

Review

# Factors That Influence Nitrous Oxide Emissions from Agricultural Soils as Well as Their Representation in Simulation Models: A Review

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**Abstract:** Nitrous oxide (N<sub>2</sub>O) is a long-lived greenhouse gas that contributes to global warming. Emissions of N<sub>2</sub>O mainly stem from agricultural soils. This review highlights the principal factors from peer-reviewed literature affecting N<sub>2</sub>O emissions from agricultural soils, by grouping the factors into three categories: environmental, management and measurement. Within these categories, each impact factor is explained in detail and its influence on N<sub>2</sub>O emissions from the soil is summarized. It is also shown how each impact factor influences other impact factors. Process-based simulation models used for estimating N<sub>2</sub>O emissions are reviewed regarding their ability to consider the impact factors in simulating N<sub>2</sub>O. The model strengths and weaknesses in simulating N<sub>2</sub>O emissions from managed soils are summarized. Finally, three selected process-based simulation models (Daily Century (DAYCENT), DeNitrification-DeComposition (DNDC), and Soil and Water Assessment Tool (SWAT)) are discussed that are widely used to simulate N<sub>2</sub>O emissions from cropping systems. Their ability to simulate N<sub>2</sub>O emissions is evaluated by describing the model components that are relevant to N<sub>2</sub>O processes and their representation in the model.

**Keywords:** denitrification; nitrification; N<sub>2</sub>O impact factor; N<sub>2</sub>O modelling; emission factors



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## 1. Introduction

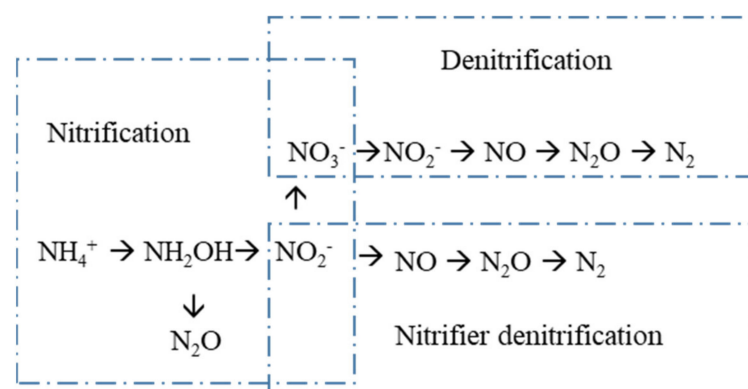
Agricultural activities are responsible for two-thirds of the total anthropogenic nitrous oxide (N<sub>2</sub>O) emissions worldwide [1]. Most of the N<sub>2</sub>O emissions stem from fertilizer and animal manure application [2–5]. A main reason for N<sub>2</sub>O emissions from agricultural soils is the application of inorganic fertilizers and/or manure when the crops cannot uptake all of the applied nitrogen (N) due to the growth stage not requiring all of it. This excess N in the soil environment leads to a lower than maximum nitrogen use efficiency [6–8]. With agricultural activities intensifying globally, N<sub>2</sub>O emissions are presently increasing at a rate of 0.25% per year [2]. Between 2001 and 2011, N<sub>2</sub>O emissions from agricultural soils increased overall, with contributions from Asia (63%), the Americas (20%), Europe (13%) and Africa (3%) [9]. In some parts of the world in recent years, a reduction in N<sub>2</sub>O emissions of 37% from 1990 levels was reported, due to both European and country specific policies on agriculture and the environment that reduced the amount of reactive nitrogen being emitted into the environment [10].

The global warming potential (GWP) is the internationally agreed method published by the Intergovernmental Panel on Climate Change (IPCC) to convert greenhouse gases

(GHG) into CO<sub>2</sub> equivalents. The GWP is defined as the time-integrated radiative forcing due to a pulse emission of a given component, relative to a pulse emission of an equal mass of CO<sub>2</sub> [8]. Based on a 100-year GWP level, the GWP of N<sub>2</sub>O emissions has been 298 times as potent as CO<sub>2</sub> as a factor in global warming [8]. N<sub>2</sub>O emissions are responsible for 6% of annual global GHG emissions in terms of CO<sub>2</sub> equivalent [11].

The IPCC also uses a metric known as the emission factor (EF) for N<sub>2</sub>O, which is calculated as kg N<sub>2</sub>O-N/kg N input, and can be used to compare N<sub>2</sub>O emissions under different conditions [12–14]. Until 2019, the default method for calculating the EF for direct N<sub>2</sub>O emissions from managed soils was to use a linear factor equal to 1% of the total N amount applied to the soil. In 2019, the IPCC revised and updated the default EF based on a much larger number of measurements available to estimate N<sub>2</sub>O emissions from managed soils [13,15]. From its Tier 1 level of methodological complexity, which corresponds to the basic method using data on fertilizer production, import/export, or sales data, the revised emission factors for direct and indirect emissions of N<sub>2</sub>O are now disaggregated by climate zone as well as by fertilizer type. In wet climates, the default EF has been set at 0.6% of organic N inputs and 1.6% of synthetic N inputs. In dry climates, the default EF has been set at 0.5% of N inputs for both organic and synthetic N [13].

The principal processes causing N<sub>2</sub>O emissions in the soil are nitrification, nitrifier denitrification, and denitrification [1,16]. These are shown in Figure 1. Nitrification is the microbial oxidation of ammonium (NH<sub>4</sub><sup>+</sup>) to nitrate (NO<sub>3</sub><sup>-</sup>), with N<sub>2</sub>O emitted as a by-product. Nitrifier denitrification is the reduction of nitrite (NO<sub>2</sub><sup>-</sup>) to nitrogen monoxide (NO), then to N<sub>2</sub>O, and finally to dinitrogen (N<sub>2</sub>). Denitrification is a two-step process whereby NO<sub>3</sub><sup>-</sup> is converted to N<sub>2</sub>O and then into inert N<sub>2</sub> under anaerobic conditions. In the denitrification pathway, NO<sub>2</sub><sup>-</sup>, NO and N<sub>2</sub>O are obligate intermediates.



**Figure 1.** Principle N transformations leading to the emission of N<sub>2</sub>O in soils.

A number of factors regulate N<sub>2</sub>O emissions during the nitrification and denitrification processes. Such factors include the soil N concentration, soil moisture, soil temperature, fertilizer application amounts, and land use management [17]. Careful consideration of these impact factors in estimating N<sub>2</sub>O emissions from agricultural soils is important to avoid overestimating the N emitted (e.g., NO<sub>x</sub> and N<sub>2</sub>, which are also produced through nitrification and denitrification processes). On the other hand, N<sub>2</sub>O emissions can also be underestimated, for example, due to the length of insufficient N<sub>2</sub>O measurements [18]. The consideration of impact factors in general is important to identify N<sub>2</sub>O emission hot spots and hot moments in a region and to identify N<sub>2</sub>O mitigation options.

Several papers have been published that classify and describe the main factors affecting N<sub>2</sub>O emissions from agricultural sites [16,19–23]. For example, Stehfest and Bouwman [18] estimated global annual N<sub>2</sub>O emissions from agricultural fields and natural vegetation by considering factors such as soil N concentration, soil organic carbon (SOC) content, soil pH and texture, fertilizer types and length of N<sub>2</sub>O emissions measurement. Weier et al. [24] analyzed the impacts of soil water content, available C and NO<sub>3</sub><sup>-</sup> concentration on denitrification in North America, as well as the N<sub>2</sub>/N<sub>2</sub>O ratio based on

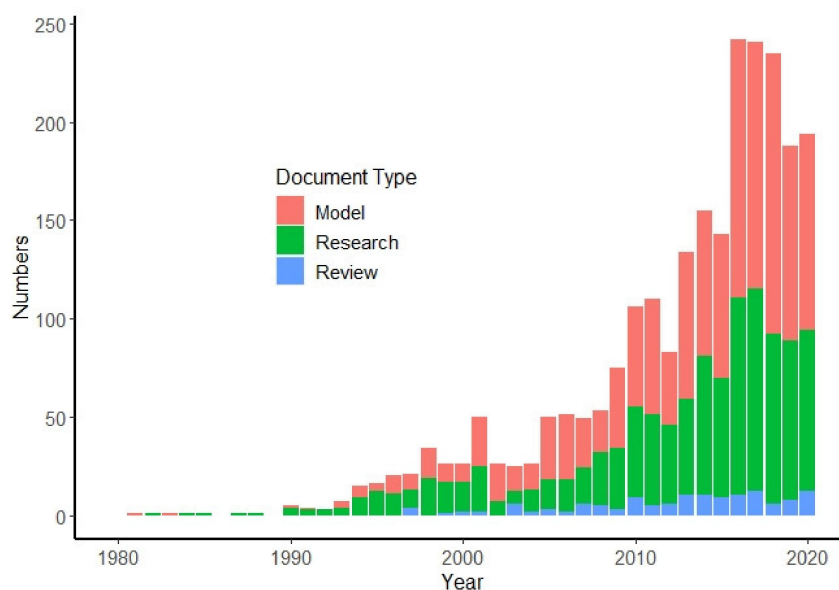
laboratory data. These laboratory data were also used by Parton et al. [25] to develop semi-empirical equations for developing an N<sub>2</sub>O emission model. In another study, Bouwman et al. [20] determined factors affecting N<sub>2</sub>O emissions and grouped them into environmental, management and measurement categories. These measurement factors are particularly important to contribute to the process of understanding N<sub>2</sub>O emissions and hence how they are represented in simulation models. Factors related to nitrification and denitrification processes have been reviewed by Cameron et al. [26], Oertel et al. [27], Signor et al. [17] and Ghimire et al. [28], while Saggar et al. [29] reviewed factors impacting denitrification and the N<sub>2</sub>/N<sub>2</sub>O ratio.

In this review we go beyond the current reviews; we review and summarize all of the relevant factors leading to N<sub>2</sub>O emissions, and we describe the impact of these factors on nitrification, denitrification and on N<sub>2</sub>/N<sub>2</sub>O partitioning. Furthermore, we identify the role of the impact factors in widely used N<sub>2</sub>O simulation models and their representation for simulating N<sub>2</sub>O effectively. Consideration of factors that influence N<sub>2</sub>O emissions is important for N<sub>2</sub>O modelling purposes, because ideally, by including as many impact factors in a model as possible, the uncertainties related to the simulation of N<sub>2</sub>O emissions may be reduced [25].

