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A dynamic model for assessing soil denitrification in large-scale natural wetlands driven by Earth observations.

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14 Abstract

- The Wetlands Soil Denitrification Model (WSDM) developed here for natural wetlands, is a physical based model that proposes: (i) the inclusion of soil moisture and temperature from satellite Earth Observations at diurnal temporal resolution, (ii) the distinction of soils under different wetland typologies (i.e., flooded forests, freshwater marshes, brackish wetlands, peatlands, and complex wetlands). Despite uncertainties involved, these two features are key
- 20 to upscale (nitrification/denitrification dynamics) in natural wetlands at landscape, regional
- and global scale. In this study, the performance of WSDM was validated with soils of flooded
- 22 forests and freshwater marshes in the central Amazonian floodplain. WSDM multiannual time
- 23 series (2012-2019) show that climate anomalies intensify denitrification events. Flooded
- 24 forests were identified with the highest annual denitrification rates. Annual denitrification and
- N_2O emissions estimated in this study are in line with previous studies.

26 Highlights

- A novel large-scale dynamic model for wetlands driven by satellite data is presented.
- Temperature and soil moisture are key to shape denitrification dynamics.
- Earth Observations data are advantageous when no field data is available.

30 Keywords

31 Nitrogen cycle, denitrification, wetlands, modelling, SMOS

1. Software and data availability

33 Name of software: Wetlands Soil Denitrification Model

- 34 Description: Wetlands Soil Denitrification Model is a parsimonious process-based model for
- 35 estimation of nitrogen denitrification fluxes in wetland ecosystems
- 36 Developers and contact information: Ahmad Al Bitar ahmad.albitar@cesbio.cnes.fr and
- 37 Columba Martinez Espinosa columba.mar.es@gmail.com
- 38 Contributors: C. Martinez-Espinosa, A. Al Bitar, J. M. Sanchez-Perez, S. Sauvage
- 39 Year first available: 2022
- 40 Program language: Python
- 41 Requirements Python3.4+; Windows, Mac OS X, or Linux; PRMS 3 or newer
- numpy (https://numpy.org/) Numerical Python library, the fundamental scientific
 python library.
- matplotlib (https://matplotlib.org/) 2D plotting library.
- scipy (https://scipy.org/) scientific python library
- basemap (https://matplotlib.org/basemap)
- 47 Program size: 9.6 MB / 4930 lines
- 48 Availability
- 49 This software is open-source and freely available since 2022 on Framagit
- 50 <u>https://framagit.org/ahmad.albitar/WSDM</u>. An online documentation to help the user going
- 51 through WSDM modules is provided <u>https://framagit.org/ahmad.albitar/WSDM/-</u>
- 52 /blob/master/README.rst

The input databases can be customized according the region of interest. For the global application the recommended databases can be found at:

- Soil characteristics database: https://www.isric.org/explore/wise-databases
- 56 Size of archive: 89,3 MB
- 57 Access form: free access
- 58 Year first available: 2016
- 59 Reference
- 60 Batjes NH 2016. Harmonised soil property values for broad-scale modelling (WISE30sec)
- 61 with estimates of global soil carbon stocks. Geoderma 2016(269), 61-68
- 62 (http://dx.doi.org/10.1016/j.geoderma.2016.01.034)
- Wetlands distribution and typologies database:
- https://www.worldwildlife.org/publications/global-lakes-and-wetlands-database-lakes and-wetlands-grid-level-3
- 66 Size of archive: 8.85 MB
- 67 Access form: free access
- 68 Year first available: 2004
- 69 Reference:
- 70 Lehner, Bernhard, and Petra Döll. "Development and validation of a global database of lakes,
- reservoirs and wetlands." Journal of hydrology 296.1-4 (2004): 1-22.
- Brightness temperature and Soil moisture catalogue:
- 73 https://www.catds.fr/Products/Available-products-from-CPDC

- 74 Access form: The CATDS-CEC Ifremer research products are freely available on FTP :
- 75 <u>ftp.ifremer.fr</u> user : ext-catds-cecos-ifremer/ password : catds2010
- 76 or ftp://ext-catds-cecos-ifremer:catds2010@ftp.ifremer.fr/
- 77 Reference:
- Al Bitar, A., Mialon, A., Kerr, Y. H., Cabot, F., Richaume, P., Jacquette, E., Quesney, A.,
- 79 Mahmoodi, A., Tarot, S., Parrens, M., Al-Yaari, A., Pellarin, T., Rodriguez-Fernandez, N.,
- and Wigneron, J.-P.: The global SMOS Level 3 daily soil moisture and brightness
- temperature maps, Earth Syst. Sci. Data, 9, 293–315, https://doi.org/10.5194/essd-9-293-
- 82 2017, 2017.

83 2. Introduction

Large scale modelling of biogeochemical cycles to quantify GHG budgets has gained importance over the last century. The increasing rate of CO_2 , CH_4 and N_2O in the atmosphere

- represent a major present and future driver of climate change and global warming (Liu and
- 87 Greaver, 2009; Pasut et al., 2021). The intensive agricultural practices and the use of N-
- fertilizers has been identified as the main source of N_2O emissions at the global scale. Current N₂O emission coming from anthropogenic origin are doubling the natural emissions (Tian et
- 89 N_2O emission coming from anthropogenic origin are doubling the natura 90 al., 2020, 2018, 2019).
- 91 In addition, fertilizers are also a major cause of eutrophication of rivers, groundwater and
- 92 oceans (Smith, 2003). Modelling of nitrogen transfer from terrestrial to aquatic ecosystems
- 93 (Boyer et al., 2006) is used to quantify nutrient carrying capacity of aquatic ecosystems and
- 94 resilience (Asaeda et al., 2000; Green et al., 2004).
- 95 Wetlands play a key role in the global nitrogen cycle (Adame et al., 2019; Martínez-Espinosa
- 96 et al., 2021), and they have been identified as large scale denitrification hotspots (Quin et al.,
- 97 2015; Thorslund et al., 2017) as they carry out complete denitrification pathways reducing
- 98 NO₃ to N₂ in four stages (Canfield et al., 2010). Quantifying where, when and how much
- 99 nitrification and denitrification occurs based only on large scale measurements remains a100 challenge.
- 101 The relative yield of the intermediates (N_2O and NO) is a function of the soil moisture, 102 nitrates availability and pH (Chen et al., 2015).
- 103 Therefore, models have become essential tools to integrate current knowledge and available
- data. Denitrification and nitrification pathways are well understood and a number of different
 approaches have been used to develop N cycling models (Adame et al., 2019; Bakken et al.,
- 2012; Burgin and Groffman, 2012; Groffman and Tiedje, 1988; Tiedje et al., 1989), yet their
 large scale suitability is still limited.
- 107 Targe scale suitability is still limited.
- 108 Wetlands Soil Denitrification Model (hereafter WSDM) was specifically conceived for 109 natural wetlands. It is established as a model with rate-controlling properties that allows
- denitrification quantification at a large scale, using satellite data. Despite all the uncertainties
- represented by satellite data, it provides data to produce temporal diurnal resolution multiyear
- 112 time series and allows access to remote locations all over the globe.
- 113 Modelling the mechanisms responsible for terrestrial N_2 emission from natural sources is still
- 114 limited. Assessment of global terrestrial N_2O emissions from natural sources vary up to a
- factor 3 and range between 3.3 and 9.0 TgN.yr⁻¹ (Ciais et al., 2014). Wetlands N_2O annual

