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# Effects of Irrigation on N<sub>2</sub>O Emissions in a Maize Crop Grown on Different Soil Types in Two Contrasting Seasons

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**Abstract:** Crop management and soil properties affect greenhouse gas (GHG) emissions from cropping systems. Irrigation is one of the agronomical management practices that deeply affects soil nitrous oxide (N<sub>2</sub>O) emissions. Careful management of irrigation, also concerning to soil type, might mitigate the emissions of this powerful GHG from agricultural soils. In the Mediterranean area, despite the relevance of the agricultural sector to the overall economy and sustainable development, the topic of N<sub>2</sub>O emissions does not have the same importance as N<sub>2</sub>O fluxes in temperate agricultural areas. Only some research has discussed N<sub>2</sub>O emissions from Mediterranean cropping systems. Therefore, in this study, N<sub>2</sub>O emissions from different soil types (sandy-loam and clay soils) were analyzed in relation to the irrigation of a maize crop grown in two contrasting seasons (2009–2010). The irrigation was done using a center pivot irrigation system about twice a week. The N<sub>2</sub>O emissions were monitored throughout the two-years of maize crop growth. The emissions were measured with the accumulation technique using eight static chambers (four chambers per site). Nitrogen fertilizer was applied in the form of ammonium sulphate and urea with 3,4 dimethylpyrazole phosphate (DMPP) nitrification inhibitors. In 2009, the N<sub>2</sub>O emissions and crop biomass measured in both soil types were lower than those measured in 2010. This situation was a lower amount of water and nitrogen (N) available to the crop. In 2010, the N<sub>2</sub>O fluxes were higher in the clay site than those in the sandy-loam site after the first fertilization, whereas an opposite trend was found after the second fertilization. The soil temperature, N content, and soil humidity were the main drivers for N<sub>2</sub>O emission during 2009, whereas during 2010, only the N content and soil humidity affected the nitrous oxide emissions. The research has demonstrated that crop water management deeply affects soil N<sub>2</sub>O emissions, acting differently for denitrification and nitrification. The soil properties affect N<sub>2</sub>O emission by influencing the microclimate conditions in the root zone, conditioning the N<sub>2</sub>O production.

**Keywords:** nitrous oxide; soil type; irrigation; plant growth; Mediterranean climate

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## 1. Introduction

Agriculture suffers from climate change (CC) while also contributing to CC by emitting large amounts of greenhouse gases (GHGs) into the atmosphere, about 14% of which is linked to soil management and livestock. Nitrous oxide (N<sub>2</sub>O) is one of the most powerful climate-altering gases,

and its concentration has significantly increased from the 270 ppb pre-industrial levels to the current levels of 340 ppb [1]. N<sub>2</sub>O is characterized by its 100-year global warming potential, which is 298 times greater than of carbon dioxide [2]. It is the main GHG emitted by agriculture, estimated to contribute more than 60% of the total anthropogenic N<sub>2</sub>O [3].

Although cultivated soils contribute largely to GHG emissions, little attention is given to N<sub>2</sub>O emissions from agricultural soils in the Mediterranean region, as compared with other regions. This makes it difficult to devise mitigating strategies targeting the impact of Mediterranean cropping systems on the climate [4].

N<sub>2</sub>O emissions from agricultural soils are closely related to microbial nitrification and denitrification. These two processes are influenced by several factors, including soil temperature, moisture content, soil pH, aeration, and nitrogen (N) availability and organic carbon contents [5,6]. N availability in the soil is the major driver for N<sub>2</sub>O emissions, and chemical fertilizers are the main source of N contents in the agricultural soils [6–9]. Soil moisture is another driver of N<sub>2</sub>O emissions as it regulates oxygen availability to soil microorganisms [10]. Soil temperature also plays an important role in regulating N<sub>2</sub>O emission from agricultural soils, and N<sub>2</sub>O emissions increase as the soil temperature increases [11]. Soil pH regulates both nitrification and denitrification. [12] Nitrification, under oxygen conditions, involves the microbial conversion of ammonium to nitrate. It generally increases with an increase in soil pH, but reaches an optimum level at pH 6–8 [13,14]. Denitrification, under limited oxygen conditions, is the microbiological process in which oxidized N species, such as nitrate (NO<sub>3</sub><sup>-</sup>) and nitrite (NO<sub>2</sub><sup>-</sup>), are reduced to gaseous nitric oxide (NO), nitrous oxide (N<sub>2</sub>O), and molecular nitrogen (N<sub>2</sub>). Soil pH affects the denitrification rate, in fact at pH values below 7, N<sub>2</sub>O is the main denitrification product, whereas N<sub>2</sub> prevails at pH values above 8 [15]. Agricultural management practices, such as the type and quantity of fertilization, tillage or ploughing, and irrigation, have an effect on GHG production, in particular on N<sub>2</sub>O [16]. Irrigation controls the soil water content in agricultural soils that directly affects oxygen availability to the soil microbes, which alternatively influences N<sub>2</sub>O emissions [17,18]. Nitrification prevails on denitrification as a source of N<sub>2</sub>O production in soils with greater oxygen availability, whereas denitrification overcomes nitrification under limited oxygen availability [19–21]. A threshold of 60% has been defined for the water filled pore space—above this level denitrification prevails, and below it nitrification prevails [22]. Soil texture also controls soil moisture; soil with a coarse texture retains less water than soil with a fine texture: as consequence, more oxygen penetrates into the soil matrix, favoring nitrification over denitrification [23,24]. It should be considered that different soil patches are often present in the same cropped field, making spatially and highly variable N<sub>2</sub>O emissions, so that it is difficult to devise a mitigating strategy applicable at a large scale [25].

