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

Authors

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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 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 forests and freshwater marshes in the central Amazonian floodplain. WSDM multiannual time series (2012-2019) show that climate anomalies intensify denitrification events. Flooded forests were identified with the highest annual denitrification rates. Annual denitrification and N₂O emissions estimated in this study are in line with previous studies.

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.

Keywords

Nitrogen cycle, denitrification, wetlands, modelling, SMOS

1. Software and data availability

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

- 42 • numpy (<https://numpy.org/>) - Numerical Python library, the fundamental scientific
43 python library.
- 44 • matplotlib (<https://matplotlib.org/>) - 2D plotting library.
- 45 • scipy (<https://scipy.org/>) - scientific python library
- 46 • 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 <https://framagit.org/ahmad.albitar/WSDM>. An online documentation to help the user going
51 through WSDM modules is provided [https://framagit.org/ahmad.albitar/WSDM/-](https://framagit.org/ahmad.albitar/WSDM/-/blob/master/README.rst)
52 [/blob/master/README.rst](https://framagit.org/ahmad.albitar/WSDM/-/blob/master/README.rst)

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

- 55 • 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>)

- 63 • Wetlands distribution and typologies database:
64 [https://www.worldwildlife.org/publications/global-lakes-and-wetlands-database-lakes-](https://www.worldwildlife.org/publications/global-lakes-and-wetlands-database-lakes-and-wetlands-grid-level-3)
65 [and-wetlands-grid-level-3](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,
71 reservoirs and wetlands." *Journal of hydrology* 296.1-4 (2004): 1-22.

- 72 • 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 <ftp.ifremer.fr> user : ext-catds-cecos-ifremer/ password : catds2010
76 or ftp://ext-catds-cecos-ifremer:catds2010@ftp.ifremer.fr/

77 Reference:

78 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.,
80 and Wigneron, J.-P.: The global SMOS Level 3 daily soil moisture and brightness
81 temperature maps, *Earth Syst. Sci. Data*, 9, 293–315, [https://doi.org/10.5194/essd-9-293-](https://doi.org/10.5194/essd-9-293-2017)
82 2017, 2017.

83 2. Introduction

84 Large scale modelling of biogeochemical cycles to quantify GHG budgets has gained
85 importance over the last century. The increasing rate of CO₂, CH₄ and N₂O in the atmosphere
86 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-
88 fertilizers has been identified as the main source of N₂O emissions at the global scale. Current
89 N₂O emission coming from anthropogenic origin are doubling the natural emissions (Tian et
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-Espinoza
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 a
100 challenge.

101 The relative yield of the intermediates (N₂O 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
104 data. Denitrification and nitrification pathways are well understood and a number of different
105 approaches have been used to develop N cycling models (Adame et al., 2019; Bakken et al.,
106 2012; Burgin and Groffman, 2012; Groffman and Tiedje, 1988; Tiedje et al., 1989), yet their
107 large 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
110 denitrification quantification at a large scale, using satellite data. Despite all the uncertainties
111 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 N₂ emission from natural sources is still
114 limited. Assessment of global terrestrial N₂O emissions from natural sources vary up to a
115 factor 3 and range between 3.3 and 9.0 TgN.yr⁻¹ (Ciais et al., 2014). Wetlands N₂O 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 $4.9\text{-}6.5 \text{ TgN.yr}^{-1}$, and inland waters, estuaries and coastal zones contribute with 0.3 TgN.yr^{-1}
119 ($0.3\text{-}0.4 \text{ TgN.yr}^{-1}$) (Tian et al., 2020).

