation is variable, between 275 and 1000 mm, such that Mediterranean climate regions range from semi-arid to humid.

In Mediterranean climates, precipitation and temperatures are suitable in winter for cultivating a variety of rain-fed crops including cereals, grain legumes, oilseeds and horticulture (Andrews et al., 2002). Cultivation of perennial crops is common in Mediterranean climate areas. Some of these crops are resistant to summer droughts, including olives, almonds, and grapes, while others are cultivated under irrigation, such as citrus and other fruit trees. Agriculture in Mediterranean climates regions, therefore, provides a high diversity of crops.

Agricultural soils are regarded as the primary source of anthropogenic N₂O emissions (Smith et al., 2008). Despite the cultural and economic importance of Mediterranean agriculture (Grigg, 1974), the number of field studies analyzing N₂O emissions from Mediterranean agricultural lands is much smaller than from other temperate areas (Stehfest and Bouwman, 2006). Recent reviews and meta-analyses of N₂O emissions do not include data from Mediterranean studies (e.g. Kim et al., 2013, Lesschen et al., 2011, Shcherbak et al., 2014). Estimating N₂O emissions and N₂O emission factors (EF, the percentage of fertilizer N applied that is transformed and emitted on site as N₂O) is essential for assessing the impact of agriculture on greenhouse gas (GHG) emissions for a particular area. Current national emission inventory methods use a direct EF for N₂O, with a default value of 1% or 1.25% (depending on the country) of the N input from manure and mineral fertilizer (IPCC, 2006). However, many studies have concluded that the response of direct N₂O emissions to N input is non-linear (Kim et al., 2013, Philibert et al., 2012, Shcherbak et al., 2014), and other recent studies highlighted the important role of environmental and management factors in determining N₂O emissions and EFs, such as climate, soil characteristics, type of fertilizer and time of application, crop type, and irrigation system (Aguilera et al., 2013a, Bouwman et al., 2002, Gerber et al., 2016, Leip et al., 2011, Lesschen et al., 2011). For example, Aguilera et al. (2013a) suggested using a lower EF for Mediterranean areas than for other temperate regions, especially in rain-fed systems.

There are three characteristics of Mediterranean regions that are fundamental to understanding why soil N₂O emissions from these regions are idiosyncratic and in-turn why the adoption of EFs which differ from other climate regions should be considered. Firstly, due to limited availability of water, irrigation is a prerequisite for the cultivation of many annual crops during summer, whereas mild, humid winters enable annual crops to be rain-fed. Different EFs are therefore needed for irrigated and rain-fed crops. Secondly, soils in the Mediterranean zone generally have a neutral to alkaline soil pH and very low concentrations of organic C (Aguilera et al., 2013b, Verheye and de la Rosa, 2005). These conditions influence denitrification rates and N₂O/N₂ ratios (Li et al., 2005, Simek and Cooper, 2002). Thirdly, soils in Mediterranean regions are rarely exposed to freeze-thaw cycles, which cause high N₂O emissions, especially in fertilized soils (Schouten et al., 2012, Tenuta and Sparling, 2011), which lead to high EFs. The aim of this study was to improve our understanding of soil N₂O emissions from Mediterranean cropping systems by (i) summarizing available field data of soil N₂O emissions; (ii) proposing a more robust and reliable regional EF; and (iii) identifying controlling factors of N₂O EFs (soil type, climate variability, irrigation and N fertilizer

management) as a basis for developing soil N_2O mitigation strategies for regions with Mediterranean climates.

2. Methods

2.1. Selection of studies and data extraction

There are varying definitions to demarcate Mediterranean climate regions worldwide, which are typically based on climate and plant associations. We chose the widely used delineation of the Mediterranean biome from the collection of ecoregions mapped by the World Wildlife Fund (Fig. 1). We selected studies in this area and in marginal areas defined as 'Mediterranean' by the authors of the original papers. Soil N₂O emission data from field-based studies investigating fertilizer-induced soil N₂O emissions were collected from these Mediterranean regions, including the Mediterranean Sea Basin, California, Australia and Chile (Fig. 1). We are not aware of any field study reporting N₂O emissions in the Mediterranean region of South Africa (Mary Scholes, Wits University, personal communication).

CALIFORNIA

dry, <450 mr medium, 450 humid, >700 rainfed drip flooded sprinkler furrow Mediterranea terrestrial ed

MEDITERRANEAN SEA BASIN

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Fig. 1. Location of the study sites included in the dataset. The dark gray area delimits the Mediterranean biome from the collection of ecoregions mapped by the World Wildlife Fund (<u>Olson et al., 2001</u>).