As only a few research works have discussed N<sub>2</sub>O emissions from Mediterranean cropping systems [26,27], the aim of this study was to evaluate the N<sub>2</sub>O emissions of two different soils (sandy-loam, and clay) cultivated with maize crops, in two contrasting years, regarding irrigation management. Soil patches with different physical–chemical properties provide the opportunity to compare the effect of irrigation management and the role of soil properties on N<sub>2</sub>O emissions under the same environmental and management conditions.

## 2. Materials and Methods

### 2.1. Experimental Site, Cropping System, and Management

This study was carried out on a farm located in Southern Italy (latitude 40°31'25.5", longitude 14°57'26.8", and mean altitude 15 m a.s.l.) during 2009 and 2010. The field was irrigated with a center pivot irrigation system. The area under study is characterized by the typical Mediterranean climate, with an annual mean temperature of 15.5 °C and annual rainfall of 908 mm (private weather station). More details can be found in Vitale et al. [28]. The field is characterized by two pedosols—the soil to the east has a clay texture, whereas the west has a sandy-loam texture (Table 1).

**Table 1.** Physical and chemical soil properties. OM—organic matter; FC—water field capacity; WFPS—water filled pore space at field capacity.

Profile	Sandy (%)	Silt (%)	Clay (%)	pH	OM (%)	Bulk Density (g cm <sup>-3</sup> )	FC (g <sub>water</sub> g <sup>-1</sup> dw)	WFPS at FC (%)	USDA
Est	29.8	22.1	48.1	7.63	3.7	1.15	0.206	45.4	Clay
West	75.0	11.0	14.0	7.65	7.8	1.01	0.391	78.3	Sandy-Loam

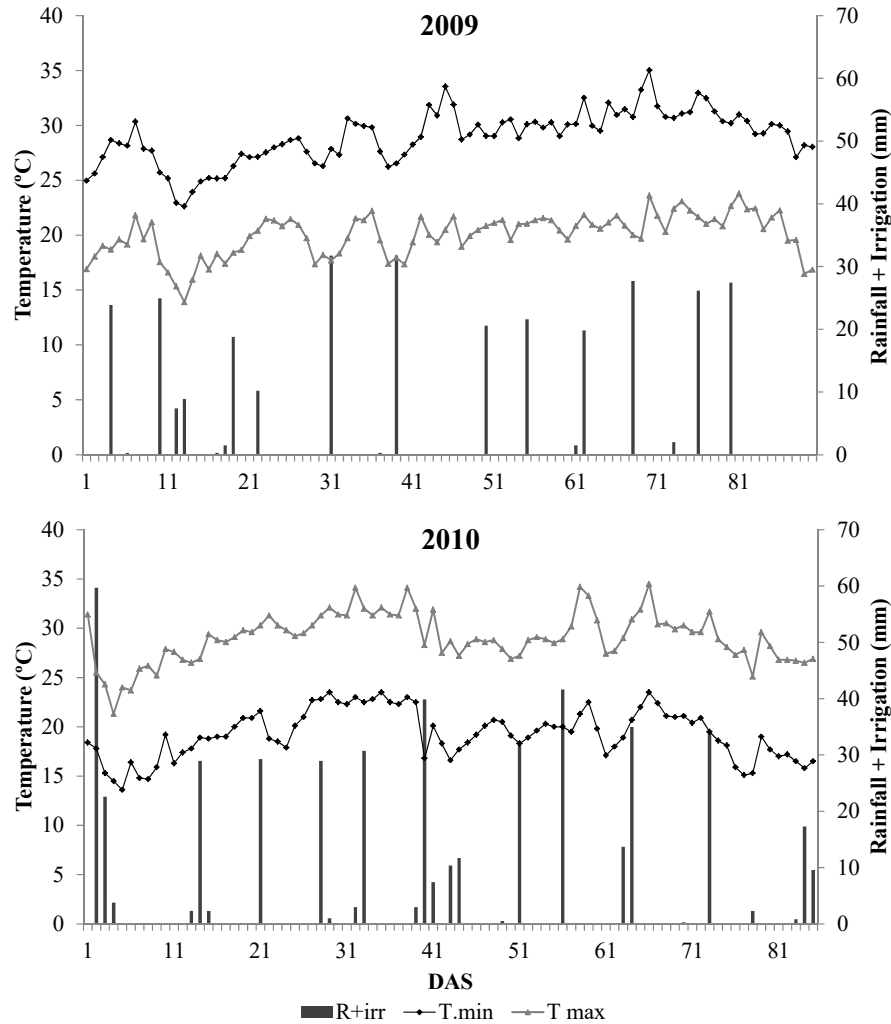
Data are means ( $n = 3$ ).