116 contribution estimation from 1981-2010 to the global budget was $0.97 \pm 0.7 \text{ TgN.yr}^{-1}$ (Tian et 117 al., 2015). Later studies reported that natural soils contribute with 5.6 TgN.yr⁻¹ in a range of 118 4.9-6.5 TgN.yr⁻¹, and inland waters, estuaries and coastal zones contribute with 0.3 TgN.yr⁻¹ 119 (0.3-0.4 TgN.yr⁻¹) (Tian et al., 2020).

These annual estimates are insightful when comparing biomes, and to identify different 120 121 wetlands entities and their contribution to the global nitrogen cycle. Yet, this assessment does not explain the role of different inland and coastal natural wetlands (i.e. freshwater marshes, 122 flooded forest, peatlands, mangroves and saltmarshes). In addition, the annual assessment 123 does not show evidence related to the hot moments (seasonality). Investigating inter-annual 124 dynamics of denitrification and their relationship with flooding or drought events is relevant 125 for future climate scenarios, WSDM aims to contribute to filling this gap, investigating 126 denitrification exclusively in natural wetlands, and emphasizing the diversity of these 127 ecosystems with spatialized information. 128

129 3. Materials and methods

130 3.1 WETLANDS SOILS DENITRIFICATION MODEL

The WSDM was developed specifically for natural wetlands ecosystems where complete 131 denitrification occurs (Adame et al., 2019; Guilhen et al., 2020; Martínez-Espinosa et al., 132 2021). The WSDM aims to model denitrification process in wetlands soils, influenced by 133 three main physical parameters; soil moisture, temperature and nitrates availability. The 134 WSDM model simplifies denitrification process by forcing available daily spatialized data to 135 enable large scale application. A software was developed to harmonize the different databases 136 and to carry out the simulations. The model is developed in Python programming language, 137 using standard scientific computation and visualisation libraries with an open-source license. 138 The code is developed in functional approach with separate modules for pre-processing, 139 140 simulation and post-processing. The WSDM model with a brief description is available at https://framagit.org/ahmad.albitar/WSDM/ 141

142 MODEL IMPLEMENTATION

WSDM needs two kind of spatialized data. On one hand, static datasets, define the wetland 143 typology and extension, and the soil characteristics (i.e. texture, bulk density, organic carbon 144 content). On the other hand, dynamic datasets (soil moisture and soil temperature) will lead 145 the nitrification and denitrification processes. Before running the physical-model, a pre-146 processing phase is carried out. The user then has to define the Region of Interest (ROI), 147 giving two latitude and two longitude points indicating ROI limits, followed by the starting 148 and end date of the simulation period. Once these criteria are established, simulation is 149 launched. Spatial harmonization of databases is the first step, to have n-dimensional data on a 150 regular grid. Soil characteristics database - WISE30sec (Batjes, 2015) was the reference grid, 151 with a spatial resolution of 30 arcsec (1 km²), well as Global Lakes and Wetlands Database 152 (GLWD) (1 km²) (Lehner and Doll, 2004). Brightness soil temperature and root zone soil 153 moisture (Ahmad and Mahmoodi Ali, 2020; Al Bitar et al., 2017) have an original grid of 154

- 25km², therefore a linear interpolation, using (https://scipy.org/) scientific python library is
 compute in every simulation, before running the physical model.
- 157 The workflow summary WSDM processes (Figure 1). The physical model has different 158 functions that are explained in the next subsections. The limitation of the approach is detailed 159 in the discussion section.
- 160



161

Figure 1. Workflow illustration of the Wetlands Soil Denitrification Model processes flow (black arrows), the blue arrows represent the main two loops of the model. After setting up the model and defining the region of interest the simulation begins with nitrate budget generation in day_i. Nitrification will be active if soil moisture is low, if not, no nitrates will be created and no denitrification will be recorded, until that condition changes. Following the workflow, day_{i+1} soil moisture will define if nitrification or denitrification will occur. This loop will continue happeninguntil the end of the defined simulation period.

169 **NITRIFICATION**

In WSDM, nitrification is the first process, as it calculates nitrate production. The first year of the model run is used for stabilization, as the nitrate budget is created at the beginning of the run, therefore a minimum of two years of input data is needed. Nitrification is linked to the stock and evolution of organic matter in the soil, both together define soil fertility. Transported nitrates (i.e. agricultural sources) are not considered in this first version. Nitrates production (Eq. 1) is modelled as follows,

$$NO_{3 nit} = (N_{org} \cdot k_2 \cdot f_{SM})$$
 Eq. 1

where $NO_{3 nit}$ corresponds to the nitrates produced by nitrification in the local soil (mgN.kg⁻¹), given by N_{org} organic nitrogen in soil (mgN.kg⁻¹) (Eq. 2),

$$N_{org} = \frac{C_{org}}{C:N}$$
 Eq. 2

where OrgC is the organic carbon in soil (gC.kg⁻¹), and C:N is the ratio of carbon and nitrogen. The destruction of humus by mineralization is variable depending on the soil and the bacteria activity expressed by k_2 coefficient, calculated from the quantity of stable humus in the soil. The rate of mineralization is always higher in warm, humid climates, and varies from 0.5 to 3%. To adjust the k_2 coefficient according to soil texture and temperature (Eq. 3), we used the model proposed for clay soils by Girard et al., (2011),

$$k_2 = \frac{1200}{(C+200) \cdot (0.3 \cdot [CaCO_3] + 200)} \cdot \rho_b \cdot (0.2 \cdot MAT - 10)$$
 Eq. 3