### *Methods*

For this review, we performed a literature search for relevant peer-reviewed scientific papers using the SCOPUS searchable scientific database. Using the combined terms “N<sub>2</sub>O” AND “agriculture” to search papers since 1990, we found more than 2000 published papers with the number of papers steadily increasing per year since 2005. In Figure 2, these papers are grouped into three groups: review related, research related, and model related. From these results, the review related papers were selected by using the terms “N<sub>2</sub>O”, AND “agriculture”, with “factors” and “review” to report on factors that influence N<sub>2</sub>O emissions (Table S1). Research related papers for the environmental factors were selected by using the terms “N<sub>2</sub>O”, “nitrification”, “denitrification”, “N<sub>2</sub>/N<sub>2</sub>O ratio” and each impact factor respectively (e.g., “soil N”, “SOC”, “soil temperature”). Research related papers for the management and measurement factors were searched by using the terms “N<sub>2</sub>O”, “agriculture”, “factors” and each factor respectively (e.g., “N fertilizer”, “tillage”). We obtained the model related papers relevant to the simulation of nitrification and denitrification from the above researched papers. Finally, the specific model related papers were searched with the terms “N<sub>2</sub>O”, “agriculture”, and the respective models “DAYCENT”, “DNDC” or “SWAT”. These three models were chosen because they are process-based models that dynamically respond to the impact factors we researched, they are widely used, and lastly are well documented in peer-reviewed literature.

This literature review firstly summarizes the empirical factors that influence N<sub>2</sub>O emissions from agricultural soils (Table S1). These factors are divided into three categories, as in Bouwman et al. [20]: environmental factors, management factors, and measurement factors. Measurement factors are not presented in the same depth as the environmental factors and management factors, because they do not directly influence N<sub>2</sub>O emissions, but are useful to compare to the model performance. We explain how each impact factor affects N<sub>2</sub>O emissions from the soil and also summarize their interactions. Secondly, the review describes three process-based simulation models that calculate N<sub>2</sub>O emissions and that are widely used for modelling agricultural systems. The process-based models include DAYCENT (Daily Century) [30], DNDC (DeNitrification-DeComposition) [31] and SWAT (Soil and Water Assessment Tool) [32]. We describe the most relevant formulas in the models for calculating N<sub>2</sub>O emissions. Each model contains process descriptions that consider different impact factors to describe N<sub>2</sub>O emissions from agricultural soils. We describe the factors in each model and how they are represented in the respective model.



**Figure 2.** Peer-reviewed publications on N<sub>2</sub>O and agriculture since 1990 searched in the SCOPUS database.

## 2. Factors That Influence Nitrous Oxide Emissions

The subcategories environmental factors, management factors and measurement factors are listed in Table 1. Due to the spatial and temporal heterogeneity of the environment and the agricultural management practices reported, the threshold values at which nitrification and denitrification occur across various catchment characteristics are rather different [12,29,33] and these are not reported in detail in this review. In the following sections, we provide a comprehensive explanation of how each impact factor affects N<sub>2</sub>O emissions from agricultural soils and we extract generalized relationships between each factor and N<sub>2</sub>O emissions.

**Table 1.** Impact factors that directly and indirectly influence N<sub>2</sub>O emissions from managed soils.

Environmental Factors	Management Factors	Measurement Factors
Microbial population	Fertilizer application	Length of measurement period
Soil available carbon	Tillage system	Types of measurements
Soil N concentration	Harvest and crop residues	
Soil moisture	Irrigation	
Soil texture		
Soil temperature		
Soil pH and salinity		

### 2.1. Environmental Factors

Soil microbial populations that are responsible for nitrification and denitrification processes leading to N<sub>2</sub>O emission require specific environmental conditions. These conditions have been measured to directly influence the activities of certain microbes and lead to instantaneous changes in the rates of nitrification and denitrification and in the N<sub>2</sub>/N<sub>2</sub>O ratio [29]. The environmental factors that impact N<sub>2</sub>O emissions by influencing nitrification, denitrification and the N<sub>2</sub>/N<sub>2</sub>O ratio are described in this section.

#### 2.1.1. Microbial Populations

Soil microorganisms are responsible for nitrification and denitrification processes [34,35]. Nitrification is primarily carried out by autotrophic bacteria (e.g., *Nitrosomonas* and *Nitrobacter*) [30]. Denitrification is carried out by microorganisms that include phototrophs, lithotrophs, and organotrophs that derive energy from light, inorganic N, and organic C, respectively.

The dominant de-nitrifiers in soils are organotrophs, and species of *Pseudomonas*, which predominate in the group, presumably because of their versatility and ability to compete for C substrates. Most of the other de-nitrifiers in soils are species of *Alcaligenes*, which are closely related to *Pseudomonas* [16,36].

Soil microorganisms can also influence N<sub>2</sub>O emissions by affecting the N product ratio (e.g., N<sub>2</sub>/N<sub>2</sub>O) of denitrification [34,35]. Chen et al. [37] isolated *Pseudomonas denitrificans* G1, which could remove 90%–98% of NO<sub>3</sub><sup>−</sup> and 97%–99% of NO<sub>2</sub><sup>−</sup> in 24 h under anaerobic conditions, in which *Pseudomonas denitrificans* G1 grew relatively slowly compared to under aerobic conditions, but could achieve effective denitrification so that the final product was N<sub>2</sub>.

Environmental impact factors also affect the distribution of soil microbes and microbial activity. For example, the suitable conditions for the denitrification of *Pseudomonas denitrificans* G1 to occur are a C/N ratio of 5–22, a dissolved oxygen of 0–4.68 mg/L, a salinity of 0–30 g NaCl/L, and a pH 7–9.5 [37].

### 2.1.2. Soil Available Carbon

The availability of soil C generally provides an energy source for soil microorganisms [17,38] and hence increases microbial activity. Nitrifiers and denitrifiers require a readily available C source for the oxidation of ammonium (NH<sub>4</sub><sup>+</sup>) and the reduction of NO<sub>3</sub><sup>−</sup>. The capacity for soil nitrification and denitrification to take place increases with increasing SOC content, especially the water-soluble C content, because this is the source most readily available for microbes and leads to an increased microbial activity [22,39,40]. Chen et al. [41] investigated the influence of soil C on the N<sub>2</sub>O emissions from a paddy field in southern China and found the mass fraction of N<sub>2</sub>O in the total N gas emissions were 35% and 50% with 28 mg kg<sup>−1</sup> and 300 mg kg<sup>−1</sup> of soil organic C, respectively.

The amount of organic C as a substrate for bacteria will determine whether de-nitrifiers produce mostly N<sub>2</sub> or N<sub>2</sub>O [42]. Weier et al. [24] analyzed the impacts of available carbon on the N<sub>2</sub>/N<sub>2</sub>O ratio emitted in a sand and silt loam soil in California with different treatment of glucose-C (0, 0.5, and 1.0 mg glucose-C g<sup>−1</sup> soil). The largest N<sub>2</sub>/N<sub>2</sub>O ratio (up to 549) was found at the highest treatment of glucose-C (1.0 mg glucose-C g<sup>−1</sup> soil). The findings indicate that SOC could increase microbial activity and the consumption of N<sub>2</sub>O, and other studies contain similar findings [43,44]. However, Saggari et al. [29] found, the impact of SOC on the N<sub>2</sub>/N<sub>2</sub>O ratio varies with soil N, which is supported by Köster et al. [45], who investigated N<sub>2</sub> and N<sub>2</sub>O emissions from soil with different C/N ratio. The low N<sub>2</sub>O emissions could be attributed to the promoting effect of SOC input on N<sub>2</sub>O reduction when soil N is low.

Research with biochar suggest its suppression of N<sub>2</sub>O emissions from soil depends on the biochar-induced soil C/N ratio, and potentially low subsequent soil N availability. Biochar is a carbon-rich material with a high C/N ratio that is applied in some farming systems as a soil amendment. Due to biochar's high sorption capacity and elevated recalcitrance to biodegradation, it can be used to sequester carbon [46]. Feng et al. [47] studied the impact of biochar on N<sub>2</sub>O emissions from maize fields in China and found the N<sub>2</sub>O emissions decreased with increasing biochar application rates. Cumulative N<sub>2</sub>O emissions from soils with additions of 0.5%, 1%, and 2% biochar were measured to be 120.9 g N/ha, 61.7 g N/ha and 47.6 g N/ha, respectively.

### 2.1.3. Soil N Concentration

All forms of N input into agricultural soils, such as inorganic N fertilizer, and organic N sources in the form of manures, slurry, legumes or post-harvest crop residues, represent a potential contribution to N substrates for N<sub>2</sub>O emissions [16,48,49]. During nitrification, NH<sub>4</sub><sup>+</sup> is oxidized to NO<sub>3</sub><sup>−</sup>. Thereafter the NO<sub>3</sub><sup>−</sup> is reduced to N<sub>2</sub>O by denitrifying bacteria. The nitrate molecule is the primary requirement for denitrification to take place. Soil NO<sub>3</sub><sup>−</sup> concentration is dynamic and at any given time depends on net mineralization and nitrification rates, the plant N uptake, the microbial immobilization rate and the NO<sub>3</sub><sup>−</sup>

movement through the soil by leaching and lateral flow [26]. In the literature, it is agreed that the relationship between N input and nitrification is positive. However, the proportion of N<sub>2</sub>O emissions as nitrified N varies according to the soil type and climate [50].

Several studies show that high soil NO<sub>3</sub><sup>−</sup> concentrations inhibit the reduction of N<sub>2</sub>O to N<sub>2</sub> [42,51,52]. In sand and silt loam soils in California, Weier et al. [24] performed experiments to analyze the N<sub>2</sub>/N<sub>2</sub>O ratio as affected by different soil NO<sub>3</sub><sup>−</sup> concentrations (0, 139, and 277 ug KNO<sub>3</sub>-N g<sup>−1</sup> soil), and found the highest soil NO<sub>3</sub><sup>−</sup> concentration (277 ug KNO<sub>3</sub>-N g<sup>−1</sup> soil) inhibited N<sub>2</sub>O reductase activity, which reduced the conversion of N<sub>2</sub>O to N<sub>2</sub> and resulted in a low N<sub>2</sub>/N<sub>2</sub>O ratio.

#### 2.1.4. Soil Moisture

Almost all studies have reported increased N<sub>2</sub>O emissions after the application of N fertilizer, especially with high soil moisture. Furthermore, N<sub>2</sub>O is generally emitted most rapidly when the soil has >60% water-filled-pore space (WFPS) [53–56]. The equations for calculating the WFPS are provided in the Supplementary Section (Equations (S3) and (S4)). When WFPS is greater than 60%, the soil pore water displaces the amount of available O<sub>2</sub> in the soil pores, and therefore leads to anaerobic soil moisture conditions, which are conducive to the production of N<sub>2</sub>O. Under such conditions, the soil NO<sub>3</sub><sup>−</sup> is reduced by facultative anaerobic bacteria (e.g., *Pseudomonas citronellolis*) to NO<sub>2</sub><sup>−</sup>, N<sub>2</sub>O and then N<sub>2</sub> [7,22,27,48]. However, the optimum WFPS for nitrification and denitrification processes to occur varies with soil texture [24,25].