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

129 3. Materials and methods

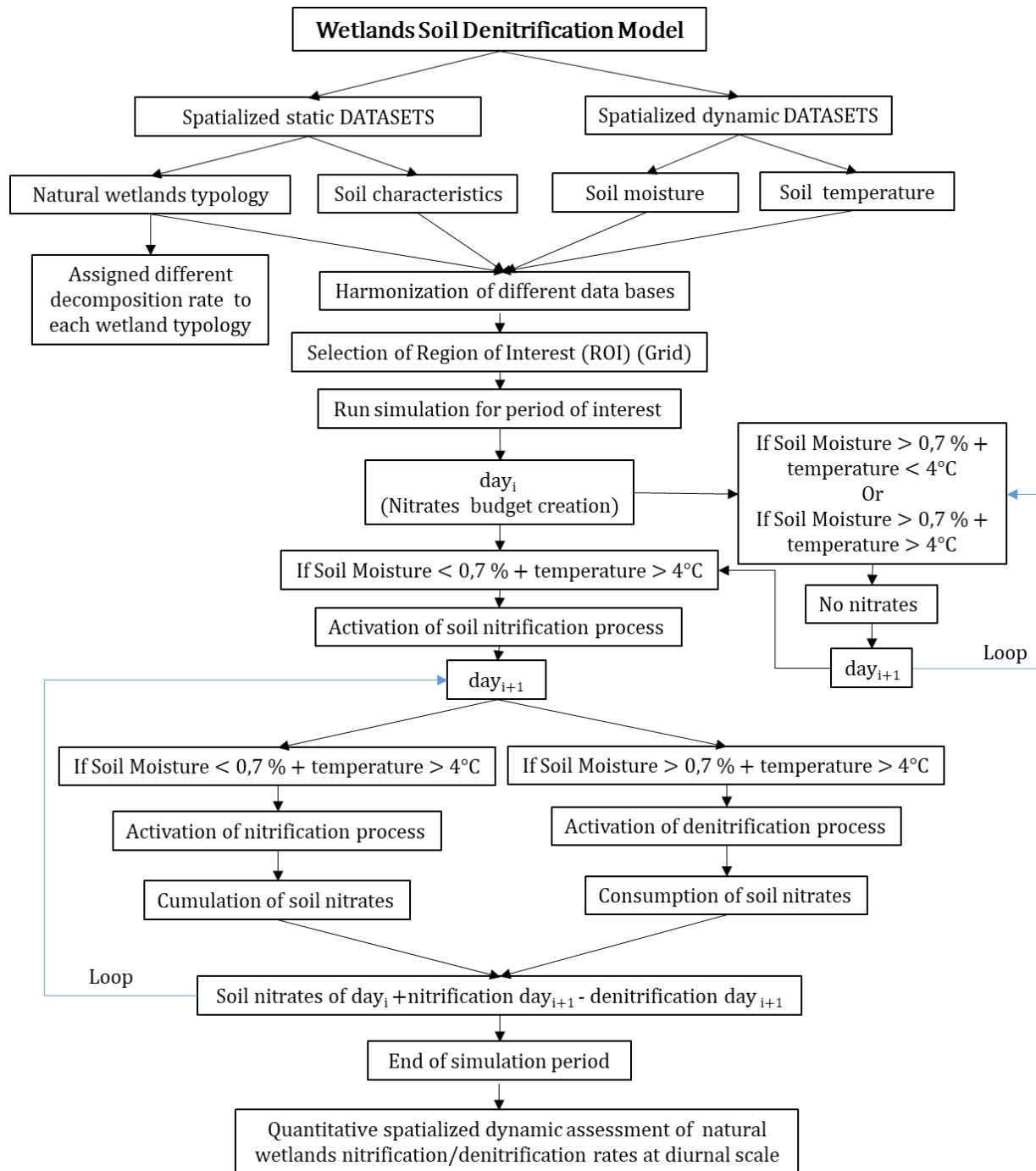
130 3.1 WETLANDS SOILS DENITRIFICATION MODEL

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

142 *MODEL IMPLEMENTATION*

143 WSDM needs two kind of spatialized data. On one hand, static datasets, define the wetland
144 typology and extension, and the soil characteristics (i.e. texture, bulk density, organic carbon
145 content). On the other hand, dynamic datasets (soil moisture and soil temperature) will lead
146 the nitrification and denitrification processes. Before running the physical-model, a pre-
147 processing phase is carried out. The user then has to define the Region of Interest (ROI),
148 giving two latitude and two longitude points indicating ROI limits, followed by the starting
149 and end date of the simulation period. Once these criteria are established, simulation is
150 launched. Spatial harmonization of databases is the first step, to have n-dimensional data on a
151 regular grid. Soil characteristics database - WISE30sec (Batjes, 2015) was the reference grid,
152 with a spatial resolution of 30 arcsec (1 km^2), well as Global Lakes and Wetlands Database
153 (GLWD) (1 km^2) (Lehner and Doll, 2004). Brightness soil temperature and root zone soil
154 moisture (Ahmad and Mahmoodi Ali, 2020; Al Bitar et al., 2017) have an original grid of

155 25km², therefore a linear interpolation, using (<https://scipy.org/>) - scientific python library is
 156 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
 162 **Figure 1.** Workflow illustration of the Wetlands Soil Denitrification Model processes flow (black
 163 arrows), the blue arrows represent the main two loops of the model. After setting up the model and
 164 defining the region of interest the simulation begins with nitrate budget generation in day_i.
 165 Nitrification will be active if soil moisture is low, if not, no nitrates will be created and no
 166 denitrification will be recorded, until that condition changes. Following the workflow, day_{i+1} soil

167 moisture will define if nitrification or denitrification will occur. This loop will continue happening
 168 until the end of the defined simulation period.

169 *NITRIFICATION*

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

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

176 where $NO_{3\ nit}$ corresponds to the nitrates produced by nitrification in the local soil (mgN.kg^{-1}
 177 $\cdot \text{day}^{-1}$), given by N_{org} organic nitrogen in soil (mgN.kg^{-1}) (Eq. 2),

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

178 where $OrgC$ is the organic carbon in soil (gC.kg^{-1}), and C:N is the ratio of carbon and
 179 nitrogen. The destruction of humus by mineralization is variable depending on the soil and the
 180 bacteria activity expressed by k_2 coefficient, calculated from the quantity of stable humus in
 181 the soil. The rate of mineralization is always higher in warm, humid climates, and varies from
 182 0.5 to 3%. To adjust the k_2 coefficient according to soil texture and temperature (Eq. 3), we
 183 used the model proposed for clay soils by Girard et al., (2011),

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

184 where C and $[CaCO_3]$ 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) ($^{\circ}\text{C}$), the
 186 coefficients are conversion units factors. The third term f_{SM} represents soil saturation factor
 187 (Eq. 4), defined as follows,

$$f_{SM} = \frac{SM_i - SM_{res}}{SM_{sat} - SM_{res}} \quad \text{Eq. 4}$$

$$\text{If } f_{SM} \geq 0.7, NO_{3\ nit} = 0$$

188 where SM_i , is the soil moisture of day (i) ($\text{m}^3 \cdot \text{m}^{-3}$), SM_{res} is the lowest soil moisture that
 189 allows the reaction to happen, and SM_{sat} , ($\text{m}^3 \cdot \text{m}^{-3}$). 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.