The criteria for inclusion of a study in the dataset were: (i) area-scaled N₂O emissions were reported for N fertilizer treatments, (ii) the number of replicates was reported unambiguously with a minimum of three replicates per treatment, (iii) only field studies were considered and (iv) only when N₂O emissions were reported for at least an entire growing season.

The cumulative N₂O emissions for each N fertilizer treatment were extracted from published papers and reports, together with a measure of variance, the number of replicates and the N application rate (kg N ha⁻¹) during the observational period. Key characteristics (location, climate data, soil type, soil management, irrigation, type of fertilizers, etc.) were collected when available (Supplementary material 1). When data were presented graphically, WebPlot Digitizer was used to extract data points (http://arohatgi.info/WebPlotDigitizer/). If cumulative N₂O emissions or other information were not reported, the authors of the field study were contacted to supply missing information. In some cases, cumulative emissions were estimated by integrating the average daily fluxes over the measurement period (Alluvione et al., 2010, Castaldi et al., 2011, Kong et al., 2009, Ranucci et al., 2011, Vitale et al., 2013). Experiments assessing the effect of nitrification/urease inhibitors were studied as a separate group (when evaluating the influence of the type of fertilization), but were not included to obtain the mean EF for Mediterranean crops (EF_{Med}) because they were not considered representative of current management practices. Fifty-three studies and 223 datasets were included in the meta-analyses (Table 1, Supplementary material 1).

Mediterranean- type climate area	Country	Studies
Mediterranean Basin	Spain	Abalos et al., 2012, Abalos et al., 2013, Abalos et al., 2014; Huérfano et al. (2015); López-Fernández et al. (2007); Maris et al., 2015a, Maris et al., 2015b; Meijide et al., 2007, Meijide et al., 2009; Plaza- Bonilla et al. (2014); Sánchez-García et al. (2016); Sánchez-Martín et al., 2008, Sánchez-Martín et al., 2010a, Sánchez-Martín et al.,

Table 1. Studies included in the meta-analyses.

Mediterranean- type climate area	Country	Studies
		2010b; Sanz-Cobena et al., 2012, Sanz-Cobena et al., 2014a; Tellez-Rio et al. (2015); Vallejo et al., 2005, Vallejo et al., 2006, Vallejo et al., 2014
	Italy	<u>Alluvione et al. (2010); Bosco et al.</u> (2015); Castaldi et al. (2011); Ranucci et al. (2011); Rees et al. (2013); Vitale et al. (2013)
	Israel/Portugal/Greece	<u>Heller et al. (2010); Kontopoulou et al. (2015); Pereira et al. (2013)</u>
Australia	Australia	Barton et al., 2008, Barton et al., 2010, Barton et al., 2013; Li et al. (2011)
California	USA	Alsina et al. (2013); Angst et al. (2014); Garland et al., 2011, Garland et al., 2014; Kallenbach et al. (2010); Kennedy et al. (2013); Kong et al. (2009); Lee et al. (2009); Pittelkow et al. (2013); Schellenberg et al. (2012); Simmonds et al. (2015); Suddick and Six (2013); Townsend-Small et al. (2011); Verhoeven and Six (2014); Zhu-Barker et al. (2015)
Chile	Chile	<u>Hube et al. (2017); Vistoso et al.</u> (2012)

Since most of the field studies in our database focus on assessing the performance of specific crop management practices over both emissions and crop yields, they often do not include post-harvest season emissions. While full year emissions are desirable for determining EFs (IPCC, 2016), in the systems we are studying, we assume that the inclusion of growing season only emissions will have minimal influence on our calculated EFs, since emissions in the intercrop period will be a) low in summer (fallow of winter crops), when the soil is dry, due to decreased microbiological activity, and b) very low in winter (fallow of summer crops) under cold conditions without freeze–thaw cycles (Aguilera et al., 2013a). In the few studies where emissions were measured over an entire year, those during the fallow period were 10% or less of the total (e.g. Sanz-Cobena et al., 2012).

2.2. Soil and land management data compilation

Soil and land management data was grouped into categories based on:

soil pH_{H20} : (i) pH < 7.5 and (ii) pH > 7.5 (The soil pH values measured with CaCl₂ were converted to values measured in distilled water using a method described by <u>Minasny et al. (2011)</u>);

soil texture: (i) coarse (sandy loam, sandy clay loam, loamy sand), (ii) medium (clay loam, loam, silty clay loam, silt, silt loam), and (iii) fine (clay, silt clay, sandy clay) (<u>USDA, 1999</u>);

topsoil organic C concentration: low (<10 g C kg⁻¹ soil), medium (10–20 g C kg⁻¹ soil), and high (>20 g C kg⁻¹ soil);

water input and management: (i) rain-fed and annual precipitation <450 mm, (ii) rain-fed and annual precipitation >450 mm, (iii) sprinklers, (iv) flooded, (v) furrow or surface irrigation, and (vi) drip irrigation;

type of N fertilizer: (i) synthetic (including all types of mineral fertilizers), (ii) organic-solid (compost, solid fraction of manures, solid organic residues), (iii) organic-liquid (pig/cattle slurries, liquid fraction of slurries, digestates), (iv) organic-synthetic mixture, and (v) inhibitors (nitrification and/or urease inhibitors: DCD, DMPP,NBPT);