Bateman et al. [53] studied N<sub>2</sub>O production during denitrification, autotrophic nitrification and heterotrophic nitrification in a fertilized (200 kg N ha<sup>−1</sup>) silt loam soil in England with the WFPS ranging from 20%–70%. They found that at 70% WFPS all of the N<sub>2</sub>O emitted was through denitrification, but at 35%–60% WFPS nitrification was the main process producing N<sub>2</sub>O. Ruser et al. [56] analyzed the impact of different soil moisture levels between 40% and 98% WFPS on N<sub>2</sub>O emissions from a fine-loamy soil in Germany. They found N<sub>2</sub>O emissions by denitrification increased when soil moisture rose above 60–70% WFPS.

The proportion of N<sub>2</sub> gas (N<sub>2</sub>/N<sub>2</sub>O ratio) during denitrification, however, is higher when the soil moisture is greater than 90%, because N<sub>2</sub>O is consumed under anaerobic conditions [55–57]. Ciarlo et al. [54] analyzed the influence of different soil moisture contents on the ratio of N<sub>2</sub>/N<sub>2</sub>O, which was emitted from a grassland in Argentina. The N<sub>2</sub>O/(N<sub>2</sub>O+N<sub>2</sub>) ratio was low (0–0.051) under 120% WFPS (with 100% WFPS plus a 2-cm surface water layer) and increased with decreasing soil moisture, but was still above 60% WFPS. The greatest N<sub>2</sub>O emissions occurred at 80% WFPS treatment. Friedl et al. [55] investigated the influence of different soil moisture contents on N<sub>2</sub> and N<sub>2</sub>O emissions from a subtropical dairy pasture in Australia. N<sub>2</sub> emissions exceeded N<sub>2</sub>O emissions by a factor of 8 when the soil was at 80% WFPS and by a factor of 17 at 100% WFPS.

It is not surprising that N<sub>2</sub>O emissions are higher in wet environments, e.g., during seasons with higher precipitation and higher soil water contents. For example, Choudhary et al. [58] confirmed this in a study on permanent pastureland on silty clay loam soil in New Zealand during dry and wet seasons. In another study on grain sorghum and sunflower in sub-tropical Australia, Schwenke et al. [59] measured the rate of N<sub>2</sub>O loss to be five times greater during the wet season compared to the dry season. During the drier season, the ratio of N<sub>2</sub>/N<sub>2</sub>O was 43%, whereas the ratio declined from 29% to 12% with increased N fertilizer rate during the wetter season.

The N<sub>2</sub>O emission factors are considered separately for dry and wet climates. In 2019, the IPCC revised the N<sub>2</sub>O EF so that in wet climates the default EF has been set at 0.6% of organic N inputs and 1.6% of synthetic N inputs. In dry climates, the default EF has been set at 0.5% of N for both organic and synthetic N applications [13].

### 2.1.5. Soil Texture

Finer textured soils can emit higher amounts of  $N_2O$  than sandy soils [60]. They have more capillary pores within aggregates than sandy soils, thereby holding soil water more tightly [24,25]. As a result, anaerobic conditions may be potentially more easily reached and maintained for longer periods within aggregates in finer textured soils than in sandy soils [18,20]. Weier et al. [24] and Parton et al. [25] found that denitrification generally increased as soil texture became finer and as the WFPS increased. When the WFPS decreases, the denitrification rate decreases most rapidly in the fine-textured soils, followed by medium- and coarse- textured soils. The best fit curve (WFPS/ $N_2O$  emissions) for clay soils increases very rapidly as WFPS increases over 40% and reaches the highest emission value for WFPS greater than 70% [25].

Soil texture mainly affects  $N_2O$  emissions by determining how likely it is for aerobic or anaerobic conditions in the soil to prevail [21,60,61]. Soil texture also affects  $N_2O$  emissions due to differences in SOC, N availability, and microbial population [62].

Site exposure (e.g., elevation, morphological position, plant cover) can also influence soil temperature and moisture.  $N_2O$  emissions are higher in depressions than on sloped land and ridges, due to the increased soil moisture content mostly found in low-lying lands. Yet lower air pressure found at higher elevation facilitates  $N_2O$  emissions due to a reduced counter pressure on the soil [27,48,63].

### 2.1.6. Soil Temperature

Soil temperature affects  $N_2O$  emissions by directly influencing the kinetic reaction and the growth of microbial communities (e.g., *Pseudomonas*) [7,16,19,60]. Moreover, soil temperature controls biological oxygen consumption by altering the growth of microbial communities, which leads to a depletion of soil oxygen concentrations and an increase of anaerobic status in soil [39,64].

In most studies, nitrification rates increase with rising temperature and the general peaks are around 20 to 35 °C [25,30], even though Lai et al. [65] reported that the temperature peaks for nitrification were between 35 and 40 °C and Prentice [66] reported the optimum temperature for nitrification to be 38 °C. Lai et al. [65] found that soil temperature variations have less impact on the proportion of  $N_2O$  emissions from nitrified N, when compared to the impact of variations in soil type [65].

Overall, studies show that nitrification and denitrification processes are similar with respect to temperature dependency and increase with increasing soil temperature, although Saggarr et al. [29] found no relationship between denitrification rate and soil temperature. Peak denitrification occurs between 40 and 60 °C [22,65,67]. It is worth noting that the temperature for peak nitrification and denitrification to occur may vary somewhat by climatic region [67].

Soil temperature also influences  $N_2O$  emissions by affecting the ratio of  $N_2/N_2O$  [16,22,68,69]. Maag et al. [70] found that  $N_2/N_2O$  increased exponentially with increasing temperature, which implies a linear relationship between the log ( $N_2/N_2O$ ) and temperature. Lai and Denton [67] analyzed  $N_2O$  and  $N_2$  emissions from a dairy farm in southwest Australia with different temperature levels (25 °C, 35 °C, 45 °C). The highest rate of  $N_2O$  emissions occurred at 35 °C. A decrease in  $N_2O$  emissions above 35 °C was partially attributed to an increase in  $N_2O$  reduction and  $N_2$  production. Increased  $N_2$  production at 45 °C decreased the  $N_2O/N_2$  ratio by 33% to 85%. The literature strongly agrees that the reduction of  $N_2O$  to  $N_2$  increases with increasing soil temperature.

Soil temperature also influences freeze-thaw cycles, which increase the availability and accessibility of the N in the soil and also create anaerobic conditions, and thus impact on the release of  $N_2O$  and  $N_2$  [29,71]. In some regions (e.g., in mid to higher latitudes and at higher elevations of the world), the topsoil is routinely frozen for parts of the winter and these soils can also be subject to successive freeze-thaw cycles. It has been determined that a substantial part of the total annual  $N_2O$  emissions may occur within a brief period after thawing [59]. The principal cause is the development of conditions that stimulate

anaerobic microbial activity, in particular the release of labile C and N compounds from dead microbial biomass, when soil-water content is high [49].

### 2.1.7. Soil pH and Salinity

Several studies show contradictory results when describing the impacts of soil pH on nitrification and denitrification. Clough et al. [72] examined the effect of raising the soil pH (through liming the soil) on N<sub>2</sub>O emissions from a silt loam. They found that autotrophic nitrification is limited at soil Ph < 4.5. Liming of acid soils can stimulate nitrification and has been shown to influence both the nitrification rate and the N<sub>2</sub>O flux. Denitrification rates decrease with decreasing soil pH. Scholefield et al. [52] developed a “flow-over” helium atmosphere core incubation technique to investigate mechanisms of denitrification in agricultural soils. They found that denitrification decreased with increasing soil pH within the range 5.1–9.4. In a review of the past 50 years of studying the impact of soil pH on denitrification, Šimek and Cooper [73] stated that it is not possible to generalize the relationship between pH and denitrification in soils.

The soil pH also affects the emission ratio of N<sub>2</sub>/N<sub>2</sub>O. It is well agreed that soil pH influences N<sub>2</sub>O emissions by affecting the activity of nitrifying and denitrifying bacteria in the soil [22,27,60]. The soil pH determines if NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> chemically decompose into N<sub>2</sub>O or into N<sub>2</sub>. Under acidic conditions N<sub>2</sub>O is emitted by denitrifier bacteria, such as *Pseudomonas* [42]. Therefore, a greater proportion of N<sub>2</sub>O relative to N<sub>2</sub> is emitted from acidic soils (pH < 6.0), whereas approximately equivalent amounts of N<sub>2</sub>O and N<sub>2</sub> are emitted from soils with pH 6.0 [74]. This is confirmed by Šimek et al. [75], who found that at a pH < 6.0, the only denitrification product was N<sub>2</sub>O, but at higher pH values, N<sub>2</sub> was the principal product of denitrification. They examined five mineral soils with a similar texture but with differing pHs in Czech Republic. In soils in which the pH was 8.3–8.5, the N<sub>2</sub>O/N<sub>2</sub> mole fraction was found to be about 0.024 from grey clay soils with irrigated cotton in Australia [74].

Soil salinity influences the production and consumption of N<sub>2</sub>O [76]. Wei et al. [77] conducted an experiment on a silty clay soils used to grow vegetables in China, and analyzed the impacts of different salinity levels (2, 5, 8 g/L) (NaCl and CaCl<sub>2</sub> of 1, 2.5, and 4 g/L equivalent) and fertilizer levels on N<sub>2</sub>O emissions. Compared to fresh water irrigated soil, cumulative N<sub>2</sub>O fluxes were reduced by 22.7% and 39.6% (0 kg N fertilizer), and 29.1% and 39.2% (120 kg N fertilizer) for soils irrigated with 2 and 8 g/L saline water, respectively. For soils irrigated with 5 g/L saline water, cumulative N<sub>2</sub>O fluxes were increased by 87.7% (0 kg N fertilizer) and 58.3% (120 kg N fertilizer). These results suggest that desalinating brackish water to a low salinity level (e.g., 2 g/L) before it is used for irrigation, might be helpful for mitigating soil N<sub>2</sub>O emissions.

Based on the above literature, we extracted generalized relationships between each environmental factor and N<sub>2</sub>O emissions in Table 2.

**Table 2.** The relationships between environmental factors and N<sub>2</sub>O emissions.

Processes	Soil N	SOC	Soil Moisture (Water-Filled-Pore-Space (WFPS))	Soil Temperature	Soil pH
Nitrification	+	+	~60%: +	+	Need more research
Denitrification	+	+	60–80%: +	+	Need more research
N <sub>2</sub> /N <sub>2</sub> O ratio	–	+ (depends on N)	>90%: +	+	<6.0: more N <sub>2</sub> O; =6.0: equivalent; >6.0: more N <sub>2</sub>



## 2.2. Management Factors

The type of field management plays an important role in influencing N<sub>2</sub>O emissions, especially as it determines the soil N input and thereby potentially changes the soil environmental and subsequent microbial conditions. Management factors include, for example, the amounts and the types of fertilizer application, the crops planted, and tillage operations undertaken, which also affect how much crop residues are left on the surface. This section provides a detailed description of how selected agricultural management operations influence N<sub>2</sub>O emissions.