Maize (*Zea mays* L.) seeds were sown in spring on rows spaced 0.75 m apart, to a nominal density of about 8.0 pt m<sup>2</sup>. At the same time, an ammonia nitrogen (0.8% 3,4 dimethylpyrazole phosphate (DMPP)) complex was applied as Entec 25 (Entec<sup>®</sup>, EuroChemAgro, Cesano Maderno, MB, Italy). Then, 30 days after sowing (DAS), fertilizer was applied as urea (0.5% DMPP; Entec 46, Entec<sup>®</sup>, EuroChemAgro, Cesano Maderno, MB, Italy). Both fertilizers contained the 3,4 dimethylpyrazole phosphate (DMPP) nitrification inhibitor. Crop management was ordinary and managed by the farm. More information about crop management is reported in Table 2.

**Table 2.** The crop management.

Year	Sowing	1° Fertilization	2° Fertilization	Harvesting	Total Water Supplied (mm)
2009	12–13 June	12–13 June 68 kg N ha <sup>-1</sup>	10 July 190 kg N ha <sup>-1</sup>	8–9 September	389
2010	18–19 June	18–19 June 65 kg N ha <sup>-1</sup>	20 July 187 kg N ha <sup>-1</sup>	21–22 September	476

Maize crops received different amounts of water during the two contrasting growing seasons (Table 2 and Figure 1). During the 2009 growing season, about 116 mm of rainfall was recorded, and to cover the water deficit, 273 mm of water was applied through irrigation. During the 2010 growing season, a reduced amount of rainfall was recorded (76 mm) compared with the 2009 season, and so about 400 mm of water by irrigation was applied.



**Figure 1.** Monthly averages minimum (black diamonds) and maximum (gray triangles) air temperature and rainfall plus irrigation (bars) during the two contrasting grown seasons.

## 2.2. Soil N<sub>2</sub>O Flux Measurement, Nitrogen Content, and Above-Ground Biomass

Soil N<sub>2</sub>O fluxes were measured with the accumulation technique using eight static chambers [29,30]; four chambers were located on the sandy-loam site and four on the clay site. Chambers (0.20 m diameter, 0.15 m height, and 4.7 L) were inserted at a 0.03 m depth into the soil and were left there for the entire measurement period. Air samples were collected between 11:00 a.m. and 13:00 p.m. solar time using a PVC syringe, and were stored in 0.20 L evacuated vials until analysis; samplings were taken before and after chamber closure within 30 min. These measurements were carried out weekly. The N<sub>2</sub>O concentration was determined using a gas chromatograph (Series 800 Fisons, Milan, Italy) and the fluxes, expressed as  $\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ , were calculated as follows:

$$f_{\text{N}_2\text{O}} = k(A/S) \quad (1)$$

where A is the slope of the line interpolating N<sub>2</sub>O concentrations in time, S is the soil surface area, and k is the coefficient used to convert measure units. The cumulative flux (fc) was determined as reported in Ranucci et al., 2001 [31], and used to calculate the CO<sub>2</sub> equivalent.

The soil temperature was measured at a 0–0.20 m depth by means of two TCAV thermocouple probes (TCAV, Campbell SkiSci. Ltd., Shepshed, UK), whereas the soil moisture was also measured at a 0–0.20 m depth by means of two soil moisture sensors (Theta Probe, Delta-T devices Ltd., Cambridge, UK), which were used to determine the water filled pore space (WFPS), as follows:

$$\text{WFPS} = \text{VSWC}/[1 - (\text{BD}/2.65)] \quad (2)$$

where 2.65 represents the average density calculated on the basis of the relative content of the different mineral constituents [32,33], BD is the bulk density, and VSWC the volumetric soil water content.