N fertilizer rate: (i) <100 kg N ha⁻¹, (ii) 100–400 kg N ha⁻¹, and (iii) >400 kg N ha⁻¹;

type of crop: (i) winter cereals (hereafter: 'cereals'), (ii) horticulture, (iii) maize, (iv) rice, (v) perennials, and (vi) other.

2.3. Calculation of emission factors

Most studies included in the meta-analysis did not explicitly report EFs since they were designed with different aims. We calculated EFs as the difference between N₂O emissions from a fertilized treatment (kg N₂O.....N ha⁻¹) and the non-fertilized (control) treatment (kg N₂O.....N ha⁻¹) divided by applied N fertilizer (kg N ha⁻¹). In 39% of cases, there was no control treatment and these missing data were obtained through

multiple imputation by chained equations (<u>Azur et al., 2011</u>) with IBM SPSS Statistics 24 (for a detailed description of missing data treatment and sensitivity tests see Supplementary material 2).

2.4. Data analysis

We performed a standard pair-wise meta-analysis using emission factors (EFs) as effect sizes with MetaWin version 2 (Rosenberg et al., 2000). Mean effect sizes for each grouping and the 95% confidence intervals (CI) generated by bootstrapping (999 iterations) were calculated using a categorical random effects model (Adams et al., 1997). For a detailed description of the statistical procedure see Supplementary material 2. Mean effect sizes were considered significantly different from each other if their 95% CI did not overlap; they were considered significantly different from the default IPCC Tier I value (1%) if the 95% CIs did not overlap with 1%. To test the possibility of publication bias (studies showing no significant effects might not be published), the Rosenthal's fail-safe N test was used (Rosenthal, 1979).

2.5. Case study: effect of EF choice on Spanish N₂O emissions estimation We chose Spain to examine the effect of applying the EFs found in this study because Spain includes both rain-fed and irrigated crops, and has one of the largest agricultural land uses within Europe. In addition, nutrient budgets at the regional scale have been well developed for Spain (Lassaletta et al., 2014, Sanz-Cobena et al., 2014b). We processed the information provided by MMARM (2010) on N fertilizer use (organic and synthetic) for rain-fed and irrigated crops (by surface) in Spanish NUTS3 (Nomenclature of territorial Units for statistics, level 3) regions to estimate the total input of fertilizer per climatic region (temperate and Mediterranean) and water management type. We then compared two methods to calculate the Spanish national N₂O emissions: 1) 'Current EF', we applied an EF = 1.0% (IPCC, 2006) on the N inputs; 2) 'New EFs', the EFs obtained in this study for rain-fed, furrow, sprinkler and drip-irrigated systems in Mediterranean areas, and the IPCC (2006) EF for temperate areas in the cropping systems of northern Spain.

3. Results

3.1. Cumulative $N_{\rm 2}O$ emissions and EF for Mediterranean regions

A total of 53 field studies analyzing N₂O emissions in Mediterranean areas have been published in the last 10 years from four of the five Mediterranean regions worldwide (see Supplementary material 2 for regional description). The cumulative emissions compiled here ranged from -0.15 kg N₂O.....N ha⁻¹ in a rice crop in California (Simmonds et al., 2015) to 43.3 kg N₂O.....N ha⁻¹ in a maize field in Israel (Heller et al., 2010), with a mean value of 2.8 kg N₂O___N ha⁻¹. N₂O emissions were on average largest for drip irrigation (4.6 kg N₂O___N ha⁻¹) and smallest for flooded irrigation (0.5 kg N₂O___N ha⁻¹) systems (Table 2). Synthetic fertilizers were the dominant type of fertilizer in all irrigation systems (Fig. S2) with drip irrigation systems receiving the most N fertilizer (295 kg N ha⁻¹), with some cases of extremely high (1500 kg N ha⁻¹) application rates (Heller et al., 2010). Treatments with a mixture of organic-synthetic fertilizers emitted the most N₂O (9.8 kg N₂O___N ha⁻¹), which is related to the high average N application rate in this group (535 kg N ha⁻¹). Organic-liquid fertilizers were applied at similar rates as synthetic fertilizers, but their emissions were on average higher (4.8 vs. 1.7 kg N₂O___N ha⁻¹). The use of organic-solid fertilizers or the addition of inhibitors led to the lowest average cumulative emissions (1.8 and 1.2 kg N₂O____N ha⁻¹, respectively) (Table 2). Maize and horticulture crops had the highest N₂O emissions (4.7 and 3.4 kg N₂O____N ha⁻¹), while rice and cereal crops had the lowest (0.5 and 0.7 kg N₂O____N ha⁻¹).