### 2.2.1. Fertilizer Application

The influence of fertilizer on N<sub>2</sub>O emissions is related to the fertilizer type, the amount and the timing of application [59,78–80]. Nitrogen fertilizer types include synthetic (mineral) fertilizers (e.g., urea, ammonium nitrate, ammonium sulfate and NPK compound fertilizers, including slow-release fertilizers), solid organic fertilizer (e.g., organic manure, composted municipal soil waste, composted animal manure, and residues of crops), and liquid organic fertilizer (e.g., raw and digested pig slurries).

In the IPCC Refinement to the N<sub>2</sub>O Guidelines, the aggregated N<sub>2</sub>O EF is set at 1% of the amount of N applied to soils [13]. In the literature, several EF values have been measured [81] and Table 3 shows the breadth of N<sub>2</sub>O EF values reported for selected crops grown in various countries and on differing soils.

**Table 3.** The emission factor (EF) for N<sub>2</sub>O as reported in the literature.

Source	Crops	EF (%)	Country	Fertilizer Type	Soil Type	N Fertilizer (kg/ha)
Rochester et al. [74]	Cotton	1.1	Australia	Mineral N	Clay	180
Dechow et al. [82]	Grassland	0.92	Germany	Mineral N		100
	Cropland	0.9	Germany	Mineral N		0–225
Hoben et al. [83]	Corn	0.6–1.5	USA	Mineral N	Loam	0–225
Lesschen et al. [60]	Grassland	1.1	Europe	Mineral N		300–400
	Grassland	0.83	Netherlands	Organic N		
Cheng et al. [84]	Corn	0.34	China	Mineral N	Sand	266
de Moraes et al. [85]	Grassland	0.51	Brazil	Mineral N	Clay	80/100
Pal et al. [86]	Pasture	1.2	New Zealand	Organic N	Clay loam	213
Gao et al. [87]	Winter wheat	0.17	China	Mineral N	Silty loam	300
	Corn	0.53	China	Mineral N	Silty loam	250
Lebender et al. [88]	Winter wheat	0.46	Germany	Mineral N		
Shi et al. [89]	Corn	0.42	China	Mineral N	Sandy loam	300
	Corn	0.29	China	Mineral N	Sandy loam	186
Sordi et al. [90]	Pasture	0.15	Brazil	Organic N	Clay	
	Pasture	0.26	Brazil	Organic N	Clay	
Zhang et al. [91]	Corn	2.5	China	Mineral N	Clay	173
	Winter wheat	2	China	Mineral N	Clay	165
Aita et al. [92]	Corn	1.39	Brazil	Mineral N	Loam	130
	Corn	1.18	Brazil	Organic N	Loam	333
	Winter wheat	1.14	Brazil	Mineral N	Loam	110
	Winter wheat	1.55	Brazil	Organic N	Loam	269
Hinton et al. [93]	Spring barley	1.35	UK	Mineral N	Sandy loam	120
Huérffano et al. [94]	Winter wheat	0.21	Spain	Mineral N	Clay loam	180
Martins et al. [95]	Corn	0.2	Brazil	Mineral N	Sandy loam	120
Shepherd et al. [96]	Corn	1.4	China	Mineral N	Clay	150
	Wheat	0.71	China	Mineral N	Silty clay	150

Table 3. Cont.

Source	Crops	EF (%)	Country	Fertilizer Type	Soil Type	N Fertilizer (kg/ha)
	Wheat	1	China	Mineral N	Clay loam	150
Bell et al. [78]	Grassland	1.06–1.34	UK	Mineral N	Sandy loam	80–320
Van der Weerden et al. [97]	Pasture	0.6	New Zealand	Mineral N		50
	Pasture	0.3	New Zealand	Organic N		101
Harty et al. [98]	Pasture	1.49	Ireland	Mineral N	Clay/sandy loam	200
Krol et al. [99]	Grassland	0.31	Ireland	Organic N	Sandy loam	280
	Grassland	1.18	Ireland	Organic N	Sandy loam	507
Macdonald et al. [100]	Sugarcane	3	Australia	Mineral N	Sandy loam	
Roche et al. [101]	Spring barley	0.35	Ireland	Mineral N	Loam	150
	Spring barley	0.27	Ireland	Mineral N	Loam	
Faubert et al. [102]	Spring barley	0.8–3.1	Canada	Organic N	Clay loam	90–120
Forte et al. [103]	Corn	0.55	Italy	Mineral N	Sandy-clay-loam	130
Gillette et al. [104]	Corn	0.66	USA	Mineral N	Clay loam	224
	Corn	0.75	USA	Mineral N	Clay loam	246
Htun et al. [105]	Winter wheat	0.43	China	Mineral N	Silty loam	220
Laville et al. [106]	Corn	1.8	Italy	Mineral N	Sandy loam	170
Krauss et al. [107]	Winter wheat	1.64	Switzerland	Organic N	Clay	
	Grassland	0.71	Switzerland	Organic N		
Pugesgaard et al. [108]	Spring barley	0.65	Denmark	Organic N	Sandy loam	150
Xie et al. [109]	Apple orchard	1.34	China	Organic N	Sand	
Zhou et al. [110]	Wheat	1.05	China	Mineral N	Loam	0–250
Badagliacca et al. [111]	Winter wheat	~1.9	Italy	Mineral N	Clay	120
Dong et al. [112]	Corn	0.308	China	Mineral N	Clay	180
Plaza-Bonilla et al. [113]	Winter wheat	~0.57	Spain	Mineral N	Loam	0–120
Reinsch et al. [114]	Grassland	0.27	Germany	Organic N	Sandy loam	180
	Corn	0.74	Germany	Organic N	Sandy loam	180
Simon et al. [115]	Pasture	0.34	Brazil	Organic N	Clay	516
	Pasture	0.11	Brazil	Organic N	Clay	
Campanha et al. [116]	Corn	0.96	Brazil	Mineral N	Clay	0–275
Kasper et al. [117]	Corn	0.71	Austria	Mineral N	Clay loam	
Mumford et al. [118]	Pasture	0.49–1.17	Australia	Mineral N	Clay	340
Myrriotis et al. [119]	Winter wheat	0.25	UK	Mineral N		
	Spring barley	0.57	UK	Mineral N		
Shen et al. [120]	Spring barley	0.085–1.1	Canada	Organic N	Clay loam	100–800
Zhang et al. [121]	Winter wheat	0.19–0.25	China	Mineral N	Loam	420/600
	Corn	0.38–0.63	China	Mineral N	Loam	
Baral et al. [122]	Spring barley	0.53	Denmark	Mineral N	Sand	169
Cowan et al. [123]	Grassland	0.9	UK	Mineral N	Clay	20–220
Krol et al. [124]	Grassland	0.58	Ireland	Mineral N	Loam	200
Kudeyarov et al. [125]	Cereal crops	0.66–0.7	Russia	Mineral N		67
Wang et al. [126]	Corn	1.85	China	Mineral N	Clay loam	130
Pareja-Sanchez et al. [127]	Corn	0.2	Spain	Mineral N	Sandy loam	0/60/120
Yang et al. [128]	Winter wheat	0.41	China	Mineral N	Silty loam	220

The blank cells in the soil type and N fertilizer columns indicate that the EFs are the average value of different soil types and N fertilizer application. The EFs are mean values for the range of N fertilizer.

The fertilizers influence the mass of N<sub>2</sub>O emissions mainly because of the different amounts of NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and organic C contained in them. Grave et al. [129] conducted experiments to determine the effects of the N sources on soil N<sub>2</sub>O emissions from a maize-wheat rotation field in Brazil. Compared to the control experiment, cumulative N<sub>2</sub>O emissions from urea and slurry in tilled soil increased by 33% and 46%, respectively. The EFs of N<sub>2</sub>O calculated with the application of urea and slurry were 0.27% and 0.76%. Chen et al. [130] studied the impact of 13 years of nitrogen fertilization on N<sub>2</sub>O emissions from temperate grassland in northeast China, and found that the soil temperature, soil water contents, SOC and soil NH<sub>4</sub><sup>+</sup> were greatly changed during the growing season, when a significant cumulative effect of fertilizer N addition on N<sub>2</sub>O emissions was measured.

The amounts of fertilizer applied add a source of N to the soil, which contributes to N<sub>2</sub>O emissions. Bordoloi et al. [131] analyzed N<sub>2</sub>O emissions from an Indian wheat cropping system under different levels of urea (from 0 to 100 kg N ha<sup>-1</sup>). Fertilized plots had higher N<sub>2</sub>O emissions than unfertilized plots by an average of up to 174% measured in the highest fertilized treatment with 100 kg N/ha, and in which the N<sub>2</sub>O EF was 3.15%. Lebender et al. [88] conducted an experiment to analyze the impact of fertilizer application rates on N<sub>2</sub>O emissions from winter wheat in north-west Germany. Nitrogen was applied as calcium-ammonium-nitrate, with application rates ranging between 0 and 400 kg N ha<sup>-1</sup>. Over a one-year period, yield-scaled N<sub>2</sub>O emissions from the 400 kg N ha<sup>-1</sup> treatment were twice as high as from the 220 kg N ha<sup>-1</sup> treatment. The N<sub>2</sub>O EFs ranged between 0.46% and 0.53%.

The time of fertilizer application influences the efficiency of fertilizer use and crop yields. Schwenke et al. [132] investigated the impacts of the timing of N fertilizer application on N<sub>2</sub>O emissions from grain sorghum field in Australia. Compared to urea applied at sowing, delayed application of urea at booting reduced the N<sub>2</sub>O emissions by 67%–81%. However, crop N uptake, grain yield and protein content tended to be lower due to dry soil conditions during the mid-season. Applying split-N (33% sowing; 67% booting) using urea reduced N<sub>2</sub>O emissions by 59% compared to urea applied at the time of sowing, but maintained crop N uptake, grain yield and protein content. When mineral fertilizer or manure are applied before or at sowing, N<sub>2</sub>O emissions can increase because of the large pool of soil N in the early crop growth stages that cannot be assimilated by the crop, and furthermore N<sub>2</sub>O can be enhanced because of potential rainfall events, which increase the soil moisture [132].

### 2.2.2. Tillage Systems

Soil tillage results in changes in the soil structure, soil aeration, microbial activity, rate of residue decomposition and loss of soil organic matter from the system, as well as soil temperature and moisture [127,133]. It was also found that the presence or absence of tillage, the tillage period and tillage implements had an influence on N<sub>2</sub>O emissions [131,134].

Grave et al. [129] studied the effects of tillage practices on N<sub>2</sub>O emissions from a maize-wheat rotation field in Brazil. Cumulative N<sub>2</sub>O emissions were 107% higher when N was applied on the no-till soil in comparison with the tilled soil. Higher N<sub>2</sub>O emissions were measured from no-till soil in response to increased WFPS (>60%) and higher N availability (C/N around 1.58) compared with tilled soil [133]. Grass is a perennial monocotyledon plant that has a longer growing season and denser rooting system than annual crops. As such, N applied to grassland is rapidly (within a few days or weeks) taken up by the grass or immobilized in the rooting system [20,60]. Due to the absence of soil tillage in grasslands (soil aeration status), in combination with high C input by grass roots and residues and manure, the organic C content of grasslands is higher than in arable cropping systems [135].