The soil  $\text{NO}_3^-$  content was determined based on the samples collected at a 0–0.20 m depth by using an auger. An integrated soil sample per chamber was obtained by collecting different soil samples near each autochamber and putting them together. The soil was air-dried and sieved (2 mm), and the soil nitrate ( $\text{NO}_3^-$ ) content was determined colorimetrically using a spectrophotometer (DR 2000 HACH Co., Loveland, CO, USA).

At harvest, for both soils on a 1 m<sup>2</sup> sampling area, the plants were collected, weighed, and oven-dried at 60 °C up to a constant weight.

### 2.3. Statistical Analysis

Statistical analysis of the data was performed by means of the Sigma-Plot package (Sigma-Plot 12.2, Systat Software, Inc., San Jose, CA, USA). Differences in the parameters between the two soil types were checked by one-way analysis of variance (ANOVA) repeated measurements, followed by Duncan's test ( $p \leq 0.05$ ). The dependence of  $\text{N}_2\text{O}$  flux on temperature, water filled pore space, and  $\text{NO}_3^-$ -N was investigated by means of an analysis of variance (ANOVA) model. The regression analyses were performed using all of the data collected during the monitoring activities. The soil  $\text{NO}_3^-$  concentration, WFPS, and T soil were limited to a different extent and at different times in the field, and the whole set of data was divided into more restricted homogeneous groups.

## 3. Results and Discussion

### 3.1. Soil Related Measurements and $\text{N}_2\text{O}$ Fluxes in Clay and Sandy-Loam Sites

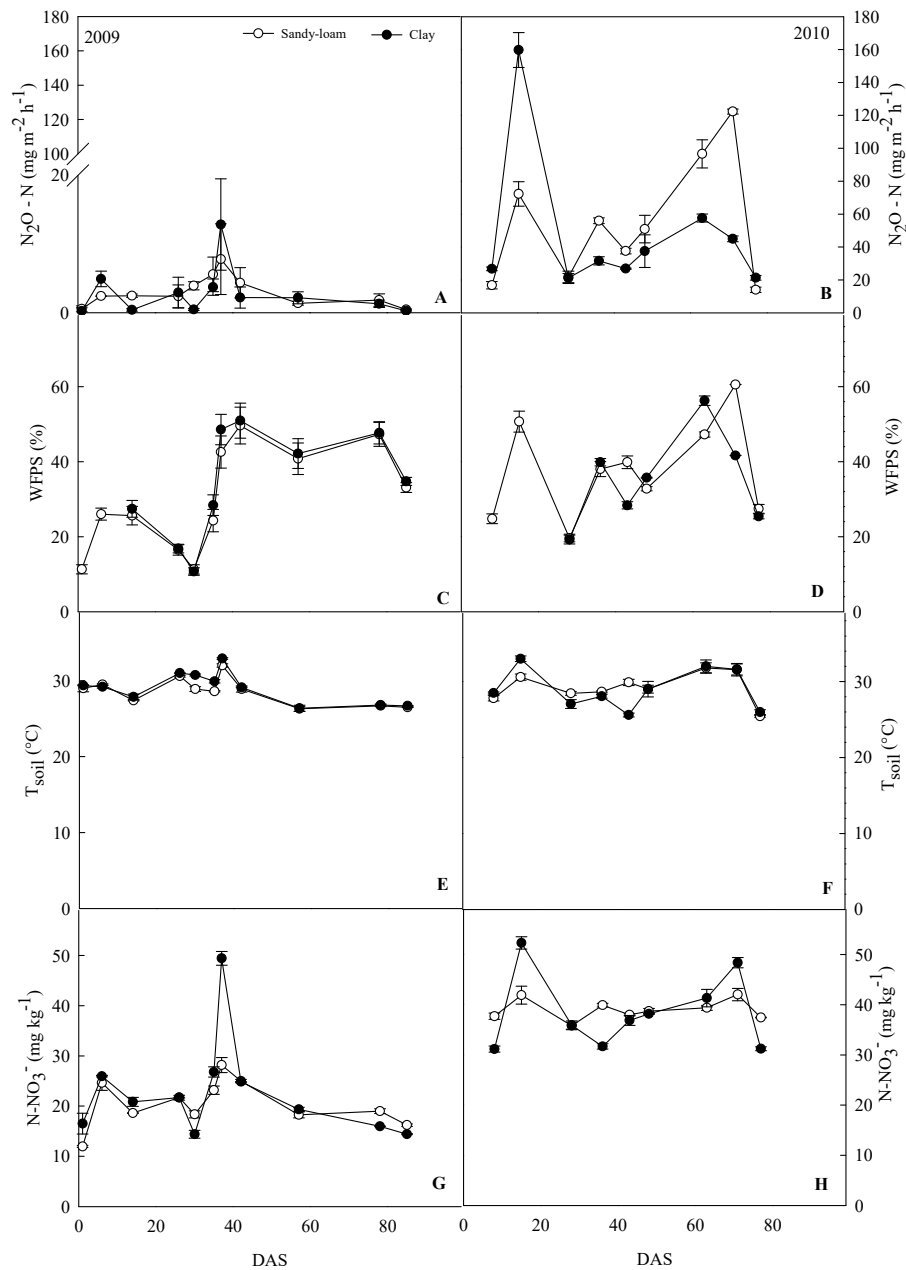
The  $\text{N}_2\text{O}$  emissions showed different trends during the two years studied (Figure 2A,B). Lower  $\text{N}_2\text{O}$  fluxes were measured during 2009 (0.57–7.8 mg m<sup>-2</sup> h<sup>-1</sup>) compared with 2010 (4.9–160 mg m<sup>-2</sup> h<sup>-1</sup>). This was due to different crop management the farmer executed in the two years, in terms of water supply, which likely also influenced the N availability in the soil. The lowest  $\text{NO}_3^-$  content in the soil found in 2009 seems to indicate a reduced dissolution of fertilizer in the soil, whereas microorganisms need nitrogen in the soil solution for their growth. It is likely that the N availability for the microbes was reduced, limiting the  $\text{N}_2\text{O}$  emissions.