184 where C and [CaCO₃] correspond to the clay (%) and carbonate content (gC.kg⁻¹) 185 respectively, ρ_b is the bulk density (kg.dm⁻³), and MAT (Mean Annual Temperature) (°C), the 186 coefficients are conversion units factors. The third term f_{SM} represents soil saturation factor 187 (Eq. 4), defined as follows,

$$f_{SM} = \frac{SM_i - SM_{res}}{SM_{sat} - SM_{res}}$$
Eq. 4
If $f_{SM} \ge 0.7, NO_{3 nit} = 0$

188 where SM_i , is the soil moisture of day (*i*) (m³.m⁻³), SM_{res} is the lowest soil moisture that 189 allows the reaction to happen, and SM_{sat} , (m³.m⁻³). A threshold indicating nitrification can 190 only happen when aerobic conditions are guaranteed. f_{SM} will be used for denitrification 191 (Eq.5), but conditioned inversely.

192 DENITRIFICATION

193 Denitrification function on WSDM was structured as the NEMIS model (Eq.5) (Hénault and 194 Germon, 2000), adapting the multi-component method (Berner, 1980) where diurnal 195 denitrification (Eq.6) is given by the potential denitrification weighted by three main 196 parameters (i.e. nitrate availability, soil moisture and temperature) adapted as follows,

$$Di_{v} = Dp \cdot f_{N} \cdot f_{SM} \cdot f_{T}$$
 Eq. 5

Where Di_{ν} is the denitrification rate in day (i), Dp is the potential denitrification rate in (mole 197 N.dm⁻³.d⁻¹) calculated from the first order kinetic model (Hunter et al., 1998). This model (Eq. 198 5), was first adapted for the hyporheic zone by Peyrard et al., (2011). Then modified and 199 tested at larger scale, to calculate the dynamic potential denitrification of flooded areas using 200 satellite data (Guilhen et al., 2020), and subsequently for daily denitrification quantification 201 202 on floodplains areas in different watershed under tropical, temperate and arctic conditions (Fabre et al., 2020). These advances were key evidence to adopt this denitrification model into 203 the WSDM as follows, 204

$$Dp = 0.8 x \cdot \rho_b \frac{1 - \varphi}{\varphi} \cdot k_{OC}[OrgC]$$
 Eq. 6

where Dp is the potential denitrification rate in (mole N dm⁻³.d⁻¹), 0.8x represent the stoichiometric proportion of nitrate consumed in denitrification compared to the organic matter used with x = 5, ρ_b is the bulk density (kg.dm⁻³), φ is the porosity (unitless), k_{oc} (d⁻¹) is organic carbon mineralization constant define for each wetland typology (Table 2), [*OrgC*] (mole.kg⁻¹) is the organic carbon available in the soil.

210 Dp is different for each wetland typology, and regulated in function of three main parameters, 211 these three unitless functions range from zero to optimal condition (one). First, f_N represents 212 nitrates soil availability (Eq. 7),

$$f_N = \frac{[NO_{3i}^-]}{[NO_{3i}^-] + K_{NO_3^-}}$$
Eq. 7

where f_N depends on the nitrates soil concentration $[NO_{3i}^-]$ (mgN.kg⁻¹) and bacteria denitrification capacity, define on the $K_{NO_3^-}$, a half saturation constant for denitrification. This constant was calibrated for wetlands ecosystems in the present study.

216 HALF SATURATION CONSTANT $k_{NO_3^-}$

217 The half saturation constant is integrated in the denitrification model in a Michaelis Menten

type function that limits the denitrification capacity, and is related to nitrates quantity

(Peyrard et al., 2011). To adjust this value to wetlands ecosystems (Eq.9), the $k_{NO_3^-}$ constant

220 was calibrated experimentally in the present study (Appendix Experimental Methodology)

using the emission results (Appendix Table A.3) as follows,

$$A = \frac{Di}{Dp}$$
 Eq. 9

where *A* is a relation factor between Dp (mgN.kg⁻¹) potential denitrification, and Di (mgN.kg⁻¹) is the control denitrification of the same soil, with no addition of nutritive solution. This factor then is substituted as f_N (Eq. 7), which allows the $k_{NO_3^-}$ to be calculated as follows,

$$k_{NO_3^-} = \frac{[NO_{3i}^-]}{A} - [NO_{3i}^-]$$
 Eq. 10

where $k_{NO_3^-}$ (mgN.kg⁻¹) is the half saturation denitrification constant cleared out from the saturation equation 7, using *A*, the unitless relation factor calculated above, as the known f_N . Then the mean $k_{NO_3^-}$ value for all the samples was stablished as the wetlands ecosystems constant (Table 2). The second term f_{SM} represents soil saturation factor, explained above (Eq. 3), conditioned as follows,

If
$$f_{SM} \leq 0.7$$
, $NO_{3 \ denit} = 0$

where a threshold indicating denitrification trigger was set at $f_{SM} = 0.7$, as denitrification can only happen when $\ge 70\%$ of water in the soil pores (Bateman and Baggs, 2005). The third term defines temperature impact on denitrification (Eq. 11),

$$f_T = e - \frac{(T_i - T_{opt})^2}{(T_i \cdot T_{opt})}$$
Eq. 11

where T_i is the temperature of the given day and T_{opt} is the optimal temperature for denitrification established as 25°C in natural ecosystems (Billen et al., 2018).

236 Denitrification Di_{v} obtained from these equations is volume based (mole N.dm⁻³.d⁻¹), in order 237 to integrate the result to the WSDM, a conversion from volume to mass (Eq. 12) was applied 238 as follows,

$$Di_m = \frac{Di_v \cdot MmN \cdot 1000}{\rho_b \frac{1-\varphi}{\varphi}}$$
 Eq. 12

where, Di_m is expressed in mgN.kg⁻¹.day⁻¹, *MmN* is the nitrogen molar mass (g), 1000 is the conversion factor g to mg, ρ_b is the bulk density (kg.dm⁻³), φ is the porosity (unitless).