From a vegetable field in the USA, Chen et al. [37] measured the impacts of strip till, no-till, tillage with black plastic mulch and bare-ground on N<sub>2</sub>O emissions, whereby the yield-scaled N<sub>2</sub>O emissions were 4.21%, 3.18%, 10.17%, 5.57%, respectively. Tillage with black plastic mulch promoted N mineralization, and the plastic mulch was found to increase the soil temperature, which contributed to greater N<sub>2</sub>O fluxes.

Choudhary et al. [58] evaluated the effects of continuous long-term tillage on N<sub>2</sub>O emissions from maize fields in New Zealand. Average annual N<sub>2</sub>O emissions from the 34-year and 17-year fields were 2.37 and 3.42 kg N<sub>2</sub>O ha<sup>-1</sup>, respectively. In the 34-year plots, due to continuous intensive cropping, low surface residue cover and a decreased water holding capacity, the depleted total C and N content were found to be low, which may have limited the denitrification process.

### 2.2.3. Harvest and Crop Residues

Applying crop residues to the soil generally increases N<sub>2</sub>O production mainly because the increased available organic C can be used in the N mineralization processes [108,136,137]. In addition, crop residues decomposition requires aerobic conditions, following which the drawdown of soil oxygen activates denitrification [44]. Badagliacca et al. [138] investigated the addition of wheat and fava bean residues on N<sub>2</sub>O emissions from two soils. In the clay soil with low-soil organic C (2.4%) and high pH (8.1), N<sub>2</sub>O emissions from fava bean residue-added pots were 0.81 kg ha<sup>-1</sup> and from pots added with wheat were 0.67 kg ha<sup>-1</sup>. In the sandy-loam soil with high organic C (4.3%) and low pH (6.6), N<sub>2</sub>O emissions in the pots added with wheat residue were 15.98 kg ha<sup>-1</sup> and that of the pots added with fava bean was 12.7 kg N<sub>2</sub>O ha<sup>-1</sup>.

Different crop harvesting frequencies and intensities influence the proportions of dead material that are left on the surface of the soil, which affect C and N cycling due to the biochemical composition (e.g., N concentration in plant tissues) and subsequently influence the soil microbial population and diversity [16]. Liu et al. [139] analyzed the impact of harvesting reeds on the N<sub>2</sub>O emissions from alkaline wetlands in northeast China. The annual average N<sub>2</sub>O flux on plots without harvesting was two times higher than that of the harvested plots, because the harvesting of reeds decreased the total organic C and total N. Da Silva et al. [140] studied how grazing intensity (light, moderate and heavy, i.e., 35 cm, 25 cm, and 15 cm height of grass, respectively) affects N<sub>2</sub>O emissions in grasslands in Brazil. Grazing intensity had a negative linear effect on annual cumulative N<sub>2</sub>O emissions.

### 2.2.4. Irrigation

Irrigation can include rain fed systems, high-watered systems (furrow, sprinkler and micro-sprinkler irrigation), and low-watered systems (surface and subsurface drip irrigation techniques). Irrigation influences the denitrification process by changing soil moisture and temperature, providing anaerobic conditions, and altering soil salinity [141–143]. An increase in WFPS may lead to reduced soil aeration resulting in low oxygen concentrations and anaerobic conditions, which support denitrification. An increased soil microbial activity may also lead to a decrease in the soil oxygen concentration [59,143]. The altered environmental factors could collectively affect dissolution/crystallization, oxidation/reduction, adsorption/desorption and other reactions that will finally change the production and consumption of N<sub>2</sub>O in the soil [19].

Sanchez-Martin et al. [144] carried out a field experiment to compare the difference between different irrigation systems on N<sub>2</sub>O emissions. They found that drip irrigation reduced total N<sub>2</sub>O emissions with respect to values for furrow irrigation. Tang et al. [145] studied the effects of irrigation regime on N<sub>2</sub>O emissions from a saline alkaline paddy field in northeast China. Continuous flooding irrigation kept the water depth on the soil at 3 to 5 cm. The main difference in N<sub>2</sub>O emissions was during the mature stage, in which continuous flooding emitted twice as much N<sub>2</sub>O compared to intermittent flooding. Ye et al. [146] analyzed the impact of irrigation methods on N<sub>2</sub>O emissions from vegetable soils in China. Compared to conventional furrow irrigation, N<sub>2</sub>O emissions from mulched drip irrigation and drip filtration irrigation decreased by 16.4% and 60.9%, respectively.

### 2.3. Measurement Factors

The measurement factors do not directly influence N<sub>2</sub>O emissions (although disturbance of natural conditions may occur when taking a sample, e.g., with chambers). However, the measurements are important factors to report because they affect the accuracy of the measured N<sub>2</sub>O amount and are useful for reporting on the uncertainties

of the N<sub>2</sub>O measurements. The N<sub>2</sub>O measurements are a link to our understanding of what happens in the soil and what can be modelled. The measurements therefore also influence various modelling stages (e.g., model development, parameter optimization and model validation). The effect of insufficient N<sub>2</sub>O sample measurements from the soil either spatially or temporally can lead to an overestimation or to an underestimation of N<sub>2</sub>O emissions [18,147]. The main factors that contribute to measurement uncertainties are the methods applied for measuring N<sub>2</sub>O emissions and the temporal and spatial scales of measurement [148–151].

### 2.3.1. Length of Measurement Period

Establishing a regionally-specific EF usually requires the measurement of a whole year of N<sub>2</sub>O emissions [20]. Shang et al. [147] reviewed 21 studies including N<sub>2</sub>O emissions measured both during the whole-year and during the growing-season. For most crop types, the whole year EF was significantly greater than the growing season EF. Vegetables showed the largest EF difference (0.19%) among all crops (0.07%), followed by paddy rice (0.11%). Neglecting to account for emissions from the non-growing season may underestimate the N<sub>2</sub>O emission factor by 30% for paddy fields, and almost three times that for non-vegetable upland crops.

Obtaining too few samples was highlighted in a study by Smith [142], who reviewed the relationship between the period length (days) of N<sub>2</sub>O being sampled to estimate N<sub>2</sub>O emissions from agricultural land, and found N<sub>2</sub>O emissions (% of N fertilizer applied) during three different lengths of measurement periods (>30, >100, >200 days) to be 0.6, 1.1 and 1.6, respectively.

### 2.3.2. Types of Measurement

Many methods are used to measure N<sub>2</sub>O emissions in terrestrial and aquatic environments, for example chamber methods, static core methods and micrometeorological techniques [148]. Chambers are widely used to study N<sub>2</sub>O fluxes spatially at different scales (e.g., landscape). The static core method is used locally to estimate potential N<sub>2</sub>O emissions from managed soils to capture nitrification and denitrification processes. Micrometeorological techniques are the preferred methods for measuring N<sub>2</sub>O fluxes on a landscape (field) scale [149,150].

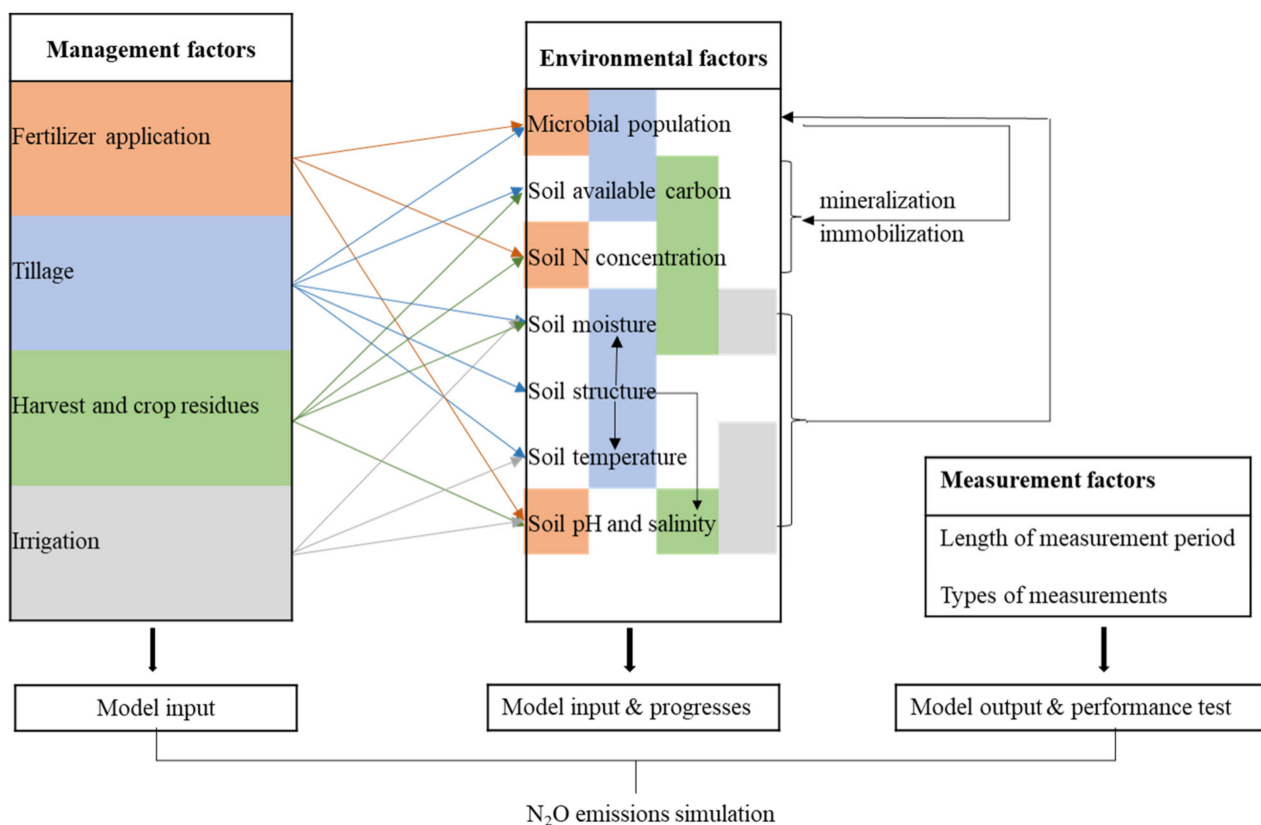
However, because of the high spatial and temporal variability of N<sub>2</sub>O emissions, each measuring method has advantages and disadvantages, even at small landscape units [22]. Chamber methods represent the most accessible techniques for measuring N<sub>2</sub>O fluxes when chambers are placed on the soil surface for short periods. Nitric oxide and N<sub>2</sub>O fluxes can be measured using open- and closed- chamber techniques [150]. The flow rate of air through the open chamber can be too high to measure differences directly between the N<sub>2</sub>O concentrations in the air streams entering and leaving the chamber, and sometimes the closed chamber is only suitable for short height crops. Micrometeorological methods have to some extent been used to measure N<sub>2</sub>O emissions from the soil, and have the advantage over chambers in terms of their spatial and temporal integration [22]. Schäfer et al. [151] reported higher N<sub>2</sub>O emissions measured by closed chambers than by micrometeorological field-scale methods. In addition, when N<sub>2</sub>O emissions are measured at the hourly time step and at small spatial scale and then upscaled to the daily time step and the field scale, N<sub>2</sub>O fluxes may be overestimated [119,151].