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,

$$Di_v = Dp \cdot f_N \cdot f_{SM} \cdot f_T \quad \text{Eq. 5}$$

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

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

205 where Dp is the potential denitrification rate in (mole $N \cdot dm^{-3} \cdot d^{-1}$), $0.8x$ represent the
206 stoichiometric proportion of nitrate consumed in denitrification compared to the organic
207 matter used with $x = 5$, ρ_b is the bulk density ($kg \cdot dm^{-3}$), φ is the porosity (unitless), k_{oc} (d^{-1})
208 is organic carbon mineralization constant define for each wetland typology (Table 2), $[OrgC]$
209 (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),

$$f_N = \frac{[NO_3^-]_i}{[NO_3^-]_i + K_{NO_3^-}} \quad \text{Eq. 7}$$

213 where f_N depends on the nitrates soil concentration $[NO_3^-]_i$ ($mgN \cdot kg^{-1}$) and bacteria
214 denitrification capacity, define on the $K_{NO_3^-}$, a half saturation constant for denitrification. This
215 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
218 type function that limits the denitrification capacity, and is related to nitrates quantity
219 (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)
221 using the emission results (Appendix Table A.3) as follows,

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

222 where A is a relation factor between Dp (mgN.kg^{-1}) potential denitrification, and Di (mgN.kg^{-1})
 223 is the control denitrification of the same soil, with no addition of nutritive solution. This
 224 factor then is substituted as f_N (Eq. 7), which allows the $k_{NO_3^-}$ to be calculated as follows,
 225

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

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

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

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

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

234 where T_i is the temperature of the given day and T_{opt} is the optimal temperature for
 235 denitrification established as 25°C in natural ecosystems (Billen et al., 2018).
 236 Denitrification Di_v obtained from these equations is volume based ($\text{mole N.dm}^{-3} \cdot \text{d}^{-1}$), in order
 237 to integrate the result to the WSDM, a conversion from volume to mass (Eq. 12) was applied
 238 as follows,

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

239 where, Di_m is expressed in $\text{mgN.kg}^{-1} \cdot \text{day}^{-1}$, MmN is the nitrogen molar mass (g), 1000 is the
 240 conversion factor g to mg, ρ_b is the bulk density (kg.dm^{-3}), φ is the porosity (unitless).
 241 Nitrates budget in the soil (Eq. 13), is calculated by integrating nitrification and denitrification
 242 processes defined as follows,

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

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

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

$$Denit_{kg.ha} = [NO_{3_i}^-]_{denit} * \rho_b * soil_{act} \quad \text{Eq. 14}$$

250 where $Denit_{kg.ha}$ is the total denitrification ($\text{N}_2\text{O-N}+\text{N}_2\text{-N}$) estimation in $\text{kgN}\cdot\text{ha}^{-1}\cdot\text{day}^{-1}$, given
 251 by $[NO_{3_i}^-]_{denit}$ ($\text{mgN}\cdot\text{kg}^{-1}$) nitrates consumed, ρ_b is the bulk density ($\text{kg}\cdot\text{dm}^{-3}$), $soil_{act}$ refers to
 252 the active soil layer, here 30 cm was used as a constant depth of the active layer.

253 $\text{N}_2\text{O-N}_2$ RATIO OUTGASSING

254 N_2O emissions are highly variable in space and time, and there has not been a consensus on a
 255 methodology that responds to bottom-up or top-down scales. However, as scale increases, so
 256 does the agreement between estimates based on soil surface measurements (bottom-up
 257 approach) and estimates derived from changes in atmospheric concentration of N_2O (top-
 258 down approach) (Grosso et al., 2008).

259 The IPCC provides guidelines for estimating regional and global N_2O emissions, which are
 260 calculated by multiplying N loading with the indirect emission factors (EF) (IPCC, 1996). The
 261 indirect N_2O emission factor associated with N leaching and runoff (EF₅: $\text{kg N}_2\text{O-N}$ per kg of
 262 NO_3^- -N) incorporates three components: (i) groundwater and surface drainage (EF_{5g}); (ii) rivers
 263 (EF_{5r}); (iii) and estuaries (EF_{5e}). In the last IPCC report (2019), the EF_{5r} and EF_{5e} were adapted to
 264 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.

266 N_2O emissions can be influence by several factors, yet to avoid adding up uncertainties we
 267 applied the constant ratios (Table 2) proposed for freshwater wetlands, for flooded soils and by
 268 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,
 270 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
ρ_b	$\text{kg}\cdot\text{dm}^{-3}$	Dry sediment density
T_i	$^{\circ}\text{C}$	Temperature
SM_i	$\text{m}^3\cdot\text{m}^{-3}$	Soil saturation
SM_{res}	$\text{m}^3\cdot\text{m}^{-3}$	Minimal soil saturation capacity
SM_{sat}	$\text{m}^3\cdot\text{m}^{-3}$	Maximal soil saturation capacity
$[OrgC]$	mole kg^{-1}	Organic carbon content
C_{org}	$\text{gC}\cdot\text{kg}^{-1}$	Organic carbon content
$[NO_{3_i}^-]$	$\text{mgN}\cdot\text{kg}^{-1}$	Nitrates concentration
$[NO_{3_i}^-]_{nit}$	$\text{mgN}\cdot\text{kg}^{-1}$	Nitrates in soil
$[NO_{3_i}^-]_{denit}$	$\text{mgN}\cdot\text{kg}^{-1}$	Nitrates denitrified
MAT	$^{\circ}\text{C}$	Mean annual temperature
$C:N$	-	C: N ratio

N_{org} mgN.kg^{-1}

Organic nitrogen

272

Table 2. Constants for Wetlands Soil Denitrification Model.