Nitrates budget in the soil (Eq. 13), is calculated by integrating nitrification and denitrification
processes defined as follows,

$$NO_{3_{i+1}}^{-} = NO_{3_{i-1}}^{-} + [NO_{3_i}^{-}]_{nit} \cdot \delta t - [NO_{3_i}^{-}]_{denit} \cdot \delta t$$
 Eq. 13

where $NO_{3_{i+1}}^{-}(\text{mgN.kg}^{-1})$ is the nitrates available in the day (i+1), given by $NO_{3_{i-1}}^{-}(\text{mgN.kg}^{-1})$ that represents the nitrates that are produced but not yet consumed, $NO_{3_{i}nit}^{-}(\text{mgN.kg}^{-1})$ is

- the nitrates produced by nitrification on a given day (*i*) and $NO_{3_j denit}^{-1}$ (mgN.kg⁻¹), the nitrates
- consumed by denitrification on the same day (*i*) and δt , (day) to denote the time span. This function is activated at the end of each day, before starting the loop. WSDM continues the
- simulation until the end of the defined period.
- 249 Transformation of denitrification rates from mass to area (Eq. 14) was calculated as follows,

$$Denit_{kg,ha} = [NO_{3i}]_{denit} * \rho_b * soil_{act}$$
Eq. 14

- where $Denit_{kg,ha}$ is the total denitrification (N₂O-N+N₂-N) estimation in kgN.ha⁻¹.day⁻¹, given by $[NO_{3i}^{-1}]_{denit}$ (mgN.kg⁻¹) nitrates consumed, ρ_h is the bulk density (kg.dm⁻³), *soil_{act}* refers to
- the active soil layer, here 30 cm was used as a constant depth of the active layer.
- 253 N₂O-N₂ RATIO OUTGASSING
- N₂O emissions are highly variable in space and time, and there has not been a consensus on a methodology that responds to bottom-up or top-down scales. However, as scale increases, so does the agreement between estimates based on soil surface measurements (bottom-up approach) and estimates derived from changes in atmospheric concentration of N₂O (topdown approach) (Grosso et al., 2008).
- The IPCC provides guidelines for estimating regional and global N₂O emissions, which are calculated by multiplying N loading with the indirect emission factors (EF) (IPCC, 1996). The indirect N₂O emission factor associated with N leaching and runoff (EF₅: kg N₂O-N per kg of NO_3^- -N) incorporates three components: (i) groundwater and surface drainage (EF₅g); (ii) rivers (EF₅r); (iii) and estuaries (EF₅e). In the last IPPC report (2019), the EF₅r and EF₅e were adapted to 0.26 according to 91 data observations compiled by (Tian et al., 2019), and a mean value of the
- $265 EF_{5g}$ for ground and surface drainage was 0.60.
- N₂O emissions can be influence by several factors, yet to avoid adding up uncertainties we applied the constant ratios (Table 2) proposed for freshwater wetlands, for flooded soils and by the IPCC applied by Guilhen et al., 2020 on the Amazon Basin.
- 269 The previously explained functions are the structure of the WSDM, the variables acronyms,
- units and description are summarised in Table 1, likewise for constants presented in Table 2.
- 271

Table 1. Variables for Wetlands Soil Denitrification Model.

Variable	Units	Description
φ	-	Porosity
$ ho_b$	kg∙dm ⁻³	Dry sediment density
T_i	°C	Temperature
SM _i	$m^3 \cdot m^{-3}$	Soil saturation
SM _{res}	$m^3 \cdot m^{-3}$	Minimal soil saturation capacity
SM _{sat}	$m^3 \cdot m^{-3}$	Maximal soil saturation capacity
[OrgC]	mole kg ⁻¹	Organic carbon content
C_{org}	gC·kg ⁻¹	Organic carbon content
$[NO_{3i}]$	mgN.kg ⁻¹	Nitrates concentration
$[NO_{3i}]_{nit}$	mgN.kg ⁻¹	Nitrates in soil
$[NO_{3i}]_{denit}$	mgN.kg ⁻¹	Nitrates denitrified
MAT	°C	Mean annual temperature
C: N	-	C: N ratio

Norg

mgN.kg⁻¹

Organic nitrogen

Constant	Value	Units	Description	Reference
T_{opt}	25	°C	Optimal temperature	Billen et al., 2018
$soil_{act}$	30	cm	Soil active layer depth	Yang et al., 2019
k_{NO_3}	0.18	mgN.kg ⁻¹	Nitrate limitation constant	This study
Freshwater Marsh k_{oc}	0.062	day	Minaralization rate	Yin et al., 2019
Flooded forest k_{oc}	0.016	uay	winieranzation rate	Bridgham et al., 1998
Freshwater wetlands R _{N2O}	0.02			Scheer et al., 2020
Flooded soils R _{N2O}	0.082	-	Emission ratio	Schlesinger, 2009
IPPC generic R _{N2O}	0.1			Guilhen et al., 2020

Table 2. Constants for Wetlands Soil Denitrification Model.

3.2 WETLANDS SOILS DENITRIFICATION MODEL VALIDATION 273

The Amazon basin was selected as it is considered to have the optimal denitrification 274 conditions, with a mean annual temperature of 26.6°C with little variations; average rainfall is 275 276 2100 mm per year (Ribeiro and Adis, 1984). Amazonian floodplains are directly linked to the lateral flood pulses (Junk et al., 1989; Keizer et al., 2014). It has a very regular annual 277 bimodal flood pulse that defines a zonation along the flooding gradient of the central amazon 278 floodplains (Kubitzki, 1989). The Amazon river discharges roughly fifteen to twenty percent 279 of the world's annual continental freshwater into the ocean (Pekárová et al., 2003), and 280 Amazonian floodplain forests cover an area of more than 97,000 km² (Hamilton et al., 2002). 281 Dimensions of this basin reflects the meaning of water movement and abundance in life 282 shaping global biogeochemical cycles (Vörösmarty et al., 1989). 283

To calibrate $k_{NO_2^-}$ and validate the WSDM, a field campaign in the central Amazonian 284 floodplain (from 14th to 24th February 2020) was carried out to collect soil samples at eight 285 sampling sites. The sampling points were distributed on the three main tributaries (Negro 286 river, Solimões river and Madeira river) with different water quality. In each river, the two 287 main wetland typologies (i.e. Freshwater marsh and Flooded forest) were sampled as shown 288 289 in Figure 2.