Table 2. The number of observations (N), mean and standard deviation (SD) of cumulative N_2O emissions, N application rate and experiment duration for some of the factors with a significant influence on N_2O emissions from agricultural fields.

Water	Cumulative N₂O emissions (kg N₂O N ha⁻¹)) 20	N application rate (kg N ha-1)		Experiment duration (days)	
	Ν	Mean	SD	Mean	SD	Mean	SD
Water							
Drip	55	4.6	9.5	295	387	299	110
Flooded	14	0.5	0.8	161	59	277	106
Furrow	29	2.9	4.7	205	94	254	92
Sprinkler	55	3.7	3.3	226	75	186	99
Rain-fed <450 mm	39	0.4	0.3	117	58	269	66
Rain-fed >450 mm	40	2.3	4.8	153	125	253	131
Fertilizer type							
Organic-liquid	30	4.8	5.4	172	95	251	71
Organic-solid	26	1.8	2.3	238	155	227	114
Mixture	22	9.8	13.5	535	523	327	73
Synthetic	131	1.7	3.1	157	77	260	108
Inhibitor	23	1.2	1.7	167	78	167	129

Water	Cumulative N₂O emissions (kg N₂O N ha⁻¹)		N application rate (kg N ha-1)		Experiment duration (days)		
	Ν	Mean	SD	Mean	SD	Mean	SD
Crop type							
Maize	56	4.7	7.0	323	298	223	129
Horticulture	36	3.4	4.6	182	67	231	125
Perennial	22	1.2	1.5	104	73	297	100
Cereal	61	0.7	0.6	138	62	277	68
Rice	14	0.5	0.8	161	59	277	106
Others	43	4.5	8.8	230	290	243	112

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inhibitor refers to treatments with synthetic and/or organic fertilizers where nitrification or urease inhibitors were applied.

The mean EF for Mediterranean crops (EF_{Med})—covering rain-fed and irrigated systems, arable and permanent crops, organically and synthetically fertilized systems (treatments with inhibitors excluded) for all Mediterranean-type climate areas was 0.50% ± 0.12 ($EF_{Med} \pm 95\%$ CI, N = 200; Rosenthal's fail-safe test: 4830). Grouping into different categories allowed us to identify which factors (soil, crop, irrigation system, type of fertilizer and application rate) had a significant impact on averaged EFs, providing key information when proposing N₂O mitigation strategies.

3.2. Influence of soil characteristics on EF

Soil pH, soil organic C or soil texture did not significantly affect EFs. Soil pHs ranged from 4.8 in a rice experimental station field site in California (Simmonds et al., 2015) to 8.5 in a cereal crop in north-eastern Spain (Plaza-Bonilla et al., 2014), with most soils having a neutral to alkaline pH (in 83% of the cases, pH > 7). The concentration of organic C in soils ranged from 4 g C kg⁻¹ soil in California (Schellenberg et al., 2012) to 133 g C kg⁻¹ soil in Chile (Vistoso et al., 2012), and the average soil organic C concentration was 15.9 g C kg⁻¹ soil. EFs did not significantly differ among soils with low (EF: 0.56, N = 59), medium (EF: 0.51, N = 94) or high (EF: 0.37, N = 5) organic C concentrations. Finally, soil texture had no significant effect on average EFs, although trends suggested that larger EFs could be expected from coarse (EF: 0.58%, N = 77) and medium-textured soils (EF: 0.48%, N = 100), than from fine-textured soils (EF: 0.27%, N = 22).

3.3. Influence of water management on EF

Rain-fed systems had an average EF of $0.27\% \pm 0.21$ (N = 62) which was significantly lower than 1% (Fig. 2). Studies under dry Mediterranean conditions (average annual precipitation <450 mm) had lower EFs (EF: $0.21\% \pm 0.26$, N = 38) than studies in areas with an average annual precipitation >450 mm (EF: $0.32\% \pm 0.33$, N = 24).