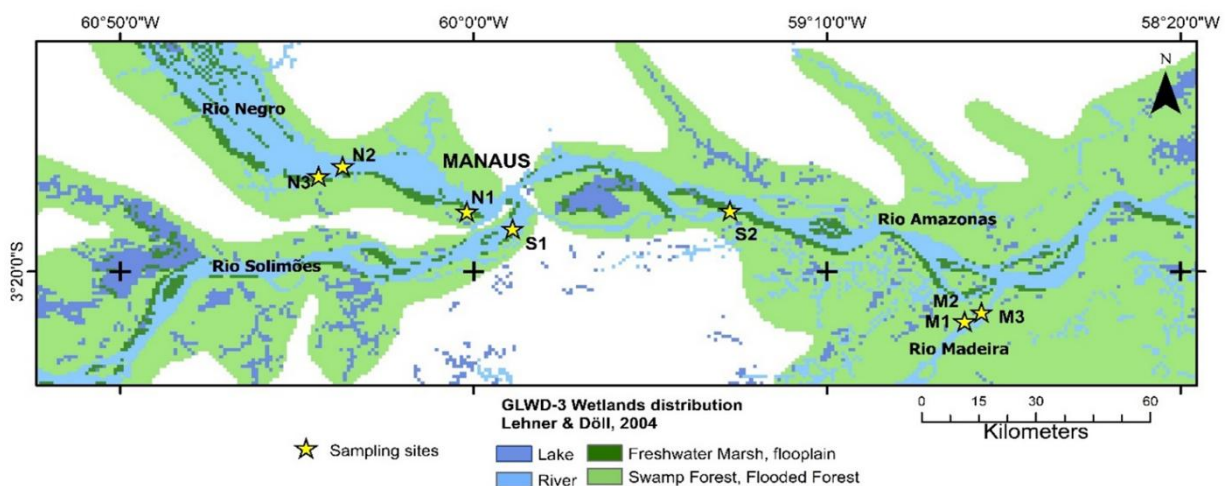
Constant	Value	Units	Description	Reference
T_{opt}	25	°C	Optimal temperature	Billen et al., 2018
$soil_{act}$	30	cm	Soil active layer depth	Yang et al., 2019
$k_{NO_3^-}$	0.18	mgN.kg^{-1}	Nitrate limitation constant	This study
Freshwater Marsh k_{oc}	0.062	day	Mineralization rate	Yin et al., 2019
Flooded forest k_{oc}	0.016			Bridgham et al., 1998
Freshwater wetlands R_{N_2O}	0.02	-	Emission ratio	Scheer et al., 2020
Flooded soils R_{N_2O}	0.082			Schlesinger, 2009
IPPC generic R_{N_2O}	0.1			Guilhen et al., 2020

273

3.2 WETLANDS SOILS DENITRIFICATION MODEL VALIDATION

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

284 To calibrate $k_{NO_3^-}$ and validate the WSDM, a field campaign in the central Amazonian
 285 floodplain (from 14th to 24th February 2020) was carried out to collect soil samples at eight
 286 sampling sites. The sampling points were distributed on the three main tributaries (Negro
 287 river, Solimões river and Madeira river) with different water quality. In each river, the two
 288 main wetland typologies (i.e. Freshwater marsh and Flooded forest) were sampled as shown
 289 in Figure 2.