272

Figure 2. Sampling sites distributed in the central Amazonian floodplain, Negro river (N1, N2, N3),
Solimões river (S1, S2, S3), Madeira river (M1, M2, M3). The sampling points are distributed in two
main non-permanent wetland types: floodplain (light green) and flooded forest (dark green). Wetlands
classification from Lehner and Doll, (2004).

295 The model validation was carried out in three steps: (a) static denitrification validation, comparing modelled potential denitrification and experimental denitrifier enzyme activity 296 297 (hereafter DEA) results. DEA was measured using acetylene-inhibition technique (AIT) as described and applied in several studies (Balderston et al., 1976; Koschorreck and Darwich, 298 2003; Tiedje et al., 1984, Tiedje et al., 1989) detailed methodology applied in this study is 299 presented in Appendix - Experimental Methodology. (b) dynamic denitrification validation, 300 nitrates soil budget and denitrification events were modelled using soil moisture and 301 302 temperature diurnal satellite input data from (2011-2019), extracted at the eight sampling points WSDM results of the eight sample sites annual denitrification rates are presented on 303 the Appendix Table A.4. (c) N_2O-N_2 ratio validation, $R_{N2O} = 0.02$ proposed for freshwater 304 wetlands ecosystems by Scheer et al., (2020) was applied to yearly denitrification WSDM 305 values for each soil sample (Appendix Table A.5). N₂O range emission was calculated for 306 freshwater wetlands and compared with other studies in order to validate the WSDM total 307 308 denitrification assessment (Appendix Table A.2).

309 4. Results

310 4.1 STATIC DENITRIFICATION VALIDATION

To illustrate the performance of the WSDM and the behaviour regarding the three main 311 physical parameters, three soil samples results, each from three different effluents (Negro 312 river -N1, Solimões river- S2, Madeira river- M2), are presented in the following figures. 313 Figure 3a. shows the soil saturation gradient, Figure 3b, the temperature gradient with 25°C as 314 the optimal temperature and 4°C, as the activation temperature, and Figure 3c shows the soil 315 316 nitrate pool. Complete modelled results for each sampling soil are compared to observed denitrification rates in laboratory-controlled conditions (Appendix Table A.2). The 317 observations and model outputs have a good fit (*p*-value < 0.001) PBIAS = 4.15 where 318 PBIAS is the percent bias between model and observation (Yapo et al., 1996), DEA and 319 model maximal denitrification have a Pearson coefficient of 0.68 with a p-value = 0.05. 320



321

Figure 3. Model responses to different limiting factors (a. soil moisture, b. temperature, c. nitrate
 concentration) of three sample sites (Madeira river (M2), Negro river (N1), and Solimões river (S2),
 compared to DEA laboratory mean observations (n=3).

325 4.2 DYNAMIC DENITRIFICATION VALIDATION

Three sampling points (Negro river - N1, Solimões river - S2, Madeira river - M2) are shown 326 as an example (Figure 4a-c). These time series show that each sampling points have different 327 soil moisture dynamics. For instance, M2, the sampling point influenced by Madeira river 328 (Figure 4.b) has an annual bimodal inundation dynamic, with one important denitrification 329 event per year. When soil moisture is very low, nitrification becomes inactive and the nitrates 330 331 soil budget of the soil stays constant. Low soil moisture events are present in 2012, 2015 and 2016 in the three wetland areas influenced by the three rivers. When the flooding of the plains 332 begins, the nitrate budget is rapidly consumed. In the case of the Negro river - N1 and 333 Solimões river - S2, soil saturation events are more frequent, so the nitrates budget is 334 consumed faster and there are more denitrification events per year. 335



Figure 4 a-c. Diurnal time series from 2011-2019, on the main y-axis, nitrate budget per day (kgN.ha⁻¹.day⁻¹) and total denitrification (N_2+N_2O) (kgN.ha⁻¹.day⁻¹) are represented, while daily soil moisture factor dynamics are represented. The nitrate budget represents the nitrates available in the soil on a certain date, this budget is not produced in one day by nitrification, but is the accumulation of several days, therefore is represented as an area, that is consumed by denitrification events (orange lines). When soil moisture factor is zero (black line), there is no nitrification and therefore the nitrates budget stays steady.

343 $4.3 N_2 O - N_2 RATIO VALIDATION$

The modelled annual denitrifications from 2012-2019 calculated in each sample site are grouped by wetland typology. The resulted emissions after applying the three different R_{N2O} from literature are compared with other studies in order to validate the WSDM total 347 denitrification assessment (Table 3). Yearly WSDM denitrification results for each soil348 sample are presented in Appendix Table A.5.

Table 3. Annual N₂O-N emissions with different emission ratio for freshwater wetlands and flooded soils

	Denitrification Rate			
Land cover, (\mathbf{R}_{N2O})	$(kgN_2O-N ha^4 yr^4)$	Reference		
	Mean value (range)			
Amazonian Forest	1.9	(Melillo et al., 2001)		
Palm swamp peat	0.5 to 2.6	(van Lent et al., 2015)		
Pantanal soil (day)	1.1-2.7	(Liengaard et al., 2014)		
High input cropping	2.3			
Low input cropping	1.2	Dorugian Amazon		
Shifting cultivation fallow	0.8	(Palm at al. 2002)		
Multistrata agroforestry	0.5	(Faili et al., 2002)		
Peach palm plantation	0.8			
Forest fallow control	0.8			
Freshwater marshes, (0.02)	0.95 (0.4-1.8)			
Flooded forests, (0.02)	3.8 (2.3-6.3)			
Freshwater marshes, (0.082)	3.8 (1.7-7.4)	This study		
Flooded forests, (0.082)	orests, (0.082) 15.5 (9.3-25.9)			
Freshwater marshes, (0.1)	4.6 (2.0-9.0)			
Flooded forests, (0.1)	18.9 (11.4-31.6)			
 	Range	D.f.		
Land cover	$(kgN_2O-N ha^{-1} yr^{-1})$	Keterence		
Amazonian Forest	1.4 - 24	(Davidson et al., 2001)		
Amazonian Forest	0.38-16.2	(Meurer et al., 2016)		
Freshwater marshes range	0.4 - 9.0	This study		
Flooded forests range	2.3 - 31.6	This study		