Irrigation controls soil water content, which in turn controls  $\text{N}_2\text{O}$  emissions. The low water supply by irrigation that occurred soon after sowing in 2009 was inadequate to elevate the WFPS to appropriate levels so as to trigger significant  $\text{N}_2\text{O}$  fluxes in both soil types. With the second fertilization, the farmer supplied more water, and this was sufficient to elevate the WFPS up to about 50% in both sites (Figure 2C,D).

On average, the temperature of the sandy-loam soil was 28.6 °C and 29.3 °C in 2009 and 2010, respectively; in the clay soil, the temperature was an average of 29 °C for both years. These temperatures are optimal for the activity of soil microorganisms (Figure 2E,F).

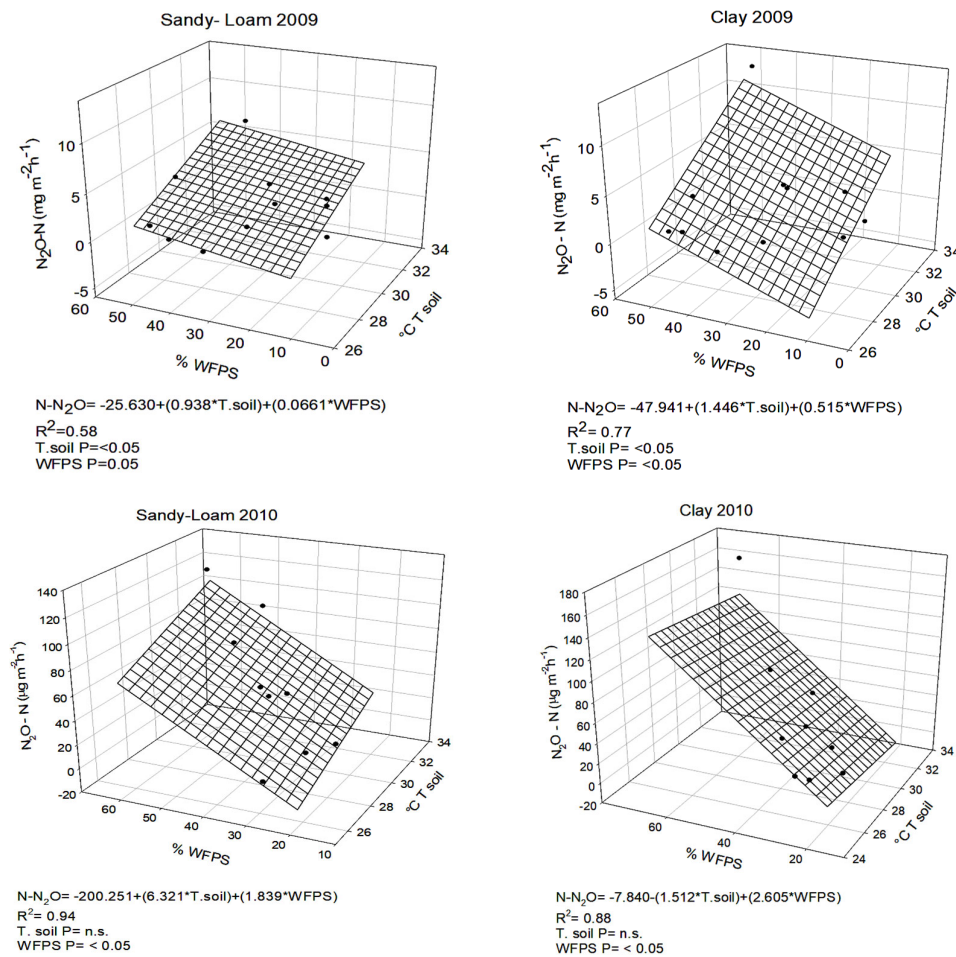
As a result, a peak in  $\text{N}_2\text{O}$  fluxes occurred at about 37 DAS, and was greater in the clay soil than in the sandy-loam soil (Figure 2A,B). This was likely because the DMPP nitrification inhibitor might have a low effectiveness in inhibiting ammonium oxidation in clay soil, as previously demonstrated by Bart et al. [34]. More studies have reported that greater soil moisture is a promoter of anaerobic conditions in the soil and, therefore, plays a more important role than denitrification, which is not affected by the inhibitory effect of DMPP [35,36]. The water amount supplied after sowing in 2010 determined greater  $\text{N}_2\text{O}$  peaks than those measured during 2009, and as a consequence, increased WFPS up to about 60% and had a greater N availability in the soil (Figure 2G,H); these peaks were greater in the clay soil compared with sandy-loam soil, proving again the role of clay particles in influencing the effectiveness of DMPP. As reported by Dobbie and Smith [37], WFPS is the main conditioning factor of  $\text{N}_2\text{O}$  emissions when the  $\text{NO}_3^-$  concentration in the soil and the temperature