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Fig. 2. The influence of different irrigation options on changes in N₂O emission factors (EFs) in Mediterranean-type climate areas. Symbols represent mean effect sizes [EFs (%)] with 95% confidence intervals. The numbers shown in parentheses correspond to observations in each class upon which the statistical analysis was based. For this analysis, treatments with nitrification inhibitors were excluded (see Methods). There was high variability in EFs between types of irrigation management (Fig. 2). Drip-irrigated (including both surface and subsurface) and furrow systems had lower EFs (EF: $0.51\% \pm 0.26$, N = 52 and EF: $0.47\% \pm 0.36$, N = 27, respectively) than sprinklers

(EF: 0.91% \pm 0.24, N = 45), which was close and not significantly differ from the IPCC default EF.

It is important to note that drip-irrigated systems had the highest level of N fertilization (<u>Table 2</u>), which could have biased the results of the meta-analysis, increasing the EF for this group. Flooded systems (rice fields) had the lowest EF ($0.19\% \pm 0.50$, N = 14), in line with <u>IPCC (2006)</u> guidelines.

3.4. Influence of fertilizer type and application rate on EF

The highest EFs corresponded with organic-liquid fertilizers (EF: $0.85\% \pm 0.30$, N = 30), which were mostly pig or cattle slurries, or the liquid fraction of their digestates (Fig. 3); this EF did not significantly differ from 1%. The rest of the fertilizer types had an EF significantly lower than 1% but were statistically similar to each other. The use of nitrification/urease inhibitors decreased the average EFs (EF: $0.14\% \pm 0.32$, N = 23) when compared with synthetic, organic-liquid, and mixtures of organic and synthetic fertilizers, but was similar to EFs from organic-solid fertilizers (EF: $0.19\% \pm 0.33$, N = 24). Crops fertilized with organic-solid fertilizers received, on average, almost double the amount of N than those with synthetic or liquid fertilizers (Table 2), which reinforces organic-solid fertilization as a strategy to decrease EFs. Although not statistically significant, higher N application rates increased EFs. Low N application rates (<100 kg N ha⁻¹) had the lowest EFs (EF: 0.27%, N = 40), whereas high N application rates (>400 kg N ha⁻¹) resulted in EFs that did not significantly differ from the 1% IPCC value (EF: 0.82%, N = 15).



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Fig. 3. The impact of the type of N fertilizer and application rate on changes in N₂O emission factors (EFs) in Mediterranean-type climate areas. Symbols represent mean effect sizes [EFs (%)] with 95% confidence intervals. The numbers shown in parentheses correspond to observations in each class upon which the statistical analysis was based.

3.5. Influence of crop types on EF

Five out of the six considered crops presented EFs significantly lower than 1% (Fig. 4). Rice and cereals (wheat, barley, and oat) had the smallest EFs (EF: $0.19\% \pm 0.51$, N = 14 for rice and $0.26\% \pm 0.22$, N = 53 for cereals). Perennials (including vineyards, almonds, and olive orchards) and others (including pasture, legumes, rapeseed, crop rotations and bare soil) had intermediate EFs (EF: 0.54%, N = 19 for perennials and EF: 0.47%, N = 33 for others). Horticultural crops (melons, onions, tomatoes, and potatoes) showed a slightly higher than average EF (EF: $0.63\% \pm 0.31$, N = 34). Finally, maize had a relatively high average EF (EF: $0.83\% \pm 0.26$, N = 47) which did not significantly differ from the 1% default.



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Fig. 4. Average N₂O emission factors (EFs) in Mediterranean-type climate areas depending on the type of crop. Symbols represent mean effect sizes [EFs (%)] with 95% confidence intervals. The numbers shown in parentheses correspond to observations in each class upon which the statistical analysis was based. For this analysis, treatments with nitrification inhibitors were excluded (see Methods).

3.6. Case study: effect of EF choice on Spanish N₂O emissions estimation

<u>Table 3</u> shows 'current EF' used by national inventories (<u>IPCC, 2006</u>) and the 'New EFs' determined from this study for rain-fed, furrow, sprinkler and drip-irrigated systems in Mediterranean crops. Nitrous oxide emissions from Spanish agriculture vary considerably depending on the calculation method. The emissions from Mediterranean

Spanish agriculture calculated with the current EF (12.5 Gg N₂O.___N yr⁻¹) exceeded the value using the new EFs (5.5 Gg N₂O.___N yr⁻¹) by a factor of two and this had a substantial impact on the estimates of total national emissions from cropping systems (<u>Table 4</u>).

Table 3. Emission factors (EFs) used to estimate total N_2O emissions in the Spanish cropping systems: current EFs according to IPCC (2006) and the new values for Mediterranean areas developed in this work for different irrigation systems. The percentages in brackets show the proportion of the area under each irrigation system in Spain.