290

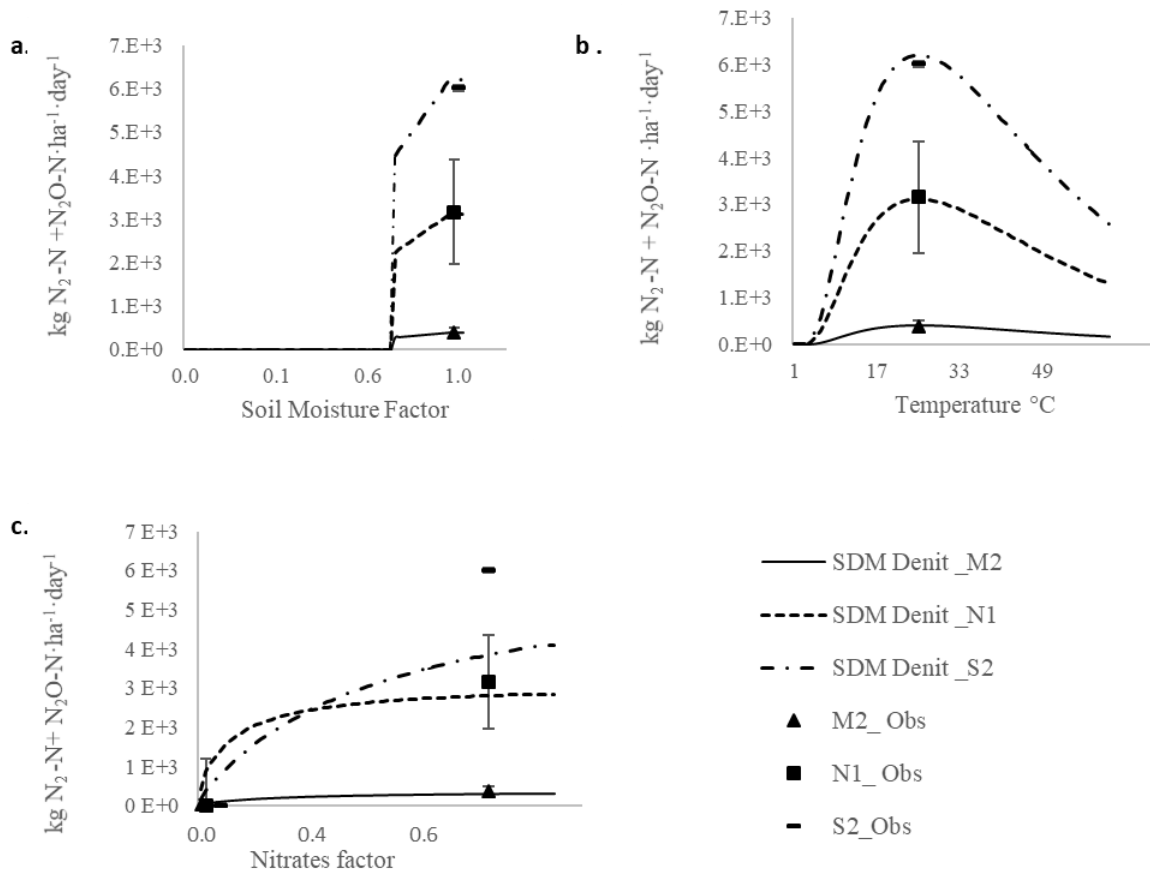
291 **Figure 2.** Sampling sites distributed in the central Amazonian floodplain, Negro river (N1, N2, N3),
292 Solimões river (S1, S2, S3), Madeira river (M1, M2, M3). The sampling points are distributed in two
293 main non-permanent wetland types: floodplain (light green) and flooded forest (dark green).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

295 The model validation was carried out in three steps: (a) *static denitrification validation*,
296 comparing modelled potential denitrification and experimental denitrifier enzyme activity
297 (hereafter DEA) results. DEA was measured using acetylene-inhibition technique (AIT) as
298 described and applied in several studies (Balderston et al., 1976; Koschorreck and Darwich,
299 2003; Tiedje et al., 1984, Tiedje et al., 1989) detailed methodology applied in this study is
300 presented in Appendix - Experimental Methodology. (b) *dynamic denitrification validation*,
301 nitrates soil budget and denitrification events were modelled using soil moisture and
302 temperature diurnal satellite input data from (2011-2019), extracted at the eight sampling
303 points WSDM results of the eight sample sites annual denitrification rates are presented on
304 the Appendix Table A.4. (c) *N₂O-N₂ ratio validation*, $R_{N_2O} = 0.02$ proposed for freshwater
305 wetlands ecosystems by Scheer et al., (2020) was applied to yearly denitrification WSDM
306 values for each soil sample (Appendix Table A.5). N₂O range emission was calculated for
307 freshwater wetlands and compared with other studies in order to validate the WSDM total
308 denitrification assessment (Appendix Table A.2).

309 4. Results

310 4.1 STATIC DENITRIFICATION VALIDATION

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

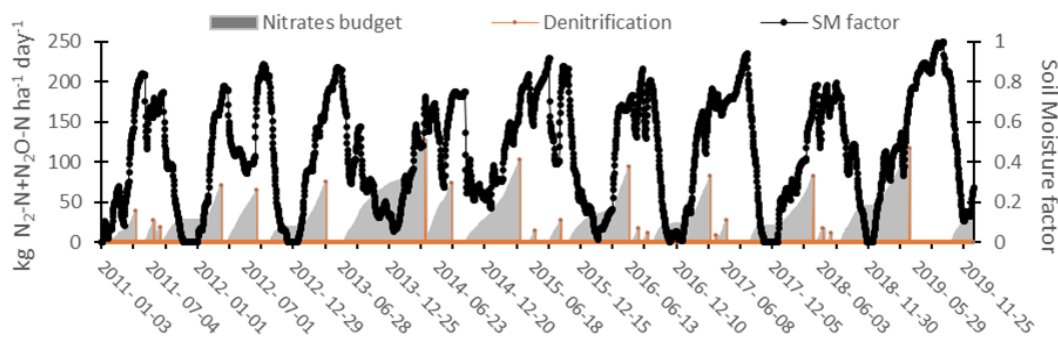


321
 322 **Figure 3.** Model responses to different limiting factors (**a.** soil moisture, **b.** temperature, **c.** nitrate
 323 concentration) of three sample sites (Madeira river (M2), Negro river (N1), and Solimões river (S2),
 324 compared to DEA laboratory mean observations (n=3).