are not limited. Following the second fertilization, the sandy-loam soil was leaking more nitrogen as N<sub>2</sub>O than the clay soil. In the latter, the N<sub>2</sub>O emissions peaked at about 63 DAS, whereas in the sandy-loam soil, the emission peak occurred eight days later (72 DAS). Forte et al. [38] reported lower N<sub>2</sub>O emissions from sandy-loam soil compared with clay soil in a study performed in previous years on the same field, whereas Vitale et al. [28] found a reduced leaf area in maize plants grown on a sandy-loam site compared with plants grown on a clay site. We speculate that the reduced canopy leaf area allowed for greater penetration of radiation into the deeper layers of the canopy, causing higher soil temperatures at the topmost soil layer where the fertilizer was applied, reducing the effectiveness of DMPP in inhibiting nitrification. The greater oxygen availability in the sandy-loam soil, due to a low WFPS (20–25%), promoted higher N<sub>2</sub>O emissions than in the clay soil.



**Figure 2.** (A,B) N<sub>2</sub>O-N fluxes, (C,D) WFPS, (E,F) soil temperature, and (G,H) nitrate content, measured on clay and sandy-loam sites during 2009 and 2010 years, respectively. DAS—days after sowing. Data are means ( $n = 3$ )  $\pm$  Standard Error.

Although N availability in the soil is the major driver for N<sub>2</sub>O emissions, soil moisture and temperature affect N<sub>2</sub>O emissions by regulating oxygen availability to the soil microorganisms and the microbial metabolism, respectively [39]. The different crop management that occurred between the two studied years determined differences in N<sub>2</sub>O fluxes, depending on the soil-related variables. In both years, we found a dependence of soil N<sub>2</sub>O emissions on nitrate and WFPS (Figure 3), and a positive relationship with soil temperature only in 2009. It could be stated that under well-watered conditions, the effect of temperature on N<sub>2</sub>O emissions could be masked by soil moisture. In fact, under a reduced water supply, the soil temperature had more weight than WFPS in driving N<sub>2</sub>O emissions (higher regression coefficients; Figure 3). In the present study, we also found a different trend of fluxes in relation to the soil type, which is reflected in the different dependence on soil-related variables (Figure 3). The latter seem to have more of an influence on nitrous oxide emissions in clay than in sandy-loam soil, highlighting the influence of the soil physical–chemical properties on the soil variables that drive GHGs fluxes. This result was confirmed by Tan et al. [39], who reported higher N<sub>2</sub>O emissions in clay soil than in sandy-loam soil. Other authors have also reported this information, concluding that soil texture is a critical characteristic for estimating future N<sub>2</sub>O emissions from agricultural fields [40].



**Figure 3.** Multiple linear regression for the relationship between N<sub>2</sub>O fluxes and soil-related measurements.