	EFs	Temperate climate	Mediterranean climate
Curront	Rain-fed crops	1.0%	1.0%
Current	Irrigated crops	1.0%	1.0%
	Rain-fed crops	1.0%	0.27%
New EFs	Irrigated furrow (27% surface)	1.0%	0.47%
	Sprinkler (24% surface)	1.0%	0.91%
	Drip (49% surface)	1.0%	0.51%

Table 4. Comparison of total N₂O emissions in Spanish cropping systems (<u>MMARM, 2010</u>) after the application of the current EFs and the new EFs obtained in this study, considering that all the irrigated crops are furrow, sprinkler or drip irrigated. The percentages in brackets show the proportion of the area under each irrigation system in Spain.

		Temperate climate	Mediterranean climate	Total
Fertilizer N input (synth + org) (Gg N yr ⁻¹)	Rain-fed crops	137	585	722
	Irrigated crops	13	664	678
	Total	151	1249	1400
Current EFs	Rain-fed crops	1.4	5.8	7.2
Total N ₂ O emissions	Irrigated crops	0.1	6.6	6.8
(Gg N yr ⁻¹)	Total	1.5	12.5	14.0
	Rain-fed crops	1.4	1.6	3.0
New EFs	Furrow (27%)	0.0	0.8	0.9
Total N ₂ O emissions	Sprinkler	0.0	1.5	1.5

		Temperate climate	Mediterranean climate		Total
	(24%)				
(Gg N yr-1)	Drip (49%)	0.1		1.7	1.7
	Total	1.5		5.5	7.0

4. Discussion

In this paper, we derived an EF for N₂O emissions from Mediterranean regions (EF_{Med}: 0.5%) and demonstrated that EFs in Mediterranean-cultivated lands are significantly lower than the 1% IPCC Tier I default value (IPCC, 2006) or the 1.25% (IPCC, 1996) used to calculate N₂O emissions in response to applying N fertilizer to land. We, therefore, recommend that Mediterranean countries, or regions, consider refining their national inventories to reflect the relatively small EF. Here, we show the implications of such a change by using the EFs obtained in this study to estimate total N₂O emissions from cropping systems in Spain and compare them to estimates using the IPCC default value.

To derive statistically robust estimates of EFs, we opted to retain studies without control measurements. We performed a sensitivity test (see Supplementary material 2) which demonstrated that including these studies had no impact on the mean EF_{Med} (EF: 0.496% including all studies and EF: 0.463% excluding cases without control, see Supplementary material 2). We, therefore, conclude that the EF_{Med} is robust, but due to the high heterogeneity of the studies included in the dataset, it was often difficult to find significant differences between different management strategies. Further field research, measuring emissions over the whole year and including control treatments, is merited to better quantify EFs for the various management options in Mediterranean systems.

4.1. Influence of soil characteristics on EF

Soil characteristics show very limited impact of EFs. This finding seems to contradict previous studies where soil organic C concentration and pH had a clear impact on denitrification and therefore N₂O emissions (<u>Li et al., 2005</u>, <u>Šimek and Cooper, 2002</u>). However, these relationships might be difficult to find in our dataset, where most soils had a neutral or slightly alkaline pH and similar (in general low) concentrations of organic C, with other variables having a stronger effect on N₂O emissions (N application rate, soil water content, type of fertilizer applied, etc.). In addition, although denitrification is generally identified as the major process generating N₂O in most cropping systems, this does not necessarily stand for studies under Mediterranean

conditions, where the importance of nitrifier-nitrification and nitrifier-denitrification have been documented (<u>Sánchez-García et al., 2014</u>, <u>Sánchez-Martín et al., 2008</u>). Nitrification (contrarily to denitrification) does not need an additional source of C and therefore if nitrification pathways dominate, the soil C availability may not play an important role on N_2O emissions.

Although not significant, we found higher EFs in coarse/medium-textured soils (EF: 0.58 and 0.48%) than in fine-textured soils (EF: 0.27%). Since denitrification needs anaerobic conditions, which are more likely to occur in fine-textured soils, this result seems contradictory. Our finding might be related to (i) complete denitrification (transformation to N₂) in less-aerated fine-textured soils (<u>Šimek and Cooper, 2002</u>) or (ii) nitrification processes having an important role in N₂O emissions, with higher nitrification rates in low water content, well-aerated soils (<u>Thomsen et al., 2003</u>). Also, previous studies found higher annual denitrification losses in loamy soils than sandy or clay-textured soils, which was interpreted as a limitation of C diffusion by adsorption to clays in fine-textured soils (<u>Barton et al., 1999</u>).