350 5 Discussion

351 5.1 MODEL PERFORMANCE WITH RESPECT TO FIELD DATA

352 The eight soil samples analysed are heterogeneous with soil properties ranging from low 353 organic carbon content (mineral soils) to rich organic soils. Even though the study area is small compared with the Amazon watershed dimension, the freshwater marshes and flooded 354 forests, (the main freshwater wetland typologies of this basin), were sampled in each of the 355 three main tributaries (i.e. Negro, Solimões and Madeira rivers). This study is not intended to 356 better understand denitrification in the Amazon, but to use Amazon soils, as examples of 357 freshwater wetlands (flooded forest and freshwater marshes) under conditions of low 358 anthropogenic impact, with a bimodal hydrological cycle. 359

These samples were key to calibrate the WSDM and were intended to model complete denitrification rates on a large scale considering wetlands heterogeneity (i.e. soil characteristics and wetland typology) as well as physical dynamics (i.e. temperature and soil moisture).

- WSDM is built up in a binary assumption, which does not allow nitrification to happen at the 364 same time as denitrification in the same point. Fixing a soil moisture threshold. This may not 365 be true when looking at the microscale, as the soil structure and the root zone has some 366 oxygen available most of the time. During wet periods, the anoxic conditions trigger three 367 different processes: denitrification, dissimilatory nitrate reduction (DNRA) and Anammox. 368 369 The WSDM, in its current configuration, does not simulate these two processes, and considers 370 denitrification as the main path in wetlands, this assumption is endorsed by previous studies (Adame et al., 2019). 371
- 372 Due to the lack of *in situ* data of N_2O emission in the selected area of interest, experiments 373 were carried out in controlled conditions (optimal temperature and saturation) allowing 374 bacterial activity to be isolated and quantify nitrate consumption exclusively. This 375 experimentation was key for the calibration and validation of the WSDM. Simulated 376 denitrification has a good fit (PBIAS: 4.15) compared with denitrification values observed in 377 controlled laboratory conditions (i.e. optimal temperature, saturated soil and limited nitrates) 378 (Appendix Table A 2)
- 378 (Appendix Table A.2).
- Flooded forest samples influenced by Negro river (N1, N3) have high organic carbon content, yet the recorded emissions are unlike. The difference lies in the concentration of nitrates in
- the soil. When there is nitrates surplus in soils the enzyme (*nosZ*) in charge of converting the N₂O to N₂ (the last step of denitrification) is withdrawn (Glass and Silverstein, 1999). This withdrawal is frequently observed in agricultural fields, where fertilizers are added and the
- type of irrigation used is flooding (Burgin and Groffman, 2012; Liu and Greaver, 2009).
- Flooded forest soil sample (N1) influenced by the Negro river located downstream of the city of Manaus recorded a N₂O emission rate of 0.32 ± 0.1 gN.kg⁻¹.h⁻¹, which is two times higher than four of the other soil samples (N3, S1, M1 and M2). These four sites register a ratio that favours N₂. On the other hand, flooded forest (N3), registered the highest N₂ emission rate $(0.23 \pm 0.02$ g N kg⁻¹ h⁻¹).
- N1 and N3 samples are examples of high potential denitrification rates of Amazonian wetlands soils. Extensive fertilizer use in this watershed will have a negative effect in wetlands denitrification, as concentration of nitrates from exogenous sources will increase the budget of nitrates produced by nitrification, that in turn will increase denitrification event intensity (fold-4) and N₂O emissions (Weier et al., 1993;Blackmer and Bremner, 1978; Pärn et al., 2021). A surplus of nitrates also affects ecosystem functionality, promotes eutrophication and biodiversity may be threatened (Huang et al., 2017; Smith, 2003).
- 397 Despite the importance of quantifying anthropogenic influence in natural wetlands, this
 398 version of the WSDM does not aim to calculate denitrification rates of anthropogenic input
 399 effects, but to identify physical parameters that shape the denitrification capacity of each
 400 wetland ecosystem, and assess these dynamics.
- The major contribution of WSDM, is that simulated denitrification is influenced by wetland vegetation typology. The influence of the vegetation in wetlands has been reported previously by Alldred and Baines, (2016), they calculated that the presence of plants increased denitrification rates by 55% on average, but they also acknowledge the need to differentiate plant communities. The WSDM modelled these two factors, including a wetland typology that

406 assumes a classification of wetlands ecosystems based on their vegetation structure (i.e. trees407 or herbs).

The link between vegetation and bacterial processes such as denitrification can be delicate. 408 The interaction occurs in the root areas, on a very local scale and depends on many physical 409 and chemical aspects. Denitrification emission ratio depends on many local variables and it 410 can exhibit drastic changes (i.e. pH, nitrate concentration). Acetylene-inhibition technique 411 412 (AIT) has limitations regarding the N₂O:N₂ emission ratio, and it has been shown to be inaccurate when recording low denitrification rates such as in groundwater. Nevertheless, AIT 413 allows an estimation of total denitrification at high temporal resolution and on small spatial 414 scales, with limited workload and costs involved (Felber et al., 2012). A stable isotope 415 416 approach might have been a preferable method to identify N₂ emissions. However, we had reservations concerning detection limits and how well the enriched solution would be 417 distributed through the soil column. 418

Therefore, in the case of the WSDM the optimal compromise between accuracy and the available information was to link wetland typology to carbon decomposition rate (k_{OC}). This immediately implies the presence of bacterial community activity and integrates the different kinds of organic matter available. This correlation was validated with the denitrification rates observed in laboratory analysis, confirming that flooded forest samples had higher denitrification rates than freshwater marshes (both in optimal conditions).

425

5.2 COMPARISON WITH EARLIER MODELLING APPROACHES

The precedent denitrification model estimates a total denitrification $(N_2-N + N_2O-N)$ rates at the Amazon floodplains from 38.8 to 142.5 kgN.ha⁻¹.yr⁻¹ with a spatial grid of 25 km² (Guilhen et al., 2020). The WSDM has a wider range (20.36 - 315.90 kgN.ha⁻¹.yr⁻¹), this difference is a consequence of model set up, the current version is sensitive to different organic carbon decomposition rates, soil moisture gradient, as well as nitrates limitation, calculated in 1 km² grid, constraints that were missing in the previous version.