The uncertainties of measured N<sub>2</sub>O emissions are also high [151,152]. Schäfer et al. [151] reported the impacts of daily meteorological conditions on N<sub>2</sub>O measurement and concluded that all measurements should run from about sunset throughout the night when the atmosphere is usually more stable. Venterea [152] reported the differences of measured N<sub>2</sub>O emissions from three chambers in the same field ranging from 0.05 to 0.5 mg N m<sup>-3</sup>. These three chambers have slightly different soil bulk density, water content, temperature and pH.

For further information on a review of the strengths and weaknesses of the N<sub>2</sub>O measurement methods, the reader is referred to Groffman et al. [148,153].

#### 2.4. Summary of Factors

In this section, the factors' interactions within and between each group are depicted, to show how the three groups are connected, which is important when modelling N<sub>2</sub>O emissions. Figure 3 shows the factors' interactions within and between each group. Crops determine the amounts of N fertilizer application, irrigation, harvest frequencies and intensities, and the amounts of crop residues. Fertilizer application influences soil microbial population, soil N concentration and soil pH. Tillage systems influence kinds of soil microbial population, soil carbon, soil moisture, soil structure, and soil temperature. Harvest and crop residues influence soil C, soil N, soil moisture and soil pH. Irrigation controls soil moisture and anaerobic conditions. Microbial population, which is affected by soil moisture, soil structure, soil pH and soil temperature, influences the soil C:N ratio by mineralization and immobilization. Soil structure influences soil moisture, soil temperature and soil pH.



**Figure 3.** Schematic diagram of the impact factors on N<sub>2</sub>O emissions, their interactions, and how they may be considered in modelling N<sub>2</sub>O emissions. Color indicates which management factor affects which environmental factors.

Management factors can be considered as an input in terms of management practices into N<sub>2</sub>O simulation models. Environment factors are considered in a model either as model inputs (e.g., precipitation, air temperature, and soil properties), or as model internal processes (soil C, soil N, soil pH, and soil temperature in model time step). Data from the measurement factors are extremely useful to test the model performance.

Process-based models used to estimate N<sub>2</sub>O emissions may include a single factor or several of the above described impact factors to simulate N<sub>2</sub>O emissions, all depending on the model's complexity and level of detail in the process-representation. Careful consideration of several important factors relevant to the research question at hand when estimating N<sub>2</sub>O emissions can avoid overestimation or underestimation of N<sub>2</sub>O amounts.

### 3. Current Process-Based Simulation Models

A number of mathematical models have been developed to simulate nitrification and denitrification (Table 4) [154–167]. These models represent N<sub>2</sub>O emission processes to varying degrees, and each model has focused on one or several of the N<sub>2</sub>O impact factors outlined above, albeit to a different extent.

**Table 4.** Dynamic models used to simulate nitrification and denitrification in agricultural fields and the impact factors considered.

Model	Description	Nitrification					Denitrification					Reference
		N	SOC	WFPS	T	pH	N	SOC	WFPS	T	pH	
APEX	APEX is a field-scale model and is used to evaluate various land management strategies at a daily time step.	✓		✓	✓	✓	✓	✓	✓	✓		Williams et al. [159]
CERES_EGC	CERES-EGC is a field-scale and process-based agro-ecosystem model and is used to simulate NO <sub>3</sub> <sup>−</sup> leaching, emissions of N <sub>2</sub> O and nitrogen oxides at a daily time step.	✓		✓	✓		✓		✓	✓		Lehuger et al. [160]
Daily Century (DAYCENT)	DAYCENT is the daily time step version of the CENTURY, and is used to simulate exchanges of C, nutrients, and trace gases among the atmosphere, soil and plants.	✓		✓	✓	✓	✓	✓	✓			Parton et al. [30]
DNDC	DNDC is a field-scale and process-based model and is used to study N and C dynamics in agroecosystems at daily time step.	✓	✓	✓	✓	✓	✓	✓		✓	✓	Li et al. [31]
DRAINMOD-N II	DRAINMOD-N II is a field-scale, daily time step and process-based model and is used to simulate C and N dynamics for artificially drained soils.	✓		✓	✓		✓	✓	✓	✓		Youssef et al. [161]
EPIC	EPIC is a field-scale agroecosystem model that simulates crop production.	✓		✓	✓	✓	✓	✓	✓	✓		Gassman et al. [162]
FASSET	FASSET is used to simulate crop growth and yield, as well as daily soil N and C fluxes in the plant–soil–atmosphere continuum.	✓		✓	✓		✓		✓	✓		Chatskikh et al. [163]
SPACSYS	SPACSYS is a field-scale model and is used to simulate daily N and C emissions from arable land and grassland.	✓	✓	✓	✓	✓	✓	✓		✓	✓	Wu et al. [33]
SWAT	SWAT is a field or catchment scale, process based model and is run at the daily time step for simulating the impacts of agricultural management practices on hydrology and water quality.	✓	✓	✓	✓		✓	✓	✓	✓		Arnold et al. [32]
TRIPLEX_GHG	TRIPLEX-GHG is developed to simulate N <sub>2</sub> O emissions from global forests and grassland.	✓	✓	✓	✓	✓	✓	✓		✓	✓	Zhang et al. [164]

where N is the N concentration and T is the soil temperature. ✓ indicates the impact factor is considered.

Empirical models are not considered in this review because they can be challenging to apply outside of known conditions and thus have limited utility to test management practices or to predict the effects of future processes, such as climate change [154,156,165]. Therefore, the uncertainty of applying empirical models to conditions other than those used for their development is very high [154,156].

Process-based modelling tools have the ability to simulate environmental conditions (e.g., soil moisture and temperature), crop growth and N fluxes under different management practices at the daily time step and at different scales (e.g., field, landscape or catchment) and once the required parameters are satisfactorily calibrated and validated they are helpful in identifying emission hot-spots and hot-moments, and are also useful in assessing the effectiveness of different management options for evaluating the impacts of

climate and land use changes [141,168–171]. Compared to other process-based models in Table 4, the biogeochemical models (e.g., DAYCENT and DNDC) and the eco-hydrological model SWAT are among the most widely used models to simulate N<sub>2</sub>O emissions from agricultural systems and are well documented [30–32,172]. The SWAT model also includes the EPIC submodule, which simulates crop growth and N transport from the field [32,173]. Table 5 summarizes these three models in simulating N<sub>2</sub>O emissions from managed soils, specifically in terms of the input data required for the model, the model components, processes and the impact factors that are considered in each model [25,30,168,173]. For the SWAT model, we also include the current SWAT N<sub>2</sub>O submodules, which are reviewed in Chimire et al. [28].

**Table 5.** Summary of three process-based models in simulating N<sub>2</sub>O emissions.

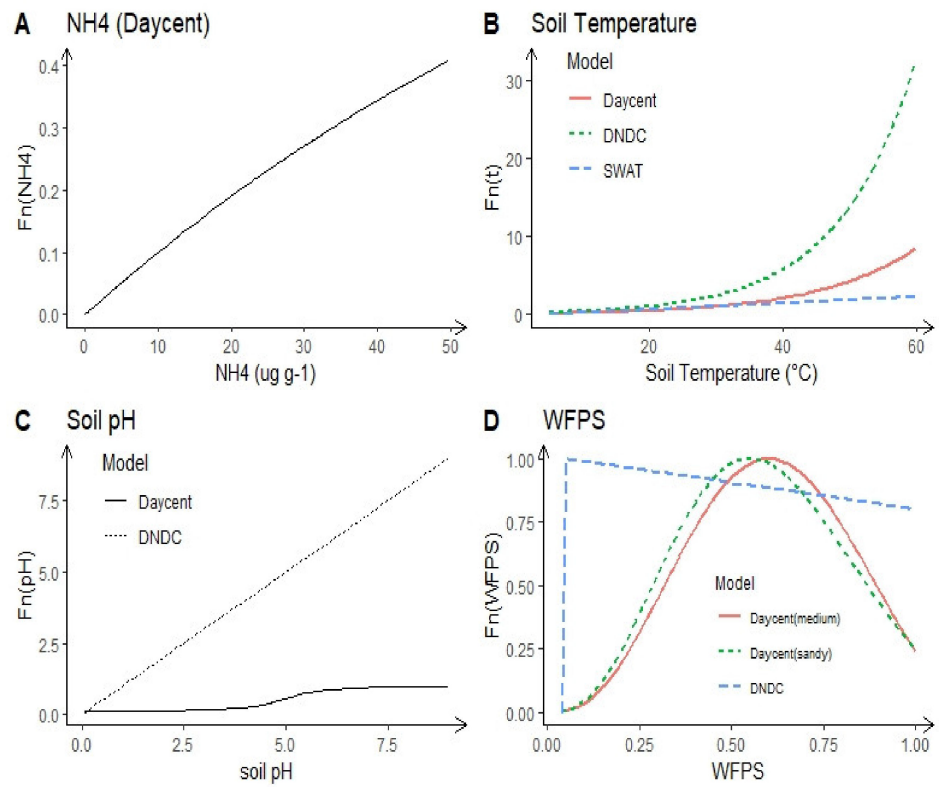
Model	Input Data	Physical Processes and Products Partitioning	Considered Environmental Factors
DAYCENT	Daily weather variables, site-specific soil properties, and land use.	Nitrification	Soil N, temperature, WFPS and pH
		Denitrification	Soil N, SOC and WFPS
		N <sub>2</sub> /N <sub>2</sub> O	Soil N, SOC and WFPS
		NO <sub>x</sub> /N <sub>2</sub> O	Soil WFPS
DNDC	Daily weather variables, soil properties, and management practices.	Nitrification	Nitrifiers, soil N, WFPS, temperature, and pH
		Denitrification	De-nitrifiers, SOC, soil N, temperature, and pH
		NO <sub>x</sub> , N <sub>2</sub>	Soil pH
SWAT	DEM, soil properties, daily weather variables, and management practices.	Nitrification	Soil N, WFPS, temperature and pH
		Denitrification	Soil N, SOC, moisture, temperature and pH

We programmed the main equations responsible for N<sub>2</sub>O emissions in the models DAYCENT, DNDC and SWAT using “R” programming language to plot and visualize the differences of the representation of each environmental factor on N<sub>2</sub>O. The results for each model are discussed below and presented in Figures 4–6. The link to related R codes refers to Supplementary materials.