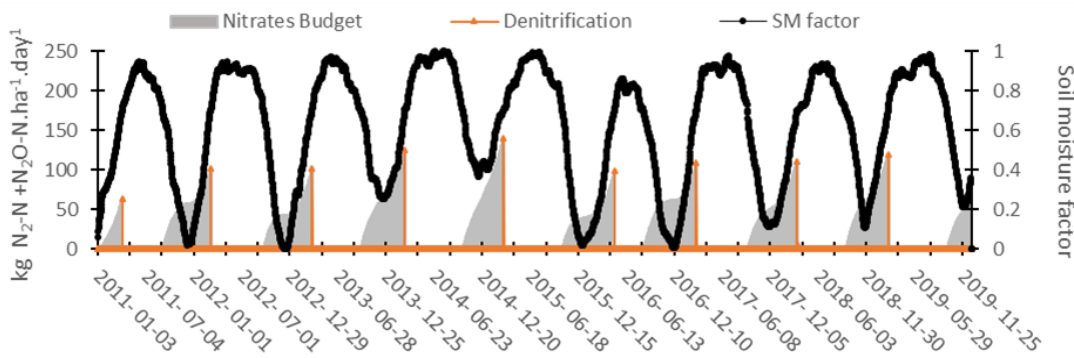
325 4.2 DYNAMIC DENITRIFICATION VALIDATION

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

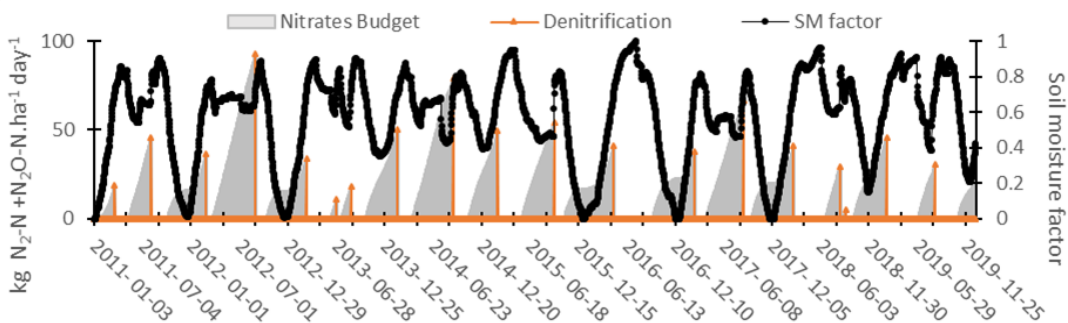
a. Negro river (N1) Flooded forest



b. Madeira river (M2) Freshwater marsh



c. Solimões river (S1) Freshwater marsh



336

337 **Figure 4 a-c.** Diurnal time series from 2011-2019, on the main y-axis, nitrate budget per day ($\text{kgN} \cdot \text{ha}^{-1} \cdot \text{day}^{-1}$)
 338 and total denitrification ($\text{N}_2 + \text{N}_2\text{O}$) ($\text{kgN} \cdot \text{ha}^{-1} \cdot \text{day}^{-1}$) are represented, while daily soil moisture factor dynamics are
 339 represented. The nitrate budget represents the nitrates available in the soil on a certain date, this budget is not
 340 produced in one day by nitrification, but is the accumulation of several days, therefore is represented as an area,
 341 that is consumed by denitrification events (orange lines). When soil moisture factor is zero (black line), there is
 342 no nitrification and therefore the nitrates budget stays steady.

343

4.3 $\text{N}_2\text{O}-\text{N}_2$ RATIO VALIDATION

344 The modelled annual denitrifications from 2012-2019 calculated in each sample site are
 345 grouped by wetland typology. The resulted emissions after applying the three different $R_{\text{N}_2\text{O}}$
 346 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 soil
 348 sample are presented in Appendix Table A.5.

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

Land cover, (R_{N2O})	Denitrification Rate (kgN₂O-N ha⁻¹ yr⁻¹) Mean value (range)	Reference
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	(Lienggaard et al., 2014)
High input cropping	2.3	Peruvian Amazon (Palm et al., 2002)
Low input cropping	1.2	
Shifting cultivation fallow	0.8	
Multistrata agroforestry	0.5	
Peach palm plantation	0.8	
Forest fallow control	0.8	
Freshwater marshes, (0.02)	0.95 (0.4-1.8)	This study
Flooded forests, (0.02)	3.8 (2.3-6.3)	
Freshwater marshes, (0.082)	3.8 (1.7-7.4)	
Flooded forests, (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)	
Land cover	Range (kgN₂O-N ha⁻¹ yr⁻¹)	Reference
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	

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
 354 small compared with the Amazon watershed dimension, the freshwater marshes and flooded
 355 forests, (the main freshwater wetland typologies of this basin), were sampled in each of the
 356 three main tributaries (i.e. Negro, Solimões and Madeira rivers). This study is not intended to
 357 better understand denitrification in the Amazon, but to use Amazon soils, as examples of
 358 freshwater wetlands (flooded forest and freshwater marshes) under conditions of low
 359 anthropogenic impact, with a bimodal hydrological cycle.

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

364 WSDM is built up in a binary assumption, which does not allow nitrification to happen at the
365 same time as denitrification in the same point. Fixing a soil moisture threshold. This may not
366 be true when looking at the microscale, as the soil structure and the root zone has some
367 oxygen available most of the time. During wet periods, the anoxic conditions trigger three
368 different processes: denitrification, dissimilatory nitrate reduction (DNRA) and Anammox.
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
371 (Adame et al., 2019).