WFPS is the parameter that influences the contributions of the nitrification and denitrification processes in  $N_2O$  production [41]

Soil moisture controls  $N_2O$  production by nitrification and denitrification, because  $O_2$  availability is closely linked to soil water status. Nitrification is an aerobic process, and  $O_2$  is an important substrate for nitrification, whereas denitrification is an anaerobic process. WFPS drives both processes, which are characterized by different optimal WFPS. It is well known that nitrification dominates over denitrification with between 20–60% WFPS, with the optimal WFPS being within the range of 45–60%, depending on the soil texture, whereas denitrification dominates over nitrification with a WFPS higher than 70–80%, depending on the soil texture [42]. In the present study, we recorded that WFPS was always lower than 60% over the entire growing seasons. Moreover, we also found a positive relationship between  $N_2O$  fluxes and nitrate. We hypothesize that nitrification was likely the main process contributing to  $N_2O$  emission in both soil types. However, the significant contribution of denitrification at a high WFPS due to local anoxia in micro-sites, especially in clay soil, characterized by a higher capacity to retain water, is not to be excluded. These results have also been observed by Dobbie et al. [43] and Ruser et al. [44], who reported a strong increase in  $N_2O$  emissions for WFPS above 60–70%, suggesting that it was denitrification and not nitrification that was the main process involved in the emissions.

The data reported in the present study show that crop management impacts not only crop productivity, but also on the environment and climate in terms of GHGs emissions. Cropping systems need an adequate water supply by irrigation in order to achieve optimal production, and this inevitably promotes conditions into the soil triggering GHG production, as it occurred during 2010, when the system had a massive source of  $N_2O$ , on average 20 times more than in 2009 (Table 3). The careful management of irrigation could mitigate GHG emissions, allowing for adequate crop productivity and making cropping systems less impactful on the climate and environment. The use of fertilizers with an added nitrification inhibitor could represent a further strategy to mitigate GHG emissions from arable soils. In this study, fertilizer with a DMPP nitrification inhibitor was used, and during the well-watered season (2010), lower amounts than other Mediterranean cropping systems with conventional management were used [26,45].

**Table 3.** Cumulative  $N_2O$  fluxes expressed as the  $CO_2$  equivalent.

Years	Soil Texture	$N_2O$ Kg $CO_2$ Equiv
2009	SL	23.15 ± 0.44
	C	25.32 ± 0.45
2010	SL	461.18 ± 14.31
	C	520.39 ± 17.88

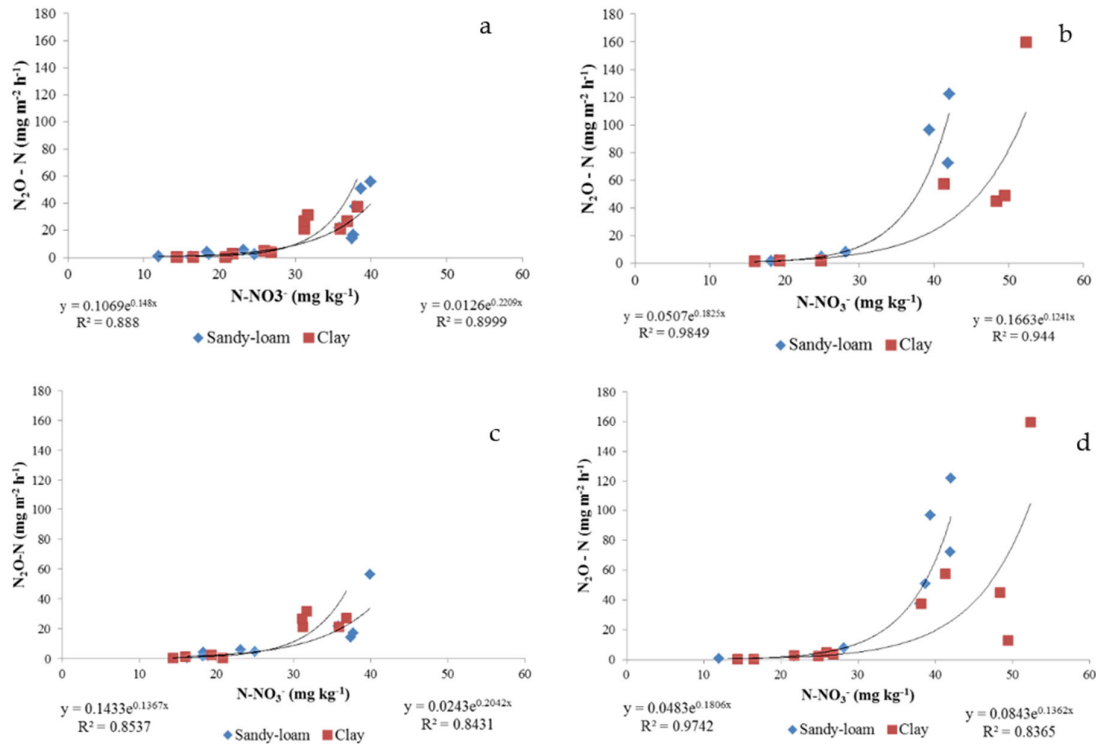
### 3.2. Regression Analysis on the Whole Dataset