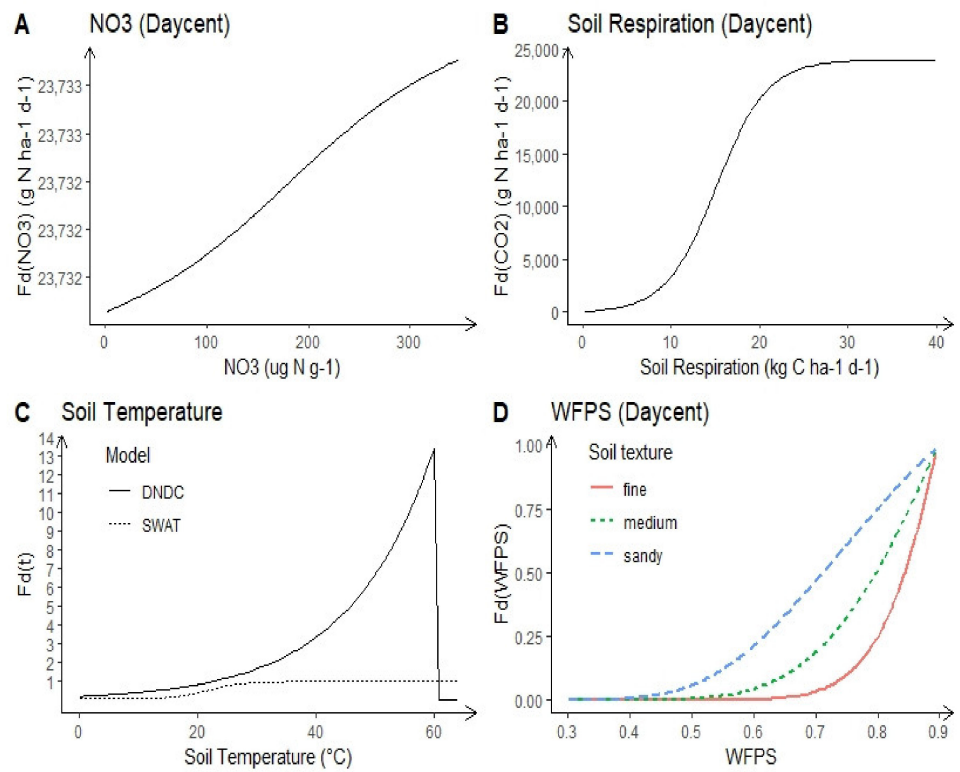
### 3.1. Nitrification Processes

The DAYCENT model calculates nitrification as a function of soil NH<sub>4</sub><sup>+</sup> level, soil temperature, soil pH, soil moisture and a N turnover coefficient (Equations (S1)–(S7)) [25]. The N turnover coefficient is a function of the soil texture, soil N fertility, N fertilizer additions, and soil management practices. In DAYCENT, the nitrification rate increases exponentially with increasing NH<sub>4</sub><sup>+</sup> levels and soil temperature (Figure 4A,B). In DAYCENT, the relationship between the nitrification rate and soil pH is the inverse of tangent function (Figure 4C). The effect of WFPS on nitrification is a function of the soil texture, whereby a maximum nitrification rate is reached for sandy soils at WFPS 0.55 and for medium texture soils at WFPS 0.61 (Figure 4D). In DAYCENT, the N turnover coefficient is treated as a site specific parameter that needs to be estimated using observed N<sub>2</sub>O data or observed potential soil N mineralized data.

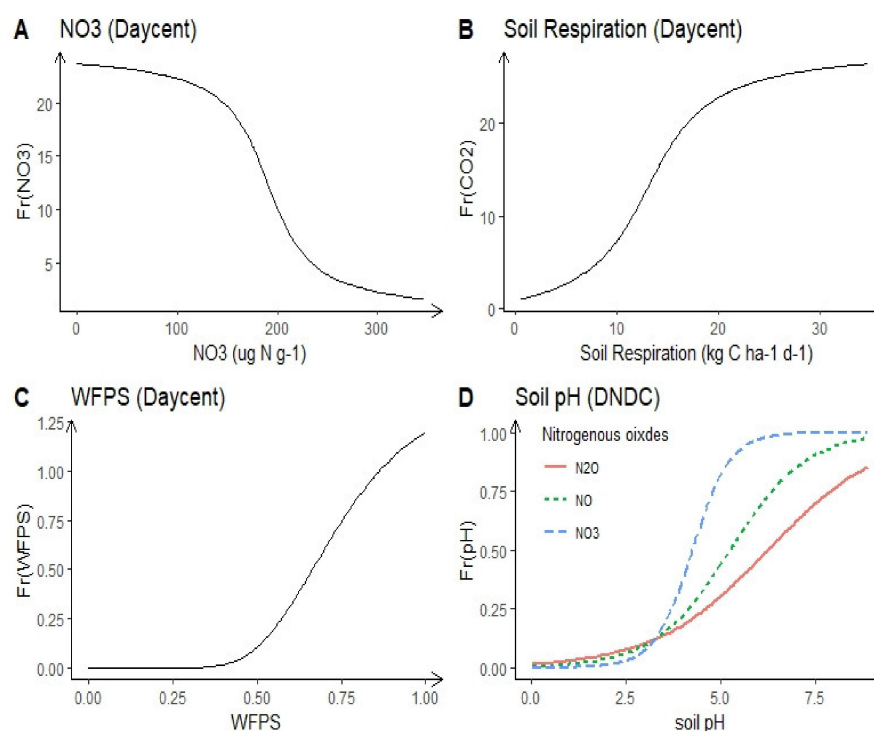




**Figure 4.** The impact of soil  $\text{NH}_4^+$  (A), soil temperature (B), soil pH (C) and WFPS (D) on nitrification processes in DAYCENT, DNDC and SWAT.



**Figure 5.** The impact of soil  $\text{NO}_3^-$  (A), soil respiration (B), soil temperature (C), and WFPS (D) on denitrification processes in DAYCENT, DNDC and SWAT.



**Figure 6.** The impact of soil  $\text{NO}_3^-$  (A), soil respiration (B), WFPS (C), and soil pH (D) on the  $\text{N}_2/\text{N}_2\text{O}$  ratio in DAYCENT and DNDC. The DNDC model shows the impact of soil pH on each nitrogenous oxide (D).

The rate of nitrification in the DNDC model is regulated by soil temperature, soil moisture, soil pH and nitrifier activity, which relies on two substrates: the dissolved organic C and  $\text{NH}_4^+$  concentration (Equations (S20)–(S27)) [136]. The nitrification rate linearly increases as the concentration of  $\text{NH}_4^+$  increases in the soil [172]. Similar to DAYCENT, the nitrification rate in the DNDC model also increases exponentially with soil temperature. However, the magnitude is much higher (Figure 4B). The effect of soil pH on nitrification is linear with a slope of 1 (Figure 4C). In the DNDC model, when  $\text{WFPS} < 0.05$ , the impact on nitrification is zero. When the  $\text{WFPS} > 0.05$ , the effect on nitrification has a negative linear association (Figure 4D).

The SWAT model considers nitrification to be a function of soil  $\text{NH}_4^+$ , soil moisture and soil temperature (Equations (S44)–(S49)) [173]. The SWAT model uses the amount of  $\text{NH}_4^+$  in each soil layer, the nitrification regulator and volatilization regulator to calculate the total amount of nitrification and ammonia volatilization, and then partitions N between the two processes. The nitrification regulator is a function of soil temperature and soil water content. The volatilization regulator is a function of soil temperature, volatilization depth and cation exchange. In SWAT, nitrification occurs only when the soil temperature exceeds  $5^\circ\text{C}$  and the correlation is linear, which is different to DAYCENT and DNDC (Figure 4B). The SWAT model calculates the impact of soil water on nitrification not by using the WFPS, but rather by using the soil water content of each soil layer, the wilting point water content, and the field capacity water content (Equations (S46) and (S47)), which vary with soil texture, climate and crop type [137]. SWAT does not take into account the changes of soil pH and therefore does not consider the impact of soil pH on nitrification.

### 3.2. Denitrification Processes

The DAYCENT model calculates denitrification to be a function of soil  $\text{NO}_3^-$ , soil respiration and the WFPS (Equations (S8)–(S11)). The impact of soil  $\text{NO}_3^-$  on denitrification is the inverse of a tangent function (Figure 5A), and the effect of soil respiration on denitrification is an exponential function (Figure 5B). Soil respiration is assumed to be cor-

related to the C substrate. The denitrification rate increases exponentially with increasing values of WFPS, and particularly when  $WFPS > 0.6$ , in all soil textures. In finer textured soil, the denitrification rate is slower at lower WFPS and only increases significantly after  $WFPS > 0.7$  (Figure 5D). The representation of the impact of soil moisture on simulated  $N_2O$  emissions fits well with the literature described in chapter 2. The DAYCENT model does not consider the impacts of soil temperature and soil pH on denitrification.

In the DNDC model, the denitrification process is a series of microbe-mediated reactions that sequentially reduce  $NO_3^-$  to  $NO_2^-$ , NO,  $N_2O$ , and finally to  $N_2$ . The rate of each reduction step is a function of denitrifiers, DOC, corresponding nitrogenous oxides, temperature, Eh and pH in soils (Equations (S28)–(S43)) [172]. The DOC and the concentration of nitrogenous oxides control the growth of denitrifiers. The relationship between soil temperature and the reduction rate is exponential when soil temperature is  $<60^\circ C$ . When soil temperature is  $>60^\circ C$ , the impact on denitrification is zero (Figure 5C). Denitrifying soil conditions are assumed if the environmental Eh drops to 500 mV or lower due to the oxygen depletion in the soil [172]. In DNDC the denitrification rate increases exponentially with increasing soil pH, and the slopes are different depending on nitrogenous oxides (Figure 6D). The impact of soil pH on simulated  $N_2O$  mimics the findings of Rochester et al. [74].

The SWAT model treats denitrification as a function of soil  $NO_3^-$ , soil organic C, soil temperature, and soil moisture (Equations (S50)–(S53)) whereby the soil organic C amount is an input value. The denitrification rate increases exponentially with increasing soil temperature (Figure 5C), but the rate never falls below 0.1. The impact of soil moisture on denitrification is based on the ratio of soil water content and the water content at field capacity, which changes with soil texture, climate and crops. The impact of soil moisture on denitrification never falls below 0.05.

### 3.3. Partitioning $N_2O$ from $N_2$

DAYCENT firstly models the total denitrification rate ( $N_2+N_2O$ ) and then partitions  $N_2$  from  $N_2O$ . It considers the  $N_2/N_2O$  ratio as a function of soil  $NO_3^-$ , soil respiration and WFPS (Equations (S12)–(S15)) (Figure 6A–C). The  $N_2/N_2O$  ratio decreases as soil  $NO_3^-$  increases (Figure 6A), and high soil  $NO_3^-$  inhibits the reduction of  $N_2O$  to  $N_2$ . The relationship of soil respiration to the  $N_2/N_2O$  ratio is the inverse of tangent function (Figure 6B) whereby the  $N_2/N_2O$  ratio increases with increasing soil respiration. When  $WFPS > 0.5$ , the  $N_2/N_2O$  ratio also exponentially increases (Figure 6C). The impact of soil  $NO_3^-$ , soil respiration and WFPS on simulated  $N_2O$  emissions in the DAYCENT model is similar to the information presented in chapter 2.