The WSDM assumed that annual input flux of carbon is greater than losses (respiration; harvesting, export, burial). Consequently, carbon budget is set constant but not unlimited. Other studies had modelled variable carbon input (Fabre et al., 2020; Guilhen et al., 2020; Peyrard et al., 2011) showing that carbon is not a limiting factor but it can enhance the denitrification signal. This assumption is compensated by the mineralization rate of organic carbon (K_{OC}), which is specific for each kind of simplified wetland ecosystem typology.

The WSDM current version does not calculates $N_2O:N_2$ ratio yet. The different N_2O rate productions (Table 3), suggest that ratio (0.02) for freshwater wetlands proposed by Scheer et al., (2020) applied to the WSDM denitrification results, gives a N_2O-N total contribution within the range of what has been reported in low impacted Amazonian soils by other studies.

442 This estimation should be taken as an indicator and could be improved by field measurements

- 443 with other methodologies as ¹⁵N isotopic tracers (Bergsma et al., 2001). Additionally, Pärn et
- al., (2021) reported by *in situ* measurements that the Peruvian palm peat swamp is a hot spot
- and that the emission ratio change depending on the season. They reported that March (the main peak) has low N_2O emissions, and very high N_2 potential. On the other hand, in

- 447 September the emission rate has a higher N_2O production ratio. The same pattern was 448 observed in the modelled time series, regarding the activation of denitrification, however the 449 WSDM in the current version does not calculate seasonal $N_2O:N_2$ ratios, but this evidence 450 could serve for developing a $N_2O:N_2$ ratio function.
- Relevant research has been done on this topic, on a large scale the Global N₂O Model 451 Intercomparison Project (Tian et al., 2018) presented a spatialized global-scale N₂O estimate 452 453 by making a comparative study of a dozen of hydrodynamic models that model the global nitrogen and carbon cycles. The resulted model, the Dynamic Land Ecosystem Model 454 (DLEM), assesses the pre-industrial emissions (CO₂, CH₄ and N₂O) and the current trend, on 455 a yearly, monthly and daily basis from 1901 to 2010 with a spatial resolution of $0.5^{\circ} \times 0.5^{\circ}$. 456 457 This model exposes the anthropogenic impact, main pollution sources and the consequences towards the biosphere. This model also takes into account different ecosystems and divides 458 wetlands into four categories (seasonal grass wetlands, seasonal forest wetlands, permanent 459 grass wetlands and permanent forest wetlands). 460
- 461 Likewise, DNDC (DeNitrification DeComposition) model is a powerful tool to evaluate N_2O
- 462 production, consumption and transport in agricultural soils, it was later modified and adapted 463 to other ecosystems. Wetland-DNDC (Gilhespy et al., 2014) was adapted to calculate carbon 464 emissions (CO_2 and CH_4). These two models have been improved by the scientific 465 community for several years, and they are currently a very robust approach to local GHG 466 emissions, and water dynamics. Both models have an empirical base that operate at watershed 467 scale and demand copious input datasets, that may not be available for several tropical 468 wetlands.
- 469 WSDM, is complementary to both models, takes into account different wetlands ecosystems 470 based on the vegetation structure, but with a simplified approach that is useful at large scale. 471 The results are given in terms of total denitrification, aiming to contribute with a particular 472 vision of natural wetlands and their positive role in the global nitrogen cycle This natural 473 wetland function via complete denitrification is often overlooked. The total denitrification 474 account non-harmful emissions (N₂), which implies the subtraction of nitrate flux into aquatic 475 ecosystems (i.e. rivers, lakes, coastal areas).

476 6 Conclusion

The WSDM main contribution is that it considers wetlands diversity, and calculates 477 denitrification in a diurnal basis while remaining parsimonious, giving a dynamic spatialized 478 479 assessment that identifies hot moments and hot spots. WSDM total denitrification can be used as an indicator tool for prioritizing conservation areas, or wetlands ecosystems that must be 480 studied in depth. The WSDM was developed for a large-scale approach, as it does not require 481 a watershed-based model. The main drivers of the model are soil moisture and temperature 482 483 input data which have been identified as key for modelling the nitrate budget, and denitrification activation-deactivation dynamics at diurnal basis. Modelling these dynamics is 484 a tool in wetlands areas where field data is not available yet. These results may be indicators 485 486 of possible scenarios when the anomalies will repeat and/or intensify. In future, this model can be applied at different scales (continents or regions) as well as in different watersheds at 487 different climatic regimes (i.e. boreal or temperate). 488

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696 Appendix

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697 Experimental methodology

Soil samples of each site were collected, conserved at 4 °C, transported to Toulouse, France 698 for further analysis. Sixty grams of each soil type were divided into three 125 ml glass flasks, 699 having ~ 20 g per flask (n=3 each soil type). Biological activity was re-established in stored 700 701 soils by incubating 48 hours at 25°C and 20 ml of deoxygenated water was added, having a saturated water-filled pore space. Each container was sealed with a screw-up lid in which a 702 703 septum had been fitted for gas sampling. Weight of the glass flasks before, and after adding the soil sample and water were taken. The gas chromatograph was used in parallel with the 704 G200 N₂O device for quantifying N₂O emission from soil activity in the control records as 705 emissions were low. For the potential denitrification concentrations recorded were within the 706 recording range of the real-time device (G200) (>1 ppm), therefore, it was used as the only 707 reading device for the rest of the experiments. To achieve potential denitrification rates, soil 708 709 cores were incubated during three hours at 25°C, under anaerobic condition, replacing the 710 headspace with helium (He), 20 ml of acetylene (C₂H₂) was added to each flask at the beginning of incubation. To identify the nitrate soil saturation linked to potential 711 denitrification, five different treatments with progression of nutrient solutions (CH₃ COOH 712 713 and KNO₃) were applied.