The whole dataset has been divided into SL and C soils, and the response functions of  $N_2O$  flux to soil nitrate concentration, WFPS, and soil have been modelled according to simple exponential and linear functions (Figure 4).

In these regressions, it was observed that for both soils at soil nitrate concentrations below 30 mg  $NO_3^-$ -N  $kg^{-1}$ ,  $N_2O$  emissions remained basal. Forte et al. [46] also observed that the rate of nitrate in the soil under which the flux  $N_2O$  emissions remained basal is 15 mg  $NO_3^-$ -N  $kg^{-1}$ .

The  $N_2O$  flows showed an exponential correlation with the soil nitrate concentration for both WFPS ranges (Figure 4), but the slope of the  $N_2O$  flux curve was higher in the sandy-loam soil than clay soil (Figure 4b). Similar trends were also observed at both temperature ranges (25–28 °C  $T_{soil}$  and 29–32 °C  $T_{soil}$ ; Figure 4c,d). The different curve slope could be related to the  $NH_4^+$  adsorption by soil colloids [47] and the higher maize production. Moreover, considering that soil porosity and water content are key parameters influencing gas diffusion in clay soils with a high WFPS,  $N_2O$  diffusion out of the soil can become restricted, and a significant amount of  $N_2O$  can be reduced to  $N_2$  before it can escape from the soil [48].





**Figure 4.** (a)  $N_2O$  fluxes vs. soil nitrate concentration in the 10–39% WFPS range and (b) 40–60% WFPS range; (c)  $N_2O$  fluxes vs. soil nitrate concentration in the 25–28 °C  $T_{soil}$  range and in the (d) 29–32 °C  $T_{soil}$  range.

### 3.3. Above-Ground Biomass on Clay and Sandy-Loam Sites

The above-ground biomass (AGB) was different between the two years (Table 4). The AGB was lower in 2009 than in 2010 because of the lower amount of water the crops received. Differences in AGB between the two sites were found only in 2010; plants grown on the clay site had a greater dry matter than the plants grown on the sand site. These data are in contrast with data previously reported by Vitale et al. [28], who found, in a study performed in 2006, no differences in plant growth and biomass between the two sites. A possible explanation of this difference could be the higher frequency of irrigation events during 2006.

**Table 4.** Dry matter yield ( $t\ ha^{-1}$ ) of the corn grown on clay and sandy-loam sites in 2009 and 2010.

Soil Type	2009	2010
Clay	19.72 ± 2.75 c	28.70 ± 1.83 a
Sandy-Loam	18.59 ± 1.15 c	24.00 ± 1.58 b

Data are mean ( $n = 3$ ) ± Standard Error. Different letters denote significant differences between years and sites ( $p \leq 0.05$ ).

## 4. Conclusions

In our research, the different soil textures affected  $N_2O$  emissions in different manners; the highest peaks of  $N_2O$  were recorded in clay soils. However, soil moisture and temperature, as well as nitrogen availability, strongly influence  $N_2O$  emissions. Under reduced moisture, soil temperature plays a significant role in driving  $N_2O$  emissions, whereas in well-wetting soils, the effect of temperature on  $N_2O$  emission could be masked by soil moisture. At a high soil moisture, the sandy-loam soil releases  $N_2O$  emissions more fast than the clay soil. Careful management of the irrigation would mitigate GHG emissions, allowing for adequate crop productivity and making

cropping systems less impactful on the climate and environment. The use of fertilizers with added nitrification inhibitors could represent a further strategy to mitigate GHG emissions from arable soils.

**Author Contributions:** conceptualization, M.M. and V.M.; methodology, L.O. and L.V.; software, I.D.M. and L.O.; validation, I.D.M., L.O., and L.V.; formal analysis, L.O.; investigation, P.D.T., I.D.M., and L.O.; resources, M.M.; data curation, L.O. and L.V.; writing—original draft preparation, L.O. and L.V.; writing—review and editing, V.M., M.M., and L.V. All of the authors have read and agreed to the published version of the manuscript.

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