Similar to the denitrification process in DNDC, the DNDC model partitions nitrogenous oxides by sequentially reducing  $NO_3^-$  to  $NO_2^-$ , NO,  $N_2O$ , and finally to  $N_2$ .

The SWAT model does not partition  $N_2O$  from nitrification and denitrification products (e.g.,  $NO_x$  and  $N_2$ ). Some studies have been undertaken to specially develop an  $N_2O$ -submodule based on the SWAT model. Yang et al. [174] enhanced the SWAT model by directly integrating the DAYCENT model into the SWAT model. Shrestha et al. [170] developed a SWAT  $N_2O$ -submodule mainly by using equations from Parton et al. [25,30], which were used to develop DAYCENT, and added the equation for the impact of soil temperature on denitrification (Equation (S52)). Wagena et al. [175] developed a SWAT-GHG model by also using the equations from Parton et al. [25]; however, their study considered the impacts of soil  $NH_4^+$  and soil moisture on nitrification that are based on the SWAT model and not directly on Parton's equations (Equations (S44)–(S47) and (S49)). Wagena et al. [175] also developed equations for considering the impacts of soil temperature and soil pH on denitrification as well as the impacts of soil pH on the  $N_2/N_2O$  ratio (Equations (S52), (S54) and (S55)). They treat soil pH as one value for the region instead of differentiating based on soil type at the local HRU level.

Based on the above analysis, we can state that the representations of soil temperature on nitrification in DAYCENT and in DNDC are as an exponential function, while in SWAT

it is linear. Furthermore, the calculated  $N_2O$  values based on the temperature formulas in these three models vary greatly.

Equations in the models showing the relations between soil  $NH_4^+$  and nitrification in SWAT and DNDC are linear, while in DAYCENT this is exponential. The impacts of soil pH on nitrification are greater in DNDC than DAYCENT while in SWAT they are neglected. The impact of WFPS on nitrification in DNDC is negative linear whereby the maximum nitrification occurs when  $WFPS = 0.05$ , then decreases as WFPS increases. This is not in accordance with the peer-reviewed literature. However, Li et al. [31] showed DNDC simulated nitrification reasonably, whereas DAYCENT overestimated the nitrification.

Other model differences are mainly related to the partitioning of  $N_2O$ . The SWAT  $N_2O$ -submodule and the DAYCENT model firstly calculate total denitrification ( $N_2O+N_2$ ) and then partition  $N_2O$  from  $N_2$ . The DAYCENT model even partitions  $N_2O$  from  $NO_x$ . The impacts of environmental factors on denitrification and the  $N_2/N_2O$  ratio are considered separately. The DNDC model simulates each stage of denitrification explicitly and the  $NO_x$ ,  $N_2O$  and  $N_2$  amounts, which are calculated directly. The impacts of soil N, SOC and soil pH on each stage depend on different functions of nitrogenous oxides, SOC and soil pH. David et al. [176] compared simulated denitrification for a corn and soybean agroecosystem from DAYCENT, SWAT and DNDC. The DAYCENT and DNDC models, which are biogeochemistry-constructed models, are more similar to each other, and overall simulate lower denitrification fluxes compared to the agronomist-developed and crop-oriented SWAT model [176]. DAYCENT predicted an even split of 50% of denitrification for  $N_2O$  and  $N_2$ , whereas the simulated  $N_2O$  from DNDC depends on the model version and its simulated denitrification (~22–75% denitrification).

The biogeochemical DAYCENT model considers partitioning  $N_2O$  from both  $N_2$  and  $NO_x$ . In DAYCENT, the semi-empirical equations for describing the impacts of environmental factors on  $N_2O$  emissions are developed based on experimental data, and are also used to develop  $N_2O$  submodules for other models [169,174,175]. Especially, the impacts of WFPS on nitrification and denitrification are considered for different soil texture. However, the DAYCENT model does not include the impacts of soil temperature and soil pH on denitrification and the ratio of  $N_2/N_2O$ . In addition, the consideration of land management strategies is not possible in the DAYCENT model, for example, fertilizer type and placement are not represented, although the current DAYCENT model can simulate limited management events (e.g., the amounts of N input) [177].

The DNDC model is also a kinetic model, which requires some parameters that are not commonly measured in the field, for example, it is difficult to measure and/or validate soil microbial biomass [178]. Even though some researchers use crop yield to validate model simulations, the uncertainty of the simulated  $N_2O$  emissions using the DNDC model still needs to be more widely quantified [179,180].

The SWAT model is an eco-hydrological model, which can be used to simulate hydrological processes, crop growth and nutrient fluxes at the catchment scale. However, SWAT does not partition  $N_2O$  from other products (e.g.,  $NO_x$  and  $N_2$ ). Even though a few studies developed SWAT  $N_2O$  submodules, the partitioning of  $N_2O$  from  $NO_x$  is still missing in all of the current developed SWAT submodules [32,169,175]. In addition, the widely used SWAT model does not simulate the dynamics of changing soil pH, thus the impact of soil pH on nitrification and denitrification is not considered. The SWAT submodules developed specifically for  $N_2O$  emissions also treat soil pH only as one value instead of differentiating at the HRU level [175].

The DAYCENT, DNDC models and the SWAT  $N_2O$ -submodule can be used to simulate long-term  $N_2O$  emissions from agricultural soils at the daily time step and at different scales. Compared to the measured  $N_2O$  data, the models' performances are highly variable and there is little agreement in the literature. Zimmermann et al. [80] reported that DAYCENT and DNDC overestimated cumulative  $N_2O$  fluxes, while Gaillard et al. [180] reported underestimation of  $N_2O$  fluxes for both models. Fitton et al. [181] showed that DAYCENT could provide a good estimation of annual  $N_2O$  emissions. The different versions of

SWAT N<sub>2</sub>O-submodules also report a wide range of performances for simulating N<sub>2</sub>O emissions [169,175].

In addition to the simulated comparisons with measured N<sub>2</sub>O data, other environmental processes can be compared to measured data. For example, DAYCENT and DNDC can simulate crop yields well when compared to observed crop yields [118,179,181,182]. Current literature on the SWAT N<sub>2</sub>O submodule did not report on SWAT performance for simulating crop yields. However, the SWAT model is based on the EPIC submodule and indeed has the ability to simulate crop growth and crop yields [32,173].

Soil moisture is another variable that can be compared in the models. DAYCENT and DNDC had relatively poor performances for simulating soil water [80], whereas SWAT could simulate soil moisture quite well, which reflects the robust hydrological processes in the SWAT model [169].

The models' performances for simulating nitrification, denitrification and N<sub>2</sub>O emissions indicates that processes and parameters governing management practices, crop growth, and water fluxes in each model show large differences and strongly influence the simulations of soil microbes, soil N, SOC, soil temperature, soil pH and soil water availability [183,184]. These environmental factors further affect the rates of nitrification, denitrification and N<sub>2</sub>O emissions as discussed in chapter 2. Different types of field observations (e.g., soil moisture, soil temperature, soil NO<sub>3</sub><sup>-</sup> and crop yields) should be compared with simulated values to improve model performance for simulating the N-cycle and N<sub>2</sub>O emissions [180,182]. In addition, the measurement of N<sub>2</sub>O emissions (e.g., length of measurements, applied method for N<sub>2</sub>O measurement and the scales) also influence the evaluation of model performance [119,185].

#### 4. Summary & Conclusions

In this review, we group factors that influence N<sub>2</sub>O emissions into environmental factors, management factors and measurement factors. Environmental factors control the rate of nitrification and denitrification. Management factors control how much N is input into soils, and influence the environmental factors. Measurement factors contribute to our process of understanding N<sub>2</sub>O emissions, and while they do not influence N<sub>2</sub>O emissions directly, they affect the accuracy (and uncertainty) of measured N<sub>2</sub>O data, which in turn is important for model development and validation. We described how these factors influence nitrification and denitrification processes and the products of the N<sub>2</sub>/N<sub>2</sub>O ratio.

Overall, there is general agreement in the literature about the main factors that influence N<sub>2</sub>O emissions; however, the factors and the significance of their impacts on nitrification, denitrification and the N<sub>2</sub>/N<sub>2</sub>O ratio vary with soil and climate types. The impacts of environmental factors on N<sub>2</sub>O emissions and the proportion of N<sub>2</sub>O emissions from nitrified N also vary with soil and climate type, and are not sufficiently researched. The effect of soil pH and how it affects denitrification is another area which is not resolved.

We compared and analyzed the algorithms responsible for N<sub>2</sub>O simulations in DAYCENT, DNDC, and SWAT for each of the impact factors. The representation of most of the impact factors in these three models are in accordance with the literature that we reviewed, although some simulated N<sub>2</sub>O results are clearly different from the literature. Current models for simulating N<sub>2</sub>O emissions use empirical equations or values, which were developed/regressed for specific soil and climate types. For example, the proportion of N<sub>2</sub>O emissions from nitrification processes are set to a single value in the DNDC model and in the recently developed SWAT N<sub>2</sub>O submodules.

The three widely used process-based models (DAYCENT, DNDC, and SWAT) have advantages and weaknesses for simulating N<sub>2</sub>O emissions from managed soils. DAYCENT and DNDC are biogeochemical models and can be used to simulate small-scale N dynamics in soils. SWAT is an eco-hydrological model and can be used to simulate N fluxes from crop production and at the catchment scale because reactive nitrogen is highly mobile and is easily transported by water. The main disadvantages of the models include the following: a particular weakness of DAYCENT is the inability to represent land management strategies,

because N<sub>2</sub>O is mainly emitted from agriculturally managed soils. Some parameters (e.g., soil microbial biomass) included in the DNDC model are difficult to validate. The SWAT model cannot completely partition N<sub>2</sub>O from NO<sub>x</sub> and N<sub>2</sub>, and does not capture the dynamic changes in soil pH.

It is difficult to conclude which simulation model is better for representing N<sub>2</sub>O fluxes, or which model consistently overestimates or underestimates N<sub>2</sub>O emissions because of the interactions of several simulated impact factors on simulated N components in the model. Most model-based studies focus on regions where field measured data are available for model calibration and validation. We recommend a more holistic approach to model calibration/validation whereby several simulated variables related to N<sub>2</sub>O emissions in the model, such as soil NO<sub>3</sub><sup>-</sup>, soil water, or crop yields should be compared with measured data when possible, as this would improve the simulation of N<sub>2</sub>O in the soil system.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/article/10.3390/agronomy11040770/s1>. Table S1. Factors that influence N<sub>2</sub>O emissions from peer-reviewed literature. Table S2. Soil texture parameters for nitrification rate. Table S3. Soil texture parameters for denitrification rate.

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