372 Due to the lack of *in situ* data of N₂O 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).

379 Flooded forest samples influenced by Negro river (N1, N3) have high organic carbon content,
380 yet the recorded emissions are unlike. The difference lies in the concentration of nitrates in
381 the soil. When there is nitrates surplus in soils the enzyme (*nosZ*) in charge of converting the
382 N₂O to N₂ (the last step of denitrification) is withdrawn (Glass and Silverstein, 1999). This
383 withdrawal is frequently observed in agricultural fields, where fertilizers are added and the
384 type of irrigation used is flooding (Burgin and Groffman, 2012; Liu and Greaver, 2009).

385 Flooded forest soil sample (N1) influenced by the Negro river located downstream of the city
386 of Manaus recorded a N₂O emission rate of $0.32 \pm 0.1 \text{ gN.kg}^{-1}.\text{h}^{-1}$, which is two times higher
387 than four of the other soil samples (N3, S1, M1 and M2). These four sites register a ratio that
388 favours N₂. On the other hand, flooded forest (N3), registered the highest N₂ emission rate
389 ($0.23 \pm 0.02 \text{ g N kg}^{-1} \text{ h}^{-1}$).

390 N1 and N3 samples are examples of high potential denitrification rates of Amazonian
391 wetlands soils. Extensive fertilizer use in this watershed will have a negative effect in
392 wetlands denitrification, as concentration of nitrates from exogenous sources will increase the
393 budget of nitrates produced by nitrification, that in turn will increase denitrification event
394 intensity (fold-4) and N₂O emissions (Weier et al., 1993; Blackmer and Bremner, 1978; Pärn
395 et al., 2021). A surplus of nitrates also affects ecosystem functionality, promotes
396 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.

401 The major contribution of WSDM, is that simulated denitrification is influenced by wetland
402 vegetation typology. The influence of the vegetation in wetlands has been reported previously
403 by Alldred and Baines, (2016), they calculated that the presence of plants increased
404 denitrification rates by 55% on average, but they also acknowledge the need to differentiate
405 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. trees
407 or herbs).

408 The link between vegetation and bacterial processes such as denitrification can be delicate.
409 The interaction occurs in the root areas, on a very local scale and depends on many physical
410 and chemical aspects. Denitrification emission ratio depends on many local variables and it
411 can exhibit drastic changes (i.e. pH, nitrate concentration). Acetylene-inhibition technique
412 (AIT) has limitations regarding the $N_2O:N_2$ emission ratio, and it has been shown to be
413 inaccurate when recording low denitrification rates such as in groundwater. Nevertheless, AIT
414 allows an estimation of total denitrification at high temporal resolution and on small spatial
415 scales, with limited workload and costs involved (Felber et al., 2012). A stable isotope
416 approach might have been a preferable method to identify N_2 emissions. However, we had
417 reservations concerning detection limits and how well the enriched solution would be
418 distributed through the soil column.

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

425 5.2 COMPARISON WITH EARLIER MODELLING APPROACHES

426 The precedent denitrification model estimates a total denitrification ($N_2-N + N_2O-N$) rates at
427 the Amazon floodplains from 38.8 to 142.5 $kgN.ha^{-1}.yr^{-1}$ with a spatial grid of 25 km^2
428 (Guilhen et al., 2020). The WSDM has a wider range (20.36 - 315.90 $kgN.ha^{-1}.yr^{-1}$), this
429 difference is a consequence of model set up, the current version is sensitive to different
430 organic carbon decomposition rates, soil moisture gradient, as well as nitrates limitation,
431 calculated in 1 km^2 grid, constraints that were missing in the previous version.

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

438 The WSDM current version does not calculates $N_2O:N_2$ ratio yet. The different N_2O rate
439 productions (Table 3), suggest that ratio (0.02) for freshwater wetlands proposed by Scheer et
440 al., (2020) applied to the WSDM denitrification results, gives a N_2O-N total contribution
441 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 ^{15}N isotopic tracers (Bergsma et al., 2001). Additionally, Pärn et
444 al., (2021) reported by *in situ* measurements that the Peruvian palm peat swamp is a hot spot
445 and that the emission ratio change depending on the season. They reported that March (the
446 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 N₂O 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 N₂O:N₂ ratios, but this evidence
450 could serve for developing a N₂O:N₂ ratio function.

451 Relevant research has been done on this topic, on a large scale the Global N₂O Model
452 Intercomparison Project (Tian et al., 2018) presented a spatialized global-scale N₂O estimate
453 by making a comparative study of a dozen of hydrodynamic models that model the global
454 nitrogen and carbon cycles. The resulted model, the Dynamic Land Ecosystem Model
455 (DLEM), assesses the pre-industrial emissions (CO₂, CH₄ and N₂O) and the current trend, on
456 a yearly, monthly and daily basis from 1901 to 2010 with a spatial resolution of 0.5° × 0.5°.
457 This model exposes the anthropogenic impact, main pollution sources and the consequences
458 towards the biosphere. This model also takes into account different ecosystems and divides
459 wetlands into four categories (seasonal grass wetlands, seasonal forest wetlands, permanent
460 grass wetlands and permanent forest wetlands).