Concentrations are shown in Table A.1 and were applied from 1 to 5. The measurement 714 principle of total denitrification (the sum of $N_2O + N_2$ fluxes), in AIT treated soil samples, 715 assumes that every N₂ molecule produced from completed denitrification which would 716 normally be emitted from the soil system, remains in the form of N₂O, which is detected in 717 our laboratory set-up by gas chromatography. A N₂O content of the headspace was 718 719 determined every half an hour within the following three hours. Soil characteristics (NO₃⁻ content, Org Carbon content, bulk density, porosity) and the mean values (n=3) for each soil 720 721 sample were done, are reported in Table A.2.

	Treatment	Vol added (ml)		Nitrogen Solution	Carbon Solution	mg N	mg C
		Ν	С	(mg/L)	(mg/L)		
-	1	5	0	100	100	0.5	0
	2	5	10	100	100	0.5	1
	3	(0.2	10000	10000	2	2
	4	(0.5	10000	10000	5	5
	5		1	10000	10000	10	10

Table A.1	Concentration	of nitrates	and carbon	solution	applied for	DEA	identification
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Between treatments, soil samples were left for 24 hours in aerated conditions before applying the next treatment. Once all the treatments were completed, the flasks were dried out in an oven at 100 °C for 24h. After that, the weight of each flask was measured. The dry samples were sieved and two grams of these homogenized samples were ignited at 500°C for 24h to obtain the organic matter content by weight difference. Pore space and bulk density were determined gravimetrically on volume samples assuming a measured particle density of 2.613 g cm⁻³. Potential denitrification rates were calculated from the linear increase of the N₂O content in the flask and expressed as $\mu g N_2 O g^{-1} h^{-1}$. All data is expressed per gram of sediment on a dry basis. The total N₂O production (Eq. 1) was calculated by the N₂O gas (g) fraction and N₂O liquid (l) fraction measured in ppm as follows,

$$N_2 O_t = N_2 O_g + N_2 O_l$$
 Eq. 1

and then converted to $\mu g N_2 O gas$ (Eq.2) and liquid (Eq. 3) as follows,

$$N_2 O_g = \frac{\frac{(2,211 \cdot 10^{-8} \cdot M_{ppm}) - (4,35 \cdot 10^{-9})}{0,00468}}{1,817 * 10^{-3}} \cdot 1000$$
 Eq. 2

$$N_2 O_l = (1,536 * 10^{-9}) \cdot M_{ppmv} \cdot W_v \cdot 10^6$$
 Eq. 3

where M_{ppm} is a density fraction is expressed in part per million of air (ppm) and M_{ppmv} refers to part per million in volume of solution (ppmv; 1 ppmv = 1 µL/L), W_v water volume was calculated with the difference between the dry sample and wet sample weight.

The N-N₂O (Eq. 4), N- N₂O+N₂ (Eq. 5) and N-N₂O (Eq. 6) production ratio were calculated in dry sediment basis as follows,

$$k_{N-N_2O} = \frac{N_2O_t}{Ds} * \frac{28}{44}$$
 Eq. 4

Eq. 5

If C₂H₂ added,

$$k_{N-N_2O+N_2} = \frac{N_2O_t}{Ds} * \frac{28}{44}$$

$$k_{N-N_2} = k_{N-N_2O+N_2} - k_{N-N_2O}$$
 Eq. 6

739 where k_{N-N_20} refers to the production rate of N₂O (µg N g⁻¹ h⁻¹) when there is no inhibition

with acetylene, and Ds is the dry soil weight (g), when acetylene is applied then the N₂O ratio

recorded is $k_{N-N_2O+N_2}$ which is the sum of (N₂ and N₂O) and is also expressed in µg N g⁻¹ h⁻¹, then k_{N-N_2} refers only to the N₂ production ratio (µg N g⁻¹ h⁻¹), as subtraction of the two previous equations.

- 744 **Results**
- 745 Static validation

 k_{NO} gu) 707 7N, -N +N,O-\$5.0 9 147,893.15 9660369 A S. E. (µmolN.kgu 9770.44 000.52 4 .003 3 0.003 0.001 0.003 0.00g I ũ 0 8 0

Table A.3. Soil samples properties and parameters used for c

C/N ratio Koc	16.17	<u>{</u> (4;1)	95096	$0.122 \\ 0.068 \\ 0.068 $	100 24	0.000	9.371	0.004	ð:264
Porosity [0rgC]	0.85	gGk <u>\$</u> 7	199.28	0.18 19:74	8 9. FG	603572	$^{40.59}_{-5.59}$	12.66	0.64
)rganic [arhon g.kg ⁻¹]	190.28	0918 ¹	19:43	80.05 80.05	030	40,40B	12.63	0.19	0.0 1

Table A.2. 746 Deni 747 trific ation rates from the Ama zon centr al flood plain wetla 748 nds soil samp les (labo rator уcontr olled cond ition s) and mod elled with WS DM

749 Dynamic validation results

ion annual

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mary of observed and modelled denitrification.

Model in mean nitr	$01\frac{2}{\mathrm{kg}}$	128	a -1.yr28	195	315	90	49.	114	20.
Ta ble	mual rate 2	12(806(0)82)	kg%o-N.h	20940-5 21	436. D6 .3	25.9 ^{92.77} .4	60.64.0	7.9.89.7	25.12
A.5 Su	ha ⁻¹ day hiteral	31(0.72) ¹	258.25	1069 b22 8 2.6	144 1.9 29	31.6 ⁶²¹¹ ∮3	106484.62	$^{11.4}_{389.230}$	1480.55
$\begin{array}{c} \text{mm} \\ \text{ary} \\ \text{of} \\ N_2 \\ O \end{array}$	kg N ₂ -N + N ₂ O-N	2.46	N.ha ⁻¹ .yr ⁻¹	7 4.54 \$	0 3.3	0 + 6.52	\$ 10.18	5 3.64	2.31

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* 2011 w. N led, as it is the first year of the model and the nitrate pool is building up, the model and the nitrate pool is building up, the model and the nitrate pool is building up.

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у	2	0.0		0.2	0.0	0.8(0.19	0.4	0.5	0.5	0.1	
and	<u>.</u>	Ŭ										
yea	Kgda	.28	18	14		.16		37	42		.66	64
rly	1 ale	2)90	-1 0.	17	_	68 (~	00	6.4	~	1 12	0.
basi	III 2	0.08	day	0.8	0.0	2.99	0.69	1.5(1.99	2.13	0.4]	
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