4.2. Influence of water management on EF

Among the irrigation technologies used in Mediterranean cropping systems, furrows are still widespread in summer-irrigated crops and sprinkler irrigation systems are on the increase in Spain (MAGRAMA, 2014). However, since many Mediterranean regions suffer from water scarcity, water-saving irrigation systems such as drip irrigation (both surface and subsurface) are being developed. The area sown to maize under drip irrigation is expected to increase due to higher water use efficiency, maintained crop yields and technical viability (Couto et al., 2013). Despite these advantages, the impact of drip irrigation systems on N₂O emissions is poorly documented. Our analyses revealed that EFs for N₂O from drip-irrigated systems are much lower than those in which water is applied through sprinklers, even when the average N application rate was higher with drip irrigation. This is consistent with other field-based research (Kallenbach et al., 2010, Sánchez-Martín et al., 2008) and a previous review under Mediterranean conditions (Aquilera et al., 2013a). The reduction in N₂O emissions with drip irrigation is probably caused by a reduction in the rate of water application compared with other conventional systems (Sharmasarkar et al., 2001). This may decrease the soil-water-filled pore space (WFPS) below the optimum range for N₂O production through denitrification, which is 60–90% depending on soil type (Barton et al., 1999, Sanz-Cobena et al., 2014a). WFPS levels below this threshold are common in many of the drip irrigation studies included in this review. For instance, in Abalos et al.

(2014), the WFPS was below 65% for 84% of the experimental period; it never exceeded 50% in the study of <u>Schellenberg et al. (2012)</u>, and it ranged from 20 to 30% and 40–60% in <u>Kallenbach et al. (2010)</u> and <u>Kennedy et al. (2013)</u>, respectively. Therefore, our results suggest that drip irrigation represents an effective N₂O mitigation practice in Mediterranean irrigated systems. These benefits, however, should be evaluated together with other effects on the GHG balance and further socioenvironmental consequences. For example, increased infrastructure material requirements and energy needs for pressurizing the irrigation water might offset drip irrigation N₂O-related emission savings in certain situations, while reduced water use (and related energy consumption) might be the main component responsible for emission reduction in other situations (<u>Sanz-Cobena et al., 2017</u>).

The lower EFs found under furrow irrigation compared to sprinkler irrigation might be related to a slightly lower average N application in the furrow systems included in our dataset and to a different soil wetting pattern, favoring complete denitrification to N₂ after irrigation events in furrows (<u>Sánchez-Martín et al., 2008</u>).

Our results show that rain-fed crops with less than 450 mm rainfall and flooded systems have the lowest EFs of all systems (Fig. 2). In contrast, rain-fed crops in areas with annual precipitation greater than 450 mm have larger emissions. These findings show the strong effect of specific climatic conditions and soil moisture on the performance of Mediterranean cropping systems in terms of N₂O emissions. The distribution of rain inputs also plays a relevant role. The first rainfall after long periods of drought (common in summers of Mediterranean areas) usually triggers N₂O emissions. This pulsing effect, also observed in the dry areas of drip-irrigated crops, is due to the accumulation of mineral N in dry soils and the reactivation of water-stressed bacteria after rainfall events (Sánchez-Martín et al., 2010a, Skiba et al., 1997).

Drip irrigation may have an adverse side-effect as its use has been associated with enhanced emissions of nitric oxide (NO) (Abalos et al., 2014). This is because the lower WFPS may favor NO production from nitrification. <u>Pilegaard (2013)</u>reported maximum NO emissions at intermediate soil moisture (40–60% WFPS) since NO is highly reactive and will be consumed at higher soil moisture.

4.3. Influence of fertilizer type and application rate on EF

Our results suggest that the use of liquid manures and inorganic N fertilizers results in greater N₂O emissions than organic-solid fertilizers such as composted manures and green wastes. Liquid and inorganic N fertilizers are likely to be more readily available to plants and microorganisms, whereas solid organically-bound N requires decomposition

and microbial mineralization to be used in N₂O-producing processes (Poodle et al., 2002). Composted organic fertilizer N is thus released more slowly, ultimately increasing N uptake by crops (Ryals et al., 2015) and decreasing the potential for N₂O emissions. It is notable that not all organic fertilizers are equivalent with regard to their potential effects on N₂O emissions. For example, fresh manures and manure slurries can result in relatively large N₂O emissions from cattle manure in the United States by an order of magnitude (Owen and Silver, 2015). Davidson (2009) also suggested that manure management was a dominant source of atmospheric N₂O concentrations, accounting for more than 40% of anthropogenic N₂O emissions. Liquid manures are rich in both N and C, potentially facilitating N₂O production in low C environments, mostly through denitrification. As already observed in Aguilera et al. (2013a), solid manure would result in lower N₂O EFs (Owen et al., 2015).