461 Likewise, DNDC (DeNitrification DeComposition) model is a powerful tool to evaluate N₂O
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 (CO₂ and CH₄). 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

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

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697 Experimental methodology

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

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

722 **Table A.1** Concentration of nitrates and carbon solution applied for DEA identification.

Treatment	Vol added (ml)		Nitrogen Solution (mg/L)	Carbon Solution (mg/L)	mg N	mg C
	N	C				
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

723 Between treatments, soil samples were left for 24 hours in aerated conditions before applying
 724 the next treatment. Once all the treatments were completed, the flasks were dried out in an
 725 oven at 100 °C for 24h. After that, the weight of each flask was measured. The dry samples
 726 were sieved and two grams of these homogenized samples were ignited at 500°C for 24h to
 727 obtain the organic matter content by weight difference. Pore space and bulk density were
 728 determined gravimetrically on volume samples assuming a measured particle density of 2.613
 729 g cm⁻³. Potential denitrification rates were calculated from the linear increase of the N₂O

730 content in the flask and expressed as $\mu\text{g N}_2\text{O g}^{-1}\cdot\text{h}^{-1}$. All data is expressed per gram of
 731 sediment on a dry basis. The total N_2O production (Eq. 1) was calculated by the N_2O gas (g)
 732 fraction and N_2O liquid (l) fraction measured in ppm as follows,

$$N_2O_t = N_2O_g + N_2O_l \quad \text{Eq. 1}$$

733 and then converted to $\mu\text{g N}_2\text{O}$ gas (Eq.2) and liquid (Eq. 3) as follows,

$$N_2O_g = \frac{(2,211 \cdot 10^{-8} \cdot M_{ppm}) - (4,35 \cdot 10^{-9})}{0,00468} \cdot 1000 \quad \text{Eq. 2}$$

$$N_2O_l = (1,536 \cdot 10^{-9}) \cdot M_{ppmv} \cdot W_v \cdot 10^6 \quad \text{Eq. 3}$$

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

737 The $\text{N-N}_2\text{O}$ (Eq. 4), $\text{N-N}_2\text{O+N}_2$ (Eq. 5) and $\text{N-N}_2\text{O}$ (Eq. 6) production ratio were calculated in
 738 dry sediment basis as follows,

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

If C_2H_2 added,

$$k_{N-N_2O+N_2} = \frac{N_2O_t}{Ds} * \frac{28}{44} \quad \text{Eq. 5}$$

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

739 where k_{N-N_2O} refers to the production rate of N_2O ($\mu\text{g N g}^{-1}\text{ h}^{-1}$) when there is no inhibition
 740 with acetylene, and Ds is the dry soil weight (g), when acetylene is applied then the N_2O ratio
 741 recorded is $k_{N-N_2O+N_2}$ which is the sum of (N_2 and N_2O) and is also expressed in $\mu\text{g N g}^{-1}\text{ h}^{-1}$,
 742 then k_{N-N_2} refers only to the N_2 production ratio ($\mu\text{g N g}^{-1}\text{ h}^{-1}$), as subtraction of the two
 743 previous equations.

746 Denitrification rates from the Amazon central flood plain wetlands soil samples (laboratory-controlled conditions) and modelled with WS DM

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748

Table A.2. Denitrification rates from the Amazon central flood plain wetlands soil samples (laboratory-controlled conditions) and modelled with WS DM

n	A	$k_{NO_3^-}$ ($\mu\text{mol N kg}^{-1} \text{d}^{-1}$)	k_{NO} (μg)
3	0.003	9770.44	
0	0.001	4797.77	4797.77
3	0.003	1077.70	1077.70
0	0.003	188.86	188.86
3	0.003	1247.97	1247.97
0	0.003	10355.91	10355.91
7	0.003	1747.59	1747.59
0	0.003	3966.80	3966.80
1	0.003	189.97	189.97
0	0.003	377.42	377.42
1	0.003	1188.50	1188.50
0	0.003	1380.42	1380.42

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

Organic carbon (kg^{-1})	Porosity [OrgC]	C/N ratio	K_{oc}
190.28	0.85	16.17	
19.45	190.49	9.99	19.45
0.04	0.18	0.122	0.122
89.05	17.74	1.08	1.08
69.30	89.62	10.04	10.04
4.08	69.32	9.99	9.99
12.66	4.43	9.271	9.271
0.19	12.66	0.004	0.004
0.64	0.39	1.204	1.204
0.06	0.64	1.204	1.204

tion annual

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summary of observed and modelled denitrification.

Table A.5

Summary of observed and modelled denitrification.

Year	Denitrification rate (kg N ₂ O day ⁻¹ ha ⁻¹)		Denitrification rate (kg N ₂ O ha ⁻¹ day ⁻¹)		Model initial mean nitrate (kg N ha ⁻¹)
	Observed	Modelled	Observed	Modelled	
2011	0.85	0.21	3170.72	20910.5	128
2012	0.01	0.00	14419.29	43616.3	315
2013	2.99	0.80	6211.93	92.77	90
2014	0.69	0.19	10648.62	60.64	49
2015	1.56	0.42	38993.7	13989.7	114
2016	1.99	0.53	1480.55	25.12	20
2017	2.12	0.57			
2018	0.41	0.11			
2019					
2020					
2021					

* 2011 was led, as it is the first year of the model and the nitrate pool is building up, the modelled denitrification rate is very low.