As expected, nitrification/urease inhibitors effectively reduced EFs from Mediterranean systems (Mosier et al., 1996). In a recent review, Gilsanz et al. (2016) developed EFs of $0.42\% \pm 2.2$ and $0.70\% \pm 3.3$ for DCD and DMPP, respectively, two commonly used nitrification inhibitors. The lower EF found in our study ($0.14\% \pm 0.32$) agrees with the low baseline EFs found in the studies included in our dataset. Thus, inhibitors seem to be a good strategy to mitigate direct N₂O emissions under Mediterranean conditions, although the potential is lowered by the relatively small baseline emissions in Mediterranean systems.

In agreement with previous studies (<u>Kim et al., 2013</u>, <u>Shcherbak et al., 2014</u>), increasing fertilizer application rates led to increased EFs. We found that applying N fertilizers over 400 kg N ha⁻¹ resulted in EFs that did not significantly differ from the 1% IPCC Tier I default value. The lack of statistical significance between N doses is probably related to the fact that in our dataset most studies only considered one N application rate, with a limited number of cases with very low or high N fertilization rates.

4.4. Influence of crop types on EF

In a previous quantitative review of Mediterranean cropping systems, <u>Aguilera et al.</u> (2013a) observed that the differences in cumulative N₂O emissions among crop types clearly respond to the management characteristics of each crop type; our results confirm these conclusions. Generally, the crop types in which water and fertilizer applications are low (see Figs. S3 and S4 and <u>Table 2</u>), such as rain-fed crops (winter cereals), have the lowest N₂O response to N applications. A low EF for rice is associated

with flooding which generates anaerobic conditions favoring complete denitrification to N_2 , thereby reducing N_2O release from the soil (<u>Conrad, 1996</u>). Maize has a high EF, possibly because it is irrigated without implementation of water-saving techniques and has on average higher N application rates. The wide confidence intervals observed for the EFs in perennials and rice are due to the lower number of observations within these crop categories.

4.5. Case study: effect of EF choice on Spanish N₂O emissions estimation In this work we have seen how the application of EFs adapted to Mediterranean conditions can significantly reduce the national estimates of total N₂O emissions from cropping systems. Applying the new EFs has consequences for determining the effectiveness of N₂O mitigation strategies in Mediterranean regions, as baseline emissions will be smaller than those suggested by Tier I emission estimates. The level of indirect emissions is, however, highly uncertain, and published information is scarce, and has thus not been assessed in this study. IPCC Tier I proposes an EF for indirect emissions of 0.75% while <u>Garnier et al.</u>, 2009, <u>Garnier et al.</u>, 2013 estimated that, for the Seine temperate basin, indirect emissions represented 13–17% of total direct emissions. Due to the regulation of water in Mediterranean agricultural areas in Spain through a dense drainage network and reservoirs (Aguilera et al., 2015), the potential for denitrification could be high and could, therefore, generate high indirect emissions. The magnitude of indirect N₂O emissions in Mediterranean areas is an interesting area for future research.

5. Concluding remarks

The average EF for nitrous oxide emissions in Mediterranean cropping systems was 50% lower than the IPCC Tier I default value (1%), which is largely based on values observed in temperate regions. The most important factors controlling the magnitude of soil N₂O EFs from Mediterranean regions were water regime (irrigation technique or precipitation amount) and fertilizer type and application rate. In rain-fed systems with precipitation below 450 mm, the EF is much lower than the IPCC values. The EF for sprinkler-irrigated systems is similar to that for temperate cropping systems, whereas drip-irrigated systems have a high potential for mitigation (EF: 0.51%). The N fertilizer rate altered EFs, suggesting a non-linear relationship between N₂O emissions and N application rate. Intensive cropping systems, such as irrigated maize, tended to have higher EFs than less intensive systems such as cereals.

Applying specific EFs would lower estimates of total N₂O emissions in countries with large areas of agricultural soils in Mediterranean climates. For example, applying

current Tier I EFs to Spanish cropping systems leads to a total N₂O emission estimate that is a factor of two higher than when applying the new EFs from our analysis (14 Gg N₂O____N yr⁻¹vs. 7 Gg N₂O____N yr⁻¹). Our results indicate that N₂O emissions from Mediterranean agriculture are much lower than expected and that with the new EFs, the effect of mitigation strategies such as drip irrigation or using nitrification inhibitors, even if highly significant, may be smaller in absolute terms (since baseline emissions will be lower).

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Appendix A. Supplementary data

The following are Supplementary data to this article: <u>Download spreadsheet (138KB)Help with xlsx files</u> <u>Download Word document (132KB)Help with docx files</u>

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